A surfactant-free route to single-crystalline CeO_2 nanowires†

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A surfactant-free route was successfully established to synthesize CeO_2 single-crystalline nanowires using H_2O_2 as oxidizer and template agent.

As a consequence of the unique electronic structures and the numerous transition modes involving the 4f shell of their ions, rare earth compounds usually have outstanding optical, catalytic, and magnetic properties, and have drawn continuous research attention for many years. In recent years, the synthesis of rare earth oxides and rare earth hydroxide nanostructures have also been reported, such as $La(OH)_3$,[1–4] $Dy(OH)_3$,[5] and other rare earth oxide.[6]

Cerium oxide is one of the most reactive rare earth metal oxides, which has been extensively studied and employed in various applications including fast ion conductors, oxygen storage capacitors, catalysts, UV blockers, and polishing materials.[7–11] Nanocrystalline CeO_2-based materials benefit not only those applications, but they also possess some other unique properties, such as the Raman-allowed modes shifting and broadening,[12] lattice expansion,[13,14] transition from boundary diffusion to lattice diffusion[15] and blue shift in ultraviolet absorption spectra.[16]

The preparation of CeO_2 materials of mesoporous[17-20] and macroporous structures,[21] nanoparticles,[22–24] and films[25,26] has widely been described, but little concerns the one-dimensional nanostructured ceriumoxide materials. The previously reported CeO_2 nanorods/nanowires, prepared by the sol–gel process using macrochannels of porous anodic alumina membranes as templates means a much more complicated procedure and a lower yield.[27,28] Very recently, several surfactant-assisted methods to prepare CeO_2 and cerium compound one dimensional nanostructures have also been reported by using expensive sodium bis(2-ethylhexyl) sulfosuccinate or cetyltrimethylammonium bromide (CTMABr) as structure-directing agents.[29–31] But the addition of surfactant in these methods means a much more complicated procedure and gives rise to an increase of the cost, and in most of the cases a usual calcination step is inevitable. Therefore surfactant-free growth of CeO_2 one-dimensional nanostructure is still a challenge.

Herein, we report a facile method to synthesize CeO_2 nanowires only using $Ce(NO_3)_3$ and H_2O_2 as starting materials in a hydrothermal system. The obtained CeO_2 nanowires are single crystalline and uniform with thin diameters of 20–70 nm and lengths up to 40 μm. On the basis of structural information and the evolution process provided by electron microscopy, thermogravimetric analysis and FTIR, a growth mechanism is proposed for the H_2O_2-assisted hydrothermal synthesis of CeO_2 nanowires. In a typical procedure, 8 ml 0.05M $Ce(NO_3)_3$ was added rapidly to 8 ml 30.0% H_2O_2 solution. After stirring for about 10 minutes, the suspension (**Sample 1**) was transferred into a 20 ml Teflon-lined autoclave, which was heated at 250 °C for 3 h. The system was then allowed to cool to room temperature naturally. The final product was washed with deionized water, and dried at 60 °C for 12 h. Then CeO_2 nanowires were obtained. **Samples 2, 3 and 4** were taken out of the furnace after the reaction had been carried out at 250 °C for 10, 15 and 20 min, respectively.

The obtained samples were characterized by powder X-ray diffraction (XRD) with a Japan Rigaku D/Max-rB rotation anode X-ray diffractometer, using Ni-filtered CuKa radiation (λ = 1.5405 Å). The morphologies of the sample were determined by a Hitachi H-800 transmission electron microscope (TEM) and a JEOLJEM-2010F high-resolution transmission electron microscope (HRTEM). Thermogravimetric analysis (TGA) was conducted in N_2 atmosphere by a NETZSCH STA- 449C.

Fig. 1 shows the X-ray diffraction pattern (XRD, Two Theta) of the nanowires. All the peaks can be indexed to cubic CeO_2 with lattice constants comparable to the values of JCPDS34-394.

Fig. 2a shows the typical TEM image of CeO_2 nanowires with diameters of 20 to 70 nm and lengths up to 40 μm. It also can be seen from the image that these nanowires are tortuous and the surfaces are smooth. Using SAED patterns taken from a single nanowire, we found that the growth direction of the nanowires is along [100]. Fig. 2b show the SAED patterns and the HR-TEM image of the individual CeO_2 nanowire, showing that the nanowire is structurally uniform and single crystalline. The interplane

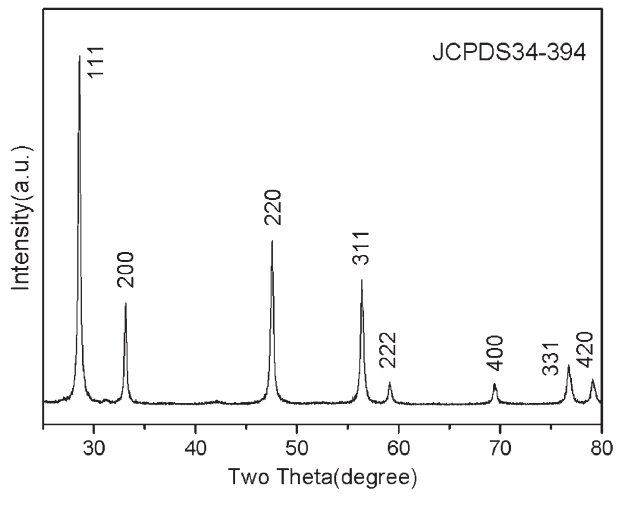

Fig. 1 The X-ray diffraction pattern (XRD, two theta) of the nanowires.

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† Electronic supplementary information (ESI) available: TEM and SEM images. See http://www.rsc.org/suppdata/cc/b5/b500708a/

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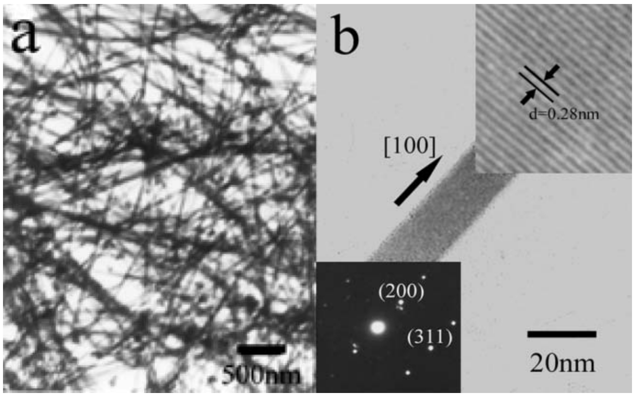

Fig. 2 a) TEM image of CeO_2 nanowires. b) HRTEM image of an individual CeO_2 nanowire, the bottom-left and the upper-right images showing the SAED pattern taken from the same nanowire and the magnified view of the middle part of the nanowire, respectively.

distance in Fig. 2b is calculated as 0.28 nm, corresponding to the separation between the (200) lattice planes of cubic CeO_2.

Hydrated ceria ($CeO_2{\cdot}nH_2O$) has been reported to possess the same crystal structure as pure CeO_2 and shows the same XRD pattern.[32,33] To confirm the component of the nanowires, thermogravimetric analysis (TGA) was carried out. Fig. 3a shows the thermal analysis of the CeO_2 nanowires. The total weight loss of the nanowires revealed by TGA is only 1.11%, which can be attributed to the absorption of a small quantity of water and carbon dioxide. Therefore, the as-prepared nanowires are composed of pure CeO_2.

To learn more about the evolution behavior of the nanostructures, hydrothermal experiments for different time were performed. TEM images for different hydrothermal time during CeO_2 nanowire formation are shown in Fig. 4. As for the **sample 1**, the suspension color is light yellow and the morphology of the particles (shown in Fig. 4a) is uniform with diameters of about 50 nm. After ten minutes, the suspension color of **sample 2** changed from light yellow to deep orange, and the particles of **sample 2** (shown in Fig. 4b) were much smaller than **sample 1**, suggesting an initial dissolution process of particles in hydrothermal reaction. After hydrothermal processing for fifteen minutes, some net-like nanostructures were formed (Fig. 4c). Following hydrothermal processing for twenty minutes, the color of the solution changed from deep-orange to light yellow again and one-dimensional nanostructures appeared (Fig. 4d). According to above results, the growth of the nanostructures can be divided into three steps in the hydrothermal process. First, the precursor aggregations dissolved to smaller particles. The dissolution process lasted for 10–15 minutes, till the deep-orange sample (**sample 1**) formed. The second step was the reorganization of the small particles and the split of large aggregations till the nanostructure skeletons formed primarily. This step lasted for about 10 minutes, and then the deep orange sample changed to light yellow again. The last step was the crystallization of the nanostructures, which lasted for a long time under hydrothermal conditions.

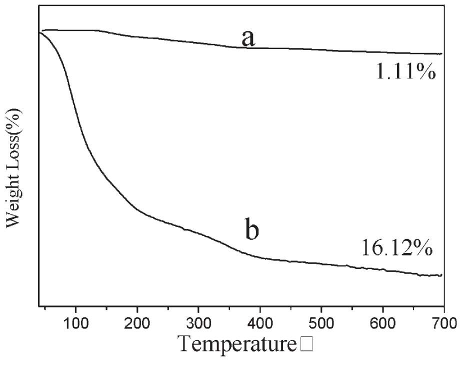

Fig. 3 Thermogravimetric analysis of a): CeO_2 nanowires and b): the deep-orange sample (**sample 2**).

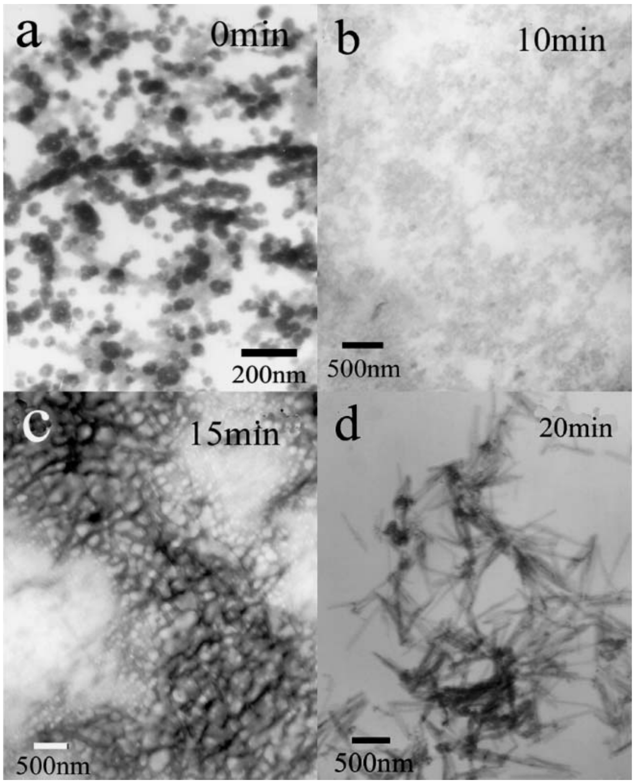

Fig. 4 TEM images of four samples, showing different stages of growth for CeO_2 nanowires. (a) **sample 1**, 0 min; (b) **sample 2**, 10 min; (c) **sample 3**, 15 min; (d) **sample 4**, 20 min.

From another experiment, we found that the precipitation mode together with the concentrations of the starting materials are very important for the formation of CeO_2 nanowire. When 8 ml 30.0% H_2O_2 was added to 8 ml 0.1M $Ce(NO_3)_3$, the particles of the suspension were much larger than that of **sample 1**, showing another type of morphology, and nanocubes were obtained in the following hydrothermal process (see supporting information†).

An experiment was carried out to confirm that H_2O_2 played an important role in the evolution of the nanowires. Before **sample 1** was transferred into an autoclave, it was washed with deionized water and centrifuged 6 times to eliminate the excess H_2O_2 in the solution, and following the washing procedure no nanowires were observed to form using the same hydrothermal process. Fig. 5 shows the TEM image of the sample, in which most of the aggregations are composed of nanoneedles with diameters of about 20 nm. **Sample 2** had been subjected to six cycles of washing with deionized water followed by centrigugation to remove

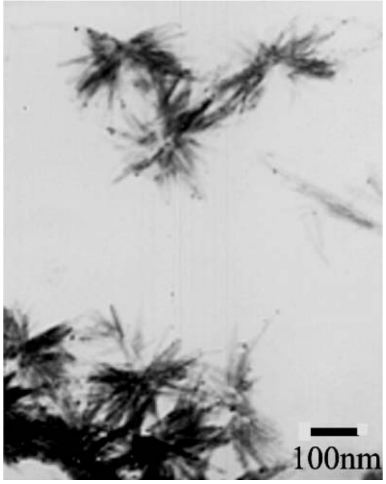

Fig. 5 TEM photograph of products obtained by placing **sample 1**, which has been washed 6 times, into deionized water at 250 °C for 3 hours.

possible ionic remnants and the excess H_2O_2 sufficiently before characterization. FT-IR and TGA were carried out in order to determine the chemical composition of the sample. From the FT-IR spectrum, the absorption peaks at around $3200\sim3400\ cm^{-1}$ and $1400\ cm^{-1}$ were observed, corresponding to the –OH and –OOH stretching vibration, respectively.[34,35] As shown in Fig. 3 (curve b), the ultimate weight loss of **sample 2** is 16.12%. **Sample 2** was also characterized with XRD, but no peak was detected, indicating that the crystallization did not take place in this step. In these experiments, owing to the H-bond interaction with other hydroxyl or hydroperoxyl groups at two-directions in **sample 2**, H_2O_2 was expected to be a template agent. It is even presumed that the template effect of residual H_2O_2 enwrapped in the aggregations results in the transformation of nanoneedles in Fig. 5.

In summary, we have demonstrated a facile approach for synthesis of single-crystalline CeO_2 nanowires only using $Ce(NO_3)_3$ and H_2O_2 as starting materials in hydrothermal system. H_2O_2, at least, takes a double role in the formation of CeO_2 nanowires. To obtain cerium(IV) oxide from Ce(III) nitrate, H_2O_2 was used as an oxidizer, and owing to the H-bond interaction with other hydroxyl or hydroperoxyl groups at two-directions, H_2O_2 was also expected to be a template agent in this experiment. Unlike most of the other templates, which mean a much more complicated process and an increase of impurity concentration in the final product, H_2O_2 makes the process very simple and does not leave any impurity in the hydrothermal reaction system. The H_2O_2-assisted hydrothermal method might offer an excellent approach to design other similar nanomaterials with anisotropic properties and have potential for industrial-scale application. Recently, ZnO, Cu_2O and In_2O_3 nanostructures have also been synthesized using H_2O_2 in a hydrothermal system.[36]

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