

Synthesis of cubic fluorite CeO₂ nanowires

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The one-dimensional (1D) nanostructures recently have attracted intensive interest because of their unique physical, and chemical properties and potential applications in nanodevices [1–3]. Many elemental and compound 1D nanowires have been synthesized by various methods, such as zinc oxide [4], single-crystal perovskite manganites [5], single-crystal germanium [6], lanthanide hydroxide single-crystal [7], silicon carbide [8], silicon [9] and others. Ceria has been widely investigated owing to its broad range of applications in catalysis [10], adsorption [11], advanced ceramics [12], high T_c superconductivity [13] and so on. However, the synthesis of a 1D single crystal nanostructured cubic ceria has little been reported. Here a simple method to synthesize single crystal cubic CeO₂ nanowires employing octadecylamine (C₁₈H₃₇NH₂) as the structure-directing agent, nitrate cerium (□) as the cerium source, and ammonia as the precipitating agent is reported.

All the reagents used were of AR grade, purchased from Beijing Chemical Reagents Company. In a typical preparation, 0.05 mol of C₁₈H₃₇NH₂, and 0.50 mol of HNO₃ were added to 166.67 ml of Ce(NO₃)₄ solution (0.3 M) under stirring. After stirring for 24 hr at 353 K, a white solution was obtained. Then, an aqueous ammonia solution (200 ml of NH₃·H₂O, 25 wt%) was added dropwise over ca 6 hr to the stirred solution. During the process, the solution turned a coffee color gradually. After that, stirring was continued for times of 2, 4, 6, 8 and 10 hr maintaining the temperature at 353 K. The prepared solid was separated by centrifuging and washed with deionized water and anhydrous ethanol. This procedure was used in order to remove the templates not incorporated within the inorganic oxide. The resulting yellow powder was dried at room temperature. The corresponding samples were named C2h, C4h, C6h, C8h and C10h respectively. The C10h sample was calcined in a muffle furnace for 3 hr at 673 K (with a heating rate of 1 K/min). The calcinations were carried out in air and the samples were placed in alumina crucibles inside the furnace. The calcined product was named C10h-673K.

The phase purity of the samples was examined by powder X-ray diffraction (XRD) with use of a Rigaku Rotoflex Dmaxa powder X-ray diffractometer with CuK α radiation. Fourier Transform Infrared (FT-IR) spectra were collected using a Nicolet-210 spectrometer. The micro-/nanostructure and morphology of samples were examined with transmission electron microscopy (TEM, Hitachi H-800, Japan) and high resolution transmission electron microscopy (HRTEM,

JEOL-JEM2010, Japan), and the crystalline phase of the samples were further confirmed by selected area electron diffraction (SAED).

Fig. 1 gives typical XRD patterns of samples C10h and C10h-673K, which show the characteristic diffraction peaks of cubic structured CeO₂ (JCPDS 34-0394). Thus, cubic CeO₂ was obtained directly by hydrothermal reaction. Comparing cures a and b, shows that calcination improves the crystallinity of the sample.

Fig. 2 shows FT-IR spectra of the cubic CeO₂ nanowires of samples C10h and C10h-673K. Fig. 2a shows that a small quantity of surfactant is still remaining in the final product (C10h). The $-(CH_2)_n-$ ($n > 4$) are detected at around 750 cm⁻¹. The bands at around 1300–1600, 2853 and 2916 cm⁻¹ are assigned to the bending vibrations of the C–H bond of methyl and methylene groups. A large band is located at 1126 cm⁻¹, corresponding to C–N stretching vibrations. Additional bands at around 3500 and 1633 cm⁻¹ are due to the O–H stretching frequency of residual water and N–H stretching vibrations. The surfactant has been eliminated at 673 K. This can be confirmed from the FT-IR spectrum of the material after calcination at 673 K (Fig. 2b). The C–H and $-(CH_2)_n-$ ($n > 4$) groups have disappeared entirely and only residual O–H groups and C–N groups are left on the surface.

As shown in Fig. 3, all cubic CeO₂ samples show nanowire morphology with lengths up to several hundreds of nanometers and diameters ranging between 10 and 25 nm. Fig. 2b shows one end of a single nanowire of C10h, which illustrates that the nanowire is solid. A typical SAED pattern (inset in Fig. 3) of the nanowire confirms that it is single crystal. A typical HRTEM image of C10h-673K is shown in Fig. 3c, which gives several nanowires with different size. The diameter of the smallest nanowire is less than 5 nm and the diameter of the biggest is more than 20 nm. It also illustrates that nanowires still possess the 1D nanostructure after calcining at 673 K for 3 hr, and the as-synthesized nanowires have good thermal stability.

After ammonia was added into the reaction system, samples with reaction times of 2, 4, 6, 8 and 10 hr were obtained. The morphologies of CeO₂ can be seen in the TEM images in Fig. 4, which illustrates that the variation of the products with time is significant and provides clues to understanding the growth process of CeO₂ nanowires. The application of complementary electrostatic interactions between surfactant molecules and charged or polarized metal oxy precursors as the inorganic component has opened a way to the

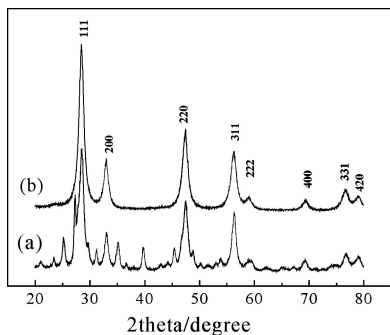


Figure 1 XRD patterns of the cubic ceria nanowires calcined at different temperatures: (a) air-dried (sample C10h), (b) 673 K (sample C10h-673K).

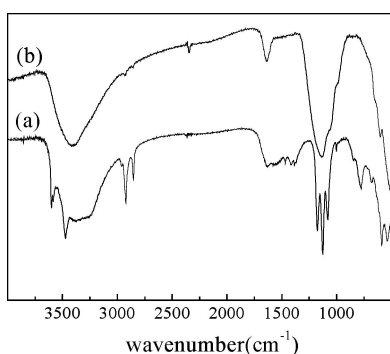


Figure 2 FT-IR spectra of the cubic ceria nanowires calcined at different temperatures: (a) air-dried (sample C10h), (b) 673 K (sample C10h-673K).

self-organized synthesis of surfactant-based periodic inorganic structures [14]. Because the octadecylamine is not dissolved by water, the superfluous nitric acid was added into the reaction system and makes the octadecylamine transform into octadecylammonium nitrite that is soluble in water. The octadecylammonium cations ($C_{18}H_{37}NH_3^+$) in aqueous solution could form clavi-form micelles by self-assembly. The Cerium hydroxide, which combined by the hydrated Ce^{+4} ions with H_2O molecules or OH^- ions [15], polymerized at the micelles-solution interface and formed the nanowire-structure clusters. With the processing of the reaction they gradually grew into the linear structure and finally have lengths up to several hundreds of nanometers and diameters ranging between 10 and 25 nm. The TEM images of C2h, C4h, C6h and C8h in Fig. 4 have proved the above growth mechanism.

A simple, at low temperature, approach has been successfully developed to synthesize single crystal CeO_2 nanowires. It has been shown that the reaction of nitrate cerium ($Ce(NO_3)_3$) with ammonia in the presence of neutral surfactant results in the precipitation of a cubic fluorite ceria/surfactant mixture, which after drying and calcination gives pure fluorite-structured CeO_2 . HRTEM observations indicate that the products have lengths up to several hundreds of nanometers and diameters around 20 nm. XRD patterns of the samples show the characteristic diffraction peaks of a cubic fluorite structured CeO_2 . SAED patterns of the samples show that the nanowires are single crystals. The FT-IR spectrum

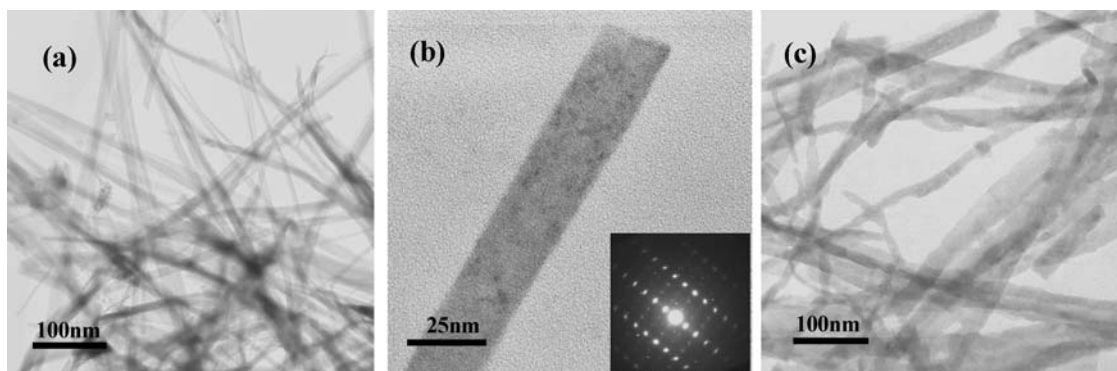


Figure 3 HRTEM images of the cubic ceria nanowires calcined at different temperatures: (a) and (b) air-dried (sample C10h); (c) 673 K (sample C10h-673K). The inset in (b) is electron diffraction (SAED) pattern of the single nanowire from (b).

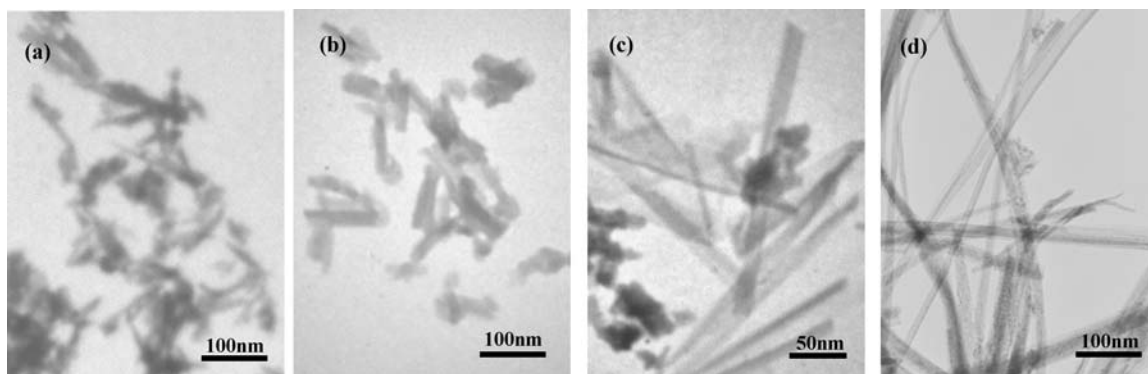


Figure 4 TEM image of the samples obtained at a molar ratio of $1.0Ce(NO_3)_4:10.0HNO_3:2.0C_{18}H_{37}NH_2:40.0NH_4OH$ with different growth periods: (a) 2 hr, (b) 4 hr, (c) 6 hr, (d) 8 hr.

of the material after calcination at 673 K shows that the surfactant has been eliminated. The growth morphologies of the cubic CeO₂ single crystal nanowires were monitored after different periods of the hydrothermal process, which clearly reveal the formation process of the CeO₂ nanowires.

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