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Research Article

Synthesis of Boron Nitride Nanotubes by Self-Propagation High-Temperature Synthesis and Annealing Method

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High-quality boron nitride nanotubes were synthesized by annealing porous precursor in flowing NH_3 gas at 1150°C. The porous precursor $B_{18}Ca_2(MgO)_9$ was produced by self-propagation high-temperature synthesis (SHS) method using Mg, B_2O_3, and CaB_6 as the starting materials, which played an important role in synthesis of BN nanotubes in large quantities. Samples were characterized by SEM, TEM, EDX, HRTEM, X-ray powder diffraction (XRD), Raman, and Fourier transform infrared (FTIR) spectroscopy. The as-synthesized BN nanotubes have an average diameter of about 150 nm with a wall/diameter ratio of 2/3. Mean length of the BN nanotubes was more than 10 μm. The effects of temperature, time, and the possible mechanism of the growth of the BN nanotubes were also discussed.

1. Introduction

Boron nitride (BN) nanotubes have a similar structure as carbon nanotubes (CNTs). They also exhibit some attracting properties, including a stable insulator, a superresistance to oxidation at high temperatures, an excellent thermal conductivity, uniform electronic properties, interesting piezoelectricity, and optical properties [1]. Moreover, in addition to these characteristics, BN nanotubes also can be used as a perfect insulating tubular shield to encapsulate some materials within and demonstrated distinctive features [2–4]. Obviously, the unique properties of BN nanotubes will be the prerequisite of the important applications in the fields of optoelectronics, nanosemiconductor devices, electronics, energy storage, and biomedical medicine [5].

In recent years, various synthetic methods have been used to grow BN nanotubes. Generally, it could be classified into two categories, the high-temperature (above 2400°C) method and the low-temperature (ranging from 400 to 1700°C) method [6]. The high-temperature methods usually need special sophisticated instruments or complex processes to meet the high-temperature requirements and only obtain single morphology BN nanotubes, which was unaffordable. In contrast to the high-temperature methods, the low-temperature methods can operate at a mild condition and normal pressure. Importantly, different types of BN nanotubes could also be prepared by changing annealing conditions, which may be suitable for popularization and application. And the catalytic chemical vapor deposition (CVD) method is one of the most popular techniques for the low-temperature synthesis of BN nanotubes. Various kinds of boron-containing precursors can be used to prepare BN nanotubes. Commonly, the precursors can be diborane (B_2H_6) [7, 8], borazine ($B_3N_3H_6$) [9, 10] and trimethyl bo rate ($C_3H_9BO_3$) [11], elemental boron [12–18], iron boride (FeB) [19, 20], and boric acid (H_3BO_3) [21]. In addition, for the CVD method, precursors with uniform dispersion of metal catalyst and boron source are especially significant. Many efforts have been made to deal with the problem, such as ball-milling process [22–27], which is very consumptive of energy and time.

Herein, we introduce a convenient way so-called SHS-annealing method to synthesize BN nanotubes using an effective porous precursor. The porous precursor can be readily produced by self-propagation high-temperature synthesis (SHS), which plays an important role in synthesis of

Figure 1: Photo of the crude product in an alumina boat. Scale bar: 7.5 mm.

large quantities of BN nanotubes. The effects of temperature, time, and possible mechanism of the growth of the BN nanotubes were also discussed.

2. Experimental

2.1. Materials. The reagents, magnesium (Mg), and boron oxide (B_2O_3) were of analytical pure grade and about 150–300 mesh (50–100 μm) powders. Calcium hexaboride (CaB_6) was made by ourselves having the particle size of 0.2 to 0.95 μm and the purity of ≥95 wt%.

2.2. Instrumentation. The resultant BN nanotube samples were characterized by X-ray powder diffraction (XRD) using a Shimadzu XD-5A X-ray diffractometer using Cu-Kα radiation (wavelength $\lambda = 1.5406$ Å). Raman spectrum was recorded at room temperature on a Nicolet DXR Raman spectrometer using Nd:YAG laser at excitation of 532 nm. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 6700 Fourier transform infrared spectrometer in transmission mode using a KBr wafer. The scanning electron microscopy (SEM) was studied using a Hitachi S-3400N scanning electron microscope and energy-dispersive X-ray (EDX) spectroscopy attached to it was employed to determine chemical contents. Samples were observed by directly spreading the samples on conductive tapes and sputtering Au or Pt on the surface. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were performed on a JEOL JEM-2100F transmission electron microscope. For HRTEM and TEM observations, samples were prepared by ultrasonically dispersing the product in ethanol and depositing on copper grids coated with carbon film.

2.3. Synthesis of Boron Nitride Nanotubes by SHS-Annealing Method. In a typical experimental procedure, 11.90 g B_2O_3, 12.20 g Mg, and 11.60 g CaB_6 were mixed by a blender mixer for about 12 minutes. The mixture was put into a SHS-furnace and heated to 750°C for 10 minutes in an argon atmosphere. After the SHS reaction, 34.80 g porous precursor was obtained. The porous precursor was placed in an alumina boat and heated to 1150°C at 6°C/min and kept for 6 h in an ammonia flowing gas at 0.3–0.9 L/min in the center of a horizontal tubular furnace at a normal pressure. After cooled to room temperature naturally, the furnace was opened, and the crude product (shown in Figure 1) was collected and washed with 5 M hydrochloric acid, ethanol, and distilled water. Finally, 20.25 g gray BN nanotube powders were obtained by drying in vacuum at 80°C for 24 hours. The yields of BN nanotubes based on boron were about 83.08 wt%.

3. Results and Discussion

3.1. Results. The typical SEM image of as-synthesized BN nanotubes is shown in Figure 2(a), which indicates the products possess a high density of one-dimensional structures with diameters in the range of 30–200 nm and an average of about 150 nm. The average lengths of the structures are more than 10 μm. Few BN flakes and particles were observed. The purity of BN nanotubes was estimated of about 95 wt%.

Figures 2(b) and 2(c) give the typical TEM images of BN nanotubes with different diameters. The thin BN nanotube reveals a diameter of 60 nm with the wall thickness of 20 nm (Figure 2(b)). However, the thick BN nanotube presents a diameter of 180 nm with the wall thickness of 60 nm, as seen in Figure 2(c). In addition, both the thin and the thick BN nanotubes had a wall/diameter rate of approximately 2/3.

To investigate the structural features of the synthesized BN nanotubes, HRTEM observation was carried out. The typical HRTEM image of the BN nanotubes suggests a well-crystallized structure, with outerwalls that are very clean (no amorphous BN coatings), as shown in Figure 2(d). The boron nitride nanotube has multiple walls with thickness of about 60 nm and clearly exhibit fringes with an average interlayer distance about 0.34 nm (see insert image of partial enlargement denoted by a frame in Figure 2(d)), which corresponds to the (002) plane of hexagonal BN crystal.

The EDX spectrum presented in Figure 2(e) demonstrates corresponding signals of boron and nitrogen, and quantitative analysis indicates that the molar ratio of B : N is 1 : 1.046, which is close to that of BN. The O peak can be ascribed to the slight surface oxidation of BN nanotubes. It is worth noting that the Ca signal also was revealed in the EDX spectrum, while no signal of Mg was observed. Probably, the Ca particles were encapsulated at the root of BN nanotubes as the metallic catalyst during the BN nanotubes growth process. A small amount of metal Ca particles still remained after the annealed precursor was washed with 5 M hydrochloric acid. On the contrary, the MgO particles only acted as a supporter during the BN nanotubes growth process and were removed after the purification processes mentioned above.

Figure 3 displays the typical XRD pattern of the as-synthesized BN nanotubes. Four peaks at d-spacings of 3.35, 2.17, 2.07, 1.67, and 1.25 Å can be indexed as (002), (100), (101), (004), and (110) planes of hexagonal boron nitride. The lattice constants are $a = 2.509$ Å and $c = 6.691$ Å, close to the reported value $a = 2.502$ and $c = 6.660$ Å in JCPDF card no. 45-0893, indicating the good crystallinity of the BN

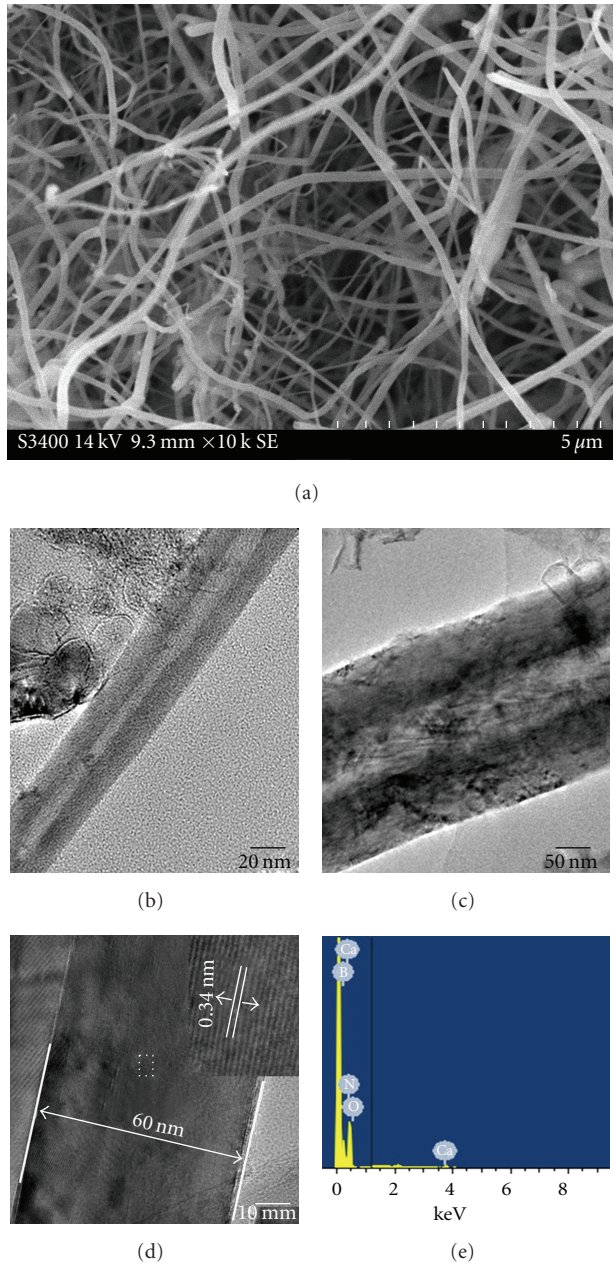

Figure 2: Typical SEM (a), TEM (b, c), HRTEM (d) images, and EDX spectrum (e) of the as-synthesized BN nanotubes. Scale bars: (a) 5 μm, (b) 20 nm, (c) 50 nm, and (d) 10 nm.

nanotubes. No noticeable peaks of other impurities, such as MgO and B_2O_3, were detected in this pattern.

Figure 4(a) shows the typical wide-scan FTIR spectrum in the range of 500 to 4000 cm^{-1} of the as-synthesized BN nanotubes sample. Two strong peaks located at 803 and 1379 cm^{-1}can be ascribed to the out-of-plane B-N TO models of the sp^2-bonded h-BN and the B-N-B in-plane bonding vibrations, respectively. The broad absorption band near 3454 cm^{-1} can be resulted from the O–H bonds due to the absorbed of water. As shown in Figure 4(b), a peak at 1535 cm^{-1} in the deconvolution spectrum should be assigned to the unique stretching of the h-BN network around the circumference of BN nanotubes [28], while the other peak at 1117 cm^{-1} in the deconvolution spectrum may be attributed to the abnormal vibrations like those of wurtzite BN, which may exist due to structure defects in the as-synthesized cylindrical BN nanotubes.

Figure 5 is the typical Raman spectrum of the as-synthesized BN nanotubes. A sharp Raman peak was showed at around 1354 cm^{-1}, which corresponded to the E_{2g} in-plane model of the h-BN networks [29], while the other weak peak at about 780 cm^{-1} may be due to the glass holder used during the analysis.

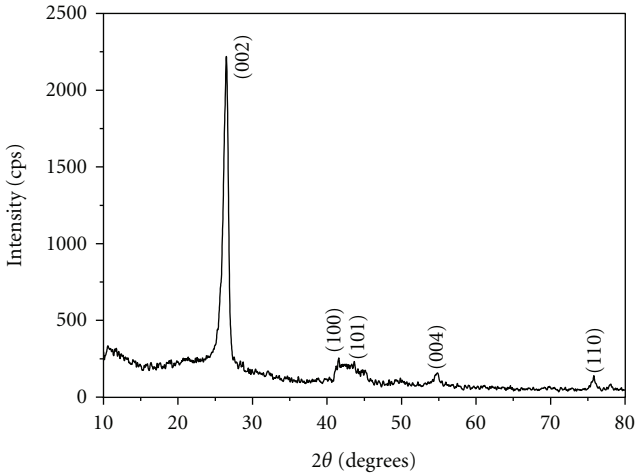

Figure 3: Typical XRD pattern of as-synthesized BN nanotubes.

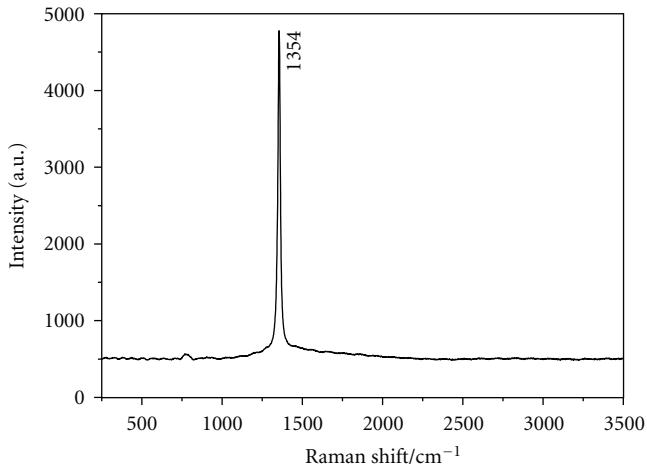

Figure 5: Typical Raman spectrum of the as-synthesized BN nanotubes.

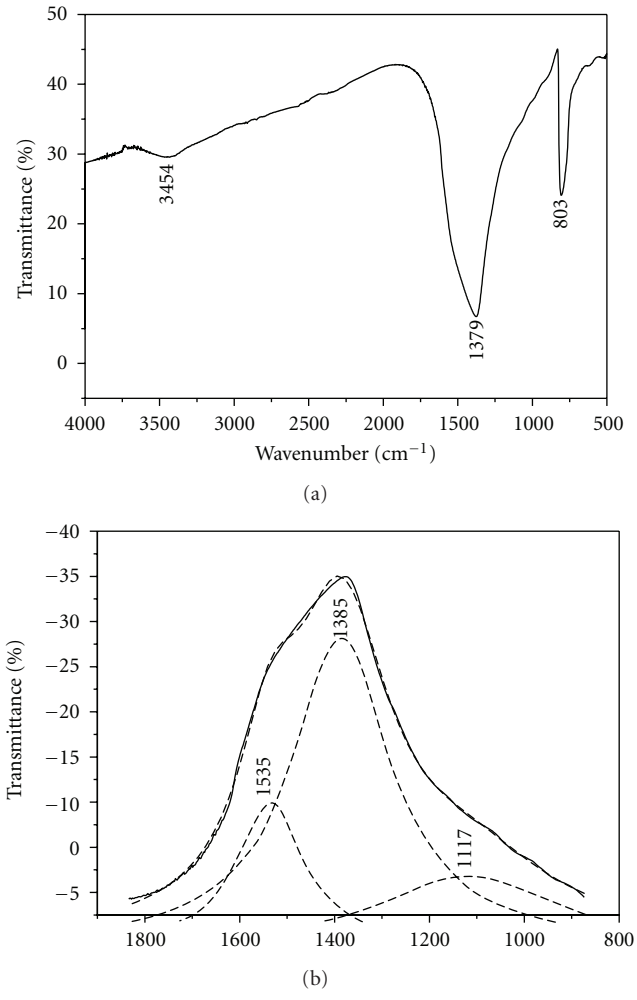

Figure 4: Typical FTIR and deconvolution FTIR spectra of the as-synthesized BN nanotubes. (a) Wide-scan FTIR spectrum and (b) deconvolution FTIR Spectrum.

3.2. Reaction Mechanism. In this experiment, the possible reactions are likely to occur as follows:

$$3\,B_2O_3 + 9\,Mg + 2\,CaB_6 = B_{18}Ca_2(MgO)_9, \tag{1}$$

$$B_{18}Ca_2(MgO)_9 + 18\,NH_3 = 18\,B^* + 18\,N^* + Ca_2(MgO)_9 + 27\,H_2, \tag{2}$$

$$x(B^* + N^*) + Ca_2(MgO)_9 = xBN_{NT} + 2\,Ca + 9\,MgO, \tag{3}$$

$$(18 - x)(B^* + N^*) = (18 - x)BN_{FL} (x = 0 \text{ to } 18,\ NT = \text{nanotubes},\ FL = \text{flakes}). \tag{4}$$

$B_{18}Ca_2(MgO)_9$ only stands for the mixed chemical elements in the precursor prepared by SHS reaction using Mg, B_2O_3, and CaB_6 as the starting materials, as in (1). NH_3 reacted with $B_{18}Ca_2(MgO)_9$ at the temperature of 1150°C and produced chemically active B* and N* vapor and hydrogen gas, as in (2). According to the VLS growth mechanism [30], boron nitride nanotubes began to grow on the surface of metal catalyst liquid supported on MgO, as in (3). However, flakes of BN may be synthesized due to lacking of metallic catalyst as vapor-solid (VS) growth mechanism, and the nanotube selectivity was $x/18$, as in (4), where the values of x were approximately estimated as about 16 to 18.

3.3. Growth Mechanism of Boron Nitride Nanotubes. According to the catalytic VLS growth mechanism [30], the diameters of nanotubes depend on the particle sizes of catalyst liquid drops. Small droplets could lead to BN nanotubes with small diameters, while large droplets could render large diameters. Therefore, the distribution of catalyst drop sizes leads to a certain diameter range of BN nanotubes. Moreover, to grow a cylindrical BN nanotube by the base growth mechanism, there is at least one initial open tip.

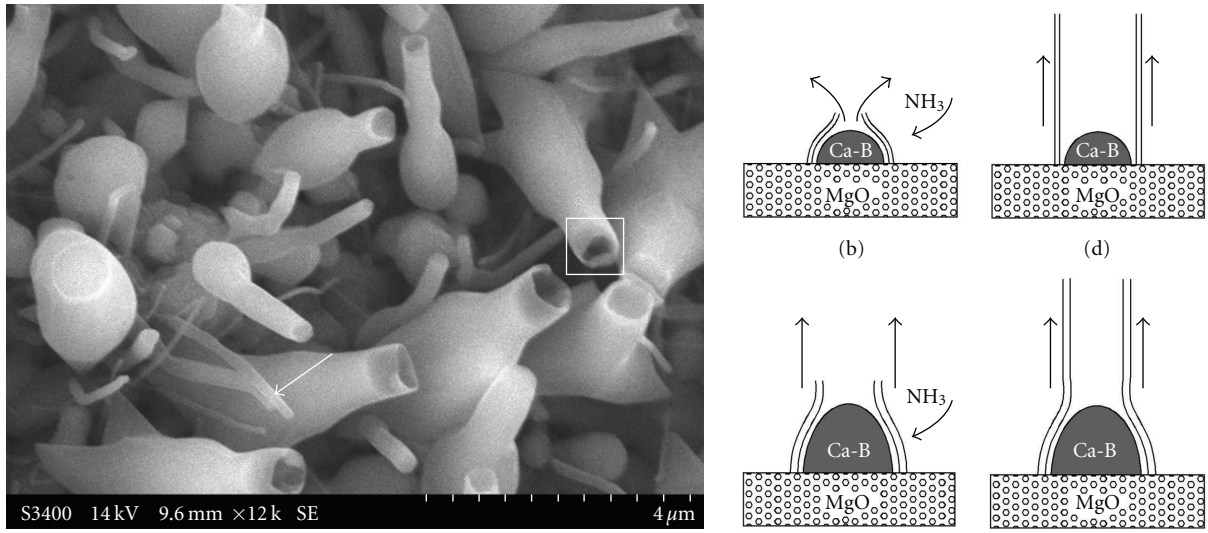

Figure 6: Typical SEM image of the porous SHS precursor at the initial annealing stage (a) and schematic illustration of base growth model of BN nanotubes with small (b) and large (c) diameters. Scale bars: (a) 4 μm.

The growth rate can be either approximately a constant or smoothly changing due to the change of microcircumstance such as the vapor constitution, temperature, and catalyst. The proposed growth model agrees well with the observed morphology of the as-synthesized BN nanotubes.

Figure 6(a) shows the typical SEM image of the porous SHS precursor at the initial annealing stage. It can be observed that there were many BN nanotube embryos of small (pointed by an arrow) and large (in a frame) sizes. Interestingly, all of these embryos revealed open tips. Therefore, we suggest a base growth scenario as schematically illustrated in Figures 6(b)–6(e).

Firstly, the Ca-B liquid drop is formed supported on MgO particle and reacts with NH_3 gas at a high temperature (1150°C). Secondly, when the concentrations of B and N species are supersaturated, BN nuclei begin to precipitate on the surface of Ca-B liquid drop and form a top-opened BN cap (Figures 6(b) and 6(c)). Thirdly, with the continuous supply of B and N atoms, the cap grows gradually up into a cylindrical BN nanotube with an open tip (Figures 6(d) and 6(e)). The growth of BN nanotube will not be terminated unless the B or N atoms are consumed. In this base growth process, BN nanotube grows from the liquid-solid interface in order to give the lowest liquid-solid interfacial energy [31].

3.4. Contrast Experiments. A collection of experiments were carried out to investigate the influence of the reaction temperature, time, and starting materials on the growth of BN nanotubes.

It was found that the optimum temperature range for the growth of the as-synthesized BN nanotubes was in the range of 1050–1150°C. The crystallinity of BN nanotubes will become better with the rise of temperature in this range. If the reaction temperature is lower than 1050°C, both selectivity and the yield of BN nanotubes will decrease. Temperature above 1150°C could mainly lead to the other shaped BN products such as flakes and grains, in spite of the yield which was increased.

The reaction time had an essential influence on the yield of BN nanotubes. In the optimum temperature range, if annealing time is less than 3 h, the reaction will become very incomplete, and as a result, the yield will be approximately less than 30 percent.

High selectivity and high yield of the BN nanotubes production could be obtained when boron ratio varies within a certain range of 25 to 35 wt%. The selectivity of the BN nanotubes will reach up to the highest value (about 95 wt%) if boron ratio is 30.5 wt% for the porous precursor $B_{18}Ca_2(MgO)_9$, which was prepared by adding 33 wt% CaB_6. It is likely that the porous precursor has an optimum porous structure and highly dispersion state of metal catalyst and the reactant. If the boron ratio is below 25 wt% or above 35 wt%, both selectivity and the yield of BN nanotubes will decrease.

4. Conclusions

In summary, we report a convenient and efficient method to prepare bulk quantity of boron nitride nanotubes with the diameter of 30–200 nm and the average length of more than 10 μm by annealing a porous precursor at 1150°C for 6 h in flowing NH_3. The porous precursor was produced by SHS method via heating the mixture of starting materials of Mg, B_2O_3, and CaB_6 powders to 750°C for 10 minutes. A base growth mechanism was proposed. The existence of metal liquid drop played an important role during the growth process of BN nanotubes. The present work demonstrates that the SHS-annealing method is effective to synthesize quantities of BN nanotubes.

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