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Purification of boron nitride nanotubes

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Abstract

A purification process was developed for the first time for boron nitride (BN) nanotubes. BN nanotubes, prepared using a ball milling and annealing method, contain a high yield of nanotubes and a small amount of BN and metal catalyst particles. The metal particles can be dissolved in an HCl solution. Fine BN nanoparticles and thin layers were first converted to water soluble B_2O_3 via a partial oxidation treatment at 800 °C. The oxide particles and layers can then be dissolved in hot water. Thermogravimetric analysis has been used to determine an adequate oxidation temperature at which fine BN particles were oxidized. © 2006 Elsevier B.V. All rights reserved.

1. Introduction

Boron nitride nanotubes (BNNTs) possess different electronic and chemical properties in comparison with carbon nanotubes (CNTs), but exhibit approximately the same structure and mechanical strength. As a wide band gap $(\sim 5.5 \text{ eV})$ dielectric material [1], BNNTs are expected to play an important role in manufacturing of nanodevices. In addition, replacing the C-C pairs in the graphene sheet with the iso-electronic B-N pairs gives BNNTs alternative functional properties, such as pyroelectric and piezoelectric behavior [2] as well as photogalvanic properties [3] which CNTs do not have. In particular, the BNNTs' band gap is independent of helicity and diameter of nanotubes [4]. BNNTs also have a better oxidation- and corrosion-resistance than CNTs at high-temperatures (up to 900 °C) [5]. These promising properties of BNNTs generate a large range of important potential applications including energy storage, nanotube electronic devices and new composite materials [6]. Obviously, these applications require high purity BNNT samples. However, similar to the case of CNTs, the as-synthesized BNNTs often contain impurities such as metal catalyst particles, BN particles and thin

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amorphous BN or boron oxide layers on the nanotube surfaces, which need to be removed. Although the purification techniques for CNTs have been well developed by many research groups [7–9]. These methods cannot be used directly on BNNTs because of different chemical properties. For example, controlled oxidation treatment can effectively burn off small C particles and amorphous layers from the surfaces of CNTs, but high-temperature oxidation of BN produces solid B_2O_3 that remains in the sample. Therefore, new purification processes need to be developed specifically for BN nanotubes. In this Letter, we demonstrate for the first time a successful approach to remove both metal and BN particles from BNNTs.

2. Experimental

In this study, BNNT samples were prepared using a ball-milling and annealing method [10,11]. The starting amorphous boron powder was first milled in a planetary mill (Fritsch, Pulverisette 5) with a stainless steel bowl and several balls for 50 h at a rotation speed of 300 rpm. The milling atmosphere was ammonia gas at a static pressure of 300 kPa. The weight ratio of the milling balls to the boron powder was 50:1. The milled boron powder was then heated in a tube furnace at 1200 °C for 8 h under a N₂ gas flow (100 ml/min) to grow BNNTs. The detailed procedure

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and formation mechanisms have been described in Ref. [10–12]. The structure and morphology of BNNT samples were characterized using X-ray powder diffraction spectroscopy (Philips 3020) (XRD) and field-emission scanning electron microscopy (Hitachi4500) (FESEM). X-ray energy dispersive spectroscopy (EDS), attached to a JEOL6400 SEM, was employed to determine sample chemical contents. Thermogravimetric analyser (Shimadzu 50) (TGA) was used to analyze the oxidization of BNNT at a heating rate of 20 °C/min in an oxygen flow of 50 ml/min.

3. Results and discussion

3.1. Dispersion of large clusters of nanotubes and particles

Dispersion of large aggregates of BN nanotubes and nanoparticles is the first step of the whole purification process. The as-synthesized BNNT samples contain some large aggregates up to several micrometers in size due to the high-temperature and solid-state formation process (1200 °C), which need to be dispersed prior to further purification treatment. A typical SEM image of a BNNT aggregate is shown in Fig. 1a. About 0.5 g of the as-synthesized BN samples was dispersed into 100 ml of ethanol under ultrasonic treatment for 1 h. After 20 min of sedimentation, the large aggregates were broken up or dropped down to the bottom of the container and thus were separated from the top solution containing fine nanotubes and particles. The above dispersion and sedimentation processes were repeated several times until most large aggregates were removed. BN nanotubes, some fine BN and Fe/Cr particles were extracted from the solution by evaporating

the solvent. The SEM image in Fig. 1b shows a mixture of loose nanotubes and particles. XRD analysis suggests some reduction in Fe content as indicated by the lower intensity of the Fe diffraction peak in Fig. 2b in comparison with the Fe peak in Fig. 2a, which was taken from the starting BNNT samples. Presumably some large and heavy metal particles or aggregates are removed during the sedimentation. The above dispersion process can be enhanced, when a large amount of BNNT sample is required, by a pre-mechanical grinding treatment in a ball mill under a low grinding intensity. However, low milling energy and a short milling time less than 1 h are critical to minimize significant damage to nanotubes.

3.2. Dissolving metal particles in acid solution

A selective chemical leaching process was used to remove metal catalysts from BN nanotubes. The starting BN nanotube samples contain catalyst particles including Fe (4.5 at%) and Cr (0.7 at%), as determined by EDS analysis. Hydrochloric acid (HCl) was found as an effective acid that could dissolve both Fe and Cr. BNNT samples were leached in an HCl solution (3 M) at 90 °C for 3 h. The leached sample was collected by filtration, and dried at 100 °C. EDS analysis revealed that the above leaching process remarkably reduced the Fe content from 4.5 to <0.1 at%, and Cr from 0.7 to 0.2 at%. XRD analysis confirmed the effective chemical leaching process. The Fe diffraction peak is absent from the XRD pattern (Fig. 2c) taken from the leached sample. The unchanged BN diffraction peaks suggest that BNNT structures are not damaged by the above treatment. Both SEM and TEM observation



Fig. 1. FESEM images of the aggregate of BNNTs and nanoparticles before purification (a); loose BNNTs and nanoparticles after a dispersion treatment in ethanol (b); after further oxidation at 800 $^{\circ}$ C for 1 h in air (c); and after dissolving oxide particles with hot water (d).



Fig. 2. XRD patterns of the BNNT samples after dispersion and chemical leaching treatment: (a) as-synthesized BN sample; (b) after dispersion; and (c) after chemical leaching.

found that some tubes were opened, presumably by the previous violent ultrasonic treatment, and enclosed catalyst particles were dissolved by the acid solution. A typical TEM image of the BNNTs in the leached sample is shown in Fig. 3a. Both two thick nanotubes have open tips and the metal particles responsible for the bamboo like structure are missing. The thin nanotube is not damaged by the treatment. Similar to the case of the purification of CNTs [7–9,13], the following reactions occurred during the leaching process:

$$Fe(Cr) + HCl \rightarrow Fe(Cr)Cl_3 + H_2 \uparrow$$

Both products $FeCl_3$ and $CrCl_3$ are soluble in hot water and can be easily removed by washing with hot water followed by filtration.

3.3. Dissolving fine BN particles

A two-step process was used to eliminate fine BN particles. A partial oxidation treatment under controlled conditions first converts BN nanoparticles into B_2O_3 but not BNNTs because nanotubes have a stronger resistance to oxidation than nanoparticles in the same size range. The B_2O_3 particles/layers are then dissolved in hot water as the B_2O_3 has a high solubility in hot water at 98 °C [14].

(1) Partial oxidation, oxidation conditions are critical for selective oxidation of fine BN particles. TGA was used to determine an optimum temperature for oxidizing BN particles since fine particles are more reactive than the nanotubes. The leached sample was analyzed up to



Fig. 3. TEM images of: (a) leached BNNT samples; (b) oxidized sample at 700 °C; (c) oxidized at 800 °C, the inset is typical EDS spectra taken from the oxidized BNNTs and nearby BN particles, indicating clearly the presence of oxygen; and (d) oxidized at 900 °C (scale bar 100 nm).

900 °C at a rate of 20 °C/min in an oxygen flow of 50 ml/ min. The TGA curve of sample weight change as a function of heating temperature is shown in Fig. 4, which shows that a slow sample weight increase until around 800 °C and a rapid weight increase above 800 °C. To clarify these changes, TGA analyses were repeated up to three different temperatures 700, 800, and 900 °C corresponding to different weight increase stages. Both XRD and TEM analyses on the three as-analyzed samples suggest that the slow weight increase at a low temperature range corresponds to the oxidization of fine BN particles and some external layers of thick BNNTs. The sharp weight increase above 800° is due to the oxidization of BNNTs [5]. The Fig. 3b shows two different BN nanotubes of the sample after heating up to 700 °C. Both thick bamboo (diameter of about 50 nm) and thin cylindrical tube (diameter of 8 nm) maintain their tubular structure without significant damage. In the sample after heating up to 800 °C, the multiwalled cylindrical structures of two tubes in Fig. 3c can be seen clearly. Thin oxide layers and particles start to form on the external surfaces as revealed by EDS analysis. The inset is typical EDS spectra taken from the oxidized BNNTs and nearby BN particles, indicating clearly the presence of oxygen. Oxidation appears to proceed more rapidly at the open tips than the wall areas. After heating up to 900 °C, sever damages can be found on BN nanotubes as shown in the TEM image in Fig. 3d. Many windows or holes are created on the tube walls due to the sever oxidation attacks. Thick bamboo tubes are almost destroyed because of the more active surfaces [11,15,16]. Many oxide particles can be seen around the nanotube. These results suggest that the oxidation temperature of BN particles should be around 800 °C. To further optimize the oxidation temperature for a larger sample quantity, the leached samples were heated in a tube furnace in air for 1 h at three different temperatures (750, 800, and 850 °C). XRD analysis of the

oxidized samples at different temperatures reveals different degrees of oxidations as indicated by the diffraction peaks of B_2O_3 phase in Fig. 5. The diffraction intensity of the B_2O_3 phase increases with increasing temperature and simultaneously the peak intensity of the BN phase decreases, suggesting different levels of oxidation. BN particles have not been fully oxidized after heating at 750 °C. Heating at 850 °C for 1 h oxidizes fine BN particles and also damages some nanotubes too. It appears that heating at 800 °C for 1 h can achieve selective oxidation of most fine BN particles and the structures of thin nanotubes remain unchanged. The possible oxidation reaction is

 $BN + O_2 \rightarrow B_2O_3 + NO \uparrow + NO_2 \uparrow$

(2) Hot water washing, partially oxidized samples were washed with hot water and filtered with a membrane of 1.0 µm pore size until all oxides were dissolved into the solution. After drying at 100 °C, a thin layer of BNNTs can be peeled off from the filter membrane. XRD analysis on the final sample no longer detected B_2O_3 as shown by the XRD pattern in Fig. 5d. The SEM analysis of the final sample revealed significant improvement in nanotube yield as shown in Fig. 1d. Almost no particles can be seen. Thick nanotubes with a diameter more than 100 nm or in bamboo structure are also missing from the samples. SEM and TEM observation also reveal smaller diameters of the purified nanotubes due to the oxidation of external layers and dissolution in hot water. Oxidation and hot water washing effectively remove amorphous BN and BO thin layers from the nanotube surface, and some structural damages are also created on the tube walls. The final purified sample contains very high density nanotubes as shown in Fig. 1d. Same as the oxidation purification process for carbon nanotubes, more than half of the starting sample has been lost in the purification process.



Fig. 4. TGA curve of HCl leached BNNTs at a heating rate of 20 $^{\circ}\text{C/min}$ in an oxygen flow of 50 ml/min.



Fig. 5. XRD patterns obtained from the samples oxidized at: (a) 750 $^{\circ}$ C; (b) 800 $^{\circ}$ C; (c) 850 $^{\circ}$ C; and (d) the sample (b) after washed with hot water.

4. Conclusions

A new and successful purification process of BNNTs has been demonstrated. The purification process consists of dispersion, selective chemical leaching (3 M, HCl), partial thermal oxidization and hot water washing steps. An optimized oxidation temperature is critical for dissolving BN particles without significant damaging or oxidizing nanotubes. This process opens up a possibility for obtaining high purity BN nanotubes required by large-scale property studies and applications. Although this process was developed based on the BNNT samples prepared using the ballmilling and annealing method, it can be used to purify BNNT samples made by other methods.

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