Communication

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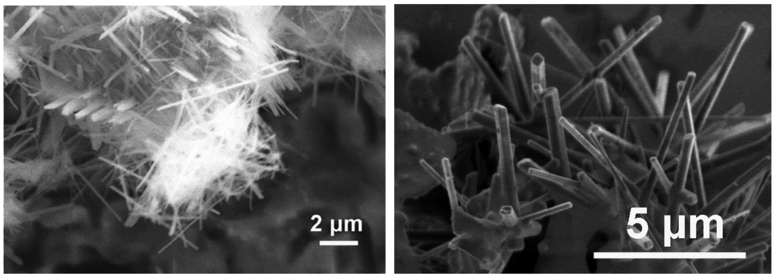

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Synthesis and Characterization of Single-Crystalline Alkali Titanate Nanowires

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The alkali metal titanates with tunnel structure are of interest, both experimentally and theoretically, as model systems for fast ionic conductors and also for their high photocatalytic activities.[1−3] A family of the alkali metal titanates, represented by the general formula $A_2O{\cdot}nTiO_2$ ($3 \leq n \leq 8$ and A = K, Na, Li), is composed of a layered structure with each layer consisting of zigzag ribbons, in which the octahedra share edges at one level in linear groups of three and are further joined together by corners. These ribbons share the terminal corners with identical ribbons, resulting in an open octahedral framework enclosing tunnels or continuous rows of interstitial positions, in which the alkali ions are situated.[3] In addition, the hollandite structure with the general formula $A_x(B_yTi_{8-y})O_{16}$, where A = K, Cs or Ba, and B is either a divalent or a trivalent cation, such as Mg^{2+}, Mn^{2+}, Al^{3+}, or Ti^{3+}, can be described as columns of four linear strings of edge-sharing octahedra parallel to the *c*-axis. The chains of octahedra are linked together, forming a framework of continuous parallel tunnels, which are only partially occupied by alkali ions.[4]

In the past decade, various strategies have been developed to fabricate one-dimensional nanostructures of most of the functional materials, due to their novel physical properties on the nanoscale. Binary oxide nanowires and nanobelts, such as TiO_2, ZnO, SnO_2, MnO_2, and Ga_2O_3, have been successfully synthesized.[5,6] However, the approach to one-dimensional nanostructure of ternary complex oxides remains a challenge, except for the template method. Recently, sodium titanate nanowires were produced by hydrothermal treatment of TiO_2[7,8] or Ti powders and H_2O_2[9] in a NaOH aqueous solution at 160−220 °C. In addition, $K_2Ti_6O_{13}$ and $K_2Ti_8O_{17}$ nanowires have also been successfully prepared by a hydrothermal reaction between TiO_2 or $Na_2Ti_3O_7$ with KOH solution.[10−12]

In this communication, we describe a simple method to synthesize sodium titanate and potassium hollandite nanowires from reactions of TiO_2 nanoparticles with molten salt in the presence of a nonionic surfactant. The morphology and structure of the single-crystalline nanowires were characterized by electron diffraction, scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

In our experimental procedure, a mixture of barium oxalate (BaC_2O_4), TiO_2 (anatase) nanoparticles, and NaCl with molar ratio of 1:1:20 was ground with 5 mL of NP-9 (Aldrich) for 20 minutes and then sonicated for 5 minutes. The mixture was first placed in a combustion boat and annealed in a tube furnace at 825 °C for 3 h and, subsequently, cooled naturally to room temperature. The pristine powders were then washed with distilled water several times to remove the NaCl and the resulting $BaTiO_3$ nanoparticles, which were suspended on the surface during washing. It was found that the use of barium oxalate would increase the yield, though it is not necessary to produce the wanted nanowires. For the potassium hollandite, KCl was used instead of NaCl, and no barium oxalate was used in the reactions. The processing parameters are almost the same, except that the reaction temperature was set at 800 °C, as has been utilized for large-scale synthesis of nanowires and nanocubes.[13] The resulting powders were washed several times with distilled water and then dried at room temperature.

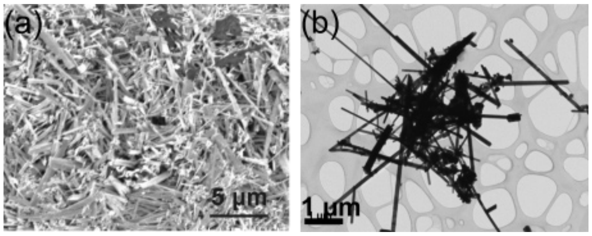

Figure 1. Morphology of the synthesized sodium titanate nanowires. (a) SEM image and (b) TEM image showing narrow distribution of nanowire diameter.

The morphology, structure, and dimensions of the synthesized nanowires were characterized with SEM (Hitachi S-4700) and TEM (JEM-2010F and JEM-100CX-II). The nanowires were first dispersed in ethanol aided by ultrasonic treatment. One drop of the suspension was then transferred to a TEM copper grid coated with a holey carbon film.

Figure 1a shows an SEM image of the synthesized sodium titanate nanowires. A large quantity of nanowires with uniform diameter around 100 nm was obtained. The length of the nanowires ranges from several to a few tens of microns. The TEM image shown in Figure 1b revealed that the distribution of diameter of the synthesized nanowires is narrow. Selected-area electron diffraction (SAED) taken from different parts of the nanowires indicates that the nanowires are single crystalline.

To identify the crystal structure of the synthesized nanowires, we examined the electron diffraction patterns and the corresponding high-resolution electron micrographs in several orientations by tilting the nanowires. Figure 2a−c shows three electron diffraction patterns taken from the same nanowire, which was identified as the monoclinic sodium hexatitanate $Na_2Ti_6O_{13}$ with space group $C2/m$ and lattice parameters $a = 15.131$ Å, $b = 3.745$ Å, $c = 9.159$ Å, and $\beta = 99.3°$ (JCPDS 73-1398). The three zone axes are [1, 0, −3] (Figure 1a), [1, −1, −3] (Figure 1b), and [1, −1, −1] (Figure 1c), respectively. The relative orientational relationships between the three electron diffraction patterns are also indicated in the figure. For example, the [1, −1, −3] (Figure 1b) zone axis electron diffraction pattern was obtained by rotating the nanowire 6.5° about its [602] direction (indicated in Figure 1a). The two-

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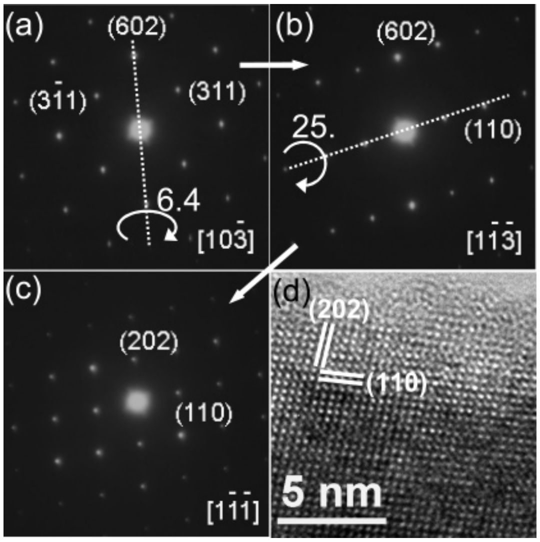

Figure 2. (a−c) Electron diffraction patterns of the same sodium hexatitanate nanowire tilted to zone axes [1, 0, −3], [1, −1, −3], and [1, −1, −1], respectively. Dashed lines indicate the tilting axes about which the nanowire was rotated to obtain the needed orientation. Circular arrows give the tilting angles, and the straight arrows indicate the tilting sequence. (d) Lattice image of $Na_2Ti_6O_{13}$ nanowire taken along zone axis [1, −1, −1], corresponding to Figure 2c.

dimensional lattice image (Figure 2d), corresponding to the electron diffraction pattern given in Figure 2c, further demonstrates that the nanowire is single crystalline and is free of crystal defects. The lattice spacings are 3.63 and 3.61 Å, respectively, which correspond to the (110) and (202) interplanar spacing of the monoclinic $Na_2Ti_6O_{13}$, as shown in Figure 2d. The growth direction of the nanowire was determined to be its [010] crystallographic direction, consistent with other alkali titanates with the same monoclinic structure.[8,11,14]

It is expected naturally that similar nanostructure should be obtained if other alkali precursors were used to substitute sodium. When the titania nanoparticles were annealed in molten KCl in the presence of the nonionic surfactant (NP-9) at 800 °C, potassium hollandite nanowires were obtained. Figure 3a shows a typical morphology of the synthesized potassium hollandite nanowires. The diameter of potassium hollandite nanowires ranges from 40 to 150 nm, and the average diameter is about 100 nm. The length of nanowires can reach up to a few tens of microns. An individual nanowire (shown in Figure 3b) was selected and tilted to obtain a series of selected-area electron diffraction patterns. From the electron diffraction patterns, the nanowires were identified as potassium hollandite $KTi_8O_{16.5}$ of tetragonal structure with lattice parameters $a = 10.15$ Å and $c = 2.962$ Å (JCPDS 41-1098). Figure 3c shows an electron diffraction pattern of the studied nanowire along the [0, −1, 0] zone axis, which indicates that the nanowire is also single crystalline with a preferential growth in the [001] crystallographic direction. Figure 3d is a lattice image of a single-crystalline potassium hollandite nanowire, which shows the clearly resolved lattice spacing of $d_{200} = 5.10$ Å, and it further confirms that the nanowire grew in the [001] direction.

By analyzing the fabrication process of ternary oxide nanowires in this work and similar results,[13] we suggest that, in a ternary oxide system, temperature is the most important parameter in determining the formation of nanowires rather than other morphologies.

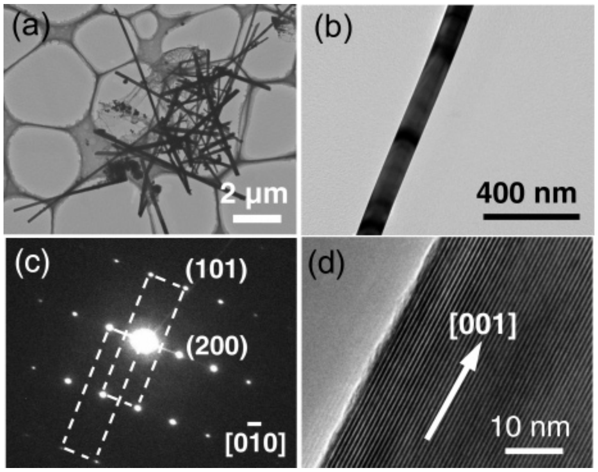

Figure 3. TEM images of synthesized potassium hollandite nanowires. (a) TEM image showing the nanowires with a diameter of 40−150 nm. (b) Low-magnification TEM image of an individual potassium hollandite nanowire. (c) Electron diffraction pattern of the nanowire depicted in (b) showing the [001] growth direction of potassium hollandite nanowire. (d) HRTEM image of an individual nanowire that also shows that the nanowire grows along the [001] direction.

In summary, anatase TiO_2 nanoparticles were found to react with molten alkali chloride to form single-crystalline sodium hexatitanate and potassium hollandite nanowires in the presence of a nonionic surfactant. The nanowires have a diameter around 100 nm and a length up to a few tens of microns. The synthesized sodium titanate and potassium hollandite nanowires were found to grow along [010] and [001] crystal direction, respectively. This method may also be extended to the fabrication of other ternary oxide nanostructures.

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