Formation of $(BN)_xC_y$ and BN Nanotubes Filled with Boron Carbide Nanowires

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Boron carbide-filled $(BN)_xC_y$ nanotubes with outer layers of pure carbon and inner layers of pure boron nitride (BN) have been synthesized for the first time in high yield by using pure carbon nanotubes (CNTs) as templates. The $(BN)_xC_y$ nanotubes form by capillary filling of boron oxide vapor condensed into the inner cavity and a subsequent substitution reaction of the boron oxide with the inner carbon layers of the CNTs in the presence of nitrogen gas. Through a CNT-confined reaction, boron oxide reacts simultaneously with gaseous carbon monoxide or the carbon layers in the interior of the nanotubes to form a boron carbide filling. The diameters of the filled nanowires typically range from 7 to 20 nm, and the thickness of BN and C tubular layers is about 5 nm. The length of the filling can be up to the entire length of the nanotubes. Boron carbide-filled pure BN−NTs also form in the product.

Introduction

The study of one-dimensional nanocomposites is of great scientific interest because these materials have unique physical, chemical, and electronic properties and might have potential applications.[1,2] It has been shown that novel nanocomposite structures based on coated[2,3] and filled[2,4−7] carbon nanotubes (CNTs) can be prepared by using CNTs as templates. Various methods, including chemical insertion, physical insertion, arc encapsulation, and encapsulation via catalytic growth from the solid phase have been used to encapsulate metals and nonmetals inside the inner core of CNTs. Many elemental metals and their respective carbides have been encapsulated by the in situ arc encapsulation technique, in which a hollow graphite anode is packed with the elemental powder to be encapsulated before performing the conventional arc deposition experiment.[2,4−7] Filled BN nanotubes are expected to be useful in nanoscale electronic devices and for the preparation of nanostructured ceramic materials. Recently, Zhang and co-workers reported the synthesis of $(BN)_xC_y$ nanotubes filled inside with a coaxial SiC and SiO_2 core by a laser ablation method.[8] Recently, Han and co-workers showed that mass quantities of BN nanotubes,[9] boron-doped carbon nanotubes,[10] BN fullerene-like nanoparticles, and $(BN)_xC_y$ nanotubes[11] can be synthesized by a substitution reaction. Boron carbide is one of the most promising advanced ceramics. Above 1100 °C and in a nonoxidizing atmosphere, boron carbide is the hardest compound known. Furthermore, boron carbide also exhibits many other attractive properties such as high modulus of elasticity, low specific weight, and high melting temperature. The high-temperature stability of this material has suggested that it can be used for high-temperature thermoelectric energy conversion.[12,13] Boron carbide nanowires have been prepared using CNTs as templates.[10,14] These nanorods are, however, not encapsulated in a nanotube. In this letter, we report a new method that combines both the CNT-confined reaction[14−17] and the substitution reaction[9−11] to synthesize mass quantities of boron carbide nanowires encapsulated in $(BN)_xC_y$ nanotubes or BN nanotubes by using CNTs as templates.

Experimental Section

The reaction was carried out in a conventional horizontal furnace with a sintered alumina tube (6 cm × 110 cm). A BN crucible was loaded with 3 g of boron oxide (B_2O_3) powder (Alfa) and placed at the center of the furnace. The relatively pure multishell CNTs with typical outer diameters of 15 nm used here were prepared by a metal-catalyzed (alumina-supported Fe_2O_3 catalyst) chemical vapor deposition (CVD) method.[14,15]

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Figure 1. Low-magnification TEM overview of the product.

The CNTs are uncontaminated by other forms of carbon or other residues except for a small amount of catalyst residue (lower than 0.2%). The alumina tube was held in a 80 sccm flowing nitrogen (99.999+%) atmosphere at 1773 K for 1 h. CNTs (8 mg) were placed just outside the central zone in a BN crucible (ca. 1693 K). After the reaction, the product was collected from the original nanotube bed. The product was dispersed on a holey carbon film after ultrasonic dispersion in ethanol. Characterization of the product was carried out by using high-resolution transmission electron microscopy (HRTEM, JEM 4000EX, JEOL) and electron energy-loss spectroscopy (EELS) in a VG HB501UX dedicated scanning TEM with a parallel EELS spectrometer (Gatan PEELS 666)-.The EELS line-scan technique was employed in addition to the spot mode.

Results and Discussion

TEM and HRTEM images reveal an abundancy of filled nanotubes in the product. The diameters and lengths of the filled nanotubes are slightly larger than and similar to those of the starting CNTs, respectively. Figure 1 is a low-magnification TEM overview of the sample that shows that many of the nanotubes are filled to their entire length. The diameters and lengths of filled (BN)$_x$C$_y$ nanotubes are slightly larger than and similar to those of the starting CNTs, respectively. Elemental concentration profiles of B, C, and N across filled nanotube were obtained by scanning a finely focused electron probe (1 nm diameter) across the structure and recording the EELS spectra. The K-edge intensities after background removal are normalized by the respective cross sections to obtain chemical profiles of all elements. Therefore, the profiles directly reveal the chemical distribution in atomic concentrations. Several tens of filled nanotubes were checked. Two types of boron carbide-filled nanotubes were observed: one, which is dominant, where the outer shells and inner shells of the tubular layers are pure carbon layers and pure BN layers, respectively (Figure 2), and another one, where the tubular layers are pure BN layers (Figure 3). Figure 2a shows the concentration profiles of all elements present in a boron carbide-filled (BN)$_x$C$_y$ nanotube representative of the dominant type of filled nanotubes. C and N profiles clearly show the tubular geometry with mirror-symmetric C and N peaks on both sides, representing the outer and inner shells, respectively. The B profile is a superposition of two contributions: one from the core filling and other from the inner BN tubular layers, the latter having unity atomic ratio with N. The C profile is also composed of two parts: one from the outer pure graphitic C tubular layers and other from the presence of C in core filling. After subtraction

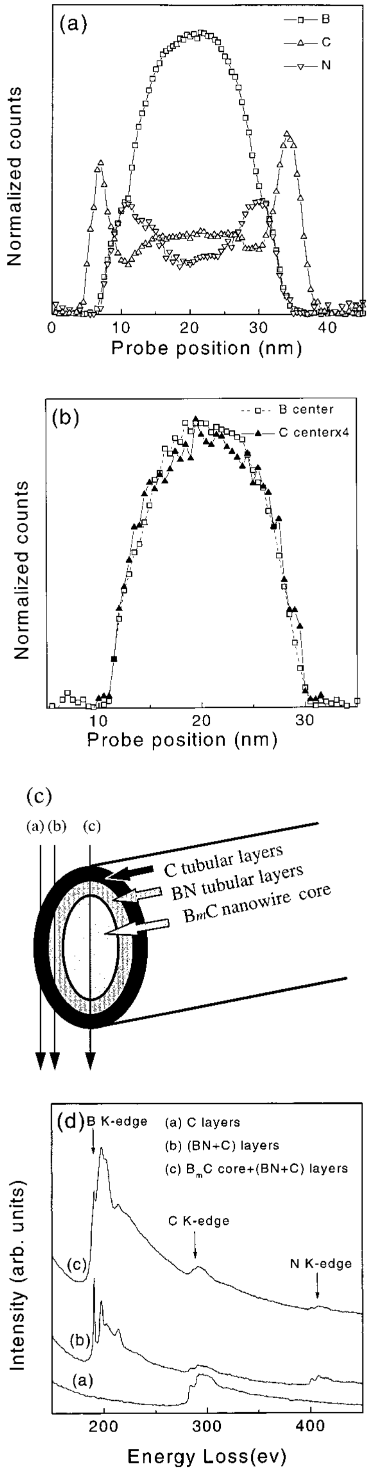

Figure 2. (a) Elemental profiles for B, C, and N across a filled (BN)$_x$C$_y$ nanotube. (b) Reduced profiles of B corresponding to the center core, obtained by subtracting the total contribution of B from the contribution of N corresponding to the BN tubular layers, and reduced profiles of C corresponding to the center core, obtained by subtracting the total contribution of C from an ideal simulation of the contribution of C corresponding to the C tubular layers. (c) Schematic illustration of a multiphase-filled nanotube. (d) Comparison of EELS spectra taken from three regions: outer carbon tubular layers, BN and carbon tubular, boron carbide (B$_m$C, $m > 2$), and (BN + C) tubular layers from top and bottom.

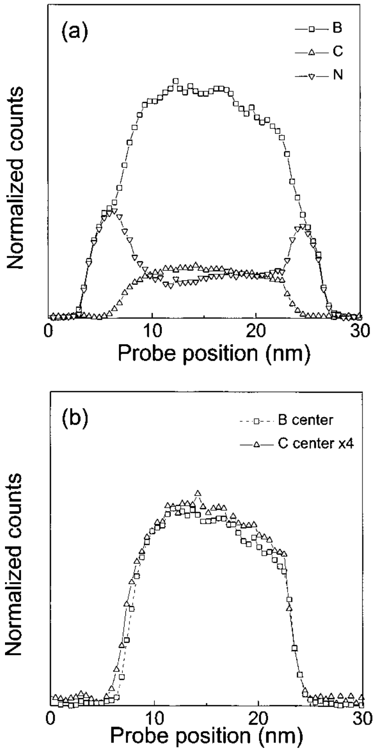

Figure 3. (a) Elemental profiles for B, C, and N across a filled BN nanotube. (b) Reduced profiles of B corresponding to the center core, obtained by subtracting the total contribution of B from the contribution of N corresponding to the BN tubular layers, and the profiles of C corresponding to the center core.

of the B and C contributions from the outer layers, the B and C profiles corresponding to the filling can be obtained (Figure 2b). A 1:4 atomic ratio of C with B in the core filling results from this analysis. Figure 2c is a schematic illustration of this multiphase-filled nanotube. Figure 2d compares a series of EELS spectra taken from three regions (solid lines with arrows in Figure 2c indicate the positions of electron probe): (a) outer carbon tubular layers, (b) the contribution from both the C and BN tubular layers, (c) the contribution from the boron carbide (B_mC, $m > 2$) nanowire core and the C and BN tubular layers on the top and bottom. The different features seen in the near-edge fine structure of the B and C K-edges reflect the graphitic bonding states (sp^2 hybridization) in the tubular layers and the characteristic carbide near-edge structure in the core. Figure 3a shows the concentration profiles of all elements present in a boron carbide-filled BN nanotube. N profiles clearly show the tubular geometry on both sides. The B profile is a superposition of two contributions: one from the core filling and other from the BN tubular layers, the latter having unity atomic ratio with N. The C profile is from the presence of C in core filling. After subtraction of the B from the outer layers, the B corresponding to the filling can be obtained (Figure 3b). A 1:4 atomic ratio of C with B in the core filling results from this analysis. The diameters of filled nanowires typically range from 7 to 20 nm, and the thickness of BN and C tubular layers is about 5 nm. Profiles recorded on the other filled nanotubes revealed that boron carbide fillings with compositions such as B_8C and $B_{25}C$ can also be found in the product.

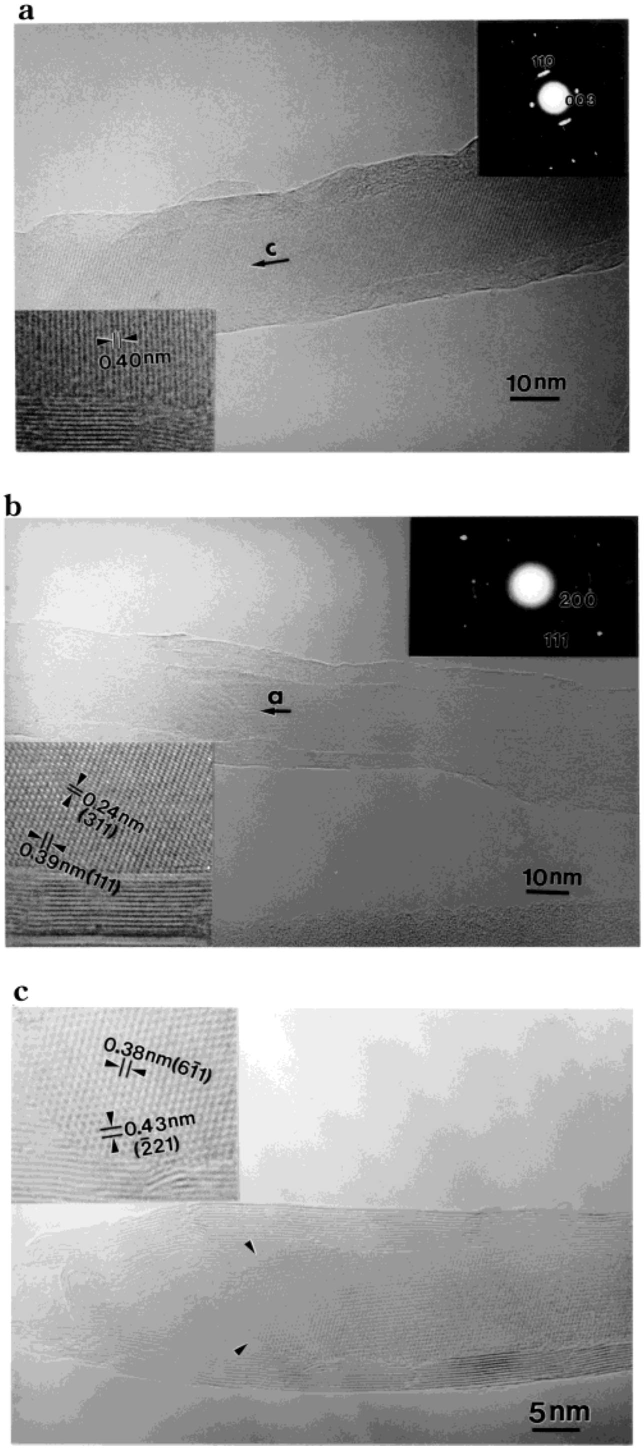

Figure 4. (a) High-resolution image of a nanotube filled with rhombohedral B_4C. The axis of the filled nanowires is along the rhombohedral B_4C crystallographic *c* direction. (b) High-resolution image of a nanotube filled with tetragonal $B_{25}C$. The axis of the filled nanowire is along a tetragonal $B_{25}C$ crystallographic *a* direction. (c) High-resolution image of a nanotube filled with orthorhomic B_8C.

Figure 4a shows a high-resolution image of a filled nanotube. The interlayer distances in the outer layers are about 0.34 nm, which is close to the value of the (002) spacing of hexagonal BN or graphitic carbon. Selected area diffraction patterns (inset of Figure 4a) correspond to B_4C or $B_{13}C_2$ with rhombohedral structure, with the <010> axis parallel to the electron beam. The axis of the filled nanowire is along the crystallographic *c* direction ([001] direction). Figure 4b shows a high-resolution image of a nanotube filled with tetragonal $B_{25}C$. The axis of the filled nanowire is along a tetragonal $B_{25}C$ crystallographic *a* direction ([100] direction). Figure 4c shows a nanotube filled with orthorhomic B_8C. The diameters of the nanowire fillings are larger than that of the inner diameter of unfilled nanotube part (the places indicated with black arrows).

The reaction process is based on the vaporization of B_2O_3 according to

$$B_2O_3\ (l) \rightarrow B_2O_3\ (g) \tag{1}$$

In the hot zone for B_2O_3 vaporization (1773 K), the B_2O_3 vapor pressure is 2.42×10^{-3} atm (calculated from JANAF[18]). The vapor is carried away by the nitrogen stream to the lower temperature region and penetrates the loose packing of the CNTs, where the B_2O_3 equilibrium vapor pressure decreases to 7.64×10^{-4} atm (calculated from JANAF[18]). The B_2O_3 vapor condenses on the surface of the CNTs and then can fill the inside hollow of the nanotubes by capillary action. CNTs prepared by the CVD method have higher defect densities than, for example, arc-discharge produced ones, such that the condensed B_2O_3 can preferably attach to the tips of the CNTs and open them by chemical reaction. After filling the inside cavity, the B_2O_3 can react with the inner carbon layers of CNTs according to the following reaction that has been proposed for the synthesis of BN−NTs by a complete C−BN substitution reaction:[9]

$$B_2O_3 + 3C\ (\text{nanotubes}) + N_2 \rightarrow 2BN + 3CO(g) \tag{2}$$

If all carbon layers are substituted, pure BN nanotubes will be formed; otherwise, $(BN)_xC_y$ nanotubes, the outer shells of which remain pure carbon and the inner shells change to BN, will form.

For the formation of the boron carbide B_mC filling, two types of reactions might be involved:

The B_2O_3 reacts with the CO vapor generated by eq 2 inside the hollow of nanotubes to form a B_mC nanowire filling by the following reaction:

$$mB_2O_3 + (3m + 4)CO \rightarrow 2B_mC\ (\text{nanowires}) + (3m + 2)CO_2 \tag{3}$$

The filling will grow along the tubular axis until it meets an obstacle or the reagents exhaust.

As a competing reaction process, the B_2O_3 inside the nanotubes can simultaneously react with the inner carbon layers of CNTs to form B_mC nanowire by the following chemical reaction:

$$mB_2O_3 + (3m + 2)C\ (\text{nanotubes}) \rightarrow 2B_mC\ (\text{nanowires}) + 3mCO \tag{4}$$

In this case, the diameter of the B_mC nanowire filling will exceed the internal diameter of the starting CNT because the inner carbon tubular layers are consumed by eq 4 (see Figure 4c). The compositional divergence of the B_mC filled inside different nanotubes may therefore result from the delicate equilibria of carbon consumption in eqs 2−4 in different nanotubes.

It is interesting to note that hollow BN−NTs are the major products under very similar experimental conditions except that the B_2O_3 powder was covered by CNTs directly.[9] This means the starting B_2O_3 powder and the CNTs were at the same temperature, such that the B_2O_3 vapor is unlikely to condense on the surface of CNTs, which is important for the filling of B_2O_3 inside of the nanotubes. In this case, only a few filled nanotubes can be observed. On the other hand, if the temperature at the zone where the B_2O_3 powder was placed is too low ($<$1473 K), no carbon tubular layers change to BN. In the present experiment, the slightly lower temperature at the zone where CNTs are placed gives rise to the condensation of B_2O_3 vapor, which originates from the hotter zone where the B_2O_3 powder was placed, on the surface of CNTs. Subsequently, the condensed B_2O_3 can fill the inside hollow of the nanotubes by capillary action.

Many details are still unresolved, i.e., why the BN−C substitution reaction seems not to start from the outer carbon layers in the present experiment. The successful synthesis of $(BN)_xC_y$ and BN nanotubes filled with boron carbide nanowires suggest, however, that this novel method, which combines both the CNT-confined reaction and the substitution reaction, can be a simple but powerful route for the synthesis of multiphase nanoscale materials by changing the starting materials used as templates. The structure and physical properties can be tailored by combining different nanowires and nanotubes.

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