Analytical TEM investigations on boron carbonitride nanotubes grown via chemical vapour deposition

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Abstract. A systematic microstructure investigation on the boron carbonitride (BCN) nanotubes, synthesized by bias-assisted hot-filament chemical vapour deposition, is reported. The BCN nanotubes were found to be well-crystallized with uniform diameters and transverse connections inside. Their lengths can be over a few tens of micrometres. Transmission electron microscopy (TEM) analyses indicate that the BCN nanotubes have near zigzag graphic-layered structures with helical angles of less than 30°. Spatial-resolved electron energy loss spectroscopy (EELS) demonstrates typical sp\textsuperscript{2} bonding configuration of the nanotubes with pronounced characteristic $\pi^*$ and $\sigma^*$ peaks of boron and carbon and characteristic K-shell ionization edges of nitrogen. EELS and energy-filtered TEM analyses reveal that the inner layer of the nanotube contains mass of carbon and some amount of boron, and the outer layer and the connections across the inner walls are rich in boron. The nitrogen is found distributing in the nanotube dispersedly and traceable amount of oxygen is measured existing in the shell of the nanotube.
1. Introduction

One-dimensional tubular nanostructures have received steadily growing interests as a result of their peculiar and fascinating properties [1]. Since the discovery of carbon nanotubes [2], extensive studies have been conducted in finding novel tubular nanostructures, among which the ternary boron carbonitride (BCN) nanotubes have attracted increasing interest for their unique electronic properties and potential nanotechnological applications [3]. Theoretical calculations have revealed that BCN nanotubes possess tunable band gaps, intermediate between those of BN nanotubes and carbon nanotubes; moreover, their band gaps can be controlled by solely changing their atomic compositions and configurations [4]. In the aspect of structural stability, however, segregation of BN, C and BCN domains tends to occur due to total energy calculations [5]. Nanotubes with either homogeneous BCN composition or separated phases of BN and C have been observed [6]. The structure and composition of the BCN nanotubes are found to be sensitive to growth methods and actual growth parameters [3]–[7]. Therefore, for BCN nanotubes grown using a specific technique, a systematic study of their structural and compositional characteristics is of great importance to both their further applications and developing the fabrication method. To do so, it is clear that analytical TEM investigation is indispensable to characterizing the nanotubes.

A few synthesis methods have been attempted to fabricate BCN nanotubes, for example, electric arc discharge and pyrolysis methods have been used with products of nanoparticles and nanotubes [3, 4, 6]. Recently, aligned BCN nanotubes have been successfully fabricated by bias-assisted hot-filament chemical vapour deposition (HFCVD) [7, 8] and their properties have been explored [8]. However, analysis on the microstructure, especially nanoscale distributions of the compositional elements, of the BCN nanotubes grown via HFCVD is far from being well understood. In this paper, analytical TEM investigations on the microstructures of the BCN nanotubes have been performed systematically.

2. Experimental procedures

A bias-assisted HFCVD apparatus was used to synthesize the BCN nanotubes, and the growth details can be found in [7, 8]. The nominal chemical composition of the nanotubes is $B_{0.06}C_{0.76}N_{0.16}$, which were measured by using Auger electron spectroscopy (AES) [8]. The structural nature of the BCN tubular materials was studied using conventional transmission electron microscopy (TEM), selected area electron diffraction (SAED), high-resolution TEM
(HRTEM), Z-contrast imaging and energy-filtered TEM (EFTEM) in a Tecnai F30 (TEM, field emission gun and accelerating voltage of 300 kV; FEI Company). The compositional details of the nanotubes were investigated by means of electron energy loss spectroscopy (EELS) in scanning TEM (STEM) mode as well as EFTEM attached to the Tecnai F30 TEM. TEM samples were prepared by dispersing the powder products in alcohol by ultrasonic treatment, dropping the mixture onto a porous carbon film supported on a copper grid and then drying the film in air.

3. Results and discussions

Figure 1 shows the microstructure of the BCN nanotubes. Low-magnification TEM bright-field (BF) images (figures 1(A)–(C)) indicate that the investigated nanomaterials have typical tubular structures with transverse connections across the inner walls. The diameters of the tubular materials are measured in the range of 40–120 nm, with a mean value around 80 nm. The lengths of the nanotubes can be over a few tens of micrometres. For each nanotube, its wall thickness is found to be uniform throughout the entire length. It can also be found that every nanotube shown in the images has a catalyst particle in its head. Detailed investigations of SAED and energy-dispersive X-ray spectroscopy (EDS) reveal that the catalyst particles are composed of Ni and exhibit two typical morphologies, i.e. oval and cone; moreover, the sizes of the catalyst particles are found to be about half of the diameters of the corresponding nanotubes (e.g. the nanotubes in figure 1(B)), which indicates that the diameters of the nanotubes are principally controlled by the sizes of the nickel particles. In addition, the smaller catalyst particles (in the nanotubes less than the average value) normally have oval morphologies with lower surface energy. The larger ones tend to have cone morphologies. Such case can be well seen in figure 1(B), where the nanotube with diameter of about 60 nm has an oval particle in its head, whereas nanotube with diameter of about 100 nm has a cone particle. The role of nickel particles in the growth of BCN nanotubes has been explored in [4], whereas here we point out the correlation between the size (small or large) and the morphology (oval or cone, respectively). In fact, the control of the catalyst particle on the size of the investigated BCN nanotube can be in a much wide range, from only a few nanometres to micrometre scale.

Figure 1(C) shows a typical BCN nanotube with average size (around 80 nm in diameter) and corresponding SAED pattern. The area selected for diffraction is marked as a bright dashed circle in figure 1(C). The wall of the nanotube in figure 1(C) may be regarded as two layers. The inner layer is well crystallized and the outer layer seems amorphous-like. In the SAED pattern, the intensities corresponding to the two equipollent (010) diffractions of the nanotube spread as two continuous arcs, which may be a result of different helical angles of the multi-wall tubule. By neglecting the cylindricality of the nanotube, the apparent semi-splitting angle \( \theta \) in the SAED pattern can be approximated as \( \alpha \), the true helical angle of the tubule [10]. The continuous arcs in figure 1(C) indicate that the helical angles of the BCN nanotube have a range from zero to a maximum, corresponding to maximum semi-splitting angle of the arcs \( \theta_{\text{max}} \). The measured \( \theta_{\text{max}} \) of the arcs is about 30°, which indicates that the helical angles of BCN nanotube in figure 1(C) are less than 30°. It should be mentioned that the vector of the centre of the (010) diffraction arcs is parallel with the axis of the nanotube, which reveals that the BCN nanotube has a near zigzag structure despite of the narrow spread of their helical angles [10]. The diffraction spots of the nickel particle (fcc, \( a = 0.3499 \) nm) are also shown in the SAED pattern and they can be
Figure 1. Morphology of the BCN nanotubes. (A) TEM BF image of the BCN nanotube at low magnification showing a large number of tubular structures with diameters of 40–120 nm and lengths up to a few tens of micrometres. Each of the nanotube has a catalyst in the head and periodical connection across the inner walls. (B) TEM BF image of two nanotubes at higher magnification. The catalysts with typical oval or cone morphologies are found in the head of the nanotubes. (C) TEM image of a single nanotube and corresponding SAED pattern (inset). The circle shows the area selected for diffraction. The arcs in the SAED pattern reveal that the nanotube is zigzag with helical angles of less than 30°. (D) Plasma energy-loss filtered TEM image of the same nanotube shown in (C).

indexed along (001) zone axis. Figure 1(D) shows the plasmon filtered TEM image of the same nanotube as that in figure 1(C). The plasmon energy loss of the sample is chosen to be 30 eV and the slit for the EFTEM is 10 eV for the fact that the plasmon energies of BCN and BN are around 25 and 31 eV, respectively [11]. By contrast with the BF image, the tubular structure with transverse connections across the inner walls can be clearly seen from the plasmon-loss image.
Figure 2. HRTEM images of BCN nanotubes. (A, B) Typical HRTEM images of a BCN nanotube with diameter of \( \sim 80 \) nm, showing layered structures of the inner walls and the transverse connections. (C, D) HRTEM images of a BCN nanotubes with smaller diameters showing the relationship between the morphogenesis of the transverse connection and the catalyst particles.

High-resolution images (figure 2) indicate that there are a great number of layers existing in the inner walls as well as in the transverse connections of the nanotubes. Figure 2(A) shows a typical HRTEM image from a BCN nanotube with dimension of \( \sim 80 \) nm. Figure 2(B) shows magnified HRTEM image from the same nanotube. The inner walls and the transverse connections are well crystallized with layer structures and form cone structures. The spacing between the layers within a transverse connection is measured to be almost identical and it
Figure 3. EELS spectrum of an individual BCN nanotube showing the ionization edges around 188, 284, 401 and 532 eV, corresponding to the K-shell ionization edges of boron, carbon, nitrogen and oxygen, respectively. The carbon and boron K edges exhibit distinct $\pi^*$ and $\sigma^*$ features, indicating a graphic structure. However, the nitrogen K edge deviates from the ideal sp$^2$ hybridization. (The signals for electron energy loss over 350 eV are magnified six times to keep the full range of the spectrum in one figure.)

is very close to that of the wall layers of the nanotube with a value ca. 0.3 nm. However, the distances between the transverse connections are measured in the range of 10–20 nm. For the BCN nanotubes with smaller diameters, the crystallized inner walls become thinner. Figure 2(C) shows such a case with an oval catalyst particle in the head. The first transverse connection across the inner layer matches the morphology of the catalyst particle very well. However, for the connections far away from the catalyst particle, their morphologies become more diverse, as shown in figure 2(D).

The chemical bonding configuration in an individual BCN nanotube was determined by spatial-resolved EELS, as shown in figure 3. The EELS spectra were recorded in diffraction mode with energy dispersions of 0.5 and 0.3 eV channel$^{-1}$ using the Gatan image filter (GIF) system attached to the Tecnai F30 TEM. The spectrum in figure 3 exhibits pronounced peaks at about 188, 284, 401 and 532 eV, corresponding to the characteristic K-shell ionization edges of B, C, N and O, respectively. Attention should be paid that the signals for energy loss over 350 eV are magnified six times. The calculated B–C–N ratio deviates from the nominal chemical composition with higher B content, which may be attributed to the fact of boron enrichment in the outer layer of the nanotube. EELS is also a powerful and efficient technique for investigation of the electronic structure of materials. The electron energy loss near edge structure (ELNES) of the carbon edge is characteristic of well-graphitized structures (sp$^2$-type bonding). The most prominent features of the ELNES are the smaller peak close to the edge onset attributed to the $1s \rightarrow \pi^*$ transition and the series of $1s \rightarrow \sigma^*$ transition peaks. The ELNES of the boron K-edges are comparable with the B edge in h-BN, which suggests that the boron is in the characteristic
Figure 4. Line profile of a BCN nanotube across the transverse connection. (A) HAADF STEM image and the position for line profile. The box was used for specimen drift correction. (B) STEM signal intensity along the scanned line. (C, D) Compositional line profiles along the scanned line probed in EELS mode. The results show that the inner layer mainly consists of carbon and the outer layer is rich in boron with dispersed nitrogen. Trace amount of oxygen is found in the shell layer.

sp$^3$-hybridized state as in h-BN and hence is substituted on carbon lattice positions into the graphic network [9]. The separations of the measured $\pi^*$ and $\sigma^*$ energy levels observed for the BCN nanotubes are measured to be 9.4 and 7.4 eV for B and C respectively, which are comparable with the previous report [3]. However, the absence of $\pi^*$ peak from the nitrogen K-edge may be explained in terms of atomic relaxation in the tubular structure, although it is also possible that the N is not incorporated in the tubular structure, which, in our case, can be excluded by STEM analysis as follows.

STEM images collected by a high-angle annular dark field detector (HAADF) attached to the Tecnai F30 TEM have also been used to characterize further the microstructure and chemical composition of the BCN nanotubes. It is well known that the STEM image with an HAADF detector is a $Z$-contrasted one, i.e. the contrast of the STEM image comes from the inelastic forward Rutherford electron scattering by the nucleus of the elements and in general is proportional to $Z^{1.5-1.7}$, where $Z$ represents the atomic number of the elements [12]. In contrast, in the diffraction contrast TEM BF images, the sidewalls of the nanotubes in the STEM images demonstrate brighter contrast due to the relatively larger number of atoms than the other parts of the nanotubes, as shown in figure 4(A). The very bright contrast in the head is the nickel
A catalyst particle. A large number of transverse connections are found to exist within the nanotube. Figure 4(B) shows the signal intensity of the STEM image along the scanned line shown in figure 4(A). Besides the central valley (marked with a hollow arrow) corresponding to the core of the nanotube, two additional valleys (marked with black arrows) have also been found in the intensity profile, indicating complex tubular structure of the BCN nanotube. Figures 4(C) and (D) depict the compositional line profiles probed in EELS mode. The spot size and distances between adjacent spots are both about 1 nm. The scan line (marked with ‘1’) is also illustrated in figure 4(A) and the box (marked with ‘2’) is used for specimen-drift correction. The position marked with ‘3’ in figure 4(A) is also marked in the compositional line profiles, as shown in figures 4(B)–(D). It should be noted that the scan line is near the transverse layer. The results reveal that the inner layer consists of mass of carbon and some amount of boron, whereas the outer layer is rich in boron. The nitrogen signals are rather lower compared with those of boron and carbon. The intensity of nitrogen in the core is apparently higher than that in the wall, because the transverse connections generate a significant number of nitrogen signals in the core. Little amount of oxygen is found in the shell of the nanotube, which is properly formed during exposure to air.

Figure 5 illustrates another compositional line profile of the same nanotube probed away from the transverse connection. The profiles for carbon and boron are found to be almost the same with those probed along the transverse connection. The obvious difference is the intensity of nitrogen in the core, which decreases apparently when probed away from the transverse connection.

EFTEM is also used to characterize the microstructure and chemical details of the nanotube. Figure 6 shows the elemental mappings of carbon, boron and oxygen rendered with different colours. The blue colour in the centre nanotube represents carbon, the green colour in the outer layer represents boron and the red colour in the shell layer represents oxygen. To get the elemental...
distributions in more detail, high-magnification EFTEM have also been conducted, as shown in figure 7. Figure 7(A) is a zero-loss filtered image with slit width of 10 eV, and figures 7(B)–(E) illustrate the elemental mappings corresponding to B, C, N and O, respectively. The EFTEM images are 256 × 256 pixels with each pixel corresponding to ~1 nm, which give images of the elemental distributions. The results are consistent with the line scan profiles shown in figures 4 and 5. The boron mapping indicates that the outer layer with a thickness of about 5 nm as well as the transverse connection is rich in boron. The carbon mapping demonstrates typical bamboo structure, which is a result of the mass-thickness contrast added to the elemental-mapping image. From the carbon and boron mappings, it can be concluded that the inner wall contains mass of carbon and some amount of boron. The mapping for nitrogen is rather noisy although it can be distinguished that the core is rich in nitrogen, indicating dispersed distribution of nitrogen. The oxygen with a thickness of less than 2–3 nm is found in the shell of the nanotube, which is properly oxidized during the fabrication and deposition of the nanotube. It should be pointed out that the nanotube subjected to the analysis has a much thinner outer layer than the average.

4. Conclusions

1. The BCN nanotubes fabricated by bias-assisted HFCVD have a graphic structure with periodic transverse connections across their inner walls. The diameters of the nanotubes are measured ranging from 40 to 120 nm with an average of about 80 nm and the lengths can be over a few tens of micrometres. Each nanotube has a nickel catalyst particle in the head. The catalyst particles in the smaller nanotubes with diameter less than the average value tend to have oval
morphology while that in the larger ones tend to have cone morphology. The BCN nanotubes are found to have near zigzag structures with helical angles less than 30°. Characteristic $sp^2$-hybridized bonding with distinct $\pi^*$ and $\sigma^*$ features in the ELNES structures of carbon and boron also proves well-graphic-crystallized structure of the BCN nanotubes.

Figure 7. EFTEM of an individual BCN nanotube at high magnification: (A) zero loss EFTEM image, (B–E) elemental mapping of B, C, N and O, respectively.
2. Detailed analytical TEM analyses reveal the complex tubular structures of the BCN nanotubes resulting from the elemental distributions. The inner wall mainly contains mass of carbon and some amount of boron, the outer layer and the transverse layers are rich in boron, and nitrogen dispersively distributed in the whole structure. Traceable amount of oxygen with a thickness of less than 2–3 nm is found in the shell layer of the nanotube.

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