Short communication

Microstructural characterization of single-crystalline potassium hollandite nanowires

C.Y. Xu[a,b], L. Zhen[a,*], Q. Zhang[b], J. Tang[c], L.-C. Qin[b,d]

[a]School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China
[b]Department of Physics and Astronomy, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3255, USA
[c]National Institute for Materials Science, Tsukuba 305-0047, Japan
[d]Curriculum in Applied and Materials Sciences, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3255, USA

ARTICLE DATA

Article history:
Received 13 February 2008
Received in revised form
14 April 2008
Accepted 14 April 2008

Keywords:
Nanomaterials
Crystal growth
Potassium hollandite
Electron microscopy

ABSTRACT

Single-crystalline potassium hollandite $KTi_8O_{16.5}$ nanowires were synthesized by the molten salt method at 800 °C. Scanning electron microscopy observation shows that the nanowires are with octagonal cross-sections, and combined analyses of transmission electron microscopy and the electron diffraction results show that the terminated planes are angled 90 or 60 degrees to the growth direction, [001] crystallography direction. Ordering of the potassium cations in the tunnels was revealed by electron diffraction. The mechanism of one-dimensional growth of the nanowires was attributed to the oriented attachment mechanism.

© 2008 Elsevier Inc. All rights reserved.

1. Introduction

The hollandite structure with general formula of $A_x(B_yTi_{8-y})O_{16}$, where A=K, Cs or Ba, and B is either a divalent or a trivalent cations, 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 [1]. Because of their particular structural features, hollandite-type compounds were considered as potential candidates for one-dimensional ionic conductivity [2]. The positions of the A cations in the tunnels have been investigated in several hollandite-type crystals by neutron diffraction or rotation photograph of X-ray scattering [3].

The conventional synthesis of potassium hollandite single-crystals involves slow O_2 oxidation of precursors, and thus the synthesis process is time-consuming and hard to control [4]. In the present work, we have prepared potassium hollandite ($KTi_8O_{16.5}$) nanowires by molten salt synthesis (MSS), and the synthesized nanowires were characterized by scanning electron microscope (SEM), transmission electron microscope (TEM) and electron diffraction technique. The growth mechanism of the nanowires was proposed based on high-resolution electron microscope observation.

* *Corresponding author*. School of Materials Science and Engineering, P.O. Box 433, Harbin Institute of Technology, Harbin 150001, China. Tel.: +86 451 8641 2133; fax: +86 451 8641 3922.
E-mail address: lzhen@hit.edu.cn (L. Zhen).

1044-5803/$ – see front matter © 2008 Elsevier Inc. All rights reserved.
doi:10.1016/j.matchar.2008.04.003

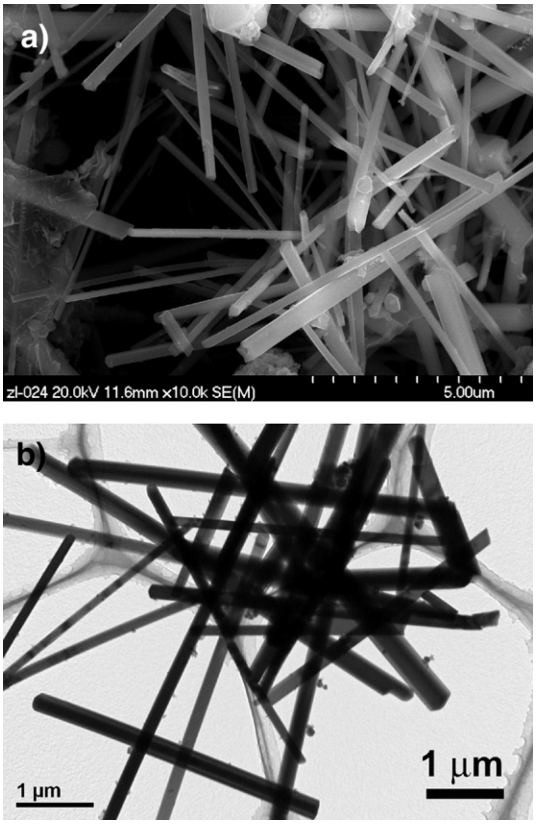

Fig. 1 – Morphology of the synthesized potassium hollandite nanowires. (a) SEM image and (b) TEM image.

2. Experimental

Single-crystalline potassium hollandite ($KTi_8O_{16.5}$) nanowires were synthesized by the molten salt method, which was reported elsewhere [5]. In brief, a mixture of TiO_2 (anatase) and KCl was ground with nonionic surfactant NP-9, and then annealed in a tube furnace at 800 °C for 3 h, and subsequently, cooled naturally to room temperature. The pristine powders were then washed with distilled water several times to remove excess KCl. Single-crystalline $KTi_8O_{16.5}$ nanowires were obtained on large scale by using this facile method. The synthesized nanowires were characterized by scanning electron microscope (SEM, Hitachi S-4700), transmission electron microscope (TEM, JEM-100CX, JEOL-2010F, JEM-3010).

3. Results and Discussion

Fig. 1a shows SEM image of the as-synthesized potassium hollandite nanowires. A large quantity of nanowires with diameters ranging from tens of nanometers to a few hundreds nanometers were obtained. The length of the nanowires ranges from several to a few tens of microns. The relative narrow diameter distribution of the nanowires was demonstrated by the TEM image, as shown in Fig. 1b. The phase of the nanowires was examined by X-ray diffraction (XRD, Rigaku D/max-γB X-ray diffractometer with Cu K_α radiation, $\lambda = 1.5406$ Å, not shown here), and the result suggests that the obtained

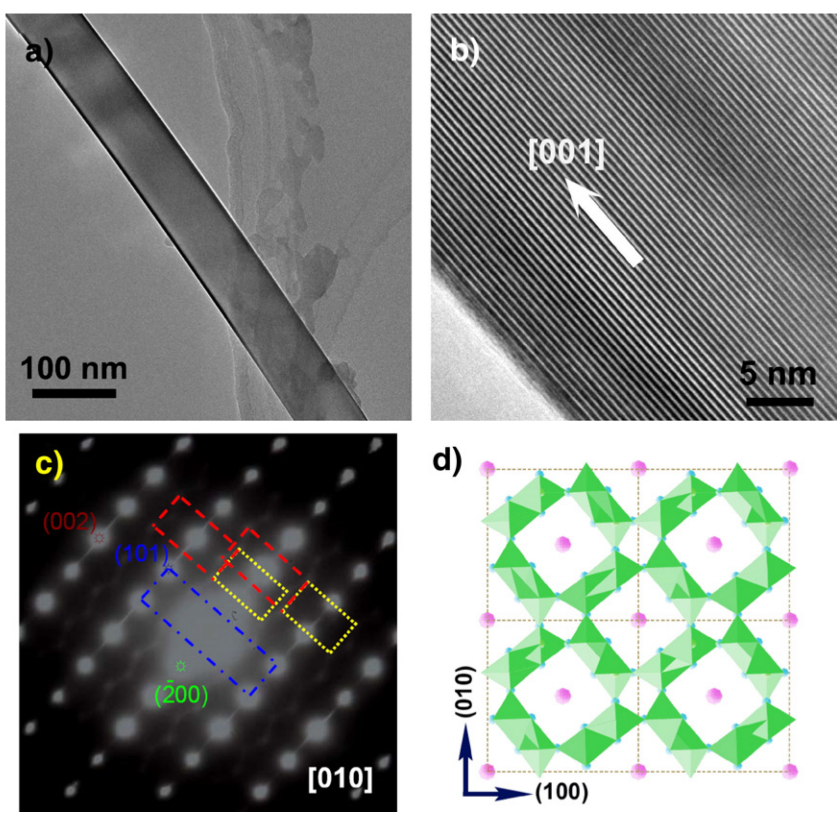

Fig. 2 – (a) TEM image of an individual $KTi_8O_{16.5}$ nanowire and corresponding HRTEM image (b) and selected area electron diffraction pattern (c). (d) Atomic structure of potassium hollandite viewed along [001] direction.

nanowires are potassium hollandite ($KTi_8O_{16.5}$, tetragonal) nanowires, with lattice parameters of $a=10.15$ Å and $c=2.962$ Å.

The synthesized potassium hollandite nanowires were furthered examined with transmission electron microscope. Selected area electron diffraction (SAED) patterns taken from a wealth of nanowires indicate that the nanowires are single-crystalline in nature. Fig. 2a shows the TEM image of an individual nanowire with diameter of c.a. 90 nm. High resolution transmission electron microscopy (HRTEM) image of the selected nanowire shown in Fig. 2b gives clearly-resolved one-dimensional lattice spacing of $d_{200}=5.10$ Å. Fig. 2c shows the SAED pattern of the studied nanowire along the [010] zone axis. Combining the image and electron diffraction pattern together, the growth direction of the nanowire is determined to be along its [001] crystallography direction, which can be also read from the streaks perpendicular to the [001] crystallography direction in the pattern. In addition, ordering phenomena in the nanowires was observed from the SAED pattern. As mentioned above, the channels surrounded by edge-sharing TiO_6 octahedras (shown in Fig. 2d) are only partially occupied by K cations, and the occupied sites are usually ordered. The zig-zag weak pattern in the diffraction pattern can be assigned to two sets of primary diffraction patterns, which was marked with dashed red rectangle plus the yellow dotted one, as shown in Fig. 2c. The primary diffraction pattern was marked with dot-by-dash blue rectangle, which is the sum of red and yellow ones. The superlattice diffraction pattern was originated from the ordering of K cations in the tunnels, and the existence of two sets of superlattice diffraction patterns suggests that the occupancy of K cations is probably ordered in three dimensional. It should be noted that the length of the red rectangle versus that of the yellow one is 1.167, indicating the incommensurate structure along [001] crystallography direction due to ordering of K cations [4].

Fig. 3a shows the top-view of the as-synthesized potassium hollandite nanowires. Rectangle cross-section of the nanowires was revealed, as marked by blue (solid line) and red (dashed line) circles. The difference between the two marked nanowires is that the angle between the terminated face and the growth direction, the blue one is 90°, while the red one is 60°. Close view of individual nanowire cross-sections shows that the cross-section is actually an octagonal cross-section, like a square cut a little from the four apexes, as shown in Fig. 3b and d. The typical angles between the terminated face and the growth direction of 90° and 60° were revealed by typical TEM images (shown in Fig. 3c and e) corresponding to Fig. 3b and d, respectively. The sketches of the terminated plane and side ones were shown in the insets of Fig. 3c and e, indicating that (001) crystallography plane is the terminated plane when the cross-section is vertical to the growth direction, while it is (−1, 0, 2) plane for the angle of 60°.

The potassium hollandite nanowires were synthesized in potassium chloride molten salt at 800°C, which is much lower than the melting point of the raw material TiO_2. Thus, conventional vapor–liquid–solid or vapor–solid mechanism cannot be used to interpret the 1D growth of the hollandite nanowires. To investigate the growth mechanism, the as-synthesized nanowires were examined carefully by HRTEM. Fig. 4a shows a high-magnification TEM image of two neighboring nanoparticles. HRTEM image of the nanoparticles (Fig. 4b) shows that both the two particles are potassium hollandite, and the lattice images are identical, suggesting

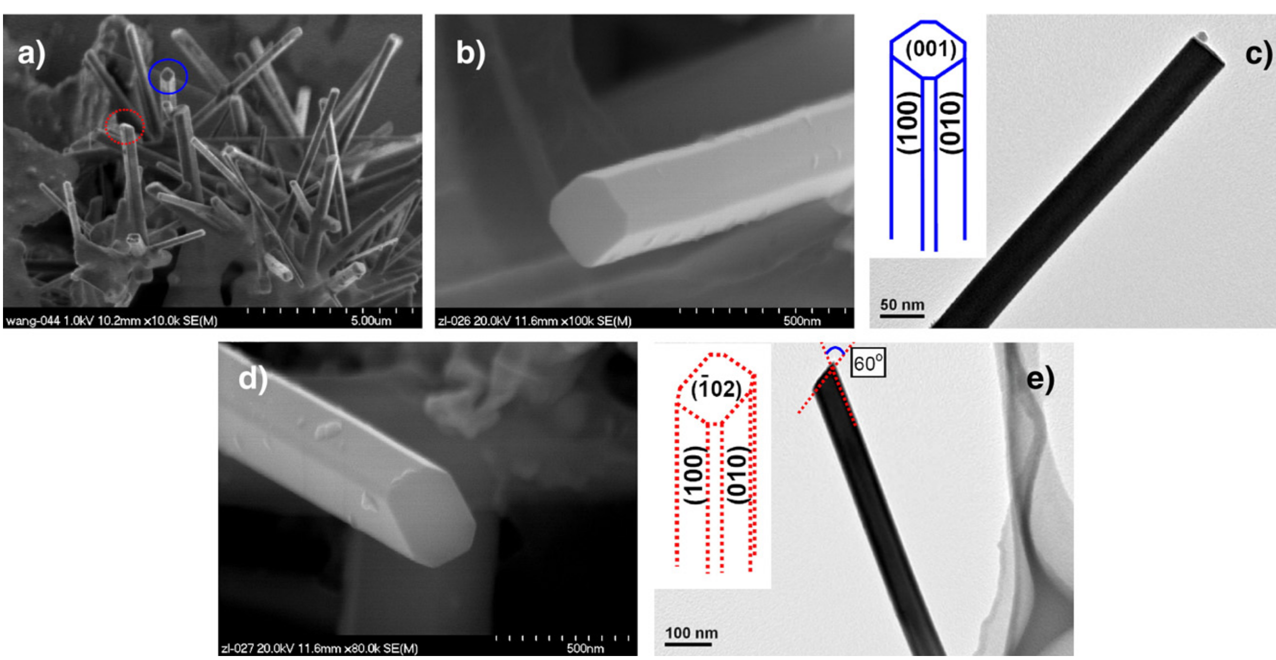

Fig. 3 – (Color online) (a) Top-view of as-synthesized potassium hollandite nanowires. Blue (solid line) and red (dotted line) circles mark different cross-section of the nanowires. (b and d) SEM images of individual nanowire showing different cross-section shapes. (c and e) TEM images showing morphology of nanowire tips corresponding to b and d. Insets in c and e show sketch of crystal plane layout at nanowire tip.

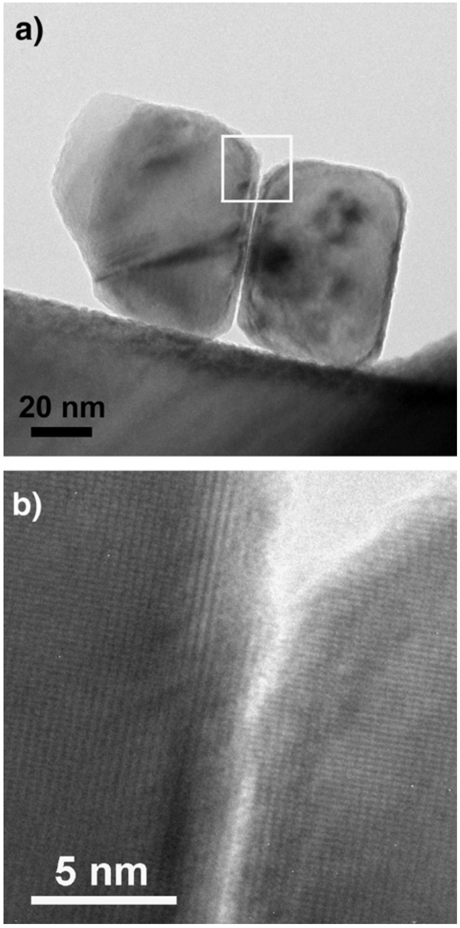

Fig. 4 – (a) High-magnification TEM image of two neighboring potassium hollandite particles. (b) HRTEM image of the boxed area in (a) showing identical lattice image of the two neighboring particles.

that the formation of the hollandite nanowires is probably based on the oriented attachment mechanism, which was first proposed by Penn and Banfield [6,7]. TiO_2 might react with K^+, which is from the molten salt, and $KTi_8O_{16.5}$ nanoparticles were formed, and then the $KTi_8O_{16.5}$ nanoparticles merged together, leading to the formation of single-crystalline nanowires.

4. Conclusions

In summary, potassium hollandite ($KTi_8O_{16.5}$) nanowires with octagonal cross-section were characterized by SEM, TEM, HRTEM and electron diffraction technique. The growth direction of the nanowire was determined to be along its [001] crystallography direction. Incommensurate structure due to the ordering of K cations in the tunnels was demonstrated by electron diffraction. Oriented attachment mechanism was employed to interpret the 1D growth behavior of the potassium hollandite nanowires synthesized by the molten salt method.

Acknowledgements

C.Y. Xu was supported by the Development Program for Outstanding Young Teachers of HIT. Thank Dr. Y.Z. Liu at Georgia Institute of Technology for fruitful discussion.

REFERENCES

[1] Bystroem A, Bystroem AM. The crystal structure of hollandite, the related manganese oxide minerals, and alpha-MnO_2. Acta Cryst 1950;3:146.
[2] Yoshikado S, Ohachi T, Taniguchi I, Onoda Y, Watanabe M, Fujiki Y. AC ionic conductivity of hollandite type compounds from 100 Hz to 37.0 GHz. Solid State Ionics 1982;7:335.
[3] Vicat J, Fanchon E, Strobel P, Qui DT. The structure of $K_{1.33}Mn_8O_{16}$ and cation ordering in hollandite-type structure. Acta Cryst B 1986;42:162.
[4] Vogt V, Schweda E, Wüstefeld C, Strähle J, Cheetham AK. Structural analysis of a potassium hollandite $K_{1.35}Ti_8O_{16}$. J Solid State Chem 1989;83:61.
[5] Xu CY, Zhang Q, Zhang H, Zhen L, Tang J, Qin LC. Synthesis and characterization of single-crystalline alkali titanate nanowires. J Am Chem Soc 2005;127:11584.
[6] Banfield JF, Welech SA, Zhang H, Ebert TT, Penn RL. Aggregation-based crystal growth and microstructure development in natural iron oxyhydroxide biomineralization products. Science 2000;289:751.
[7] Penn RL, Banfield JF. Imperfect oriented attachment: Dislocation generation in defect-free nanocrystals. Science 1998;281:969.