



## Research paper

## Boron nitride nanotubes grown on stainless steel from a mixture of diboron trioxide and boron

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## ABSTRACT

Boron nitride nanotubes (BNNTs) can be grown on stainless steel by annealing a mixture of diboron trioxide (B<sub>2</sub>O<sub>3</sub>) and boron (B) at 1200–1300 °C under ammonia (NH<sub>3</sub>). In previously reported boron oxide chemical vapor deposition methods for the synthesis of BNNTs, diboron dioxide (B<sub>2</sub>O<sub>2</sub>) is generated in situ by the reaction of boron and metal oxides. In this study, we directly used a mixture of B<sub>2</sub>O<sub>3</sub> and boron as boron sources, thereby, avoiding the use of metal containing species in the starting material. The concentration of B<sub>2</sub>O<sub>3</sub> significantly influenced the formation, quality and quantity of BNNTs.

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Recently, it has been reported that boron nitride nanotubes (BNNTs) can be massively produced by several routes [1], such as thermal plasma process [2,3] and pressurized vapor/condenser method [4], which presented high conversion rate and quality for BNNTs. However, these methods were often realized by the special home-made equipment and could not be easily conducted in general laboratories. In reality, BNNTs are still very difficult to fabricate in traditional horizontal tube furnace, particularly those with small diameters and few walls. Because common gaseous and liquid boron containing species, such as borazines, boranes, and their derivatives are either explosive or poisonous, they are not suitable for using as BNNTs precursors. Thus, solid boracic materials have been used, including boron powder [5], boron nitride (BN) [6], diboron trioxide (B<sub>2</sub>O<sub>3</sub>) [7], borate [8], and boric acid (H<sub>3</sub>BO<sub>3</sub>) [9]. Methods for preparing BNNTs using these materials include arc discharge [10], laser heating [11], ball-milling and annealing [12], CNTs substitution [13], and chemical vapor deposition (CVD) [14]. Of these methods, CVD is the most popular and has been intensively studied because of its broad applicability and high operability. The most common CVD process for the production of BNNTs is boron oxide chemical vapor deposition (BOCVD), [15] which uses B<sub>2</sub>O<sub>2</sub> as a boron source. Almost all of

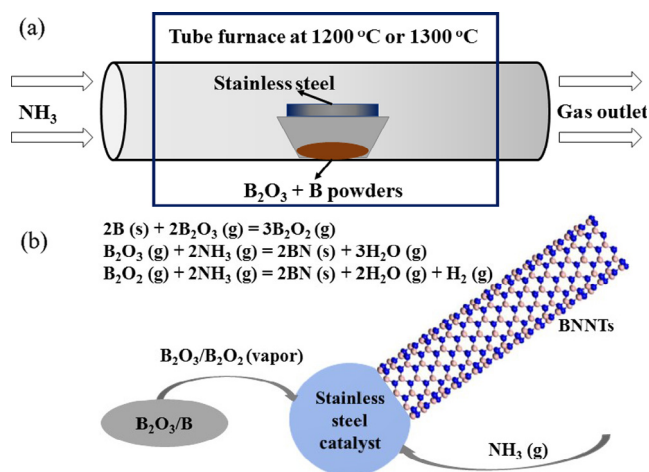
the previously reported BOCVD methods produce B<sub>2</sub>O<sub>2</sub> by the reaction of boron powder and metal oxides; a mixture of boron, MgO, and FeO is the most typical precursor [16]. MgO, FeO, and Fe-Mg-O species have been reported to function as catalysts and BNNTs are produced by the reaction of B<sub>2</sub>O<sub>2</sub> and NH<sub>3</sub> [17]. In addition to B<sub>2</sub>O<sub>2</sub>, it has been reported that BN can also be produced by the reaction of B<sub>2</sub>O<sub>3</sub> and NH<sub>3</sub> [18]; this route is widely used for industrial synthesis of BN. Furthermore, pure B<sub>2</sub>O<sub>3</sub> can be transformed into B<sub>2</sub>O<sub>2</sub> via single electron capture at a high temperature [19], such as 1300 K, which suggests that B<sub>2</sub>O<sub>3</sub> has chemistry identical to B<sub>2</sub>O<sub>2</sub> at high temperatures. Additionally, B<sub>2</sub>O<sub>3</sub> can also be used as an oxidizing agent to oxidize boron and give B<sub>2</sub>O<sub>2</sub> [19]. Based on these considerations, we hypothesized that B<sub>2</sub>O<sub>3</sub> could be used as an alternative of metal oxides to improve the atom economy and to avoid the introduction of other metals into BNNTs.

In this study, we demonstrated that BNNTs can be grown on stainless steel by annealing a mixture of B<sub>2</sub>O<sub>3</sub> and boron at 1200–1300 °C under ammonia (NH<sub>3</sub>). B<sub>2</sub>O<sub>3</sub> functioned as a boron source for the fabrication of BNNTs. Furthermore, no metal oxides were introduced into the precursor mixture.

The 200-mg mixture of B<sub>2</sub>O<sub>3</sub> and boron was finely ground and poured into an alumina crucible. Then, the crucible was covered with stainless steel and placed into a horizontal tube furnace. The mixture was annealed under NH<sub>3</sub> and atmosphere pressure at 1200 °C or 1300 °C for 2 h. After that, the furnace was cooled to room temperature under Ar, and white BNNTs were found on the stainless steel substrate. The experimental setup for fabricating BNNTs is depicted in Fig.1(a).

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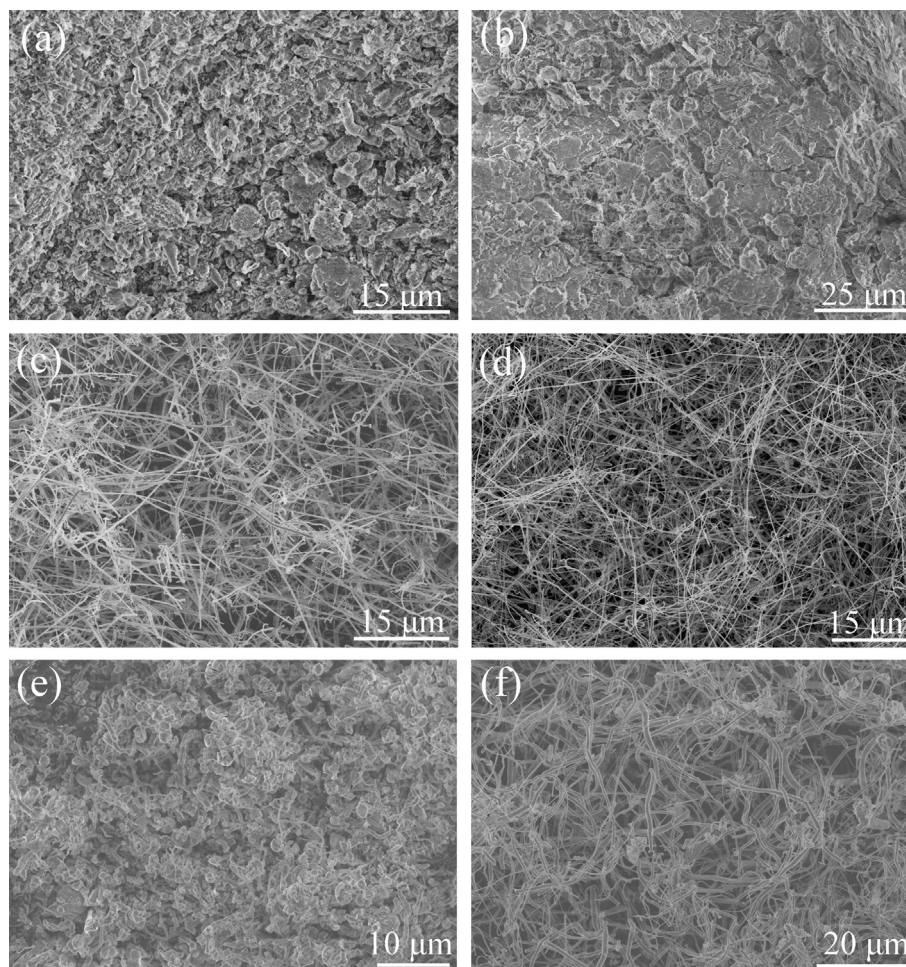


**Fig. 1.** Schematic diagram of (a) experimental setup, (b) the chemical reactions and mechanism for the formation of BNNTs.

A schematic diagram of the chemical reactions that occur during annealing process and the growth mechanism of BNNTs is presented in Fig. 1(b). The growth mechanism is attributed to a vapor-liquid-solid (VLS) mechanism [20].  $\text{B}_2\text{O}_2$  was formed by the reaction between  $\text{B}_2\text{O}_3$  and boron (Fig. 1(b)). Because of the importance

of the total  $\text{B}_2\text{O}_3$  and  $\text{B}_2\text{O}_2$  content in this study, we used  $\text{B}_x\text{O}_y$  as a general chemical formula for the mixture of  $\text{B}_2\text{O}_3$  and  $\text{B}_2\text{O}_2$  in this paper.

To determine the influence of the proportion of precursors on the target product, mixtures of  $\text{B}_2\text{O}_3$  and boron with mass ratios of 0.5:3, 4:3, and 10:3 were used to fabricate BNNTs, as described above. The volume flow of  $\text{NH}_3$  for these tests was fixed at 200 standard cubic centimeters per minute (sccm). As shown in Fig. 2 (a) and (b), BNNTs were not successfully fabricated using the 0.5:3 and 10:3 mixtures. In the case of the 0.5:3 mixture (Fig. 2 (a)), many small granules were formed. Abundant, large, and disordered blocks were formed from annealing the 10:3 mixture (Fig. 2 (b)). When the mass ratio of  $\text{B}_2\text{O}_3$  to boron was 4:3, BNNTs with uniform distribution were obtained on stainless steel at 1200 °C and 1300 °C, as shown in Fig. 2(c) and (d), respectively. By comparing Fig. 2(c) and (d), it is evident that the BNNTs sample grown at 1300 °C exhibits less debris than that fabricated at 1200 °C, indicating that 1300 °C is more suitable for growing BNNTs via the method used in this experiment. The products obtained at different temperatures and precursor mass ratios demonstrate that the concentration of  $\text{B}_2\text{O}_3$  and annealing temperature have a significant effect on the fabrication of BNNTs. Meanwhile, the influence of the volume flow of  $\text{NH}_3$  was also investigated. By comparing Fig. 2(d), (e) and (f), it can be seen that the 100 sccm  $\text{NH}_3$  led to the formation of disordered BN particles, and the thick BN fibers with many impurities were formed under the 300 sccm  $\text{NH}_3$ . The



**Fig. 2.** Scanning electron microscopic (SEM) images of products obtained using  $\text{B}_2\text{O}_3$  to boron mass ratios of (a) 0.5:3 and (b) 10:3 at 1300 °C and 200 sccm  $\text{NH}_3$ . SEM images of the resultants obtained using a precursor mass ratio of 4:3 at (c) 1200 °C and 200 sccm  $\text{NH}_3$ , (d) 1300 °C and 200 sccm  $\text{NH}_3$ , (e) 1300 °C and 100 sccm, and (f) 1300 °C and 300 sccm  $\text{NH}_3$ .

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