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Industrialization of boron nitride nanotubes: Synthesis, chemistry, assemblies and composites

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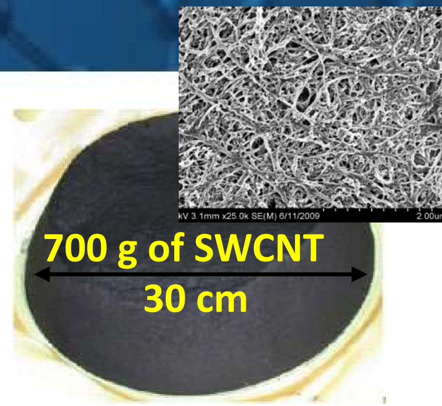
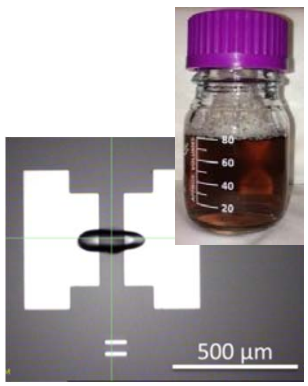
NRC·CNRC

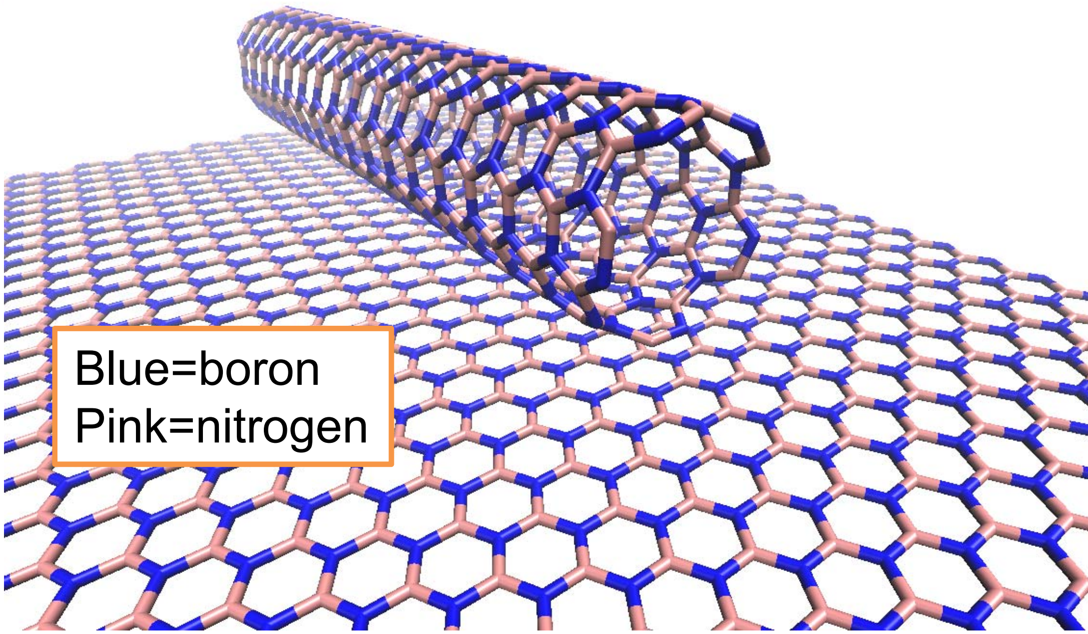
Nanotubes@NRC (since 1999)

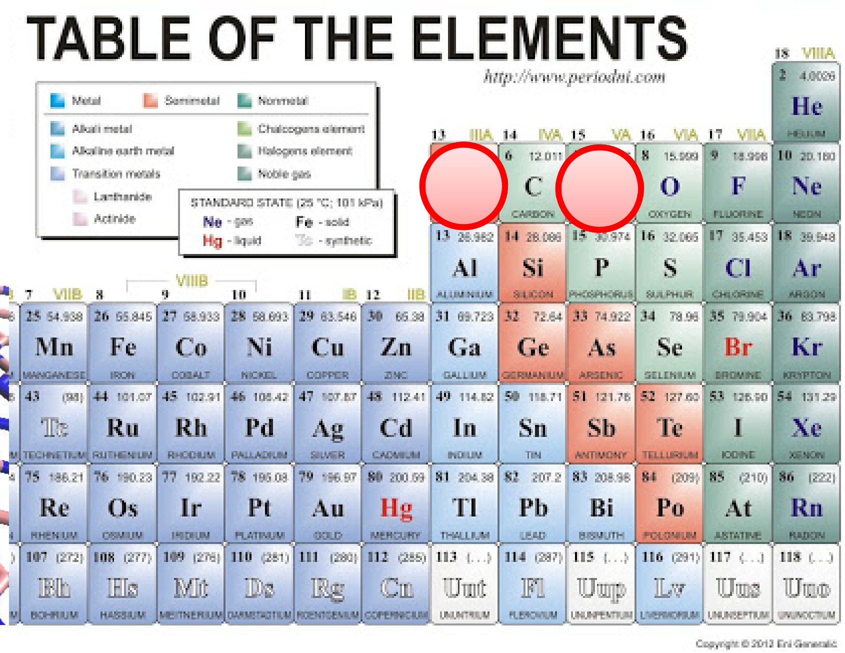
- Synthesis of SWCNTs & BNNTs
- CNT assemblies (sheets, films, fibers)
- Composite materials
    - Polymers
    - Metals
    - Ceramics
    - Inks





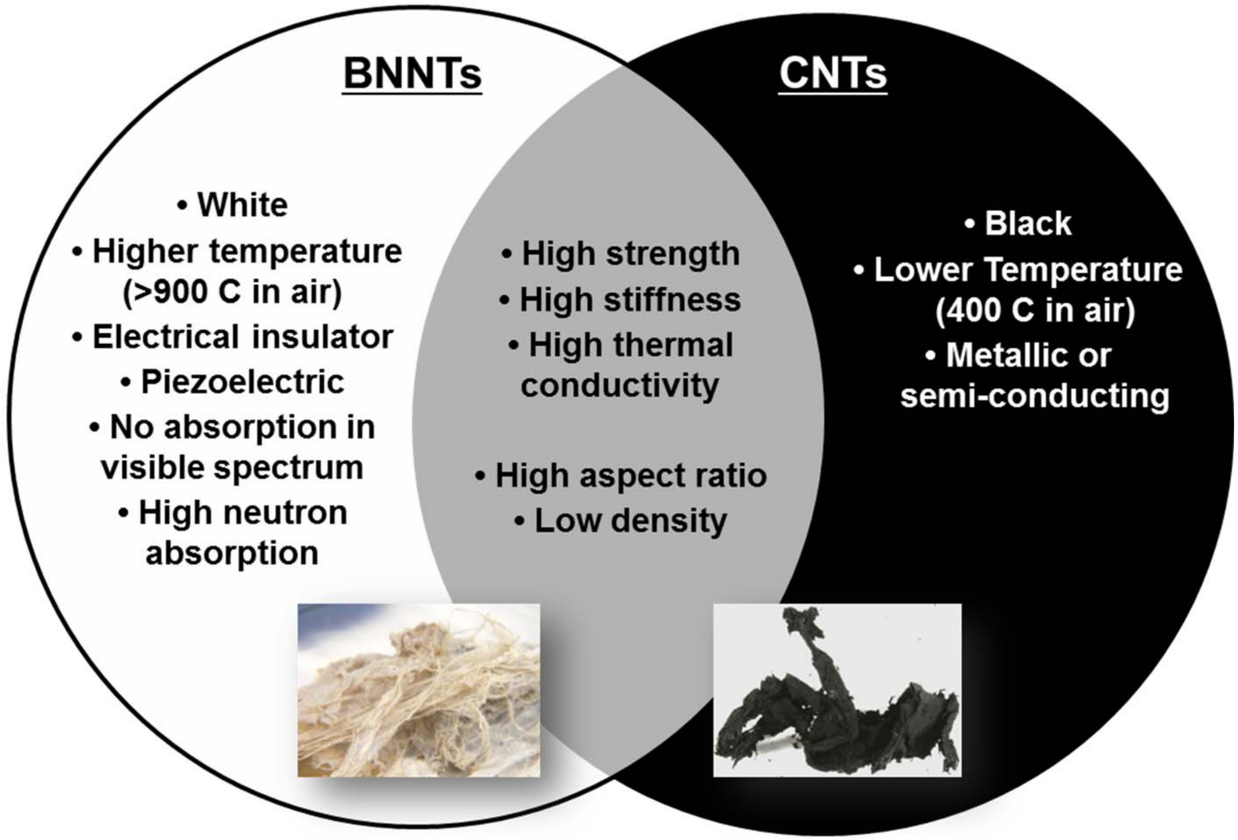
Boron Nitride Nanotubes (BNNTs)





- Theoretically proposed in 1994, and first synthesized in 1995
- Rolling up a hexagonal BN monolayer composed of alternating B and N
- Structurally similar to CNTs, thus mechanical properties as compelling as those of CNTs
- Other distinct physical and chemical properties, such as large band gaps, piezoelectricity, neutron adsorption, etc..

Nanotubes: Carbon and Boron Nitride

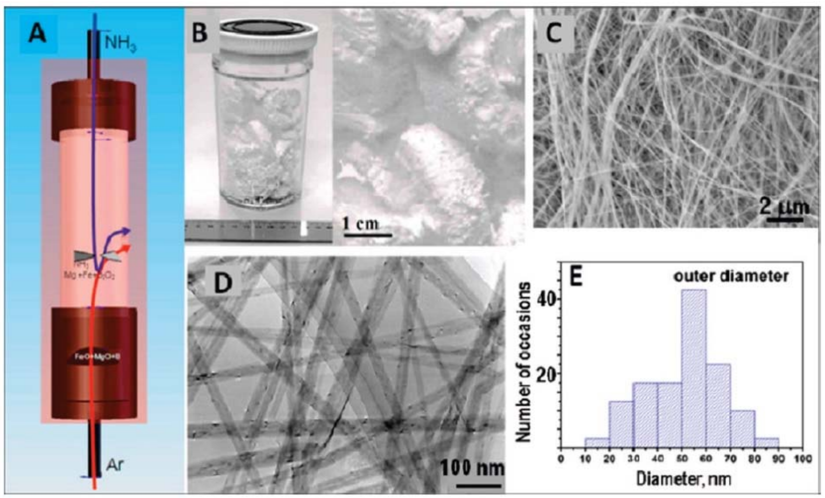


Potential composites advantages of BNNTs: e.g.,

- High-temperature composites
- Thermally conductive insulators
- Transparent composites
- Radiation shielding
- Piezoelectrics
- Flame resistance

BNTs Synthesis Methods

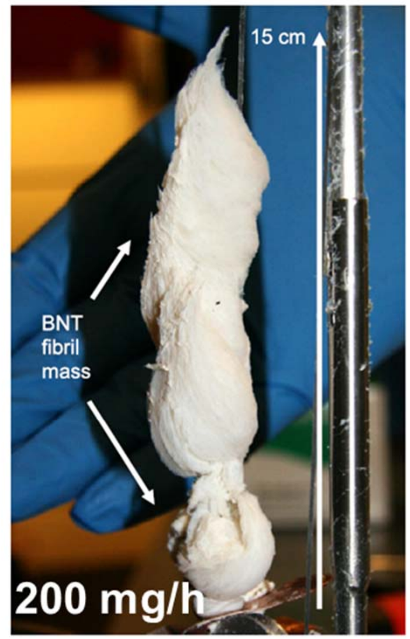
- **Low temperature routes (< 2,000 K)**
  - Chemical vapor depositions (CVD)
  - Floating catalysts CVDs
  - Ball-milling & annealing
  - Carbothermal reactions

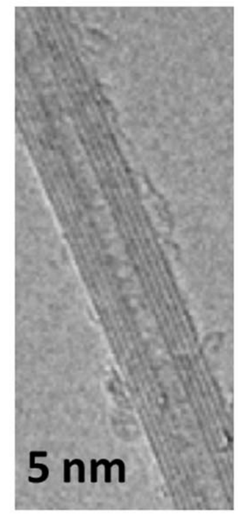


Zhi *et al*., Solid Stat. Comm., **135**, 67 (2005)

- **High temperature routes (>4,000 K)**

Smith *et al*., Nanotech. **20**, 505604 (2009)

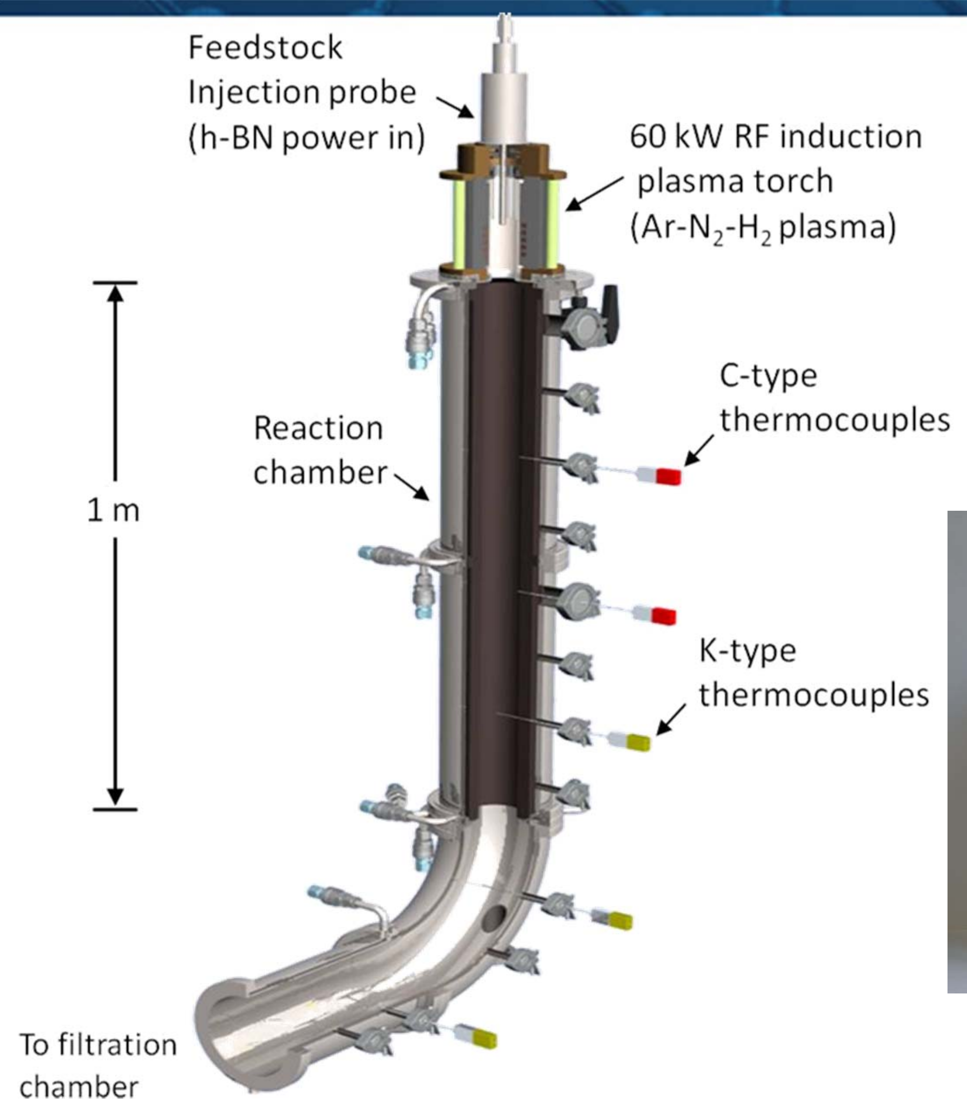




NASA @ Langley
Commercialization by BNNT LLC

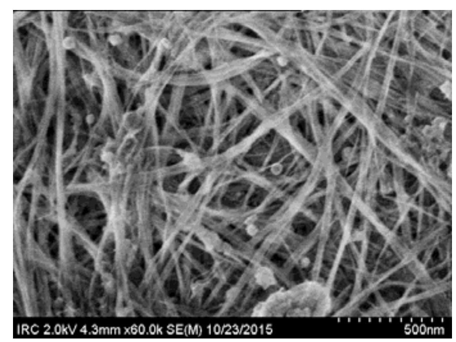
✓ High pressure laser process
✓ Small-diameter, few-walled BNNTs

Pilot-Scale BNNT Synthesis: Induction Thermal Plasma



- Atmospheric pressure
- Yield rate: > 25 g/h
- BNNT type: few-walled
- BNNT diameter: < 10 nm
- Hydrogen is essential.

No metal catalyst is needed !

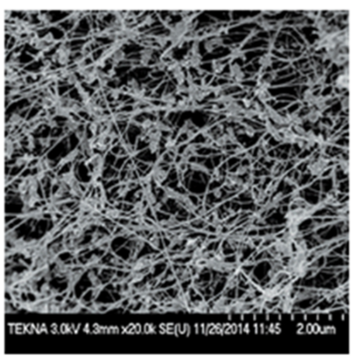


Towards Industrialization of BNNTs

- Literature: first synthesis reported in 1995, sub-gram yields are typical
- Lack of availability previously limited development (*Until now!*)
- Last year, NRC reported pilot-scale production of high-quality, small diameter BNNTs
- Accessibility of multigram-to-kg quantity → new opportunities for composites

TEKNA

NEW TEKMAT™ BNNT-R – Boron Nitride Nano Tubes



Typical Properties

- ☑ BNNT >60%
- ☑ Elemental B <25%
- ☑ Balance: h/BN and BNH derivatives
- ☑ No Metal Catalyst
- ☑ Nanotube diameter (nm): ~5
- ☑ Surface Area (BET): >100m^2/g

Available from SIGMA-ALDRICH: **802824**

Volume 92 Issue 21 | p. 41 | Concentrates
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C&EN
CHEMICAL & ENGINEERING NEWS

Making Boron Nitride Nanotubes In Bulk

Large-scale production of small-diameter nanostructures provides an opportunity to explore this material's applications

Email Print

By Bethany Halford

Department: Science & Technology
News Channels: Nano SCENE, Materials
Keywords: nanotubes, boron nitride, ind

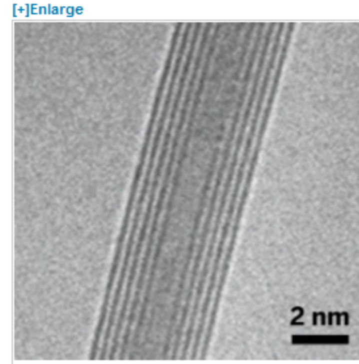
> ***"…kg quantities of high-purity and highly crystalline BNNTs are now accessible for the first time"!***
> *-Kim et al (ACS Nano, 2014)*

Science & Technology Concentrates

- Image-Guided Drug Design
- Diabetes-Related Enzyme Modulates Insulin, Amylin, And Glucagon
- To Uncover Substrates For Mystery Enzymes, Fragment-Based Approaches May Be A Poor Fit
- Simple Method Stabilizes Li-Ion Conductor
- Metal Whisker Growth Clarified
- Making Boron Nitride Nanotubes In Bulk
- Reducing CO_2 In Ionic Liquids
- Old Paintings' Egg White Coatings Unveiled
- All Concentrates

Like their all-carbon cousins, boron nitride nanotubes (BNNTs) possess exceptional mechanical properties, thanks to similarities in geometry. In certain areas, BNNTs even outperform carbon nanotubes. For example, they have a higher thermal stability, making them an attractive additive for high-temperature composites. But researchers have struggled to come up with a way to produce enough of these novel nanotubes to truly make them useful for real-world applications. Now, a team led by Benoit Simard of Canada's National Research Council has come up with an induction thermal plasma process capable of making 20 g of BNNTs per hour (*ACS Nano* 2014, DOI: **10.1021/nn501661p**). The resultant nanotubes (shown) have few walls, excellent cylindrical geometry, and a small diameter of about 5 nm. Simard and colleagues propose that during the synthesis boron condenses into droplets that nucleate the growth of the tiny tubes. They also found that hydrogen plays a crucial catalytic role in nanotube formation. "The yields demonstrated by this plasma synthesis process mean that kilogram quantities of high-purity and highly crystalline BNNTs are now accessible for the first time," the authors note.

[+]Enlarge



A transmission electron micrograph of a boron nitride nanotube.

Credit: *ACS Nano*

Chemical & Engineering News
ISSN 0009-2347

Patent appl.: Kim et al., US#61/813,324 (2013) | Kim et al, *ACS Nano* 8, 6211 (2014)

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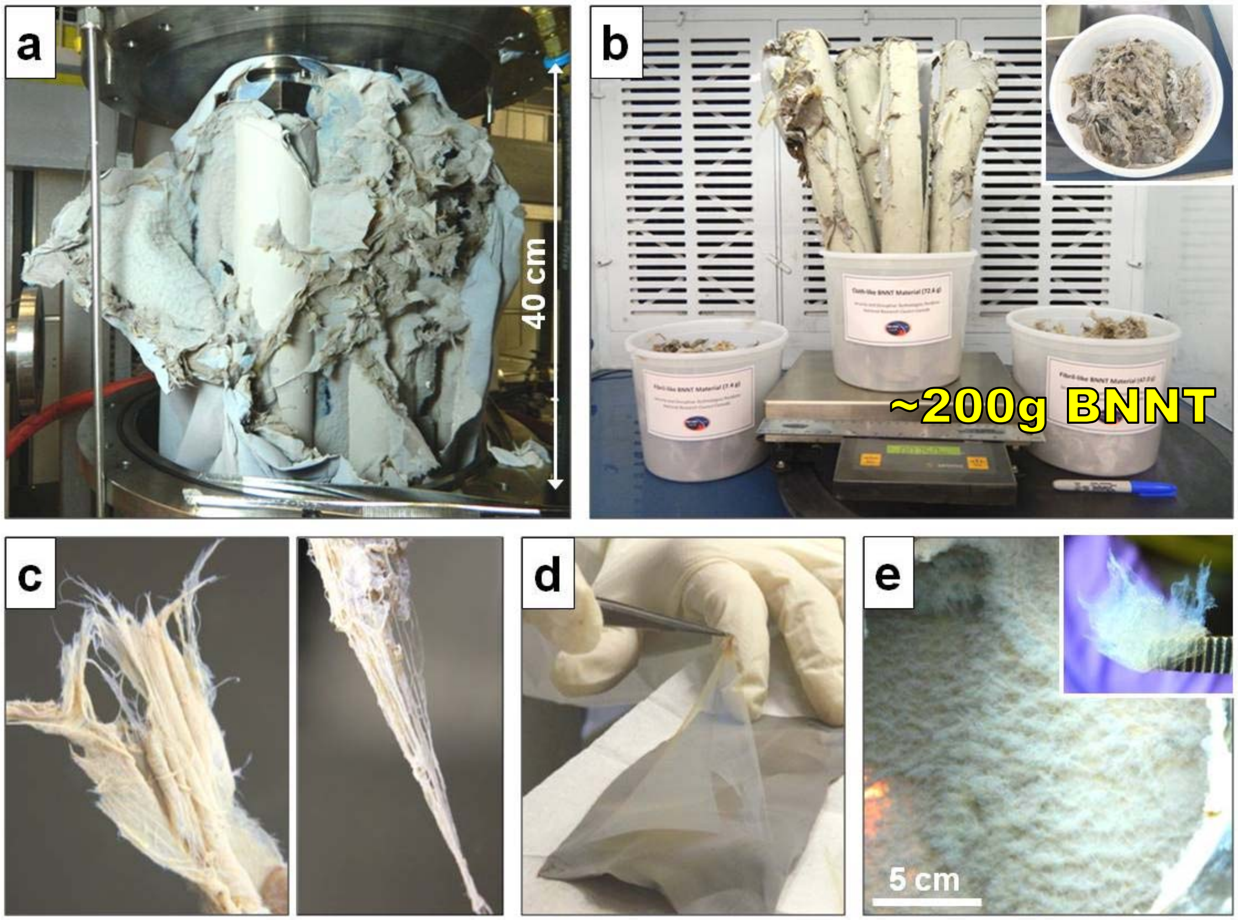
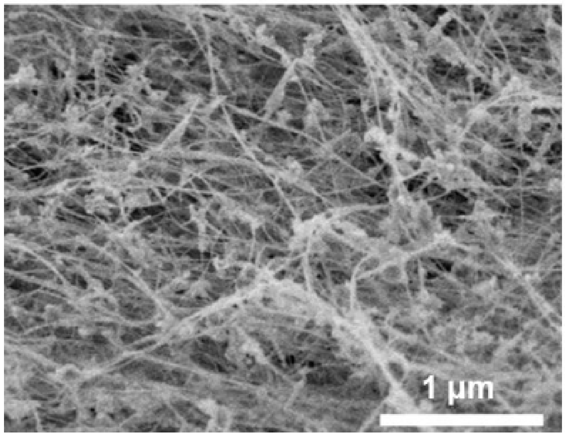
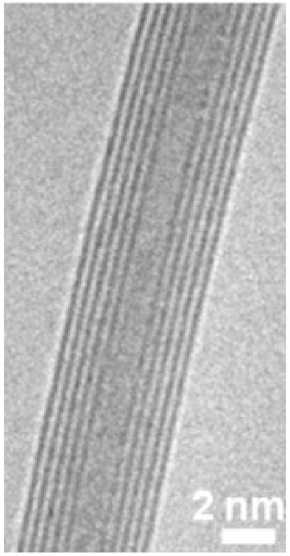
Large-scale Synthesis of BNNT (>20 g/h): Raw Materials



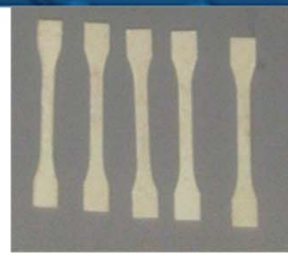


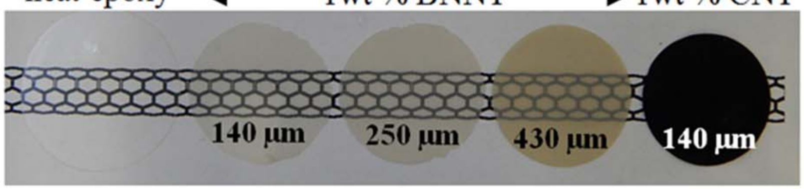


Kim et al, *ACS Nano* 8, 6211 (2014)

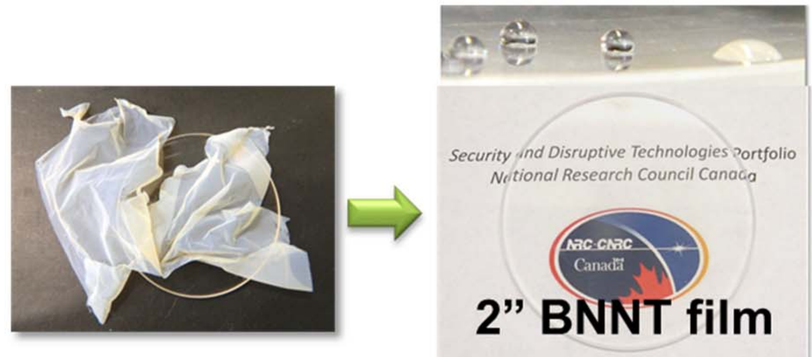
Development of BNNT Engineering Materials

Polymer Nanocomposites

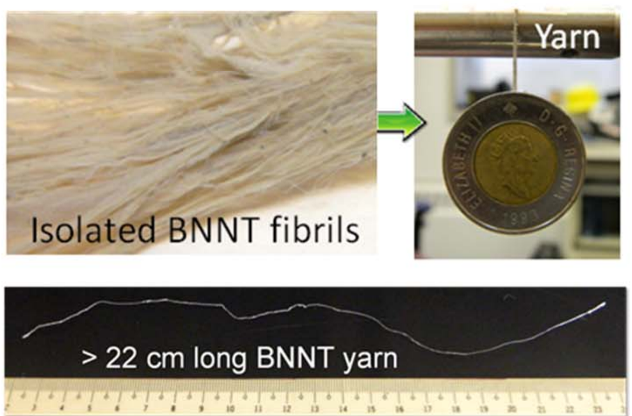




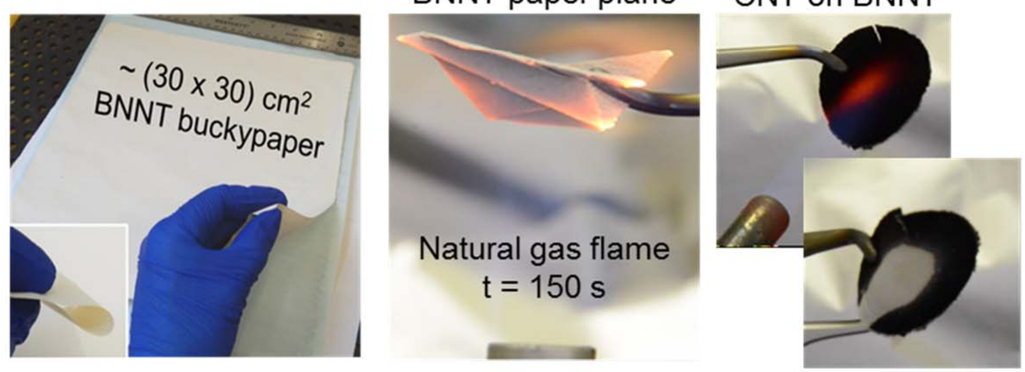
Thin films and coatings



Macroscopic Fibres



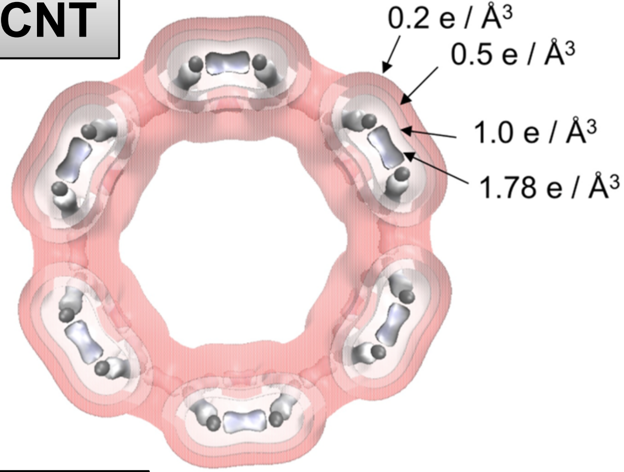
Multifunctional NT papers

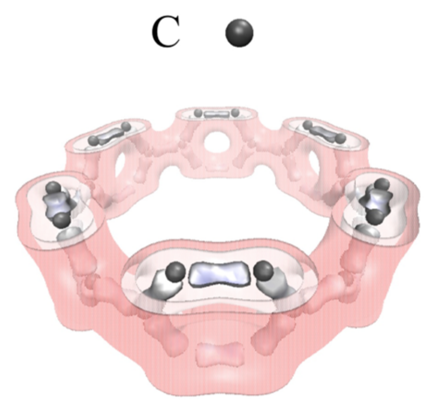


Valence electron density distributions

Shin *et* al., ACS Nano, 9, 12573 (2015).

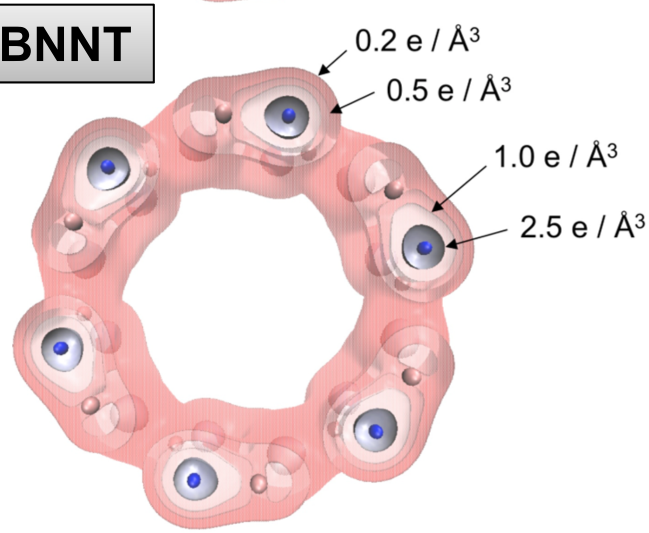
(6,6) CNT

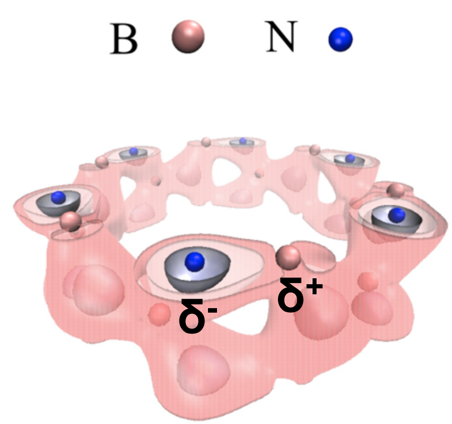




- Charge density is equally distributed around C atoms
- Strong covalent C-C bonds
- Delocalized π electrons

(6,6) BNNT





- Valence charges are concentrated around the N atoms
- Electronegativigy of B (2.04) and N (3.04) → partial charges±0.2~0.5e
- Mixed covalent-ionic bonding characteristics

NRC·CNRC

Chemistry of reduced BNNT-Computational studies

Shin *et al.*, ACS Nano, 9, 12573 (2015).

$$E_b^n = E_{tot}(NT + radical) - E_{tot}(NT) - E_{tot}(radical)$$

$$E_b^r = E_{tot}(NT^- + radical) - E_{tot}(NT^-) - E_{tot}(radical)$$

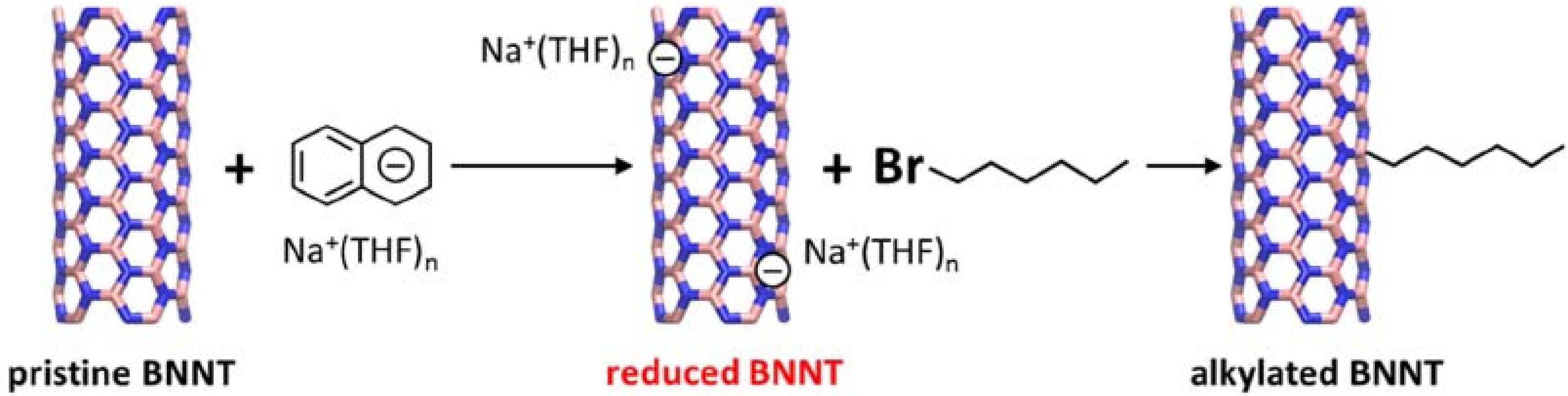
ρ=-1/*60* (*e*/atom)

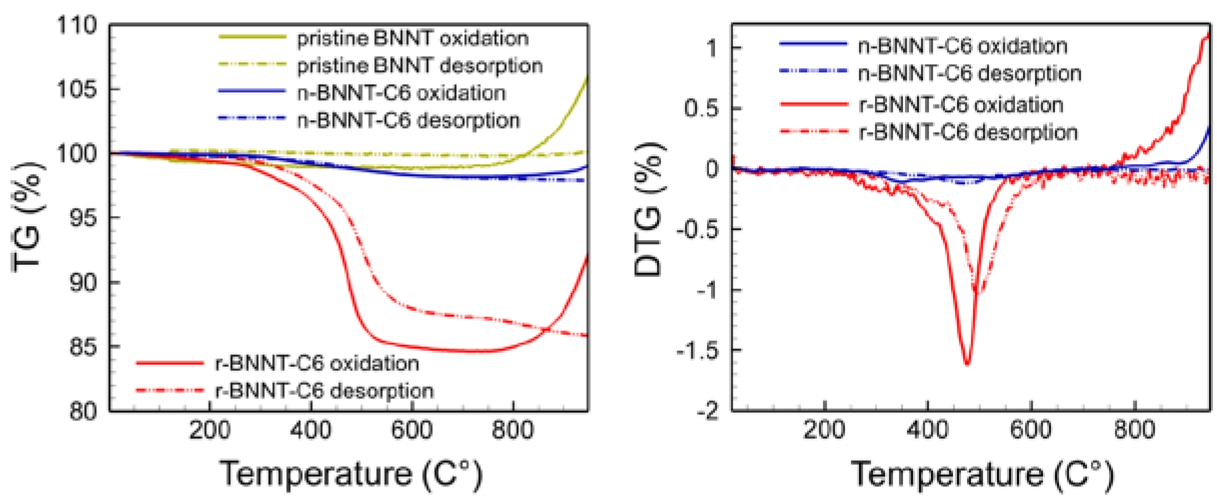
neutral tubes	E_b^n (eV)	reduced tubes	E_b^r (eV)	ΔE_b (eV)	ΔE_b^T (eV)
$B_{30}N_{30} + \bullet CH_3$	0.06	$B_{30}N_{30}^- + \bullet CH_3$	-2.86	2.91	4.14
$B_{30}N_{30} + \bullet NH_2$	-0.64	$B_{30}N_{30}^- + \bullet NH_2$	-3.54	2.89	4.26
$B_{30}N_{30} + \bullet OH$	-1.36	$B_{30}N_{30}^- + \bullet OH$	-4.70	3.34	5.00
$B_{30}N_{30} + \bullet NH$	-2.34	$B_{30}N_{30}^- + \bullet NH$	-3.26	0.93	2.41
$B_{30}N_{30} + NH_3$	-0.43	$B_{30}N_{30}^- + NH_3$	-0.60	0.17	-
$C_{60} + \bullet CH_3$	-1.01	$C_{60}^- + \bullet CH_3$	-1.24	0.24	0.12
$C_{60} + \bullet NH_2$	-1.01	$C_{60}^- + \bullet NH_2$	-1.33	0.32	0.19
$C_{60} + \bullet OH$	-1.63	$C_{60}^- + \bullet OH$	-2.09	0.46	0.22
$C_{60} + \bullet NH$	-3.14	$C_{60}^- + \bullet NH$	-1.82	-1.32	-2.39
$C_{60} + NH_3$	-0.23	$C_{60}^- + NH_3$	-0.34	0.11	-

1) Upon **reduction**, **BNNTs drastically improve their binding affinity** toward radical molecules, due to the extra electron localization
2) The reduction of CNTs only moderately increases their binding affinities with radical molecules
3) No significant changes for non-radical molecules, such as ammonia

Chemistry of reduced BNNT-Experimental studies

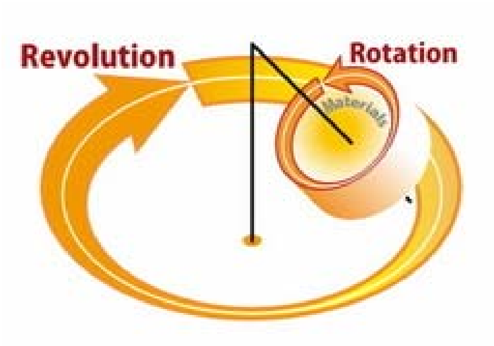
Shin *et* al., ACS Nano, 9, 12573 (2015).



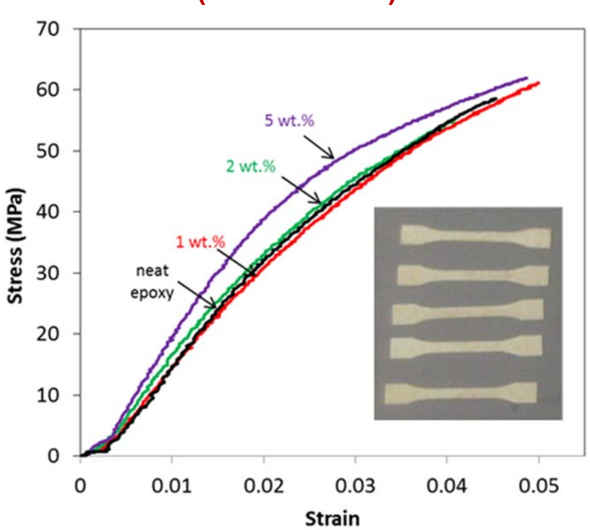


Thermoset Nanocomposites with Dispersed BNNTs

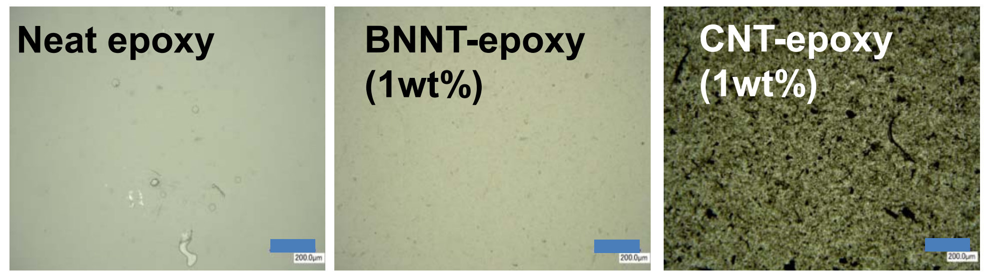
Filler: as produced BNNTs
Matrix: EPON 828 Epoxy

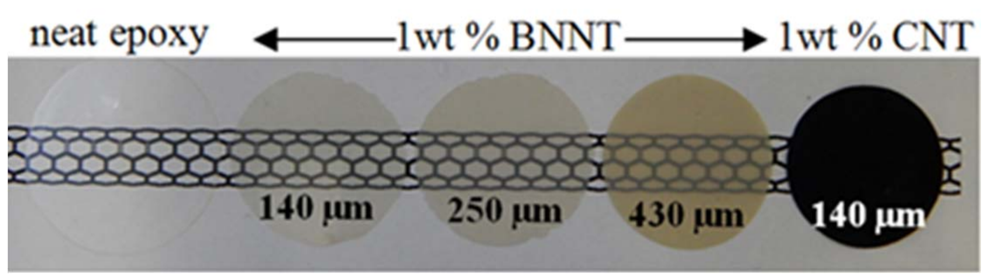


Planetary Centrifugal Mixer (solvent-free)



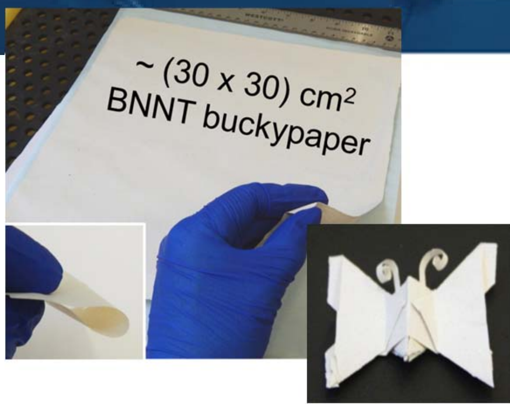
Transmission Optical Images





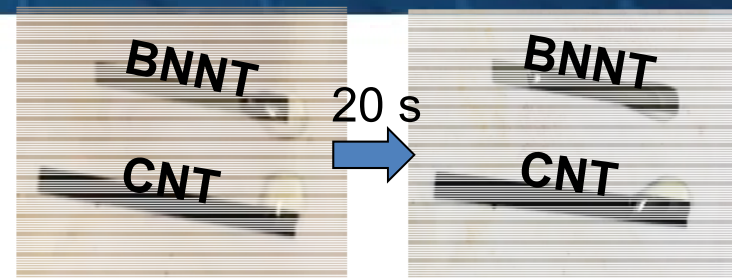
- Integration by planetary mixing (solvent-free)
- Small viscosity increase (up to 2 wt%), *c.f.*, large increase with small-diameter MWCNTs
- Potential for transparent coatings and composites

High BNNT content composites:
Epoxy-impregnated buckypaper (30 wt.% BNNTs)

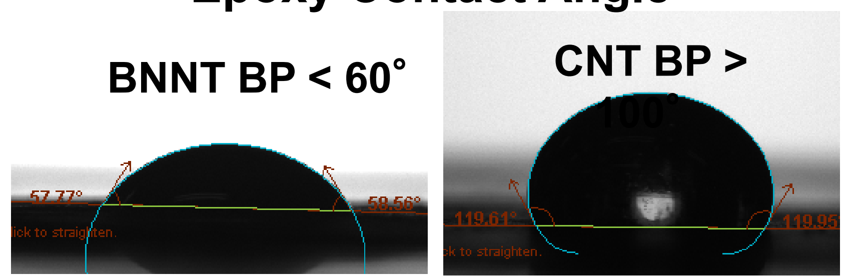


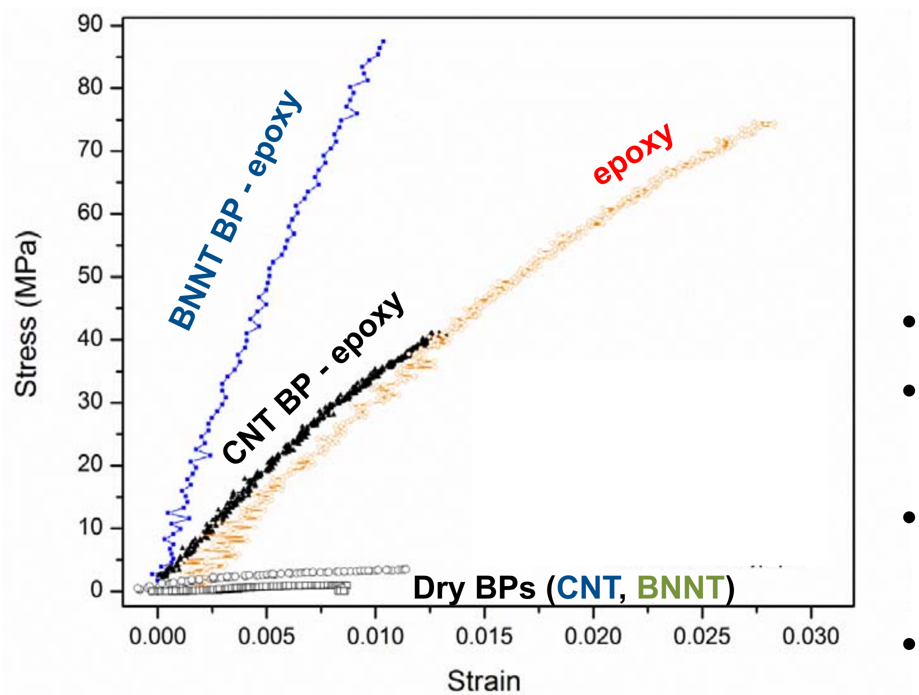
MY0510-epoxy/BNNT

Wicking



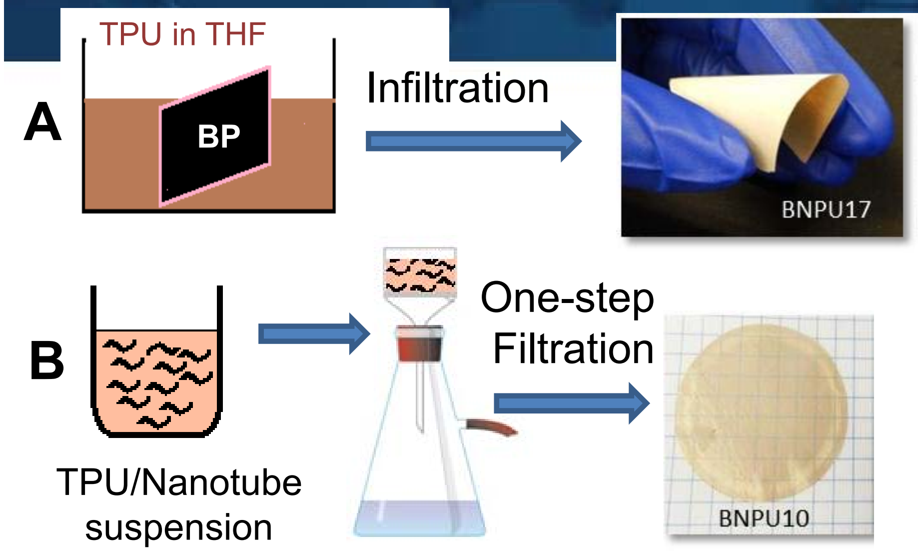
Epoxy Contact Angle





- Partially transparent (60 µm thick)
- Better interaction between BNNT and resin than CNT (wicking, contact angle)
- Young's modulus: over 2x neat epoxy and 20x unimpregnated BP
- Encouraging thermal conductivity results

Polyurethane-Modified Buckypaper Composites

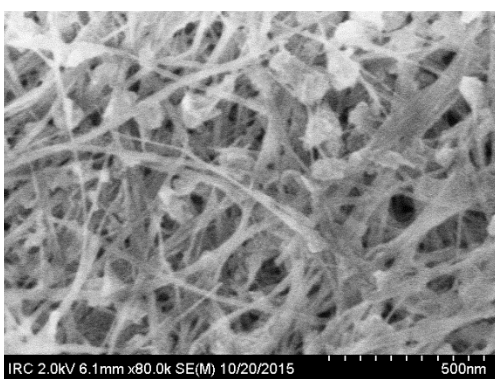


Characteristics of BNNT/TPU buckypapers

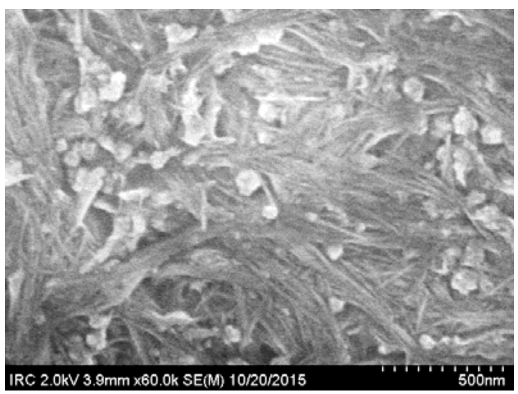
Sample	Method	BNNT:TPU (wt. ratio)	Density (g/cm^3)
BNNT		100:0	0.38
BN80PU20	**A**	80:20	0.50
BN90PU10	**B**	90:10	0.61
BN80PU20	**B**	80:20	0.70
BN60PU40	**B**	40:60	1.2

Method B

BNNT/TPU 80:20 (wt. ratio)



BNNT/TPU 40:60 (wt. ratio)



- Low-density, porous nanotube-network morphology can be retained → intermediate step to other composite fabrication

- The one-step filtration method enabled control of the TPU content → tailor properties from buckypaper-like to PU-like

Confidential

Kim et al, *RSC Advances* 5, 41186 (2015)

Summary on BNNT

- Small-diameter BNNTs synthesized at high purity and high yield by thermal plasma technology.
- Largest production capacity for BNNTs; Technology now in industry hands.
- Enabling technology for development of BNNT composites and other large scale applications.
- Dispersed BNNT composites: easier dispersion than CNTs (better CNT-epoxy interaction for materials tested), transparent coatings, electrical insulating equivalent of CNTs for joint enhancement. Dramatic increase in thermal stability (+50 ^{o}C) in PC and T_g (+40^{o}C) in epoxy.
- BNNT buckypaper: easy handling, high wt.% BNNT nanocomposites; potential for structural & multifunctional composites.
- Multifunctional materials opportunities, including in combination with CNT (complimentary properties) and other nanomaterials.

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