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A convenient catalytic approach to synthesize straight boron nitride nanotubes using synergic nitrogen source

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Abstract

Straight boron nitride nanotubes (BNNTs) with pure hexagonal phase were conveniently prepared by heating the mixture of $Mg(BO_2)_2 \cdot H_2O$, NH_4Cl , NaN_3 and Mg powder in an autoclave at 600 °C for 20–60 h. These BNNTs had diameters mainly ranging 30–300 nm and lengths up to ~5 µm, and a majority of them had at least one closed end. Besides the traditional end tips, additional cone-like tips were frequently found to be attached on the BNNTs. The effects of temperature, reactants and the possible mechanism of the catalytic formation of the BNNTs are discussed.

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1. Introduction

Since the first discovery of crystalline and pure boron nitride nanotubes in 1995 [1], the synthesis, characterization and studies of the structures and properties of this unique material have generated great interest. Continued experimental and theoretical efforts [2] have shown that BNNTs are nanomaterials with constant band gaps that are nearly independent of their radius and helicity [3]. In addition, they possess unusual mechanical and thermal properties (such as high thermal conductivity and stability) as well as high oxidation resistivity and chemical inertness [4],which make BNNTs a promising material for developing nanotube-based electronic devices or composite materials that can be used in oxidative, hazardous, high-temperature environments, or those serviceable for hydrogen storage at room temperature [5].

BNNTs are normally prepared by methods similar to those employed for production of carbon nanotubes, such as arc-discharge [1], laser ablation [6], chemical vapor

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deposition [7], and template-grown method [8]. Other approaches based on specially designed chemical reactions have also been reported. For example, BNNTs were produced by annealing of B and h-BN powders in NH₃ gas at 1200 °C [9], through heating B and Li powders at ~1200 °C under an N₂ atmosphere [10], or via pyrolysis of B₃N₃H₆ at ~1100 °C [11]. Recently, bulk amounts of BNNTs were synthesized by reacting B, MgO and NH₃ at 1300 °C [12], and BNNTs were also produced by annealing of Fe₄N and B particles at 1000 °C in N₂ atmosphere [13,14]. The above-mentioned methods have produced pure and crystalline BNNTs, but they usually needed high temperature, or special apparatus, or complex synthesis processes. Therefore, further approaches for designing novel schemes of fabrication have been awaited.

Solid state pyrolysis of synergic boron and/or nitrogen sources has been proved to be a convenient way to fabricate BNNTs at low temperature [15]. In line with this method, we have developed in the present study a low-cost and carbon-free approach for fabrication of straight BNNTs at 600 °C for 20–60 h. A majority of these asobtained BNNTs are found to have at least one closed end, besides the traditional end tips, and additional cone-like tips are frequently contained jointly with the BNNTs. Based on the results of contrast experimental analyses, we have explored the effects of reaction temperature on the reactants and the formation mechanism of BNNTs.

2. Experimental section

All the chemical reagents were of analytical-grade purity (Shanghai Chem. Co.) and were used directly. In a typical procedure, $Mg(BO_2)_2 \cdot H_2O$ (20 mmol), Mg powder (110 mmol), NH_4Cl (131 mmol) and NaN_3 (33 mmol) were mixed together and were put into a 55 ml autoclave. The autoclave was sealed and heated in an electric stove with an increasing speed of 10 °C/min and maintained at 600 °C for 60 h, and then it was naturally cooled to room temperature. The raw product was collected and washed with diluted HCl acid and distilled water several times until the solution became neutral. The final product was washed with ethanol and dried in a vacuum at 50 °C for 3 h.

The phases of the products were measured using a Bruker D8 X-ray powder diffractometer. Fourier transform infrared spectroscopy of the samples was conducted on an AVATAR-370 (Thermonicolet) spectrometer. The sizes and structures of the products were examined by transmission electron microscopy (Hitachi-600) and high-resolution TEM (JEOL-2100).

3. Results

3.1. XRD and IR analyses

Fig. 1 shows typical XRD patterns of the products before and after the acid treatment. The distinct diffraction peaks in Fig. 1a can be indexed to be MgO (JCPDS card no. 65-476) and Mg₃(BO₃)₂ (JCPDS card no. 38-1475), while those of hexagonal BN (h-BN) are weak in intensity. Fig. 1b presents the XRD pattern of the product obtained



Fig. 1. Typical XRD patterns of the products: (a) before and (b) after acid treatment.

after washing with HCl, in which all the reflection peaks can be indexed as pure h-BN with lattice constants a = 2.503 Å and c = 6.662 Å, because these values are close to those reported for h-BN (JCPDS card no. 34-0421). No noticeable peaks of other impurities such as B₂O₃ and B were detected in this pattern.

Fig. 2 shows a typical FTIR spectrum of the sample after the acid treatment. Two strong peaks located at 1377 and 819 cm⁻¹ can be ascribed to the characteristic absorption peaks of h-BN. The former absorption band centered around 1377 cm^{-1} should be assigned to the in-plane B–N to modes of the sp² bonded h-BN, while the latter one can be ascribed to the B–N–B out-of-plane bending vibration [16]. The result of this analysis combined with that of XRD patterns further proves the pure phase of the final product.

3.2. TEM analyses

The results of the TEM microscope analyses indicated that the products were composed of BNNTs, nanocages, and flake-like BN powder. Most of the BNNTs produced were multilayer straight tubes generally with diameters ranging from 30 to 300 nm and lengths up to $\sim 5 \,\mu\text{m}$. Fig. 3a shows a typical TEM image of the BNNTs obtained at 600 °C for 60 h. The inset BNNTs have relative uniform diameters, but their lengths varied greatly; some of them have lengths of only ~ 400 nm (as arrowed), while the longest BN nanotubes have lengths up to $\sim 5 \,\mu m$. It can also be observed that these BNNTs usually have one or two closed ends, being different from the BNNTs reported in Refs. [16,17]. An individual BNNT having two closed ends is displayed in Fig. 3b, and its corresponding SAED pattern is depicted in Fig. 3c, where the arcs and rings can be indexed as 002, 101 and 110 diffractions, respectively. The HRTEM image of a part of the individual BNNT (in Fig. 3b), displayed in Fig. 3d, has multiple walls and clearly exhibit fringes with an interplanar distance $d_{002} = 3.401$ Å, which is close to the diffraction spacing



Fig. 2. A typical FTIR spectrum of the product after acid treatment.

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Fig. 3. Representative TEM micrographs, SAED pattern and EDX spectrum: (a) TEM image; (b)–(e) an individual BNNT, its corresponding SAED pattern, part of its HRTEM image and EDX spectrum and (f) a TEM image of BN nanocages.

of 002 planes. A typical EDX spectrum of the BNNT (in Fig. 3b) presented in Fig. 3e indicates that this BN nanotube is composed of B and N elements only. The Cu and C signals originate from the supporting Cu grid and the specimen holder-carbon film, respectively. As the synthetic processes are free of carbon, the present nanotube is proved to be a pure BN nanotube. Besides the BNNTs, BN nanocages are also found in different areas of the same copper grid under TEM observations. Fig. 3f shows a typical TEM image of BN nanocages, in which spherical and polygonal hollow BN nanocages exist apart from the BNNTs.

3.3. Characteristic features of BNNTs

The as-obtained BNNTs are straight, and their diameters are larger than the BNNTs reported previously [12]. A majority of them have at least one closed end, which might be used for protective shields of large-capacity dielectric nano-containers for encapsulated species [17]. Besides the traditional tip-ends, additional cone-like tips have also been discovered frequently. This is another notable feature of these BNNTs. Fig. 4 show a variety of TEM images of such cone-like tips and their corresponding HRTEM images. For example, the images of the front of the tip (Figs. 4a and b) show two sets of stacked parallel layers meeting at a sharp angle, while the backs of these layers enter into the curled layers that belong to the traditional end-tips.

4. Discussion

4.1. Possible reaction mechanism

In this experiment, the following reactions are likely to occur with the increasing temperature:

- $NH_4Cl \rightarrow NH_3 + HCl$ (2)
- $2NaN_3 \rightarrow 2Na + 3N_2 \tag{3}$

$$B_2O_3 + 3Mg \rightarrow 2B + 3MgO \tag{4}$$



Fig. 4. Representative TEM and the corresponding HRTEM images of the cone-like tips indicated with arrows: (a) TEM image; (b) HRTEM image of the part arrowed on the right side and (c)-(f) the parts as arrowed.

 $B_2O_3 + 2NH_3 \rightarrow 2BN + 3H_2O \tag{5}$

 $B_2O_3 + 3Mg + N_2 \rightarrow 2BN + 3MgO \tag{6}$

 $2\mathbf{B} + 2\mathbf{N}\mathbf{H}_3 \to 2\mathbf{B}\mathbf{N} + 3\mathbf{H}_2 \tag{7}$

 $2\mathbf{B} + \mathbf{N}_2 \to 2\mathbf{B}\mathbf{N} \tag{8}$

The Gibbs energies for the formulas from (2)–(8) were calculated as -62.75, -462.24, -478.03, -7.72, -830.98, -449.92, $-352.95 \text{ kJ} \cdot \text{mol}^{-1}$ at 600 °C, respectively. The negative values imply correctness of the formulas proposed above. Because B_2O_3 has a relatively low melting point (~450 °C), a part of the B_2O_3 may be reduced by the Mg powder that is excessively loaded in the initial step to form B powder. As the initial molar ratio of N atom to B was 5.75, h-BN could be easily produced between the reactions of chemically activated B and B_2O_3 with NH₃/N₂ (and/or their decomposers; see formulas in (5)–(8)). Of course, the byproducts including MgO and Mg₃ (BO₃)₂ could also be formed, as proved by the XRD pattern (Fig. 1a), and the appearance of additional cone-like tips conjunct on the BNNTs (see Fig. 3) might prove the processes of two boron sources discussed above.



Fig. 5. Representative HRTEM images: (a) a core-shell composite; (b) part of the composite in Fig. 5a and (c) the product obtained for 20 h.

It is found that no BN was produced if Mg powder was substituted by Al, Fe, Co or Zn powder. This suggests that Mg powder plays a catalytic role during the formation process of BNNTs. This point might further be evidenced partly by the occasionally observed Mg-filled BNNT under many times of HRTEM observations. Figs. 5a and b show typical HRTEM images of a cable-like composite, which are composed of two kinds of materials according the strong contrast color. The resolved fringes with an interlayer distance of $d_{001} = 5.12$ Å is close to that of Mg (JCPDS card no. 01-1141) 001 planes. It is also found that the thickness of the outer BN layer coated on the interior Mg nanorod varies at different areas of the composites, which is consistent with the reasonable speculation that catalysts-assisted (Mg or/and Mg based materials) tip (or root) growth process (see Fig. 5c) might be responsible for the growth of BNNTs; however, the exact formation mechanism still needs further research. This supposition could tentatively be supported by the observation of the HRTEM images (Fig. 5) and the related reports in Refs. [12,17].

4.2. Contrast experiments

A series of contrast experiments were further carried out in order to study the effects of reaction temperature, time and reactants on the final formation of BNNTs. For instance, the following results were obtained: (a) the optimum temperature for the formation of BNNTs was 600 °C; other temperatures such as 500 °C, 550 °C and 650 °C only led to the production of irregularly shaped BN and less yield of BNNTs. (b) The reaction time had no essential influence on the yield augment of BNNTs but had an effective influence on their length-extension. Fig. 5c shows a typical TEM image of the BNNTs obtained at 600 °C for 20 h; their lengths were significantly shorter than those obtained at 600 °C for 60 h (see Fig. 3a). A very short BNNT with a closed end-tip, as arrowed in Fig. 5c, indicates a growth termination. A similar scene is also observed in Fig. 3a, where the appearance of these phenomena might attribute to the impingement of growing BN nanotubes with small metal catalyst clusters [18]. (c) When NH₄Cl or NaN₃was used solely as the nitrogen source, BNNTs were hardly observed under TEM observations. Therefore, it is likely that NH₄Cl and NaN₃ have a synergic effect on the fabrication of BNNTs in this experiment.

5. Conclusions

In this study, BNNTs were produced at 600 °C using a synergic nitrogen source. Most of the as-obtained BNNTs are straight and with multi-walls. A majority of them have at least one closed end. A possible catalytic process is considered to be responsible for the formation of these BNNTs. This unique feature of the synthesized products

might bring a new insight into the experimental and theoretical studies of BN nanotubes.

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