Facile preparation of BCN nanofibers with tunable band gaps

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Abstract. As a new synthetic metal-free material, BCN has aroused great interests in the field of photocatalyst materials due to its lower cost as well as higher reliability and better sustainability. In this work, we prepared BCN nanofibers by electrospinning of precursor solution containing polyacrylonitrile and ammonia borane, and then pyrolyzed the polymer fibers in NH_3 . Infrared spectroscopy (FT-IR), Scanning emission microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were used to analyse the composition and structure of the samples. The results show that the BCN nanofibers have an average diameter of 50-100 nm and mainly compose of BN nanocrystals. C atoms are distributed at the BN grain boundary in terms of B-C and B-N bonds. The band gap of the fibers is between 2.1-2.7 eV and can be adjusted by changing the ratio of PAN and AB in the raw materials.

1 Instruction

Metal-free catalysts are catalysts containing only non-metallic elements, such as carbon, silicon, phosphorus, nitrogen, oxygen, and hydrogen [1]. In comparison with traditional metal-based catalysts, the metal-free catalysts cost less, show superior sustainability and have longer durability [2]. Moreover, the majority of these non-metal elements are also key elements in biological systems. Therefore, metal-free catalysts are more environmentally friendly than catalysts containing metals.

Common metal-free catalysts include graphitic carbon nitride [3], boron nitride [4], boron carbide [5], boron phosphide [6], and so on. These catalysts usually have a two-dimensional (2D) planar structure, which brings them excellent conduction and transportation properties. However, as typical 2D materials, graphite and BN cannot be used directly as catalysts because their band gaps are not in the effective catalysis range [7]. Fortunately, intermediates of them, denoted as ternary BCN compounds, are medium-bandgap semiconductors [8]. Therefore, construction of BCN compounds with adjustable band gap is a new way to develop efficient catalysts [9].

Preparation methods of BCN compounds include chemical vapor deposition (CVD) [10], solvothermal synthesis [11], hot press [12], precursor pyrolysis [13], and so on. Among these methods, precursor pyrolysis has the advantages of high production efficiency, low preparation cost, easy shaping and tunable composition, thus are widely used to prepare low-dimensional materials. Electrospinning is a fast, simple and efficient fiber production technology [14]. Nanofibers prepared by electrospinning usually have a higher specific surface

area and sufficient active sites, which is very beneficial to improve the catalytic performance of the material [15, 16].

In this paper, we present a facile method to prepare BCN nanofibers with controllable composition and tunable band gaps. The influence of raw material ratio and pyrolysis temperature on fiber composition and structure was systematically studied.

2 Experimental

2.1 Materials

Polyacrylonitrile (PAN) was obtained from Shenzhen Lute New Material Technology Co., Ltd. Ammonia borane (AB) was obtained from Shanghai McLean Biotechnology Co., Ltd. N-N-dimethylformamide (DMF) was purchased from Shanghai Qian shun Chemical Reagent Co., Ltd. All the reagents were analytically pure.

2.2 Preparation of the BCN nanofibers

PAN was dissolved into DMF to obtain a 10wt% PAN/DMF solution. PAN/AB/DMF spinning solutions were prepared by dispersing a given amount of AB into the PAN/DMF solution. The spinning solution was drawn into a 5 mL syringe with a 0.8 mm diameter needle and then was electrospun into polymer fibers by using an electrospinning machine. The working voltage, spinning rate and collecting distance was set to 15 kV, 1 ml/h and 10 cm, respectively.

The as-spun polymer fibers were placed in a horizontal tube furnace and then were calcined followed

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a two-step procedure. In the first step, the heating temperature rises from 30°C to 500 °C with a heating rate of 2 °C /min in N₂ gas protection. When the calcination temperature reaches 500 °C, the cracking gas was changed to NH₃ with a flow rate of 400 mL/min. The samples were heated to a determined calcining temperature with a heating rate of 2°C/min under NH₃ atmosphere and holding at the highest temperature for 1 hour to give the BCN fibers. These obtained samples were named BCN-x, where x is the highest calcining temperature. Fig. 1 illustrates the whole fabrication process and heating procedure of BCN nanofibers.

Figure 1. Schematic diagram of preparing BCN nanofibers.

2.3 Characterization of the BCN nanofibers

Fourier transform infrared spectroscopy (FT-IR) of the polymer fibers and BCN fibers were recorded on a Fourier transform-infrared spectrophotometer (Bruker TENSOR-27). The surface morphologies of the BCN fibers were examined using scanning electron microscope (SEM, Hitachi, S-4800, Japan). Transmission electron microscopy (TEM) was conducted using a Tecnai G2 F20 S-TWIN TMP (FEI Inc., U.S.). The crystal phases of the BCN fibers were identified with an X-ray diffractometer (XRD, Rigaku Co., Type Max 2550, Tokyo, Japan) using Cu K α radiation, and the apparent size of BN crystallite was calculated from the half value width of (111) peak by using Scherrer 's formula. X-ray photoelectron spectroscopy (XPS) was investigated using K-Alpha 1063 type with focused monochromatized Al K α radiation. UV-vis diffuse reflectance spectra (DRS) were carried out on a HITACHI U4100 spectrophotometer using BaSO₄ as the reference.

3 Results and Discussion

Figure 2 shows the morphology of polymer fibers and BCN-1000 fibers. As can be observed from Figure 2(a) and (b), the diameter of the polymer fibers ranges from 100 to 200 nm. There are some holes on the fiber surface. This may be the result of solvent volatilization during the electrospinning process. As shown in Figure 2(c) and (d), after heat treatment, the BCN fibers became curly and the diameter of the fibers shrinks to 20 ~ 100 nm.

Figure 2. (a) and (b) SEM graphs of polymer fibers before calcination. (c) and (d) SEM images of BCN fibers heat treated at 1000°C.

Figure 3 shows the IR spectra of the polymer fibers and BCN-1000 fibers. The characteristic peaks of polymer fibers are consistent with the known values of PAN and AB. There are absorptions for PAN at 2240 cm⁻¹ and 1600 cm⁻¹ (C $\equiv$ N stretching), 1450 cm⁻¹ and 1375 cm⁻¹ (CH₂ deformation). There are also peaks for AB at 3312 cm⁻¹(N-H stretching), 2380 cm⁻¹(B-H stretching), 2276 cm⁻¹(B-H stretching), 1160 cm⁻¹(B-H deformation) and 782 cm⁻¹ (B-N stretching). The appearance of the B-O bond (peaks at 1063 cm⁻¹ and 924 cm⁻¹) may due to the hydrolysis of AB in the air. Compare with the polymer fibers, the characteristic peaks of C $\equiv$ N, CH₂, N - H, B - H and B - O bond of BCN fibers disappeared after heat treatment. But the absorption for B - N bond at around 780 cm⁻¹ increased. Moreover, a new absorption peaks for C=C, C=N bond at around 1600 cm⁻¹ appears. This indicated that the polymer fibers undergo a series of reactions, including dehydrogenation, crosslinking and cycloaddition, during the pyrolysis process.

Figure 3. IR spectra of the polymer fibers before calcination and BCN-1000 fibers heat-treated at 1000°C.

Figure 4 shows the XRD patterns of the BCN fibers pyrolyzed at different temperatures. Peaks at around 2 θ = 27° and 41° is indexed to be (002) and (100) lattice plane of hexagonal boron nitride (*h*-BN, JCPDS Card No. 41-1487)[17]. It can be seen from the figure that as the heat treatment temperature increases from 900 °C to 1000°C, the diffraction peak becomes sharper, indicating a better crystallization in BCN-1000 fiber. However, as the temperature further increases, the intensity of the

diffraction peak in the curve becomes weaker. This means that heat treatment over 1000 °C will cause deterioration of the internal crystalline properties of the material. Moreover, according to Bragg's law, the (002) crystal plane of h-BN in BCN-1000 fibers is 0.33 nm.

Figure 4. XRD patterns of the BCN fibers pyrolyzed at different temperatures.

Figure 5 shows TEM, HR-TEM and SAED images of the BCN-1000 nanofibers. As can be seen from the Figure 5a, the diameter of the BCN-1000 is relatively uniform, which is ranging from 50-90 nm. The interplanar distance of the graphitized crystal structure (002) of the BCN-1000 nanofibers is approximately 0.34 nm (inset in Fig.3c), which is in well accordance to the XRD results. The SAED image (inset in Fig. 3c) reveals that the BCN samples are polycrystalline. Therefore, it is assumed that most of the C atoms are distributed at the BN grain boundary [18]. The XPS analysis was utilized to confirm this speculation and the results are shown in Figure 6.

Figure 5. TEM images of BCN nanofiber heat-treated at 1000°C.

As can be observed from the Figure 6a, the survey spectra of BCN fibers have four peaks at around 532 eV, 400 eV, 285 eV and 191 eV, which indicated the presence of O, N, C and B atoms in the fiber, respectively. The high-resolution spectrum of B(1s) was deconvoluted into three peaks, which correspond to B-O bonds (191.6 eV), B-C bonds (190.0 eV) and B-N bonds (190.7 eV). The C 1s spectra were deconvoluted into three typical peaks at 285.1, 284.1 and 285.7 eV, which, respectively, correspond to the C atoms in graphitic carbon, C-B and C-N bonds. As shown in Figure 6d, N atoms in the BCN fibers could be assigned to three categories: The N atoms in N-B coordination (397.6 eV), the N atoms in B-N-C bond (298.3 eV) and the bridging

N atoms bonded to three C atoms (401.1 eV). In summary, the XPS results prove that the B, C, and N atoms in the BCN fibers are chemically bonded to each other.

Figure 6. XPS analysis of BCN nanofiber pyrolyzed at different temperature.

Furthermore, relationship between pyrolysis temperature and atomic percentages of products was calculated according to the XPS analysis. Results are summarized in Table 1. It can be seen from the table that as the temperature increases, the content of elements B and N gradually increase, while the content of elements C and O gradually decrease. During the pyrolysis process, In the pyrolysis process, cleavage and cyclization of the side groups of PAN occurs first. Therefore, BCN-900 has higher C content than N. As the temperature increases, elements such as B and C in the fiber begin to react with NH_3 , resulting in an increase in the N content of the product. The O in the fiber is mainly introduced by the hydrolysis of AB. During the pyrolysis process, the B-O bond gradually breaks, so the O content in the product gradually decreases with the increase of pyrolysis temperature.

Table 1. Elemental analysis of BCN nanofiber pyrolyzed at different temperature (raw material ratio PAN/AB=5:1).

Sample	B1s			C1s			N1s			O1s	
	at%	Bond	RI	at%	Bond	RI	at%	Bond	RI	at%	
BCN-900		B-N	1.00		C-B	1.00		N-B	0.98		
	39.88	B-C	0.96	17.23	C-C	0.95	27.58	B-N-C	1.00	15.31	
		B-O	0.87		C-N	0.92		Graphitic N	0.95		
BCN-1000		B-N	1.00		C-B	1.00		N-B	0.97		
	44.12	B-C	0.98	12.02	C-C	0.98	30.65	B-N-C	1.00	13.21	
		B-O	0.87		C-N	0.95		Graphitic N	0.95		
BCN-1100		B-N	0.96		C-B	1.00		N-B	0.96		
	46.35	B-C	1.00	9.69	C-C	0.97	32.85	B-N-C	1.00	11.1	
		B-O	0.69		C-N	0.94		Graphitic N	0.97		

Table 2 presents the influence of raw material ratios on the composition of products. It is clear that the B content in the BCN fiber decreases as the AB content in the raw material ratio decreases, and the C content

increases as the PAN ratio increases. However, the N content in the product did not change significantly due to the change of the raw material ratio. It implied that N in BCN fibers is mainly introduced through the reaction of precursor fibers and NH_3 .

Table 2. Elemental analysis of BCN nanofiber derived from different raw material ratio (pyrolyzed at 1000°C).

PAN/AB	B 1s (at%)	C 1s (at%)	N 1s (at%)	O 1s (at%)
1:1	44.43	2.30	36.01	17.26
3:1	37.54	11.52	36.42	14.52
5:1	33.78	19.63	37.01	9.58

The optical absorption performance of BCN fibers derived from different raw material ratios are examined by UV-vis diffuse reflectance spectra (Figure 7a). It is clear that all samples have obvious absorption between 300–500nm. In particular, the sample with a raw material ratio of PAN/AB=8:1 has strong absorption in the entire visible light range. This is mainly due to the high content of graphite carbon in the fiber, which is consistent with the black appearance of the sample (other products are light yellow). Figure 7b shows the band energy levels calculated based on the DRS results. As the proportion of PAN in the raw material increases, it can be seen that the band gap of BCN fibers gradually narrows from 2.62 eV to 2.13 eV.

Figure 7 (a) UV/vis diffuse reflectance spectra of samples derived from different raw material ratios and (b) the corresponding Tauc plots.

Conclusion

In this study, a series of BCN nanofibers with different composition and bandgaps were prepared. The B content in the fiber is mainly determined by the AB content in the raw material, while the N content mainly depends on the pyrolysis temperature.

The BCN nanofibers are mainly composed of *h*-BN crystallites. C atoms are distributed at the grain boundaries and are connected to the crystallites through B-C covalent bonds and B-N coordination bonds. As the heat treatment temperature increases, the crystallization of *h*-BN gradually improves. However, heat treatment over 1000°C will cause degradation of the crystal structure.

As the proportion of PAN in the raw material increases, the band gap of the product gradually narrows. This is beneficial for improving the light absorption performance of the fiber. However, high PAN content

will result in excess C content in the product. This may have adverse effects on the formation of the BCN ternary system.

In summary, the best conditions for preparing BCN fibers are: PAN/AB ratio between 3:1 and 5:1, pyrolysis temperature of about 1000°C . The as-obtained BCN fiber has an adjustable band gap between 2.1 and 2.7 eV, which has potential applications in the field of photocatalysis.

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