Synthesis and Characterization of Polycrystalline CeO_2 Nanowires

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(Received February 12, 2004; CL-040161)

Polycrystalline CeO_2 nanowires have been synthesized via a solution-phase route using sodium bis(2-ethylhexyl) sulfosuccinate as a structure-directing agent. The obtained CeO_2 nanowires were 30–120 nm in diameters and 0.2–5 µm in lengths. The CeO_2 nanowire consists of many tiny interconnected nanocrystallites of about 7 nm in size. The Raman spectrum of CeO_2 nanowires shows size-dependent effect.

Cerium oxide (CeO_2) is a technologically important material because of its wide applications as a promotor in three-way catalysts for the elimination of toxic auto-exhaust gases,[1–3] in addition to oxygen sensors[4,5] and fuel cells.[6–8] These applications are mainly related to storage and transport behaviors of oxygen in CeO_2. One-dimensional nanostructured materials have significant advantages in view of kinetics and reactivity and are potential building elements for future nanodevices. Particularly interesting, the electronic conductivity of CeO_2 can be enhanced four orders of magnitude when its microstructure changes from micro- to nanocrystalline region.[9] However, there are few reports for the synthesis of 1-D nanostructure of CeO_2. Herein we report firstly the synthesis of CeO_2 nanowires by a novel solution-phase route.

In a typical synthesis, 0.02 mol sodium bis(2-ethylhexyl) sulfosuccinate (NaAOT, 96%, Acros Organics) was dissolved into a solution containing 40 mL of deionized water and 40 mL absolute ethanol. Hydrated cerium(III) acetate ($Ce(C_2H_3O_2)_3 \cdot 1.5H_2O$, 99%, Alfa Aesar) powder was added into the NaAOT solution with a molar ratio of 1:2 ($Ce(C_2H_3O_2)_3 \cdot 1.5H_2O$: NaAOT) under mechanical stirring. An aqueous ammonia (80 mL of $NH_3 \cdot H_2O$, 5 wt %) was added dropwise to above solution. A gelatinous deep pink solid was precipitated gradually. After that, the slurry was stirred for one hour to ensure the sufficient attachment of cerium ions on the head groups of NaAOT. Then the mixture was sealed in a glass beaker and placed in a thermostatic bath at 340 K for 72 h. A pale yellow final product was obtained. The product was washed with ethanol solution, separated by a centrifuge and calcinated at 673 K in air for 4 h.

The phases of the samples were identified by X-ray diffraction (XRD) measurement performed on a Rigaku X-ray diffractometer with Cu Kα radiation. The obtained CeO_2 nanowires are pure phase products with face-centered cubic structure (Figure 1). The grain size of CeO_2 nanowires is about 12 nm estimated from the Scherrer equation.

Scanning electron microscopy (SEM, XL30s-FEG) and transmission electron microscopy (TEM, H-9000 NAR) have provided insight into the morphologies and structure details of these CeO_2 nanowires. The length and diameter of obtained nanowires range from 0.2 to 5 micrometer and from 30 to 120 nm, respectively (Figure 2). CeO_2 nanowires are straight and have uniform diameter (Figures 3a and 3b) and the SAED pattern confirms further that the nanowires are polycrystalline face-centered cubic phase CeO_2 (Figure 3b, inset). The HRTEM image indicates clearly that the nanowire is composed of many tiny grains at different orientations (average grain size of 7 nm, Figure 3c). It seems a porous nanowire, which may enable the gas to access all the surfaces of CeO_2 nanoparticles contained in the device unit.[10]

Prepared CeO_2 nanowires were also investigated by Raman spectrometry on a multichannel modular triple Raman system with 488.0 nm radiation at room temperature. The Raman spectra of the samples of CeO_2 nanowires are far different from that of the samples of bulk CeO_2. In general, the mode at ca. 465 cm^{-1} is related to a first-order symmetrical stretching mode of the Ce–O8 vibration unit, which is very sensitive to any disorder in the oxygen sublattice resulting from thermal and/or grain size-induced nonstoichiometry.[11,12] As shown in Figure 4 (left inset), the band located at 465 cm^{-1} for bulk CeO_2 red-shifts to 462 cm^{-1} and broadens significantly in the case of CeO_2 nanowires. Such a size-dependent variation is related to combined effects of strain and phonon confinement and has been observed in the Raman spectra of nanocrystalline CeO_2 (particles and thin film).[12,13] Second-order peak at 262 cm^{-1} (2TA mode)

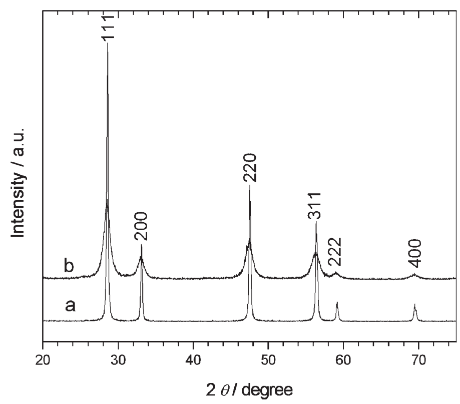

Figure 1. (a) XRD pattern of the samples of bulk CeO_2 (commercially purchased spectral-pure CeO_2 powder); (b) XRD patterns of the samples of CeO_2 nanowires.

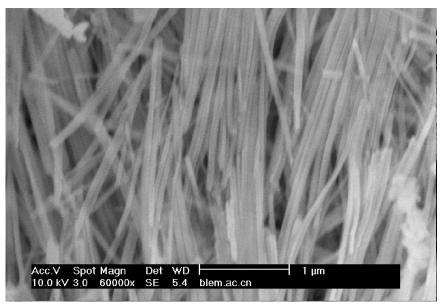

Figure 2. SEM image of CeO_2 nanowires.

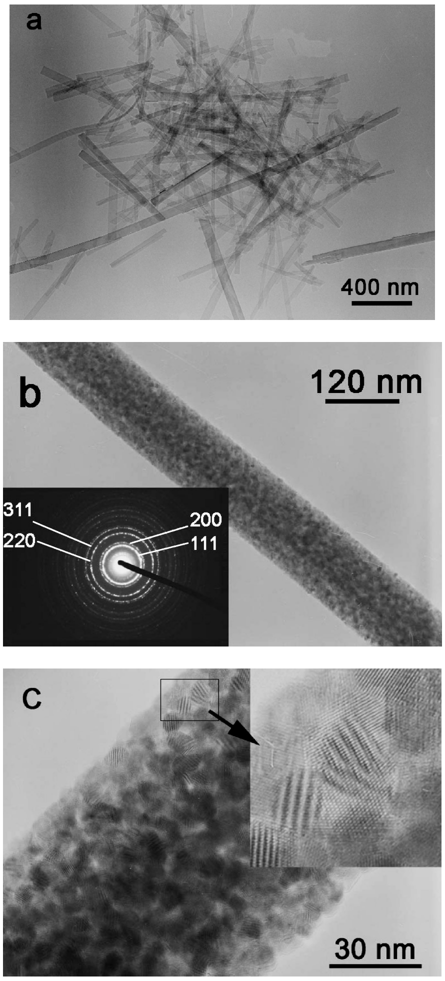

Figure 3. The typical TEM and HRTEM images of the CeO_2 nanowires. (a) overview of TEM images of CeO_2 nanowires; (b) amplified TEM image of single CeO_2 nanowire, the inset is the SAED pattern of single CeO_2 nanowire; (c) HRTEM image corresponding to single CeO_2 nanowire.

is observed in both cases. However, the second-order peaks at 600 cm^{-1} (2TA mode) and 670 cm^{-1} (2LO mode) for bulk CeO_2 are merged into one broad peak at 612 cm^{-1} for CeO_2 nanowires (Figure 4, right inset). The peak at 1171 cm^{-1} (2LO mode) is splitted into two weak peaks at 1128 and 1171 cm^{-1} in the spectrum of CeO_2 nanowires. In addition, an extra band at 1010 cm^{-1} can be observed clearly in the Raman spectrum of CeO_2 nanowires. It might be a second-order peak designated to $2\omega_R(X)$ mode.[14] It is obviously that the relative intensities of the second-order bands in CeO_2 nanowires are much stronger than that in the bulk CeO_2 powder as shown in Figure 4.

In summary, for the first time, polycrystalline CeO_2 nanowires have been successfully prepared by a novel solution-phase method. Our method is facile, less costly and reproducible. Such a microstructure is very interesting for further studies on its

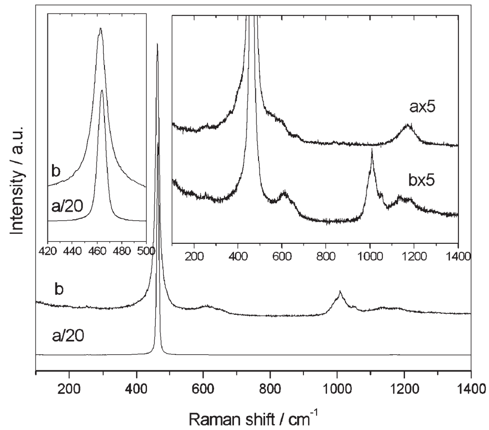

Figure 4. (a) Raman spectrum of the sample of bulk CeO_2 (spectral pure CeO_2 powder); (b) Raman spectrum of the sample of CeO_2 nanowires. The intensities are magnified in order to highlight local information.

physical and chemical properties. Further work is in progress to study the interaction between the surfactant and inorganic precursor, oxygen storage and transport properties of this novel 1-D nanostructured material.

Valuable discussions with Prof. X. L. Chen and Dr. M. He are acknowledged. This work was financially supported by the National Science Foundation of China (NSFC) and National 863 Key Project.

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Published on the web (Advance View) May 10, 2004; DOI 10.1246/cl.2004.662