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Preparation and Optical Properties of ThO$_2$ and Eu-Doped ThO$_2$ Nanotubes by the Sol–Gel Method Combined with Porous Anodic Aluminum Oxide Template

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In this paper, we report the synthesis of thorium oxide and Eu-doped thorium oxide nanotubes for the first time using the sol–gel method in porous anodic aluminum oxide template. Transmission electron microscopy, X-ray diffraction, and X-ray photoelectron spectroscopy were applied to characterize the morphology and structure of the as-prepared nanotubes. It has been demonstrated that Eu$^{3+}$ ions were homogeneously doped into the ThO$_2$ crystal lattice. The optical properties resulting from Eu-doped products were investigated by means of photoluminescence spectroscopy. Strong visible light emissions were observed at low doping concentration, and the luminescent intensity decreased at high doping concentration. The luminescent centers were concluded to be the Eu$^{3+}$ ions in the cubic ($O_h$) sites rather than the $C_{3v}$ sites, which accounted well for the decrease of luminescent intensity at high doping concentration.

1. Introduction

Nanostructured materials have been intensively studied for the past decade because of their unique properties and the potential to tailor these properties toward specific applications. Among the kinds of nanostructures, hollow nanostructures attract increasing attention due to potential applications in many areas such as small containers for encapsulation and host materials for loading catalysts, etc. With the development of nanoscience and nanotechnology, various synthetic techniques have been developed to prepare hollow nanostructured materials, including template-assisted methods and template-free methods. Among these methods, the porous anodic aluminum oxide (AAO), a well-known hard template, plays an important role in the preparation of one-dimensional nanotubes and their arrays. Meanwhile, sol–gel method has many unique advantages in the preparation of nanomaterials, such as high purity and easy to control synthesis procedures and components. Herein, we combine the sol–gel and AAO template methods for a simple preparation of thorium dioxide (ThO$_2$) and Eu-doped ThO$_2$ nanotubes.

ThO$_2$ is a new and important material used in ceramics, sensors, catalysts, and electrodes. Although there are many studies on the separation and preparation of ThO$_2$ grains, few papers have been concerned with the preparation and properties of nanostructured thorium oxide. Especially, synthesis of ThO$_2$ nanotubes or nanowires has not yet been reported to our knowledge. Furthermore, there has been an increasing interest in rare-earth (RE)-doped materials for their potential application in photonics and optoelectronics.

In particular, the luminescence of Eu$^{3+}$ is fascinating because the major emission band is centered near 612 nm, which is one of the three primary colors. In this paper, we reported an AAO template-assisted sol–gel method to prepare high-yield ThO$_2$ nanotubes. Eu$^{3+}$ ions were successfully doped into ThO$_2$ nanotubes by introducing Eu$_2$O$_3$ powder during the preparation process. The optical properties resulting from Eu-doping were investigated by means of the photoluminescence spectroscopy.

2. Experimental Section

The AAO templates were prepared using a one-step anodizing process as reported in our previous paper. After preparation of the porous AAO film, the pores of AAO were widened to about 80 nm by dipping the AAO film into 5% phosphoric acid solution for a half-hour at room temperature. Then, the AAO template was rinsed with distilled water and kept in a desiccator under low pressure for more than 8 h in order to drive out the gases trapped inside the pores. The pore depth of the AAO templates was about 20 μm.

ThO$_2$ and Eu-doped nanotubes were synthesized via an AAO template-assisted sol–gel method. The thorium nitrate and europium oxide powder (totally about 1.0 g) with proper proportions (the atomic mole ratios between thorium and europium are about 1.0:0, 1.0:0.1, 1.0:0.3, 1.0:0.6, 1.0:1.0, and 1.0:1.2, respectively) were dissolved by adding nitric acid (60 wt %) in 50 mL of distilled water, and the resulting mixture was stirred in a water bath of 100 °C until a white sol was obtained. The pH value of the resulting sol is about 2–3. The AAO templates were immersed into the sol for 2 h under relative vacuum ambiance. The AAO templates were then placed in a furnace and heated to 500 °C within 20 min. The AAO templates were kept at 500 °C for 2 h and then cooled to room temperature...
photoelectron spectroscopy (XPS) analyses were performed on the source, and the excited wavelength was 250 nm. The X-ray (F-4500) using a Xenon discharge lamp as the excitation light spectra were measured by a photoluminescence spectrometer. The fluorescence using Cu Kα radiation, TEM (Hitachi H600), and high-resolution TEM (HRTEM, TECNAI F-30). The morphology and structure of final products were characterized by X-ray powder diffraction (XRD, Panalytical X-pert) using Cu Kα radiation, TEM (Hitachi H600), and high-resolution TEM (HRTEM, TECNAI F-30). The fluorescence spectra were measured by a photoluminescence spectrometer (F-4500) using a Xenon discharge lamp as the excitation light source, and the excited wavelength was 250 nm. The X-ray photoelectron spectroscopy (XPS) analyses were performed on a PHI quantum 2000 scanning ESCA microprobe equipped with an Al Kα monochromatic X-ray source.

3. Results and Discussion

3.1. Structure Characterization of ThO₂ and Eu-Doped ThO₂ Nanotubes. The AAO templates used in the experiment have an average pore diameter of 80 nm and a thickness of about 20 μm. Since previous reports showed that large quantities of alumina nanotubes/nanowires were obtainable by etching porous AAO templates in an aqueous NaOH solution at room temperature,27 special attention should be paid not to mistake alumina nanotubes for the as-prepared nanotubes. To ensure all the aluminum oxide is dissolved, a high concentration of NaOH solution (4 M) was used to dissolve the corresponding AAO templates and the dissolving time was kept long enough (usually more than 10 h). Figure 1a shows a typical TEM image of as-prepared products without Eu³⁺-doping. It can be seen that the final products consist of one-dimensional nanotubes.

The nanotubes are straight and have a uniform diameter of about 80 nm, which basically equals the pore size of the AAO template employed. The size and the morphology of the nanotubes do not change with the time for dissolving the AAO template, showing that the high concentration NaOH solutions do not affect the as-prepared nanotubes. It is also testified that the diameter of as-prepared nanotubes can be adjusted by choosing AAO templates with different pore size, indicating that the diameters of nanotubes are confined by the AAO pores during their growth. The lengths of these nanotubes are shorter than the pore depth of the AAO templates because the nanotubes are easily broken into short tubes during the ultrasonic dispersion process. At the same time, some bamboo-like nanotubes are observed in the product, as shown in Figure 2b. It is clearly found that the contrast of the nanotubes varied periodically along the long axes of the nanotubes. It should be pointed out that the morphologies have no obvious difference between undoped nanotubes and Eu³⁺-doped samples with relatively low doping concentrations (such as the case in which the atomic mole proportion between thorium and europium is below 1.0:1.0).

When the doping concentration was too high (for example, the atomic mole proportion between thorium and europium is 1.0:1.2), many irregular nanorods were observed. Figure 1c is a magnified TEM image of the nanotubes, showing that the wall thickness of the nanotubes is about 8 nm. The selected area electron diffractions (SAED) of the nanotubes display a set of diffraction rings (see inset of Figure 1c), revealing that the nanotube is polycrystalline. According to the electron diffraction formula, the diffraction circles can be indexed as the diffractions from a cubic structure of thorium oxide. The HRTEM image taken from the wall of a nanotube confirms the polycrystalline nature of the nanotube, where the crystallite size is about 3–5 nm, as shown in Figure 1d. The lattice fringes in the HRTEM image are spaced 0.32 nm apart, which corresponds to the d value of (111) planes of the cubic thorium oxide (JCPDS No. 42-1462).

The typical XRD pattern of undoped ThO₂ nanotubes is shown in Figure 2a, in which all peaks are consistent with those of a cubic phase ThO₂ (JCPDS No. 42-1462). The relatively broadened diffraction peaks reveal that the nanotubes are composed of small nanoparticles. According to the Scherrer formula, the average diameter of the crystallites is estimated to be 4 nm. This result is in good agreement with the HRTEM observations.

It has been mentioned that the morphologies of the Eu-doped nanotubes have no obvious difference from that of the undoped ThO₂ nanotubes. To get deep insight into the structure of the Eu-doped nanotubes, the X-ray diffraction was carried out for...
ThO$_2$ and Eu-Doped ThO$_2$ Nanotubes


Figure 3. XPS spectra of (a) Th 4f and (b) Eu 3d as a function of Eu$^{3+}$ concentration in Eu-doped ThO$_2$ nanotubes.

TABLE 1: Lattice Constants $a$ (nm) of Eu-Doped ThO$_2$ Nanostructures

<table>
<thead>
<tr>
<th>Th$^{4+}$:Eu$^{3+}$</th>
<th>$a$ value (nm)</th>
<th>Th$^{4+}$:Eu$^{3+}$</th>
<th>$a$ value (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0:0</td>
<td>0.5596 ± 0.0001</td>
<td>1.0:1.0</td>
<td>0.5586 ± 0.0003</td>
</tr>
<tr>
<td>1.0:0.1</td>
<td>0.5595 ± 0.0002</td>
<td>1.0:1.2</td>
<td>0.5574 ± 0.0002</td>
</tr>
<tr>
<td>1.0:0.3</td>
<td>0.5591 ± 0.0002</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

...a serial of Eu$^{3+}$-doped ThO$_2$ samples with different doping concentrations (Figure 2b–e). It can be found that no additional crystal phase was observed after introducing Eu$^{3+}$, and all Eu-doped samples keep the same crystal phase as that of ThO$_2$. The results imply that the Eu$^{3+}$ ions were homogeneously doped into the ThO$_2$ crystal lattice. Because the ionic radius of Eu$^{3+}$ (0.095 nm) is smaller than that of Th$^{4+}$ (0.104 nm), the replacement of Th$^{4+}$ with Eu$^{3+}$ results in the contraction of the crystal lattice. From the XRD patterns, the trend of the diffraction angles slightly shifting to high angle with the increase of the doping amount of Eu$^{3+}$ is well-consistent with the hypothesis of lattice constant contraction after doping Eu$^{3+}$. Table 1 summarizes the crystal lattice parameters calculated from the XRD patterns for the Eu-doped products with different doping concentrations. The results show the decrease of crystal lattice parameters with the increase of Eu$^{3+}$ concentration.

The doping of Eu$^{3+}$ has further been checked by XPS, which is known to probe the elemental information of the surface of the materials. Parts a and b of Figure 3 respectively show the XPS spectra of the Th 4f region and the Eu 3d region of the ThO$_2$ nanotubes with different Eu$^{3+}$ doping concentration. On the basis of the *Handbook of X-ray Photoelectron Spectroscopy*, we assign the peaks around 334.4 and 343.1 eV to the binding energies of Th 4f and the peak around 1134.0 eV to that of Eu 3d. It can be seen that the intensities of the Th 4f peaks decrease and those of Eu 3d increase with the increase of the Eu$^{3+}$ concentration, confirming the successful doping of Eu$^{3+}$. Furthermore, with the increase of Eu-doping, the apexes of the Th 4f peaks shift to low binding energy, which could be due to replacement of the quadrivalence Th$^{4+}$ by trivalence Eu$^{3+}$.

It is well-known that the sol–gel method is based on the hydrolysis and condensation of precursor solution such as organic metal alkoxides in organic solvents or inorganic salts in aqueous media. The biggest advantage of this sol–gel method is that the constituent materials can be easily homogeneously mixed at the molecular level by means of properly controlling the hydrolysis and condensation process. Therefore the sol–gel method can be an effective and versatile method for the preparation of homogeneous multicomponent materials. The successful doping of Eu$^{3+}$ ions in the ThO$_2$ lattices at a wide doping concentration range in our experiments shows such a universality of the sol–gel method.

In recent years, the hard synthetic templates bring new opportunity for the preparation of one-dimensional (1D) mono-component and multicomponent nanostructures such as nanowires/nanotubes. Especially, porous AAO template plays an increasingly important role in the synthetic field of 1D nanostructures and their arrays due to its size-limiting effect and the high order of the pores. Combined with the sol–gel method, numerous monocomponent and multicomponent nanostructures have been successfully prepared by using porous AAO template.

The successful examples of high-yield and well-shaped nanotubes are seldom reported. During the preparation of the sol in our experiment, we simply use metallic nitrate. Although the detail mechanism of the nanotube formation by our method is still unknown, the as-prepared gels could tend to heterogeneously adsorb and nucleate on active sites on the AAO pore walls and thus form a tubular structure. By means of the analogous method, we have also succeeded in obtaining a series of rare-earth metal oxide nanotubes from rare-earth metal nitrate recently. Therefore, our proposed porous AAO template assisted sol–gel method could be a versatile method and has potential application in the preparation of the polycrystalline nanotubes.

3.2. Optical Properties of ThO$_2$ and Eu-Doped ThO$_2$ Nanotubes. Figure 4 shows the room-temperature photoluminescence spectra from the original ThO$_2$ nanotubes, Eu$_2$O$_3$ powder, and Eu-doped ThO$_2$ nanotubes (atomic ratio of 1.0:0.1 between Th$^{4+}$ and Eu$^{3+}$ ions) under excitation at 250 nm, respectively. We divide the spectra into 300–480 nm (left) and 530–700 nm (right), as a very high second-order line appears at about 500 nm. It can be seen that there is no strong emission peak in the wave range of visible light for the pure ThO$_2$ nanotubes and the Eu$_2$O$_3$ powder. However, the emission spectrum shows several very strong peaks located at 590, 610, and 626 nm for the Eu-doped nanotubes in the case of the atomic ratio of 1.0:0.1 between Th$^{4+}$ and Eu$^{3+}$ ions. Clearly, the
formed for the charge compensation after doping the Eu$^3^+$ ions are in the displays. The luminescence center of Eu$^3^+$ symmetry. It is reasonable to suppose that Eu$^3^+$ ions in the cubic ($O_h$) sites. At low concentration, the doped Eu$^{3+}$ ions predominantly occupy the cubic sites ($O_h$ symmetry), and the intensities of the luminescent peaks increase with the doping density. While the doping concentration further increases, the Eu$^{3+}$ ions occupy the $C_{3v}$ sites and the Eu$^{3+}$ ions in cubic sites decrease. Therefore, these three strong luminescent peaks decrease at high doping concentration. In the pure Eu$_2$O$_3$ powder, there is no Eu$^{3+}$ ion in cubic ($O_h$) sites, and thus the three emission lines cannot be observed.

4. Summary

In summary, both pure and Eu-doped ThO$_2$ nanotubes have been successfully fabricated by sol–gel method with the assistance of porous AAO templates. The Eu-doped ThO$_2$ nanotubes adopt the same cubic structure as that of ThO$_2$. The walls of the nanotubes are polycrystalline and their crystallite size is about 3–5 nm. Combining XRD and XPS measurements, we confirm the Eu$^{3+}$ ion has been successfully doped into ThO$_2$. Photoluminescence properties of Eu-doped in ThO$_2$ nanotubes are also studied, which shows strong visible light emission occurs at low concentration doping, and the luminescence intensity decreases at high concentration doping. The Eu$^{3+}$ ions in the cubic ($O_h$) sites are thought to be the luminescent center in the Eu-doped ThO$_2$ nanotubes, which can well account for the decrease of luminescent intensity at high doping concentration.

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References and Notes


Figure 5. Room-temperature fluorescence emission spectra as a function of Eu$^{3+}$ concentration in Eu-doped ThO$_2$ nanotubes.
ThO₂ and Eu-Doped ThO₂ Nanotubes