Ceria Nanostructures

DOI: 10.1002/ange.200500992

Large-Scale Nonhydrolytic Sol–Gel Synthesis of Uniform-Sized Ceria Nanocrystals with Spherical, Wire, and Tadpole Shapes**

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In the last decade, nanocrystals have been intensively studied, not only for their fundamental scientific interest owing to their size-dependent properties, but also for their many technological applications.[1] Cerium oxide (ceria, CeO_2) is a rare earth oxide that has attracted a great deal of interest owing to its unique properties, including high mechanical strength, oxygen ion conductivity, and oxygen storage capacity. Because of these characteristics, ceria has been widely used as an oxygen ion conductor in solid oxide fuel cells, oxygen pumps, and amperometric oxygen monitors.[2] Ceria has also been used as a polishing agent for the chemical mechanical planarization (CMP) process, as a gate oxide in metal oxide semiconductor devices, and as a catalytic material for three-way catalysis (TWC) of exhaust gas from automobiles and fluid catalytic cracking (FCC).[3] Several methods have been employed to synthesize ceria nanoparticles. Deshpande et al. synthesized nanoparticles of CeO_2, ZrO_2, and $Ce_{1-x}Zr_xO_2$ by hydroxide coprecipitation of a precursor solution composed of cerium ammonium nitrate and zirconyl chloride.[4] Inoue et al. obtained a colloidal solution of 2 nm ceria particles by the solvothermal process.[5] Adachi and co-workers fabricated 2.6 and 4.1 nm ceria particles using reverse micelles.[6] Gedanken and co-workers synthesized 3.3 nm ceria nanoparticles using sonochemical treatment.[7] Zhu and co-workers also prepared 2.8 nm ceria nanoparticles by the sonochemical and microwave-assisted heating methods.[8] However, the ceria nanoparticles synthesized by these methods are often highly aggregated, and a very small quantity is usually produced. Recently, Yan and co-workers synthesized nanocrystals of ceria and other rare earth oxides with various shapes from the thermolysis of metal benzoylacetonate complexes in a solvent mixture composed of oleic acid and oleylamine.[9]

Nonhydrolytic sol–gel processes have been employed to synthesize various oxide materials.[10] Recently, they were

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[**] This work was supported by the National Creative Research Initiative Program of the Korean Ministry of Science and Technology.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

successfully applied to the synthesis of various nanocrystals of transition metal oxides. For example, Colvin and co-workers[11] synthesized TiO_2 nanocrystals by a nonhydrolytic alkyl halide elimination reaction. We employed a similar procedure[12] to produce uniform-sized tetragonal ZrO_2 nanocrystals on the multigram scale by high-temperature reaction of zirconium halides and zirconium isopropoxide. Recently, Brus and co-workers[13] further extended these synthetic methods to produce nanocrystals of HfO_2 and $Hf_xZr_{1-x}O_2$. Stucky and co-workers reported the synthesis of nanocrystals of various metal oxides from the reaction of metal chlorides and benzyl alcohol,[14] and Niederberger and co-workers developed a halide-free approach to synthesize nanocrystals of various oxides from the reaction of metal alkoxides and benzyl alcohol.[15]

One-dimensional (1D) nanocrystalline materials such as nanorods and nanowires have been intensively studied because of their unique properties, which are derived from their low dimensionality and possible quantum-confinement effects.[16] For extensive application of nanocrystals, an economical mass production method for the synthesis of uniform-sized nanocrystals must be developed. Recently, we reported the ultra-large-scale synthesis of monodisperse nanocrystals of many transition metal oxides and sulfides by thermolysis of metal–surfactant complexes.[17] Here we report on the large-scale synthesis of uniform-sized ceria nanocrystals with sphere, wire, and tadpole shapes by the nonhydrolytic sol–gel reaction of cerium(III) nitrate and diphenyl ether in the presence of appropriate surfactants. All of the ceria nanocrystals were produced on a scale of more than 10 g in a single reaction. In particular, we were able to synthesize ceria nanowires with the ultrasmall diameter of 1.2 nm on a multigram scale. The size and shape of the ceria nanocrystals were controlled by adjusting the experimental conditions such as the molar ratio of the surfactants, and the reaction time.

Spherical ceria nanocrystals with an average diameter of 3.5 nm were synthesized from the reaction of cerium(III) nitrate and diphenyl ether in oleylamine at 320 °C. A low-magnification transmission electron microscopy (TEM) image revealed uniform particles with an average size of 3.5 nm and a quasispherical shape (Figure 1 a). A high-resolution TEM (HRTEM) image of the ceria nanocrystals showed a cross-lattice pattern, which demonstrates their highly crystalline nature (Figure 1 a). The powder X-ray diffraction (XRD) pattern (Supporting Information) of the nanocrystals revealed that they have a cubic fluorite structure ($Fm3m$, $a = 5.41134$ Å, JCPDS Card No. 34-0394). The size of the ceria nanocrystals, calculated by using the Scherrer formula, was 3.65 nm, which matched very well with the TEM data. Larger ceria nanocrystals were synthesized by adding tri-*n*-octylamine (TOA) as a cosurfactant in addition to oleylamine. The TEM image showed that uniform quasispherical ceria nanocrystals with an average particle size of 5.2 nm were produced in this case (Figure 1 b). Under optimized synthetic conditions, we were able to synthesize both of these quasispherical ceria nanocrystals on a scale of more than 10 g in a single reaction in 200 mL of solvent (Supporting Information). The UV/Vis absorption spectrum of the 3.5 nm nanocrystals was significantly blue-shifted compared to that of the 5.2 nm nanocrystals (Supporting Information).

Recently, various anisotropic nanocrystals, including nanorods and nanowires, were synthesized by using two different kinds of surfactants.[18] In our synthesis, adding oleic acid as a cosurfactant in addition to oleylamine led to production of anisotropic wire- and tadpole-shaped ceria nanocrystals. When cerium nitrate (1.7 g, 4 mmol) dissolved in a mixture of oleic acid (3.39 g, 12 mmol) and oleylamine (20 mL, 60 mmol, 16.26 g) was treated with diphenyl ether and the resulting solution slowly heated and aged at 320 °C for 2 h, a mixture of ceria nanowires (1.2 nm in diameter and 71 nm in length) with 3.7 nm quasispherical nanocrystals was produced. The diameter of these nanowires is very similar to that of single-wall carbon nanotubes[19] and is among the thinnest of reported nanowires. Although nanowires with diameters of about 1 nm or less have been reported, they were generally produced in extremely small quantities.[20] The TEM image showed that the product was composed of about 70 % nanowires and about 30 % nanospheres (Figure 2). More careful investigation of the TEM images revealed that some nanowires were attached to nanospheres in a tadpolelike structure. The XRD pattern (Supporting Information) showed that the product had a cubic fluorite structure. The HRTEM image showed the {111} faces of a cubic fluorite structure of ceria grown along the [100] direction (Figure 2). By increasing the amount of oleic acid, while keeping the other experimental conditions unchanged, we were able to

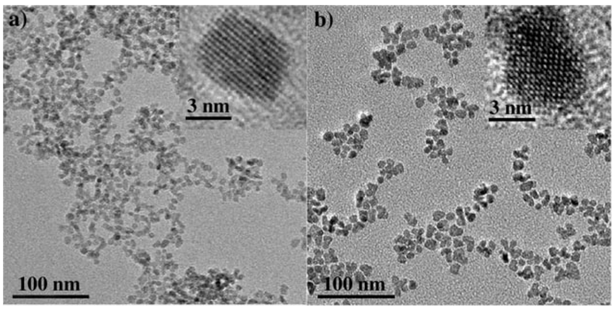

Figure 1. TEM images of a) 3.5 nm spherical ceria nanocrystals and b) 5.2 nm spherical ceria nanocrystals. Insets are their HRTEM images.

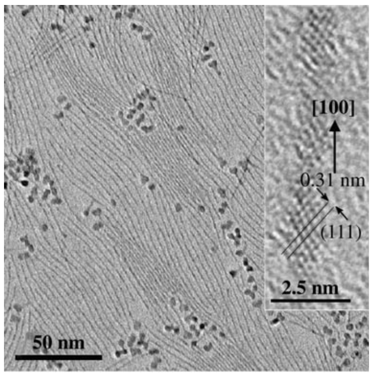

Figure 2. TEM images of 1.2×71 nm wire-shaped ceria nanocrystals. The inset is the HRTEM image of a wire-shaped nanocrystal.

synthesize longer nanowires without changing the diameter. By using different amounts of oleic acid, nanowires of various lengths with a nearly constant diameter of 1.2 nm were produced (Supporting Information). We were able to synthesize the nanowires in large quantities (>10 g) in a single reaction in 200 mL of solvent (Supporting Information).

During a shape-evolution experiment with a relatively large amount of oleylamine, we determined the optimum conditions for predominant formation of the tadpole-shaped nanowires. Tadpole-shaped nanowires consist of a spherical head with a diameter of 3.5 nm and a wire-shaped tail with a diameter of 1.2 nm and length of 27 nm. The low-magnification TEM image revealed that most of these nanocrystals were tadpole-shaped and uniform in size (Figure 3). Recently,

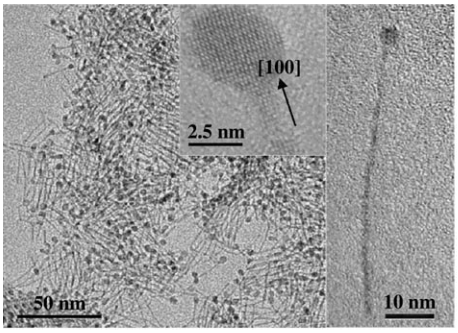

Figure 3. TEM images of the tadpole-shaped ceria nanocrystals. The inset is the HRTEM image of a tadpole shaped nanocrystal.

tadpole-shaped gold nanocrystals were produced.[21] The (HRTEM) image (Figure 3; see Supporting Information for further images) of a single tadpole-shaped ceria nanocrystal revealed that the spherical head and the wire-shaped tail grew epitaxially along the (200) planes with an interplanar distance of 0.27 nm. The XRD pattern showed that the tadpole-shaped ceria nanowires have a cubic fluorite structure (Figure 4).

In conclusion, uniform-sized ceria nanocrystals with quasispherical, wire, and tadpole shapes were synthesized from the nonhydrolytic sol–gel reaction of cerium(III) nitrate and diphenyl ether in the presence of appropriate surfactants. The synthetic procedures described in this study offer several important advantages for the production of ceria nanocrystals. First, this process allows uniform-sized nanocrystals to be obtained on a scale of tens of grams in a single reaction without the need for a further size-sorting process. When reactors are set up in parallel, several kilograms of monodisperse nanocrystals can be readily obtained. Second, ceria nanocrystals with various shapes can be produced simply by changing the experimental conditions. In particular, novel tadpole-shaped nanowires with an extremely small diameter of 1.2 nm were produced.

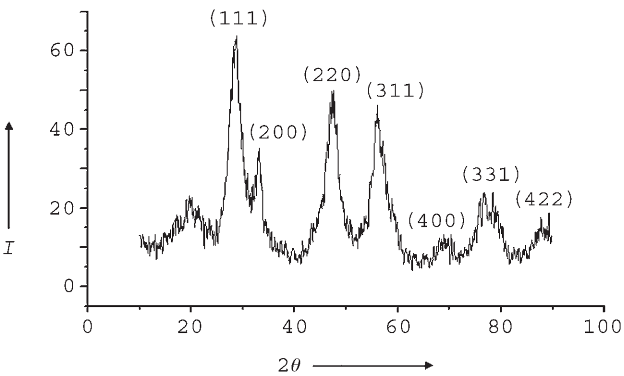

Figure 4. XRD pattern of the tadpole-shaped ceria nanocrystals.

Experimental Section

Synthesis of quasispherical ceria nanocrystals: Cerium(III) nitrate hexahydrate (1.7 g, 4 mmol) was added to oleylamine (technical grade, 20 mL, 16.26 g, 60 mmol) or a mixture of olyelamine (technical grade, 3.21 g, 12 mmol) and tri-*n*-octylamine (20 mL, 16.18 g, 45 mmol) at room temperature. The resulting solution was heated to 90 °C under vacuum, and a homogeneous, clear, black solution formed. Diphenyl ether (2 mL, 2.1 g, 12 mmol) was injected into the solution at 90 °C, and the observed increase in solution temperature to 120 °C demonstrated that the reaction between cerium nitrate and diphenyl ether did indeed occur. The resulting mixture was heated to 320 °C and aged at that temperature for 2 h to give a black colloidal solution. Ethanol (100 mL) was added to precipitate the CeO_2 nanocrystals. The precipitate was retrieved by centrifugation to give white-brown CeO_2 nanocrystals. The nanocrystals were dispersible in many organic solvents, such as toluene, hexane, and octane.

Synthesis of ceria nanowires: Cerium (III) nitrate hexahydrate (4 mmol, 1.7 g) was added to a mixture of oleylamine (technical grade, 20 mL, 16.26 g, 60 mmol) and oleic acid (3.39 g, 12 mmol) at 90 °C. The rest of the synthetic procedure was similar to that used for the synthesis of the spherical nanocrystals. Using 1.7, 3.39, 5.08, and 6.78 g (6, 12, 18, and 24 mmol) of oleic acid in the synthesis gave ceria nanowires with a uniform diameter of 1.2 nm and average lengths of 27.8, 71.1, 115.5, and 164.5 nm, respectively.

Synthesis of tadpole-shaped ceria nanowires: The synthetic procedure for the tadpole-shaped ceria nanowires was very similar to that used for the synthesis of the ceria nanowires. A reaction mixture composed of cerium (III) nitrate (0.85 g, 2 mmol), oleylamine (technical grade, 20 mL, 16.26 g, 60 mmol), of oleic acid (1.69 g, 6 mmol), and diphenyl ether (1 mL, 1.07 g, 6 mmol) was aged at 320 °C for 1 h.

UV/Vis spectra of 3.5 and 5.2 nm spherical nanocrystals, XRD patterns of 3.5 and 5.2 nm spherical nanocrystals and nanowires, TEM images of ceria nanowires of various lengths, and photographs of ceria nanocrystalline powders can be found in the Supporting Infomation.

Received: March 18, 2005
Published online: October 25, 2005
Publication delayed at author's request.

Keywords: cerium · nanocrystals · nanostructures · sol–gel processes

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