

Synthesis of boron nitride nanotubes by boron ink annealing

Lu Hua Li^{1,2}, Ying Chen¹ and Alexey M Glushenkov¹

¹ Institute for Technology Research and Innovation, Deakin University, Waurn Ponds, VIC 3217, Australia

² Department of Electronic Materials Engineering, Research School of Physics and Engineering, Australian National University, Canberra, ACT 0200, Australia

E-mail: ian.chen@deakin.edu.au

Received 14 November 2009, in final form 20 January 2010

Published 15 February 2010

Online at stacks.iop.org/Nano/21/105601

Abstract

Ball-milling and annealing is one effective method for the mass production of boron nitride nanotubes (BNNTs). We report that the method has been modified to a boron (B) ink annealing method. In this new process, the nanosize ball-milled B particles are mixed with metal nitrate in ethanol to form an ink-like solution, and then the ink is annealed in nitrogen-containing gas to form nanotubes. The new method greatly enhances the yield of BNNTs, giving a higher density of nanotubes. These improvements are caused by the addition of metal nitrate and ethanol, both of which can strongly boost the nitrating reaction, as revealed by thermogravimetric analysis. The size and structure of BNNTs can be controlled by varying the annealing conditions. This high-yield production of BNNTs in large quantities enables the large-scale application of BNNTs.

 Online supplementary data available from stacks.iop.org/Nano/21/105601/mmedia

1. Introduction

Boron nitride nanotubes (BNNTs) are attracting more and more attention in the wake of the great enthusiasm for carbon nanotube (CNT) research. BNNTs not only have superior thermal conductivity and similar mechanical properties to CNTs [1, 2], they also exhibit some unique properties that cannot be found in CNTs. For example, BNNTs are more stable at high temperature and less chemically reactive than CNTs [3, 4]. They have a uniform wide bandgap close to 6 eV [5, 6] and provide excellent radiation shielding due to the presence of the ¹⁰B isotope [7]. Therefore, BNNTs are promising composite fillers that can not only greatly improve the mechanical properties and thermal conductivity of the composite, but also help meet high temperature and electrical insulating requirements. BNNTs are found to have luminescence in the deep-ultraviolet (DUV) range [8] and a giant Stark effect [9], which make them potential candidates for optoelectronic applications. A recent theoretical study also predicts that BNNTs could enable faster and more effective desalination [10].

Various synthesis techniques have been proposed in the past decade to produce BNNTs, including arc-discharge [11],

laser ablation [12], chemical vapor deposition (CVD) [13], high temperature chemical processes [14, 15], and the ball-milling and annealing method [16, 17]. The ball-milling and annealing method was first proposed by one of the current authors at the Australian National University in 1999 [16, 17]. It has successfully produced BNNTs, BN nanorods and BN nanowires in much larger quantities than the other methods, and made commercial application of BNNTs possible for the first time [18–21]. Recently, the longest BNNT (over 1 mm) has been produced using this method [22]. Here we report that the ball-milling and annealing method has been modified to a liquid B ink method, which can greatly enhance the yield and density of BNNTs in the product. The yield of BNNTs in the new process is comparable to that of CNTs produced in the CVD process. This improvement is mainly due to the addition of nitrate and ethanol to the ball-milled B particles.

2. Experimental details

Fine B particles were first produced by intensive ball-milling. 2 g of amorphous B powder (95%–97%, Sigma-Aldrich) were sealed in a steel-milling vial with four hardened steel balls. The ball-to-powder weight ratio (BPR) was 132:1. Anhydrate

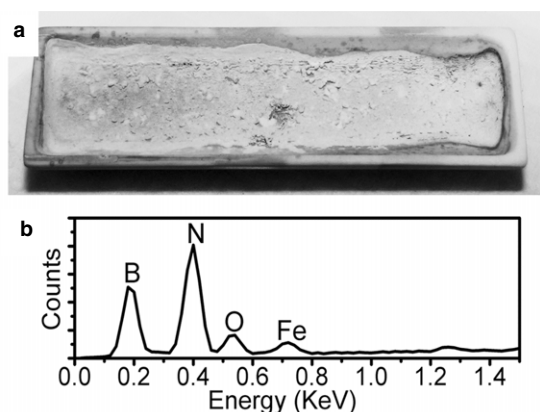


Figure 1. (a) Photo of the white BNNT layer in an alumina crucible produced by the B ink annealing method. The top inner size of the crucible is 68 mm \times 19 mm; (b) EDS spectrum showing the elements B and N predominate, along with some O and Fe.

ammonia (NH_3) as the reaction gas was purged into the vial and a static pressure of 300 kPa was established prior to the milling treatment. The ball-milling process lasted for 150 h with a slow laboratory rolling mill to ensure the formation of nanosized B particles with metastable structures [16, 23]. B ink was prepared by mixing the ball-milled B particles with ferric nitrate (98%, Sigma-Aldrich) or cobalt nitrate (98%, Sigma-Aldrich) in ethanol solution under 1 h ultrasonic bath treatment. The ink-like solution was then poured into a crucible and isothermally annealed using a horizontal tube furnace at temperatures between 1000 and 1300 $^\circ\text{C}$ for several hours in different atmospheres: nitrogen with 5% hydrogen (N_2 -5% H_2) or NH_3 . During the annealing, the B particles reacted with the N-containing gas via the chemical reaction $\text{B} + \text{N} \rightarrow \text{BN}$, and were transformed into BNNTs.

Nanotubes were investigated using a Philips 3020 x-ray diffraction (XRD) diffractometer. A Hitachi 4300SE/N scanning electronic microscope (SEM) operated at 3 kV was employed to examine the nanotube morphology. The chemical composition of the nanotubes was examined using x-ray energy dispersive spectroscopy (EDS) attached to the SEM. Transmission electron microscopy (TEM) investigations

were performed using a Philips CM300 (300 kV) instrument. Thermogravimetric analysis (TGA) was conducted with a Shimadzu TGA-60 instrument.

3. Results and discussion

3.1. Large quantity synthesis

BNNTs in large quantities and higher yield were synthesized by using the new B ink annealing method. The photo in figure 1(a) shows a layer of white fluffy material covering the bottom of a ceramic combustion boat (size: 68 mm \times 19 mm). The EDS spectrum (figure 1(b)) reveals that the annealed sample was predominantly the elements B and N, along with some O and Fe impurities. The Fe was from both the ball-milling process and the $\text{Fe}(\text{NO}_3)_3$ added to the B ink. Larger quantities of BNNTs can be produced by using bigger crucibles. For example, 0.5 g of BNNTs was synthesized in a rectangular stainless steel boat of 100 mm \times 40 mm. The morphologies and structures of the materials are discussed below.

The diameter and structure of BNNTs can be adjusted by adopting different annealing atmospheres and temperatures, similar to the old ball-milling and annealing method [17, 22, 23]. BNNTs with cylindrical structure and small diameters were synthesized by annealing in NH_3 gas. In this process, 0.034 M $\text{Co}(\text{NO}_3)_2$ ethanol solution was chosen to prepare the B ink, because Co is an effective catalyst for both NH_3 decomposition and BNNT growth [24]. The SEM image in figure 2(a) shows a high density of small tubes obtained after annealing in NH_3 at 1300 $^\circ\text{C}$ for 6 h. The tube lengths are mainly 3–5 μm . Investigation by TEM (figure 2(b)) showed that they have small diameters, in the range of 2–10 nm, and a well-crystallized, multi-walled cylindrical structure.

When B ink (with 0.02 M $\text{Fe}(\text{NO}_3)_3$ ethanol solution) was annealed at 1000 – 1100 $^\circ\text{C}$ for 3–4 h in N_2 -5% H_2 gas, longer BNNTs with larger diameters were produced. The SEM image in figure 3(a) reveals a high density of nanotubes with lengths of 100–200 μm . The longest BNNT found by SEM observation was more than 300 μm (see supplementary data, figure S1 available at stacks.iop.org/Nano/21/105601/mmedia).

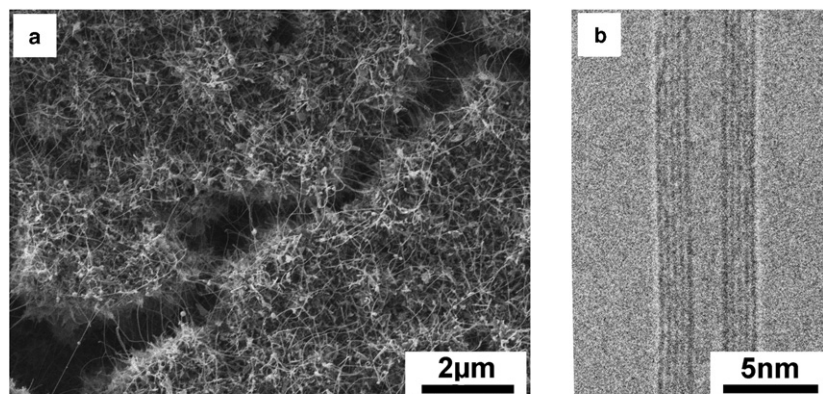


Figure 2. (a) SEM image of the BNNTs produced with $\text{Co}(\text{NO}_3)_2$ in NH_3 gas at 1300 $^\circ\text{C}$; (b) TEM image revealing the small diameter and cylindrical structure of the nanotubes.

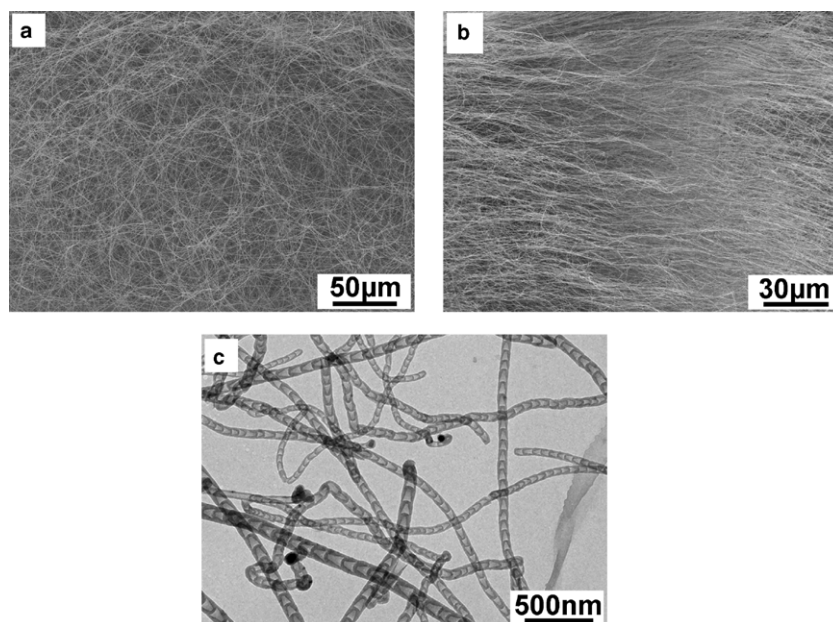


Figure 3. (a) SEM image showing high purity BNNTs produced with $\text{Fe}(\text{NO}_3)_3$ in N_2 -5% H_2 gas at 1100 °C; (b) SEM image showing the aligned BNNTs found near the crucible edge; (c) TEM image showing most of these nanotubes have a bamboo-like structure with a metal catalyst at the tip.

The tube diameters are in the range of 50–80 nm. No BN or unreacted B particles were observed. Although the majority of the nanotubes grew in random directions (figure 3(a)), well-aligned BNNTs were often found at the edge of the boat (figure 3(b)), which is believed to be caused by the gas flow during annealing [25, 26]. TEM analysis revealed that most of the tubes had a bamboo-like structure and usually contained metal catalyst at the tip (figure 3(c)). The detailed structural information and growth mechanism of the bamboo-type tubes have been reported previously [3, 16, 17]. The formation of different tubular structures is related to the different annealing atmospheres and temperatures [27].

The arc-discharge and laser ablation methods are able to produce small amounts of highly crystallized BNNTs with few walls and short lengths [11, 12]. The CVD method usually produces BNNTs with large diameters [13]. The size, length and structure of BNNTs from high temperature chemical processes are highly dependent on the chemical reaction involved. For example, Zhi *et al* reported an effective method of producing large quantities of BNNTs of more than 50 nm diameter [14], while Singhal *et al* reported another simple chemical method that produced similar quantities of fine BNNTs with diameters as small as 10–30 nm [15]. The B ink annealing method can produce larger quantities of BNNTs than the arc-discharge or laser ablation methods. The density of nanotubes produced by the new method is higher than those from the CVD method and the increased yield overcomes a drawback of the chemical method reported by Singhal *et al*. The new method can also produce different sized BNNTs with different structures by varying the annealing conditions.

3.2. The role of metal nitrates

TGA was used to investigate the roles of both ethanol and nitrate in the annealing process. The TGA curve in figure 4(a)

shows the weight change of B ink during heating in N_2 -5% H_2 gas. In the analysis, 0.1 M $\text{Fe}(\text{NO}_3)_3$ ethanol solution was used to prepare the B ink (100 mg B in 1 ml solution) and the heating rate was 20 °C min^{-1} . Because of the similar catalytic effects from $\text{Fe}(\text{NO}_3)_3$ and $\text{Co}(\text{NO}_3)_2$, only $\text{Fe}(\text{NO}_3)_3$ was used in this analysis. In the curve, three different stages corresponding to three different physical and chemical changes in the B ink during the annealing can be seen. The first stage is from room temperature to 145 °C, in which the weight of the sample plummeted dramatically from 48.5 to 5.6 mg. This rapid weight loss was caused by ethanol evaporation. The next stage is from 145 to 400 °C. During this stage, nitrate, $\text{Fe}(\text{NO}_3)_3$, thermally decomposed into metal oxide, Fe_2O_3 , which was further reduced into nanosized metal particles that acted as catalysts to assist the nanotube growth [28, 29]. The last stage is from 400 to 1100 °C, where the weight of the sample rebounded due to the nitriding reaction between B particles and N_2 gas with the formation of BN phases.

Metal nitrate plays an essential catalytic role in the high-yield synthesis of BNNTs. In the ball-milled B powder, small steel particles, 2.09 at.% Fe, are formed from the high energy collisions between the milling vial and balls during ball-milling. So even if no nitrate is added to the ball-milled B particles, these metal particles can still act as catalysts to grow BNNTs [17, 23]. However, they are not numerous or efficient enough to transform all the B particles into BNNTs. The nanosized metal particles decomposed from the nitrate added in the B ink can compensate for this deficiency, as shown below. The nitriding reaction rates of five samples: (i) ball-milled dry B particles only, (ii) ball-milled B particles added with pure ethanol, (iii), (iv) and (v) B ink prepared using 0.013 M, 0.04 M and 0.1 M $\text{Fe}(\text{NO}_3)_3$ ethanol solution, were compared (figure 4(b)). In the TGA curves, the percentage weight gain is based on the minimum weight of each sample

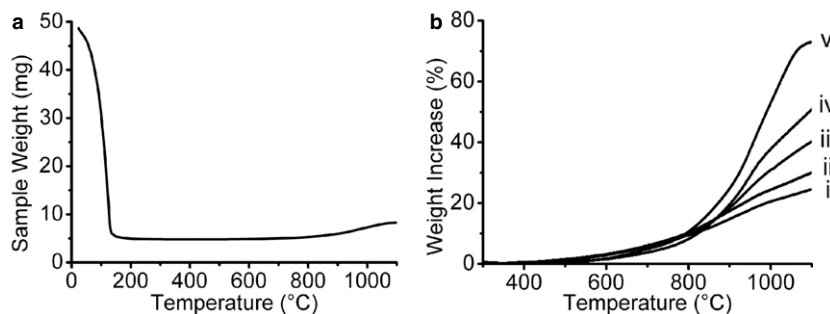


Figure 4. (a) TGA curve showing the B ink weight change during annealing to 1100 °C in $N_2-5\%H_2$ gas; (b) five TGA curves comparing the nitriding reaction rates of: (i) ball-milled dry B particles; (ii) ball-milled B particles with pure ethanol; (iii) B ink with 0.013 M $Fe(NO_3)_3$ ethanol solution; (iv) B ink with 0.04 M $Fe(NO_3)_3$ ethanol solution; and (v) B ink with 0.1 M $Fe(NO_3)_3$ ethanol solution. All B inks were prepared by adding 100 mg of ball-milled B particles to 1 ml of solution.

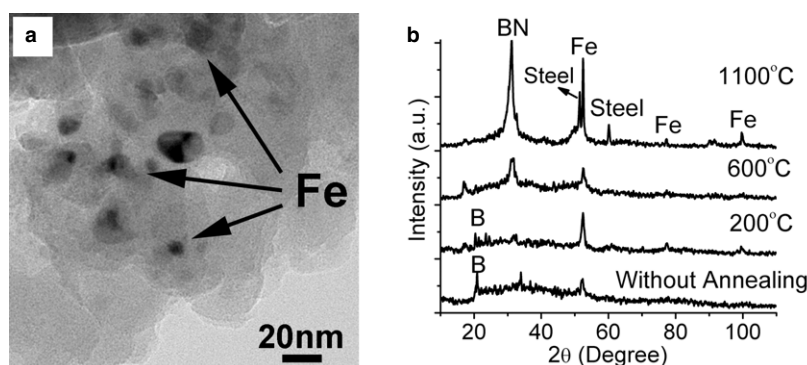


Figure 5. (a) TEM image of B ink after 800 °C annealing in $N_2-5\%H_2$ gas, and the small dark dots with diameters 5–10 nm are Fe catalysts from decomposed and reduced $Fe(NO_3)_3$; (b) XRD spectra showing the BN phase formation with increased temperature.

during annealing. For the ball-milled dry B particles and the B particles with pure ethanol, the weight gains were only 24.7% and 30.2% during annealing. In contrast, there were much larger weight gains for the B ink with added $Fe(NO_3)_3$, and the weight gain increased with increased concentration of nitrate. The B ink with 0.013M, 0.04M and 0.1 M $Fe(NO_3)_3$ showed weight increases of 40.2%, 50.9% and 73.2%, respectively. The increased weight gains seen by TGA mean faster nitriding reactions, which lead to more BN phases. Therefore, metal nitrate is the main reason for the improvement in the nanotube yield. The detailed TGA investigation of the heating process of $Fe(NO_3)_3$ in $N_2-5\%H_2$ gas revealed that most of the $Fe(NO_3)_3$ thermally decomposed into Fe_2O_3 at 350 °C, and then these oxides were largely reduced by H_2 into Fe particles at around 850 °C. The TEM image (figure 5(a)) shows the Fe particles (dark) reduced from the B ink after annealing at 800 °C in $N_2-5\%H_2$ are as small as 5 nm, while the 20 nm particles could be steel particles from ball-milling or the agglomeration of Fe decomposed from $Fe(NO_3)_3$. These Fe particles created more reaction sites for nitriding and acted as seeds for nanotube growth [28]. The highest yields of BNNTs were produced when 0.08–0.2 mg $Fe(NO_3)_3 \cdot 9H_2O$ was added to 1 mg of ball-milled B powder (see supplementary data available at stacks.iop.org/Nano/21/105601/mmedia). If less $Fe(NO_3)_3$ is added, the yield of BNNTs is lower because there is still not enough catalyst; and if too much is added, particle

impurities will be found in the product, due to the loss of the catalytic function of the large Fe particles [30, 31].

3.3. The role of ethanol

Although most of the ethanol evaporated below 145 °C, it still slightly enhanced the BNNT growth. TGA (figure 4(b)) shows that even by adding pure ethanol to the B particles without nitrate, there was still a bigger weight gain than for dry B particles. The role of ethanol can be explained as follows. Firstly, ethanol can help to break up the agglomerates of B particles during ultrasonication. The nanosized B particles normally agglomerate into large clusters under the ball impacts during milling. The agglomeration slows down the nitriding reaction and hence reduces nanotube yield. The ultrasonic treatment in ethanol can break these large agglomerates into loose B particles, giving better contact with the reaction gas so that an enhanced nitriding reaction was achieved during annealing. Secondly, ethanol helps to protect the metastable B particles from oxidation. The ball-milling process produces the metastable disordered B structures that are highly reactive in air even at room temperature. The oxidation of these structures may cause them to lose their chemical reactivity. The ethanol can cover the surface of these ball-milled particles, preventing the oxidation. Thirdly, ethanol assists homogeneous mixing of the nitrates with the nanosized B particles. On the other hand, ethanol does not leave C contamination in BNNTs, if excessive

volumes are avoided. TGA (figure 4(a)) shows that ethanol can be evaporated away at low temperature (below 145 °C) and thus it is not involved in any chemical reactions at high temperature. The EDS analysis of the final BNNT products does not show significant C residues (figure 1(b)).

The metastable disordered B structures produced by the ball-milling treatment can react with the nitrogen-containing gas at relatively lower temperature to form BN phases [16, 17]. The XRD spectra of the B ink annealed at different temperatures in figure 5(b) clearly show the formation and increase of the BN phases with increased annealing temperature. At room temperature, there were only disordered B structures. The (002) BN phase appeared at 600 °C. At 1100 °C, this peak became dominant. The XRD results confirm the weight gains in TGA were caused by the nitriding reaction or the hBN phase increase between 400 and 1100 °C. Because the ball-milled B particles are preferable for growing one-dimensional BNNTs with the presence of metal catalysts at lower growth temperatures [7, 27, 32], large quantities and high densities of BNNTs are able to be fabricated in synthesis.

4. Conclusions

A new B ink annealing method was developed to synthesize larger quantities of BNNTs with a higher yield. The B ink was prepared by mixing $\text{Fe}(\text{NO}_3)_3$ or $\text{Co}(\text{NO}_3)_2$ with ball-milled B particles in ethanol solution. Small-diameter cylindrical multi-walled BNNTs were produced in HN_3 at 1300 °C and bamboo-structured BNNTs were produced in N_2 -5% H_2 at 1000–1100 °C. TGA analysis showed that both the metal nitrate and ethanol contributed to the significant improvement in the nitriding reaction. The nitrate provided extra metal catalysts and the ethanol helped to intimately mix the B particles with the nitrate. This method opens the door for potential large-scale application of BNNTs.

Acknowledgments

The research is supported in part by the Australian Research Council under the Centre of Excellence for Functional Nanomaterials. We are grateful to Dr Peter Lamb for assistance in preparing the manuscript.

References

- [1] Xiao Y, Yan X H, Cao J X, Ding J W, Mao Y L and Xiang J 2004 *Phys. Rev. B* **69** 205415

- [2] Suryavanshi A P, Yu M F, Wen J G, Tang C C and Bando Y 2004 *Appl. Phys. Lett.* **84** 2527
- [3] Chen Y and Chadderton L T 2004 *J. Mater. Res.* **19** 2791
- [4] Golberg D, Bando Y, Kurashima K and Sato T 2001 *Scr. Mater.* **44** 1561
- [5] Blase X, Rubio A, Louie S G and Cohen M L 1994 *Europhys. Lett.* **28** 335
- [6] Yu J, Yu D, Chen Y, Chen H, Lin M-Y, Cheng B-M, Li J and Duan W 2009 *Chem. Phys. Lett.* **476** 240
- [7] Yu J, Chen Y, Elliman R G and Petravic M 2006 *Adv. Mater.* **18** 2157
- [8] Jaffrennou P et al 2008 *Phys. Rev. B* **77** 235422
- [9] Khoo K H, Mazzoni M S C and Louie S G 2004 *Phys. Rev. B* **69** 201401
- [10] Hilder T A, Gordon D and Chung S-H 2009 *Small* **5** 2183
- [11] Chopra N G, Luyken R J, Cherrey K, Crespi V H, Cohen M L, Louie S G and Zettl A 1995 *Science* **269** 966
- [12] Laude T, Matsui Y, Marraud A and Jouffrey B 2000 *Appl. Phys. Lett.* **76** 3239
- [13] Lourie O R, Jones C R, Bartlett B M, Gibbons P C, Ruoff R S and Buhro W E 2000 *Chem. Mater.* **12** 1808
- [14] Zhi C Y, Bando Y, Tan C C and Golberg D 2005 *Solid State Commun.* **135** 67
- [15] Singhal S K, Srivastava A K, Singh B P and Gupta A K 2008 *Indian J. Eng. Mater. Sci.* **15** 419
- [16] Chen Y, Chadderton L T, FitzGerald J and Williams J S 1999 *Appl. Phys. Lett.* **74** 2960
- [17] Chen Y, Fitz Gerald J D, Williams J S and Bulcock S 1999 *Chem. Phys. Lett.* **299** 260
- [18] Zhang H Z, Yu J, Chen Y and FitzGerald J 2006 *J. Am. Ceram. Soc.* **89** 675
- [19] Chen Y J, Chi B, Mahon D C and Chen Y 2006 *Nanotechnology* **17** 2942
- [20] Lim S H, Luo J Z, Ji W and Lin J 2007 *Catal. Today* **120** 346
- [21] Li Y J, Zhou J E, Zhao K, Tung S M and Schneider E 2009 *Mater. Lett.* **63** 1733
- [22] Chen H, Chen Y, Liu Y, Fu L, Huang C and Llewellyn D 2008 *Chem. Phys. Lett.* **463** 130
- [23] Chen Y, Conway M, Williams J S and Zou J 2002 *J. Mater. Res.* **17** 1896
- [24] Sorensen R Z, Nielsen L J E, Jensen S, Hansen O, Johannessen T, Quaade U and Christensen C H 2005 *Catal. Commun.* **6** 229
- [25] Xin H J and Woolley A T 2004 *Nano Lett.* **4** 1481
- [26] Liu Y T, Xie X M, Gao Y F, Feng Q P, Guo L R, Wang X H and Ye X Y 2007 *Mater. Lett.* **61** 334
- [27] Yu J, Li B C P, Zou J and Chen Y 2007 *J. Mater. Sci.* **42** 4025
- [28] Wiczorek-Ciurowa K and Kozak A J 1999 *J. Therm. Anal. Calorim.* **58** 647
- [29] Tang C C, Ding X X, Huang X T, Gan Z W, Qi S R, Liu W and Fan S S 2002 *Chem. Phys. Lett.* **356** 254
- [30] Kind H, Bonard J M, Forro L, Kern K, Hernadi K, Nilsson L O and Schlapbach L 2000 *Langmuir* **16** 6877
- [31] Klinke C, Delvigne E, Barth J V and Kern K 2005 *J. Phys. Chem. B* **109** 21677
- [32] Yu J, Chen Y, Wuhrer R, Liu Z W and Ringer S P 2005 *Chem. Mater.* **17** 5172

Supplementary Data

Synthesis of boron nitride nanotubes by boron ink annealing

Lu Hua Li^{1,2}, Ying Chen¹ and Alexey M. Glushenkov¹

¹ Institute for Technology Research and Innovation, Deakin University, Waurn Ponds, Victoria 3217, Australia

² Department of Electronic Materials Engineering, Research School of Physics and Engineering, the Australian National University, Canberra, ACT 0200, Australia

E-mail: ian.chen@deakin.edu.au

1. BNNTs with length more than 300 μm

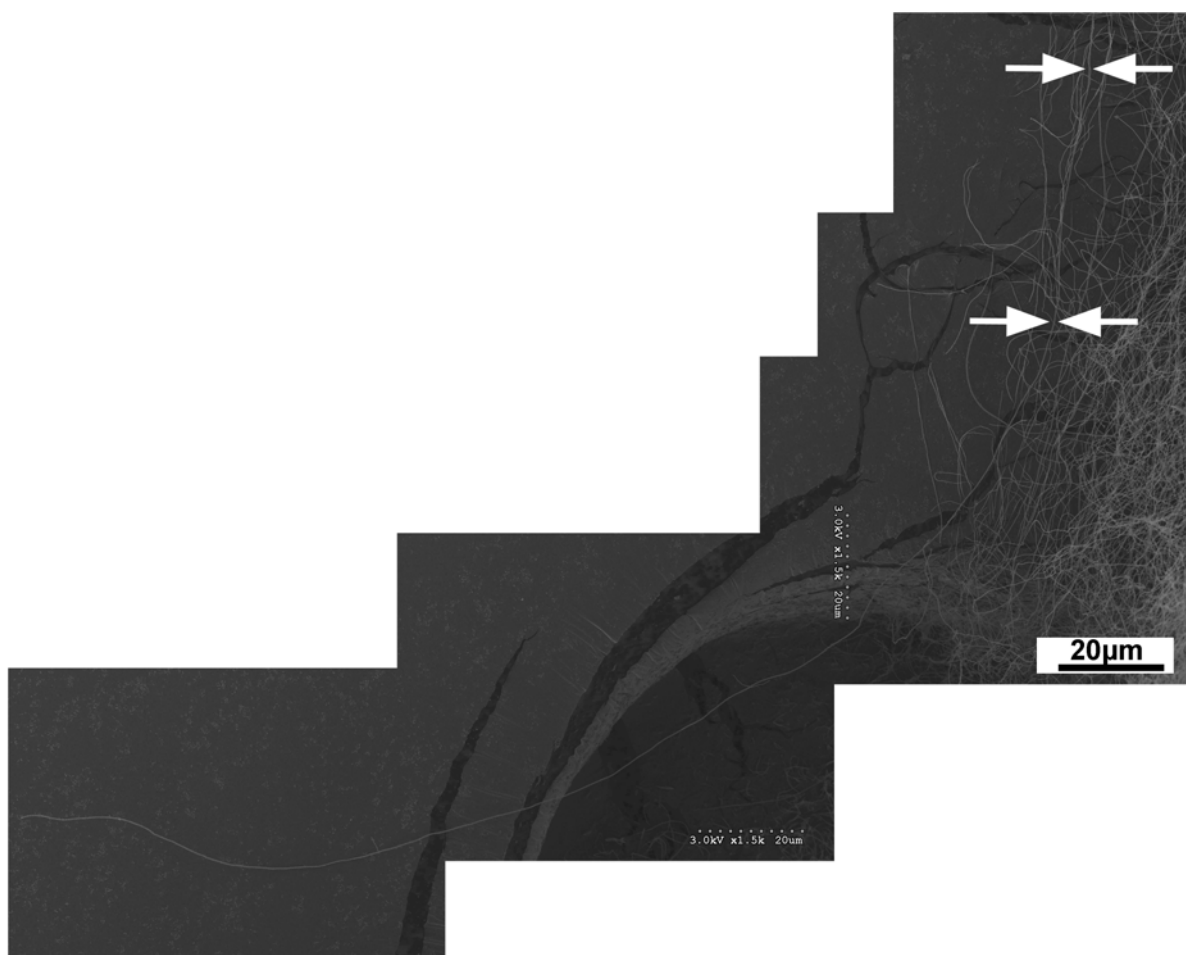


Figure S1 SEM images showing a BNNT greater than 300 μm in length (arrowed).

2. The SEM images of BNNT products using different amount of $\text{Fe}(\text{NO}_3)_3$

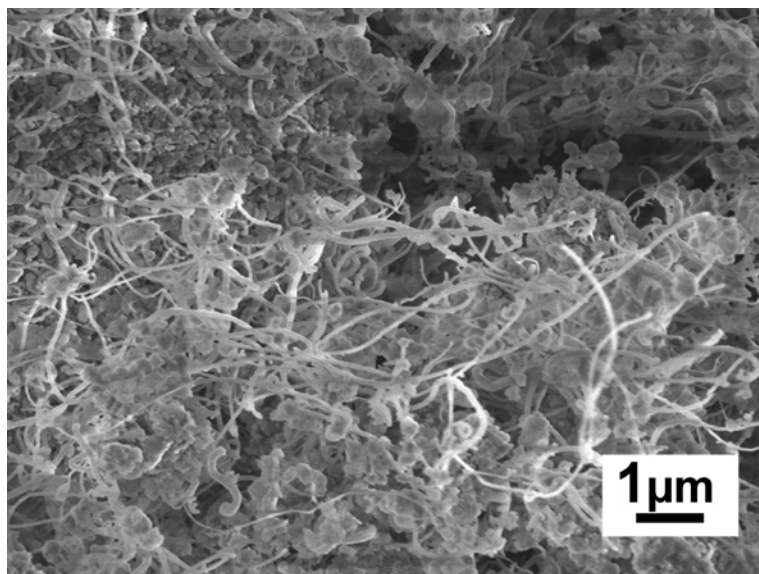


Figure S2.1 SEM image showing low density of BNNTs in product when ball-milled B particles with pure ethanol without adding any $\text{Fe}(\text{NO}_3)_3$ was used in annealing. There are more particles than BNNTs.

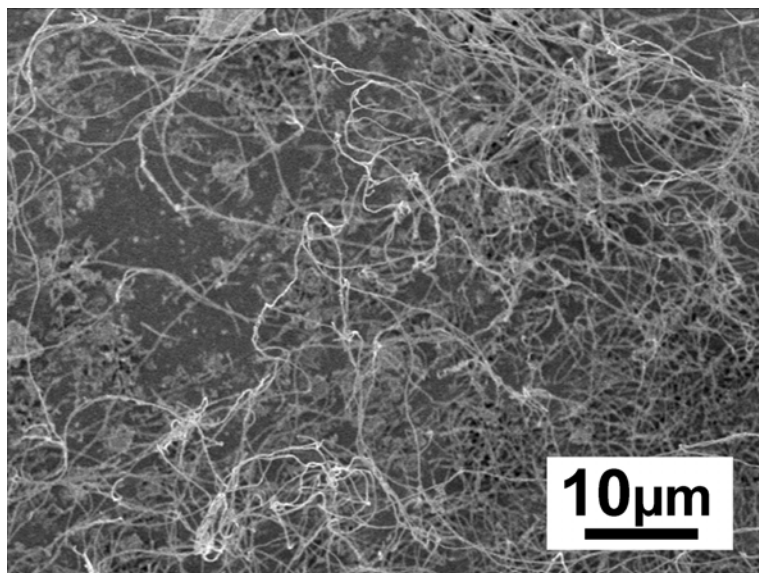


Figure S2.2 SEM image showing improved density of BNNTs in product when 0.04mg $\text{Fe}(\text{NO}_3)_3$ was added to every mg of ball-milled B (still not enough $\text{Fe}(\text{NO}_3)_3$). But there were still particulate contaminants.

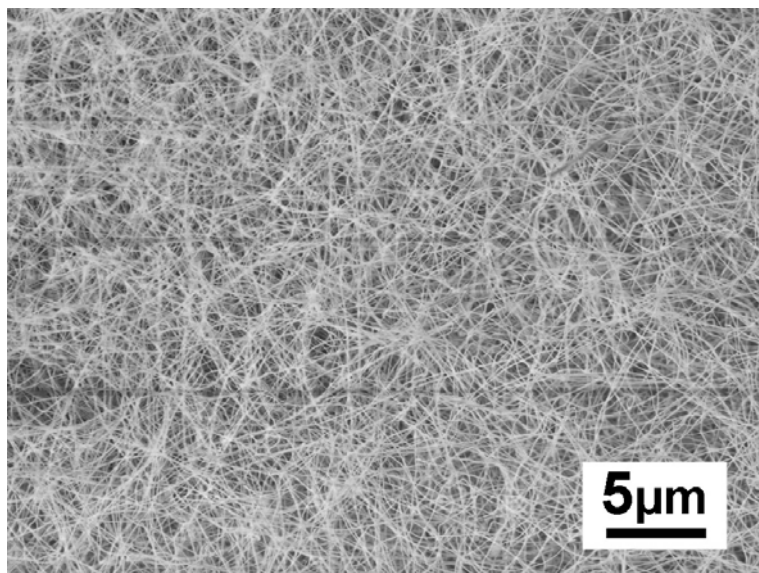


Figure S2.3 SEM image showing very high density of BNNTs in product when 0.2mg $\text{Fe}(\text{NO}_3)_3$ was added to every mg of ball-milled B (within the range of optimum amount).

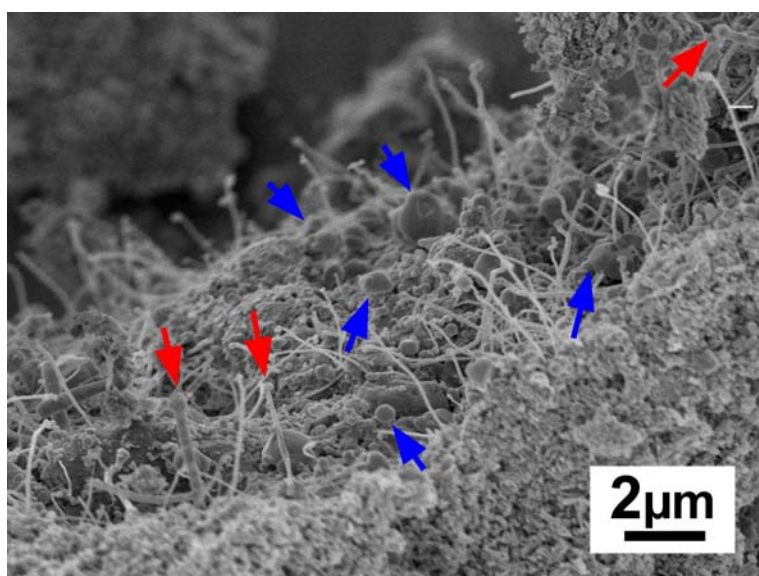


Figure S2.4 SEM image showing BNNT in product when 0.29mg $\text{Fe}(\text{NO}_3)_3$ was added to every mg of ball-milled B (too much $\text{Fe}(\text{NO}_3)_3$). The big round Fe particles were found in the product (blue arrowed), which have almost lost their catalytic function; while a small number of BNNTs grew up with big catalysts on the tip (red arrowed).

All the SEM images shown above were from samples annealed in N_2 -5% H_2 at 1100°C for several hours.