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Preparation of h-BN nano-tubes, -bamboos, and -fibers from borazine oligomer with alumina porous template

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Abstract

h-BN nano-tubes, -bamboos, and -fibers were prepared separately from borazine oligomers using an alumina porous template at different wetting times of 20 h, 40 h and 2 weeks at room temperature, respectively. The borazine oligomer in the template was transformed to the h-BN nano-materials by two-step heat-treatment at 600 and 1200 °C in flowing N_2. The FT-IR result confirmed the formation of BN. TEM and SEM images showed the formation of the nano-tubes in diameters 200–300 nm with thin walls about 10–20 nm thick, nano-bamboos 200–300 nm wide with knots at the separations of 0.5–1 μm, and the nano-fibers 15–20 μm long with fine crystallized BN particles. The mechanism for the formation of h-BN nano-tubes, -bamboos and -fibers is proposed.

Keywords: A. Nanostructures; A. Nitrides; A. Organometallic compounds

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1. Introduction

Hexagonal boron nitride (h-BN) is an important material with many unique properties such as a low dielectric constant, and high thermal conductivity, high temperature stability and strength, high corrosion and oxidation resistance [1]. Therefore, h-BN attracts much interest as an important material applicable in many advanced fields. However, the inherent brittleness of BN sets a hurdle to prepare BN materials in a complex form such as films or fibers [2].

Recently, much attention has been paid to nano-materials such as nano-tubes, -fibers or -belts [3]. BN nano-tubes have been prepared by arc-discharge technique [4], laser heating of hexagonal BN (h-BN) at high nitrogen pressures [5], thermal annealing of amorphous boron powder under lithium vapour in h-BN crucible [6], and CVD from borazine using NiB powders as a catalyst [7]. Almost all these methods require complicated and expensive apparatus or severe preparation conditions, resulting in the small amount production. Therefore, a new simple and efficient synthetic method to make BN nano-tubes or -fibers has been highly desired.

Currently, the template-aided synthesis has been considered as one of the major strategies to produce new nano-materials [8]. A selection of templates and precursors is important to control the size and shape of the nano-materials. Various types of templates have been utilized to produce various forms of nanostructured BN [9,10]. Alumina anodic membrane (AAM) has been used as one of the suitable templates for synthesis of 1D nanostructures, due to its tunable pore dimensions, narrow pore size distribution, and good mechanical and thermal stability [8,11].

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Several starting materials are reported for synthesis of BN materials, for instance, polyvinylpentaborane, polyvinylborazine, or dibromoboranedimethyl sulphide, which is known to be a good precursor to form BN upon ammonia thermolysis. Alternatively, borazine ($B_3N_3H_6$) is proved to be one of the almost ideal precursors to synthesis of boron nitride, because of its high ceramic yield to BN, no carbon content, and easy change to BN upon thermal treatment without NH_3 [1,12]. This report describes the interesting preparation of BN nano-tubes, -bamboos and -fibers from borazine oligomer formed at different wetting times using alumina anodic membrane as a template.

2. Experimental

A borazine oligomer was formed from borazine monomer solution which was prepared from a mixture of sodium borohydride ($NaBH_4$) and ammonium sulfate ($(NH_4)_2SO_4$) in tetraglyme at 135 °C in dynamic vacuum [13]. The borazine solution with 97 wt.% $B_3N_3H_6$ and 3 wt.% BH_3NH_3 obtained thus was heated in a glass flask sealed with a teflon cap at 40 °C while stirring for 40 h, after which time borazine liquid oligomer $(B_3N_3H_4)_x$ with a low viscosity was formed; the x value was not determined at present.

A commercially available alumina anodic membrane 60 μm thick with a nominal pore diameter of 100 nm was used as the template (Whatman Ltd., Anodisc 13). The alumina templates were treated by ultrasonic cleaning in acetone, ethanol and distilled water and successive drying at 50 °C. Fig. 1 shows the experimental procedure for synthesis of BN nano-materials. The template was immersed in a borazine oligomer for periods of 20 h, 40 h and 2 weeks in a glove box filled with N_2 at room temperature. The template containing the borazine oligomer was heated at 10 °C min^{-1} from room temperature to 600 °C, then kept for 24 h and subsequently heated to 1200 °C at 10 °C min^{-1}, at which temperature it was maintained for 30 min. The N_2 gas was kept flowing into the glove box during the heat-treatment and cooling to room temperature. The template containing BN was dissolved in a 40% NaOH solution at 60 °C to separate BN materials from the template. The BN nano-materials were carefully washed several times with water and ethanol.

The texture and morphology of BN nano-materials were observed by scanning electron microscopy (SEM) (JEOL JSM 6500F) and high resolution transmission electron microscopy (HRTEM) (JEM2000) with electron diffraction at an accelerating voltage of 200 kV and energy dispersive spectroscopy (EDS). FT-IR spectra of BN nano-tube, -bamboos and -fibers (Thermo Nicolet AVATAR 320) were taken to determine the formation of BN.

3. Results and discussion

3.1. Formation of h-BN nano-tubes by 20 h wetting

Fig. 2 shows SEM images of the side and top views of h-BN nano-tube bundles formed by 20 h wetting of the borazine oligomer. BN nano-tubes are seen to have diameters of 200–300 nm, corresponding to the pore diameters of the template. The lengths of the BN nano-tubes are several tens micrometers. Some chipped walls are observed on the tube surfaces,

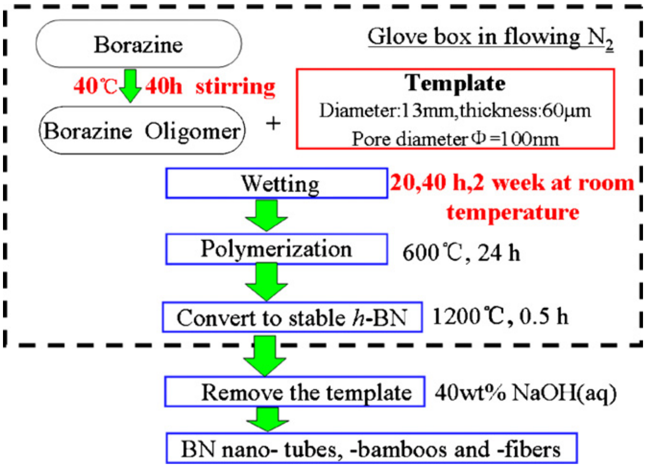

Fig. 1. A flow chart for the process of making BN nano-materials.

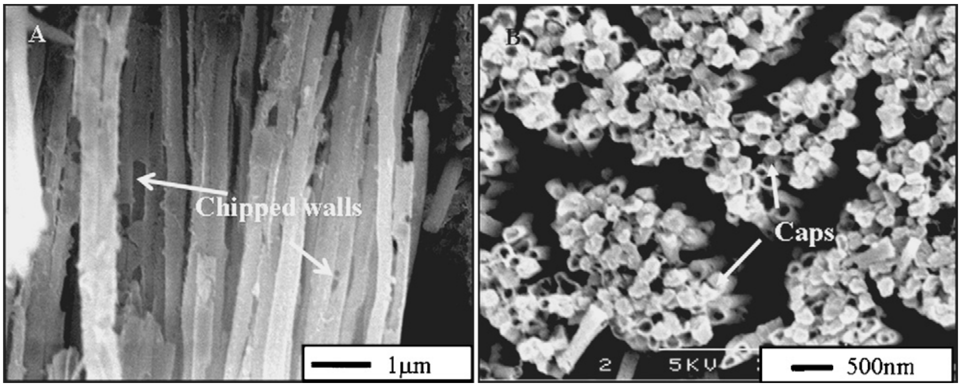

Fig. 2. SEM images of nano-tubes obtained for 20 h wetting: (A) side view bundles of BN nano-tubes and (B) top view of BN nano-tubes.

showing the hollow structure of the nano-tubes (Fig. 2A). In addition to this observation, the recognition of nano-tubes comes from the open ends of the tube bundle array (Fig. 2B). BN caps formed from the borazine oligomer remain on the top tube surfaces. It is proposed that the tubes with open ends were formed by either the expansion of gases trapped in the templates pores during the heat treatment or mechanical damages received during the preparation of SEM.

Microstructural observation of BN nano-tubes was performed by TEM with selected-area electron diffraction (SAED) (Fig. 3). A long straight hollow nano-tube about 200 nm wide with a wall thickness of 10 nm is seen (Fig. 3A). In addition, there are many short tubes with both ends closed. A high magnification image shows a BN nano-tube consisting of fine particles, with their SAED at a small rectangular area giving the BN (0 0 2), (1 0 0), (0 0 4) and (1 1 0) reflection rings (Fig. 3B). Of these, the (0 0 2) and (0 0 4) reflections are strong arcs, suggesting that BN nano-tubes have a turbostratic structure with the 0 0 1 planes running parallel to the wall. In a HRTEM image, the layer structure can be observed on the nano-tube surface (Fig. 3C). The lattice fringes with a regular spacing of about 0.32 nm close to the theoretical one (0.333 nm) [14] of h-BN (0 0 2) are seen, supporting the formation of h-BN. EDS analysis of BN nano-tubes did not detect the presence of an Al-containing impurity.

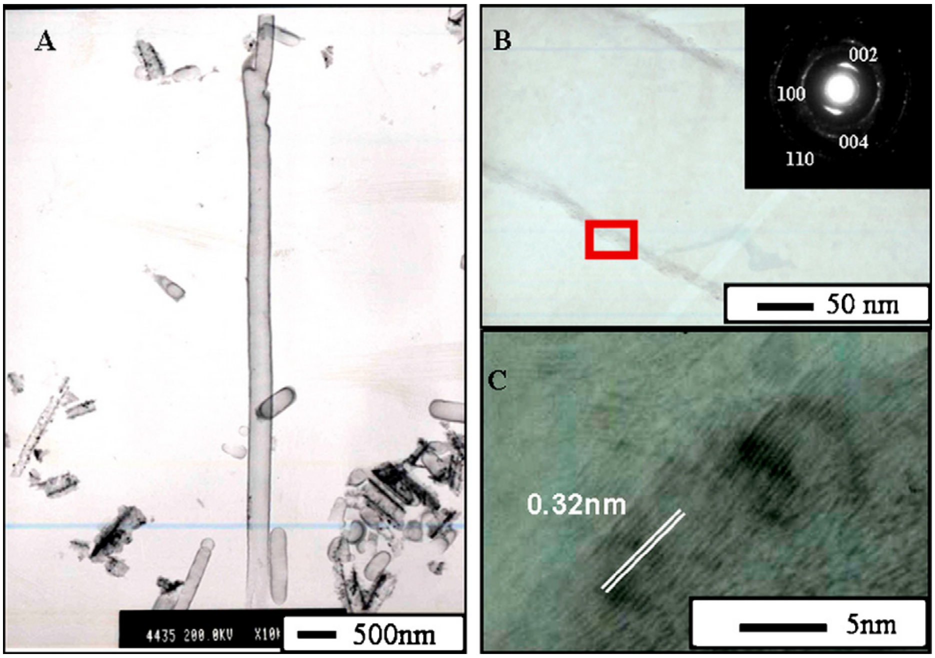

Fig. 3. A TEM images of BN nano-tubes (A), a higher magnification of TEM image of wall of BN nano-tubes with a SAED pattern (B) and HRTEM image at the wall of BN nano-tube (C).

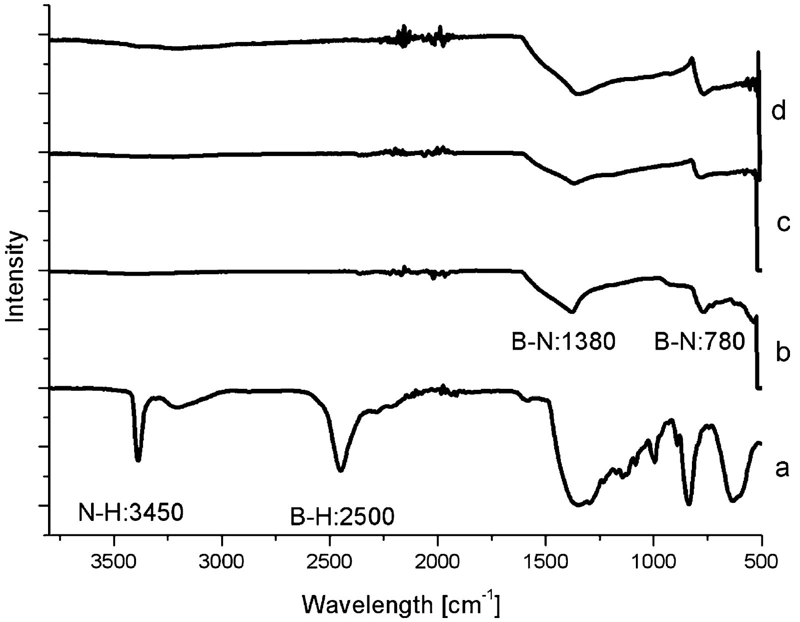

Fig. 4. FT-IR spectra of borazine oligomer (a) BN nano-tube (b) BN nano-bamboos (c) and BN nano-fibers (d).

FT-IR spectra of the borazine oligomer, BN nano-tubes, -bamboos and -fibers are exhibited in Fig. 4. The spectrum of the oligomer shows the characteristic N-H, B-H, and B-N stretchings at 3450, 2500, and 1380 cm^{-1}[2], respectively. After the heat-treatment at 1200 °C, the peaks of B-H and N-H stretchings in the borazine oligomer disappeared, but the peaks at 1380 and 780 cm^{-1} assigned to h-BN stretching appear The FT-IR spectra of BN nano-bamboos and -fibers were almost the same as those of the nano-tubes.

3.2. Formation of h-BN nano-bamboos by 40 h wetting

When the wetting time was extended to 40 h, the BN nano-bamboos 40 μm long and 300 nm thick were formed, with knots at the separations of 0.5–1 μm, as shown by Fig. 5A. An enlarged TEM image shows that the bamboo walls are about 20 nm thick and the knots 30–100 nm thick (Fig. 5B). The SAED patterns taken at the positions a and b reveal that the turbostratic structures similar to those of the BN nano-tubes are formed on the walls of the bamboos, while the crystallographic orientations of BN are randomly distributed in the knots. Very fine particles (<10 nm) were deposited on the bamboo walls (see thick arrows) in Fig. 5B.

3.3. Formation of h-BN nano-fibers by 2 weeks wetting

When the wetting time was taken as 2 weeks, BN nano-fibers 20 μm long and 300 nm thick were formed as observed by TEM (Fig. 6A). Additionally, several tens of nano-sized bubbles formed at the sides of the fiber (see arrows), a large one being included in the fiber. These bubbles are assumed to be formed when H_2 gas was released during the polymerization of borazine oligomer. The ED patterns of the fibers show the strong h-BN (0 0 2) and (1 1 0) rings and the weak (1 0 0) one at cores and walls of the fibers, respectively, suggesting that the crystallographic orientations of the BN particles are randomly distributed in the fiber. Small fine particles less than several nanometers are observed to deposit the external surfaces (Fig. 6B).

3.4. The formation of h-BN nano-tubes, -bamboos and -fibers

It has been reported that BN can be obtained from borazine by heating at 40–1200 °C in N_2 [2,12]. In the present study, borazine changed to borazine oligomer with increasing viscosity by release of H_2 when heated at 40 °C. A mechanism for the formation of BN nano-materials is proposed, as schematically shown in Fig. 7. There are two

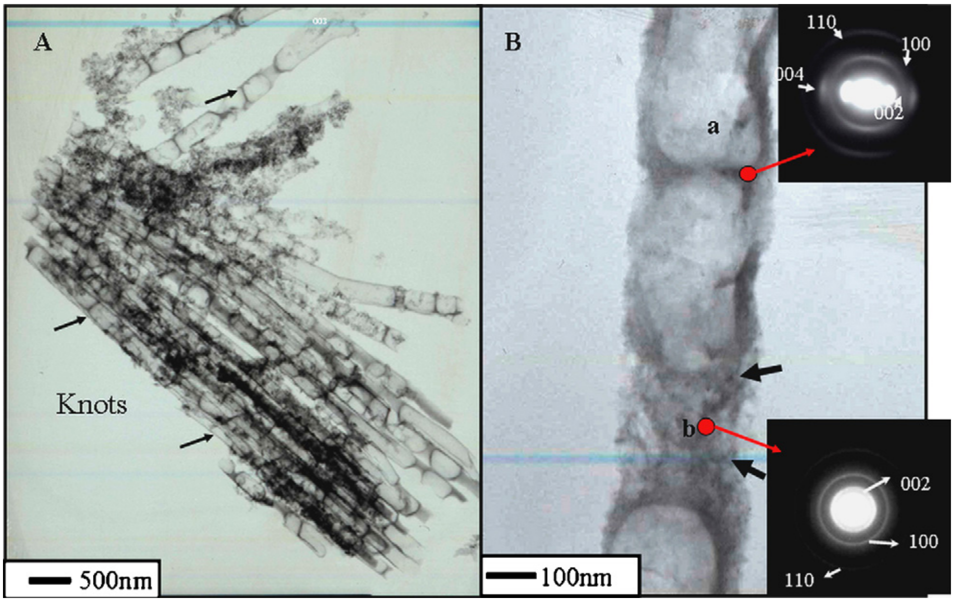

Fig. 5. TEM image of BN nano-bamboos (A) and an enlarged TEM image (B) with SAED patterns at the wall (a) and the knot (b) of a bamboo.

forces affecting the wetting behavior of borazine oligomer in alumina anodic templates, a cohesive force due to the surface tension between the liquid molecules and an adhesive force due to the surface tension between liquid borazine oligomer and the solid surface of pore walls. When a porous alumina template was wetted with borazine oligomer, a thin surface film is formed on the walls. The oligomer gradually covers the pore walls in an initial stage and then pores are filled with the oligomer with increasing wetting time [15,16]. In the first 20 h, the adhesive forces are dominant over the cohesive forces, resulting in the formation of BN nano-tubes by heat treatment at 1200 °C (Route A). At the times $\geq$20 h, the borazine oligomer continues to flow down slowly along the walls or briefly stagnate at the wall, and fills in the pores with increasing thickness, probably because the template channels or pores are neither perfectly cylindrical nor smooth and have very small cracks in the anodic alumina template [17] or contaminations inside the channels [18]. When borazine oligomer happens to catch on projections of the walls and eventually imperfectly fill in the channels, the bamboo structures are formed after heat treatment at 1200 °C (Route B). It is thought that the bamboo structure is in the transition to the nano-fiber one in the wetting process. The fiber structure is finally produced after 2-week wetting, the time being sufficient to fill the pores with oligomer to form nano-fibers of BN (Route C).

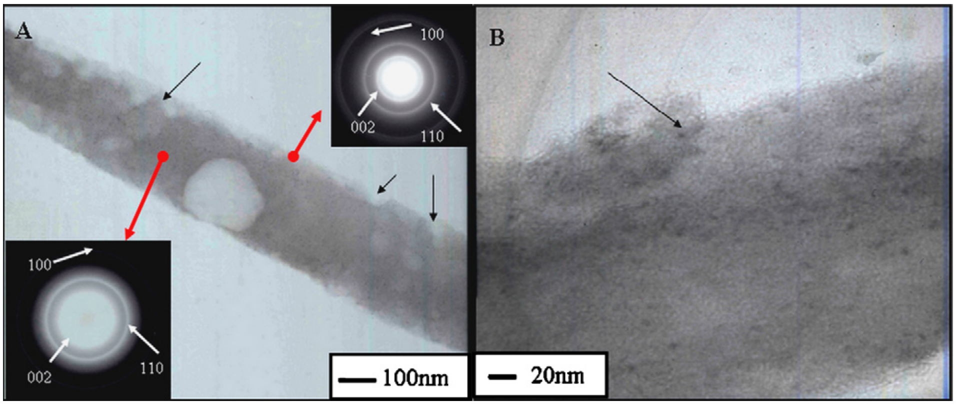

Fig. 6. A TEM image of nano-fibers with SAED patterns of core and wall in a fiber (A) and a higher magnification image of a BN nano-fiber (B).

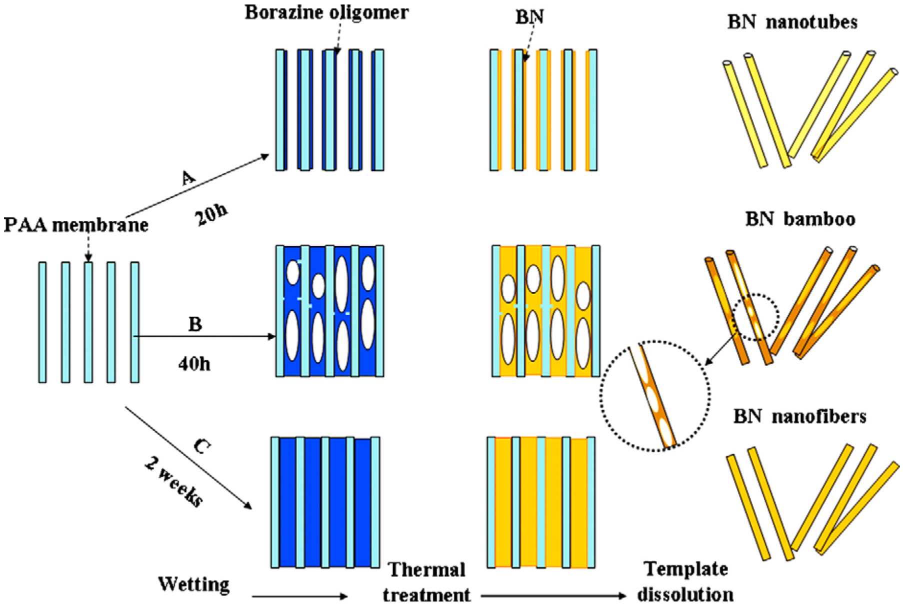

Fig. 7. A schematic diagram of the formation process of BN nano-tubes, BN nano-bamboos and BN nano-fibers.

4. Conclusion

We have successfully fabricated the h-BN nano-tubes,-bamboos and -fibers by the heat-treatment of borazine oligomer at 1200 °C in a N_2 flowing glove box using an alumina porous membrane as a template. The formation of the BN nano-materials depended on the wetting times of 20 h, 40 h and 2 weeks. The microstructures of nano-tube, -bamboo and -fiber were observed by TEM. The SAED and FT-IR provided the evidence of the formation of h-BN. A mechanism of the formation of h-BN nano-tubes, -bamboos and -fibers was proposed.

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