Preparation and photoluminescence of yttrium hydroxide and yttrium oxide doped with europium nanowires

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Abstract

Single-crystalline Y(OH)\textsubscript{3}:Eu nanowires have been prepared by polymer-assisted hydrothermal method. The yields of the nanowires were higher than 95%. XRD patterns showed that the products were the hexagonal Y(OH)\textsubscript{3} structure. SEM images displayed that the nanowires consisted of nanobelts and nanorods. The nanorods have the diameter of about 85 nm and length up to several tens of microns, and the nanobelts have the width of \sim 95 nm, and the thickness of 20 nm, and the length of several tens of microns. Y(OH)\textsubscript{3}:Eu nanowires were converted to Y\textsubscript{2}O\textsubscript{3}:Eu nanowires by thermal decomposition at 500 °C for 3 h. The morphologies still remained. The photoluminescence (PL) properties of Y(OH)\textsubscript{3}:Eu and Y\textsubscript{2}O\textsubscript{3}:Eu nanowires were studied. There are four strong peaks at 592, 616, 651 and 696 nm for the Y(OH)\textsubscript{3}:Eu nanowires under the excitation of 396 nm. There is only strong peak at 611 nm for the Y\textsubscript{2}O\textsubscript{3}:Eu nanowires under the excitation of 465 nm.

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1. Introduction

Phosphors are essential materials in display applications. The high performance of display requires high-quality phosphors for sufficient brightness and long-term stability. To enhance the luminescent characteristic of phosphors, extensive research has been carried out on rare-earth-activated oxide phosphors. Among these
oxide-based phosphors, Y$_2$O$_3$:Eu nanoparticles are one of the most promising oxide-based red phosphors systems due to its excellent luminescence efficiency, color purity, and stability [1]. In the preparation of Y$_2$O$_3$:Eu nanoparticles, many different techniques have been reported such as spray pyrolysis [2], chemical vapor deposition [3], sol–gel [4] and so on. One-dimensional (1D) quantum wires have attracted much attention for both their importance in mesoscopic physics and potential applications in fabricating novel nanoelectronic, optoelectronic, electrochemical, and electromechanical device [5–8]. Therefore, it is important to fabricate Y(OH)$_3$:Eu and Y$_2$O$_3$:Eu quantum wires to meet demand in fabricating nanodevices. There have also been a few reports related to the synthesis of Y$_2$O$_3$:Eu 1D nanostructures such as Y$_2$O$_3$:Eu nanowire array with anodic aluminum oxide template [9], Y$_2$O$_3$:Eu nanotubes [10], Y(OH)$_3$ and Y$_2$O$_3$ nanotubes [11] and Y$_2$O$_3$:Eu nanobelts [12]. However, Y(OH)$_3$:Eu nanowires and their photoluminescence (PL) properties have not been reported until now. Here, we report the synthesis of Y(OH)$_3$:Eu nanowires via (polyethylene glycol) PEG 20000-assisted hydrothermal reaction. Y$_2$O$_3$:Eu nanowires were prepared by thermal decomposition of Y(OH)$_3$:Eu nanowires, and their morphologies were characterized in detail, and their PL properties were studied.

2. Experimental section

All the reagents used in our experiments were of analytical purity and were used without further purification. Yttrium oxide, sodium hydroxide and PEG 20000 were purchased from Shanghai (China) chemical reagent company. Nitric acid was purchased from Nanjing (China) chemical reagents factory.

In a typical procedure, 0.6 mmol Y$_2$O$_3$ and 0.03 mmol Eu$_2$O$_3$ powders were dissolved in 2 ml concentrated nitric acid, and were adjusted to pH $\approx$ 13 with sodium hydroxide. The solution was added with 0.5 g PEG 20000 and distilled water, and the total volume of the solution was 30 ml. After the solution mixture was stirred for 20 min, it was transferred into a Teflon-lined stainless autoclave with 40 ml. The autoclave was maintained at 170 °C for 24 h, and cooled to room temperature. The products were collected and washed with the distilled water and ethanol, and dried at 80 °C for 4 h. They were converted into Y$_2$O$_3$:Eu nanowires after the as-prepared Y(OH)$_3$:Eu nanowires were calcined in alumina crucible at 500 °C at a rate of 5 °C/min and maintained for 3 h in air. The hydroxide samples of the different times such as 2 and 12 h were prepared for investigation into growth process of the nanowires. Bulk Y(OH)$_3$:Eu was synthesized according to the above similar method, without PEG 20000, but reaction time was prolonged to 36 h. Bulk Y(OH)$_3$:Eu was converted to bulk Y$_2$O$_3$:Eu at 500 °C.

The products were characterized on a Shimadzu XD-3A X-ray diffractometer with graphite monochromatized Cu Kα-radiation ($\lambda = 0.15418$ nm) and nickel filter. TEM images and SAED (selected area electron diffraction) pictures were recorded on a JEOL-JEM 200CX transmission electron microscope, using an accelerating voltage of
200 kV. SEM pictures were, respectively, taken by LEO-1530VP scanning electron microscope. The PL spectra were taken by time resolved fluorescence spectrometer. (SLM 48000DSCF/AB2, SLM Inc.)

3. Results and discussion

3.1. Structure characterization

The powder XRD pattern of Y(OH)$_3$ and Y(OH)$_3$:Eu nanowires have been shown respectively as Fig. 1a and b, which can be indexed to be a pure hexagonal phase with the cell constants of $a = 0.6268$ nm and $c = 0.3547$ nm, identical to the reported data in JCPDS cards (JCPDS 24-1422). Perhaps, because Eu content of Y(OH)$_3$:Eu nanorods is low or because radius of Y$^{3+}$ approaches that of Eu$^{3+}$, there is almost no change in the lattice parameters. Y(OH)$_3$:Eu nanowires were calcined at 500 °C to be converted to Y$_2$O$_3$:Eu nanowires. The powder XRD pattern of the samples is shown as Fig. 1c, which is a cubic phase with the cell constants of $a = 1.0604$ nm (JCPDS 25-1200).

3.2. Morphologies

Fig. 2a is a low-magnification SEM micrograph of Y(OH)$_3$:Eu nanowires, which shows that the
samples are composed of the nanowire bundles with the diameter of 1–3 \( \mu \)m and length up to several tens of microns. Further observation shows the coexistence of nanorods and nanobelts. As Fig. 2b shows, a single nanowire has the diameter of about 85 nm. Fig. 2c reveals the Y(OH)\(_3\):Eu nanobelts with the width of \( \sim 95 \) nm, and the thickness of \( \sim 20 \) nm. Fig. 2d is a low-magnification SEM image of Y\(_2\)O\(_3\):Eu nanowires. Fig. 2e reveals that the Y\(_2\)O\(_3\):Eu nanobelts have a width of about 53 nm, and thickness of about 20 nm. Fig. 2f indicates morphologies of Y\(_2\)O\(_3\):Eu nanorods with diameters of about 80 nm. Compared with Y(OH)\(_3\):Eu nanowires, the morphologies of Y\(_2\)O\(_3\):Eu nanowires almost remain the same, but the diameter (width) decreases slightly.

Fig. 3a is TEM micrograph of a bundle of Y(OH)\(_3\):Eu nanowires. Fig. 3b shows TEM image of a single nanowire, and inset is its SAED pattern along [\(1\overline{1}0\)] direction, which indicates the nanowire grows along [0 0 1] direction. Fig. 3c is TEM image of Y\(_2\)O\(_3\):Eu nanowires. The SAED pattern (Fig. 3d) of a single Y\(_2\)O\(_3\):Eu nanowire supported the results indexed by XRD. Fig. 3e shows TEM images of a bundle of Y\(_2\)O\(_3\):Eu nanobelts, and the typical belt was indicated by the arrow in Fig. 3e.
3.3. Photoluminescence properties

Fig. 4a presents the room-temperature excitation spectrum of Y(OH)$_3$:Eu nanowires, which the strongest peak is at 396 nm, so it is selected as the excited light. Fig. 4b is the emission spectrum of the sample under 396 nm excitation. The peak at 592 nm derives from the allowed magnetic dipole transition ($^5$D$_0$$^7$F$_1$) (Eu$^{3+}$ site with inversion symmetry). Peak at 616 nm is due to the forced electric dipole transition ($^5$D$_0$$^7$F$_2$), which is allowed on condition that the europium ion occupies a site without an inverse center. Its intensity is hypersensitive to crystal environments. Peaks at 651 and 696 nm are, respectively, attributed to $^5$D$_0$$^7$F$_3$ and $^5$D$_0$$^7$F$_4$ transitions [13]. In accordance with Judd–Ofelt theory, transitions to even J-numbers have much higher intensity than those to corresponding neighboring odd J-numbers, however, the intensity of the $^5$D$_0$$^7$F$_1$ transition is higher than that of the $^5$D$_0$$^7$F$_2$ as for Y(OH)$_3$:Eu nanowires, which is an abnormal phenomenon, and the same phenomenon also appears on bulk samples, therefore investigation into them will remain further.

Fig. 5a presents the room-temperature excitation spectrum of Y$_2$O$_3$:Eu nanowires, which shows the double excitation peaks at 394 and 465 nm, and the strongest peak is at 465 nm, so we select it as the excited light. Fig. 5b is the room-temperature emission spectrum of the sample under 465 nm excitation. The strongest peak at 611 nm is attributed to the forced electric dipole transition ($^5$D$_0$$^7$F$_2$) (the europium ion occupies a site without an inverse center). The PL spectrum of
Y$_2$O$_3$:Eu nanowires is similar to that of Y$_2$O$_3$:Eu nanocrystallites [14], which shows their Eu coordination environments are similar. In order to compare PL properties of bulk Y(OH)$_3$:Eu and Y$_2$O$_3$:Eu with corresponding nanowires, we synthesized bulk Y(OH)$_3$:Eu and Y$_2$O$_3$:Eu, however, there are no differences. PL spectra of bulk Y(OH)$_3$:Eu or Y$_2$O$_3$:Eu are shown in Fig. 6.

3.4. Growth process

Fig. 7a and b shows the TEM images of the samples taken at different stages of the hydrothermal reaction: (a) 2h and (b) 12h. A large number of nanoparticles appeared after hydrothermal reaction for 2h. The particles and rods coexisted after hydrothermal reaction for 12h. After 24h, the particles were almost dissolved, and the nanowires were formed completely. If no PEG were added, there were more the particles (Fig. 7c). It shows that PEG plays a polymer-template role. The growth process could be included as follows: (1) PEG coordinated with Y$^{3+}$ to form a long chain complex—PEG–Y(NO$_3$)$_3$ [11] (Fig. 8b); (2) in the alkaline solution, the unstable complex were converted into Y(OH)$_3$–PEG gel and amorphous
particles, and under the present hydrothermal condition, the gel could convert to Y(OH)$_3$ molecule chains along PEG long chains (Fig. 8c); (3) as the reaction proceeded, some little amorphous particles dissolved, and Y$^{3+}$ and OH$^-$/CO$_3$$^-$ ions transferred to the surface of Y(OH)$_3$ molecule chains, condensed and formed ultrafine nanowires. If there were less polymer chains connected with the side of the ultrafine nanowires, as Y$^{3+}$ and OH$^-$ ions attacked around ultrafine nanowires, the section of the nanowires approached a circle. If there were more polymer chains connected with the side of the ultrafine nanowires, as polymer chains resisted Y$^{3+}$ and OH$^-$ ions to attack around the ultrafine nanowires, the nanobelts were formed. Such a process is illustrated as Fig. 8. In fact, it is a process of solid–liquid–solid (SLS) under direction with PEG 20000 long chain. If no polymers were added, a little of the nanowires could be formed. Because of the anisotropy hexagonal structure of Y(OH)$_3$, there was an intrinsic tendency to grow into rod-like morphologies.

4. Conclusions

We have demonstrated an effective approach to prepare single-crystalline Y(OH)$_3$:Eu and Y$_2$O$_3$:Eu nanowires. Growth process of Y(OH)$_3$:Eu nanowires has been thought as SLS mechanism under the direction of polymer-templates. Photoluminescence (PL) properties of Y(OH)$_3$:Eu and Y$_2$O$_3$:Eu nanowires are obviously different. It can be attributed to change of the symmetry of Eu$^{3+}$ coordination environments.

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References