

Synthesis of Eu_2O_3 Nanotube Arrays through a Facile Sol–Gel Template Approach

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The tubular nanostructure has attracted much attention since the discovery of carbon nanotubes.¹ The potential applications of nanotubes in the electric devices, sensors, and others due to their special physical and chemical properties have been also proposed.² Up to now, some inorganic nanotubes such as sulfides, nitrides, and oxides have been fabricated.^{3–8} Rare earth compounds have been widely used as high-performance luminescent devices, magnets, catalysts, and other functional materials based on the electronic, optical, and chemical characteristics arising from their 4f electrons.⁹ Recently, some rare earth compound nanotubes have been produced by many researchers.^{10–12} Among the rare earth elements, the luminescence of Eu^{3+} is particularly interesting because the major emission band is centered near 612 nm, which is one of the three primary colors. Therefore, Eu^{3+} has been studied intensively as a luminescent activator in many host lattices.¹³ Eu_2O_3 is one of the most important oxide phosphors and has been investigated thoroughly. Eu_2O_3 nanoparticles have been prepared by means of laser evaporation,¹⁴ sol–gel,¹⁵ and colloidal chemistry.¹⁶ However, to the best of our knowledge, no reports on the synthesis of Eu_2O_3 nanotube have been published to date.

Here, the Eu_2O_3 nanotube arrays were prepared successfully by an improved sol–gel method combined with porous anodic alumina templates. In a traditional sol–gel template process, the templates are usually dipped into the relevant sols directly; the only driving force of this technique is capillary action. If a higher-concentration sol is used, filling the pores will be difficult, especially for small-pore diameter templates, but low concentration leads to nanomaterials with serious shrinkage and cracking. In recent years, the sol–gel electrophoresis deposition has been developed to fabricate 1D nanostructures.¹⁷ However, this process is usually very complex and requires special equipment; moreover, some element oxides cannot be obtained by this method because the suitable sols are difficult to prepare and the relative negative redox potentials make electrophoresis deposition impossible in aqueous solution, for example, binary rare earth oxides. In this work, the method used to prepare Eu_2O_3 nanotubes can overcome these limitations to a certain extent.

The porous anodic alumina (PAA) templates used in this work were prepared by a two-step aluminum anodic oxidation process in a 0.3 M oxalic acid solution, which are similar to those described previously.^{18,19} Nitrate of Eu was prepared via dissolved Eu_2O_3 in nitric acid, and urea used in this experiment was A.R. grade. In a typical experiment, an amount of nitrate of Eu was dissolved into deionized water to form a 0.01 M aqueous solution of nitrate, the pH value of the solution was adjusted to near neutral using ammonia, and then urea was added into the solution; the molar ratio of Eu and urea was 1:20. The PAA template was put into a vessel which contained an appropriate amount of the above-mentioned nitrate solution. Then, the temperature of the vessel was kept at 80 °C for 72 h. Subsequently, the PAA template was taken out and put into a tube furnace. The temperature of the tube furnace

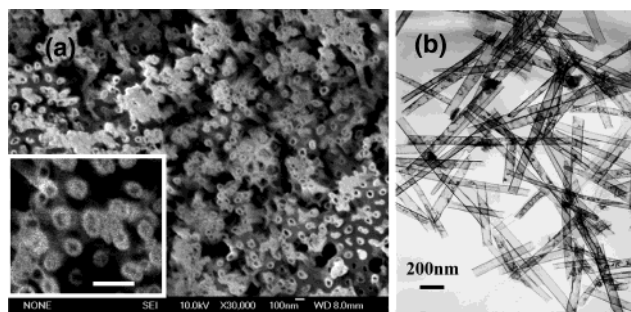


Figure 1. (a) Typical SEM image of Eu_2O_3 nanotube arrays; inset shows the zoom in view of vertical Eu_2O_3 nanotube array with a scale bar of 200 nm. (b) Typical TEM image of the Eu_2O_3 nanotubes.

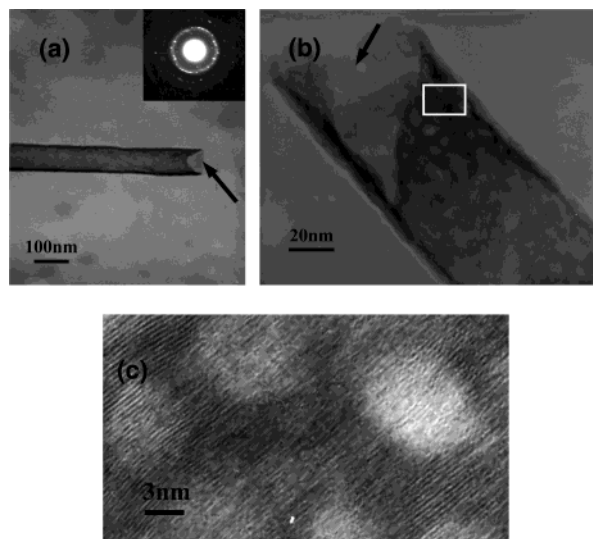


Figure 2. (a) Single Eu_2O_3 nanotube and its SAED pattern (inset). (b) HREM image of a nanotube. (c) HREM image of nanotube indicated in (b).

was increased to 150 °C and kept constantly at this temperature for 1 h, then was increased to 700 °C and kept for 10 h.

The as-synthesized sample was examined by X-ray diffraction (XRD) measurements on a Philips X'pert PRO diffractometer with $\text{Cu K}\alpha$ radiation. The diffraction peaks can be indexed to a cubic-structured Eu_2O_3 phase with a cell constant of $a = 1.085$ nm, which are close to the reported values of the bulk (JCPDS File No. 86-2476).

The morphology of the as-synthesized sample was obtained with field emission electron microscopy (FE-SEM). Figure 1a illustrates the top view image of the Eu_2O_3 nanotube arrays grown within a PAA template. The micrograph shows that the nanotubes are roughly parallel to each other, vertically oriented on the PAA template to form an array, and the outer diameter of these nanotubes is about 50–80 nm, corresponding to the diameter of channels in

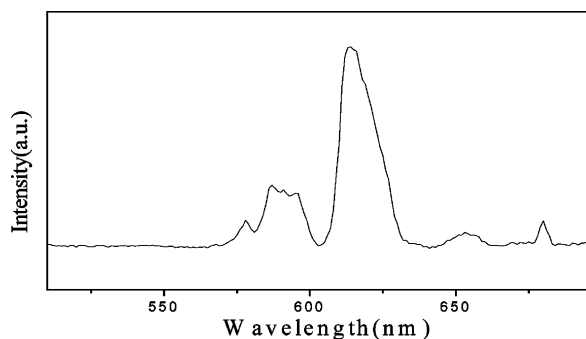
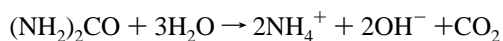


Figure 3. Luminescence spectrum (excitation at 254 nm) of Eu_2O_3 nanotubes at room temperature.

the PAA template. The inset of Figure 1a is a high-magnification FE-SEM image showing clearly the morphology of the vertical nanotube arrays. It is found that almost all the pores in PAA templates are filled with Eu_2O_3 nanotubes. A typical TEM image of Eu_2O_3 nanotubes is depicted in Figure 1b. It can be observed that large-scale Eu_2O_3 nanotubes were produced and that the outer diameters of the Eu_2O_3 nanotubes obtained are about 70 nm with their shapes clearly replicating the pore structure of PAA templates. The thickness of the wall is estimated to be around 5 nm. The image of a single Eu_2O_3 nanotube is shown in Figure 2a. The open end of nanotube can be seen clearly. The inset of Figure 2a presents the selected area electron diffraction (SAED) pattern taken from a single nanotube. While the presence of the ring pattern evidences the formation of polycrystalline Eu_2O_3 , the strong (222) ring indicates that the crystals do have preferred growth orientation. Figure 2b shows a high-resolution electron microscopy (HREM) image of a nanotube. Figure 2c is the enlarged image of the frame in Figure 2b. This image reveals that the nanotube is polycrystalline with interplanar spacing of about 0.319 nm, which corresponds to (222) planes. It can be seen that most of the particles align to the same direction, which is consistent with the SAED image. To further confirm the composition of the as-prepared nanotube, the energy dispersion X-ray (EDX) spectrum was recorded. Eu and O are observed with an estimated atomic ratio of 2:3.

The optical property of the Eu_2O_3 nanotubes was characterized by a fluorescence spectrometer with an excitation wavelength of 254 nm. The strong emission peak at 612 nm, which is due to the forced electric dipole transition (${}^5D_0 \rightarrow {}^7F_2$) can be seen clearly (Figure 3). It indicates that the cubic phase Eu_2O_3 has been produced.²⁰ The peak is obviously broadened compared with that of bulk Eu_2O_3 .

A schematic of the possible formation process of Eu_2O_3 nanotubes is shown in Figure 4. In our experiments, the templates were dipped into the mixed solution containing europium nitrate and urea. Because the viscosity of the solution was lower than that of sol, the solution was easier to fill into the pores of the templates. When the solution was heated, the pH value of the solution rose because of urea undergoing hydrolysis heated at above 60 °C as follows.



The OH^- ions then combined with europium ions to form $\text{Eu}[(\text{OH})_x(\text{H}_2\text{O})_y]$ sol, depending on the solution concentration of

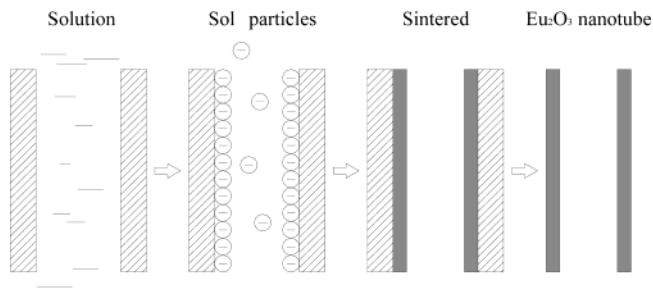


Figure 4. Schematic illustration of the sol-gel template process for making Eu_2O_3 nanotubes.

Eu^{3+} and the pH value. This process took place within the pores and the solution simultaneously. In this experiment, the sol particles were negatively charged; meanwhile, the pore walls of the PAA were positively charged.²¹ Thus, the density of sol particles was larger near the wall of pores, and it was reasonable that the nanotubes first formed near wall areas of the pores and then extended to the center area gradually. Subsequently, the template was taken out of the sol and sintered in a tube furnace. During the sintering process, the sol within the PAA's nanochannels would be changed into gel by the condensation reactions, and the gel was further turned into Eu_2O_3 nanocrystallines.

Acknowledgment. This work was supported by the Ministry of Science and Technology of China (Grant No. 1999064501).

Supporting Information Available: X-ray diffraction pattern of Eu_2O_3 nanotubes; EDX of the single Eu_2O_3 nanotube. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Iijima, S. *Nature* **1991**, *254*, 56.
- (2) Ajayan, P. M. *Chem. Rev.* **1999**, *99*, 1787.
- (3) Feldman, Y.; Wasserman, E.; Srolovitz, D. J.; Tenne, R. *Science* **1995**, *267*, 222.
- (4) Hamilton, E. J. M.; Dolan, S. E.; Mann, C. E.; Colijin, H. O.; McDonald, C. A.; Shore, S. G. *Science* **1993**, *260*, 659.
- (5) Lin, H. P.; Mou, C. Y.; Liu, S. B. *Adv. Mater.* **2000**, *12*, 103.
- (6) Kobayashi, S.; Hanabusa, K.; Hamasaki, N.; Kimura, M.; Shirai, H. *Chem. Mater.* **2000**, *12*, 1523.
- (7) Lakshmi, B. B.; Dorhout, P. K.; Matrin, C. R. *Chem. Mater.* **1997**, *9*, 857.
- (8) Ono, Y.; Nakashima, K.; Sano, M.; Hojo, J.; Shinkai, S. *Chem. Commun.* **1998**, 1477.
- (9) Xu, A. W.; Cao, Y.; Liu, H. Q. *J. Catal.* **2002**, *207*, 151.
- (10) Yada, M.; Mihara, M.; Mouri, S.; Kuroki, M.; Kijima, T. *Adv. Mater.* **2002**, *14*, 309.
- (11) Xu, A. W.; Fang, Y. P.; You, L. P.; Liu, H. Q. *J. Am. Chem. Soc.* **2003**, *125*, 1494.
- (12) Wang, X.; Sun, X. M.; Yu, D. P.; Zou, B. S.; Li, Y. D. *Adv. Mater.* **2003**, *15*, 1442.
- (13) Blasse, G. *Struct. Bonding* **1976**, *26*, 43.
- (14) Eilers, H.; Tissue, B. M. *Chem. Phys. Lett.* **1996**, *251*, 74.
- (15) Patra, A.; Sominska, E.; Ramesh, S.; Koltypin, Y.; Zhong, Z. *J. Phys. Chem. B* **1999**, *103*, 3361.
- (16) Wakefield, G.; Keron, H. A.; Dobson, P. J.; Hutchison, J. L. **1999**, *215*, 179.
- (17) Steven, J.; Cao, G. *Zh. Adv. Mater.* **2003**, *15*, 427.
- (18) Li, A. P.; Muller, F.; Birner, A.; Nielsch, K.; Gosele, U. *Adv. Mater.* **1999**, *11*, 483.
- (19) Masuda, H.; Yamada, H.; Satoh, M.; Asoh, H.; Nakao, M.; Tamamura, T. *Appl. Phys. Lett.* **1997**, *71*, 2270.
- (20) Carnell, W. T. *Handbook on the Physics and Chemistry of Rare Earths*; North-Holland Publishing Company: Amsterdam, 1979; Vol. 3, p 171.
- (21) Diggle, J. W.; Downie, T. C.; Goulding, C. W. *Chem. Rev.* **1969**, *69*, 365.

JA039012L