Two-step Synthesis of Eu-doped Lu$_2$O$_3$ Ultrathin Nanorods and its Luminescent Property

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Ultrathin Eu-doped lutetium hydroxide oxide (LuOOH:Eu) nanorods with different sizes in diameter about 10 nm have been synthesized for the first time via hydrothermal treatment of colloidal Lu(OH)$_3$:Eu nanoparticles. After calcining, the Eu-doped Lu$_2$O$_3$ nanorods were obtained.

Nanostructured one-dimensional materials, such as nanorods, nanotubes, and nanowires, have attracted worldwide attention because they have potential application in many fields since the discovery of carbon nanotube.[1–3]

Rare-earth oxides are a kind of advanced material and have been widely used as high-performance phosphors, catalysts and other functional materials. If rare-earth oxides were obtained in a nanosized form, they should show more effective functions resulting from nanosize effect. Many rare earth (Sm, Er, Yb, Tm, Dy, Eu, Ho, etc.) hydroxides with various nanosized morphologies have been synthesized via a hydrothermal routine and the corresponding nanostructured rare earth oxides were made by calcining them.[4–8] Here, we report that the Eu-doped lutetium hydroxide oxide (LuOOH:Eu) nanorods are made through treating the colloid solution of Lu(OH)$_3$:Eu under hydrothermal treatment for the first time and the high-quality phosphor with high purity of phase, narrow size distribution and microstructural uniformity was obtained by calcining the LuOOH:Eu nanorods at 600 °C.

The procedure employed here is described as following. The appropriate amount of Lu$_2$O$_3$ and Eu$_2$O$_3$ was dissolved in diluted nitric acid to get the 0.4 M Lu(NO$_3$)$_3$ solution and 0.1 M Eu(NO$_3$)$_3$ solution, respectively. 10% NaOH solution was added into the mixed solution of 25 mL of Lu(NO$_3$)$_3$ solution and 6 mL of Eu(NO$_3$)$_3$ solution under a stirred condition at room temperature. The final pH value of the colloidal solution was maintained at about 13. After stirring for half an hour, the solution was sealed in a 100-mL autoclave then put into an oven at 170 °C for 24 h. The solid product was recovered by filtration, washed with a large amount of deionized water and then anhydrous alcohol, and later dried at 50 °C for 48 h. The Lu$_2$O$_3$:Eu nanorods were made through calcining the LuOOH:Eu nanorods at 600 °C for 2 h in air.

X-ray powder diffraction patterns were collected on a Rigaku D/MAX-γB instrument using Cu Kα ($\lambda = 0.15406$ nm) radiation at 40 kV and 60 mA. The TEM images and HRTEM were obtained on a JEM-2010 transmission electron microscope using an accelerating voltage of 200 kV. The photoluminescence spectrum was recorded on a Shimadzu RF-5301PC spectrofluorophotometer at room temperature.

The XRD pattern of LuOOH:Eu powder synthesized by hydrothermal treatment at 170 °C for 24 h was shown in Figure 1a. All of the reflections could be readily indexed to the monoclinic

phase of LuOOH, the calculated lattice constants $a = 5.811$ nm, $b = 3.551$ nm, $c = 4.239$ nm, and $\beta = 109.45°$ are compatible with the standard values of $a = 5.836$ nm, $b = 3.552$ nm, $c = 4.247$ nm, and $\beta = 109.33°$ (JCPDS 72-0928). Figure 1b shows the XRD pattern of the final Lu$_2$O$_3$:Eu powder calcined at 600 °C for 2 h. All peaks can be indexed to a pure cubic phase of Lu$_2$O$_3$:Eu with lattice constant $a = 1.036$ nm, which is very consistent with the literature value of $a = 1.037$ nm (JCPDS 76-0162). On the basis of the XRD analysis, the final phase Lu$_2$O$_3$:Eu should be the result of high-temperature crystallization and phase transformation of LuOOH:Eu. So, TEM technique was used to give a strong evidence for the transformation.
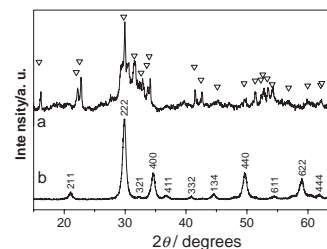

Figure 1. Powder XRD patterns of a) monoclinic LuOOH and b) cubic Lu$_2$O$_3$ nanorods.

Figures 2a and 2b are TEM images of as-synthesized LuOOH:Eu nanorods with narrow size distribution. The rods are close to monodispersed (Figure 2a) and the diameters are 6–10 nm (Figure 2b) and lengths range from 20 nm to 300 nm except for several nanoparticles. As seen in Figure 2b, the obtained LuOOH:Eu nanorods possess very smooth surface. After calcining in air, Lu$_2$O$_3$:Eu nanorods obtained seemly congregate are seen from Figure 2c, but it is easy to observe many nanorods with different lengths. From low magnification of HRTEM of the Lu$_2$O$_3$:Eu nanorods, it can be seen that the diameters are also $\approx$10 nm, but its surface is apparently cruder than the LuOOH:Eu nanorods. And a single Lu$_2$O$_3$:Eu nanorod is built up by several small crystals assembled in one-dimensional order (Figure 2d). It implies that the transformation of the precursor LuOOH:Eu into Lu$_2$O$_3$:Eu made the nanorods flaw, so the Lu$_2$O$_3$:Eu nanorods with knots were formed as clearly seen in Figure 2d. The HRTEM image of the Lu$_2$O$_3$:Eu nanorod can be seen in Figure 2e with the clearly resolved interplanar distance $d_{222} = 0.30$ nm. EDS analysis performed on a single nanorod identified Eu and Lu with an atom ratio of nearly 5.4:100, which is close to the designed atom ratio of 6:100, and the doped Eu^{3+} has gone into the framework of Lu$_2$O$_3$. And no other elements were detected except the carbon and copper peaks from the sample grid.

Photoluminescence (PL) spectrum was used to investigate the photoluminescence of the powder. Figure 3 shows the
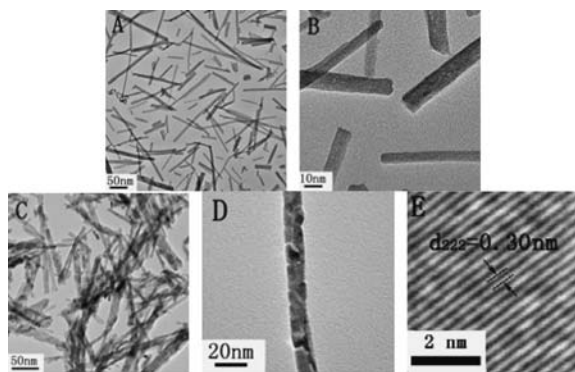
Figure 2. (A) Typical TEM micrographs and (B) low magnification HRTEM image of the LuOOH:Eu nanorods. (C) Representative TEM, (D) low magnification HRTEM, and (E) HRTEM image of the Lu_2O_3:Eu nanorods.
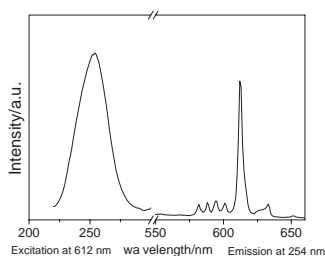

Figure 3. Excitation and emission spectra from Lu_2O_3:Eu nanorods.

excitation spectra (left) and emission spectra (right) of rod-like Lu_2O_3:Eu powder. The excitation spectra (left) and emission spectra (right) are taken at an emission wavelength of 612 nm and an excitation wavelength of 254 nm, respectively. The emission peak at 612 nm is due to the forced electric dipole transition of Eu ($^5D_0 \rightarrow {}^7F_2$).[10] The broad peak on the excitation spectra at ≈ 254 nm is excitation from the ground state of the 4f shell to a Eu–O change-transfer state.[11] From the emission spectra, the ultrathin Lu_2O_3:Eu nanorods shows strong light emission in the red region.

Finally, we discuss the formation mechanisms of the nanorods. Figure 4 shows the TEM micrograph of the colloid before hydrothermal treatment. The precursor $Lu(OH)_3$:Eu is composed of many nanoparticles with irregular morphologies whose sizes are about 10–20 nm and most of them are connected with each other. After hydrothermal treatment, the obtained LuOOH:Eu nanorods with different lengths have smooth surface as shown in Figures 2a and 2b. It can be considered that the formation of LuOOH:Eu nanorods cannot be explained by induced scrolling process[9] which is used to make clear the formation mechanism of one-dimensional nanosized rare-earth compounds. The so small nanoparticles, not sheet, cannot scroll into nanorods with length high to 300 nm. So, we think that the growth of LuOOH:Eu nanorods is through a dissolution–recrystallization-growth process when the colloid solution is hydrothermally treated. It has been reported that lanthanide hydroxides have a strong tendency to form one-dimensional nanostructure in hydrothermal treatment.[8] The precursor $Lu(OH)_3$:Eu was
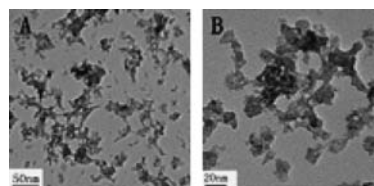

Figure 4. (A) TEM micrographs and (B) low magnification HRTEM image of the $Lu(OH)_3$:Eu precursor before hydrothermal treatment.

dissolved and then Lu^{3+} and Eu^{3+} grew into $Lu(OH)_3$:Eu nanorods in a strongly basic condition under hydrothermal treatment. At the same time, $Lu(OH)_3$ dehydrated to produce LuOOH as affirmed by the result of XRD under hydrothermal treatment at 170°C. The dehydration process is supposed to be: $Lu(OH)_3 \rightarrow$ LuOOH + H_2O. When the hydrothermal treatment was carried out at lower temperature, the obtained powder was crystalline $Lu(OH)_3$ powder, not LuOOH which is only obtained at higher temperature in hydrothermal condition. Further dehydration was carried out by calcination of the LuOOH:Eu powder. The basic principle for dehydration is to make LuOOH which loses water gradually to produce Lu_2O_3, the morphology of which inherits its precursor LuOOH and not to sinter to form massive solid. The calcination temperature was determined by TG-DSC characterization, the result of which shows that the precursor LuOOH was entirely converted to Lu_2O_3 at 600°C (not shown here). The dehydration process of calcination is: 2LuOOH $\rightarrow$ Lu_2O_3 + H_2O.

In summary, by a designed two-step route, Eu-doped Lu_2O_3 nanorods with uniform diameter of ≈ 10 nm and different lengths were successfully synthesized. PL spectra of the Lu_2O_3:Eu nanorods shows light emission in the red region, which may be a kind of highly efficient red phosphor.

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