Fabrication of Single Crystalline Neodymium Oxide Nanowires under Mild Conditions

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Nanowires of single crystalline neodymium oxide have been successfully synthesized under mild conditions using surfactant-assisted assemblies composed of laurylamine hydrochloride and neodymium alkoxide modified with acetylacetone. The nanowire structure was characterized by XRD, TEM, SEM, and nitrogen adsorption isotherms. Nd_2O_3 nanowires have a single crystalline structure with diameters ranging from 10 to 50 nm and lengths of several hundred nanometers. This newly developed synthetic method can be easily extended to other rare earth metal oxides.

Oxides are the most stable rare earth compounds; the cations in these oxides are typically in the trivalent state.[1] Rare earth oxides are widely used as high-performance luminescent devices, magnets, catalysts, and other functional materials based on the electronic, optical, and chemical characteristics arising from their 4f electrons.[1–4] Most of these advanced functions depend strongly on the compositions and structures, which are sensitive to the bonding states of rare earth atoms or ions. If rare earth oxides were fabricated in the form of a 1-D nanostructure, they would hold promise as highly functionalized materials as a result of both shape-specific and quantum confinement effects. They could also act as electrically, magnetically, or optically functional materials. Recently, the synthesis and characterization of lanthanide hydroxide nanowires, composite nanowires containing rare earth metal or lanthanide oxides nanparticles have been reported.[5–8] However, few studies have focused on the synthesis of nanostructured lanthanide-related compounds. Such materials would be of great significance because of the possible novel properties induced by their reduced dimensionality. We have also succeeded in synthesis of silica nanotubes using the surfactant-templating mechanism by LAHC/tetraethoxysilane system.[9] Herein, we present a novel chemical route toward the growth of well-proportioned and crystallized Nd_2O_3 nanowires using complex molecular assemblies composed of laurylamine hydrochloride (LAHC) and rare earth metal alkoxides modified with acetylacetone (ACA). The novelty of this procedure can be characterized by the successfully well-ordered growth of single crystal Nd_2O_3 nanowires under easily controllable and mild conditions.

In a typical synthesis process, LAHC was dissolved in distilled water. Neodymium tri-*n*-butoxide (NTB, $Nd(OC_4H_9)_3$) was mixed with the same moles of ACA in a glass and immediately added to LAHC aqueous solution of pH 4.2. The mole ratio of NTB to LAHC was 4. When the two solutions were mixed, the color of the solution became violet. The solution was stirred for several days at 313 K to obtain homogeneous sol. The temperature was then changed to 353 K. After 1 week, the solution became a violet gel with a colorless liquid. After drying at 353 K for 1 day, the dried sample was calcined in air at 773 K for 4 h.

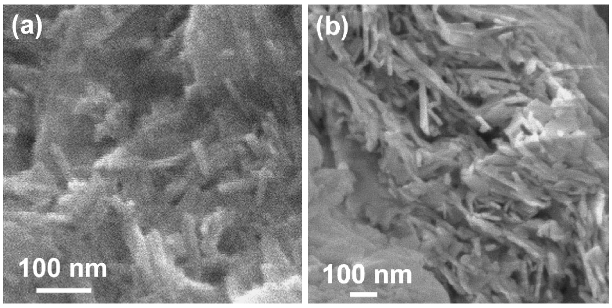

Figure 1. FE-SEM images of Nd_2O_3 nanowires dried at 353 K for 1 day (a), and calcined at 773 K for 4 h (b).

Figure 1 shows the field emission scanning microscopy (FE-SEM; JEOL JSM-5510) images of Nd samples dried at 353 K (a) and calcined at 773 K (b). As shown in Figure 1a, the dried samples consist of a wire-like structure with diameters of 15–20 nm and lengths ranging from 100–150 nm. This result suggested that the wire structure had been formed during the early reaction stage by interaction between NTB and the surfactants. In Figure 1b Nd_2O_3 calcined at 773 K showed clear nanowires. The length of the calcined sample became longer than that of the dried sample. As shown later, the wire structure formed in the early reaction stage leads to longer single crystal nanowire formation after calcination at high temperature.

The X-ray diffraction (XRD; Rigaku RAD-IIC using Cu Kα radiation at 35 kV, 20 mA) patterns of Nd sample dried at 353 K containing LAHC surfactants (a) and calcined at 773 K (b) are shown in Figure 2, respectively. The diffraction peak in Figure 2a can be indexed to hexagonal phase (space group: $P6_3/m$) of $Nd(OH)_3$ with lattice constants $a = 6.421$ Å, $c = 3.740$ Å, i.e., the peaks agreed quite well with the standard data file (JCPDS file no. 06-0601). About half of the XRD peaks in Figure 2b

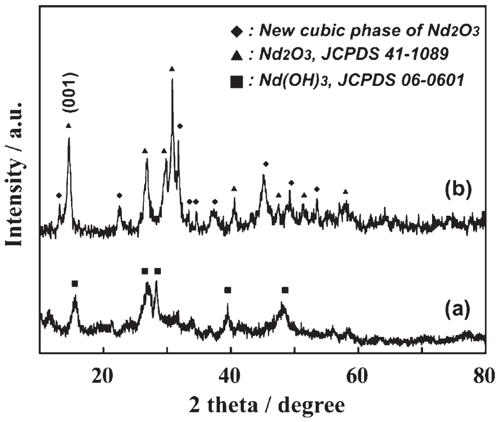

Figure 2. XRD patterns of $Nd(OH)_3$ nanowires: (a) the samples dried at 353 K for 1 day, and (b) Nd_2O_3 nanowires calcined at 773 K for 4 h.

could be indexed to hexagonal phase (space group: $P3m1$) of Nd_2O_3 with lattice constants $a = 3.830$ Å, $c = 5.999$ Å (JCPDS file no. 41-1089), but the other half of the peaks could not be indexed to any possible phase such as Nd_2O_3, NdO and $Nd(OH)_3$. None of the data in the JCPDS card matched these peaks well by XRD searching. We thus assumed that the lattice parameter a of cubic unit cell changed. The most suitable value of lattice parameter was sought, and the interplanar spacing d was calculated on the basis of the lattice parameters of cubic phase. The experimental and calculated interplanar spacings d corresponding to the different plane indices are listed in Supporting Information 1. Satisfactory agreement was obtained between experiment and calculation. Consequently, a cubic unit cell with parameters $a = 11.066$ Å has been adopted, and it was concluded that the space group ($Ia3$) of Nd_2O_3 with cubic phase (JCPDS 21-0579; $a = 11.08$ Å) had changed. Thus, the XRD pattern shown in Figure 2b matches best with the mixture of hexagonal phase (JCPDS file no. 41-1089) and new cubic phase of Nd_2O_3 with lattice constant $a = 11.066$ Å. In contrast, Nd_2O_3 synthesized using the sol–gel method generally has hexagonal phase 1. This result shows that Nd_2O_3 with the new cubic structure can be selectively synthesized by control of hydrolysis and condensation reactions using chemical modifications with surfactant molecules.

Both XRD patterns of Figures 2a and 2b show broad peaks. Since the Nd sample calcined at 773 K shown in Figure 3b shows many lattice images on a high-resolution transmission electron microscope (HRTEM; JEOL JEM-200CX operated at 200 kV) image, as shown later, the Nd sample calcined at 773 K has high crystalinity, and the particle size is small. The relative intensity of the diffraction peaks deviates from that of the bulk, suggesting a differently oriented growth direction of the nanowires. Comparing the intensity of the (001) peak of the sample with those of the hexagonal phase of bulk Nd_2O_3, it was found that the relative intensity of (001) was dramatically increased from 0.1% in the bulk phase to 80% in the present sample. This finding clearly shows that the nanowire growth occurs along the [001] direction.

We also synthesized Nd samples using NTB modified ACA system without LAHC, in order to make clear the influence of the surfactants. The sample was prepared in the same way by mixing NTB modified ACA with water without LAHC, and the products were calcined at 773 K for 4 h. As shown in Supporting Information 2, Nd_2O_3 plate-like particles were formed in the same system. Thus, we can conclude that LAHC plays an important role in the formation of Nd_2O_3 nanowires. The XRD pattern of the sample without LAHC matches best with the mixture of cubic phase (JCPDS 21-0579) and new cubic phase of Nd_2O_3 with lattice constant $a = 11.066$ Å.

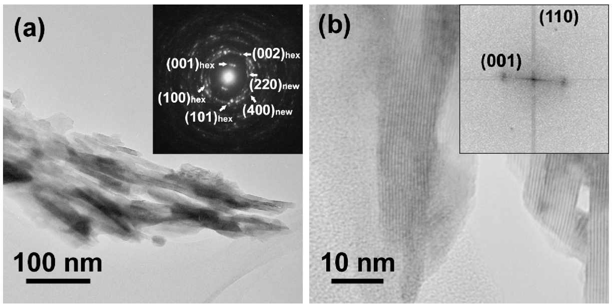

Figure 3. (a) TEM image of aggregated Nd_2O_3 nanowires calcined at 773 K for 4 h. Inset: SAED pattern obtained from the same nanowires. (b) High-resolution TEM (HRTEM) image of Nd_2O_3 nanowires calcined at 773 K for 4 h. Inset: FFT pattern obtained from HRTEM.

Figure 3a shows the low magnification TEM images of the Nd_2O_3 nanowires calcined at 773 K with diameter of 10 nm, although the majority of Nd_2O_3 nanowires were assembled into the aggregates. The selected area electron-diffraction (SAED) pattern (inset) of these aggregated nanowires in Figure 3a shows the Debye–Sherrer rings and diffraction points of Nd_2O_3 hexagonal phase and new cubic phase. To study further the fine structure of the aggregated nanowires, HRTEM combined with a fast Fourier transform (FFT) analysis technique was used. The HRTEM image of the aggregated nanowires in Figure 3b shows the single crystalline structure with a lattice spacing of 5.99 Å corresponding to the (001) planes of hexagonal phase by FFT pattern (inset) in Figure 3b; the nanowires grow along the c axis. This result confirms that selective growth of nanowires along the [001] direction gave a dramatic increase in the intensity of (001) in XRD analysis shown in Figure 2b and elongation of nanowires by calcination shown in Figure 1b. The nitrogen adsorption–desorption isotherm pattern (BEL Japan BELSORP-18 Plus) of the Nd sample calcined at 773 K was a typical IUPAC II, indicating that a nonporous shape was formed. The BET surface area of the same Nd_2O_3 was calculated to be $27\,m^2/g$.

In summary, we have developed a novel alkoxide-surfactant-assisted method to prepare Nd_2O_3 nanowires under mild conditions with high crystallinity at diameters of 10–50 nm, and length of several hundred nm. Selective growth of nanowires along the [001] direction of hexagonal phase was observed. Without LAHC, Nd_2O_3 nanowires could not be formed.

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