

CVD synthesis of boron nitride nanotubes without metal catalysts

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Abstract

An efficient CVD synthetic route for bulk quantities of boron nitride nanotubes (BN-NTs) was developed, where a B–N–O precursor generated from melamine diborate ($C_3N_6H_6 \cdot 2H_3BO_3$) was employed as the precursor and no metal catalyst was used. The resultant tubes all show remarkable ordering of the concentric atomic layers and exhibit stoichiometric BN composition. It is commonly found that the nanotubes have bulbous tips showing B–N–O amorphous clusters encapsulated in BN cages. The amorphous clusters might play the catalytic role in the nanotube ‘tip-growth’ process as the metal catalysts do in the metal-catalyzed CVD method. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Boron nitride nanotubes (BN-NTs), predicted to have a uniform electronic bandgap independent of the diameter and chirality, have been the subject of intense recent investigations [1,2]. As BN-NTs are analogous to carbon nanotubes (CNTs) [3], many methods for BN-NTs synthesis were inspired from carbon, i.e. arc-discharge technique using various electrodes [4–6] or laser ablation method [7,8]. However, none of these methods can make an equivalent of carbon production. A process for substitution of CNTs into BN-NTs with B_2O_3/N_2 mixture has also been developed [9]. But, the usage of CNTs as the starting materials hinders it from being a popular method.

CNTs can now be routinely prepared in bulk amounts by the metal-catalyzed chemical vapor deposition (CVD) method [10,11]. But the previous attempts to prepare BN-NTs by the same pyrolysis process are disappointingly unsuccessful [12,13]. Bourgeois et al. [14] previously reported an iron-related growth of tubular fibers by heating BN powder between 1750°C and 2100°C in a N_2 atmosphere. The synthesized fibers are appeared in the bamboo-like rather than uniform tube structures. Very recently, some success has been achieved in growing BN-NTs on nickel boride catalysts from the precursor borazine ($B_3N_3H_6$) [15]. However, the yield is consistently low. In addition, the borazine generation is potentially dangerous. In a word, BN-NTs are not readily formed by the metal-catalyzed CVD process. It is likely due to the poor wetting property of BN with metal catalysts at relatively low temperature. So the challenge still remains to develop efficient CVD method for large synthesis of BN-NTs.

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Here we describe an efficient CVD synthetic route to bulk production of BN-NTs, where a ternary B–N–O compound generated from melamine diborate ($\text{C}_3\text{N}_6\text{H}_6 \cdot 2\text{H}_3\text{BO}_3$) [16] was chosen as the precursor and no metal catalyst was used. An alternative growth mechanism will also be discussed based on the morphological analysis of these nanotubes.

2. Experimental

Melamine diborate was prepared as white powder by cooling a hot aqueous solution of melamine and boric acid in a molar ratio of 1:2. It was then calcined at 500°C in air for 3 h and annealed at 800°C in N_2 for 1 h. The following chemical reaction takes place [16]: $2(\text{C}_3\text{N}_6\text{H}_6 \cdot 2\text{H}_3\text{BO}_3) = \text{B}_4\text{N}_3\text{O}_2\text{H} + 4\text{H}_2\text{NCN} + 2\text{CO}_2 + \text{NH}_3 + 6\text{H}_2\text{O}$. The obtained powder precursor is a B–N–O intermediate product, $\text{B}_4\text{N}_3\text{O}_2\text{H}$ as empirical formula, containing BN skeleton and about 27 wt% of oxygen.

The powder precursor was charged into a graphite crucible, itself placed into a graphite susceptor. Then the system was heated rapidly by induction heating and held at 1700°C for 2 h in a N_2 gas stream. The N_2 gas stream, first bubbling from distilled water (H_2O) at 25°C and then passing through carbon black at 1500°C, was introduced into the susceptor at the flowing rate of 1 l/min.

After the reaction, white products were observed on the outwall of the crucible and inner wall of the susceptor, where the temperature is in the order of 1200°C. Samples of raw materials removed from the walls were observed by scanning electron microscopy (SEM). Some powders were ultrasonically dispersed in CCl_4 and dripped onto a holey carbon-coated-copper grid for characterization with a JEM-3000F (JEOL) high resolution transmission field emission electron microscopy (HRTEM) operated at 300 kV attached with parallel detection Gatan-666 electron energy loss spectrometer (EELS). EELS experiments were performed by using a stationary focused 1 nm electron probe with a Gatan spectrometer.

3. Results and discussion

Fig. 1 shows the SEM examination result of the raw white powders taken from walls. The image reveals abundant entangled fibrous structures. The straight fibrous structures are nanometer dimension in diameter and several micrometers in length. The most interesting feature of these fibers is that they commonly exhibit bulbous tips. TEM analysis demonstrates that the synthesized fibers are multi-walled nanotubes. Fig. 2 shows a low magnification TEM image of the nanotubes. The nanotubes may be partially filled with amorphous materials. It also indicates that the tubes are likely to grow out of the bulbous tips.

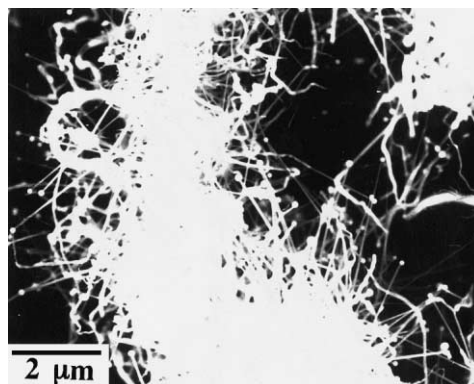


Fig. 1. SEM image of the collected white products. The straight fibers are nanometer dimension in diameter and several micrometers in length.

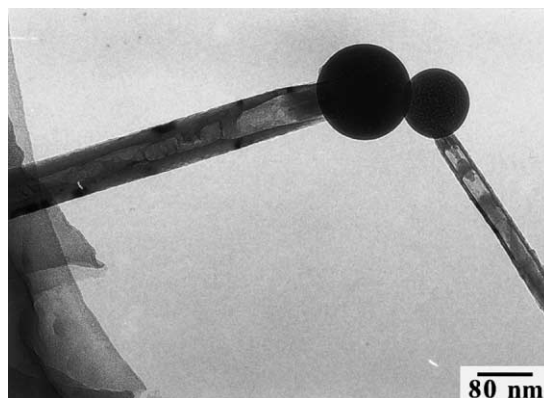


Fig. 2. Low magnification TEM image of the synthesized nanotubes, showing the tubes may be growing out of the bulbous tips.

EELS spectra showed that the nanotubes in the product were all BN-NTs. Under HRTEM examination, a typical well-grown BN nanotube is shown in Fig. 3a. The dark bands in the figure are considered as the BN layers. The perfectly straight fringes exhibit that the tubes are well ordered. The particular tube has 12 concentric layers, with inner and outer diameters of 5.2 and 13.1 nm, respectively, indicating an inter-layer spacing of about 0.33 nm. The data are in good agreement with the inplanar distance of 0.333 nm in bulk h-BN [17,18]. A representative EELS spectrum taken from the tubes is shown in Fig. 3b. It demonstrates distinct absorption peaks of B and N characteristic *K*-edge at 188 and 401 eV, respectively, with no-

table absence of carbon *K*-edge at 284 eV. The B/N ratios calculated from our spectra obtained from many tubes range from 0.8 to 1.15. Taking into consideration a typical error of $\sim 20\%$ due to the background subtraction, the synthesized nanotubes exhibit a stoichiometric BN composition.

Carefully examining the bulbous tips of the tubes, we found that the tips are BN cages with amorphous B–N–O clusters encapsulated inside. A HRTEM image of the tip morphology is shown in Fig. 4a. The peculiar tip morphology, which to our knowledge had not been observed in prior studies, may be related to the growth process of the BN-NTs. In terms of the growth mechanism of BN-NTs in the present CVD method without adding metal catalysts, the following process is proposed. At the experimental temperatures (1700°C), some species such as B_2O_3 and some amorphous B–N–O

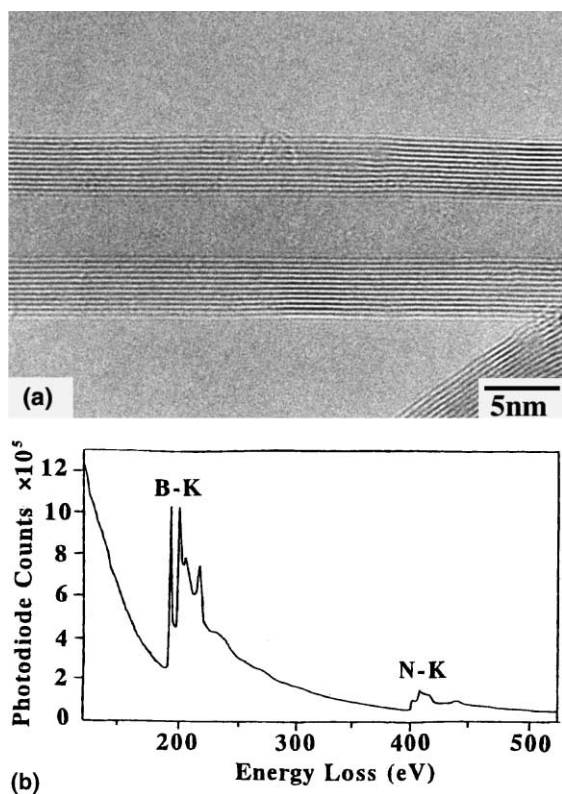


Fig. 3. HRTEM image of a multi-walled nanotube and the typical EELS spectrum. (a) A well-grown nanotube with 12 layers on either side of a hollow and uniform layer separation ($D = 13.1$ nm, $d = 5.2$ nm). (b) A typical EELS spectrum taken from the nanotubes. The distinct *K*-edge peaks at 188 and 401 eV identifies that the composition of the tube is boron and nitrogen.

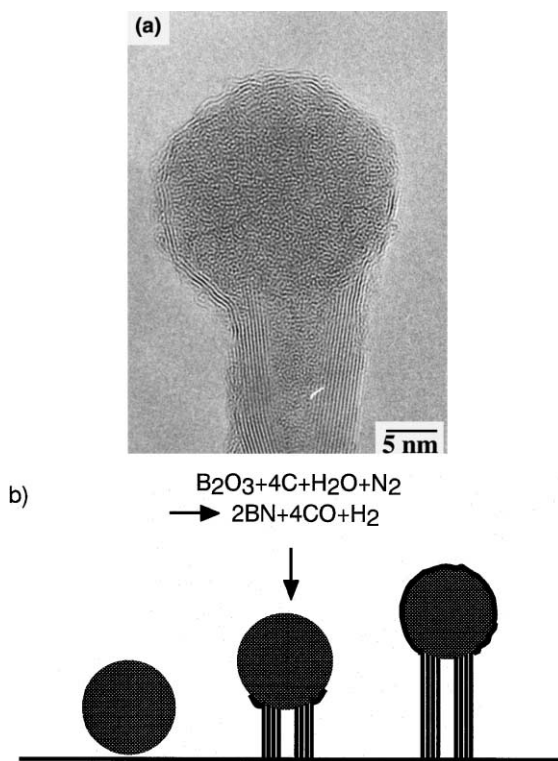


Fig. 4. The peculiar tip morphology and proposed growth mechanism: (a) HRTEM image of a bulbous tip, showing BN cage filled with amorphous materials; (b) a postulated model for the nanotube growth under the present condition, similar to the nanotube 'tip-growth' in the metal-catalyzed CVD method.

clusters may originate from the decomposition of the precursor. Then the cloud of B_2O_3 vapor and amorphous B–N–O clusters is carried away by the flowing N_2 stream to the lower temperature region, here is in the order of 1200°C , where amorphous B–N–O clusters condense onto the walls of the graphite crucible and susceptor. Almost simultaneously, the vapor phase reaction between B_2O_3 and other species in the atmosphere may take place, expressed as: $B_2O_3 + 4C + H_2O + N_2 \rightarrow 2BN + 4CO + H_2$ [19–21]. The formed BN possibly precipitates onto or diffuses through the amorphous clusters, forming nanotubes [22]. The nanotube growth continues with the amorphous cluster detach and moves at the head of the growing tubes. The process stops when the amorphous cluster becomes inactive (for example the temperature decreases or itself is fully covered by BN layers as in Fig. 4a). Such a postulated mechanism, somewhat similar to the nanotube ‘tip-growth’ in the metal-catalyzed CVD method [10,11,23,24], is illustrated graphically in Fig. 4b. In this model, the amorphous clusters play an active role as the metal catalysts do.

4. Conclusions

To summarize, BN-NTs were successfully prepared in good yield with melamine diborate as the starting material. The bulbous tips of these tubes, BN cages filled with amorphous clusters, appear to be related to the growth process. The CVD method present here may provide a solution to bulk production of pure BN-NTs. Furthermore, as the nanotubes are deposited in the temperature region of 1200°C and no metal catalyst is needed, it may also be employed to grow BN-NTs films on some substrates (e.g., Si substrate) for potential device application.

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