Large-scale Synthesis of Luminescent Y_2O_3:Eu Nanobelts

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A two-step method was developed for the large-scale synthesis of luminescent Y_2O_3:Eu nanobelts. The structure and composition of the as-prepared Y_2O_3:Eu were characterized by XRD, TEM, and EDX. The luminescent performance of the nanobelts was also characterized and the result was different from that of the other Y_2O_3:Eu materials observed before.

Nanostructured materials have received much attention because of their novel properties which differ from those of bulk materials. There has been great interest in controlling the shapes of materials and in finding novel properties. In the past ten years, many one dimensional (1D) nanotubes[1,2] and nanowires[3,4] have been extensively investigated owing to their distinguished properties. Recently nanobelts, a new kind of nanoblock, which was distinctive from nanowires, have attracted extensive interest for their promising applications in building nanodevices, nanosensors, and functional nanomaterials.[5] Eever since, many nanobelts, such as ZnO,[5,6] SnO_2,[7] PbO,[8] Ge_3N_4,[9] GaN,[10] Zn,[11] etc. have been synthesized by the high-temperature method. Li and his coworkers also developed a novel hydrothermal method to synthesize sodium and potassium titanate[12] and MoO_3[13] nanobelts in rather low temperature. However, the exploration for the belt-like nanostructures and the application are still limited. Here we reported a new functional oxide nanobelts, Y_2O_3:Eu synthesized in large-scale by a two-step method.

Rare earth compounds have been extensively applied to high-performance magnets, luminescence devices, catalysts, and other functional materials. Recently, Li and his coworkers reported a hydrothermal method to synthesize a series of lanthanide hydroxide nanowires.[14] Because of the similarity of the properties between Y and lanthanide, we also could develop the hydrothermal method to synthesize $Y(OH)_3$ and its derivatives in theory. Among the derivatives of the $Y(OH)_3$, Y_2O_3 is one of the most important functional materials. When doped with one or several trivalent-rare-earth ions, such as Eu^{3+}, Tm^{3+}, Ho^{3+}, Yb^{3+}, Er^{3+}, etc.,[15–19] it could have some attractive luminescent[15–17] or upconversion luminescent[18,19] performance. In this paper, we successfully synthesized $Y_4O(OH)_9(NO_3)$:Eu nanobelts as precursor by hydrothermal method and then converted it into Y_2O_3:Eu with the nanobelt structure by calcination. We also studied the luminescent properties of the as-prepared Y_2O_3:Eu nanobelts.

In order to obtain Y_2O_3:5% Eu, the typical synthesis procedure is as follows. 0.678 g of Y_2O_3 powder (3.00 mmol, purity: 99.99%) and 0.0556 g Eu_2O_3 (0.158 mmol, purity: 99.99%) were dissolved in concentrated nitric acid. Then rapidly adjusted the solution to pH = 10 using 40% KOH solution, and a large amount of white amorphous precipitate appeared immediately. After stirring for about 10 min, the precipitate was then transferred into a Teflon-lined autoclave of 50-mL capacity which was filled with deionized water up to 60% of the total volume. The autoclave was sealed into a stainless steel tank and kept at 160 °C for 24 h, and then cooled to room temperature naturally. The resulting products were collected and washed with water and dried at 50 °C in air. Then the as-prepared precursor was converted to Y_2O_3 nanobelts in air at 500 °C for 6 h.

The precursor and the final product were both examined by X-ray diffraction (XRD) using a Bruker D8-advance X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). Figure 1a shows the XRD pattern of the precursor. All the reflections can be readily indexed as a pure monocline phase [space group: $P2_1$] of $Y_4O(OH)_9(NO_3)$ with lattice constants $a = 9.376$ Å, $b = 16.37$ Å, $c = 3.623$ Å, identical to the reported data in the JCPDS cards (79-1352). The amount of Eu was hardly examined. This result was a little different from the previous work[14] in which the corresponding hydroxide nanowires were often obtained in hydrothermal condition. In this case, $Y(OH)_3$ reacted with nitrate ion in the hydrothermal progress and formed certain nitrate hydroxide. This may be explained by the differences in ionic radii of their trivalent forms responsible for their coordination numbers and basicities.[16] After calcination, the precursor could be completely transformed into Y_2O_3. The XRD pattern is shown in Figure 1b. All of the peaks can be indexed as a pure cubic phase [space group: $I2_13$] of Y_2O_3 with lattice constants $a = 10.60$ Å (JCPDS 76-0151).

The morphologies and structure of the prepared products were further examined with transmission electron microscopy [TEM, Hitachi (Tokyo, Japan) H-800]. Figure 2a reveals almost entirely the belt structure of the $Y_4O(OH)_9(NO_3)$:Eu product with a width of 150–350 nm and a length of 6–8 μm. The width-to-thickness ratio is 5 to 15. After calcination, the nanobelts morphology was still maintained in the product Y_2O_3:Eu which is shown in Figure 2b. And the Y_2O_3 was quite the same with $Y_4O(OH)_9(NO_3)$ in length, width and thickness. This phe-

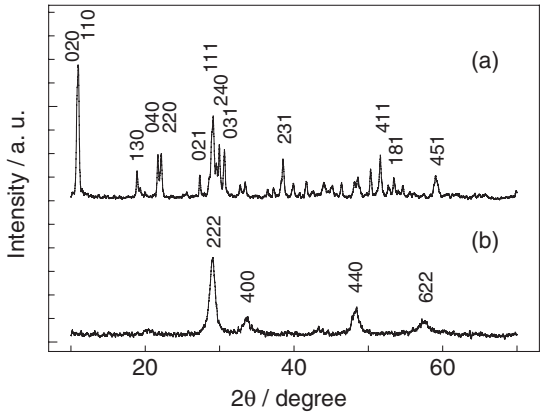

Figure 1. XRD patterns of the products (a) $Y_4O(OH)_9(NO_3)$:Eu, (b) Y_2O_3:Eu.

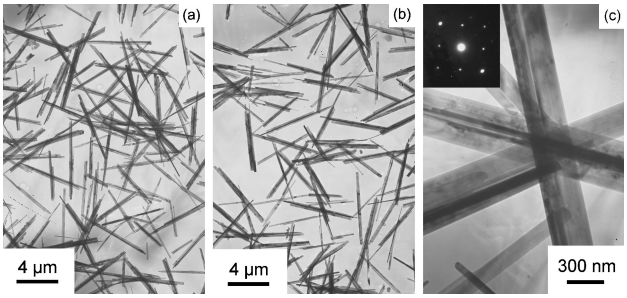

Figure 2. (a) TEM image of as-prepared $Y_4O(OH)_9(NO_3)$:Eu precursor; (b) TEM image of as-prepared Y_2O_3:Eu nanobelts; (c) Enlarged TEM image of Y_2O_3:Eu nanobelts.

nomenon was attributed to the shape memory effect.[20] Figure 2c shows the enlarged image of Y_2O_3:Eu nanobelts which are thin and overlap in part with each other. The inset shows the ED (Electron Diffraction) pattern of the product which reveals the single crystalline structure. Energy dispersive X-ray analysis (EDXA) indicates that only the elements Y and Eu are detected (except the peaks arising from Cu grid), just as Figure 3 shows. The Y/Eu ratio was evaluated to be about 19:1 in everywhere in the nanobelts after calcination. This reveals that Eu was uniformly distributed in the products. The EDXA result of the product before calcination was quite the same. It is reasonable that Eu has the similar property and trivalence in its oxide with Y, so they could grow uniformly with each other in the hydrothermal process.

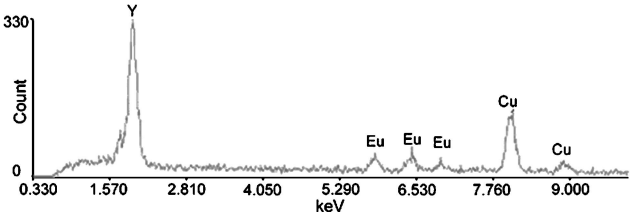

Figure 3. Typical EDXA spectrum of the nanobelts after calcinations.

Figure 4 presents the room-temperature luminescent spectrum of the as-prepared Y_2O_3:Eu nanobelts, excited at 253 nm. The peak at 610 nm is due to the forced electric dipole transition ($^5D_0$–$^7F_2$), which is allowed on condition that the Eu^{3+} ion occupies a site without an inverse center. The broad peak near 590 nm derives from the allowed magnetic dipole transition ($^5D_0$–$^7F_1$). And the peak near 625 nm hasn't been detected in the luminescent spectra of neither the nanoparticle[15,17] nor the nanotube[16] structures. In addition, the whole spectrum is quite different from them. This is probably due to the nanobelt structure, in which the Eu^{3+} occupies the different site in the cubic yttria.[16] The luminescent spectrum also indicates that the Eu^{3+} ions have been effectively distributed into the yttria materials. So we can predicted that other trivalent-rare-earth ions, such as Tm^{3+}, Yb^{3+}, Er^{3+}, can be used to realize the upconversion luminescent properties[18,19] as well by this method. This part of work is still in progress.

In summary, we successfully synthesized luminescent Y_2O_3:Eu nanobelts by a two-step method which includes the hydrothermal and calcination processes. This is a new way to obtain doped Y_2O_3 and its derivatives with nanobelt structure.

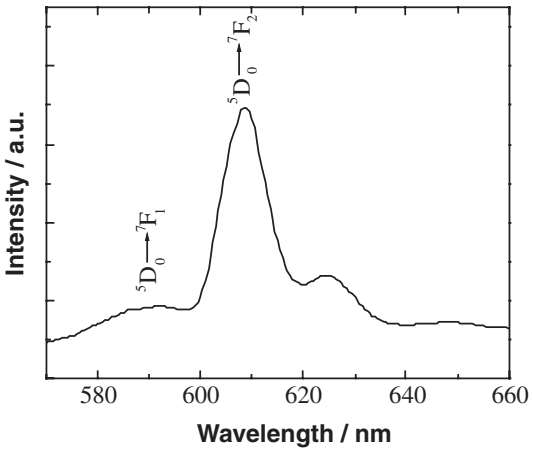

Figure 4. Emission spectrum of Y_2O_3:Eu nanobelts, excited at 253 nm.

By studying the luminescent spectrum of the as-prepared Y_2O_3:Eu, we found that the nanobelt structure affects the luminescent performance greatly.

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