Highly reducible CeO₂ nanotubes

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1. Experimental details

Ce(OH)₃ nanotubes/nanorods were prepared by a standard alkali thermal treatment process. In a typical experiment, 0.5 g of Ce₂(SO₄)₃·9H₂O was loaded into a 50 mL Teflon-lined stainless steel autoclave and then an aqueous NaOH solution (10 M, 40 mL) was poured with stirring. The autoclave was sealed and held at a temperature of 130 °C for 15 h. Upon leaving the solution to cool to room temperature, a precipitated powder was collected. The powder was washed with distilled water. The sample for characterization was further dried at 50 °C for 12 h under a nitrogen flow.

CeO₂ nanotubes with extended cavities were prepared by a facile oxidation-coordination assisted dissolution process of these hydroxide precursors. First, the newly prepared 1D hydroxide was exposed in the air at room temperature for 24h to partially oxidize the Ce(OH)₃; then the partially oxidized Ce(OH)₃ were dispersed in the distilled water, treated under ultrasonic for 2 h after appropriate 15% H₂O₂ was added.

The products were analyzed using an X-ray diffractometer with CuKα radiation, TEM (H8100) and HRTEM (JEM-2010).

Hydrogen temperature-programmed reduction (TPR) was conducted with a conventional apparatus equipped with a TCD detector. Before the TPR analysis, the samples were treated in pure oxygen at 450 °C for 45 min. A molecular sieve trap was placed before the detector to adsorb the water produced. TPR was performed by heating of the sample (50 mg) at 10 °C/min to 950°C in a 5% H₂-N₂ mixture flowing at 40 ml/min.

2. Characterization and formation of 1D Ce(OH)₃ and ceria nanotubes

Cerium hydroxide could be synthesized by hydrothermal treatment of Ce₂(SO₄)₃·9H₂O with a 10 M NaOH solution at 130 °C. The phase purity of the products was examined by X-ray diffraction (XRD). A typical X-ray diffraction (XRD) pattern of the as-synthesized products is shown in Supplemental Figure 1a. All detectable peaks in this pattern can be readily indexed to a pure hexagonal phase [space group: P6₃/m (176)] of Ce(OH)₃ with lattice constants of a = 0.6489 nm and c = 0.3806 nm (JCPDS 74-0665). No evidence was found for the existence of impurity in the products.

Supplemental Figure 1. XRD patterns of the products. a) the newly prepared 1D Ce(OH)₃; b) the partially oxidized the Ce(OH)₃ after exposing in the air at room temperature for 24 h; c) Ce(OH)₃ exposed to air for 3 days, fluorite-type CeO₂ phase is obtained; d) CeO₂ nanotubes synthesized via the oxidation-coordination assisted dissolution process.

Supplemental Figure 2. TEM images of the products. a) the newly prepared 1D $\text{Ce}(\text{OH})_3$; b) one $\text{Ce}(\text{OH})_3$ nanotube and corresponding SAED pattern. c) HRTEM image of one $\text{Ce}(\text{OH})_3$ nanotube; d) HRTEM image of one $\text{Ce}(\text{OH})_3$ nanorod; e) TEM image of 1D CeO_2 obtained after a) exposed to air for 3 days.

The size and morphology of the as-synthesized products were further examined by transmission electron microscopy (TEM). All the $\text{Ce}(\text{OH})_3$ synthesized reveal a 1D structure and most of them display a nanotube-like morphology. As shown in

Supplemental Figure 2a, a typical TEM image of the products show diameter of 15-25 nm and lengths up several hundreds of nanometers. These characteristics are similar to the nanostructures obtained by Tang et al. The electron diffraction pattern (Supplemental Figure 2b, inset) taken from a single $\text{Ce}(\text{OH})_3$ nanotube reveals the single-crystalline nature of the sample and the tube growth is documented to be along the $[10\bar{1}0]$ direction. A high-resolution TEM (HRTEM) image (Supplemental Figure 2c) shows that the nanotube is structurally uniform with good crystallinity. The HRTEM image displays the clearly resolved plane of $\{110\}$ planes with a d-spacing of 0.33 nm and the fringes are parallel to the nanotube-growth axis. The TEM images also reveal that some rod-like structure can be found. A typical HRTEM image of one hydroxide nanorod is shown in Supplemental Figure 2d and the fringes of $\{110\}$ planes paralleling to the rod-growth axis are well displayed.

3. TEM and HRTEM images of the ceria nanotubes

Supplemental Figure 3. TEM images of the CeO_2 nanotubes synthesized via the oxidation-coordination assisted dissolution process.