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Boron nitride nanotubes and nanowires

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Abstract

Simple methods of preparing boron nitride nanotubes and nanowires have been investigated. The methods involve heating boric acid with activated carbon, multi-walled carbon nanotubes, catalytic iron particles or a mixture of activated carbon and iron particles, in the presence of NH_3. While with activated carbon, boron nitride nanowires constitute the primary product, high yields of clean boron nitride nanotubes are obtained with multi-walled carbon nanotubes. Aligned boron nitride nanotubes are produced when aligned multi-walled carbon nanotubes are employed as the starting material suggesting the templating role of the nanotubes. Boron nitride nanotubes with different structures have been obtained by reacting boric acid with NH_3 in the presence of a mixture of activated carbon and Fe particles.

1. Introduction

Nanotubes and nanorods of boron nitride (BN) have attracted considerable attention in the last two years. Nanotubes of BN were first prepared by Chopra et al. [1] by a carbon-free plasma discharge between a BN-packed tungsten rod and a cooled copper electrode. Arc discharge between ZrB_2 electrodes in a nitrogen atmosphere also yields BN nanotubes [2]. BN nanotubes have been prepared by the carbothermal reduction of ultradisperse amorphous boron oxide and B_4C in the presence of nitrogen between 1100 and 1450 °C [3], and by thermal annealing of ball-milled boron powder in an ammonia atmosphere [4]. Most of the recent efforts, however, employ chemical methods involving suitable catalysts. Thus, Lourie et al. [5] have synthesized BN nanotubes by the CVD deposition of borazine over nickel boride catalyst particles at a temperature of about 1100 °C. A chemical vapor deposition route employing melaminediborate at 1700 °C yields BN nanotubes, although the material occurs along with amorphous B–N–O clusters [6]. Carbon nanotubes have been used to prepare BN nanotubes by the reaction with B_2O_3 in a nitrogenous atmosphere. Thus, Golberg et al. [7] have synthesized multi-walled BN nanotube ropes by carrying out the reaction of

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a mixture of B_2O_3 and multi-walled carbon nanotubes (MWNTs) at 1500 °C in a nitrogen atmosphere in the presence of a MoO_3 catalyst. Tang et al. [8] have obtained nanotube and nanobamboo structures of BN by the reaction of boron and iron oxide in flowing ammonia gas in the 1200–1500 °C range.

It was our interest to develop simple chemical methods for preparing BN nanotubes and nanowires and have explored various strategies for this purpose. We find that a variety of BN nanotubes and nanowires can be readily produced by the reaction of boric acid with ammonia in the presence of activated carbon or carbon nanotubes, with or without catalytic iron particles. By using aligned carbon nanotube bundles, we have obtained aligned BN nanotubes. Furthermore, the temperature of the reaction can be as low as 1000 °C. In these preparations, NH_3 acts as a nitriding agent and also provides the reducing atmosphere, required for the reaction. Since we submitted this Letter for publication, we have noticed that Han et al. [9] have employed the reaction between B_2O_3 and NH_3 in the presence of carbon nanotubes to obtain $B_xC_yN_z$ nanotubes. We, however, obtain pure BN nanotubes which get collected at the mouth of the reaction tube after sublimation.

2. Experimental

In order to prepare BN nanotubes and nanowires, the following methods of synthesis were employed. Procedure (i) involved the carbothermal reduction of a mixture of activated carbon and boric acid in the presence of ammonia at 1300 °C. The activated carbon was prepared by decomposing polyethylene glycol (600 units) in argon atmosphere at 700 °C for 3 h [10]. An intimate mixture of finely ground activated carbon and H_3BO_3 (mole ratio 3:1) was taken in an 8 mm quartz tube closed at one end, and held vertically inside a larger quartz tube placed in a tubular furnace. NH_3 gas was passed through the quartz tube (flow rate 10 sccm) and the temperature of the furnace, maintained initially at 200 °C for 2 h, was slowly raised to 1300 °C and maintained at that temperature for 3 h. Procedure (ii) was similar to procedure (i), except that a mixture of 0.36 g of multi-walled carbon nanotubes and 0.62 g boric acid was taken in the inner quartz tube. Reactions with the carbon nanotubes were also performed at a lower temperature of 1000 °C. Multi-walled carbon nanotubes were prepared by the arc evaporation of graphite while aligned carbon nanotube bundles were prepared by the pyrolysis of ferrocene in the presence of acetylene at 1100 °C [11].

Procedure (iii) employed a homogeneous solution of an iron catalyst and H_3BO_3 in silica gel as the starting material. About 0.6183 g of H_3BO_3 (0.1 mol) and 0.404 g of $Fe(NO_3)_3 \cdot 9H_2O$ (0.001 mol) were dissolved in 20 ml methanol. To this solution, 2 ml of tetraethylorthosilicate (TEOS) was added and stirred for 20 min. About 1.5 ml of 48% HF was added dropwise and the solution stirred till it formed a gel. This gel was dried at 60 °C for 12 h and was powdered. This homogeneous mixture containing finely divided Fe particles was calcined at 200 °C and subsequently heated in NH_3 (flow rate, 10 sccm) at 1200 °C for 4 h. In procedure (iv), an intimate mixture of 0.36 g of activated carbon with 0.618 g of H_3BO_3 and 0.404 g of ferric nitrate (mole ratio of 3:1:0.1) was dried in the oven at 60 °C for 6 h, and then heated in a flow of NH_3 (flow rate, 10 sccm) at 1300 °C for 4 h.

The products in the above procedures were generally obtained as light grey powders formed at the bottom of the inner quartz tube. White deposits formed at the mouth of the inner quartz tube and also at the outlet of the outer quartz tube. The white product was identified as pure BN. The grey product had some carbon depending on the carbon content in the starting composition.

X-ray diffraction (XRD) patterns of the products were recorded using the Seifert (XRD, XDL, TT, and Cu target) instrument. Scanning electron microscope (SEM) images were obtained with a Leica S-440 i microscope. Transmission electron microscopic (TEM) images were obtained with a JEOL (JEM 3010) operating with an accelerating voltage of 300 kV. Powder samples for TEM were dispersed in CCl_4 using an ultrasonic bath, and a drop of the suspension placed on a copper support grid covered with holey carbon film. X-ray photoelectron spectra of the BN nanotubes were recorded with an ESCALAB MKIV spectrometer employing AlKα radiation (1486.6 eV) to establish the composition.

3. Results and discussion

All the four procedures employed by us gave BN nanotubes although their yields varied from one method to another. By procedure (i), involving the reaction of H_3BO_3 with activated carbon and NH_3, we obtained a high proportion of nanowires. The reaction of H_3BO_3 with carbon nanotubes and NH_3, however, gave a high yield of BN nanotubes at a relatively low temperature of 1000 °C. While the reaction of H_3BO_3 with NH_3 in the presence of a Fe catalyst gave a mixture of nanotubes and nanowires at 1200 °C, the reaction of H_3BO_3 with NH_3 in presence of the Fe catalyst and activated carbon at 1300 °C yielded nanotubes with varied structures. The nanostructures obtained by the various methods generally showed the hexagonal structure ($a = 2.54$ Å, $c = 6.70$ Å; JCPDS file: 34-0421), but were in mixture with a small proportion of the rhombohedral structure, of the type reported by Tang et al. [8] and Golberg et al. [12], in some of the preparations.

In Fig. 1a, we show an SEM image of the nanostructures obtained by reacting a mixture of H_3BO_3 and activated carbon with NH_3 at 1300 °C by procedure (i). These nanostructures comprise of both nanowires and nanotubes as revealed by the TEM investigations. We show typical TEM images of single crystal nanowires in Fig. 1b and of a nanotube in Fig. 1c. While the nanowires have a

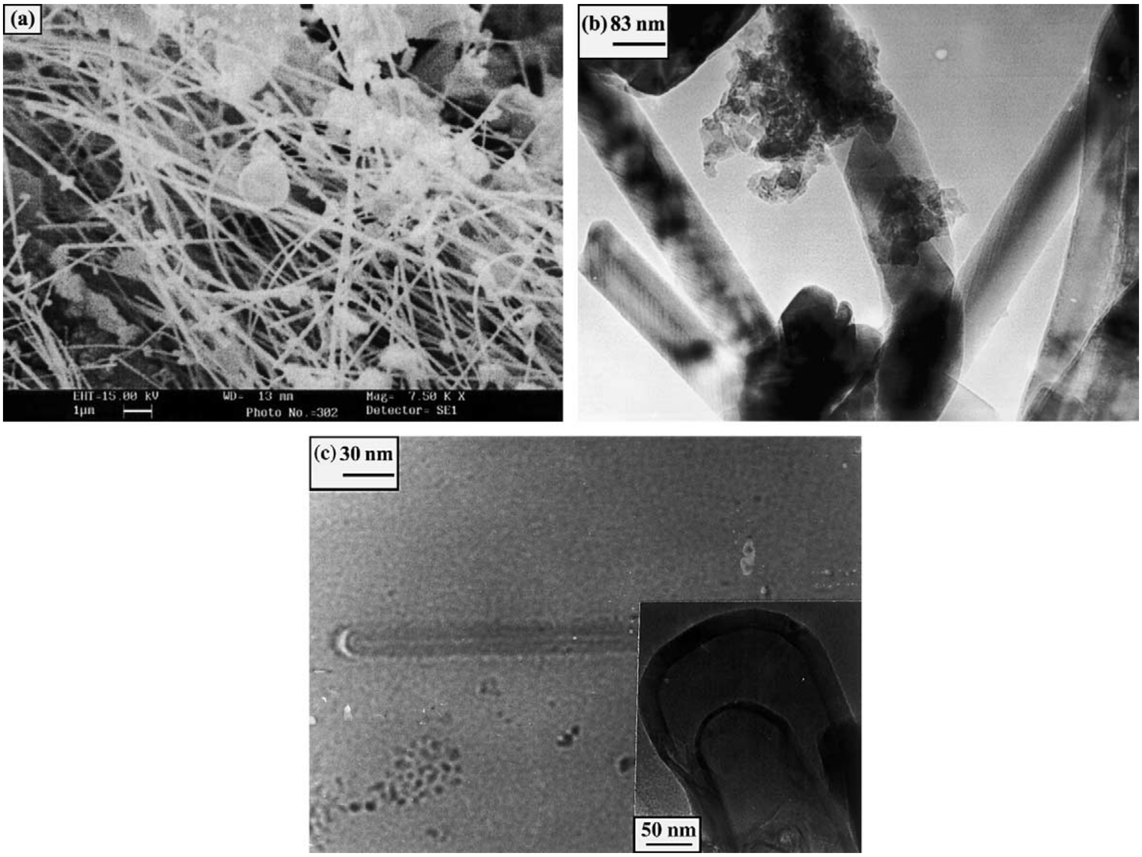

Fig. 1. Nanostructures obtained by the reaction of H_3BO_3 and activated carbon with NH_3 by procedure (i): (a) SEM image; (b) TEM image of nanowires; (c) TEM image of a nanotube. Inset shows an interesting nanotube in a nanotube.

diameter in the range of 75 nm, the nanotube has an outer diameter of 20 nm. The inset in Fig. 1c shows a BN nanotube, inside a bigger one. This procedure gave nanowires as the majority product rather than nanotubes. The basic chemical reaction involved here can be written as,

$$2H_3BO_3 + 3C + 2NH_3 \rightarrow 2BN + 3CO + 3H_2 + 3H_2O \qquad (1)$$

Unlike the reaction of activated carbon with H_3BO_3, the reaction with carbon MWNTs by procedure (ii) gave good yields of BN nanotubes, although the basic chemical reaction remains as (1). While BN nanotubes were obtained with MWNTs prepared by arc-discharge as well as precursor pyrolysis methods, by using aligned MWNT bundles, we could obtain aligned BN nanotube bundles at the bottom of the inner quartz tube as shown in the SEM images in Fig. 2a and b. In Fig. 2c we show the TEM image of pure BN nanotubes obtained at the mouth of the inner quartz tube. The images clearly reveal BN nanotubes aligned in two different orientations and establish that the carbon MWNTs not only take part in the reaction, but also serve as templates. Shelimov and Moskovits [13] have reported that aligned BN nanotubes can be prepared by the decomposition of trichloroborazine on porous alumina templates. The present method appears to be considerably simpler. We show typical TEM images of the individual BN nanotubes in Fig. 3a. The average outer diameter of the nanotubes

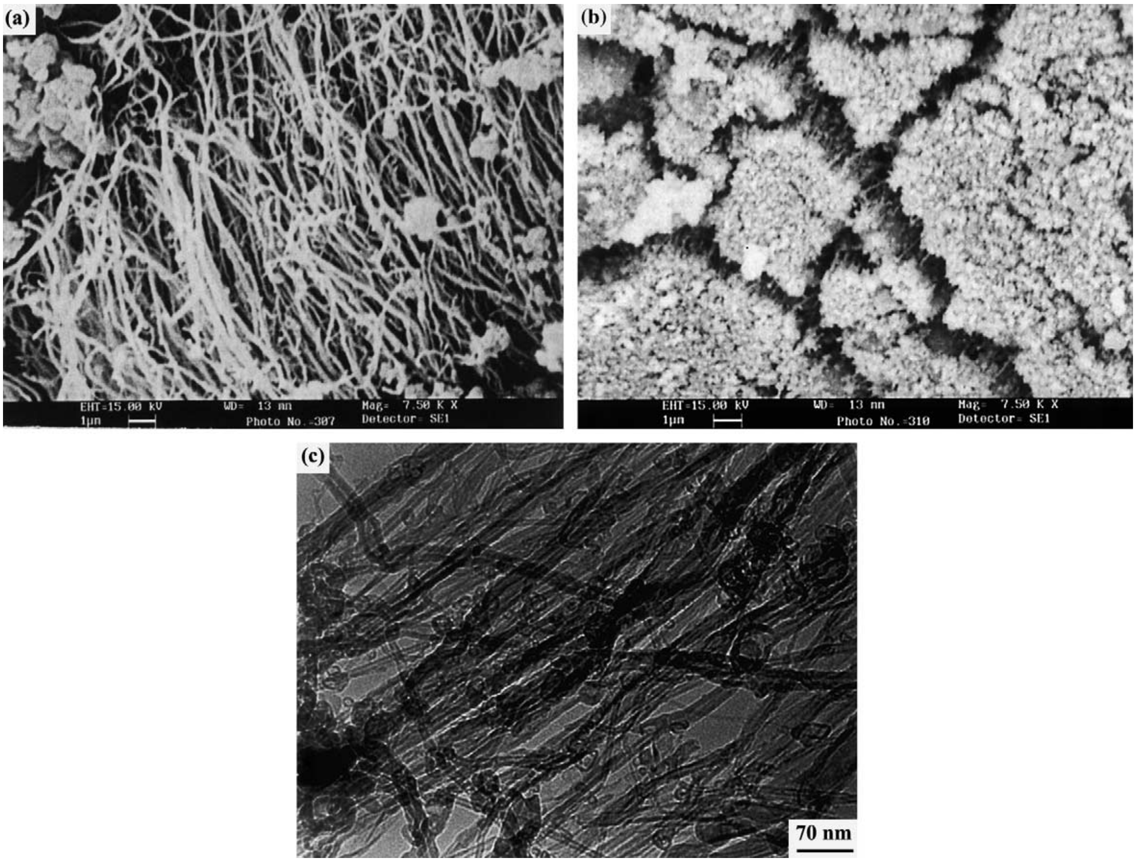

Fig. 2. SEM and TEM images of aligned BN nanotube bundles obtained by the reaction of H_3BO_3 and aligned multi-walled carbon nanotubes with NH_3 by procedure (ii): (a) and (b) give side and top view SEM images, respectively; (c) TEM image of pure BN nanotubes obtained at the mouth of the inner quartz tube.

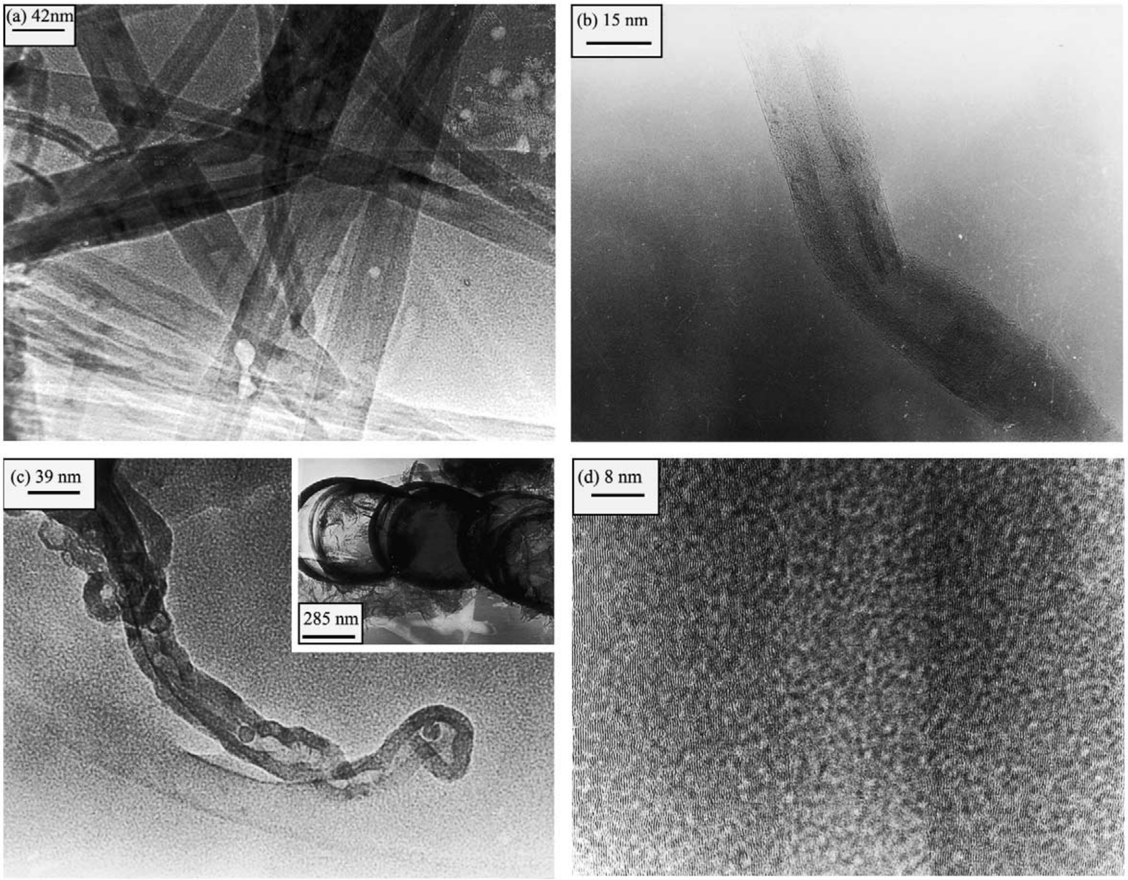

Fig. 3. TEM images of BN nanotubes obtained by procedure (ii): (a) a collection nanotube; (b) a nanotube with an interesting bend or kink; (c) nanotube showing an unusual cap; (d) a high-resolution image indicating the discontinuous lattice planes. Inset in (c) show bulbous structures found occasionally with the nanotubes.

varies from 15 to 40 nm. Fig. 3b reveals an interesting bend or kink of the type generally encountered in multi-walled carbon nanotubes. Fig. 3c shows an interesting BN nanotube tip with a triangular flag-like shape, similar to the one reported by Saito and Maida [2]. Such capped structures in BN nanotubes arise from the presence of odd numbered rings, for example, by introducing four B_2N_2 squares and two B_3N_4 heptagons into the hexagonal network. In the inset of Fig. 3c, we show hairy bulb-like structures with a diameter of 550 nm. The high-resolution TEM image in Fig. 3d shows discontinuous lattice planes with a spacing of 0.33 nm corresponding to the interplanar distance between (0 0 2) planes (0.333 nm in bulk hexagonal BN). The irregularity of the layers may be because of the high beam sensitivity of these nanotubes. An important aspect of the reaction of H_3BO_3 with carbon nanotubes by procedure (ii) is that the reaction temperature can be as low as 1000 °C. BN nanotubes are not obtained at such a low temperature by the other methods of synthesis. Furthermore, there is no need for an additional catalyst in the present procedure.

We have recorded the X-ray photoelectron spectra of the BN nanotubes and nanowires obtained by the different procedures. Core level spectra of these samples gave distinct B(1s) and N(1s) signals at 190 and 398.5 eV, respectively. These binding energy values correspond well with those reported for BN thin films in the literature [14]. After normalizing with respect to the photoionization cross-sections, the intensities of the signals gave B:N ratios close to 1:1. To ensure reproducibility, the samples were subjected to two cycles of Ar etching (4 keV for 15 min). The proportion of boron and nitrogen remained the same after etching. The composition of the white product at the mouth of the reaction tube in procedure (ii) was found to be BN with no carbon. The C/B ratio was, however, high (0.5–3) in the grey samples collected from the bottom of the reaction tube in procedure (ii). Han et al. [9] have obtained such high C/B ratios in $B_xC_yN_z$ nanotubes. This is surprising since the reaction of B_2O_3 with carbon alone gives lower C/B ratios in the range 0.1–0.2 [15]. Furthermore, pure BN nanotubes have been obtained from the reaction of MWNT and B_2O_3 in an atmosphere of N_2 [16]. In order to ensure the composition of the products obtained by procedure (ii), we have varied the C/B ratios in the starting compositions and found that the white powder collected at the mouth of the quartz tube by sublimation always contained pure BN nanotubes without any carbon. We consider the variable C/B ratios in the grey product at the bottom of the reaction tube to be due to the unreacted carbon nanotubes left over after the reaction with boric acid. The oxygen content in the BN nanotubes was negligible. Considering that pure BN nanotubes constitute almost the entire product by procedure (ii), we estimate the conversion of boric acid to BN to be 100%.

We have carried out the reaction of H_3BO_3 and catalytic Fe particles in an ammonia atmosphere at 1300 °C by procedure (iii). We obtain plates and whiskers of BN as shown in the SEM image in Fig. 4a. In addition, nanowires are obtained in small

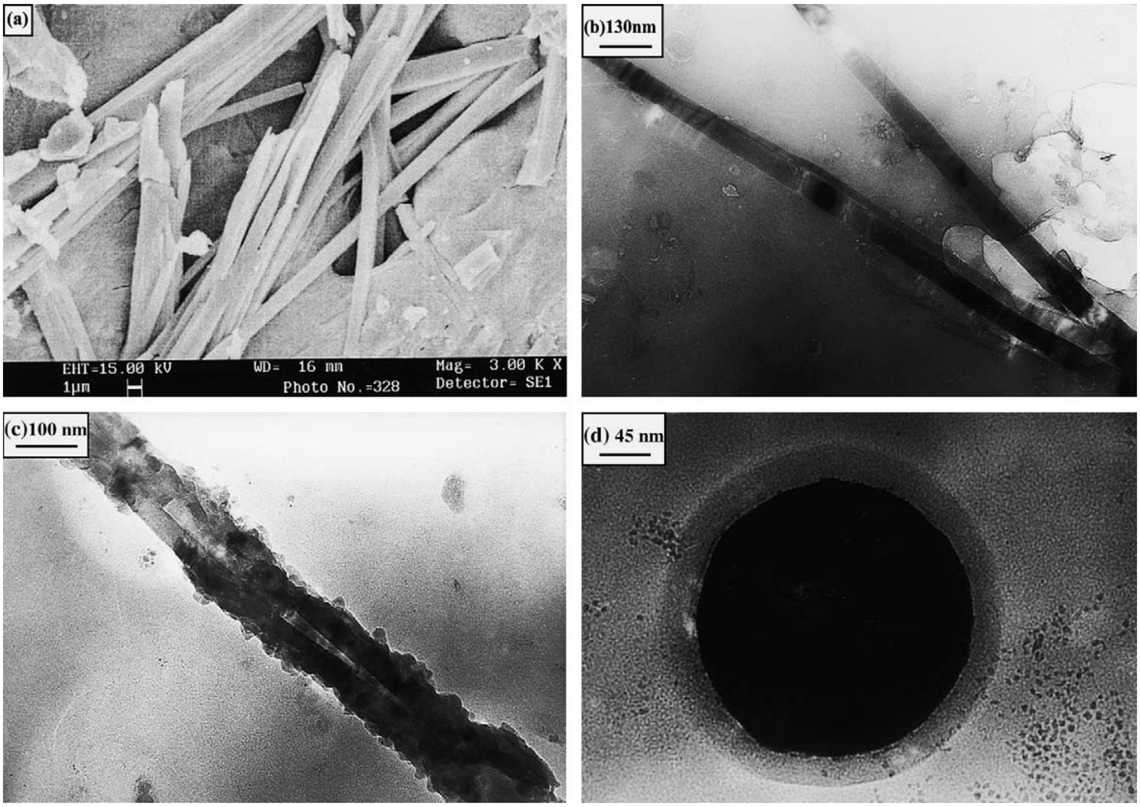

Fig. 4. Nanostructures of BN obtained by the reaction of H_3BO_3 and catalytic Fe particles (dispersed over silica) with NH_3 by procedure (iii): (a) SEM image of plates and whiskers; (b) TEM image of nanowires; (c) TEM image of a nanotube and (d) TEM image of a BN-coated Fe particle.

quantities. We show TEM images of the nanowires in Fig. 4b. The nanowires have a diameter of 60 nm, with the lengths going upto 1 μm. The occasional presence of BN nanotubes is revealed by the TEM image in Fig. 4c. The nanotube has an inner diameter of 30 nm and an outer diameter of 140 nm. Iron particles coated with an amorphous layer of BN are also formed in this procedure, along with nanowires and other structures. We show a typical TEM image of a BN-coated iron particle in Fig. 4d. It appears that the growth of BN nanotubes originally starts by the deposition of amorphous BN onto a metal particle. The BN coating may pull away from the innermost layer and grow outward to form a tube. The tube growth is likely to terminate when a metal particle collides with the growing end of a tube and attaches itself to the dangling bond, forming a stable nitride or boride [1]. The chemical reaction involved in the formation of BN by procedure (iii) is given by

$$2H_3BO_3 + 2Fe + 2NH_3 \rightarrow 2BN + Fe_2O_3 + 3H_2 + 3H_2O \quad (2)$$

The catalytic Fe particles are regenerated by reduction of Fe_2O_3 by H_2. The composition of the nanotubes obtained by procedure (iii) had a B:N ratio of 1:1.

Procedure (iii) using catalytic Fe particles alone is not satisfactory to produce BN nanotubes. We

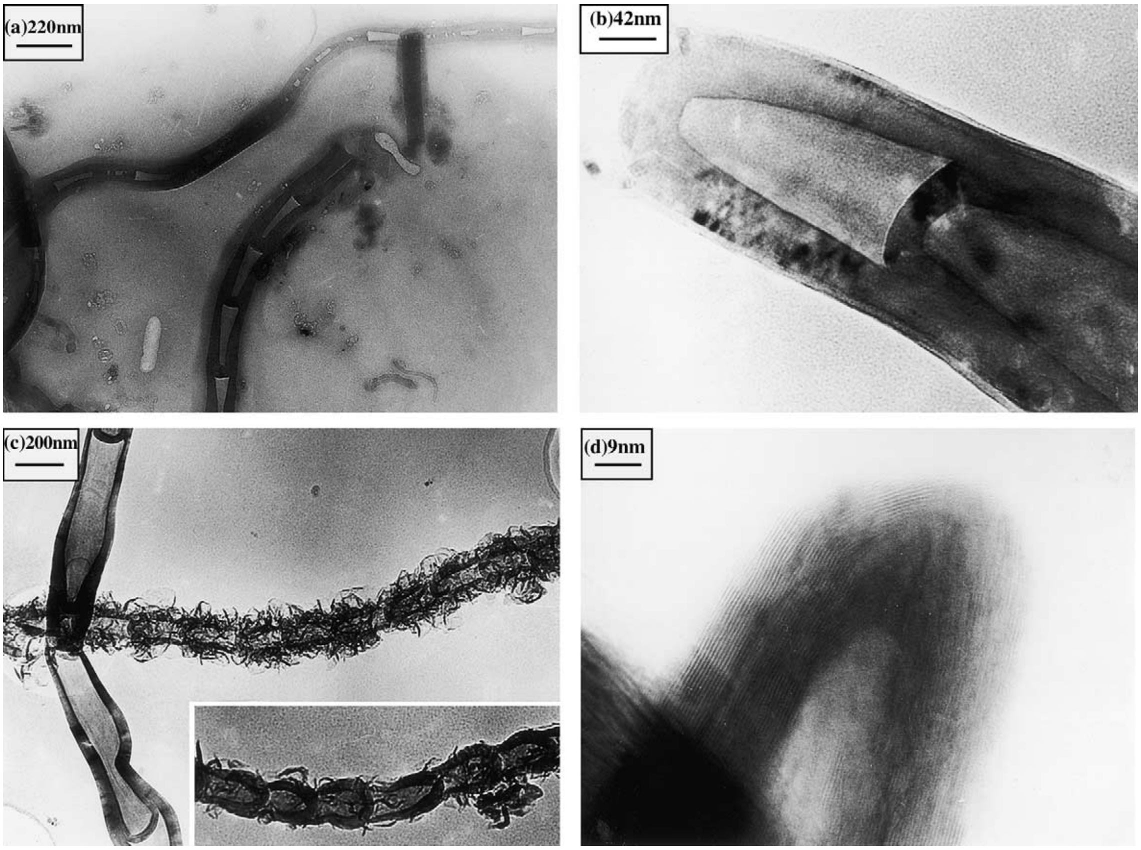

Fig. 5. TEM images of nanotube structures of BN obtained by the reaction of H_3BO_3 and activated carbon with NH_3 in the presence of catalytic Fe particles by procedure (iv): (a) TEM image of a BN nanotube with nested cones; (b) magnified TEM image of nested cones; (c) bamboo structure of BN with hair-like species attached to the outer surface; (d) high resolution image of a nanotube with a spherical cap. Inset in (c) shows the magnified image of the hair-like bamboo structure.

have, therefore carried out the reaction of H_3BO_3 and activated carbon with ammonia at 1300 °C in the presence of catalytic Fe particles by procedure (iv). This had the twin objective, one to achieve the reduction of boric acid by carbon and the second to provide catalytic particles for the growth of the BN nanostructures. This procedure yields various types of nanotubular structures, noteworthy among them being the nested cone and the bamboo structures. In Fig. 5, we show the various types of nanotube structures obtained by this procedure. The TEM image in Fig. 5a reveals the presence of nested truncated cones along the axis of growth of the tube. This is clearly revealed by the magnified image (Fig. 5b). The growth of the nanotube here progresses outwards with an increase in the diameter as further layers are added during the formation [3]. A bamboo structure with tiny hair-like features attached to the outer surface is shown in Fig. 5c. A BN nanotube with the conventional spherical tip is shown in the HREM image in Fig. 5d. The layer spacing here is 0.34 nm and the concentric layers bend nicely at the tip. The B/N ratio of these nanotubes was also 1:1, with a very small carbon content ($\leqslant 0.1$).

4. Conclusions

The present study shows that clean BN nanotubes are obtained in high yields by heating boric acid with multi-walled carbon nanotubes in the 1000–1300 °C range. That the BN nanotubes are produced at a temperature as low as 1000 °C is noteworthy. Interestingly, aligned BN nanotubes are obtained by using aligned carbon nanotube bundles as the starting materials. The conversion of boric acid to BN in the presence of nanotubes is $\sim 100\%$. Reaction of boric acid with activated carbon in the presence of catalytic Fe particles gives BN nanotubes exhibiting a variety of structures. In order to prepare BN nanowires, however, a mixture of boric acid with activated carbon appears to be the appropriate starting material.

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