Research Article

Solvothermal Synthesis of Gd$_2$O$_3$ : Eu$^{3+}$ Luminescent Nanowires

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Uniform Gd$_2$O$_3$ : Eu$^{3+}$ luminescent nanowires were prepared on a large scale by a facile solvothermal method using polyethylene glycol (PEG-2000) as template and ethanol as solvent; the properties and the structure were characterized. X-ray diffraction (XRD) patterns and Fourier transform infrared spectrometry (FTIR) showed that the precursors are hexagonal phase Gd(OH)$_3$ crystals, and the samples calcined at 800°C are cubic phase Gd$_2$O$_3$. Transmission Electron Microscopy (TEM) images indicated that the samples are nanowires with a diameter of 30 nm and a length of a few microns. Photoluminescence (PL) spectra showed that the ratio of $^5D_0 \rightarrow ^7F_2$ to $^5D_0 \rightarrow ^7F_1$ transition peak of the calcined samples is stronger than that of the precursors, which confirmed that the color purity of the Gd$_2$O$_3$ : Eu$^{3+}$ is better than that of the precursors. The as-obtained Gd$_2$O$_3$ : Eu$^{3+}$ luminescent nanowires show a strong red emission corresponding to $^5D_0 \rightarrow ^7F_2$ transition (610 nm) of Eu$^{3+}$ under ultraviolet excitation (250 nm), which have potential application in red-emitting phosphors and field emission display devices.

1. Introduction

Recently, 1D nanomaterials have been attracted much attention for their unique properties owing to their low dimension and high surface/volume ratio; therefore, they have potential applications in fabricating nanoscale electronic, optoelectronic, and magnetic devices and also provide an ideal model system to quantify conductance and size effects [1]. 1D rare earth oxide nanomaterials are a kind of advanced materials and have extensive applications on the fields of high-performance luminescent devices, catalysts, and other functional materials for their special electronic, optical, and chemical characteristics arising from their 4f electron. Several strategies have been developed for preparing 1D rare earth oxide nanomaterials, including template method [2–7], hydrothermal or solvothermal method [8–18], and chemical reaction [19–22]. Among these methods, the hydrothermal or solvothermal techniques are powerful and important means to synthesize 1D rare earth oxide nanomaterials due to their great chemical flexibility and synthetic tenability.

As well known, in rare earth oxide luminescence materials, Europium-doped Gd$_2$O$_3$ phosphor is one of the most important red-emitting phosphors and has been widely used in X-ray scintillator materials, high definition projection televisions, flat panel displays, and photoelectronic apparatus [23]. Over the past decade, Gd$_2$O$_3$ : Eu$^{3+}$ nanoparticles have been investigated extensively [24–27]. When Gd$_2$O$_3$ : Eu$^{3+}$ is prepared in the form of one-dimensional nanomaterials such as nanowires, nanorods or, nanotubes, its application would be widely extended due to the shape-specific and quantum confinement effects. However, compared with the study of Gd$_2$O$_3$ : Eu$^{3+}$ nanoparticles, there have been few reports on the synthesis of 1D Gd$_2$O$_3$ : Eu$^{3+}$ nanomaterials; for example, Jia et al. [19] had prepared Gd$_2$O$_3$ : Eu$^{3+}$ nanotubes via a wet-chemical route and a subsequent heat-treatment. Li et al. [28] had prepared Gd$_2$O$_3$ : Eu$^{3+}$ nanowires via AAO templated method, the method is complex, and the size of the obtained samples is limited by the template. Zhang et al. [29] had prepared Gd$_2$O$_3$ : Eu$^{3+}$ nanorods by surfactant-assisted hydrothermal method. Liu et al. [30] used MWCNTs as a template, coating gadolinium compounds on the carbon nanotube surface, followed by firing the carbon nanotube to obtain the Gd$_3$O$_7$ : Eu$^{3+}$ nanotubes, but the MWCNT template was difficult to remove afterwards. Herein, a large-scale uniform Gd$_2$O$_3$ : Eu$^{3+}$ nanowires were successfully prepared by a simple solvothermal method at the presence of polyethylene glycol followed by a subsequent calcination process, and the structure and properties were characterized.
2. Experimental Section

2.1. Preparation. In a typical synthesis, first, 4.5349 g Gd₂O₃ and 1.7608 g Eu₂O₃ (purity: 99.99%, Shanghai Yuelong Non-Ferrous Metals Limited, China) were dissolved in a minimum amount of diluted nitric acid (V_{HNO₃} : V_{H₂O} = 1 : 1) and evaporated to dryness then dissolved in distilled water to form 0.1 mol·L⁻¹ gadolinium nitrate and 0.05 mol·L⁻¹ europium nitrate solutions.

Secondly, 30 mL absolute ethanol and 12.8 g polyethylene glycol (PEG, A.R., molecular weight is 2000, Shanghai Linger Chemical Company, China) were added into the mixture of a certain amount of Gd(NO₃)₃ and Eu(NO₃)₃ solutions according to the molar ratio of Gd/Eu = 95 : 5, in which the molar ratio of rare earth ion and the surfactant PEG is 1 : 2. And then 4 mol·L⁻¹ NaOH was added to adjust pH of 13; after being stirred for 30 minutes, the mixture was transferred into a 50 mL autoclave, sealed and heated at 180°C for 36 hours. After the autoclave was cooled to room temperature naturally, the precursors were filtered and washed with distilled water and absolute ethanol for three times, respectively. The final white products were obtained through a heat-treatment at 800°C in air for 2 hours after being dried at 80°C for 2 hours.

2.2. Characterization. The sample crystal structure was characterized by an Aolong Y-2000 X-ray Diffractometer (XRD) equipped with a Cu Kα radiation source (λ = 0.154056 nm) and Ni filter at a scanning rate of 4°·min⁻¹ (2θ from 10 to 80°), X-ray tube voltage and current were 40 kV and 20 mA, respectively, and the step was 0.02°. FTIR spectra were measured with Perkin-Elmer 580B Infrared Spectrophotometer using a KBr pellet technique. The morphologies of the samples and the selected area electron diffraction (SAED) pattern were observed using a JEOL JEM-2010 Transmission Electron Microscopy (TEM), and the voltage was 160 kV. Photoluminescence (PL) excitation and emission spectra of the samples were recorded with a HITACHI F-4500 Fluorescence Spectrophotometer using a Xe lamp as the excitation source, the measurement range is 200–800 nm, scanning rate is 1200 nm/min, and step length is 0.2 nm. All the measurements were performed at room temperature.

3. Results and Discussion

3.1. XRD Patterns. XRD patterns of the precursors and the calcined samples are shown in Figure 1, it is noted that the precursors are well indexed to be a pure hexagonal phase Gd(OH)₃, identical to the reported data in JCPDS card (83-2037), because the Eu content is low, there are no peaks of Eu(OH)₃, and the cell constants of Gd(OH)₃ are almost not changed. After annealing at the temperature of 800°C, the intensities and the positions of the peaks are all changed, and the diffraction peaks are coincided with the data of JCPDS card of (12-0797), which indicated that the calcined samples are pure cubic phase Gd₂O₃. Moreover, it can be observed that the diffraction peaks of the calcined samples are very sharp and strong, indicating that the Gd₂O₃ samples with high crystallinity are synthesized by this method.

3.2. FTIR Spectra. Figure 2 shows the FTIR spectra of the precursors and the calcined samples; from Figure 2(a), the absorption peak at 3440 cm⁻¹ is due to vibration of –OH in H₂O, and the peaks at 1510 cm⁻¹ and 1390 cm⁻¹ are ascribed to the vibration of NO₃⁻ [31], which originated from the residue NO₃⁻ in the sample. The peak near 703 cm⁻¹ is designed to vibration of Gd–OH, which indicated that the precursors are Gd(OH)₃. From Figure 2(b), it can be seen that the absorption peaks at 3440 cm⁻¹, 1510 cm⁻¹ and 1390 cm⁻¹ are stronger than those of the precursors; it is reported that the peaks in the wavelength range of 1400–1600 come from the carbonate groups and a weak peak at 847 cm⁻¹ is due to the absorption of CO₃²⁻ [32]. Perhaps...
the samples absorbed the CO₂ and H₂O from the atmosphere during the measurement process and the storage course, and which led to the overlap of CO₃²⁻ and the residue NO₃⁻. The important absorption peak at 547 cm⁻¹ is ascribed to vibration of Gd–O, suggesting that the Gd(OH)₃ had converted to Gd₂O₃ after calcining; this result confirms the analysis from XRD patterns.

3.3. TEM Images. In order to study the morphology and the size of the as-prepared Gd₂O₃:Eu³⁺ nanomaterials, the samples were investigated by TEM, which are shown in Figures 3(a) and 3(b). It is seen clearly that the samples comprise wire shapes and are generally well dispersed. The diameter of the wires is about 30 nm and the length reaches to micrometer scale. It is also observed that the samples are smooth and uniform. Figure 3(c) is the corresponding SAED pattern; one can see the (211), (222), (400), and (440) planes of the cubic phase Gd₂O₃, which is in agreement with the XRD results.

3.4. Photoluminescence Spectra. The uniform Gd₂O₃:Eu nanowires obtained by the solvothermal method exhibit a strong red emission under short UV irradiation, and the spectral properties are typical of the well-known Gd₂O₃:Eu [24, 25, 27].

The excitation spectra of the precursors and the samples calcined at 800°C are drawn in Figure 4; the monitoring wavelength is 5D₀→7F₂ transition at 610 nm of the Eu³⁺. It is noted that the excitation peaks of the precursors are weaker than those of the calcined samples. From the magnified spectrum of the inset, it is obvious that the strong excitation peak is near 250 nm, which originated from the charge transfer band of O²⁻–Eu³⁺, and the weak peak near 394 nm is due to the 7F₀ → 5L₆ transition of Eu³⁺. After being calcined at 800°C, the excitation spectrum becomes stronger and it consists of an intense broad band near 232 and 247 nm, the former is due to the host absorption of Gd₂O₃, and the latter is attributed to the charge transfer band (CTB) of O²⁻–Eu³⁺ [33]. The weak shoulder at 276 nm superimposed on the CTB of Eu³⁺ can be assigned to the 8S–6I transition line of Gd³⁺ [34]. The presence of the Gd₂O₃ host band and Gd³⁺ excitation line in the excitation spectrum of Eu³⁺ indicates that there exists an energy transfer from the Gd₂O₃ host band to the doped Eu³⁺ [34]. At the same time, a series of weak intensity peaks near 314 nm, 394 nm, and 465 nm can be seen, which is supported to the 7F₀ → 5L₆, 7F₀ → 5D₂ energy level transition of Eu³⁺ [33–35].

Figure 5 shows the emission spectra of the precursors and the calcined samples, the excitation wavelength is the CTB of Eu³⁺ at 250 nm. From the magnified spectrum of the precursors, it can be seen that the emission spectrum consists of 5D₀→7F₆ line emissions of Eu³⁺, the strongest emission peak is near 610 nm, which corresponds to the hypersensitive 5D₀→7F₂ transition of Eu³⁺, and the line peak at 590 nm is due to 5D₀→7F₁ magnetic dipole transition, which emits orange red light. After being calcined at 800°C, the emission spectrum consists of 5D₀→7F₁, 7F₀→5L₆, 7F₀→5D₂ energy level transition of Eu³⁺ [34, 35].

Figure 3: TEM images of the calcined samples ((a), low magnification (b), high magnification) with its SAED pattern (c).
precursors). Annealing at 800 \degree \text{C} and the calcined samples are pure cubic phase Gd$_2$O$_3$. The ratio of $\frac{5D_0}{7F_1}$ of the calcined samples (Gd$_2$O$_3$ : Eu$^{3+}$) is much stronger than that of the precursors, confirming that the color purity of Gd$_2$O$_3$ : Eu$^{3+}$ is better than that of Gd(OH)$_3$ : Eu$^{3+}$ for red phosphors. The as-prepared Gd$_2$O$_3$ : Eu$^{3+}$ luminescent nanowires are potentially applied in red-emitting phosphors and field emission display devices. This facile method can be used to synthesize other rare earth oxide luminescence materials.

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\section*{References}


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