Highly Efficient Synthesis of Hexagonal Boron Nitride Nanofibers with High Specific Surface Area

Hongshou Liu, Zhaqian Yan, Zhihao Sun, Anran Li, Zihao Guo and Lei Qian*

Abstract

Hexagonal boron nitride nanofibers with high specific surface were successfully prepared through precursor pyrolysis method via boric acid, melamine and polyethylene glycol (PEG) as raw materials. The field emission scanning electron microscopy images showed that hexagonal boron nitride (h-BN) nanofibers were well aligned, and exhibited good fibrous structure. Chemical composition of the synthesized h-BN nanofibers was analyzed by X-ray diffraction, fourier transform infrared spectroscopy and thermogravimetric. Effects of precursor drying method and the PEG contents on morphologies and the specific surface area were investigated and optimized. Results indicated that the diameter of h-BN nanofibers increased with the ratio of boric acid to melamine, and their aspect ratios were greatly improved from 20 to 30 after freeze-drying treatment. Specific surface area of the h-BN nanofibers was increased from 65.25 to 319.07 m²/g due to the freeze-drying treatment. Besides, the content of PEG also obviously improved specific surface area. When the PEG content reached 2%, specific surface area of the h-BN nanofibers from the air-dried precursor was increased by 12.4 times to 874.58 m²/g. The resulted h-BN nanofibers show promising and potential applications in many fields including catalysis, hydrogen storage and environment.

Keywords: BN nanofibers; PEG; Freeze-drying; Specific surface area.

Received: 27 September 2021; Accepted: 30 October 2021.

Article type: Research article.

1. Introduction

Boron nitride (BN) has been widely used because of its excellent thermal stability, high thermal conductivity, corrosion resistance and other excellent properties.[1-8] It possesses several typical heteromorph structures including hexagonal BN (h-BN), rhombohedral BN (r-BN), cubic BN (c-BN) and wurtzite BN (w-BN).[9-12] Among them, h-BN alternately forms a planar hexagonal ring network structure via sp² hybridization, which has many superiorities including good thermal conductivity, thermal stability and chemical inertness.[13-18] In recent years, due to their potential applications in prospective electronic and mechanical devices many preparation methods of BN with different microstructures such as nanoparticles, nanotubes and nanowires have been reported in many literatures.[19-24] BN nanotubes were obtained by using NiB/Al₂O₃ as the catalyst to catalyze the reaction of boron and amine.[21] The 3D BN fibers were synthesized by multi-stage calcination of the precursor containing boric acid and melamine.[19] Among many different microstructures, h-BN nanofibers with one-dimensional structure have attracted widespread attention owing to their low density, chemical inertness, high stability and good adsorption performance. Moreover, the h-BN nanofibers can be used in the manufacture of fuel cells as catalytic carriers in high temperature oxidation atmosphere due to their chemical inertness and excellent oxidation resistance.

However, specific surface area of synthetic h-BN nanofibers is usually not high and the synthesis methods are also more complicated, which greatly hinder their applications in environment and catalysis.[25-30] Hence, it is urgent and necessary to develop a new method for convenient synthesis of h-BN nanofibers with high specific surface area.[31-35] There are already many different methods to synthesize h-BN nanofibers such as hydrothermal method, templating, high-pressure reaction and precursor pyrolysis method.[36] Among them, the precursor pyrolysis method is conducive to the production of h-BN nanofibers due to its advantages of simple operation, low energy consumption, high efficiency and controllability. Lin et al.[37] synthesized BN nanofibers using the precursor pyrolysis method with specific surface area of 515 m²/g at 1100 °C. Liu et al.[38] obtained the BN with a fibrous morphology through multi-stage heating treatment of...
the precursor. However, these reported methods were complicated and the specific surface area was not easily controlled.

In this paper, the h-BN nanofibers with high specific surface area were fabricated by precursor pyrolysis method. The effects of different drying methods (freeze-drying and air-drying) of precursors and PEG contents on morphology and specific surface area of h-BN nanofibers have been investigated. The results indicated that specific surface area of the h-BN nanofibers could be tuned by the precursor drying methods and PEG content. During the freeze-dried process, specific surface area of the h-BN nanofibers increased because the ice sublimation process effectively resisted the collapse of nanofiber structures in the precursor. In addition, the gradual decomposition and release of PEG as a template also increased the specific surface area of h-BN nanofibers during the pyrolysis of the precursor. This work provided important and practical guidance for the efficient synthesis of h-BN nanofibers with high specific surface area.

2. Experimental Section

2.1 Chemicals and reagents
Polyethylene glycol (PEG, purity > 99%) and Melamine (C₃N₆H₁₂, purity > 99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Boric acid (H₃BO₃, purity > 99%) was purchased from Tianjin Guangcheng Chemical Reagent Co., Ltd.

2.2 Synthesis of h-BN nanofibers
Fig. 1 briefly shows the preparation route of h-BN nanofibers. Boric acid (BA) and melamine (M) with different molar ratios (1:1, 3:2, 2:1 and 3:1) were added to 200 mL of distilled water. The mixed solution was heated at 90 °C for 2 h until the solution became transparent. Then the transparent solution was naturally cooled to room temperature to obtain the white flocculent, which was filtrated and dried in air at 60 °C to obtain the precursor (M·2B₃). After annealing the precursor at 900 °C for 2 h under a flowing nitrogen atmosphere (with heating rate of 5 °C/min, nitrogen flow rate of 100 mL/min), the h-BN nanofibers (BNNF-D) were obtained.

In order to investigate the effects of different drying methods on the morphology and specific surface area of h-BN nanofibers, the white flocculent after filtration was freeze-dried to obtain the precursor (M·2B₃). Finally, h-BN nanofibers (BNNF-F) were obtained from calcinating the freeze-dried precursor at 900 °C for 2 h in a flowing nitrogen atmosphere.

2.3 Fabrication of h-BN nanofibers with high specific surface area
PEG with different mass concentration (0.5%, 1%, 2%) was added to the aqueous solution of BA and M with the molar ratio of 3:1, respectively. The mixed solution was heated at 90 °C for 2 h until the solution became transparent. As a result, the precursor (M·2B₃) was obtained by air-drying the white flocculent precipitated at 60 °C from the transparent solution. Then the precursor was heated to 900 °C for 2 h in a flow of nitrogen atmosphere to perform the pyrolysis treatments. Finally, the obtained h-BN nanofibers (BNNF-PD) were further calcined at 500 °C in air to remove the left carbon in h-BN nanofibers. Besides, the h-BN nanofibers (BNNF-PF) were synthesized from the precursor produced by freeze-drying the white flocculent to investigate the effect of the drying methods.

2.4 Characterization
The morphology and microstructures were characterized by field emission scanning electron microscope (FESEM, Hitachi SU-70, Tokyo, Japan) and transmission electron microscope (TEM, JEOL JEM 2100F). X-ray diffraction (XRD, MiniFlex 600, Japan) was used to identify the phases of h-BN nanofibers. Thermogravimetric (TGA) was carried out (in 30-1000 °C with 10 °C/min) by using a thermo gravimetric analyzer (TGA5500) under N₂ to characterize the pyrolysis process of the M·2B. Fourier transform infrared spectroscopy (FT-IR, Nicolet iS50, USA) was used to analyze the chemical groups

Fig. 1 Schematic diagram for preparation of h-BN nanofibers.
and bonds of h-BN nanofibers. Specific surface area of the h-BN nanofibers was tested by a Brunner-Emmett-Teller (BET) surface analyzer (ASAP 2460, Micromeritics Instrument Corporation, USA).

3. Results and Discussion

3.1 Chemical composition of h-BN nanofibers

Fig. 2a shows the FTIR spectra of BNNF-D with different BA:M ratios. The absorption bands around 1393 and 798 cm⁻¹ corresponded to B-N tensile vibration and B-N-B bending vibration, respectively. The wide band near 1300-1800 cm⁻¹ was resulted from the asymmetric stretching of B-O-B bond and C-N bond. The other weak adsorption band located at 3300-3500 cm⁻¹ was due to the stretching vibration of O-H bond. The appearance of B-N bond and B-N-B bond indicated that the h-BN nanofibers were successfully synthesized. The absorption peak of B-N-B bond at 798 cm⁻¹ had the shift toward the lower wavenumber compared with the standard absorption peak (820 cm⁻¹), indicating an increase of the interlayer distance d002 in the h-BN nanofibers.⁴⁰,⁴¹

XRD was used to further characterize increase of the interlayer distance of h-BN nanofibers as shown in Fig. 2b. The reflection peaks at 2θ = 25.3° and 43.5° indexed to the (002) and (100) planes of the h-BN nanofibers, respectively. The weak diffraction peak indicated that the crystallinity of the obtained h-BN nanofibers was relatively poor due to the existence of C and O impurities. Compared with the standard card (JCPDS#45-1171), a slight shift of the (002) peak toward to the smaller degree was observed. The corresponding d002 spacing for the h-BN nanofibers was calculated between 0.35-0.36 nm, which was much larger than that from the h-BN nanotubes and bulk h-BN of 0.33 nm. The decrease of d002 and the broad peak at 2θ = 43.5° confirmed the turbostratic BN phase of h-BN nanofibers.⁴²,⁴³

The TGA curve was obtained by calcining the precursor in N₂ atmosphere to analyze the converting process of the h-BN nanofibers. As shown in the Fig. 3a, the weight decreased in three stages with the increase of temperature for the M-2B₃D precursor. The precursor had a layer-like morphology from the interlinked planar triangular H₂BO₃ and C₃N₆H₆ molecules via the hydrogen-bonded structure.⁴⁴ When the temperature was raised to 185 °C, the weight loss rate reached 15 wt% due to the evaporation of CO₂, free water and constitution water. When the temperature was raised to 356 °C, the weight loss rate was increased by 35.5 wt%, which possibly was caused by volatilization of gases, such as NH₃ and H₂O. During this heating process, the intermediate compound BCNO was formed due to constant volatilization of water and gas in the precursor. Finally, the weight loss rate reached 82 wt% with the temperature increased to 805 °C, and the h-BN nanofibers were finally obtained with the continuous decomposition of the precursor.⁴⁵

Besides, the thermal decomposition process of the M-2B₃D precursor was studied to analyze the effect of PEG on the thermal decomposition process. The obvious difference was that there were only two stages of weight decrease with the temperature as shown in the Fig. 3b. In the first stage, CO₂ and water were released from the precursor. Besides, the addition of PEG increased the chance of intermolecular entanglement in the precursor which improved the thermal stability of the precursor. As a result, the first stage continued until 290 °C rather than 185 °C, and the weight loss rate reached 29 wt% compared with the precursor without the PEG. When the temperature was increased to 738 °C, the CO₂ was further released from PEG and the h-BN nanofibers were obtained with the weight loss rate of 75.8%.

3.2 Morphology of h-BN nanofibers

Fig. 4 shows the morphology of the BNNF-D obtained from the air-dried precursor. The h-BN nanofibers had typical 1D fibrous morphology with high aspect ratios. The length of nanofibers varied from 10 to 100 µm and the diameter between 0.5 – 5 µm. When the BA: M molar ratio was 1:1, the h-BN nanofibers were mainly lath-like nanofibers mixed with some round-shaped nanofibers, which were shown as I and II in Fig. 4a, respectively. As shown in the Figs. 4a-d, the length and diameter of the h-BN nanofibers were increased with the molar ratio of BA: M. When the molar ratio of BA:M increased to 3:1, the length of h-BN nanofibers significantly reached to 200 µm and the aspect ratio had also reached 20. It
was confused that the BNNF-D had a high porosity structure as shown in the Fig. 4e. The low-magnification TEM image showed the pore diameter of the BNNF-D was in the range of 5 ~ 10 nm. Moreover, the high resolution TEM image in Fig. 4f revealed a turbine layered structure of the h-BN nanofibers. These BN layers had a certain orientation and uniform layer spacing, and the different layers were superimposed on each other to form the turbine layered structure. And the interlayer spacing in this BNNF-D was calculated as 0.356 nm, which was consistent with the result obtained from XRD.

The morphology of h-BN nanofibers from freeze-dried precursor was analyzed to explore the effect of freeze-drying treatment on h-BN nanofibers (Fig. 5). The diameter of the BNNF-F was in the range of 2 ~ 5 µm and the length was more than 150 µm. When the ratio of BA: M was 3:1, the aspect ratio of the BNNF-F reached 30, and it was greatly improved.

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**Fig. 3** TGA curves (a) M·2B_{D}; (b) M·2B_{P2D}.

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**Fig. 4** FESEM images of the BNNF-D obtained at different BA:M ratios as: (a) 1:1; (b) 3:2 (c) 2:1; (d) 3:1; (e) Low-magnification TEM image of BNNF-D with the ratios of BA:M as 3:1; (f) HRTEM image of BNNF-D with the ratios of BA:M as 3:1.
compared with BNNF-D of 20. Fig. 5e shows TEM image of the BNNF-F. It was observed that the pore size of BNNF-F was reduced to 2 ~ 8 nm and the pores were mainly concentrated in the middle part of the BNNF-F. The possible reason was that during the freezing process, ice crystals was formed due to the supercooling influence provided by the temperature gradient, and grew vertically along the freezing gradient. As a result, the M·2B\text{F} crystal nuclei continued to move closer to the middle due to the growth and extrusion of ice crystals. In the subsequent dried process, the ice crystals in the M·2B\text{F} were removed by sublimation to obtain the precursor with a larger aspect ratio. It confirmed that the freeze-dried process was beneficial to increase the aspect ratio of the h-BN nanofibers. Besides, the extrusion of ice crystals during the freeze-drying process may cause the reduction of the interlayer spacing, and the high-resolution TEM image in Fig. 5f confirmed that the interlayer spacing of BNNF-F was 0.349 nm which was smaller than the 0.356 nm of BNNF-D. Fig. 6 shows the morphology of the h-BN nanofibers (BNNF-PD and BNNF-PF) obtained from the precursor with the different content of PEG. It was observed that the cross section of all BNNF-PD was square with the diameter of 5 ~ 9 μm. From the Figs. 6a-c, it was found that the diameter of the h-BN nanofibers remained the same and the length increased with the content of PEG. When the content of PEG increased to 2%, the length of the BNNF-PD increased to 300 μm from 100 μm. Besides, BNNF-PD also had many uniformly dispersed pore structures like BNNF-D as shown in the Fig. 6g. The low-magnification TEM image showed the pore diameter of the BNNF-PD was in the range of 6 ~ 12 nm. And from Fig. 6h, it was found that the interlayer spacing of BNNF-PD was calculated as 0.357 nm which was also close to the interlayer spacing of BNNF-D. In addition, all of the BNNF-PF had a ribbon-like morphology after being freeze-dried treatment, and the aspect ratio of all BNNF-PF was also increased due to the freeze-drying treatment. As shown in the Figs. 6d-f, the diameter of all BNNF-PF was 2 ~ 8 μm, and the length was greatly improved from 150 to 500 μm with the content of PEG. This further proved that the freeze-drying treatment was beneficial to increase the aspect ratio of h-BN nanofibers.
3.3 Specific surface area of h-BN nanofibers

Fig. 7 shows the N₂ adsorption and desorption isotherms of the h-BN nanofibers, and the inserts correspond to the Barrett–Joyner–Halenda (BJH) pore-size distribution. A typical N₂ adsorption/desorption isotherm of h-BN nanofibers synthesized under different conditions was classified as type IV isotherm based on the International Union of Pure and Applied Chemistry (IUPAC) classification, and exhibited a H4 type hysteresis loop.[46] Besides, the pore size distribution of h-BN nanofibers was discussed based on the BJH equation and the results were shown in the Table 1.

In this experiment, the most of the pore structure in the BNNF-D was microporous because the hysteresis ring in the range of \( p/p₀ = 0.4 \sim 1.0 \) was extremely small, which also suggested that the adsorption-desorption process was almost completely reversible although the adsorption and desorption isotherms of the BNNF-D (Fig. 7a) accorded with IV isotherm. The pore structure of BNNF-D was also confirmed by its main characteristic pore sizes of \( \sim 1.4, \sim 2.1 \) and \( \sim 2.5 \) nm. Moreover, specific surface area of the BNNF-D was only 65.25 m²/g and
Fig. 7 Nitrogen adsorption/desorption isotherms of h-BN nanofibers: (a) BNNF-D; (b) BNNF-F; (c) BNNF-P₂D; (d) BNNF-P₂F (The inset is corresponding BJH pore-size distribution of h-BN).

Table 1. Specific surface area of the produced h-BN nanofibers.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Drying methods</th>
<th>PEG (%)</th>
<th>BET (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Main characteristic pore sizes (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BNNF-D</td>
<td>Air-dried</td>
<td>0</td>
<td>65.25</td>
<td>0.74</td>
<td>1.4, 2.1, 2.5</td>
</tr>
<tr>
<td>BNNF-F</td>
<td>Freeze-dried</td>
<td>0</td>
<td>319.07</td>
<td>1.45</td>
<td>1.3, 3.2</td>
</tr>
<tr>
<td>BNNF-P₀.5D</td>
<td>Air-dried</td>
<td>0.5</td>
<td>687.28</td>
<td>2.37</td>
<td>1.5, 2.7</td>
</tr>
<tr>
<td>BNNF-P₁D</td>
<td>Air-dried</td>
<td>1</td>
<td>714.23</td>
<td>2.64</td>
<td>1.4, 2.3</td>
</tr>
<tr>
<td>BNNF-P₂D</td>
<td>Air-dried</td>
<td>2</td>
<td>874.58</td>
<td>3.21</td>
<td>1.3, 2.6</td>
</tr>
<tr>
<td>BNNF-P₂F</td>
<td>Freeze-dried</td>
<td>2</td>
<td>416.75</td>
<td>1.85</td>
<td>1.4, 2.3</td>
</tr>
</tbody>
</table>

The pore volume was 0.74 cm³/g (including the volume of micropores as 0.12 cm³/g and mesopores as 0.62 cm³/g).

The pore volume of BNNF-F (Fig. 7b) reached 1.45 cm³/g with the micropores of 0.62 cm³/g and the mesopores of 0.83 cm³/g. And the volume of micropores had reached 42% from 16% with the main characteristic pore sizes of ~ 1.3 and ~ 3.2 nm. Besides, specific surface area of BNNF-F reached 319.07 m²/g. The possible reason for the increase in specific surface area and pore volume of the BNNF-F was as follows. During the freeze-drying process, the pore collapse caused by the surface tension of the solid-liquid interface was minimized through the sublimation process of ice crystals. As a result, the pore structure of the BNNF-F was preserved to the maximum extent and specific surface area of BNNF-F was greatly improved by inhibiting the formation of agglomerates.

Further, different contents of PEG were added to the precursor to study the effect of PEG content versus specific surface area of the h-BN nanofibers. As is shown in the Figs. 7c-d, the adsorption/desorption isotherm of N₂ increased rapidly in the relatively low-pressure range after the addition of PEG, indicating that there were a large number of micropores in the h-BN nanofibers.³⁵ The specific surface area of the BNNF-P₀.5D reached 687.28 m²/g accompanied by the addition of 0.5% PEG. When the content of PEG reaches 1%, specific surface area of the BNNF-P₁D reached 714.23 m²/g. It was worth noting that the specific surface area of
BNNF-P:D (Fig. 7c) reached 874.58 m²/g under the condition of 2% PEG with the main characteristic pore sizes of ~1.3 and ~2.6 nm and a high pore volume of 3.21 cm³/g (including the volume of micropores as 1.58 cm³/g and mesopores as 1.63 cm³/g). It was increased by 12.4 times compared with BNNF-D that without PEG. The increase in the specific surface area of BNNF-PD was due to the decomposition of PEG during the calcination process.

Fig. 7d shows the nitrogen adsorption/desorption isotherms of BNNF-PF undergoing freeze-drying treatment with the addition of PEG. When the content of PEG reached 2%, specific surface area of BNNF-P2F (Fig. 7d) was 416.75 m²/g with a pore volume of 1.85 cm³/g (including the volume of micropores as 0.83 cm³/g and mesopores as 1.02 cm³/g). This was an increase of 30% compared with that of BNNF-F (319.07 m²/g). From the above results, it was found that different drying treatment (air-drying and freeze-drying) of precursors containing PEG increased the specific surface area of h-BN nanofibers. However, the specific surface area of h-BN nanofibers calcined from the freeze-dried precursor with PEG was lower than that of nanofibers from the air-drying treatment. The possible reason was that during the freeze-dried process, the solutes (PEG and M-2B precursor) were precipitated and excluded from the vertical growth of ice crystals. The process resulted in the partial agglomeration of PEG molecules in the precursor, which influenced the formation of mesopores in the subsequent sintering process. As a result, the specific surface area of BNNF-PF was lower than that of BNNF-PD.

4. Conclusions
The h-BN nanofibers with high specific surface area were successfully obtained through precursor pyrolysis method. The effects of the precursor drying and the addition of PEG on the morphology and specific surface area of the h-BN nanofibers were analyzed. The diameter of the h-BN nanofibers gradually increased with the ratio of boric acid to melamine. The aspect ratio of BNNF-F increased to 30 from 20 due to the freeze-drying treatment and specific surface area also increased to 319.07 m²/g from 65.25 m²/g. In addition, specific surface area of the h-BN nanofibers increased with the content of PEG. It was worth noting that with the addition of 2 wt% PEG, the h-BN nanofibers synthesized from the air-dried precursor exhibited the largest specific surface area of 874.58 m²/g. This work provides a new synthetic method of h-BN nanofibers with high specific surface area, which makes the h-BN nanofibers have a wider application prospect in hydrogen storage, water treatment and catalysis.

Conflict of Interest
There is no conflict of interest.

Supporting Information
Not applicable.

References

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