

High-yield Synthesis of Boron Nitride Nanotubes by Annealing Fe₃BO₆

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Boron nitride (BN) nanotubes were obtained in high yield via chemical vapor deposition by annealing Fe₃BO₆ under NH₃ atmosphere at 1100 °C. The XRD and FTIR spectra indicate the products are high pure hexagonal phase BN. SEM, TEM, and HRTEM were used for observing the morphology of the products. The possible chemical reactions and growth mechanism are also proposed.

Boron nitride (BN) nanotubes have many excellent properties, such as unusual mechanical, thermal, oxidation resistivity, and chemical inertness properties, so they may be applied potentially in various fields, for instance electronic and mechanical devices, fabrication of BN nanotube-reinforced glass composites, hydrogen adsorption, and biomedicine. In recent years, BN nanotubes have been synthesized by various methods, such as arc-discharge,^{1,2} laser ablation,^{3,4} ball-milling,^{5,6} template-confined,^{7,8} chemical reaction,^{9,10} and chemical vapor deposition (CVD) methods.^{11,12} Catalytic CVD is one of the most common techniques for the synthesis of BN nanotubes. Some research groups have synthesized BN nanotubes via CVD using Fe/B compounds. Huo et al.¹³ have synthesized periodic spindle-unit BN nanotubes with buglelike open-end tips simply by nitriding low-boron-content Fe–B nanoparticles in a N₂/NH₃ atmosphere at 1100 °C. Loh et al.¹⁴ have prepared hexagonal BN nanotubes from the liquid flow of iron boride (FeB) nanoparticles. Fu et al.¹⁵ have synthesized BN nanotubes through the reaction of a gas mixture of NH₃/N₂ with Fe–B precursor at 1100 °C. In addition, BN nanotubes, nanohorns, and nanocoils have been synthesized by annealing Fe₄N and B powders in a furnace at 1000 °C in nitrogen atmosphere.¹⁶ But it is still difficult to produce BN nanotubes on a large scale, which limits the application of them in various fields.

In this paper, we report an effective CVD method to prepare BN nanotubes in high yield by annealing Fe₃BO₆. To our best knowledge, Fe₃BO₆ has not been reported to be employed as a reagent to prepare BN nanotubes at low temperature so far. Based on the characterization results, the possible chemical reactions are discussed, and the growth mechanism in the presence of catalyst is also proposed to interpret the growth of BN nanotubes.

In a typical procedure, 23.4 g of Fe(OH)₃ and 4.5 g of H₃BO₃ were used to prepare 19.7 g of Fe₃BO₆ as in our previous work.¹⁷ The previous Fe₃BO₆ was heated in a vertical furnace under NH₃ atmosphere (ca. 0.8 L min⁻¹) at 1100 °C for 24 h and then cooled on standing to room temperature. The raw product was purified by excess HCl (15 wt %), centrifuged, and then washed with distilled water several times. 1.52 g of gray powder was collected after the purified product was dried under vacuum at 80 °C for 12 h.

The resultant sample was characterized by X-ray powder diffraction (XRD) using a Shimadzu XD-5A X-ray diffractometer. Fourier transform infrared (FTIR) spectrum was recorded on a Nicolet 6700 Fourier transform infrared spectrometer. Scanning

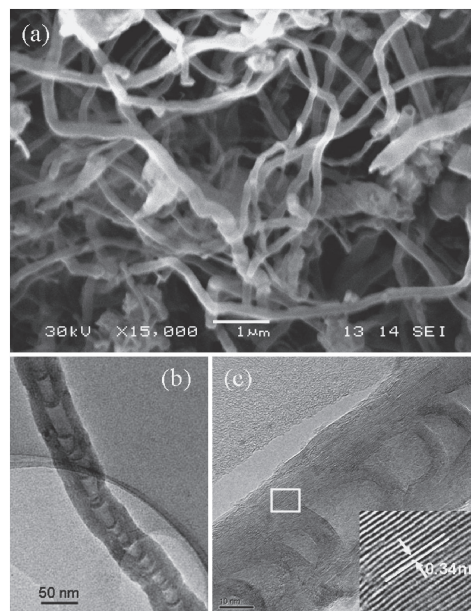


Figure 1. Typical SEM (a), TEM (b), and HRTEM (c) images of the products. Scale bar: (a) 1 μm, (b) 50 nm, and (c) 10 nm.

electron microscopy (SEM) was conducted using a Hitachi S-3400N scanning electron microscope. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were performed on a JEOL JEM-2100F transmission electron microscope.

Figure 1 shows typical SEM, TEM, and HRTEM images of the as-synthesized BN nanotubes. Figure 1a is a typical SEM image of the sample. It reveals that the product contains a large amount of BN nanotubes and few BN nanoflakes impurities. The total BN nanotubes content of the products is about 90 wt % according to statistical analyses by SEM and TEM microscopy. The average diameter of BN nanotubes is less than 150 nm, and the length more than 10 μm. To confirm the detailed morphology and structure of BN nanotubes, an extensive TEM investigation was carried out. Figure 1b, a representative TEM image of an individual BN, shows that the nanotube is consist of many bamboo-like structures. It also clearly displays that the tube has an outer diameter of about 60 nm and an inner diameter of about 20 nm. The outer walls of the tubes are very clear, suggesting no amorphous BN coatings or other impurities exist in the product. Figure 1c is a corresponding HRTEM image recorded from a part of the BN nanotube. It is demonstrated that the lattice fringes are well-defined, indicating that the nanotube wall has a high degree of crystalline perfection. The high-magnification inset image reveals the clear parallel fringes with an average interplanar distance of 0.34 nm, which is close to the *d*₀₀₂ spacing of the hexagonal phase of BN.¹⁸

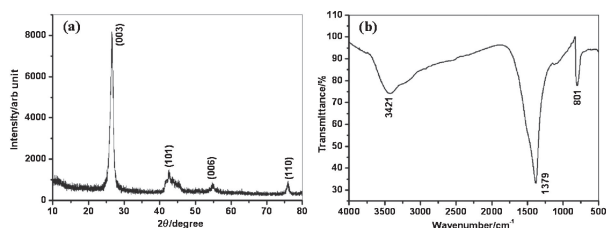
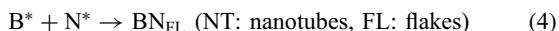
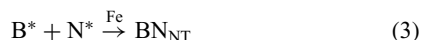
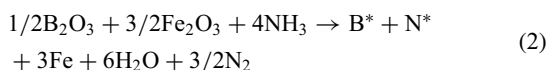
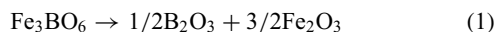


Figure 2. Typical XRD pattern (a) and FTIR spectrum (b) of the products.

The as-synthesized BN nanotubes were also characterized by XRD and FTIR spectroscopy. As shown in Figure 2a, the XRD pattern reveals four peaks at d spacings of 3.351, 2.122, 1.674, and 1.251 Å, that can be indexed as the (003), (101), (006), and (110) planes of hexagonal phase of BN. The lattice constants are $a = 2.505$ and $c = 10.049$ Å, which are close to the value $a = 2.504$ and $c = 10.000$ Å in JCPDS card No. 45-1171. No distinct diffraction peaks of impurity phases are detected in the XRD spectrum. Figure 2b shows a typical FTIR spectrum of the as-synthesized product. Two strong peaks located at 1379 and 801 cm can be ascribed to the characteristic absorption peaks, assigned to the in-plane B–N TO modes of the sp-bonded h-BN and the B–N–B out-of-plane bending vibration, respectively.¹⁹ The broad absorption band near 3421 cm can be result from the O–H bonds due to absorbed water.

The chemical reaction mechanism for the growth of the as-synthesized BN nanotubes may be described in eqs 1–4.



As shown in eq 1, Fe_3BO_6 decomposed promptly and generated B_2O_3 and Fe_2O_3 at the first stage of annealing. The newly produced B_2O_3 and Fe_2O_3 reacting with NH_3 yielded nascent boron (B^*) and nitrogen (N^*) vapor (eq 2). According to the vapor–liquid–solid (VLS) growth mechanism,²⁰ BN nanotubes can be grown from the B^* and N^* vapor in the presence of catalyst droplet Fe (eq 3). Meanwhile, a small amount of BN flakes may also be produced by a rival growth process through a vapor–solid (VS) growth mechanism due to a lack of catalyst Fe (eq 4).

The growth of the as-synthesized BN nanotubes is due to the three-dimensional movement of catalyst droplets. We propose the base growth model for the as-synthesized BN nanotubes based on the catalytic VLS growth mechanism. During annealing, catalyst liquid droplet and boron sources disperse uniformly in the porous precursor (Figure 3(1)). Then boron sources reacting with NH_3 form BN species on the surface of the catalyst liquid droplet (Figure 3(2)). When the BN species are supersaturated, they begin to precipitate layer by layer in the form of BN sheets around the surface of catalyst liquid droplets. An interface is formed between the catalyst and BN shells (Figure 3(3)). With gradual growth of the nanotube, an increasing backward compressive force builds up consequentially and applies to the forward liquid drops. When the negative compressive force reaches a certain level, a sudden disjunction occurs at the interface. While the inner space is reopened, a puff of outside vapor containing B^* and N^* rushes

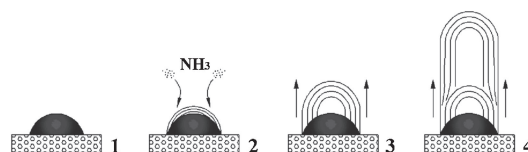


Figure 3. Growth mechanism of bamboolike BN nanotubes.

inside to balance the negative pressure, leaving an achieved inner bamboolike structure (Figure 3(4)). Finally, the bamboolike nanotube grows up through repeating the above process until boron source is used up. In fact, the catalyst droplet is the growth point of the BN nanotubes.

The porous structure of precursor Fe_3BO_6 plays a critical role in the bulk syntheses. The porous structure could result from the expansion of some gases, such as N_2 , O_2 , and H_2O , produced in the synthesis of Fe_3BO_6 . During annealing, the porous structure of precursors Fe_3BO_6 can expose more space for the reaction with ammonia. The unique structure also can maintain the growth of BN nanotubes at random in the base growth model. Consequently well-designed precursors with uniform pore structure and highly dispersed composition are very significant for large batch and selective production of BN nanotubes.

In summary, BN nanotubes with bamboolike structures were batch produced by annealing porous precursor Fe_3BO_6 under NH_3 atmosphere at 1100 °C. The BN nanotubes have a well-crystallized hexagonal phase with diameters less than 150 nm and lengths more than 10 μm on average. The porous structure of precursor Fe_3BO_6 plays a key role in the bulk synthesis. This is a novel method to produce BN nanotubes, and it may contribute to the larger yield and all-sized applications of BN nanotubes in the future.

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