

Development and Characterization of Commercial Boron Nitride Nanotube Product Forms

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ABSTRACT

Boron nitride nanotubes (BNNTs), like carbon nanotubes (CNTs), possess an impressive collection of properties that motivate their use in areas where CNTs are limited (e.g., high temperature processing and applications) or unsuitable (e.g., electrical insulation). The recent advent of commercially available BNNTs offers improved opportunities to study BNNT science and develop applications. Here we highlight BNNT product forms based on a pilot-scale BNNT manufacturing process, which have subsequently been transitioned to commercial products by Tekna Advanced Materials, and describe the appearance of these BNNTs in common characterization methods useful for evaluating nanotube composition, quality and purity.

Keywords: boron nitride nanotubes, nanotube characterization, buckypaper

1 INTRODUCTION

Boron nitride nanotubes (BNNTs) are structurally analogous to carbon nanotubes (CNTs) and possess equally impressive mechanical properties along with a different set of multifunctional features (Figure 1) including higher thermal stability, electrical insulation, high neutron absorption, and transparency in the visible region. Advances in large-scale BNNT production [1], including the hydrogen-assisted BNNT synthesis (HABS) process at NRC Canada [2], are now enabling broader availability of BNNT-based materials for research and applications. In recent years, a handful of BNNT producers/suppliers have made commercial BNNT materials available (Table 1); however, in terms of broad availability of commercial nanotube materials, BNNTs are still an emerging material. Reliable characterization of such materials, in particular the composition, purity, and quality of BNNTs is critical to build the user base for these nanomaterials products, as was the case for carbon nanotubes, and enable evaluation and comparison of studies using BNNT materials.

In this presentation we highlight the development and characterization BNNT materials derived from the HABS process, which have subsequently been transitioned to BNNT product forms by Tekna Advanced Materials (Sherbrooke, Canada) using standardized protocols for

batch-to-batch consistency. This includes a commercial product (Tekna BNNT-R [3]) derived from the “raw”, unpurified BNNTs, which was released in 2015 and followed quickly by purified (BNNT-P [3]) and buckypaper (BNNT-BP [3]) products. Characterization discussed includes scanning and transmission electron microscopy, atomic force microscopy, thermogravimetric analysis, absorption spectroscopy, Raman, X-ray diffraction, and X-ray photoelectron spectroscopy, and properties of BNNT buckypaper sheets.

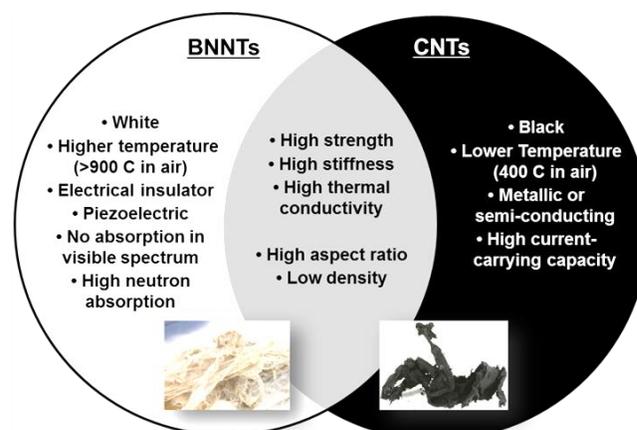


Figure 1. Comparison of BNNT and CNT properties (Credit: National Research Council Canada)

2 HYDROGEN-ASSISTED BNNT SYNTHESIS & BNNT PRODUCT FORMS

In our typical synthesis, hexagonal boron nitride (h-BN) powder is fed along with nitrogen and hydrogen gas into an atmospheric pressure, high-temperature plasma. This converts the feedstock to its constituent atoms and through the detailed features of the process, including the high cooling rate and control of the gas composition, leads to the nucleation and growth of small diameter, highly crystalline BNNTs at high yield [2]. The production rate, now over 30 g/hr, can be sustained over extended periods, with close to 200 g demonstrated in a continuous run [2]. Unique to this process is use of a high partial-pressure of hydrogen (15 to 30 vol. % H₂), which led to the moniker of hydrogen-assisted BNNT synthesis (HABS) [1].

Table 1. Commercially available BNNT products

	BNNT LLC ^a	Tekna (BNNT-R) ^b	Tekna (BNNT-P & BNNT-BP) ^b	Nano Innovations ^c	Deakin University ^d	Deakin University ^d
Method	PVC	HABS	HABS	CVD	Ball milling	
Type	crystalline, few-wall	crystalline, few-wall	crystalline, few-wall	multiwall	multiwall	Multiwall, bamboo-like
Diameter		5 nm	5 nm	60 nm	< 15 nm	40-80 nm
Wall #	2, 3 most common					
impurities	hBN and elemental B	elemental B, hBN derivatives	hBN derivatives			
Purity	40-50%	50%	75%	99.90%	<50%	~70%
Length	up to 200 μm			>10 μm		
Surface area	up to 200 m^2/g	>100 m^2/g	> 100 m^2/g			
bandgap	5.7 eV	5.5 eV	5.5 eV	6 eV		

Source: supplier websites (^awww.bnnt.com; ^bwww.tekna.com; ^cwww.nano-innov.com; ^dwww.deakin.edu.au/ifm)

This BNNT material exhibits three distinct morphologies (entangled fibrils, cloth-like sheets, and low-density deposits) depending on where it deposits within the reactor [2]. While local density and BNNT purity may differ, the BNNTs appear to be of equivalent structural quality. In one approach the synthesis products are harvested together and mechanically shredded and homogenized to produce a fluff-like, *raw* BNNT form, which is a suitable starting point for further processing including integration into polymer composites [4-6]. Alternatively, this material can be *purified* using chemical processes to remove elemental boron and washing/filtration to reduce hBN-like impurities, which converts the beige-brown of the as-synthesized material to the characteristic

white color of purified BNNTs due to removal of an elemental boron impurity. Following solvent dispersion, the BNNTs can also be formed into non-woven sheets (e.g., by vacuum filtration) similar to CNT *buckypaper* [2,4-6]. Figure 2 illustrates the as-synthesized BNNTs along with purified/homogenized and buckypaper forms.

3 BNNT CHARACTERIZATION

3.1 Imaging

Scanning electron microscopy (SEM) images shows nanofibrous features and transmission electron microscopy (TEM) confirms that these are hollow nanotubes with several, highly crystalline walls (Figure 3). From imaging over 60 BNNTs, the average diameter was estimated as ~ 5 nm, and the majority of the nanotubes have between 2 and 5 walls [2]. Considering those diameter and wall number observations in a geometrical model described for CNTs [7], we estimated a density of ~ 1.9 g/cc for the individual BNNTs [6]. Determining length poses practical challenges as bundling can lead to overestimates of length and, conversely, longer BNNTs may be under-sampled due to lower dispersibility and processes for purification or sample preparation can shorten nanotubes. Comparisons should use a consistent preparation and imaging method. AFM observations (e.g., Figure 3) are underway and analyzing approximately 200 BNNTs indicates typical lengths of 2-3 microns for a case of polymer-dispersed, purified BNNTs.

3.2 Composition

Elemental composition was assessed by X-ray photoelectron spectroscopy (Figure 4 a,b), which shows the material, both raw and purified, is boron-rich and that the ratio of B:N gets closer to 1:1 in purified BNNTs. The elemental composition was also mapped using TEM-electron energy loss spectroscopy (EELS) measurements [2], showing that the nanotube walls are composed of B and N (Figure 4 c). The lower intensity carbon signal smeared



Figure 2. Clockwise from top-left: ~ 20 g of as-synthesized BNNTs (reproduced from [4] with permission of The Royal Society of Chemistry), purified/homogenized BNNT powder (fluff-like), BNNT buckypaper sheet, and a folded origami butterfly (reproduced from [2] with permission) made with BNNT buckypaper

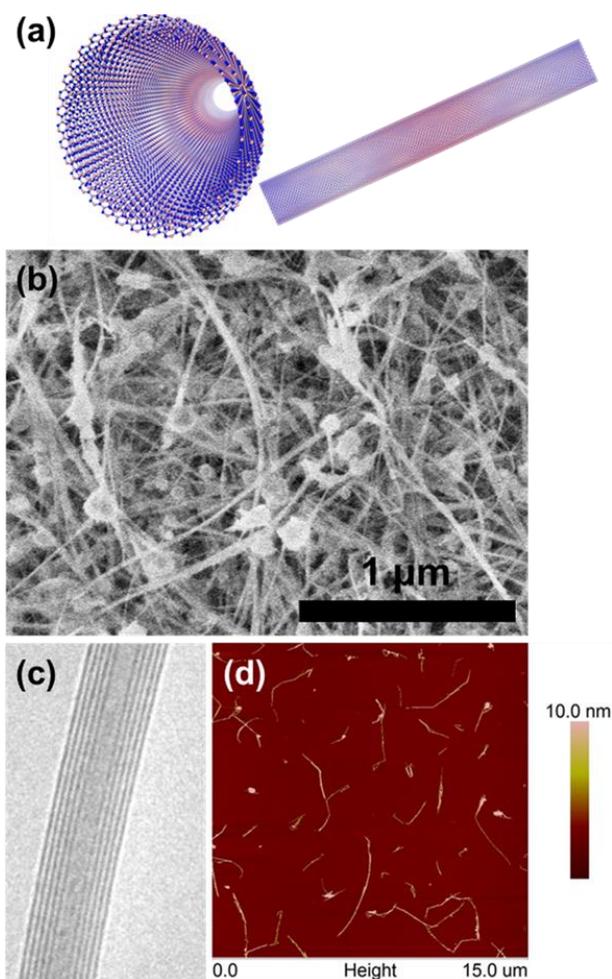


Figure 3. (a) Model of a typical size, $d = 5\text{ nm}$, 3-wall BNNT, (b) SEM of BNNT buckypaper, (c) TEM of an isolated, 4 nm BNNT (adapted from [2] with permission), (d) AFM of BNNTs spun coated on a mica surface.

over the nanotube is attributed to the solvent used to prepare the TEM grid, and the fine structures of the B and N K-shell ionization edges [2] displayed sharply defined π^* and σ^* peaks, which are characteristic of the sp^2 -hybridized BN of an hBN-like nanotube wall [2].

3.3 Purity & Quality

Of key interest for assessment of nanotube products are the quality (i.e., crystallinity and uniformity) and purity (i.e., percentage of nanotubes) of the material. In contrast to CNTs, where reasonably straightforward spectroscopic assessment methods are established, much of the assessment of BNNT quality and purity is imaging-based. While screening by SEM has been a valuable tool to adjust our purification protocols and the observation of well-defined, straight nanotubes in TEM indicates high crystallinity and uniformity, there is a need for more objective and spectroscopic characterization methods.

Thermogravimetric analysis (TGA) in air and (even simpler) the sample color can identify the presence of an

elemental boron impurity [2,4], which leads to mass increase above $\sim 650\text{ C}$ due to oxidation of boron (Figure 5). However, TGA does not differentiate BNNT from non-oxidizable impurities (i.e., other hBN-like material or boron oxides). We estimate a boron-impurity of $< 25\%$ in the raw BNNTs based on yield after chemical conversion, and $< 1\%$ from TGA for purified BNNTs. One approach to assess the “BN purity” of BNNTs is to quantify both the B:N ratio and the components of the B 1s peak in the XPS spectrum. The component of the B 1s signal assigned to B-B vanishes (Figure 5) and the B:N ratio improves upon going from raw (B:N = 1:0.77) to purified (B:N = 1:0.89) BNNTs from the HABS process. In some sense this can be used analogously to the reporting of “carbon purity” of CNT materials from TGA. Similar to that assessment of CNTs, this does not differentiate BNNTs from other BN. Other standard tools like Raman and infrared absorption spectroscopy also indicate B-N in the BNNT materials [2,4], but do not readily differentiate hBN from BNNTs. Indirectly, we have shown differentiation of hBN from the BNNTs based on a shift in absorption of a conjugated polymer in the presence of BNNTs that is not observed with hBN [8]. Routine approaches to assess the relative BNNT purity, including differentiating between BNNT and hBN, are needed to both compare and improve BNNT materials.

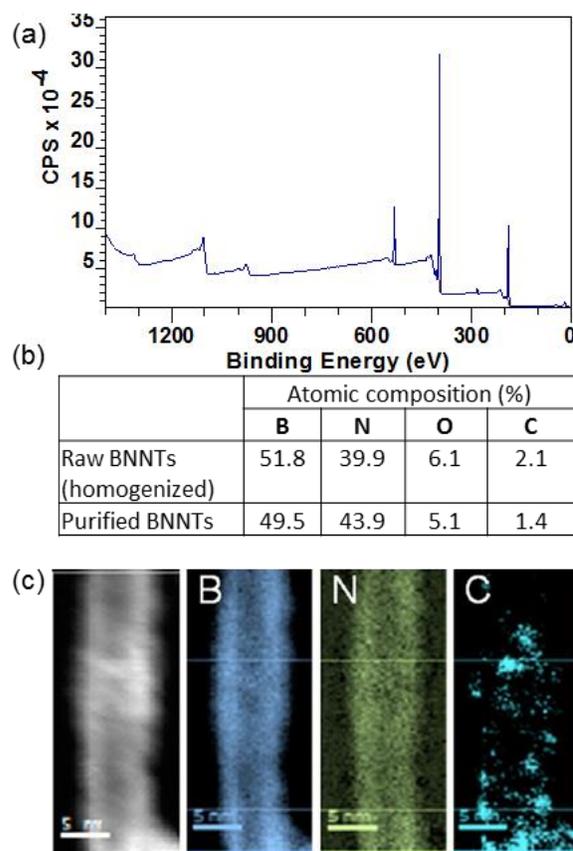


Figure 4. (a) XPS spectrum of raw BNNTs and (b) XPS-derived atomic compositions. (c) TEM-EELS based elemental map (reproduced from [2] with permission) showing B and N in the nanotube wall.

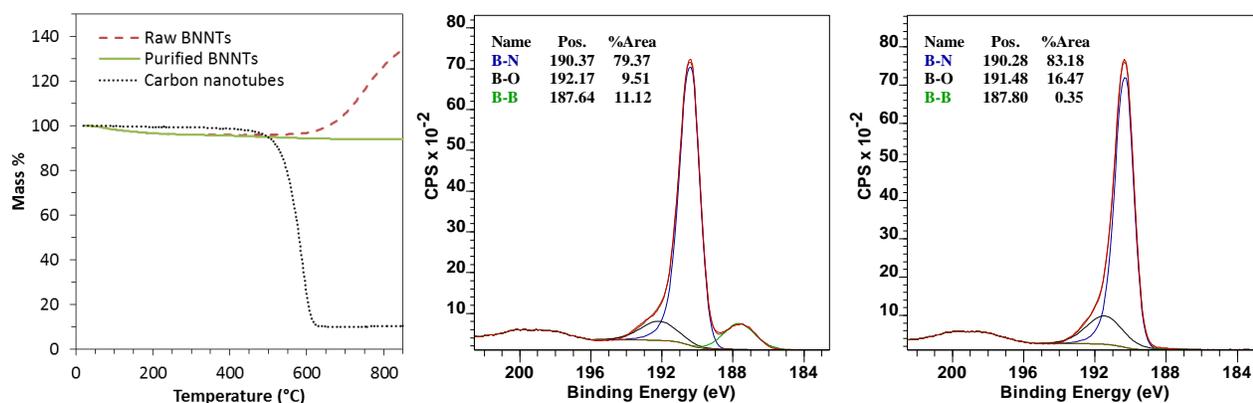


Figure 5. Comparisons from TGA (air-oxidation) for raw and purified BNNTs (left), and XPS of raw (center) and purified (right) BNNTs. TGA also shows comparison to oxidation of CNTs, which is used in purity assessment of CNTs.

X-ray diffraction (Figure 6) adds to the assessment of BNNT quality. The sharp, double-peaks just above 40° , which are at slightly higher angles than for hBN due to the rolled hBN sheet structure, suggest uniform crystalline nanotubes. The peak near 25° reflects the interwall spacing ($\sim 3.4 \text{ \AA}$), which is slightly higher spacing (lower angle) and more variable (broader peak) than for hBN.

4 BNNT BUCKYPAPER

BNNT buckypaper offers convenient form for handling, reducing the difficulty of handling low density BNNT powder/fluff and enabling high BNNT content composites [4-6]. Additionally, the quality of the paper appears to offer a practical method to assess the effect of purification and processing on BNNT quality. BNNT buckypaper formed from HABS-derived BNNTs have modest properties (e.g., strengths of 1-3 MPa, Young's Modulus of 300-500 MPa [4]); however, they can be handled similarly to paper and flexed/folded/creased (e.g., Figure 2). Conversely, when the BNNTs were subjected to more intense sonication or chemical processes, which are suspected to cause shorter and more damaged BNNTs, the resulting paper is much more brittle and cracks on folding. The BNNT BP and BP-epoxy composites combine thermal conductivities in the range of $1.5 - 3.5 \text{ W m}^{-1} \text{ K}^{-1}$ with high electrical resistance and breakdown strength [5,6].

5 CONCLUSIONS

New BNNT products have recently become available through commercial suppliers, making the material much more broadly available for research and development, and additional products and suppliers are expected to emerge. We described BNNT product forms based on NRC's pilot-scale process for hydrogen-assisted BNNT synthesis and the appearance of these BNNTs in common characterization methods useful for evaluating BNNT composition, quality and purity. Development of new methods for routine characterization, in particular to differentiate between hBN and BNNTs is ongoing.

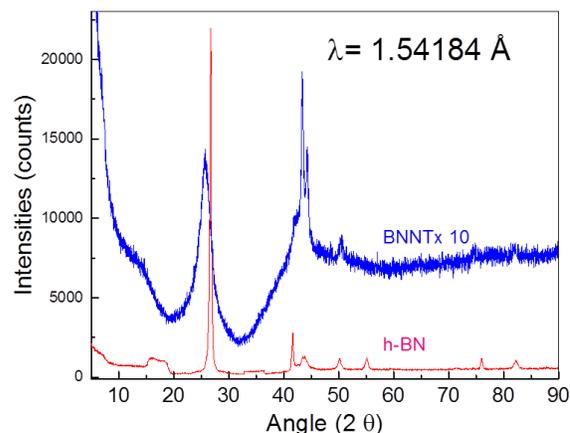


Figure 6. XRD spectra for purified BNNTs in comparison to hBN.

6 ACKNOWLEDGEMENTS

The authors thank Mark Plunkett and Dean Ruth (BNNT production), Gordon Chan (SEM), and Kodra Oltion (XPS) for technical support, as well as Jérôme Pollak and Richard Dolbec (Tekna Advanced Materials) for helpful discussion. Funding was provided by the National Research Council Canada through the Security Materials Technology Program.

REFERENCES

- [1] K.S. Kim *et al.*, Semiconductor Science and Technology 32, 013003, 2017.
- [2] K.S. Kim *et al.* ACS Nano, 8, 6211, 2014.
- [3] www.tekna.com (last accessed: March 22, 2017)
- [4] K.S. Kim *et al.*, RSC Adv 5, 41186, 2015.
- [5] M.B. Jakubinek *et al.*, Physica Status Solidi A 213, 2237, 2016.
- [6] B. Ashrafi *et al.*, Submitted, 2017.
- [7] Ch. Laurent, E. Flahaut, A. Peigney. Carbon 48, 2994, 2010.
- [8] Y. Martinez-Rubi *et al.*, Journal of Physical Chemistry C 119, 26605, 2015.