Highly Reducible CeO$_2$ Nanotubes
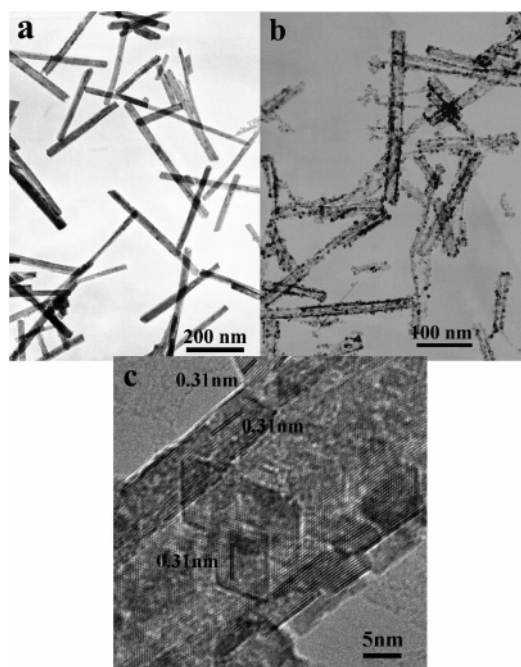
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Fluorite-structured ceria (CeO$_2$) has proved to be a material of exceptional technological importance because of its unique properties and is being extensively used for preparing catalysts, fuel cells, solar cells, UV blocks, and polishing materials.[1] Stimulated by both the promising applications and the fantastic properties, much attention has been directed to the controlled synthesis of CeO$_2$ nanostructured materials. Over the past few years, remarkable process has been made in the synthesis of nanosized ceria with different morphologies and the investigation of their size/shape-dependent properties. Nanospheres, nanorods, nanowires, and nanocubes of CeO$_2$ have been prepared by us and other research groups.[1a,2]

Since the discovery of carbon nanotubes by Iijima,[3] one-dimensional (1D) tubular nanostructures have been the subject of considerable research. Up to now, several strategies have been demonstrated to process a broad range of materials into nanotubes, such as arc discharge, chemical vapor deposition, template-directed synthesis, and hydrothermal treatment.[4] However, the synthesis of nanotubes of CeO$_2$ is difficult because of its unique structural characteristics. Most recently, Han et al.[5] reported the production of ceria nanotubes via a two-step procedure: precipitation at 100 °C and aging at 0 °C for 45 days. Tang et al.[6] also reported layer-structured rolling Ce(OH)$_3$ nanotubes through an alkali thermal-treatment process under oxygen-free conditions and ceria nanotubes by annealing Ce(OH)$_3$ in a reducing atmosphere. However, these methods either were time-consuming

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Figure 1. (a) TEM image of the newly prepared 1D Ce(OH)$_3$. (b) TEM image of the CeO$_2$ nanotubes synthesized via the oxidation−coordination-assisted dissolution process. (c) High-resolution TEM images of the CeO$_2$ nanotubes.

or required special equipment; moreover, the cavities of the obtained ceria nanotubes were quite small, and there were also a great deal of rod-like concomitant in the products. There is still a lack of effective methods for production of high-quality ceria nanotubes in terms of yield, uniformity, large cavities, and thin walls, as well as control over dimension.

Herein, we report a facile rational synthesis of CeO$_2$ nanotubes with large cavities and thin walls by a simple oxidation−coordination-assisted dissolution process of the Ce(OH)$_3$ nanotubes/nanorods. The redox property of the ceria nanotubes for application in catalysis was further investigated, and excellent reducibility of these materials has been demonstrated.

Cerium hydroxide could be synthesized by hydrothermal treatment of Ce$_2$(SO$_4$)$_3$·9H$_2$O with a 10 M NaOH solution at 130 °C. All the Ce(OH)$_3$ synthesized displays 1D structures, and most of them own nanotube-like morphology. As shown in Figure 1a, a typical transmission electron microscopy (TEM) image of the products shows diameter of 15−25 nm and lengths of up several hundreds of nanometers. The TEM images also reveal that some rod-like structure can be found.
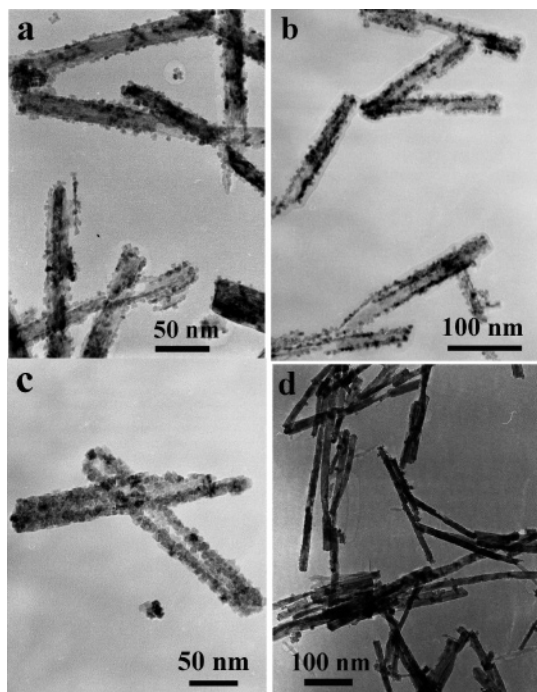
Although most of the 1D Ce(OH)$_3$ possesses the tubular structure, the cavities of the nanotubes are quite narrow. Therefore extending the cavities is of technical importance for practical applications, for example, catalysis. A simple method was designed to realize this purpose. CeO$_2$ nanotubes with larger cavities could be prepared by treating the partially oxidized Ce(OH)$_3$ nanotubes/nanorods with H$_2$O$_2$ under ultrasonic conditions. First, the newly prepared 1D Ce(OH)$_3$
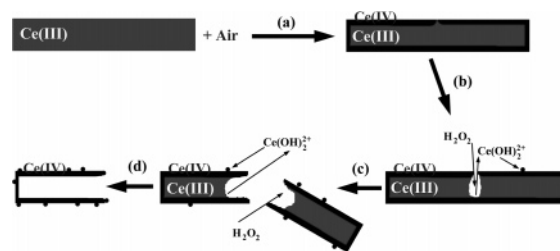
Figure 2. (a–c) TEM images of the products at different reaction stages: (a) $t = 30$ min; (b) $t = 60$ min; and (c) $t = 90$ min. (d) TEM images of the products when the newly as-prepared 1D Ce(OH)$_3$ were used as the starting materials.

Figure 3. Schematic illustration summarizing all the major morphological changes involved in the synthesis of ceria nanotubes by oxidation complex dissolution reaction: (a) formation of a ceria layer on the surface of the Ce(OH)$_3$ nanotubes/nanorods through partial oxidation by air. (b) Pitting at a specific site on the surface of the 1D nanostructure, oxidation of Ce(III) inside by H$_2$O$_2$, formation of Ce(OH)$_2{}^{2+}$ that migrated outside, and formation of ceria nanoparticles on the surface. (c) Formation of hollow structures after further etching of the interior of the 1D nanostructure and breaking into shorter ones. (d) Formation of a completely empty ceria nanotube.

was exposed in the air at room temperature for 24 h to partially oxidize the Ce(OH)$_3$; then, the partially oxidized Ce(OH)$_3$ nanotubes were dispersed in the distilled water and treated under ultrasonic for 2 h after appropriate 15% H$_2$O$_2$ was added.

The X-ray diffraction (XRD) analysis reveals that all the peaks of the products can be readily indexed to a pure cubic phase [space group: *Fm3m* (No. 225)] of CeO$_2$ (JCPDS 34-0394). The size and morphology of the as-synthesized products were examined by TEM. As shown in Figure 1b, a typical TEM image of CeO$_2$ nanotubes displays the outer diameter of about 15–25 nm and lengths of about 100 nms with open ends, and there are many nanoparticles with the size about 8 nm attached on the walls. The thickness of the wall is about 5–7 nm, and the inner diameters of the nanotubes are about 10–15 nm, which are much larger than those of previously reported (about 5 nm).[5] A high-resolution TEM image (Figure 1c) reveals that the nanotube is of good crystallinity and the existence of defects can be discerned. The octahedral nanoparticles on the wall are all of ceria phases.

TEM was used to follow the morphological and structural changes and their growth mechanism involved in various stages of the formation process (Figure 2a–c). The product obtained after 30 min (Figure 2a) shows that some nanotubes have been broken, and the cleaning of the cerium compounds from the cavities begins. As the process was prolonged to 60 min, the cavities were further enlarged and the nanotubes became shorter (Figure 2b). After 90 min treatment, the product consists predominantly of nanotubes that are completely hollow, and some walls of the nanotubes are broken into several pieces of slender rods (Figure 2c).

To further clarify the mechanism, we carried out two additional comparative experiments, which was similar to

the process used to prepare the ceria nanotubes except for some modifications. First, the newly as-prepared 1D Ce(OH)$_3$ were used as the starting materials instead of the partially oxidized ones, and most of the resulting products were not nanotubes but rod-like ceria with the decrescent diameter (Figure 2d). Second, H$_2$O$_2$ was not introduced to the system, and almost no morphological and structural changes could be discerned with respect to the starting partially oxidized Ce(OH)$_3$ nanostructures. Therefore, both H$_2$O$_2$ and partial oxidation of the Ce(OH)$_3$ are essential to the ceria tubular structure formation. The H$_2$O$_2$ here acts as oxidant for Ce^{3+}. The Ce^{3+} ions present in the Ce(OH)$_3$ nanotubes can be converted to a Ce^{4+} complex (Ce(OH)$_2{}^{2+}$) by hydroxyl free radicals in the hydrogen peroxide solution:[7]

$$2Ce^{3+}(s) + 2OH^- + H_2O_2 \rightarrow 2Ce(OH)_2{}^{2+}(aq) \qquad (1)$$
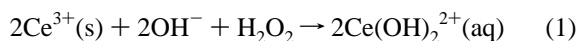
thus, the Ce(OH)$_2{}^{2+}$ transfer into the solution. As the concentration of the Ce(OH)$_2{}^{2+}$ increased, ceria can be formed easily under the following reaction:

$$Ce(OH)_2{}^{2+}(aq) + 2OH^- \rightarrow CeO_2(s) + 2H_2O \qquad (2)$$
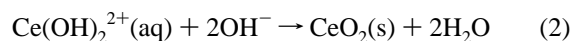
Therefore, an oxidation–coordination-assisted dissolution was involved during the whole process. When the newly as-prepared Ce(OH)$_3$ were used as the starting materials, the above oxidation complex dissolution reaction occurred directly at the outer wall of the Ce(OH)$_3$ nanostructures, and slender rod-like ceria could be formed. In the case of the partially oxidized Ce(OH)$_3$, since most of the outer wall had been oxidized into ceria, the oxidation–coordination-assisted dissolution process was limited inside the 1D nanomaterials; thus, the ceria nanotubes with extended cavities formed finally. The formation mechanism of the ceria nanotubes is depicted in Figure 3.

The large cavities and thin walls indicate the ceria nanotubes may be served as excellent catalytic materials. In redox catalysis, the role of ceria is usually to act as an oxygen transferring component.[8] The oxygen storage capacity (OSC)

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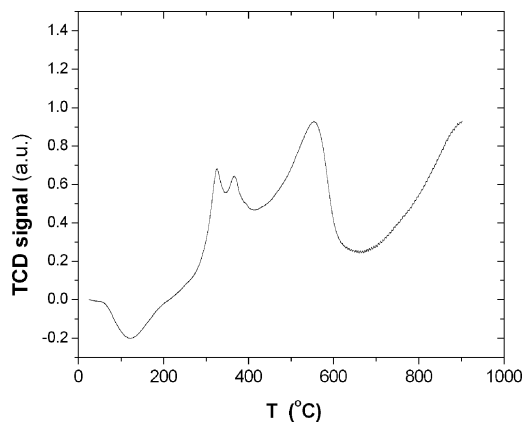
Figure 4. TPR profiles of the ceria nanotubes. The negative peak at about 120 °C is attributed to the desorption of the hydrogen.

and the reducibility are important characteristics to determine its catalytic properties. Temperature-programmed reduction (TPR) by H_2 was used to measure these characteristics. The ceria nanotubes exhibit a broad low-temperature reduction profile from 200 °C to 650 °C and a high-temperature reduction peak above 700 °C (Figure 4). The area under the low-temperature peak is of particular interest since the oxygen contributing to the low-temperature reduction peak is the most readily available during catalytic operation.[9]

Quantitative evaluation of the low-temperature reduction peak (below 650 °C, representation for OSC) reveals that hydrogen consumed by ceria nanotubes is 758 μmol H_2/g (ceria), which is about 4 to 5 times higher than the conventional ceria materials (the value is about 150−200 μmol H_2/g (ceria)).[2b] This indicates the ceria nanotubes are much more reducible and active than the conventional ceria materials. The novel properties exhibited by this novel nanomaterial lead us to believe that ceria nanotubes will find wide application in catalytic fields.

In summary, ceria nanotubes with extended cavities can be obtained by a facile oxidation−coordination-assisted dissolution process of their hydroxide precursors. These results provide a new strategy to synthesize inorganic nanotubes, and it could be applicable to the synthesis of other tubular nanostructures. Moreover, the ceria nanotubes with large cavities and thin walls exhibit excellent reducibility and high OSC, indicating they are potential novel catalytic materials.

Supporting Information Available: Synthetic, characterization, and experimental details about the 1D $Ce(OH)_3$ and CeO_2 nanotubes (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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