

High-Aspect-Ratio Aluminum Borate Nanowire Bundles Supported by Sucrose

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High-aspect-ratio and single-crystal aluminum borate ($\text{Al}_{18}\text{B}_4\text{O}_{33}$) nanowire bundles with an ordered orientation were synthesized by using an innovative sucrose-assisted growth process. The process involves the dehydration and polycondensation of aluminum borate–sucrose solution to form a highly viscous precursor. The sucrose plays a crucial role in the growth of the nanowire bundles by supporting as a polymeric substrate and a type of adhesive template. Electron microscopy was used to characterize the high-aspect-ratio nanowire bundles. A possible growth mechanism for the nanowire bundles is proposed.

1. Introduction

One-dimensional nanostructures and nanomaterials, such as nanotubes, nanowires, and nanorods, have attracted special interest in recent years because of their great potential for increasing the understanding of fundamental physics and for various nanotechnological applications.^{1–4} Considerable research has been done for the synthesis of such nanostructures, as well as for the corresponding properties. Some nanostructures are believed to be able to exhibit a range of interesting properties superior to their bulk counterparts.^{5–7}

Considering the important role played by traditional whisker-reinforced ceramic composites in current commercial applications, SiC nanowires are particularly interesting and used widely to strengthen composite materials by incorporation of SiC whiskers into some brittle matrices. However, nanoscale SiC is prone to be oxidated at high temperature, resulting in a marked degradation of strength and toughness.^{8,9} Aluminum borate whiskers/nanowires meet these expectations based on their excellent mechanical properties, chemical inertness, high-temperature stability, low thermal expansion coefficient, and much lower cost compared to SiC nanowires.^{10–13}

Because of the superior properties of aluminum borate nanocomposites, $\text{Al}_{18}\text{B}_4\text{O}_{33}$ whiskers and fibers have been fabricated by several different techniques.^{14,15} Microtubes, nanowires, and coated $\text{Al}_{18}\text{B}_4\text{O}_{33}$ have been synthesized by the direct reaction between aluminum source and boron source.^{16–21} In addition, nanowires with high aspect ratios possess the significant third (or z) dimension leading to increased surface and cross section areas, which is important for the enhancement of mechanical properties.²² However, from the reported literature the largest aspect ratio of aluminum borate whiskers only gets to a few tens.^{16–21} To expand the application field of the aluminum borate nanowires and further enhance the mechanical properties, it is important to prepare the aluminum borate nanowires with a higher aspect ratio (up to hundred).

Besides the low aspect ratio, the free-standing appearance of the reported nanowire/microtube-based aluminum borate is another difficulty for the possible applications in automotive engines, photonics, and electronic materials. Little attention has

been paid to the preparation of the ordered aluminum borate nanowires so far.^{11,23}

In this work, we report a novel approach for the growth of the ordered orientation $\text{Al}_{18}\text{B}_4\text{O}_{33}$ nanowire bundles, which was synthesized by a sucrose-assisted growth method. We use sucrose as the monodispersed solvent and a novel adhesive template to prepare $\text{Al}_{18}\text{B}_4\text{O}_{33}$ nanowire bundles. The monodispersed precursor was obtained first, and a thermal treatment process was applied to prepare aluminum borate nanowire bundles. Sucrose is a cheap and safe reactant, combined with easy control of preparing parameters and highly viscous property. These make the present method facile for the large-scale production of high-aspect-ratio ordered orientation nanowire bundles by using sucrose as the assisted reactant.

2. Experimental Section

Commercially available aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 99.0% purity), boric acid (H_3BO_3 , 99.5% purity), and sucrose were used as the starting materials. The molar ratio of aluminum nitrate and boric acid was 1:2, and the weight ratio of the sucrose to the addition mass of aluminum nitrate and boric acid was 1:1. The following two steps were used to prepare the aluminum borate nanowire bundles.

Preparation of the Precursor. The starting materials (200 mg weight in total, in the fixed ratio mentioned above) in a 300 mL capacity of the beaker were dissolved slowly by 200 mL of the distilled water. After the sonication of the mixture for 20 min, the solution was further stirred vigorously at 80 °C until a highly viscous black gelatin appeared. The precursor was then obtained by keeping the gelatin in a vacuum system at 120 °C for 8 h.

Thermolysis of the Precursor. The precursor was placed in an alumina crucible located in an alumina tube, which was mounted in a traditional resistance-heating furnace. The system was first purged with a high purity argon for 30 min. The argon flow was then kept at 40 standard cubic centimeters per minute (sccm) when the furnace was heated to 1300 °C in 90 min. After the reaction for 2 h, the furnace was allowed to cool naturally in the argon flow. When the temperature decreased to 800 °C, the argon flow was shut off and the reaction crucible was exposed directly to the ambient atmosphere in order to

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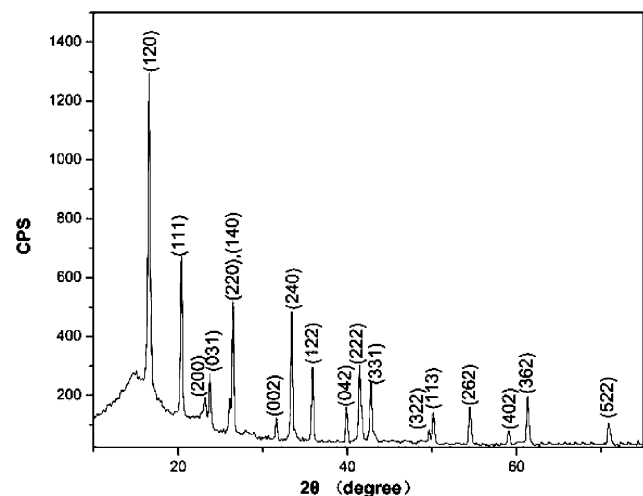


Figure 1. XRD pattern of the product. The peaks of the pattern can be well indexed as the orthorhombic-structured aluminum borate $\text{Al}_{18}\text{B}_4\text{O}_{33}$.

remove the remnant carbon-contained reactants. After the reaction, a light-gray powder was obtained.

The product was identified by means of X-ray diffraction (XRD, D/max-rB, Cu $\text{K}\alpha$ radiation) analysis. The overview of the sample morphology was checked by a field emission scanning electron microscope (SEM, JSM-6700F, JEOL). The powder sample was also ultrasonically dispersed in ethanol solution and was then transferred onto a copper grid covered with carbon film for the transmission electron microscopy (TEM, JEM-2100F, JEOL) examination.

3. Results and Discussion

The XRD pattern of as-synthesized aluminum borate is shown in Figure 1. All of the diffraction peaks can be well indexed to the phase of orthorhombic aluminum borate with the calculated lattice parameters of $a = 0.768$ nm, $b = 1.501$ nm, and $c = 0.566$ nm, which is in agreement with the standard parameters (JPDs 32-0003). No diffraction peaks from any impurity were observed in the XRD pattern, indicating a high purity and crystallinity of the final sample.

A low-magnification SEM image of the aluminum borate is shown in Figure 2a, indicating that the product consists of bundle-like particles. Each bundle consisted of straight nanowires with lengths up to several tens of micrometers (ranging from 10 to 30 μm). All of the nanowires in each bundle show an ordered orientation, relative to the bundle bottom. Indeed, the bundle usually has an irregular substrate (arrowed in Figure 2a) and all inside nanowires grow from the substrate. The magnified SEM image (Figure 2b) depicts the detailed morphology of one bundle. A great amount of empty pores exist within the bundle, which is an essential indicator that the bundle growth involves a template-based method. (Empty pores resulted from the template removal.)²⁴ An EDS spectrum (Figure 2c) taken from the individual bundle confirms the element composition of the Al, B, and O with the molar ratio approaching 1:1:3, indicating that some amorphous boron oxides exist in the bundle or the substrate.

To understand the role of sucrose played in the formation of aluminum borate nanowire bundles, we have synthesized aluminum borate without the addition of sucrose. The other experimental details are the same as the above experiment with sucrose. Figure 3 shows a SEM image of the synthesized sample. Figure 3a is the overview morphology, and Figure 3b is the magnified SEM image. From the image it can be seen that the

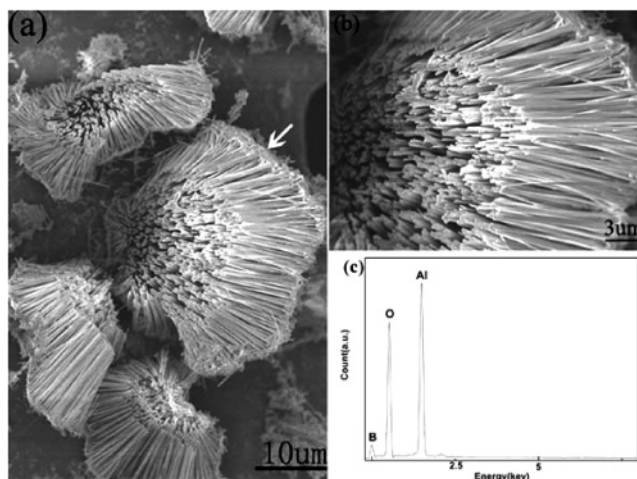


Figure 2. Morphologies and EDS spectra of the aluminum borate nanowire bundles: (a and b) typical SEM images: (a) overview of the bundles, the arrow shows the position of the substrate; (b) magnified image for a single bundle; (c) EDS image from the bundle shown in Figure 2b.

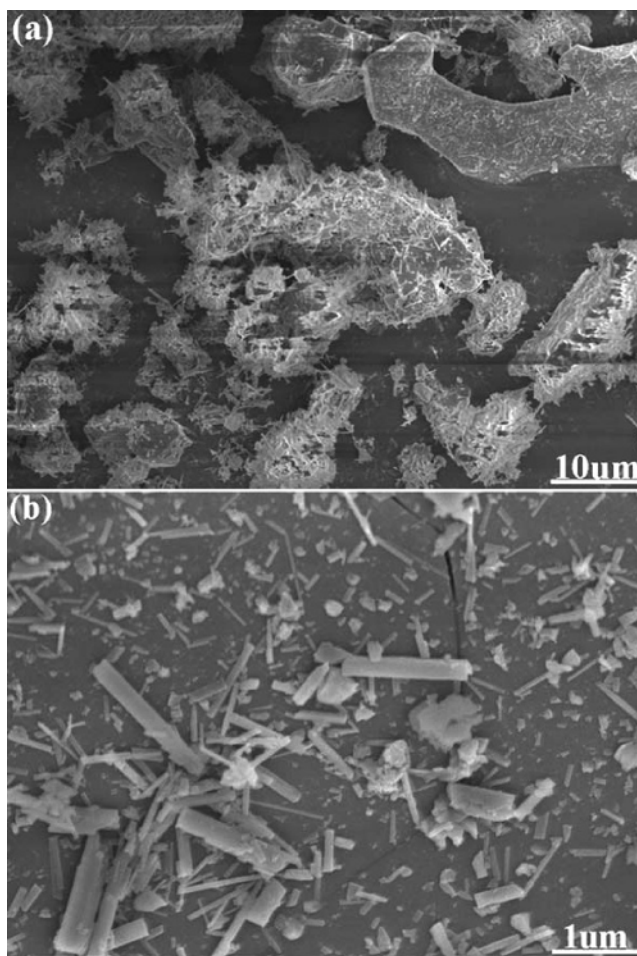


Figure 3. Images of the experiment without sucrose: (a) the overview morphology; (b) the magnified SEM image.

main product is particle-like, and there are also several short, uneven in diameter nanorods existing in the product. Therefore, it reveals that we cannot synthesize the nanowire bundles without the supporting sucrose.

TEM analyses further show the ordered orientation of the aluminum borate nanowire bundles. A small fragment from the bundle was found from the TEM specimen, as shown in Figure 4a. The nanowires within the fragment are basically parallel to

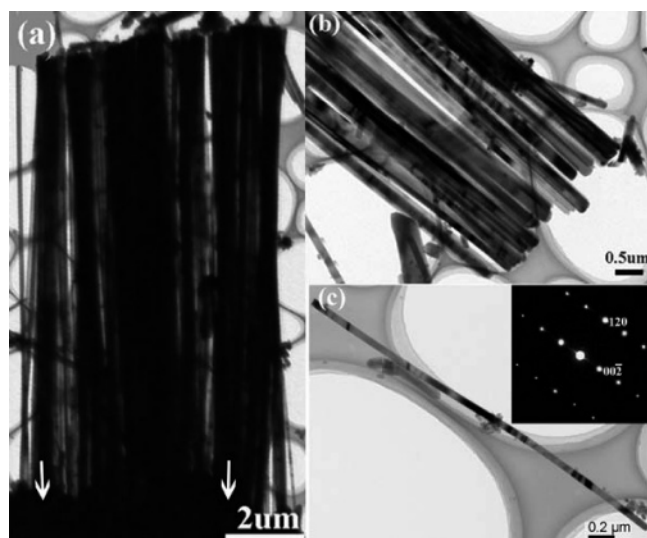


Figure 4. (a) TEM image of a fragment of the bundle, arrows point to the bottom substrate observed in SEM examination; (b) End-tip morphology of the bundle top; (c) Individual nanowire separated from the bundle, and its selected area electron diffraction pattern (inset) recorded from the direction perpendicular to the axis. The pattern can be indexed to the $[-210]$ zone axis of orthorhombic $\text{Al}_{18}\text{B}_4\text{O}_{33}$.

each other. The irregular substrate was observed again (as arrowed in the Figure), which tightly attaches to one end of the nanowire bundle. EDS and selected area electron diffraction (SAED) analyses indicate that the substrate is made of amorphous boron oxide. The product of the polysaccharide of sucrose was removed during the posttreatment process that exposed the as-prepared product to the ambient atmosphere at 800 °C. No amorphous oxide was observed from another end of the bundle, as shown in Figure 4b.

Indicated in Figure 4c is an individual $\text{Al}_{18}\text{B}_4\text{O}_{33}$ nanowire with the diameter ca. 60 nm and the corresponding SAED pattern. The pattern can be indexed as the orthorhombic $\text{Al}_{18}\text{B}_4\text{O}_{33}$ single-crystal recorded from the $[-210]$ zone axis with the same crystalline parameter as the calculated results from XRD measurement. Combining high-resolution TEM with defocus SAED technique, the axis direction of $\text{Al}_{18}\text{B}_4\text{O}_{33}$ nanowires could be determined as $[001]$ c axis growth.

Taking account of the previous reports about the synthesis of aluminum borate nanomaterials,^{14–21} we believe that sucrose plays an important role in the formation of the ordered orientation of nanowire bundles. We tempt to propose a formation mechanism, involving a novel template process discussed as follows.

Beginning with a mixture solution of aluminum nitrate, boric acid, and sucrose, the ions are well mixed on a molecular scale. After the sonication, mixed at 80 °C and dried at 120 °C, reactant particles were uniformly dispersed into sucrose polymer. It has been reported that monodispersed particles can self-assemble easily into two- or three-dimensional arrays by entropy-driven force with the evaporation of used solvent.^{25–27} Therefore, in this study, the precursor of the aluminum borate should align with the confinement of the sucrose. The deduction can be confirmed from the SEM observations for the precursor images, as shown in Figure 5. Although the precursor contains a great amount of lumps (Figure 5a), the magnified SEM images (Figure 5b) indicate the detail structure of the lumps that small particles (diameter ~ 30 nm) adhesive to each other nearly align in one direction, forming a channel-like morphology. These quasi-aligned channels should be generated by the reaction

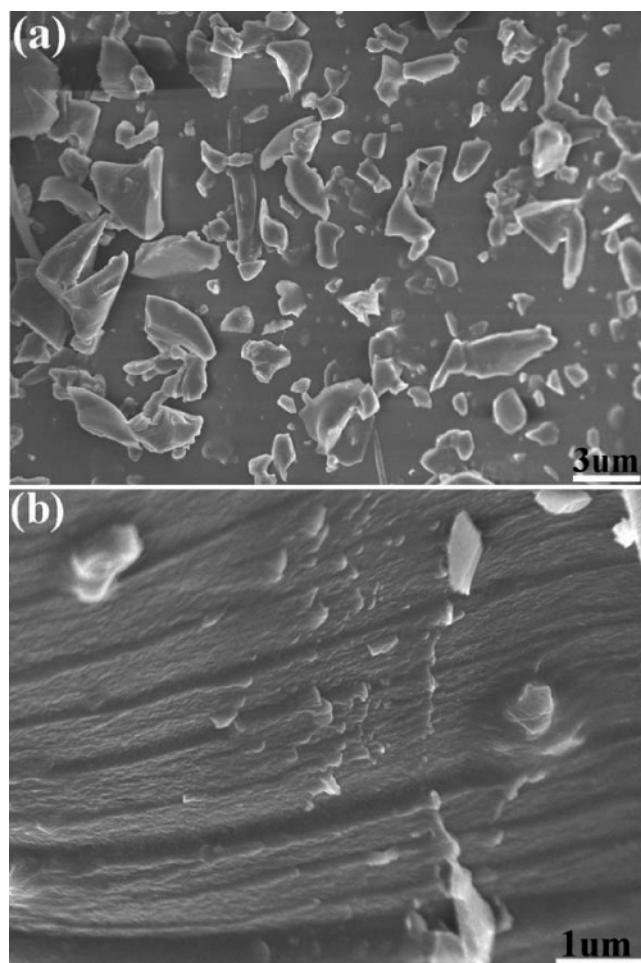


Figure 5. Morphologies of the precursor (a) SEM image of the overview of the precursor, indicating that the precursor contains lump-like particles all over the image; (b) The magnified SEM image of one lump-like particle in Figure 5a, shown that much small particles adhesive to each other and present channel-like morphology quasi-aligned in one direction.

between the starting reactants and sucrose, possibly in a chemical way, forming the AIB–sucrose complex.

When the thermolysis temperature gets to more than 200 °C, the aluminum nitrate in situ decomposes thoroughly into the aluminum oxide. The sucrose gradually undergoes polycondensation reactions and converts to a higher melting point polysaccharide, resulting in a high viscous polymeric resin. With raising the temperature, the interface between the crucible and the reactants was gradually converted into a porous-rich substrate because boron oxide (from decomposition of boric acid) becomes amorphous and glassy.

The monodispersed reactants might undergo a local vapor–solid (LVS) growth process to produce the nanowires. Some carbon decomposed from the sucrose reacts with B_2O_3 and alumina to generate the vapors containing B_2O_2 and Al_2O , which promote the growth of $\text{Al}_4\text{B}_2\text{O}_9$ between 800 °C and 1035 °C.²⁸ $\text{Al}_4\text{B}_2\text{O}_9$ is a low-temperature stable phase and will be converted to $\text{Al}_{18}\text{B}_4\text{O}_{33}$ at high temperature.²¹ At the same time, $\text{Al}_{18}\text{B}_4\text{O}_{33}$ crystallizes in a bundle-like morphology with the help of the template confinement of sucrose polysaccharide and the substrate. The crystallized position depends on the starting reactants, which was confined by the sucrose template. Therefore, the sucrose naturally fixes the growth orientation of the nanowires, and the high viscous liquid polysaccharide existing in the reactants ties the nanowires tightly to form bundles. The air heat-treatment at 800 °C removed the carbonaceous template,

and left the empty pores, as observed in SEM and TEM examinations.

Without the assistance of sucrose, aluminum borate will crystallize freely and no one-dimensional bundle morphology can be found, as confirmed by our experiments.

4. Conclusions

In summary, large-scale uniform nanowire bundles have been synthesized by the reaction between aluminum nitrate and boric acid in the presence of sucrose. The nanowires within the bundle have an ordered orientation, with a diameter distribution from 50 to 90 nm and a length ranging from 10 to 30 μm . Highly viscous polysaccharides of sucrose at high temperature are responsible for the formation of the nanowire bundles. We expect that the novel method reported here can be useful for the preparation and potential applications of aluminum borate and other nanomaterials in the future.

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