A New Class of Boron Nitride Nanotubes via the Pressurized Vapor/Condenser Method

By *Michael W. Smith *, Kevin C. Jordan, Cheol Park **, Jae-Woo Kim, Peter T. Lillehei, Roy Crooks,* and *Joycelyn S. Harrison*

[*] Dr. Michael W. Smith (synthesis)
MS 493,
NASA Langley Research Center
Hampton, VA 23681 (USA)
E-mail: Michael.W.Smith@NASA.gov

[**] Dr. Cheol Park (microscopy/analysis)
National Institute of Aerospace
MS 226, 6 West Taylor Street
NASA Langley Research Center
Hampton, VA 23681 (USA)
E-mail: Cheol.Park-1@NASA.gov

Boron nitride nanotubes (BNNTs) are desired for their exceptional mechanical, electronic, thermal, structural, textural, optical, and quantum properties. Golberg [1] gives an excellent review of possible applications. To date, BNNTs have been grown by a number of techniques which can be divided roughly into two categories based on the class of material produced. One is the high temperature category in which energy is concentrated into a B or BN target at a level which can vaporize elemental boron. BNNTs form in the deposits of the liberated vapors. The energy is input by laser [2-6] or by arc discharge [7-9] . Only small quantities (mg's) of material have been produced by this method, but the tubes are high quality. They have one or just a few walls, and most importantly, the tube walls are low in defects and parallel to the axis of the nanotube. The second category is low temperature synthesis, between about 600 C and 1700 C, well below the vaporization temperature of pure boron (~4000 C). These low temperature synthesis methods can be further divided into two catagories. In the first category, ball-milled precursor powders of boron and catalyst are annealed in a nitrogen or ammonia gas atmosphere, sprouting nanostructures on their

surfaces [10-13]. In the second category, a boron-containing vapor, usually B_2O_2, reacts with

a nitrogen-containing gas, usually ammonia, to deposit nanostructures on a substrate by

chemical vapor deposition (CVD) [14-16]. Hundreds of milligrams to grams of raw material

can be produced by ball-milling and CVD and the nanostructures contain a very high fraction

of hexagonal BN (h-BN), however the morphology is very different than that produced via the

high temperature route. Most often, the h-BN layers of low-temperature-grown tubes are not

parallel to the axis of the structure, containing angled slip planes, wavy walls, elbows, and

bamboo-like cells. Also, these pipe-like nanostructures have typical diameters about an order

of magnitude greater than those made by the high temperature techniques (~50 nm, vs ~5 nm)

and correspondingly, many more, sometimes hundreds of layers of h-BN. Fullerenes are

caged molecules, round, spheroid, or tubular, with one to a few walls which are parallel to and

define the boundary of the molecule. These low temperature morphologies do not meet the

normal definition of a fullerenic nanotube.

In this paper we introduce a technique for producing a new class of BNNTs which is scalable,

yet embodies the structure of fullerenic nanotubes. **Fig. 1A** is a schematic representation of

the technique which we call the `pressurized vapor/condenser' (PVC) method. A flow of pure

boron vapor ascends vertically in a chamber of nitrogen at elevated pressure.   A condenser, in

this case a refractory metal stick, is placed in the boron flow triggering the formation of

BNNT fibrils in its wake. The fibrils are similar in appearance to spider silk and grow up to

10 cm in length. These long fibrils grow at extraordinary rates, requiring only 100 ms to form

the full 10 centimeters. The fibrils also exhibit natural alignment along the axis of growth and

pulp-like masses of these fibrils can be produced with the appearance of combed cotton balls.

Such a cottony mass is seen in Fig. 1B. This 60 mg mass was produced by translating the

metal condenser about 20 cm over the course of about 30 minutes of continuous production.

The process of fibril formation is very efficient as about 80% of the boron vapor that flows over the condenser is converted to BNNT raw material.

Carbon nanotube yarns have been reported [17-19], but in Fig 1C we report the world's first BNNT yarn, a section about 3 cm in length. It was spun directly from a cotton-like BNNT mass similar to that seen in Fig 1B. A group of fibrils weighing about 10 mg (representing ~5 minutes of synthesis time) was separated from the mass, drawn slightly in the growth direction, and finger-twisted to form a simple one-ply yarn with a twist angle of about 45 degrees. Before twisting, the fibrils were delicate to the touch with little mechanical strength, but within the yarn could support a small load, demonstrating the improved strength due to spinning. The yarn in Fig 1C had a relatively large diameter of about 1 mm, was loosely packed, and was spun dry from unpurified raw material—all unfavorable conditions for mechanical strength. This implies that the underlying staple fibers (BNNT tubes and bundles) must have been relatively long to counteract these disadvantages and that considerable improvement in strength can be expected with a more refined spinning process.

In **Fig. 2**, a 200 mg sample of as-grown PVC-BNNT material is shown. This cottony material shows a much lower as-grown density than typical ball-milled or CVD material [14], suggesting a raw BNNT product with a much higher surface area than previously available. Most importantly, these PVC nanotubes meet the strict definition of a nanotube, one with straight, parallel, low-defect h-BN walls aligned with the axis of the tube. **Figs. 3A-D** show the raw material under progressively higher levels of magnification. In Fig 3A, a scanning electron microscope (SEM) image of a short section of a single, unpurified, as-grown, ~ 1 mm wide BNNT fibril is shown. The fibril is composed of a number of distinct vertical strands which extend the full height of the image (~ 1 mm), indicating that the raw material has an alignment axis parallel to the growth direction. Along the growth axis, the raw material could

be stretched elastically like a cobweb. Transverse to the growth axis, the material could easily

be separated into individual strands with light mechanical force. On the micron and sub-

micron scale (Figs. 3B and C), the structure is a network of long, branching nanotubes and

tube bundles, often linked at nodes, which often contain nanodroplets. As seen in Fig 3C, the

ratio of tubes to droplets, one measure of purity, can be extremely high. On these SEM

images the tubes are light colored and the droplets dark indicating a different composition for

the droplets, presumably elemental boron. This presumption was verified by the results in Fig.

4.

In Fig. 4A, an unusually large diameter, yet highly crystalline 8-walled tube is shown.

Characteristic of PVC BNNTs, all 8 walls are are smooth and parallel to the axis of the tube.

A representative electron energy loss spectroscopy (EELS) plot is shown in the inset of Fig.

4A. The BN composition of this individual tube was directly confirmed by EELS; the B-to-N

ratios from several EELS spectra were repeatably found to be 1:1. Elemental map images

created with energy-filtered transmission electron microscopy (EFTEM) are shown in Fig 4C

and D. One shows the location of elemental boron and the other nitrogen. These maps show,

as expected, that the tubes contain both boron and nitrogen but also confirm that the observed

droplets are boron. Also of note--the boron particles are coated with a uniform layer of boron

nitride, a layer that has been theorized to play an important role in BNNT formation [6].

In summary, we have demonstrated a conceptually simple method of producing a new class of

BNNTs which we call the, `pressurized vapor condenser,' or PVC method. The BNNTs

formed by the PVC method have three important characteristics. One, they grow without

catalyst using only boron and nitrogen as the reactants, eliminating the need to use acid or

other destructive purification treatments common to carbon nanotube processing. Two, they

have natural alignment on an extraordinary macroscopic length scale, producing an as-grown

appearance similar to conventional fiber pulp or cotton. This allows them to be handled with textile techniques as demonstrated by the yarn spun in Fig 1. And three, they are genuine fullerenic nanotubes having one or a few, smooth, low-defect walls parallel to the tube axis. Only this class of nanotube can be expected to fulfill the theoretical predictions of desirable mechanical, electronic, thermal, optical, piezo, and electronic properties, as these calculations generally assume a highly crystalline fullerenic structure. As useful as the may turn out to be for some applications, the bulk `nanotubes' produced to date by low temperature techniques generally possess tens or hundreds of layers, wavy walls, bamboo strutures, or h-BN planes askew to the tube axis, and thus cannot be expected to perform in the manner of genuine fullerenic nanotubes.

Experimental

An Hitachi S-5200 High Resolution Scanning Electron Microscope (HRSEM) equipped with scanning transmission (STEM) mode, with a field emission electron gun and in-lens detector, was used to image as grown BNNT bundles and fibrils. Energy filtered images of solute-isolated individual BNNTs were collected with a Gatan GIF system on a Philips CM30 Transmission Electron Microscope (TEM), with a $LaB6$ filament operated at 200kV.

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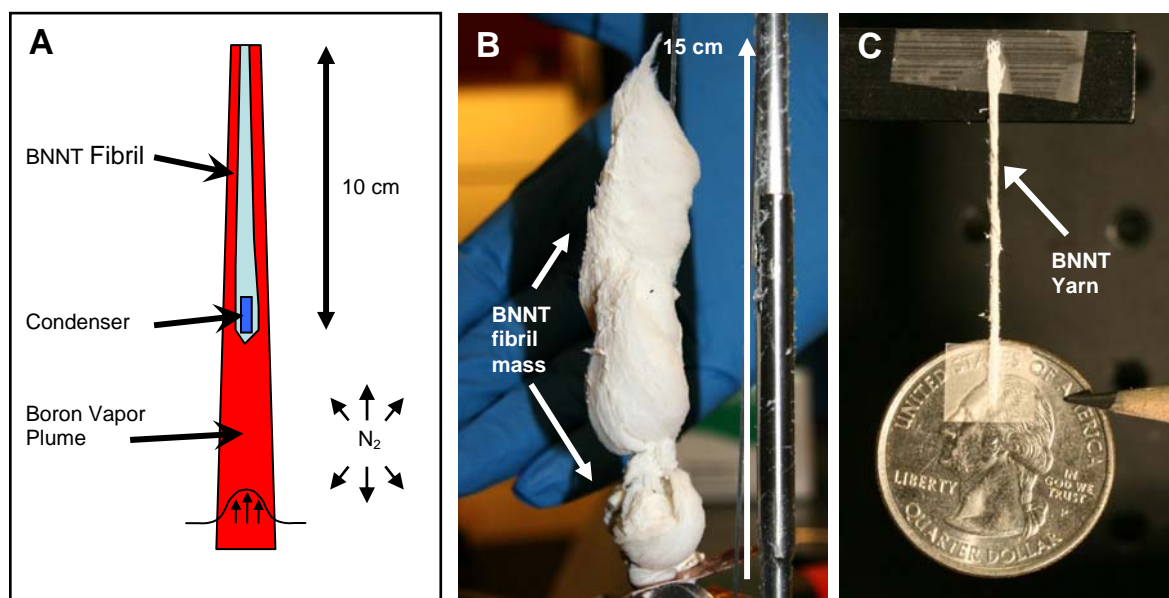*Adv. Mat. **2006**, 18*, 3160.

Figure 1. A) Schematic of the pressurized vapor/condenser (PVC) method. B) A 60 mg
cotton-like mass of BNNT grown by the PVC method in about 30 minutes. C) A 3 cm long
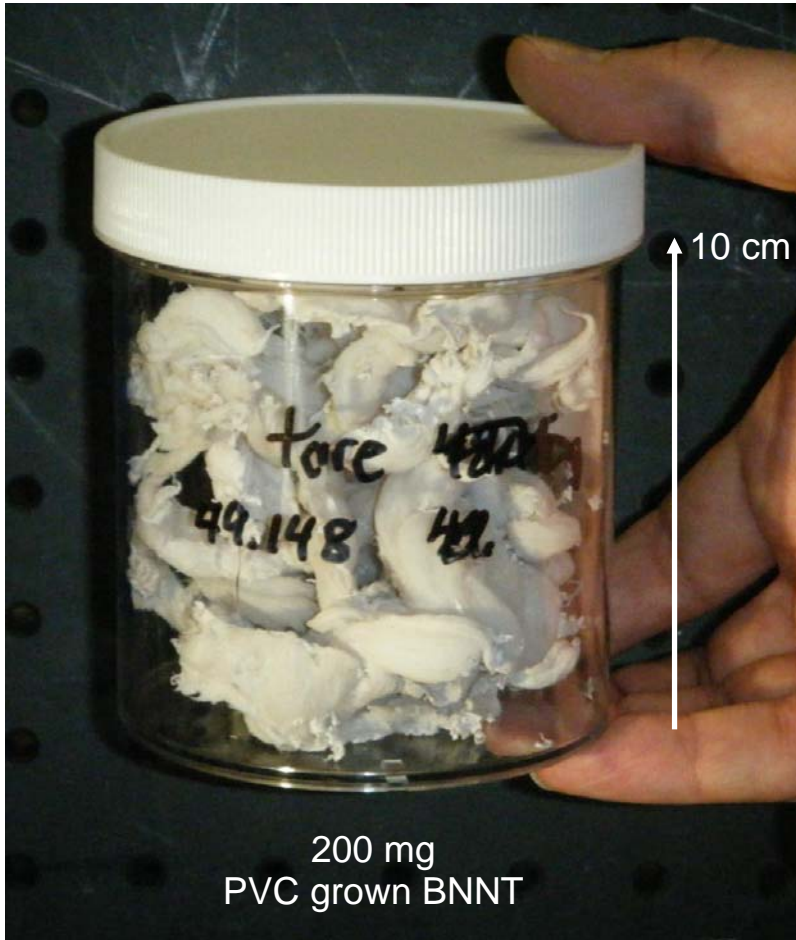section of yarn spun directly from PVC-BNNT.

Figure 2. The results of a 200 mg PVC BNNT production run. The unprocessed material has the appearance of cotton balls, though the texture is somewhat softer and the material finer-grained.
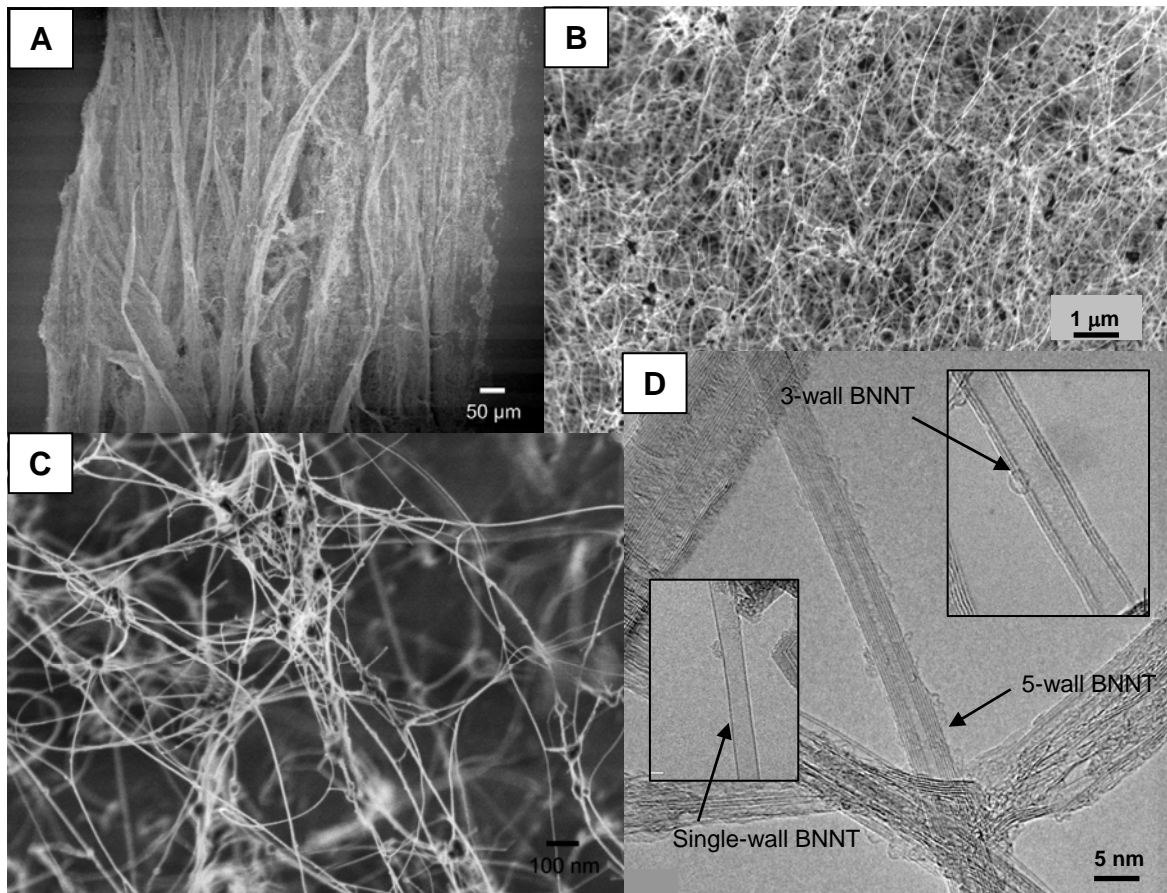
Figure 3. Scanning (A-C) and transmission (D) electron microscope images showing the structure of PVC-grown BNNT fibrils at increasing magnifications. Panel D shows 1, 3, and 5 wall tubes. Although as many as 8 walls have been observed (see Fig. 4, below), 2 to 5 walls are most common.
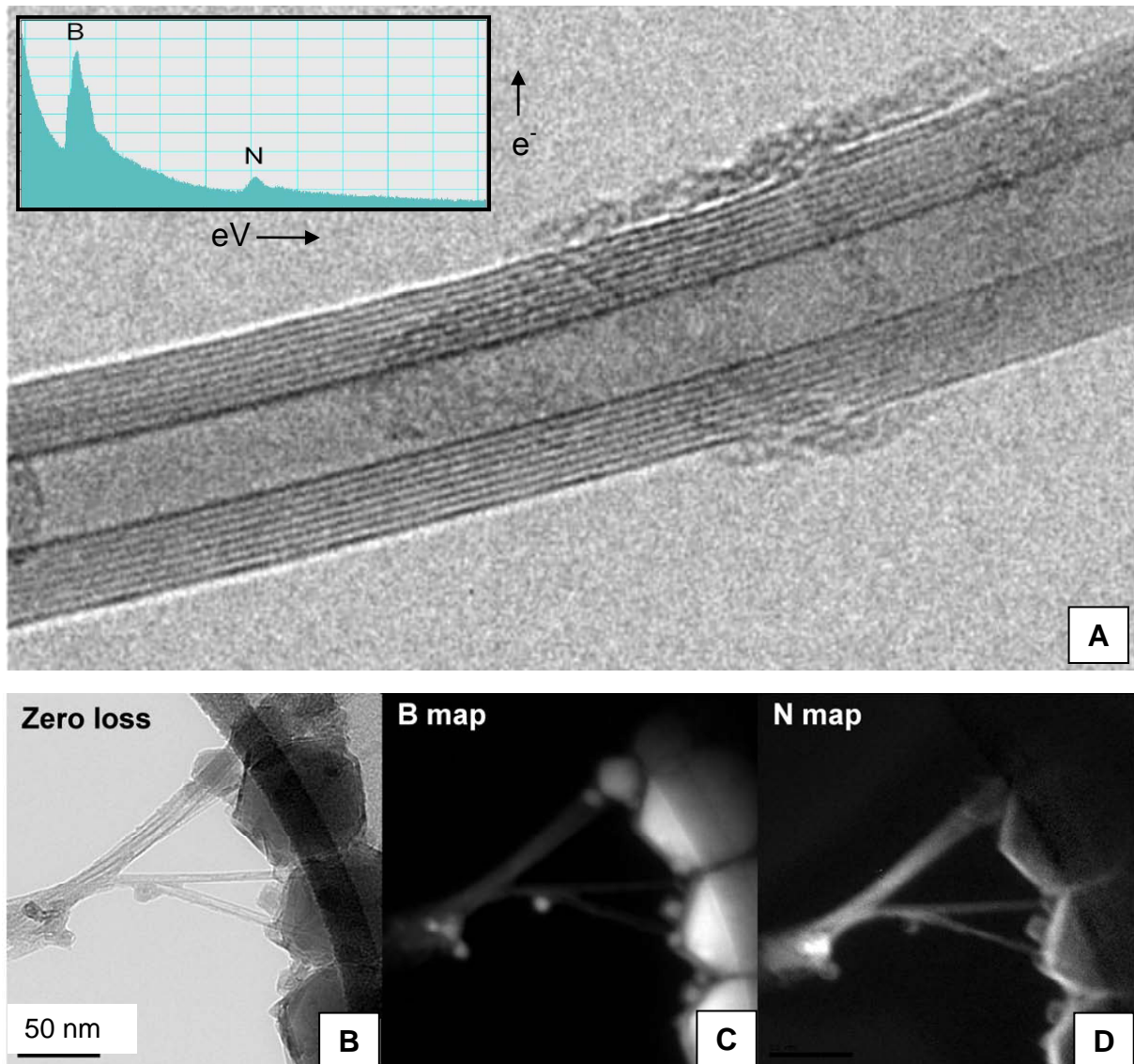
Figure 4. (A) High resolution TEM image of an 8-walled BNNT. Inset is an EELS spectrum showing 1:1 ratio of B to N. (B) Zero-loss image of BNNT bundle at junction with supporting nanoparticles. (C), (D) EFTEM maps showing elemental distribution of boron and nitrogen, respectively.