



Chemical Physics Letters 308 (1999) 337-342



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Single-walled B-doped carbon, B/N-doped carbon and BN nanotubes synthesized from single-walled carbon nanotubes through a substitution reaction

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Received 3 April 1999; in final form 6 May 1999

Abstract

Bundles of single-walled boron-doped carbon (B_xC_{1-x}) , boron- and nitrogen-doped carbon $(B_xC_{1-x-y}N_y)$ and boron nitride (BN) nanotubes were prepared by thermal treatment of a mixture of boron trioxide and bundles of single-walled carbon nanotubes at 1523–1623 K in a nitrogen flow. The $(B_xC_{1-x} + B_xC_{1-x-y}N_y)/BN$ nanotube yield ratio increased with decreasing temperature in the reaction zone. The nanotubes were characterised by using high-resolution transmission electron microscopy and electron energy loss spectroscopy. The diameter of the individual nanotubes in the resultant bundles was 1.2-1.4 nm, which was similar to the diameter of the starting C-nanotubes. The B/C ratio of the B-doped carbon nanotubes was of ≤ 0.1 , whereas the BN nanotubes exhibited a B/N stoichiometry of ~ 1.0. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Doping of carbon nanotubes by B and N [1-4] or synthesizing nanotubes with exact BN stoichiometry [5-8] offers the possibility of nanotube electrical transport tailoring over a wide range [9]. The electronic structure of such tubes is assumed to be controlled by their chemistry rather than their geometry (helicity and diameter) as for their pure carbon counterparts [10].

Theoretical calculations [11] and conductivity measurements [12] have shown that B-doped nan-

otubes are intrinsically metallic, while the conductivity of the pure C nanotube varies between metal and semiconductor type depending on the nanotube's chirality [10]. In addition, B is known to increase the oxidation resistance of carbon-based materials [13] which is of prime importance for practical applications.

A BN nanotube is predicted to have stable insulating properties with a band gap of 5.5 eV [14], which, however, may drop to 1.5-2.0 eV under cross-section polygonization [15]. In combination with a higher resistance to oxidation, this makes a BN nanotube a perfect nanoinsulating shield for any encapsulated material.

Among nanotubular structures, special attention has been focused on single-walled nanotubes (SWNT) [10,16], since they open up a real-life labo-

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ratory for one-dimensional physics due to the absence of effects important in multi-walled nanotubes (MWNT): lip-lip interactions between shells and helicity distribution for the individual shells.

BN SWNT were found in low yields relative to MWNT in the resultant product of an arc-discharge process utilising HfB_2 [7] or ZrB_2 electrodes [17] and in relatively high yields after excimer laser ablation in different carrier gases [18].

Recently, a new route for the synthesis of MWNT in the B–C–N system has been proposed by Han et al. [19,20]. It is a general substitution chemical reaction of carbon nanotubes during which carbon atoms are partially or completely substituted by B and N atoms without topological changes of the starting material. The prime advantage of this technique is its simplicity, low cost, and a practically unlimited yield of nanotubes, which depends only upon the quantity of the starting C nanotubes.

Application of this new technique to synthesizing SWNT in the B-C-N system is the goal of the present study.

2. Experimental

High purity untreated carbon SWNT were bought from Carbolex (USA). Encapsulated metal catalyst particles (Fe/Ni), carbon nanospheres and an amorphous-like carbon residue were present as impurity phases. The nanotube product consisted of SWNT bundles (10–200 nanotubes per bundle). The estimated volume fraction of the SWNT product was approximately 50–70 vol.%.

The carbon SWNT product, in the form of a black powder, was placed in a carbon crucible together with B_2O_3 and the resultant powder mixture was heated in an induction furnace with a susceptor made of graphite at temperatures ranging between 1523 and 1803 K over 30 min in a flowing nitrogen atmosphere. The temperature in the reaction zone was controlled with the aid of an optical pyrometer with an estimated accuracy of ± 10 K. More details on specimen preparation are presented in recent papers [19,20].

The extracted reaction product was mixed with a CCl_4 solution. Finally, a few drops of the mixture were dripped onto a standard \emptyset 3 mm carbon-film-

coated copper grid. High resolution transmission electron microscopy (HRTEM) observations were carried out by means of a JEOL-3000F field emission type electron microscope operating at 300 kV. The HRTEM images were taken at the optimum defocus of the microscope ~ -56 nm at a magnification of 4×10^5 . The chemical composition and the bonding character of the product were characterized by means of a parallel Gatan-666 electron energy loss spectrometer (EELS) using an ultrafine electron probe focused down to \emptyset 0.8–1.6 nm for the diffraction mode with a 12 cm camera length.

3. Results and discussion

Fig. 1 shows the HRTEM images of the starting carbon SWNT bundle (Fig. 1a) and the resultant SWNT bundles of B_xC_{1-x} (Fig. 1c) and BN (Fig. 1e) obtained after thermal treatments at 1523 and 1623 K, respectively. Corresponding typical EELS spectra taken from the bundles are shown in Fig. 1b,d,f. The B/C ratio of the spectrum in Fig. 1d was measured to be ~ 0.1, whereas the B/N ratio of the spectrum in Fig. 1f was ~ 1.0. The estimated scatter of the measured B/C and B/N ratios was ~ 20% because of uncertainty in the background subtraction and the precise evaluation of the pure B-, C- and N-K edges.

With a decrease in the thermal treatment temperature from 1623 to 1523 K, we observed $B_{\nu}C_{1-\nu}$ SWNT bundles only (occasionally containing negligible traces of N) in the resultant product (Fig. 1c,d). Though $B_x C_{1-x}$ and $B_x C_{1-x-y} N_y$ SWNT bundles form preferentially even after increase in temperature to 1623 K, we were able to detect some fraction of pure BN bundles as a by-product in this case (Fig. 1e,f). Typically, SWNT formed in the bundles, although individual isolated SWNT were occasionally observed. A further increase in processing temperature to 1803 K leads to the complete transformation of the C SWNT bundles to bulk BN product consisting of hexagonal, rhombohedral and turbostratic BN with a minor fraction of BN nanoscale structures: polygonal particles, nanocones, nanorods, and MWNT, with no traces of the SWNT bundles remaining.



Fig. 1. HRTEM images of the starting carbon SWNT bundles (a) and the resultant $B_x C_{1-x}$ (c), and BN (e) SWNT bundles prepared through a partial (at 1523 K (c)) or complete (at 1623 K (e)) substitution chemical reaction. The corresponding EELS spectra taken from the starting C SWNT bundle (b), the $B_x C_{1-x}$ SWNT bundle (d), and the BN SWNT bundle (f) are also shown. The B-, C- and N–K edges at 188, 283, and 401 eV, the characteristic π^* -peaks indicating sp²-hybridization in the nanostructures, and the calculated B/C and B/N ratios are labelled.

The diameters of the individual SWNT in the $B_x C_{1-x}$, $B_x C_{1-x-y} N_y$ and BN bundles exactly cor-

responded to that of the starting SWNT and were in the range of 1.2–1.4 nm (Fig. 1a,c,e). Thus, it can be

presumed that the starting C SWNT are not simply the source of carbon atoms during the synthesis, but that C atoms in the SWNT are partially or completely substituted by the B and N atoms, while the topology of the SWNT is kept unchanged, although a slight undulation of the individual SWNT in the bundles may have taken place (Fig. 1e).

The following chemical reactions have been proposed for the incomplete and complete substitution reactions, respectively, leading to the formation of MWNT B $_{x}C_{1-x}$ and BN [19,20]:

$$xB_2O_3 + (2+3x)C \text{ (nanotubes)}$$

$$\rightarrow 2B_xC \text{ (nanotubes)} + 3xCO, \quad (1)$$

$$B_2O_3 + 3C \text{ (nanotubes)} + N_2$$

 $\rightarrow 2BN (nanotubes) + 3CO$. (2)

It appears that these reactions are indeed applicable in the case of SWNT synthesis. During the reactions, the SWNT C were oxidised and the C atoms were partially or completely substituted by B and N atoms and flowed away as CO vapor. The sources of the B and N atoms were boron trioxide vapour and flowing nitrogen gas, respectively. Although the details of the substitution mechanism need to be clarified, we expect that the intra-tube tunnels between the individual tubes in the bundles may serve as effective pathways for O, B and N atom diffusion, which allows them to reach the individual SWNT and react with them.

Numerous EELS runs taken on the $B_{x}C_{1-x}$ SWNT bundles (Fig. 1d) revealed that their B-content never exceeded ~ 10 at.%. It is of interest that the same composition limit was realised for $B_x C_{1-x}$ MWNT synthesized through the substitution reaction [20], and for $B_{\kappa}C_{1-\kappa}$ fullerenes prepared by intense electron irradiation of the graphitic B-doped materials [21]. In the case of the B-doped fullerenes, this limit was found to correlate with the minimum in energy of the $B_n C_{60-n}$ series (n = 2, 4, 6, 8, 10) at n = 6, i.e., a B content of ~10 at.% [22]. According to density functional theory (DFT) calculations, the chemical potential difference at which B₆C₅₄ becomes more stable than the C_{60} molecule was found to be 2.826 eV/atom, compared to a very consistent value of 2.836-2.837 eV/atom for the structures with 2, 4, 8, and 10 atoms [22]. Analogous energy calculations for $B_x C_{1-x}$ SWNT are underway [23].

We note that the maximum B-content and the arrangement of B-atoms in B-doped nanostructures is a questionable issue. To date, B-doped MWNT with high B-content (~ 25 at.%) have only been reported by Weng-Seih et al. [24]. However, lower B-contents were observed for $B_{\nu}C_{1}$, MWNT in later studies by various authors [20,25]. The B content in $B_{\nu}C_{1}$, thin films grown by chemical vapor deposition (CVD) was found to be 17 at.% [26]. It was also mentioned that a B-content greater than this value would result in the presence of B-atoms in interstitial positions and produce a significant increase in d_{002} spacing, or in defect generation within the graphitic sheet (i.e., B-rich islands). The intrinsic metallic behaviour of the B-doped MWNT [11,12] was accounted for by the existence of the B-rich islands (e.g., BC₃) in the graphene sheet. No data have so far been reported for the $B_{x}C_{1-x}$ SWNT. Thus, presently it is rather difficult to determine both the reasons for the experimentally observed 10 at.% B-content limit in $B_{r}C_{1-r}$ SWNT, and the precise distribution of the B-atoms in the $B_{x}C_{1-x}$ SWNT bundles prepared through the substitution reaction, although a pronounced π^* -peak in the B-K edge at 188 eV (Fig. 1d) allows one to assume that the B-atoms are in the same sp²-hybridised state within the graphitic shells as their C counterparts and are not gathered in the $B_{r}C_{1-r}$ SWNT bundle intra-tube tunnels.

The B/C and N/C ratios for the $B_{r}C_{1-r-v}N_{v}$ SWNT bundles varied over a wide range from bundle to bundle (Fig. 2a,b). In addition, these ratios were found to depend on the position of the EELS probe across or along the bundle axis. It is suggested that such a variety reflects the deviations in chemical composition between the individual tubes in the bundles and/or within the graphitic shell of the elemental tubes. The nearly equal B/C and N/Cratios measured in every particular EELS run (Fig. 2a,b) may reflect the fact that the substitution reaction proceeded gradually by formation of pure BN areas incorporated into C graphitic shells, rather than by a random substitution of the C atoms by the B and N ones, thus, leading to the altering of the pure BN and C SWNT within the bundle and/or pure BN and C areas within the individual shells. Similar to the B-doped SWNT, for which B-rich islands seemed to be favoured [11,12], BN-rich islands in the individual graphitic shell may also be presumed to exist, forming heterojunctions between C and BN nanodomains [9].

The BN SWNT bundles (Fig. 1e) do not show any traces of residual carbon (Fig. 1f) confirming that the substitution chemical reaction proceeded to completion (Eq. (2)). Occasionally, individual isolated BN nanotubes were observed in the product. Fig. 3 shows such a BN SWNT exhibiting a characteristic dimension in a cross-section of approximately 2.5 nm.

The exciting feature of the BN SWNT in Fig. 3 is the HRTEM contrast observed in the core region, resembling the 2-D image of a nested 4-shelled entirely closed cage. Since the HRTEM contrast under the focusing conditions of Fig. 3 is exactly the same for the areas of the SWNT that are at a tangent



Fig. 2. Representative core-loss K-shell EELS spectra taken from the BN-poor (a) and BN-rich (b) $B_x C_{1-x-y} N_y$ SWNT bundles prepared through an incomplete substitution reaction at 1623 K. The B-, C- and N–K edges and corresponding B/C and N/C ratios are shown.



Fig. 3. An isolated individual BN SWNT found in a specimen processed from the C SWNT bundles at 1623 K, exhibiting a nested 4-shelled octahedral BN fullerene encapsulated within. The fullerene HRTEM image resembles a hexagon, which would be consistent with an octahedral BN cage viewed in an orientation close to $\langle 111 \rangle$ [27,28].

to the electron beam and for the 4-shelled object in the core region, we consider that the cage is encapsulated in the SWNT rather than mounted on the SWNT surface. Recently, encapsulated C_{60} molecules have been observed in C SWNT [29]. The 2-D cage image in Fig. 3 is obviously not spherical as it should be for a C_{60} type fullerene and would be consistent with a nested octahedral BN fullerene viewed in an orientation close to $\langle 111 \rangle$ (hexagon-like HRTEM image) [27,28]. The dimensions of the nested encapsulated 4-shelled object match well those of the $B_{12}N_{12}@B_{76}N_{76}@B_{208}N_{208}@B_{412}N_{412}$ nested octahedral fullerene [28]. A perfect fit between the BN octahedral fullerene and the BN SWNT in Fig. 3 with no gap between their shells leads us to suggest that the individual BN SWNT cross-section may not be a sphere but a polygon.

4. Conclusions

Bundles of B-doped carbon, boron/nitrogendoped carbon and boron nitride SWNT were obtained through a partial or complete substitution chemical reaction from carbon SWNT bundles by thermal heating of C SWNT with boron oxide in a nitrogen flow at 1523 and 1623 K. The B-doped and B/N-doped SWNT were the only fractions in the SWNT product obtained at the lower temperature and those yields were markedly higher than that of pure BN SWNT after thermal treatment at the higher temperature. The B/C ratio in the B-doped SWNT was limited to ~ 0.1, whereas the BN SWNT revealed an exact stoichiomety of the B/N-1.0. Occasionally, octahedral BN nested fullerenes were found to be encapsulated within the individual BN SWNT in a similar way as C_{60} molecules in C SWNT [29].

Acknowledgements

This work was carried out under the project of the Japan Science and Technology. The authors are grateful to Dr. L. Bourgeois and Dr. O. Louchev at the National Institute for Research in Inorganic Materials, Tsukuba, and to Dr. C. Goringe at the Australian Key Centre for Electron Microscopy, University of Sydney, for the stimulating discussions, and to Dr. J. Hester of the Australian Nuclear Science and Technology Organization for reading the manuscript and providing useful suggestions.

References

- O. Stéphan, P.M. Ajayan, C. Colliex, Ph. Redlich, J.M. Lambert, P.M. Bernier, P. Lefin, Science 266 (1994) 1683.
- [2] M. Terrones, A.M. Benito, C. Manteca-Diego, W.K. Hsu, O.I. Osman, J.P. Hare, D.G. Reid, H. Terrones, A.K. Cheetham, K. Prassides, H.W. Kroto, D.R.M. Walton, Chem. Phys. Lett. 257 (1996) 576.
- [3] R. Sen, A. Govindaraj, C.N.R. Rao, Chem. Phys. Lett. 287 (1998) 671.
- [4] Y. Zhang, H. Gu, K. Suenaga, S. Iijima, Chem. Phys. Lett. 279 (1997) 264.
- [5] N.G. Chopra, R.J. Luyken, K. Cherrey, V.H. Crespi, M.L. Cohen, S.G. Louie, A. Zettl, Science 269 (1995) 966.
- [6] M. Terrones, W.K. Hsu, H. Terrones, J.P. Zhang, S. Ramos, J.P. Hare, R. Castillo, K. Prassides, A.K. Cheetham, H.W. Kroto, D.R.M. Walton, Chem. Phys. Lett. 259 (1996) 568.
- [7] A. Loiseau, F. Willaime, N. Demoncy, G. Hug, H. Pascard, Phys. Rev. Lett. 76 (1996) 4737.

- [8] D. Golberg, Y. Bando, M. Eremets, K. Takemura, K. Kurashima, H. Yusa, Appl. Phys. Lett. 69 (1996) 2045.
- [9] X. Blase, J.-C. Charlier, A. De Vita, R. Car, Appl. Phys. Lett. 70 (1997) 197.
- [10] S.J. Tans, M.H. Devoret, H. Dai, A. Thess, R.E. Smalley, L.J. Geerlings, C. Dekker, Nature 386 (1997) 474.
- [11] D.L. Caroll, Ph. Redlich, X. Blase, J.-C. Charlier, S. Curran, P.M. Ajayan, S. Roth, M. Rühle, Phys. Rev. Lett. 81 (1998) 2332.
- [12] M. Terrones, W.K. Hsu, A. Schilder, H. Terrones, N. Crobert, J.P. Hare, Y.Q. Zhu, M. Schwoerer, K. Prassides, H.W. Kroto, D.R.M. Walton, Appl. Phys. A 66 (1998) 307.
- [13] L.R. Radovic, M. Karra, K. Skokova, P. Thrower, Carbon 36 (1998) 1841.
- [14] X. Blase, A. Rubio, S.G. Louie, M.L. Cohen, Europhys. Lett. 28 (1994) 335.
- [15] M. Terrones, W.K. Hsu, H.W. Kroto, D.R.M. Walton, in: A. Hirsch (Ed.), Topics in Current Chemistry, Vol. 199, Springer, Berlin, 1999, p. 220.
- [16] S. Iijima, T. Ichihashi, Nature 361 (1993) 603.
- [17] Y. Saito, M. Maida, T. Matsumoto, Jpn. J. Appl. Phys. 38 (1999) 159.
- [18] D.P. Yu, X.S. Sun, C.S. Lee, I. Bello, H.D. Gu, K.M. Leung, G.W. Zhou, Z.F. Dong, Z. Zhang, Appl. Phys. Lett. 72 (1998) 1966.
- [19] W. Han, Y. Bando, K. Kurashima, T. Sato, Appl. Phys. Lett. 73 (1998) 3085.
- [20] W. Han, Y. Bando, K. Kurashima, T. Sato, Chem. Phys. Lett. 299 (1999) 368.
- [21] D. Golberg, Y. Bando, K. Kurashima, T. Sato, Appl. Phys. Lett. 72 (1998) 2108.
- [22] C. Goringe, in: Y. Bando et al. (Eds.), Proc. 6th Int. Conf. on Advanced Materials, Tsukuba, 1999, p. 95.
- [23] C. Goringe, personal communication.
- [24] Z. Weng-Seih, K. Cherrey, N.G. Chopra, X. Blase, Y. Miyamoto, A. Rubio, M.L. Cohen, S.G. Louie, A. Zettl, R. Gronsky, Phys. Rev. B 51 (1995) 11229.
- [25] Ph. Redlich, J. Loeffler, P.M. Ajayan, J. Bill, F. Aldinger, M. Rühle, Chem. Phys. Lett. 260 (1996) 465.
- [26] C.T. Hach, L.E. Jones, C. Crossland, P.A. Thrower, Carbon 37 (1999) 221.
- [27] D. Golberg, Y. Bando, O. Stéphan, K. Kurashima, Appl. Phys. Lett. 73 (1998) 2441.
- [28] O. Stéphan, Y. Bando, A. Loiseau, F. Willaime, N. Shramchenko, T. Tamiya, T. Sato, Appl. Phys. A 67 (1998) 107.
- [29] B.W. Smith, M. Monthioux, D.E. Luzzi, Nature 396 (1998) 323.