

Transformation of $B_xC_yN_z$ nanotubes to pure BN nanotubes

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(Received 17 April 2002; accepted for publication 6 June 2002)

We demonstrate that multiwalled $B_xC_yN_z$ nanotubes can be efficiently converted to BN multiwalled nanotubes via an oxidation treatment. The microstructure and composition of the precursors and final products have been characterized by high-resolution transmission electron microscopy, electron energy-loss spectroscopy, and energy dispersive x-ray spectroscopy. The conversion process is monitored by thermogravimetric analysis. Carbon layers of $B_xC_yN_z$ nanotubes start to oxidize at 550 °C, thereby transforming $B_xC_yN_z$ nanotubes into pure BN nanotubes. The remarkable thermal stability of pure BN nanotubes in an oxidizing environment is also established. © 2002 American Institute of Physics. [DOI: 10.1063/1.1498494]

Boron nitride (BN) nanotubes (NTs)¹ and $B_xC_yN_z$ nanotubes^{2,3} are candidates for potential nanosized electronic and photonic devices with a large variety of electronic properties. Since their electronic properties are primarily determined by composition, they are relatively easy to control. Previously, BN nanotubes, BN conical nanotubes, and $B_xC_yN_z$ nanotubes have been synthesized by various methods including a carbon-nanotube-confined reaction using chemical-vapor-deposition (CVD)-derived carbon nanotubes together with boron oxide (B_2O_3) and nitrogen (N_2) at temperatures ranging from 1300 to 2000 °C.⁴⁻⁷ In the product, $B_xC_yN_z$ nanotubes are often found mixed with a small amount of pure BN nanotubes. In previous work,^{8,9} pure carbon nanotubes were oxidized to open their tips. In this letter, we present our studies on the oxidation of $B_xC_yN_z$ nanotubes and show that $B_xC_yN_z$ nanotubes can be efficiently transformed to BN nanotubes by a simple oxidation process. Since $B_xC_yN_z$ nanotubes are in general easier to prepare than pure BN nanotubes, our findings provide an important synthesis route for pure BN nanotubes. We also demonstrate the exceptional thermal stability of pure BN nanotubes.

$B_xC_yN_z$ nanotubes (including BN nanotubes, $y=0$) were synthesized via the carbon nanotube-confined reaction^{4,5} at 1600 °C for 0.5 h. Carbon nanotubes are made by CVD methods using ethene and catalyst of iron oxide with alumina nanoparticles as support. The resulting sample was characterized by high-resolution transmission electron microscope (TEM), using a Philips CM-200 FEG equipped with a parallel electron energy-loss spectroscopy detector (EELS) (Gatan PEELS 666) and energy dispersive x-ray spectrometer (EDS). The oxidation behavior of $B_xC_yN_z$ nanotubes and carbon nanotubes was characterized using a thermogravimetric analyzer (TGA) (7, Perkin Elmer).

For comparison purpose, we first investigate the behavior of pure carbon nanotubes (multiwalled CVD-derived) to an oxidizing environment. Figure 1(a) shows TGA results for carbon nanotubes heated from room temperature to 1000 °C in an 80% N_2 /20% O_2 (by volume) atmosphere at a rate of

3 °C/min and then held at 1000 °C for 2 h. The mass of the CVD-carbon nanotubes starts to decrease at about 500 °C,¹⁰ drops to about 10% of its original value between 500 and 600 °C, then remains constant up to 1000 °C. The final remaining material is reddish-yellow in color. This final product was determined by EDS to be an Fe–Al–O mixture, reflecting the original catalyst material used in the CVD synthesis of carbon nanotubes.

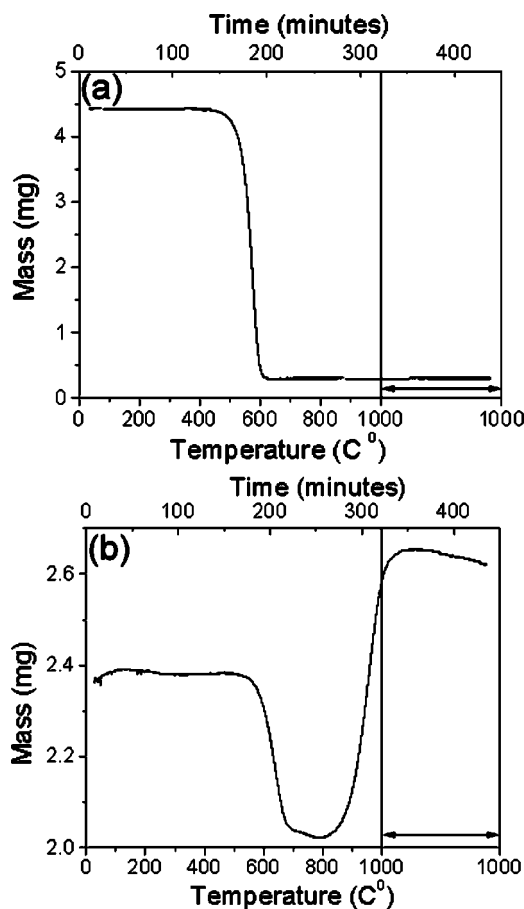


FIG. 1. (a) Plot of the mass of CVD-carbon nanotubes vs temperature and reaction time, (b) plot of the mass of $B_xC_yN_z$ nanotubes vs temperature and reaction time. The TGA is heated from room temperature to 1000 °C in an 80% N_2 /20% O_2 (by volume) atmosphere at a rate of 3 °C/min and then held at 1000 °C for 2 h.

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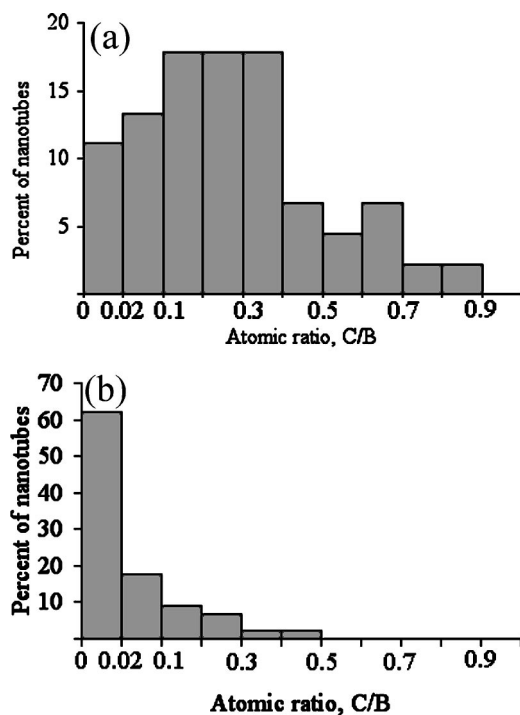
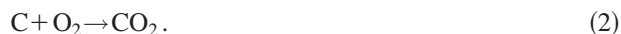
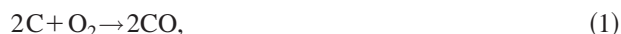


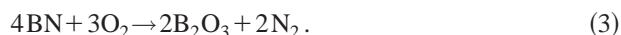
FIG. 2. (a) Histograms of the y/x atomic ratio of $B_xC_yN_z$ -NTs produced by carbon nanotube-substitution reaction, (b) histograms of the y/x atomic ratio of $B_xC_yN_z$ -NTs and BN nanotubes after oxidation. Note: There are 2 bins for $y/x < 0.1$ to differentiate between BN ($y/x < 0.02$) and $B_xC_yN_z$ ($0.02 < y/x < 0.1$). The data are from EELS.

$B_xC_yN_z$ nanotubes behave very differently from carbon nanotubes in an oxidative environment. Figure 1(b) shows TGA results for $B_xC_yN_z$ nanotubes heated from room temperature to 1000°C in an 80% N_2 /20% O_2 (by volume) atmosphere at a rate of $3^\circ\text{C}/\text{min}$ and then held at 1000°C for 2 h. The mass of the $B_xC_yN_z$ nanotubes decreases between 550 and 675°C . In this temperature region, the sample mass decreases by about 14%. The mass stabilizes considerably from about 675 to 800°C . Above 800°C , the mass begins to increase and stabilizes after the sample is held at 1000°C for about 50 min. The mass increases to about 10% greater than its original value (about 35% from its carbon depleted value). The final product here was determined by EDS to be B_2O_3 .

The conversion of $B_xC_yN_z$ nanotubes to B_2O_3 can be described by a four-stage process. In the first stage (550 – 675°C), excess carbon in the $B_xC_yN_z$ nanotubes is removed by oxidation



In the second stage (675 – 800°C), the mass stabilizes because the all the excess carbon has been oxidized, exiting the system as vapor. In the third stage (800 – 1000°C holding for 50 min), BN layers oxidize



From reaction (3), the mass theoretically increases by 40%, which is close to our experimentally observed mass increase of 35%. After the temperature has been held at 1000°C for more than 50 min, the BN nanotubes have com-

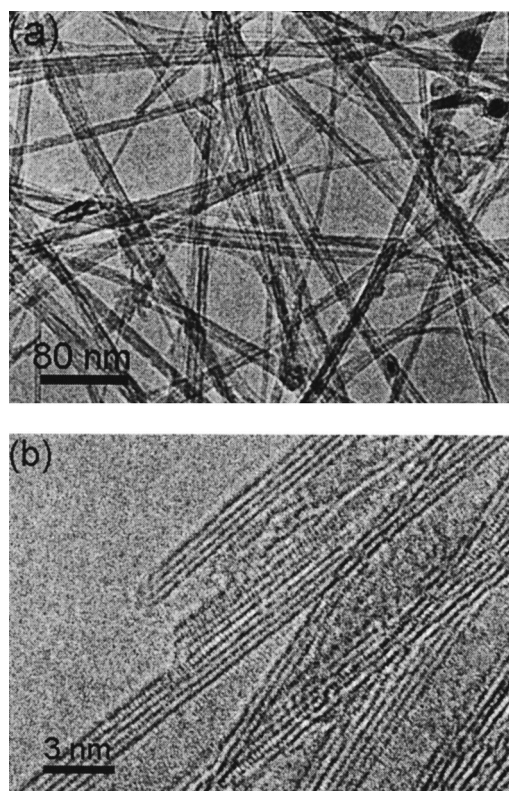


FIG. 3. (a) Low-magnification TEM image showing a general view of the oxidation-treated nanotubes, (b) high-magnification TEM micrograph showing a bundle of BN nanotubes. The tip of one nanotube is visible and it is open.

pletely oxidized to B_2O_3 . The slight mass loss in this fourth and final stage [observed in Fig. 1(b)] can be explained by the vaporization of B_2O_3 .

The earlier results suggest that controlled oxidation of $B_xC_yN_z$ nanotubes can be used to obtain pure BN nanotubes. To achieve this selected reaction, we oxidized $B_xC_yN_z$ nanotubes in air at 700°C for 30 min in order to remove only the carbon. Several tens of nanotubes for both the starting $B_xC_yN_z$ material and the oxidation-treated BN product were analyzed by EELS. Characterization of the K -edge absorption for boron, carbon, and nitrogen was used to estimate the stoichiometry of the nanotubes. Spectra were obtained using a spot size of about 5–10 nm.

Figure 2(a) shows histograms of the carbon/boron atomic ratio (y/x) of unoxidized $B_xC_yN_z$ nanotubes, determined using EELS, in 45 randomly selected nanotubes. The y/x ratio ranges from less than 0.02 (constituting about 11% of the nanotubes) up to 0.9 (constituting about 2% of the nanotubes). Figure 2(b) shows corresponding histograms of the carbon/boron ratio (y/x) of oxidized $B_xC_yN_z$ nanotubes. The maximum y/x ratio is reduced to 0.5, while the amount of pure BN nanotubes (or with carbon content below 2%) has increased to about 62%. The atomic ratio of boron to nitrogen of BN and $B_xC_yN_z$ nanotubes for most nanotubes is close to 1:1. This result suggests that B and N prefer to incorporate into the network of nanotubes in a 1:1 ratio.^{4,11}

Figure 3(a) is a typical low-resolution TEM image of BN nanotubes obtained by the earlier-mentioned oxidation process. The BN nanotubes appear either as individuals or in bundles. These nanotubes usually have only a few layers.¹²

TEM shows that the number of nanotubes layers decreases after oxidation. Figure 3(b) shows a bundle of BN nanotubes with one NT having an open tip. This shows that oxidation is good for opening the tips of BN nanotubes. Most of the BN nanotubes produced by oxidation have a near-perfect layer-structure.

Suenaga *et al.* have shown that $B_xC_yN_z$ nanotubes produced by arc discharge with a HfB_2 anode and a carbon cathode can have a strong phase separation between BN layers and carbon layers along the radial direction.¹³ Our results suggest that the BN layers and carbon layers of $B_xC_yN_z$ nanotubes prepared by carbon nanotube-confined reaction are also strongly phase separated. If each wall has a mixture of B, N, and C, one would expect to see large defects in the walls of the tubes, due to the removal of the carbon. However, the walls of the oxidized nanotubes are well ordered and free of defects, suggesting that the nanotubes are separated into BN layers and C layers.

Han *et al.* have previously suggested three possible structures for $B_xC_yN_z$ nanotubes made from carbon nanotube-confined reaction.⁴ In the first two configurations, the carbon nanotube shells are segregated in the structure and comprise the outer few (first configuration) or inner few (second configuration) layers of the multiwall tube. In both of these configurations, the carbon layers are susceptible to attack from an oxidizing environment (in the first configuration, the pure carbon outermost shells are removed by oxidation, leaving a pure BN nanotube, while in the second configuration the pure carbon innermost layers are removed by oxidation, again leaving a pure BN nanotube. Of course, some nanotubes may be a combination of “first” and “second” configurations, with BN tubes sandwiched between carbon layers in a C–BN–C geometry. The third configuration is again a sandwich structure, but here the innermost and outermost tubes are BN, while the “core” of the sandwich is comprised of pure carbon nanotube shells. In this third configuration, the sidewalls of the carbon shells are protected from an oxidizing environment by the surrounding BN layers. Thus, in this third configuration, it is difficult to selectively remove the carbon layers. This suggests that the thermal stability of BN could in certain applications be used as a beneficial as a shield for less robust materials.

In summary, $B_xC_yN_z$ nanotubes have been converted to

pure BN with an efficiency of about 60%. It is postulated that the reason it is not 100% efficient is due to protection of the carbon by the boron nitride layers for a minority of BN–C–BN sandwich-like nanotubes. Boron nitride could be used in a wide range of applications to isolate materials from harsh environments.

This research was supported in part by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy, Contract Number No. DE-AC03-76SF00098. J.C. acknowledges support from an IBM Fellowship.

¹N. G. Chopra, R. J. Luyken, K. Cherrey, V. H. Crespi, M. L. Cohen, S. G. Louie, and A. Zettl, *Science* **269**, 966 (1995).

²Z. Weng-Sieh, K. Cherrey, N. G. Chopra, X. Blasé, Y. Miyamoto, A. Rubio, M. L. Cohen, S. G. Louie, A. Zettl, and R. Gronsky, *Phys. Rev. B* **51**, 11229 (1995).

³X. Blase, J.-Ch. Charlier, A. De Vita, and R. Car, *Appl. Phys. A: Mater. Sci. Process.* **A68**, 293 (1999).

⁴W. Han, Y. Bando, K. Kurashima, and T. Sato, *Appl. Phys. Lett.* **73**, 3085 (1998).

⁵W. Han, Y. Bando, K. Kurashima, and T. Sato, *Jpn. J. Appl. Phys., Part 2* **38**, L755 (1999).

⁶W. Han, L. Bourgeois, Y. Bando, K. Kurashima, and T. Sato, *Appl. Phys. A: Mater. Sci. Process.* **A71**, 83 (2000).

⁷D. Golberg, Y. Bando, K. Kurashima, and T. Sato, *Chem. Phys. Lett.* **323**, 185 (2000).

⁸S. C. Tsang, P. J. F. Harris, and M. L. H. Green, *Nature (London)* **362**, 520 (1993).

⁹T. W. Ebbesen, P. M. Ajayan, H. Hiura, and K. Tanigaki, *Nature (London)* **367**, 519 (1994).

¹⁰As a comparison, we also measure the amorphous porous carbon and graphite particles by TGA. The masses of amorphous porous carbon graphite particles start to decrease at about 400 and 600 °C, respectively.

¹¹W. Han, J. Cumings, X. Hunag, K. Bradley, and A. Zettl, *Chem. Phys. Lett.* **346**, 368 (2001).

¹²There are about 50% nanotubes in the sample. Others are $B_xC_yN_z$ and BN particles, wires and Fullerene-like nano particles. There are not pure carbon materials in the sample. For $B_xC_yN_z$ nanotubes, there are no amorphous carbon coating. The mass loss data by TGA is from all the stuffs of the sample (14%). The mass loss data (9%) by EELS is only from nanotubes. The mass loss data difference comes from two reasons: (1) the measurement error (e.g., due to uncertainties in background subtraction of EELS data, the calculated B/C ratio has an estimated error of 20%); (2) the non-nanotubes $B_xC_yN_z$ materials might have more carbon content than that of nanotubes.

¹³K. Suenaga, C. Colliex, N. Demoncey, A. Loiseau, H. Pascard, and F. Willaime, *Science* **278**, 653 (1997).