Highly Ordered Boron Nitride Nanotube Arrays with Controllable Texture from Ammonia Borane by Template-Aided Vapor-Phase Pyrolysis

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An efficient approach for the preparation of good-quality boron nitride nanotubes (BNNTs) is developed. BNNTs with specific texture were prepared from ammonia borane (BH$_3$NH$_3$) by vapor-phase pyrolysis with the aid of a template in two independent temperature-controlled furnaces. Two kinds of BNNTs, 200–300 nm wide × 60 μm long and 70–80 nm wide × 40 μm long, were produced after removal of the templates. The as-produced BNNTs were heated at different temperatures in the range of 1300–1700°C in NH$_3$. FT-IR and XPS results confirmed the formation of BN from BH$_3$NH$_3$. Ordered arrays of BNNTs without cracks on the surface were seen using microstructural observations. The diameter and length of the BNNTs are controlled using templates with different pore sizes and thickness. The wall thickness of the nanotubes was increased by increasing the number of deposition cycles. The crystallinity of the BNNTs was improved by heating at a high temperature (1700°C) in NH$_3$.

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1. INTRODUCTION

Recently, one-dimensional (1D) nanostructured materials, such as nanotubes, nanowires, and nanobelts, have attracted much attention on account of their novel chemical and physical properties. Boron nitride nanotubes (BNNTs), which are structurally similar to carbon nanotubes (CNTs), display several outstanding properties for technological applications, including gas absorption, field emission measurement, and thermal conductivity [1–7]. BNNTs are considered to be more suitable than carbon nanotubes for several applications since BNNTs demonstrate high oxidation resistance up to 800°C in air, in contrast to CNTs that are readily oxidized at around 400°C. Furthermore, the electronic properties of BNNTs, independent of the diameter and chirality, allow for novel applications in nanoelectronics and optoelectronics.

There have been many studies on CNTs, whereas there have been relatively fewer reports on the preparation and applications of BNNTs, probably because the synthesis of BNNTs with high quality as well as the control of texture (i.e., diameter, length, and inner space) is more difficult and expensive compared to CNTs. Thus far, BNNTs have been synthesized using arc discharge [8], substitution reaction with CNTs [9], ball milling of BN powder [10], thermal annealing of a mixed powder of boron and hexagonal boron nitride (h-BN) [11], and chemical vapor deposition (CVD) using a mixture of B and MgO vapor [5]. However, almost all of these methods require complicated and expensive apparatus or severe preparation conditions. In particular, all methods have difficulty with the control of the texture of nanotubes and the assembly of individual nanotubes into highly ordered arrays. To the best of our knowledge, no previous approach to the synthesis of BNNTs that can fulfill all these requirements has been reported.

To produce ordered arrays of nanotubes with controlled diameter and length, template-aided synthesis has been suggested as one of the major approaches. A porous alumina anodic (PAA) membrane has been used as a suitable template for the synthesis of 1D nanostructures because of its tunable pore dimensions, narrow pore size distribution, and good mechanical and thermal stability [12]. Although PAA membranes are commercially available, it is of interest to use homemade ones with different textures (e.g., uniform length and pore diameter) to produce different kinds of nanotubes.
Several starting materials have been reported for the synthesis of BN materials, including borazine, polyvinylpentaborane, or dibromoboranedimethyl sulphide, which is known to be a good precursor to form BN upon ammonia thermolysis. In our previous study, BNNTs with highly ordered arrays were successfully prepared by wetting the PAA template with borazine (B₃N₃H₆) [13]. However, both ends of the BNNTs were sealed by a thin BN film formed by the deposition of the liquid polymer precursor on the template surface, causing difficulties with further adjusting functionality and applications of the BNNTs. In addition, it was also difficult to control the wall thickness or inner diameter of the nanotubes by the wetting approach.

In order to overcome these problems in our previous study, it was recommended to use a gaseous organometallic precursor of BN for the formation of BNNTs in the PAA template. In this respect, ammonia borane (BH₃NH₃) is considered to be a suitable precursor for the preparation of BNNTs through vapor-phase pyrolysis since BH₃NH₃ is a stable crystalline solid with less toxicity without C and O and can be easily transformed into the gas phase by moderate temperature heating [14, 15]. In addition, no catalyst is needed to synthesize BN using BH₃NH₃. This study reports the successful preparation of BNNTs with high quality in highly ordered arrays and controllable texture from BH₃NH₃ using template-aided vapor-phase pyrolysis.

2. EXPERIMENTAL DETAILS

2.1. Materials

Ammonia borane was synthesized from sodium borohydride (NaBH₄) and ammonium sulfamate (NH₄NH₂SO₃), as described by Suenram and Thorne [16]. The composition of this product using ¹H-NMR was found to be 97 wt% BH₃NH₃ and ≈3 wt% (BH₂NH₂)ₓ (x<3).

Two types of PAA templates were used in this study. One was a commercially available alumina anodic membrane 60 μm thick with a nominal pore diameter of 100 nm (Anodisc 13, Whatman Ltd.). The other was a homemade membrane, about 40 μm thick with pore diameters ≤80 nm, which was formed based on the method reported by Thompson (Figure 1) [12]. Before being used, the PAA templates were cleaned in an ultrasonic bath using distilled water, ethanol, and acetone, and successively dried at 50°C in air.

2.2. Preparation of BNNTs

The experimental apparatus used is shown in Figure 2(a). Two independent temperature-controlled furnaces (I and II) were set in a glove box filled with N₂. One-side-closed silica glass tube functioned as the reaction chamber in the furnaces. An amount of 0.3 g of BH₃NH₃ was placed in the glass tube positioned in furnace (II), while the alumina template was attached to the outlet of the silica glass tube in furnace (I). However, furnace (I) was first heated to 550°C, and then furnace (II) was heated from room temperature to 250°C at a heating rate of 10°C min⁻¹, and maintained for 1 hour at this temperature. After furnace (II) was cooled down naturally, furnace (I) was kept at 550°C for another 24 hours. Consequently, amorphous BNNTs were formed in the PAA template. To obtain BNNTs with different wall thicknesses, the deposition step was repeated using the same template. The template filled with the BNNTs was then moved out from the glove box and heated in a horizontal tube furnace using a two-cycle heat treatment program, as shown in Figure 2(b). Also, BN heated at high temperature (>1300°C) is chemically inert in a strong base solution. Crystallized BN obtained by the 1st cycle heat treatment at 1300°C was not dissolved by the NaOH solution. The template with the BNNTs was then heated to 1300°C at a rate of 10°C min⁻¹ and then kept for 1 hour in NH₃ flowing at 100 mL min⁻¹ (1st cycle) and washed with ethanol for 30 minutes in an ultrasonic bath. The template with BNNTs was etched in a 40 wt% NaOH solution to dissolve the template. The BNNTs free of alumina were washed several times using dilute water and ethanol, and then successively dried at 100°C in air. As shown by the 2nd cycle of the heat treatment, alumina-free BNNTs were placed in a BN boat and heated from room temperature to 1400°C at 10°C min⁻¹. They were maintained at this temperature for 1 hour, followed by further heating at 1500, 1600, and 1700°C for 1 hour in NH₃ gas (100 mL min⁻¹).

2.3. Characterization

The texture and morphology of the BN nanotubes obtained after heat treatment at the final temperature of 1300, 1500, 1600, and 1700°C were observed using scanning electron microscopy (SEM; JEOL JSM 6500F) and high-resolution transmission electron microscopy (HRTEM; JEM2000) with selected area electron diffraction (SAED) at an accelerating voltage of 200 kV and energy dispersive spectroscopy (EDS). Fourier transform infrared spectroscopy (FT-IR; Thermo Nicolet AVATAR 320) measurements were carried out to determine the formation of BN.

3. RESULTS AND DISCUSSION

FT-IR spectra of BH₃NH₃ and BNNTs after heating using a two-step heat treatment at 1400/1700°C in NH₃ are shown.
in Figure 3. Typical peaks due to stretching of N–H and B–H bonds in BH$_3$NH$_3$ appear at 3280 and 2320 cm$^{-1}$, respectively, with the N–H deformation at 1560 cm$^{-1}$ (Figure 3(a)). After the heat treatment at 1400/1700°C, these peaks disappeared because of dehydrogenation with polymerization and condensation [17]. Peaks corresponding to B–N stretching were observed at 1380 and 780 cm$^{-1}$ (Figure 3(b)). On the other hand, XPS spectra of the BNNTs formed at the final temperature of 1700°C showed N$_{1s}$ and B$_{1s}$ peaks at the binding energy of 397.65 and 190.15 eV [18], respectively. The B:N ratio was given to be about 1:1 from the areas under the peaks. The formation of BN from BH$_3$NH$_3$ by pyrolysis was confirmed on the basis of the FT-IR and XPS results. Since neither oxygen nor carbon was seen to exist in BH$_3$NH$_3$, it is obvious that BNNTs can be prepared without oxygen and carbon impurities.

Figure 4 shows bundles of template-free BNNTs prepared by heating at 1300°C (1st cycle). Highly ordered arrays of BNNT bundles can be observed, with the maximum length of the BNNTs reaching 60 μm (Figure 4(a)). As seen in Figure 4(b), straight BNNTs were formed with diameters ranging from 200 to 300 nm, corresponding to the pore sizes of the PAA template. Neither cracks nor residual alumina can be seen on the surfaces of the BNNTs. An enlarged image (Figure 4(c)) of the middle part from Figure 4(a) shows broken BNNTs which were probably formed during SEM sample preparation. Figure 4(c) confirms the hollow structure of the BNNTs, as indicated by the arrows. Also, Figure 4(d) shows that BNNTs with open ends were formed without the formation of films on the top surfaces.

Figure 5 shows TEM images of BNNTs produced at 1300°C (1st cycle) in NH$_3$. Long, straight, and hollow nanotubes about 200 nm wide including Y-shaped ones were observed (Figure 5(a)). The Y-shaped nanotube should be inherited from channels of the template. The wall thickness of the BNNT was about 8 nm (Figure 5(b)). It was found that the wall thickness of the as-prepared BNNTs had a narrow range from 5 to 10 nm. Because of the thin walls, the BNNTs have very large inner diameters ranging from 180 to 280 nm, several tens of times larger than those of BNNTs prepared using other approaches [5, 10, 11]. SAED from the walls of the nanotubes yielded BN (002), (100), and (110) reflections (inset in Figure 5(b)), and the strong arcs of (002) revealed the turbostratic structure of the BNNTs. EDX analysis showed the absence of Al and O elements in the BNNT samples. When the BNNTs that were formed at 1300°C were directly heated to temperatures higher than 1500°C, the original morphology of the BNNTs was broken. Therefore, a two-step heat treatment, shown in Figure 2(b), was applied to maintain the morphology of the BNNTs with high crystallinity.

Figure 6 shows high-resolution TEM images of BNNTs obtained by the one-step heat treatment at 1300°C and the two-step heat treatment at 1400/1500°C, 1400/1600°C, and 1400/1700°C (2nd cycle). Compared with the BNNTs prepared using the single-step process at 1300°C (1st cycle)
Figure 4: SEM images of highly ordered BNNT arrays obtained at 1300°C (1st cycle) after removal of the PAA template. Cross-section of BNNTs ((a) and (b)), fragments of broken BNNTs (c), and top view of the BNNT bundles (d).

Figure 5: TEM images of BNNTs formed at 1300°C (1st cycle) in NH₃ ((a) and (b)); the inset in image (b) shows the ED pattern of the nanotube wall.

(Figure 6(a)), the crystalline planes of the BNNTs obtained by the two-step heat treatment tend to run along the long axis of the nanotubes parallel to the c-axis of h-BN (see arrows). The BNNTs treated at 1700°C (Figure 6(d)) show regular spacings of about 0.34 nm, close to the theoretical value of 0.333 nm of h-BN (002) (Joint Committee on Powder Diffraction Standards (JCPDS) Card no. 73-2095), which also confirms the formation of h-BN. The order degree of the stacking layers of BN was gradually increased by heating from 1300 to 1700°C. The angle of inclination of the crystallites from the long axis of the nanotube decreased gradually from 1300 to 1700°C. It is to be noted that the BNNTs obtained at 1700°C show a well-ordered layer structure similar to the BNNTs deposited on graphite at 1200°C from the B–N–O precursor vapor generated at 1700°C by the CVD method [19]. The distribution of plane crystallites in the BNNTs after heat treatment at 1300, 1500, 1600, and 1700°C is shown in Figure 7(a). The lengths of the crystallites became longer with increasing heat treatment from 1300 to 1700°C. The average length of the BN crystallites exponentially increased with temperature (Figure 7(b)). In particular, the mean length of the crystallites grew to 17 nm when the BNNTs were heated to 1700°C. It is understood that the crystallinity of the BNNTs can be distinctly improved by heating at high temperatures in NH₃.

The BNNTs after heat treatment at 1300–1700°C were washed in distilled water and ethanol to remove contamination on the surface. When BNNTs heated at 1300°C (1st cycle) were inadequately dried and moved into the vacuum chamber of the SEM or TEM, some of the BNNTs became
flat and were bent, curling the bundles (Figure 8(a)). It is of interest to observe a flat, twisted BNNT without cracks (Figure 8(b)).

In order to increase the thickness of the walls of the BNNTs, a template was reversed after the first deposition and the B–N–H containing polymer was subsequently deposited again in such a manner as mentioned in experimental procedure. As a result, we obtained the wall of BNNTs doubly thick. The wall thickness was increased from 9 to 20 nm by the double deposition (Figure 9), indicating that the wall thickness can be controlled by the number of deposition cycles. When the homemade template with a pore diameter ≤80 nm and a thickness of 40 μm was used, BNNTs with corresponding sizes (i.e., diameter ≤80 nm and length ≈40 μm) were successfully prepared after heating at 1300°C (1st cycle) (Figure 10(a)). The wall thickness in this case was less than 10 nm (Figure 10(b)), comparable to that of the BNNTs fabricated using the commercial template, suggesting that the wall thickness is determined by the amount of starting BH\textsubscript{3}NH\textsubscript{3} material, independent of the template size. In addition, flat and bent BNNTs surrounding the bundles also were observed (see arrows).

The overall reaction for the formation of BNNTs from BH\textsubscript{3}NH\textsubscript{3} can be expressed as follows [14, 16, 20]:

\[
\text{BH}_3\text{NH}_3 \rightarrow \text{BN} + 3\text{H}_2. 
\] (1)

A mechanism for the formation of BNNTs is schematically shown in Figure 11. The formation of BNNTs from BH\textsubscript{3}NH\textsubscript{3} consists of two steps. First, BH\textsubscript{3}NH\textsubscript{3} is heated to 250°C in furnace (II) and it decomposes to gaseous H\textsubscript{3}, BH\textsubscript{2}NH\textsubscript{2}, and B\textsubscript{3}N\textsubscript{3}H\textsubscript{6} [20]. These gaseous precursors BH\textsubscript{2}NH\textsubscript{2} and B\textsubscript{3}N\textsubscript{3}H\textsubscript{6} are carried upward with H\textsubscript{2}. Second, when these gases go through the narrow channels of the template at 550°C in furnace (I), pyrolysis of BH\textsubscript{2}NH\textsubscript{2} and B\textsubscript{3}N\textsubscript{3}H\textsubscript{6} readily occurs, resulting in deposition of solid, amorphous BN films at the surfaces of the walls of the channels. As the reaction proceeds, BN films without cracks on the surface are uniformly thickened to several nanometers. After heat treatment (≥1300°C), with subsequent removal of the PAA template, highly ordered BNNTs arrays with a specific texture are produced.
4. CONCLUSIONS

We report a simple and efficient route to the production of highly ordered BNNT arrays with controllable texture from BH$_3$NH$_3$. Two kinds of BNNTs, 200–300 nm wide × 60 μm long and 70–80 nm wide × 40 μm long, were obtained with a wall thickness less than 10 nm. It was found that the BNNT wall thickness could be increased by repeating the deposition. The crystallinity of the BNNTs improved by heat treatment at ≥1300°C in NH$_3$, and BN crystallites grew to 17–44 nm at 1700°C. A mechanism for the formation of BNNTs from BH$_3$NH$_3$ was proposed including several steps involving the pyrolysis of BH$_3$NH$_3$, deposition in the PAA templates, and crystallization of BN.
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