Pyrolytic-grown B–C–N and BN nanotubes

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Abstract

We report the growth of pyrolytic boron–carbon–nitrogen (B–C–N) nanotubes on iron (Fe) and nickel (Ni) catalysts. It was discovered that different catalysts had effect on the elemental compositions of B–C–N nanotubes, which may allow one to tune the transport properties of B–C–N nanotubes in a wide range. A new synthetic route was also developed to generate H3N:BH3 as the precursor and yield boron nitride (BN) nanotubes by pyrolysis. The typical growth scenario of multi-wall BN tubes will be discussed.

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1. Introduction

Since the discovery of carbon (C) nanotubes [1], much interest has been attracted to the syntheses and characterizations of nanotubes with multi-element compositions particularly in boron–carbon–nitrogen (B–C–N) system. Investigations on nanotubes with various B, C and N stoichiometries were carried out [2–24]. B–C–N nanotubes constitute possible hybrid systems of boron nitride (BN) and graphite, which may be semiconductors. For example, BN nanotubes have a constant energy gap (Eg) of ~5.5 eV [7]. The gaps for BC3 nanotubes and BC2N nanotubes are approximate 0.5 and 2.0 eV, respectively [8,9]. Bundles of B–C–N nanotubes with few layers displayed semiconducting behavior with an estimated gap of ~1.0 eV [10]. In general, the energy gap of B–C–N nanotubes is largely independent of the geometry and the degree of perfection in the constituting nanotubes, instead, is determined by their chemical compositions. So there is an apparent advantage to control the energy gap of B–C–N nanotubes by simply adjusting their compositions. Preparation of ternary B–C–N nanotubes of various compositions may allow one to tune the transport properties over a wide range.

Carbon nanotubes can be routinely obtained by pyrolyzing different carbon–hydrogen (C–H) precursors at a suitable temperature regime (700–900 °C) [11–14]. B–C–N nanotubes and nanofibers were also synthesized by catalytic pyrolysis of different starting materials containing B–C–N [15–17]. Here we add a new precursor, DMAB ((CH3)2NH·BH3), for the catalytic growth of B–C–N nanotubes. Our work also demonstrates that different catalysts may affect the elemental compositions of as-grown B–C–N nanotubes.

On the other hand, growing pyrolytic BN nanotubes proves to be more difficult as there is few precursors, containing stoichiometric BN and without carbon deterioration, available for the pyrolysis. Borazine (B3N3H6) or related materials (e.g. H3N:BH3) might be ideal for the pyrolytic growth of BN nanotubes [17–21]. Sen et al. attempted to pyrolyze H3N:BH3 from the reaction of LiBH4 and (NH4)2SO4 in ether [17]. Shelimov et al. employed 2,4,6-trichloroborazine (B3N3H3Cl3) to yield BN nanotubes in alumina filter membrane [18]. B3N3H6 was also generated from NaBH4 and (NH4)2SO4, which was subsequently pyrolyzed to grow BN nanotubes on nickel boride catalyst particles [19]. All these methods were either not very successful in generating B3N3H6 or somewhat dangerous. In the current work, a new mild route to generate H3N:BH3 and grow BN nanotubes will be presented.

2. Experimental procedures

The precursor for B–C–N nanotubes is commercially available DMAB ((CH3)2NH·BH3). BN nanostructures were

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synthesized from NaBH₄ + NH₄Cl, which were obtained by well mixing NaBH₄ and NH₄Cl powders under the protection of Ar in a grove box. DMAB or NaBH₄ + NH₄Cl was charged into a flask and connected to a quartz tube furnace. An alumina boat containing Fe or Ni nanoparticles (~20 nm) was laid on the center part of the quartz tube. The flask was mantle-heated to 100 °C (for DMAB precursor) or 300 °C (for NaBH₄ + NH₄Cl precursor) while the quartz tube furnace was maintained at 1050 °C under N₂ atmosphere. The conditions were kept for 1 hour and then the furnace was cooled to room temperature.

The products were collected from the alumina boat and directly observed by scanning electron microscopy (SEM). Some products were also dispersed in CCl₄ solution. A drop of the suspension was dipped onto a carbon-coated copper grid. Microscopic characterizations were performed using a high-resolution transmission electron microscopy (HRTEM, JEM-3000F, JEOL) with electron energy-loss spectrometer (EELS, Gatan-666). EELS were collected using a nanobeam (~1.0 nm).

3. Results and discussion

3.1. B–C–N nanotubes

Fig. 1 shows the SEM images of the product obtained from the pyrolysis of DMAB on Fe nanoparticles. Fiber-like structures are abundant in the images. Notably, they are usually entangled together. Fig. 2A displays a typical TEM image revealing that the fiber-like structures are nanotubes. The nanotubes generally have diameters of 30–50 nm. All the nanotubes exhibit hollow cores albeit not hollow through the entire tube length. In fact, continuous compartments are formed in the tube core area with cross-linked layers. Some particles in darker contrast are also clearly seen at the nanotube tip ends, which identified to be Fe-rich species. This indicates that Fe nanoparticles act as the catalyst for the nanotube growth.

Fig. 2B depicts the high-resolution TEM image of a typical nanotube. The cross-linked layers in the tube core area are very apparent. The inter-layer spacings in the wall fragments are measured to be ~0.34 nm, close to the inter-plane distances of (002) in graphite or BN. EELS analyses revealed that these nanotubes are composed of B, C, N with distinct adsorption edges at 188, 284, 401 eV (Fig. 2C and D). The spectra in Fig. 2C and D are collected from locations 1 and 2 in the same nanotube as indicated in Fig. 2B, respectively. The atomic ratio of B to N in the spectra was always close to unity (B:N ≈ 1). However, the C concentrations to B (or N) are quite different. In Fig. 2C, the C atomic ratio to BN was quantified to be approximate 1.8–2.0, i.e. BCₓN (x ≈ 1.8–2.0). This elemental composition is very close to BCₓN. On the other hand, the C atomic ratio to BN is much less in Fig. 2D. The quantification result gave a composition formula expressed as BCₓN (x ≈ 0.2–0.3).

It thus may conclude that the nanotube is enriched in C near location 1 while the vicinity near location 2 is composed of almost pure BN. So the C to BN atomic ratios may change dramatically in different parts even in one individual nanotube. This feature may be useful to controllably synthesize a variety of B–C–N nanostructures with different compositions [22–24]. It appears that the composition variance also induces some morphology changes. As can be seen in Fig. 2B, the nanotube segment near location 1 is stacked up with very short compartments while the part near location 2 consists of somewhat elongated ones.

When Ni nanoparticles were used, abundant nanotubes were also obtained. Fig. 3 depicts the typical TEM images. The diameters of the nanotubes are very similar to the Fe-catalyzed ones, ranging 30–50 nm. Nanoparticles, which are identified mainly containing Ni, are also encapsulated in the tube ends. Fig. 3B clearly shows the tip part of a nanotube containing a wedge-shaped encapsulation. The inset in Fig. 3B is the electron diffraction pattern from the tip. It can be indexed to be [001] zone axis projection of cubic metallic Ni. The wedge-shape of Ni particles is very different from the case of Fe catalysts, which are
droplet-shaped. Fig. 3C is a HRTEM image of a typical Ni-catalyzed nanotube. In contrast with the Fe-catalyzed nanotubes, it does not exhibit apparent compartments or interlinks in the tube core area.

EELS measurements identified that the Ni-catalyzed nanotubes are also B–C–N (Fig. 3D). The quantifications showed that the concentrations of C to B (or N) are generally higher than 3.0 (i.e. $\text{BC}_x\text{Ni}_y$, $x > 3.0$). That is, the carbon concentration in the Ni-catalyzed nanotubes is much higher than that of Fe-catalyzed ones. It is most likely that the difference in carbon concentrations is derived from the effect of catalyst species. It has been proposed that Ni catalyst yields the formation of C–N bonds in a graphitic environment while Fe gives rise to C–N pyridine-like bonds [16]. When the C is alloyed with Fe (i.e. carbide phase), the melting point of Fe drops and the Fe catalysts are supposed to be in the molten state. This might be the reason why the Fe encapsulates are in droplet-shapes. Carbon is also able to form an alloy with Ni. However, N–Ni alloy formation is

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Fig. 2. TEM and EELS characterizations of Fe-catalyzed B–C–N nanotubes. (A) A typical TEM image. Note the cross-linked layers in the tube core area and Fe particles in darker contrast at the tips. (B) A typical HRTEM image. The locations 1 and 2 are indicated where the spectra were collected. (C and D) EELS from locations 1 and 2, respectively. Both have elemental compositions of B (188 eV), C (284 eV) and N (401 eV). It is apparent that the carbon concentrations are different in the two spectra.

Fig. 3. (A) TEM images of Ni-catalyzed B–C–N nanotubes. (B) The wedge-shaped encapsulate at the tip is cubic Ni. (C) HRTEM of a Ni-catalyzed nanotube. (D) EELS reveals that the Ni-catalyzed nanotubes have more carbon content than Fe-catalyzed ones.
almost unlikely to happen. As the result, Ni–catalyzed nanotubes may have higher carbon concentration.

3.2. BN nanotubes

Fig. 4 shows the SEM images of the product synthesized from NaBH₄ + NH₄Cl precursor. Some short tube-like structures are observed in the product (Fig. 4A and B). The diameters of the tubes are somewhat huge (100–300 nm). The tubes clearly exhibit hollow cores. As shown in Fig. 4B, the cross sections of the tubes are generally cylindrical. Some ring-like structures were also identified in the product (Fig. 4C). It seems reasonable to consider that the tubes are grown from these ring-like embryos.

In the product, some tiny and long fibers were also encountered (Fig. 4D). Under TEM, they were characterized to be nanotubes with diameters 3–30 nm. Fig. 5A and B depict two tiny nanotubes with only four layers and a few nanometers in the diameter. One of the 4-layer tubes is empty (Fig. 5A), the other is filled with some amorphous based materials (Fig. 5B). The nature of the filling is not well understood. Preliminary characterizations gave indications that it might be amorphous boron-rich species. The perfect ordering of the wall layers in the two 4-layer nanotubes are significantly different from that of B–C–N nanotubes. It is also noteworthy that they do not encapsulate any metallic particles at the tips as observed in B–C–N nanotubes. A typical EELS is shown in Fig. 5C. It only detects the existence of B–K and N–K at 188 and 401 eV, respectively, with no apparent incorporation of C (C–K at 284 eV). So the nanotubes comprise of stoichiometric BN, free from carbon.

Fig. 6A shows another intriguing multi-wall BN nanotube. The nanotube appears to have terminated the growth suddenly, leaving a growth front as indicated by arrows. Based on the TEM image, a model for the probable nanotube growth is illustrated in Fig. 6B. It is believed that the nanotubes are grown in a layer-by-layer sequence. The previously formed layer acts as the template for the subsequent layers. This layer-by-layer sequence does not indicate that the growth must be a single layer following a single layer. A few layers may be growing simultaneously.

Fig. 4. SEM images of the product synthesized from NaBH₄ + NH₄Cl. (A and B) Huge tubes (100–300 nm). (C) Ring-like structures are regarded as embryos for the tubes. (D) Occasionally observed tiny and long fibers.

Fig. 5. TEM images of one empty (A) and one filled (B) 4-layer nanotubes. The perfect ordered wall layers are very significant. (C) EELS identifies that the nanotube are of stoichiometric BN composition free from carbon.
The peripheric velocities of these layers are likely to be different, causing an elliptical growth front as depicted in Fig. 6B. There have been some growth mechanisms suggesting that the chemical bonding between adjacent coaxial layers, i.e. lip–lip interactions, can stabilize the open ends of multi-layer carbon nanotubes [25]. The open end geometry enables a high degree of chemical activity and easily accommodates incoming carbon atoms. Due to the structural similarity between carbon and BN, we suspect that the open ends of BN nanotubes can also be stabilized by such lip–lip interactions. BN feeding also happens to the open ends when the tube growth occurs.

4. Conclusions

We have revealed that B–C–N nanotubes could be synthesized from DMAB with the use of either Fe or Ni catalysts. The different chemical compositions in an individual nanotube as well as morphological change were characterized. The catalyst species play a role in affecting the carbon concentrations of the resultant nanotubes. It may be useful for the rational synthesis of B–C–N nanotubes with various elemental compositions. BN nanotubes were also successfully produced from H₃N:BH₃, which were in-situ generated employing NaBH₄ + NH₄Cl. The nanotube quantity from pyrolyzing H₃N:BH₃ is relatively low. Further work is under way to explore the optimal growth of BN nanotubes from this promising precursor.

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