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## Synthesis of aligned $B_xC_yN_z$ nanotubes by a substitution-reaction route

Wei-Qiang Han, John Cumings, Xiaosheng Huang, Keith Bradley, Alex Zettl \*

*Department of Physics, University of California – Berkeley, Berkeley, CA 94720, USA  
Materials Science Division Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA*

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### Abstract

A substitution-reaction is used to synthesize highly aligned  $B_xC_yN_z$  nanotubes ( $B_xC_yN_z$ -NTs) with uniform length and small diameter. Aligned carbon/nitrogen nanotubes ( $CN_x$ -NTs) or aligned carbon nanotubes (C-NTs) are reacted with  $B_2O_3$  under ammonia atmosphere. The length and diameter of the aligned  $B_xC_yN_z$ -NTs are similar to the starting aligned nanotubes. For example, the aligned  $B_xC_yN_z$ -NTs produced from aligned  $CN_x$ -NTs are 10–30  $\mu\text{m}$  in length and 20–90 nm in diameter. The  $x/z$  ratio of  $B_xC_yN_z$ -NTs for most nanotubes is close to 1:1. The  $x/y$  ratio of  $B_xC_yN_z$ -NTs ranges from 0.3 to 1.7. © 2001 Published by Elsevier Science B.V.

### 1. Introduction

Nanotubes and nanorods of various materials can be synthesized using a template-based approach [1]. Nitride [2,3] and carbide [4,5] nanorods can be prepared by the conversion of hollow C-NTs to solid nanorods by reaction with respective volatile oxide or halide species under inert or reactive atmosphere. The growth of the nanorods involves a template mechanism in which the C-NTs confines the overall morphology of the produced nanostructure [2]. Recently, oriented SiC nanowires were synthesized by the reaction of SiO with aligned C-NTs [6]. BN,  $B_xC_yN_z$  and B-doped multiwall and single wall nanotubes have been synthesized by a carbon nanotube-substitution reaction in which carbon atoms of starting C-NTs

have been substituted partially or totally by boron and/or nitrogen atoms by reaction with  $B_2O_3$  with C-NTs under Ar or  $N_2$  atmosphere [7–10].

Composite  $B_xC_yN_z$ -NTs offer a large variety of electronic properties and are suggested to be candidates for nanoscale electronic and photonic devices. The advantage of such nanotubes is that their electronic properties are easier to control, since they are determined only by composition [11].  $B_xC_yN_z$ -NTs have been synthesized by arc-discharge, laser ablation, pyrolysis, and substitution-reaction [12–17]. Recently, Bai et al. [18] have reported the formation of aligned B–C–N nanotubes by bias-assisted hot filament chemical vapor deposition from the source gases of  $B_2H_6$ ,  $CH_4$ ,  $N_2$  and  $H_2$ . The diameters of these nanotubes range from 50 to 260 nm.

In the present Letter, we describe the use of a substitution-reaction to synthesize highly aligned  $B_xC_yN_z$ -NTs with uniform length and small diameter from aligned  $CN_x$ -NTs and aligned C-NTs.

\* Corresponding author. Fax: +1-510-6438497.

E-mail address: azettl@physics.berkeley.edu (A. Zettl).

## 2. Experimental

The aligned  $CN_x$ -NTs and aligned C-NTs used in these studies were prepared in a two-stage furnace system fitted with temperature controllers. The aligned  $CN_x$ -NTs ( $x < 0.1$ ) were prepared by the following procedure: A (1:4) mixture (by weight) of powdered ferrocene (dicyclopentadienyliron, Aldrich, 98%, ca. 20–50 mg) and melamine ( $C_3H_6N_6$ , Fluka,  $\geq 99\%$ ) was introduced into a quartz tube and pyrolyzed at 1050 °C in an  $NH_3$  flow (ca. 20–40 ml/min) [19,20]. Subsequently, the system was allowed to cool to room temperature, and soot-like deposits, containing the aligned pure C-NTs, were collected from the silica tube. For the aligned C-NTs, the synthesis is similar to the above procedure for the aligned  $CN_x$ -NTs, but the mixture is composed of ferrocene (dicyclopentadienyliron, Aldrich 98%, ca. 20–50 mg) and a mixture of  $C_{60}$  and  $C_{70}$  (Bucky, USA, 70%  $C_{70}$  + 30%  $C_{60}$ ) (1:1, by weight), and  $NH_3$  gas was replaced by Ar [21,22]. The substitution-reaction was performed in a horizontal high temperature furnace with molybdenum disilicide heating elements.  $B_2O_3$  powder (Alfa,  $\geq 99.99\%$ ) was placed in an open platinum crucible and then covered with aligned  $CN_x$ -NTs or aligned C-NTs. The crucible was held in a flowing ammonia atmosphere at 1260 °C for 0.5 h. After the reaction, the product was collected from the bed of aligned nanotubes. The originally black nanotubes were found to have turned into a brown colored layer of product. The resulting samples were characterized by scanning electron microscopy (SEM) using a JEOL JSM-6340 field emission microscope and high-resolution transmission electron microscopy (HRTEM) using a Philips CM200 FEG equipped with a parallel electron energy-loss spectroscopy detector (EELS, Gatan PEELS 678).

## 3. Results

### 3.1. Aligned $B_xC_yN_z$ -NTs from aligned $CN_x$ -NTs

Fig. 1 shows a typical SEM image of bundles of highly aligned  $B_xC_yN_z$ -NTs produced from aligned

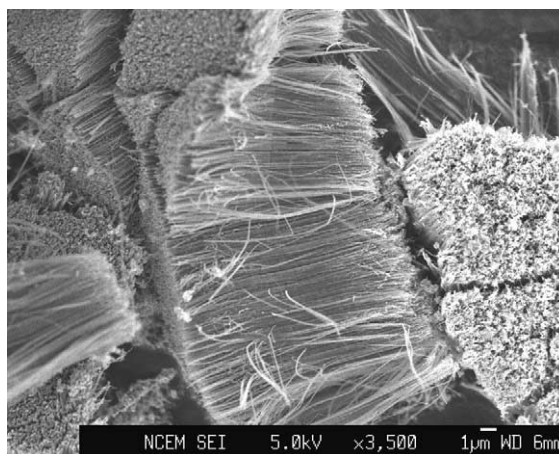


Fig. 1. SEM image revealing a high density of highly aligned  $B_xC_yN_z$ -NTs produced from aligned  $CN_x$ -NTs.

$CN_x$ -NTs precursor material. The  $B_xC_yN_z$ -NTs are 10–30  $\mu m$  in length and 30–90 nm in diameter, which is similar to the sizes of the starting aligned  $CN_x$ -NTs [19,20]. Fig. 2 shows typical TEM images of the produced nanotubes, which feature

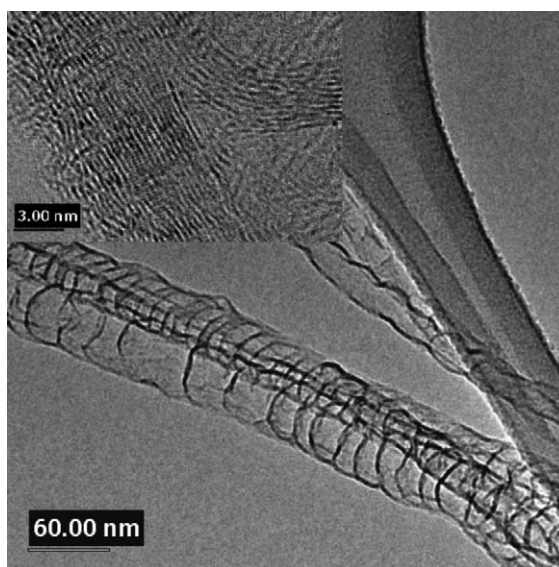


Fig. 2. TEM image showing aligned nanotubes of  $B_xC_yN_z$  produced from aligned  $CN_x$ -NTs. The NTs possess irregular bamboo-like morphologies. The inset reveals that the nanotube walls are composed of graphite-like layers, which make up the stacked bamboo-like tubules.

irregular bamboo-like morphologies with wide core diameters, similar to those of aligned  $CN_x$ -NTs nanotubes reported elsewhere [19,20]. The inset reveals that the nanotube walls are composed of graphite-like layers, which make up the stacked bamboo-like tubules.

EELS characterizations of the K-edge absorption for boron, carbon and nitrogen were used to estimate the stoichiometry of the nanotubes. Spectra were obtained using a probe beam diameter of 5–10 nm. A typical EELS spectrum from an individual nanotube is shown in Fig. 3. Three distinct absorption features are apparent, starting from 188, 284 and 401 eV, corresponding to the known B–K, C–K and N–K edges, respectively. The B/C and N/B atomic ratios of the nanotube are 1.5 and 0.92.

Several tens of nanotubes have been checked by EELS measurement, and all are shown to be  $B_xC_yN_z$ -NTs. Fig. 4a, b shows histograms of the  $x/y$  and  $x/z$  ratio of  $B_xC_yN_z$ -NTs determined using EELS in 40 randomly selected nanotubes. The  $x/y$  ratio of  $B_xC_yN_z$ -NTs ranges from 0.3 to 1.7. The  $z/x$  ratio of  $B_xC_yN_z$ -NTs ranges from 0.7 to 1.1. Taking into consideration the experimental error of about 10%, due mainly to background subtraction when the EELS spectra are analyzed, the  $x/z$  ratio of  $B_xC_yN_z$ -NTs for most nanotubes is close to 1:1. This suggests that B and N radicals prefer to incorporate into the network of the nanotubes in the ratio of 1:1. No

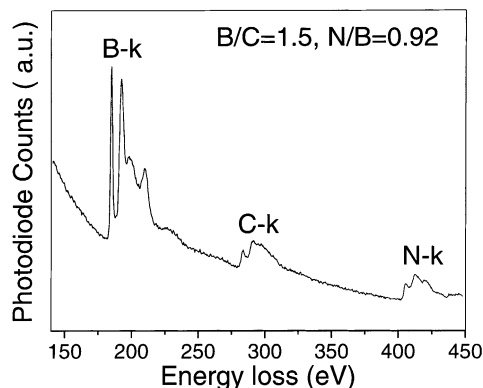


Fig. 3. A typical EELS core electron K-shell spectrum taken from an individual nanotube of aligned  $B_xC_yN_z$ -NTs produced from aligned  $CN_x$ -NTs.

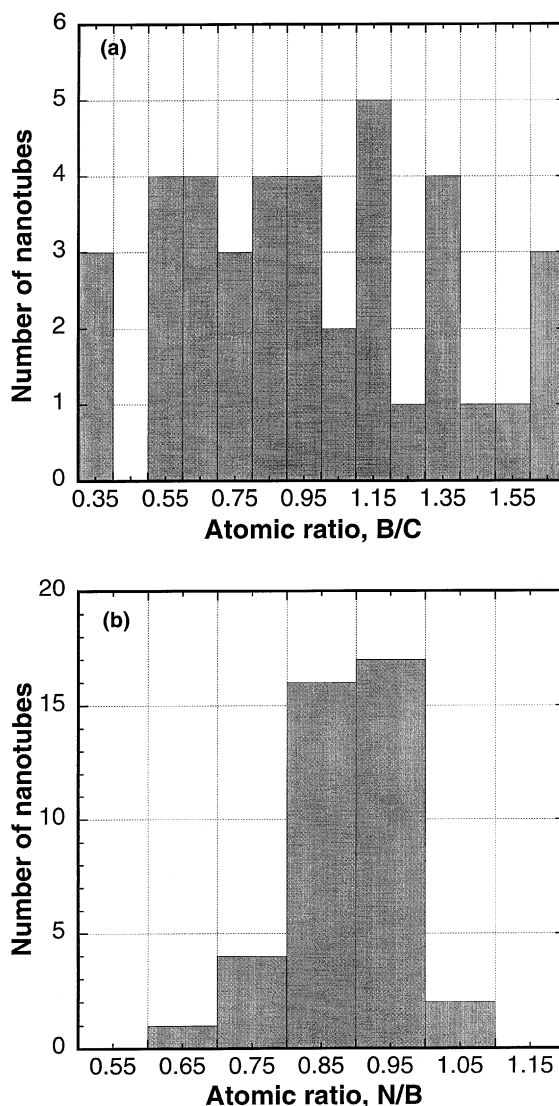


Fig. 4. (a) Histograms of the  $x/y$  ratio of  $B_xC_yN_z$ -NTs produced from  $CN_x$ -NTs. (b) Histograms of the  $x/z$  ratio of  $B_xC_yN_z$ -NTs produced from aligned  $CN_x$ -NTs.

pure BN or pure carbon nanotubes were found in the product.

### 3.2. Aligned $B_xC_yN_z$ -NTs from aligned C-NTs

Fig. 5 is the typical SEM images of the aligned  $B_xC_yN_z$ -NTs produced from aligned C-NTs precursor material. It shows bundles of highly aligned

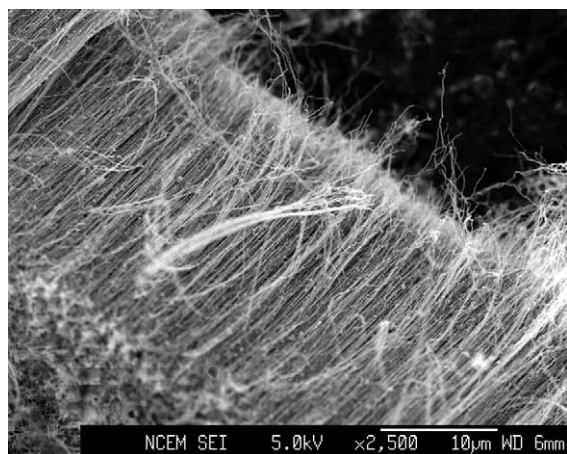


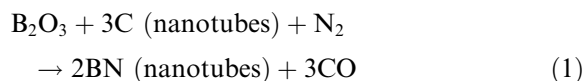
Fig. 5. SEM images of the highly aligned  $B_xC_yN_z$ -NTs produced from aligned C-NTs.

nanotubes. The aligned nanotubes are 20–50  $\mu\text{m}$  in length and 20–70 nm in diameter, similar to the original aligned C-NTs [21,22]. HRTEM shows that nanotubes have regular morphologies with straighter fringes that indicate a more ordered structure, similar to those of aligned C-NTs [21,22].

EELS characterizations of the K-edge absorption for boron, carbon and nitrogen were used to estimate the stoichiometry of the nanotubes. Several tens of nanotubes have been characterized by EELS measurement. The  $x/y$  ratio of  $B_xC_yN_z$ -NTs is up to 0.8. The  $x/z$  ratio of  $B_xC_yN_z$ -NTs for most nanotubes is close to 1:1. This result is similar to that from aligned  $B_xC_yN_z$ -NTs produced from aligned  $CN_x$ -NTs. A small amount of pure C-NTs remain in the product.

#### 4. Discussion

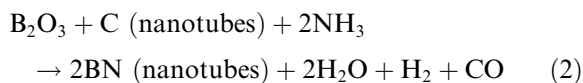
The following chemical reaction has been proposed for the synthesis of BN-NTs and  $(BN)_xC_y$ -NTs from C-NTs through complete or partial substitution of C atoms by B and N under  $N_2$  atmosphere [7,10,17]:



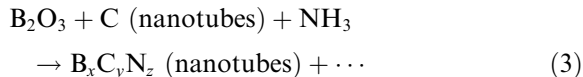
The reaction above is efficient for CVD-C-NTs when the reaction temperature is higher than 1300  $^\circ\text{C}$  [10,17]. However, when the reaction temperature is over 1300  $^\circ\text{C}$ , for both aligned  $CN_x$ -NTs and aligned C-NTs, the nanotube alignment deteriorates. The substitution ratio is also not very high.

By using  $NH_3$  atmosphere to replace  $N_2$  atmosphere, the efficient temperature of substitution reaction can be decreased to about 1260  $^\circ\text{C}$ , so that the nanotube alignment can be preserved. Although aligned nanotubes are closely packed, the spaces between nanotubes are large enough for the passage of  $NH_3$  and boron oxide vapor.

The atomic ratio of B and N for most of the nanotubes in the product is close to 1, as achieved in the previous study [7,17]. The reaction can be expressed as



For  $B_xC_yN_z$ -NTs, the reaction can be expressed as



When the reaction temperature is over 1300  $^\circ\text{C}$  under  $NH_3$  atmosphere, the nanotube alignment deteriorates, although the  $x/y$  ratio of  $B_xC_yN_z$ -NTs is increased.

As a comparison, control experiments with the same experimental conditions for aligned  $B_xC_yN_z$ -NTs as reported above were performed with nitrogen instead of ammonia. The products were primarily carbon nanotubes and only small amounts of  $B_xC_yN_z$ -NTs, because 1260  $^\circ\text{C}$  is too low for the substitution reaction under  $N_2$  atmosphere.

EELS spectra show that the substitution ratio for aligned  $CN_x$ -NTs is greater than that for aligned C-NTs. The reason might be that the aligned  $CN_x$ -NTs used here have much higher densities of defects and distortions than the aligned C-NTs used here, so that the aligned  $CN_x$ -NTs provide many more accessible active surface sites in the nanotube lattice structure during the substitution reaction. The existing C–N bonding in

aligned  $CN_x$ -NTs might also be advantageous for the substitution-reaction.

## 5. Conclusion

The substitution-reaction route has been demonstrated as an efficient synthesis route for producing uniform arrays of highly aligned  $B_xC_yN_z$ -NTs. The use of  $NH_3$  is crucial, since it can decrease the efficient reaction temperature, which is important for maintaining nanotube alignment. We have found that the conversion of  $CN_x$ -NTs into  $B_xC_yN_z$ -NTs is more efficient than the conversion of CNTs into  $B_xC_yN_z$ -NTs.

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