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A novel precursor for synthesis of pure boron nitride nanotubes†

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Received (in Cambridge, UK) 1st March 2002, Accepted 9th May 2002
First published as an Advance Article on the web 21st May 2002

A novel precursor, a mixture of B_2O_2 and Mg which is generated *in situ* by reacting B and MgO at 1300 °C, can be used to effectively synthesize bulk amounts of pure BN nanotubes with Mg evaporated from the final product; transmission electron microscope observation for the synthesized BN nanotubes indicates that defects present strongly depend on the tube diameter.

Much research on boron nitride nanotubes has followed the discovery of carbon nanotubes.[1] In view of the structural similarity of graphite and bulk BN, it is usual to discuss the properties and formation mechanism of BN nanotubes in terms of carbon nanotube models. However, BN nanotubes should exhibit unique physical and chemical properties that are obviously different to those of carbon nanotubes. The electronic structure of a pure carbon nanotube is known to be either metallic or semiconducting, depending on the tube diameter, wrapping angle, twisting and topological defects,[2] while BN nanotubes exhibit a wide band gap of about 5 eV that is insensitive to tube diameter and chirality but could be controlled by chemical composition,[3] a phenomenon that has been attributed to the ionic origin of the band gap.

Strong ionic B–N bonding should also have an influence on the formation of BN nanotubes. Indeed, BN nanotubes have been synthesized using methods similar to those used to form carbon nanotubes, such as arc-discharge,[4] laser ablation,[5] and chemical vapor deposition (CVD).[6] Many other novel synthesis methods have also been proposed such as carbon nanotube- and template-confined methods.[7] However, to our knowledge, there is no reliable method to produce bulk amounts and more importantly, impurity-free BN nanotubes. The low quantity and/or impure BN nanotubes produced so far have made the characterization of certain physical and chemical properties difficult, if not impossible.[8] Therefore, large-scale and impurity-free synthesis of BN nanotubes is desired, and has attracted intense recent interest. Recently, bulk quantities of double-wall and single-walled BN nanotubes have been synthesized *via* the improved arc-discharge method and continuous laser vaporization.[8,9]

CVD of catalytic decomposition of carbonaceous vapors has been confirmed to be an effective method for the large-scale synthesis of pure carbon nanotubes. However, the synthesis of BN nanotubes has been hindered by carbon contamination when employing the CVD method, because carbon is the first solid phase to appear upon cooling vapors containing B, N and C.[10] Therefore, the key to the synthesis of pure BN nanotubes is to design a carbon-free precursor and catalyst. Very recently, some success has been achieved in growing BN nanotubes on nickel boride catalysts from the dangerous carbon-free precursor borazine.[6] In fact, an earlier work showed that some specially designed chemical reactions might result in the formation of BN tubular structures,[11] and that the size of catalysts within the framework of vapor–liquid–solid growth mechanism[12] plays an important role in defining the nanoscale size of one-dimensional structures. Therefore, we have recently been studying inorganic carbon-free precursors and catalysts for using the CVD method to synthesize bulk amounts of pure BN nanotubes.[13]

The method described here produces pure and large-scale BN nanotubes without introducing transition metals as catalysts. BN nanotubes as the only resultant phase present in the reaction area; other reactants, which mainly consist of metaliic magnesium, are evaporated and transported far from the product area.

A mixture of boron and magnesium oxide (with molar ratio of 1 : 1) located in a BN-made reaction tube was heated to 1300 °C using an RF inducting furnace. At this temperature, boron reacted with MgO to form B_2O_2 and Mg vapor.[14] The vapors were argon-transported into a reaction chamber the temperature of which was controlled to *ca.* 1100 °C and a flow of ammonia was then introduced. BN was synthesized by the simple reaction of B_2O_2 and ammonia. The chemical reactions are given by eqns. (1) and (2):

$$2B\ (s) + 2MgO\ (s) \rightarrow B_2O_2\ (g) + 2Mg\ (g) \tag{1}$$

$$B_2O_2\ (g) + 2NH_3\ (g) \rightarrow 2BN\ (s) + 2H_2O\ (g) + H_2\ (g) \tag{2}$$

After fully evaporating the mixture (1.55 g), 310 mg of white product could be collected from the BN wall of the chamber. The conversion rate from boron to boron nitride reached up to 40%.

The phase purity of the product was examined by X-ray diffraction (XRD) using Cu-Kα radiation. All of the reflections of the XRD pattern could be indexed to a mixed phase of hexagonal and rhombohedral BN (Fig. S2, ESI†), no peaks associated with B_2O_3, turbostratic BN[15] or other crystalline forms related with the starting reactants could be detected in the pattern, indicating the product is of high purity and crystallinity.

Scanning electron microscope observations show that the product only exhibits a one-dimensional nanostructure with the diameter ranging from several nanometers to about 70 nm, and a length of up to 10 micrometers. Fig. 1(a) shows the typical resulting morphology of curved nanotubes twisted around one another. The transmission electron microscopy (TEM) image shown in Fig. 1(b) establishes that the nanostructures having a small diameter around 10 nm are straight nanotubes with concentric-tube structures that do not contain internal wall closures or internal cap structures; defects usually observed for BN nanotubes with large diameters. We also found that the defects strongly depend on the tube diameters. For nanotubes with diameter of around 60 nm, the inner diameter of nanotubes gradually decreases until an internally closed segment occurs (marked by arrow in Fig. 1(b)). Such defect morphology has been reported for BN nanotubes with large diameters synthesized by chemical reactions without obvious catalyst assistance.[16,4] For medium diameters of about 30 nm, the coaxial nanotubes grow inside the outer nanotubes to form an internal cap structure (Fig. 2(a)). The nanotubes of diameter around 10 nm exhibit a perfectly cylindrical structure, although edge dislocations can be occasionally observed from the rhombohed-

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† Electronic supplementary information (ESI) available: (a) experimental apparatus and details; (b) Fig. S2, XRD pattern of BN nanotubes; (c) XRD pattern of the product formed by dispersive Mg at the surface of the graphite susceptor; (d) Fig. S4, EELS spectrum of BN nanotubes; (e) Fig. S5, selected-area electron diffraction; (f) Fig. S6, EDS analysis of open tip. See http://www.rsc.org/suppdata/cc/b2/b202177c/

DOI: 10.1039/b202177c

rally stacking ordered nanotubes (Fig. 2(c)), which are common defects of nanotubes caused by the inherent strain in concentric nanotubes.[17,18]

Regardless of the defects, all nanotubes exhibit the parallel-fringe patterns characteristic of multi-walled BN nanotubes in the high-resolution TEM images and only contain boron and nitrogen with a B : N ratio of about 1, as estimated from the measurements of electron energy loss spectroscopy. In addition, after examining a considerable number of diffraction patterns we found that BN nanotubes exhibit a near zigzag arrangement (see Fig. S5, ESI†).[17]

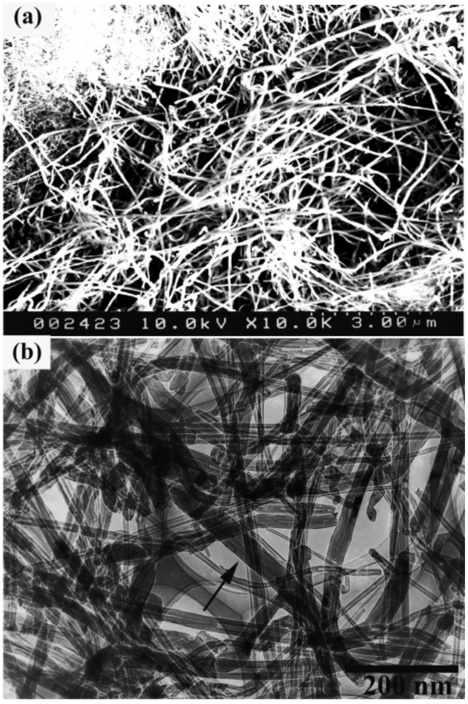

Fig. 1 (a) SEM images from the product; (b) typical TEM image showing the morphology of the nanotubes.

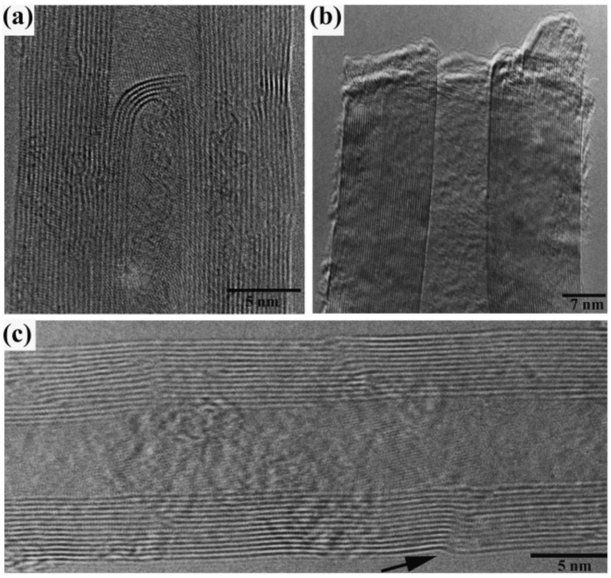

Fig. 2 High-resolution TEM images of individual BN nanotubes: (a) coaxial BN nanotube, (b) BN nanotube tip with fracture surface, (c) morphology of BN nanotubes with small diameter, the arrow points to an edge dislocation. The lattice contrasts in the inner part of the BN nanotubes are due to part of the layers lying normal to the electron beam.

It is worth noting that independent of their diameter, most nanotubes possess an open tip usually showing irregular fracture surfaces (Fig. 2(b)). Moreover, we also occasionally observed some encapsulated matter near the fracture surface. Energy-dispersive X-ray analysis shows that the inclusion consists of N, Mg, B, O and Si (Fig. S6, ESI†, Mg–Si–O solid solutions usually possess a high melting point from 1600 to 2000 °C and low saturated vapor pressure). Silicon probably arises from contamination from the reactants or the chamber. We therefore speculate that magnesium should exist at the end of BN nanotubes during the growth process, and that nanotube growth is also based on the vapor–liquid–solid mechanism. The liquid-phase magnesium could be expected to deposit on the walls of BN boat, act as a catalyst, and then evaporate after reaction. However, the proposed growth mechanism is speculative since we have not found any solidified Mg particles at the tube tip. Indeed, it has been reported that BN nanotubes could be synthesized without the assistance of any catalyst.[4,8,16]

The synthesis of large-scale and impurity-free BN nanotubes indicates that a mixture of boron and magnesium oxide can be used to be an effective precursor, since it does not contain carbon impurities and the byproduct magnesium can be easily removed. Although the formation mechanism warrants further investigation, we believe that pure BN nanotubes with uniform diameter distribution could be obtained by using a nanoscale-supported catalyst.

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