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Single Unit Cell Thick Samaria Nanowires and Nanoplates

Taekyung Yu, Jin Joo, Yong Il Park, and Taeghwan Hyeon*

National Creative Research Initiative Center for Oxide Nanocrystalline Materials and School of Chemical and Biological Engineering, Seoul National University, Seoul 151-744, Korea

Received October 25, 2005; E-mail: thyeon@plaza.snu.ac.kr

Nanowires have received a tremendous amount of attention because of their unique properties derived from low dimensionality and possible quantum confinement effect.[1] These 1-D nanostructured materials have found applications in interconnects and functional blocks for fabricating nanoscale electronic, magnetic, and optical devices.[2] Although various nanowires have been synthesized using different synthetic procedures, their diameters are usually larger than 10 nm and they are often nonuniform. In particular, the synthesis of uniform nanowires with feature sizes of ~1 nm is a major challenge. Although nanowires with diameters in the sub-nanometer or ~1 nm range have been reported, they were usually produced in extremely small quantities or their diameters were often nonuniform.[3] Recently, several research groups reported the fabrication of ultrathin nanostructures of lanthanide oxides. For example, Cao synthesized square-shaped Gd_2O_3 nanoplates with a thickness of 1.1 nm.[4] Yan and co-workers synthesized various nanostructures of lanthanide oxides, including ultrathin Eu_2O_3 nanoplates.[5] Our research group synthesized tadpole-shaped ceria nanowires with a 3.5 nm sized spherical head and a 1.2 nm sized tail.[6] Herein, we report on the large-scale synthesis of uniform rectangular-shaped samaria (Sm_2O_3) nanowires with a single unit cell thickness (1.1 nm).

Samarium oxide (samaria, Sm_2O_3) nanowires having a rectangular shape were synthesized from the thermal decomposition of hydrated samarium(III) acetate in the presence of a mixture of oleylamine and a long-chain carboxylic acid under argon atmosphere. In a typical synthesis, 0.64 g of hydrated samarium(III) acetate (2 mmol) was added to a mixed solvent composed of 20 mL of oleylamine (technical grade, 60 mmol, 16.26 g) and 3.10 g of decanoic acid (18 mmol) at room temperature. The resulting solution was heated to 90 °C in a vacuum to remove hydrated water, forming a homogeneous and clear white−yellow solution. The resulting mixture was heated to 240 °C and aged at that temperature for 6 h, resulting in a white colloidal solution; 100 mL of ethanol was added to cause the precipitation of the nanocrystals. The precipitate was retrieved by centrifugation, producing white samaria nanocrystals.

A transmission electron microscopic (TEM) image of the nanowires revealed that they possess an extremely uniform thickness (Figure 1a; more TEM images in Supporting Information, Figure S1) and width (Figure 1b) of 1.1 and 2.2 nm, respectively, with lengths of more than 1 μm. These nanowires self-assembled to generate parallel arrays due to their high surface energy. A tilting experiment in TEM showed that the nanowires have a rectangular shape rather than a circular shape (see Supporting Information, Figure S2). The TEM image of the microtomed sample clearly showed a rectangular cross-section with dimensions of 1.1 nm × 2.2 nm (Figure 1c). Recently, Park and co-workers synthesized vanadium dioxide nanowires with a rectangular cross-section of 60 nm thickness.[7]

The powder X-ray diffraction (XRD) and electron diffraction patterns (see Supporting Information, Figure S3) indicated that the samaria nanocrystals have a body-centered cubic (bcc) Sm_2O_3 structure (La3, a = 10.92 Å, JCPDS Card No. 86-2479). The lattice constant of the unit cell of samaria is about 1.1 nm, which matched the thickness of the nanowires. The dimensions of the cross-section of the nanowires were 1.1 nm (thickness) × 2.2 nm (width), which corresponded to the size of two unit cells (Figure 1d).

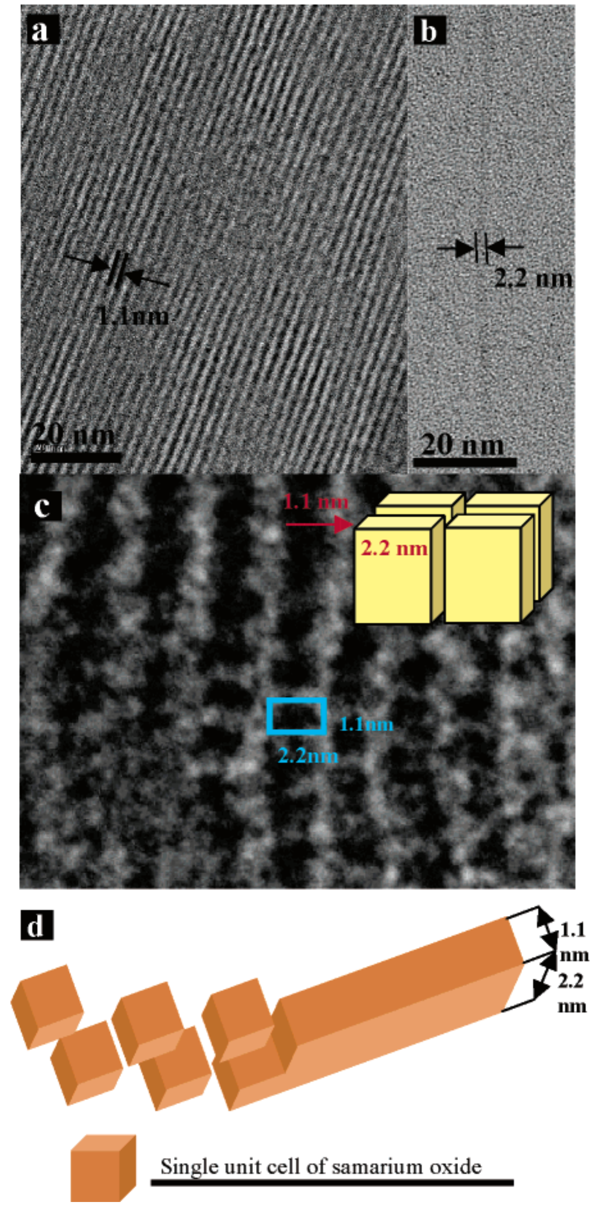

Figure 1. TEM images of rectangular-shaped samaria nanowires (a and b). (c) Microtomed TEM image of samaria nanowires. (d) Proposed model for the structure of the rectangular-shaped samaria nanowire.

Recently, various anisotropic nanocrystals, including nanorods and nanowires, were synthesized using two different kinds of

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surfactants having different binding capabilities. In our current synthesis, decanoic acid was added as a cosurfactant, in addition to oleylamine, leading to the production of anisotropic rectangular-shaped samaria nanowires. It is known that decanoic acid tends to bind more strongly than oleylamine to the surface of the nanocrystals, due to its higher oxophilicity. In a control experiment, in which only oleylamine was used without decanoic acid, large rod-shaped nanocrystals having diameters of >100 nm were obtained (see Supporting Information, Figure S4). On the other hand, nearly no nanocrystals were produced when only decanoic acid was used as the solvent. Moreover, under optimized synthetic conditions, we were able to synthesize the samaria nanowires on an extremely large scale of over 10 g in a single reaction using 400 mL of the solvent (see Supporting Information, Figure S5).[8] Furthermore, when the synthesis was performed in mixed surfactant solutions composed of variable ratios of oleylamine and octylamine along with a fixed amount of oleic acid, the aspect ratios of the nanowires were able to be systematically controlled while maintaining a uniform thickness of 1.1 nm. For example, when a 1:1 mixture of octylamine (30 mmol) and oleylamine (30 mmol) was used in the synthesis, nanoribbons with a width of 3.4 nm and a length of 80 nm were produced. On the other hand, when a 2:1 mixture of octylamine (40 mmol) and oleylamine (20 mmol) was used, wider and longer nanoribbons with a width of 10 nm and a length of 150 nm were produced (see Supporting Information, Figure S6).

To further study the influence of surfactants on the formation of the nanocrystals, we used different surfactants in the synthesis. When oleic acid (18 mmol) was employed as the surfactant along with oleylamine (60 mmol), square-shaped samaria nanoplates with a uniform thickness of 1.1 nm were generated (Figure 2). These nanoplates had a relatively uniform side dimension of 10.6 nm and self-assembled side by side to form aligned arrays, as shown in Figure 2b. A high-resolution transmission electron microscopic (HRTEM) image showed that the nanoplates grew along the {400} facets of the body-centered cubic structure of samaria with an interplanar distance of 0.27 nm (Figure 2b). When the amount of the samarium precursor was changed to 1 and 4 mmol, and keeping the other experimental conditions unchanged, samaria nanoplates with a uniform thickness of 1.1 nm and side dimensions of 7 and 15 nm were produced, respectively (see Supporting Information, Figure S7). Nanoplates of other rare-earth metal oxides, including La_2O_3, Nd_2O_3, Y_2O_3, and Pr_2O_3, were synthesized using a procedure very similar to that employed for the synthesis of the samaria nanoplates, and the detailed characterization is underway.

In conclusion, we synthesized samaria nanowires and nanoplates with a thickness of 1.1 nm, corresponding to a single unit cell dimension. By varying the experimental conditions, such as the kinds of surfactants and the amount of samarium precursor, we were able to vary the shapes and sizes of the samaria nanostructures. Under optimized conditions, we were able to synthesize as much as 10 g of the nanowires. We are currently working on the synthesis of ultrathin nanowires of other rare-earth oxides using a similar synthetic procedure. For example, we synthesized uniform lanthanum oxide nanowires with a thickness of 1.1 nm.

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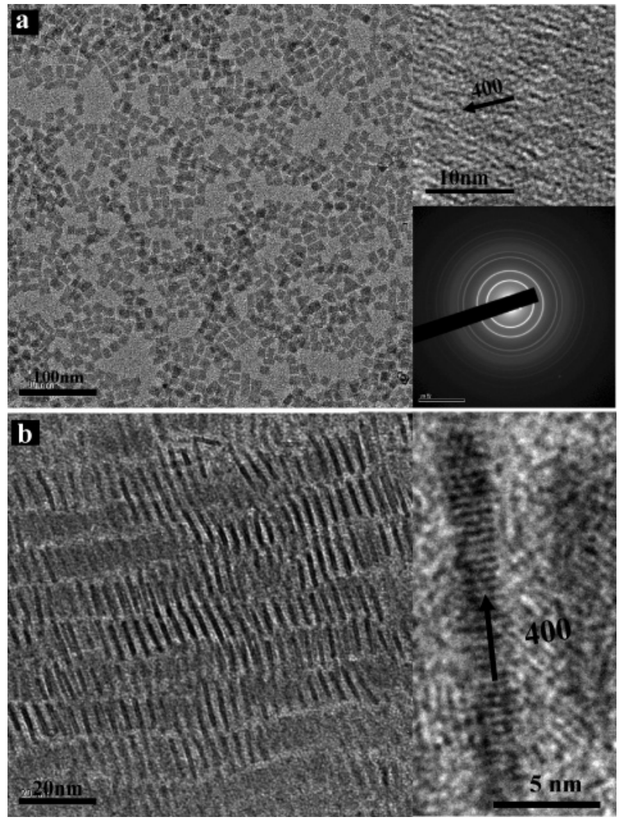

Figure 2. TEM images, HRTEM images, and electron diffraction pattern of square-shaped samaria nanoplates.

Supporting Information Available: TEM and XRD results of various sized and shaped samaria and other rare-earth oxide nanocrystals. Photographs of the powders of samaria nanowires. This material is available free of charge via the Internet at http://pubs.acs.org.

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