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## Synthesis of boron nitride nanotubes from carbon nanotubes by a substitution reaction

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A method involving carbon nanotubes substituted reaction was developed for the synthesis of mass quantities of boron nitride nanotubes. Boron oxide vapor was reacted with nitrogen gas in the presence of carbon nanotubes to form boron nitride nanotubes, whose diameters and lengths are similar to those of the starting carbon nanotubes. It is proposed that carbon atoms of carbon nanotubes can be fully substituted by boron and nitrogen atoms through a general chemical reaction. The results suggest that the synthesis methodology developed here may also be extended to form nanotubes from other novel materials. © *1998 American Institute of Physics*. [S0003-6951(98)02447-4]

Boron nitride nanotubes (BN-NTs), whose electronic properties are independent of helicity and the number of layers according to theoretical predictions<sup>1</sup> offer highly promising for the creation of nanostructure electronic devices. BN-NTs have recently been synthesized by arc-discharge<sup>2,3</sup> high pressure laser heating<sup>4</sup> and oven-laser ablation,<sup>5</sup> but these methods have only resulted in low yields. Here we show that a simple and easily accessible technique involving a carbon nanotubes (CNTs) substituted reaction can generate mass quantities of BN-NTs.

Since the discovery of CNTs,<sup>6</sup> this hollow nanostructure has been used as a template to produce new one dimensional nanoscale materials by filling,<sup>7–9</sup> coating,<sup>9,10</sup> and confined reaction (carbide<sup>11,12</sup> and nitride nanorods<sup>13–15</sup>) (Fig. 1). In the present study, we claim that CNTs could be exploited as templates to prepare other nanotubes. We call this method CNTs substituted reaction, which means that through this chemical reaction the carbon atoms of CNTs are substituted reaction is quite different from the CNTs confined reaction<sup>13</sup> because the latter results in solid rod-like nanostructures, rather than hollow nanotubes.

For confirming the speculated CNTs substituted reaction, BN-NTs were chosen to be synthesized because BN-NTs have the same layered structure and also close lattice constants compared with CNTs. The designed reaction can be expressed as

 $B_2O_3+3C$  (nanotubes)+ $N_2\rightarrow 2BN$  (nanotubes)+3CO.

It was expected that boron oxide gas generated from the  $B_2O_3$  powder would flow up towards the region containing the carbon nanotubes and react with the nanotubes and the nitrogen (N<sub>2</sub>) gas.

The reaction was carried out in an induction-heating system with susceptors made of graphite.  $B_2O_3$  powder was placed in an open sintered graphite crucible and then covered with CNTs. Relatively pure multishell CNTs with typical

diameters of approximately 10 nm used here were prepared by a metal-catalyzed chemical vapor deposition (CVD) method. The crucible was held in a flowing nitrogen atmosphere at 1773 K for 0.5 h.

After the crucible from the furnace was recovered, the starting black carbon nanotubes were found to have turned into a grey colored layer of a wool-like product. The product and the starting CNTs were characterized with Ragaku RINT 2000 x-ray diffractometer (XRD) with Cu  $K\alpha$  radiation. Figure 2(a) is an XRD pattern of the product, which is identified as a mixture of hexagonal BN (h-BN) (two-layered repeating units) and the rhombohedral BN (r-BN) (three-layered repeating units). As can be seen from Fig. 2(a), the intensity of the peak assigned to (100) *h*-BN is almost the same with that of the peak assigned to (101) r-BN, indicating that the content of the h-BN is almost the same with that of r-BN in the product. For the product the strongest peak corresponding to both (002) h-BN and (003) r-BN has a distinguished lower value (0.335 nm) compared to that (0.345 nm) of the starting CNTs [Fig. 2(b)]. It was also clear that the degree of crystallization of the BN product is better than that of the starting CNTs.



FIG. 1. Schematic illustrations of carbon nanotubes as a template to produce new one dimensional nanoscale materials by (a) filling, (b) coating, (c) carbon nanotubes confined reaction to produce carbide and nitride nanorods, and (d) carbon nanotubes substituted reaction to produce boron nitride nanotubes.

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FIG. 2. X-ray diffraction patterns of (a) product, which is identified as a mixture of hexagonal and the rhombohedral BN, and (b) starting carbon nanotubes.

The product was characterized by high resolution lattice images with the use of a field emission type transmission electron microscope (TEM) (JEOL-3000F), operating at 300 kV, equipped with an apparatus for both energy dispersive x-ray spectroscopy (EDS) and parallel recording electron energy loss spectroscopy (EELS).<sup>16</sup> EELS experiments were performed by using a stationary focused 1 nm electron probe with a Gatan spectrometer. Figures 3(a) and 3(b) are typical high resolution TEM micrographs showing a general view of the starting CNTS and the product, respectively. Abundant nanotubes are visible in the product [Fig. 3(b)], and they appear either as the individual nanotubes or as the bundles. The interplanar spacing of these nanotubes is approximately 0.335 nm, which is consistent with the interplanar distance 0.333 nm in both bulk h-BN and r-BN. These nanotubes have relative straight fringes indicating a well ordered structure, which is consistent with the result of XRD. The diam-



This a FIG. 3. High resolution TEM images of (a) starting carbon nanotubes, and (b) boron nitride nanotubes.



FIG. 4. A typical EELS core electron K-shell spectrum taken from an individual BN-NT.

eters of these nanotubes are a few nanometers and lengths are up to a few micrometers, which are similar to the diameters and the lengths of starting CNTs. A few of encapsulated nanocages and nanowires were also observed in the product.

EELS spectra showed that the nanotubes in the product were all BN-NTs. A typical EELS spectrum from an individual nanotube corresponds to B-N  $sp^2$  bonds (Fig. 4). Two distinct absorption features are revealed, one starting at 188 eV and another at 401 eV, corresponding to the known B-K and N-K edges, respectively. Noteworthy is the absence of the feature at 284 eV, the K-edge absorption for carbon. The B/N ratio of this spectrum is determined to be approximately 1.02, which is consistent with a stoichiometry of BN (due to uncertainties in background subtraction, the calculated B/N ratio has an estimated error of 20%). The EELS spectra revealed that the nanowires and the nanocage shells were also BN. EDS measurements showed that the nanoparticles encapsulated inside the BN nanocages were iron, which was used as a catalyst for the synthesis of the starting CNTs and was encapsulated inside the starting CNTs.

In summary, the successful preparation of BN-NTs with the average diameters and lengths similar to the starting CNTs confirms the applicability of this method—CNTS substituted reaction. Although the final BN-NTs nanotubes do not contain carbon element, CNTs may play an important role as precursors and in particular supply the skeletons for the growth of BN-NTs during the substitution reaction. After fully substituting the carbon atoms of CNTs by B and N atoms, the B and N atoms of BN-NTs may be involved in a rearrangement process for more suitable and ordered positions at high temperature. Although a deeper understanding of the BN-NTs growth mechanism is clearly needed, we note that this simple and cheap CNTs substituted reaction technology could in principle produce BN-NTs of any quantity. Only sufficient amount of CNT is needed, which have been synthesized in a large quantity<sup>17,18</sup> and are commercially available. The CNTs substituted reaction developed here is easily accessible to others with an interest in BN-NTs and may also be extended to form nanotubes of other novel materials (for instance, the  $B_x N_y C_z^{19-21}$  or C-BN-C sandwich structure<sup>22</sup> nanotubes). The ready availability of large amounts of these nanotubes should offer more opportunities for both new fundamental science and useful nanotechnological applications.

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