

Large-scale preparation of aluminum borate-coated aluminum oxide nanowires

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Abstract

Single-crystal and uniform aluminum borate ($\text{Al}_4\text{B}_2\text{O}_9$)-coated aluminum oxide nanowires have been synthesized in high purity and in large yield via a reaction of metal aluminum with boron oxide in the presence of carbon nanotubes (CNTs). The aluminum oxide nanowires exhibit a well-crystallized one-dimensional structure with diameters ranging from 50 to 70 nm, and the $\text{Al}_4\text{B}_2\text{O}_9$ have a coating thickness of about 1–5 nm. CNTs play a crucial role in the formation of the important ceramic nanowires, by providing a platform to grow the composite structure. The growth mechanism was proposed by the detailed microscopy observations.

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1. Introduction

One-dimensional nanomaterials are currently being researched throughout the world due to their unique applications in fabricating nanoscale electronic, photonic, electrochemical, electromechanical, and sensing devices [1–4]. Carbon nanotubes (CNTs) have been the most important research topic pointing to these applications and have also been widely used as the precursor for other important nanomaterials with one-dimensional morphology [5]. Great efforts have been put into the synthetic researches on CNTs in bulk quality [6]. Therefore, there has been the widespread interest in the fabrication of novel one-dimensional nanoscale materials with improved properties by decorating CNTs in the fashion of filling, coating [7–9], template reaction or substitution reaction [10,11].

Aluminum oxide is an important structural ceramic material due to its high strength, elastic modulus,

thermal stability, and low density [12,13]. There have also been interests for the Al_2O_3 -based composites in order to enhance its toughness. Many investigations have demonstrated that it is possible to toughen the ceramic matrix by implanting various materials having higher toughness. Recent researches have indicated that the strength and ductility of nanostructured ceramics and nanoscale whiskers are greatly superior to those on the micrometer or bulk scale. For example, the strength of SiC nanowires is a factor of 2 times the best previously observed SiC whiskers in micrometer diameter [14,15]. Therefore, nanowires or nanotubes made of SiC are very useful to reinforce the ceramic by constructing SiC– Al_2O_3 composites. However, nanoscale SiC is prone to be oxidated at high temperatures, resulting in a marked degradation of strength and toughness [16,17]. There have thus been many investigations on BN-based composite one-dimensional nanowires, due to the excellent chemical and thermal stability of BN nanotubes [18]. The process of producing composite nanowire structure BN– Al_2O_3 is difficult and the costly price is also a consideration for commercial applications.

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Aluminum borate whiskers are one of the traditional ceramic materials at the cheap prices with enhanced mechanical properties, high melting point and stability in oxidizing environments [19]. With these characteristics, aluminum borate nanowires may have potential in oxidation-resistant reinforced composites. Free-standing nanowires made of aluminum borate have been synthesized by several groups [20–22]. If the aluminum borate could be synthesized in a composite form, coating on the Al_2O_3 nanowires, the expected one-dimensional composites would have considerable potential for a wide range of applications due to the mechanical properties enhancement as a result of the shape-specific and quantum-size effects.

Here we report a simple method to synthesize the aluminum borate-coated aluminum oxide with the composite structure in a high yield by using CNTs as templates for the first time. Structural analysis and growth mechanism of the composite nanowires are discussed in the present paper.

2. Experimental

Multi-walled CNTs were prepared by metal catalytic decomposition of ethylene and hydrogen in a traditional chemical vapor deposition system, in the presence of the nanoscale alumina supported iron catalysts. The catalytic growth yields CNTs with a typical diameter of ~ 20 nm. The product contains a small amount of catalyst impurities. The CNTs used in this study were further purified by refluxing the as-synthesized nanotubes with concentrated HNO_3 solution for 2 h, then washing with distilled water, vacuum drying in an oven at 60°C for 12 h.

The mixture of Al and B_2O_3 with the weight ratio of 1:3 was homogenized with an agate pestle and mortar. The mixture was used as an initial reactant, which was placed in a quartz crucible and was then covered by the purified CNTs. The crucible was placed in the center of a sintered alumina tube held in a traditional resistance-heating horizontal furnace. Argon was flowing during the overall reaction period as a transport gas to maintain the inert atmosphere of reaction system. The furnace was heated to reach 1000°C and held for 90 min. After reaction, the reaction gas was shut off and the furnace was cooled to room temperature naturally.

Upon completing the reaction, the original product was converted into a gray rigid shell. The product was physically scrapped from the crucible and washed with distilled water at the temperature of about 60°C several times to remove the residual B_2O_3 . In order to eliminate the residual CNTs, the product was further heated at 700°C in air for 1 h.

The product was examined by means of X-ray diffraction (XRD, D/max-rB, Cu K_α radiation) analysis

at room temperature. The overview of the sample morphology was checked by scanning electron microscopy (SEM, JSM-6700F, JEOL). The sample was also ultrasonically dispersed in CCl_4 solution and was then transferred onto a copper grid covered with holey carbon for transmission electron microscopy (TEM, JEM-2100F, JEOL) equipped with the system of energy-dispersive X-ray (EDX) analysis.

3. Results and discussion

Fig. 1 (top) shows the XRD pattern of the product after purification by washing with water and heating in the ambient atmosphere, indicating that the remnant reactants like incompletely reacted CNTs and boric oxide were fully removed. The sharp diffraction peaks shown in the pattern can be well assigned to cubic Al, corundum $\alpha\text{-Al}_2\text{O}_3$ and orthorhombic $\text{Al}_4\text{B}_2\text{O}_9$ in their peak positions. The residual reactant Al could also be removed by treating the product with a dilute hydrochloric acid solution, confirmed by the XRD diffraction measurement shown in Fig. 1 (bottom). We also noticed that, although the observed diffraction patterns of aluminum oxide and aluminum borate in peak positions are consistent with the patterns from the counterpart bulk materials (see JCPDS 83-2081 and JCPDS 29-0010), their peak intensities exhibit considerable difference between the present XRD patterns and the patterns of bulk materials. The ideal intensity ratio of Al_2O_3 corundum between (012) and (113) is about 0.7, whereas the measured ratio in this study is smaller than 0.4. The intensity from (113) diffraction is obviously enhanced. This phenomenon has also been observed for GaP nanorods [23] and Al_2O_3 whiskers [24], which was

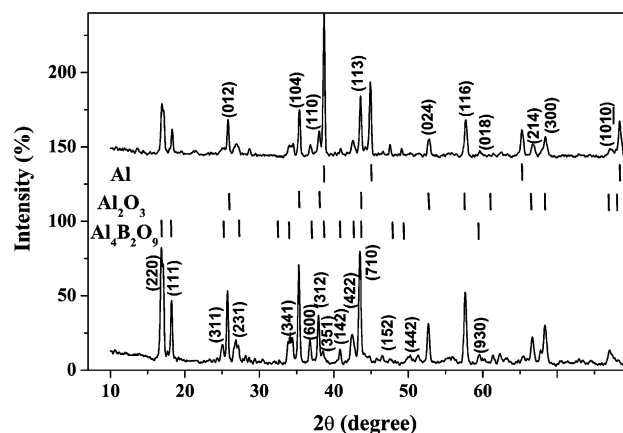


Fig. 1. XRD patterns of the product washed with water and heated at 700°C in air (top), followed by treating with dilute hydrochloric acid solution (bottom). Al remnant was fully removed by the acid treatment. The peak positions of Al_2O_3 and $\text{Al}_4\text{B}_2\text{O}_9$ are marked by their indices, and shown in the top and bottom of the figure, respectively.

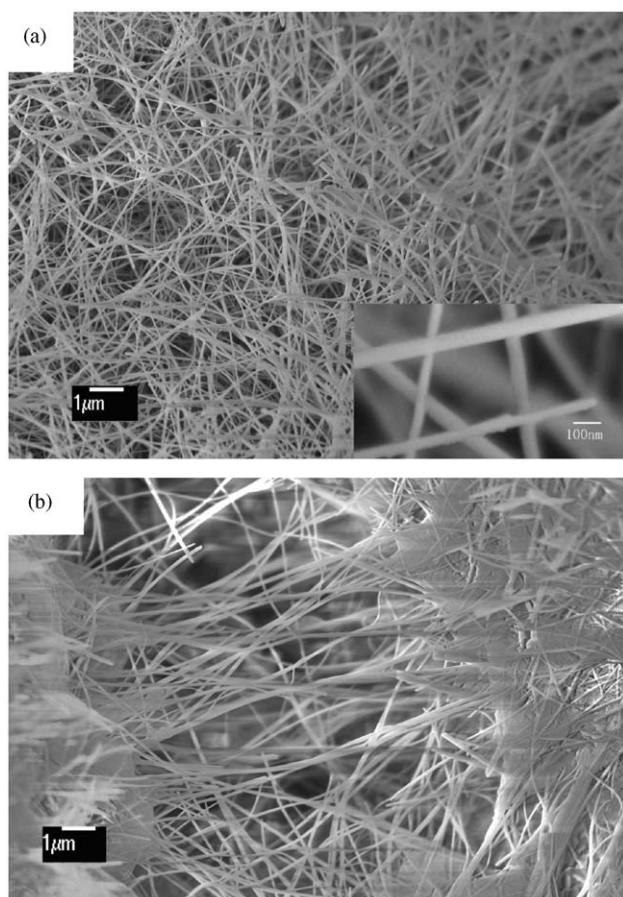


Fig. 2. Commonly observed SEM images of the product after the purification: (a) free-standing and twisted nanowires, (inset) a high-magnification image of this type of nanowires; and (b) hedge-like nanowires grown from an aggregated lump.

attributed to preferential growth of wire-like structure. As a result, the present Al_2O_3 crystal should have a preferential epitaxial axis perpendicular to (113) plane. The intensity ratio between (111) and (220) of $\text{Al}_4\text{B}_2\text{O}_9$ was ~ 0.6 , whereas the ratio is only ~ 0.15 observed in the bulk counterpart, indicating a texture structure with an epitaxial axis.

Fig. 2 shows the typical SEM images of the product after the purification, indicating that the product is the free-standing nanowires with uniform diameter of 50–70 nm and typical length of several tens of micrometers (Fig. 2a). However, some curvy nanowires could also be found clearly from the SEM image as shown in Fig. 2b, which grow radiantly from some irregular particles. EDX measurements for the particles show the presence of Al, B and O in the particles.

TEM observation allows us to confirm the uniformity and the cylindrical morphology of the synthesized nanowires. A low-magnification TEM image of the product is shown in Fig. 3a. Besides the wire-like nanowires, wool-like aluminum borate was also found

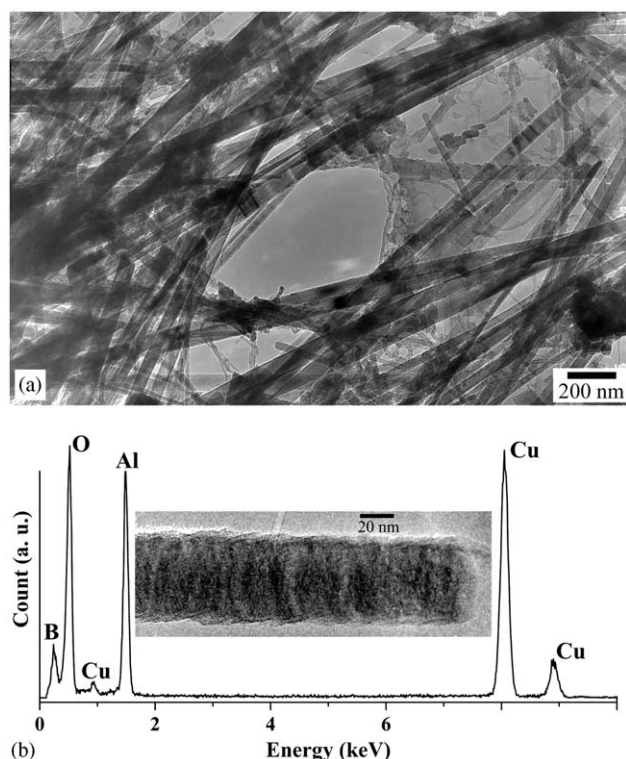


Fig. 3. (a) Typical TEM images of the composite nanowires; wool-like materials could be easily observed during TEM observation; (b) individual nanowire having the non-cylindrical fragment-like ending and the corresponding EDX spectrum.

from TEM observation. The wool product should result from the aggregated lump shown in the SEM image, implying that the aggregates were dispersed fully in the process of preparing TEM sample using the ultrasonic dispersion method. We also noticed that all nanowires have the non-cylindrical fragment-like morphologies at their ends, no other elements except Al, B and O can be observed. Shown in Fig. 3b is its chemical composition examined by EDX technique, indicating that the tip ending and the nanowire contain Al, B and O with the same Al/O molar ratio of $\sim 2.0/2.8$. In fact, chemical composition analyses for the large amount of the nanowires show that the Al/O ratio is basically constant, ranging from 2.0/2.8 to 2.0/2.5. This indicates that the present nanowires should be made of $\text{Al}_4\text{B}_2\text{O}_9$ and Al_2O_3 , as exhibited from XRD measurement.

It is worth noting that $\text{Al}_4\text{B}_2\text{O}_9$ and Al_2O_3 were detected simultaneously from individual nanowires. High-resolution TEM examination gave the further details for the crystalline structure of the aluminum borate-coated aluminum oxide nanowires. The composite nanowire structures were imaged by HRTEM, as shown in Figs. 4a and b. Two different contrasts are clearly visible in most of the individual nanowire. The outer coating walls are $\text{Al}_4\text{B}_2\text{O}_9$, and the cores with

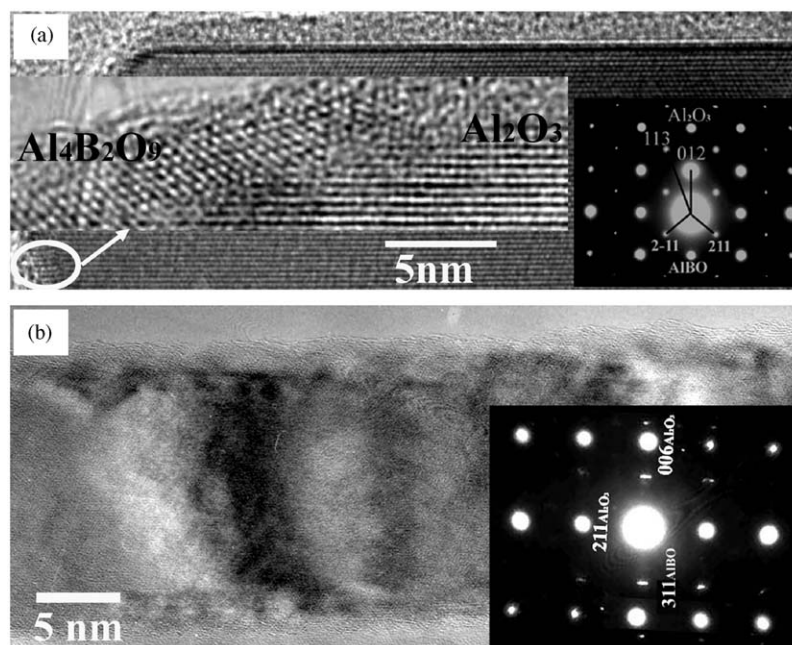


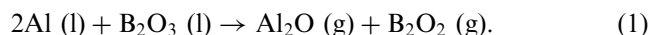
Fig. 4. High-resolution TEM images of composite $\text{Al}_4\text{B}_2\text{O}_9/\text{Al}_2\text{O}_3$ nanowires: (a) $\alpha\text{-Al}_2\text{O}_3$ corundum viewed along its $[0\bar{1}1]$ zone axis, (inset) SAED patterns showing the orientation $(102)_{\text{AlBO}}/(012)_{\text{AlO}}$ and the enlargement image from the circled area; (b) Al_2O_3 zone axis along $[110]$, (inset) SAED pattern with the orientation $(311)_{\text{AlBO}}/(001)_{\text{AlO}}$.

darker contrast are Al_2O_3 . After examining over 100 of the one-dimensional structures, it was found that most of the nanowires (over 90%) exhibit the composite structure. We also observed that the thickness of the outer layers has a wide distribution ranging from ~ 1 to ~ 5 nm.

Fig. 4a shows a high-resolution TEM image of the composite nanowire with coating thickness of ~ 1 nm and the corresponding selected area electron diffraction (SAED) pattern. The SAED pattern can be indexed as the mixture of $[0\bar{1}1]$ zone axis of Al_2O_3 and $[\bar{1}02]$ of $\text{Al}_4\text{B}_2\text{O}_9$. The orientation relationship was $(102)_{\text{AlBO}}// (012)_{\text{AlO}}$. The Al_2O_3 core has an interlayer spacing of 0.21 nm, which corresponds well to the interplanar distance of the (113) planes. It is also noteworthy that there are some stacking faults of atomic arrangement between Al_2O_3 and $\text{Al}_4\text{B}_2\text{O}_9$. Al_2O_3 nanowires thus grow basically along $[110]$ direction, also determined using defocus technique. Fig. 4b shows the high-resolution TEM image and SAED pattern from another nanowire with coating thickness of ~ 3 nm. The diffraction pattern from the top layer of $\text{Al}_4\text{B}_2\text{O}_9$ can be well accounted for by the $[110]$ zone axis of Al_2O_3 and $[0\bar{1}1]$ of $\text{Al}_4\text{B}_2\text{O}_9$.

Comparing with the previous report about the synthesis of aluminum borate nanowires [22], we believe that CNTs used in this study are essential to the formation of the composite nanowires. The formation mechanism should involve in a vapor–solid reaction process, and CNTs provide the platform to start

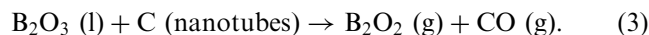
growing the composite structure. A possible growth process will be discussed as follows. The following reaction starts when heating B_2O_3 and Al at a high temperature:



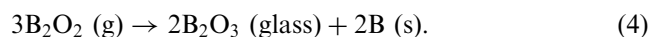
The generated Al_2O vapors transfer and deposit onto the surfaces of CNTs to form Al_2O_3 lumps, or form Al_2O_3 nanowires along with CNTs, according to the process



Once the nanowires are formed, this trend might be maintained and Al_2O_3 nanowires would grow continuously along the initially formed crystal directions. Simultaneously, the vapor B_2O_2 reacts with Al_2O or Al_2O_3 to form $\text{Al}_4\text{B}_2\text{O}_9$ crystal. At the same time, B_2O_2 gas can also be supplied by the chemical reaction



Therefore, the existence of CNTs avoids the formation of the glassy B_2O_3 in the product due to the decomposition of B_2O_2 to B_2O_3 at low temperature according to the reaction



B_2O_2 gas can escape and react with Al or its oxides, forming $\text{Al}_4\text{B}_2\text{O}_9$ coating at the surface of the as-grown Al_2O_3 .

The diameters of the Al₂O₃ nanowires coated by aluminum borate layers may be larger than those of the starting CNTs due to the epitaxial growth discussed above when the total reaction time is long and the reactants are supplied continuously. This phenomenon has been explained in the other works of synthesizing nanowires via CNTs reaction [25,26].

We speculate that the defects of Al₂O₃ nanowires are one of the driving forces for the one-dimensional growth. The presence of these defects at the tip areas we observed in this study should result in the fast growth of Al₂O₃ nanowires along a certain direction since dislocations are known to play an important role in crystal growth [27].

4. Conclusions

High quality of single-crystal structured aluminum borate—aluminum oxide nanowires have been synthesized by using CNTs as a reaction template. A possible mechanism for the growth of the composite nanowires was proposed based on the TEM and XRD examinations. Considering the simplicity of the procedure, the method described here is likely to be of interest to commercial-scale production in order to find application in metal reinforcing materials.

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