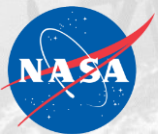


Boron Nitride Nanotube: Synthesis and Applications

Cheol Park

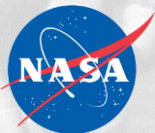
Advanced Materials and Processing Branch
NASA Langley Research Center, Hampton, VA USA

*Macromolecular Science and Engineering, University of Michigan
Ann Arbor, MI, March 10, 2014*



NASA Langley Research Center

Acknowledgements



NASA Langley Research Center

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Mohammad Adnan, Matteo Pasquali



NASA Langley Research Center: C&I, B&P, OD, IRAD, NIAC



AFOSR Low Density Materials: FA9550-10-1-0451

Outline

- BNNT Research Motivation
- Synthesis
- In-situ Diagnostics/ex-situ Characterizations
- Modeling/Simulation
- BNNT Properties
- BCN Nanotubes (BCNNT)
- Summary

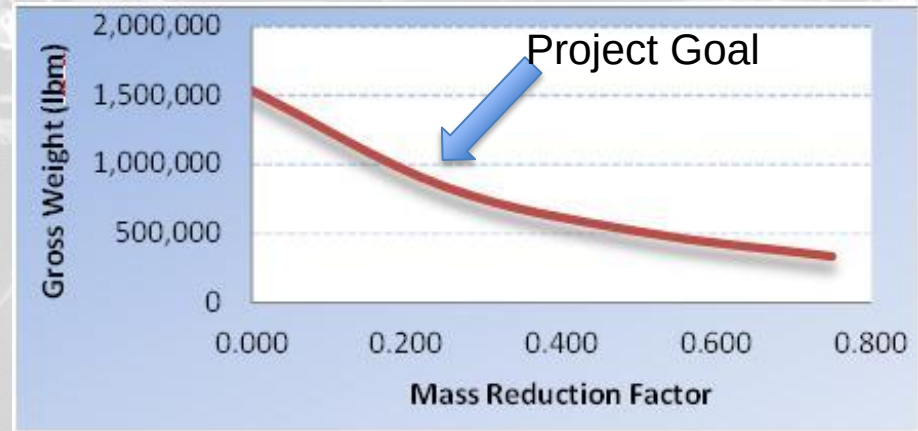
Strategic Overview

- Vehicle weight is a primary driver for most NASA missions.

Reducing vehicle weight can:

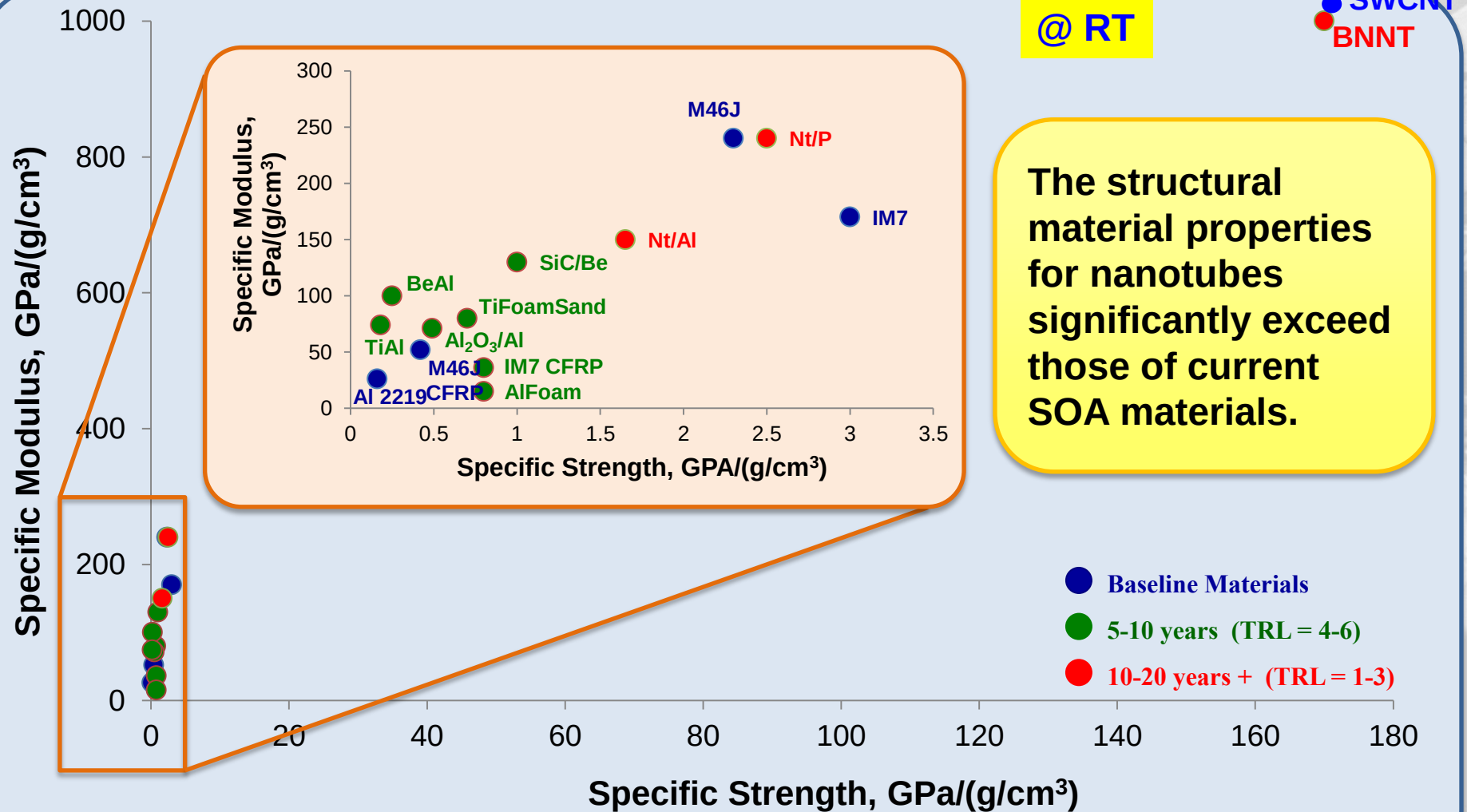
- Expand mission capability
- Reduce launch costs
- Reduce fuel consumption
- Systems analysis shows that **reducing materials mass by 20% leads to a 30% reduction** in launch vehicle gross weight
- Same study indicates a **50% reduction in materials mass reduces launch vehicle gross weight by >60%**, enables potential single stage to orbit designs
- Additional **multifunctionality**: thermal, radiation protection, sensing capabilities, no corrosion

Effect of Materials Mass Reduction on Launch Vehicle Gross Weight

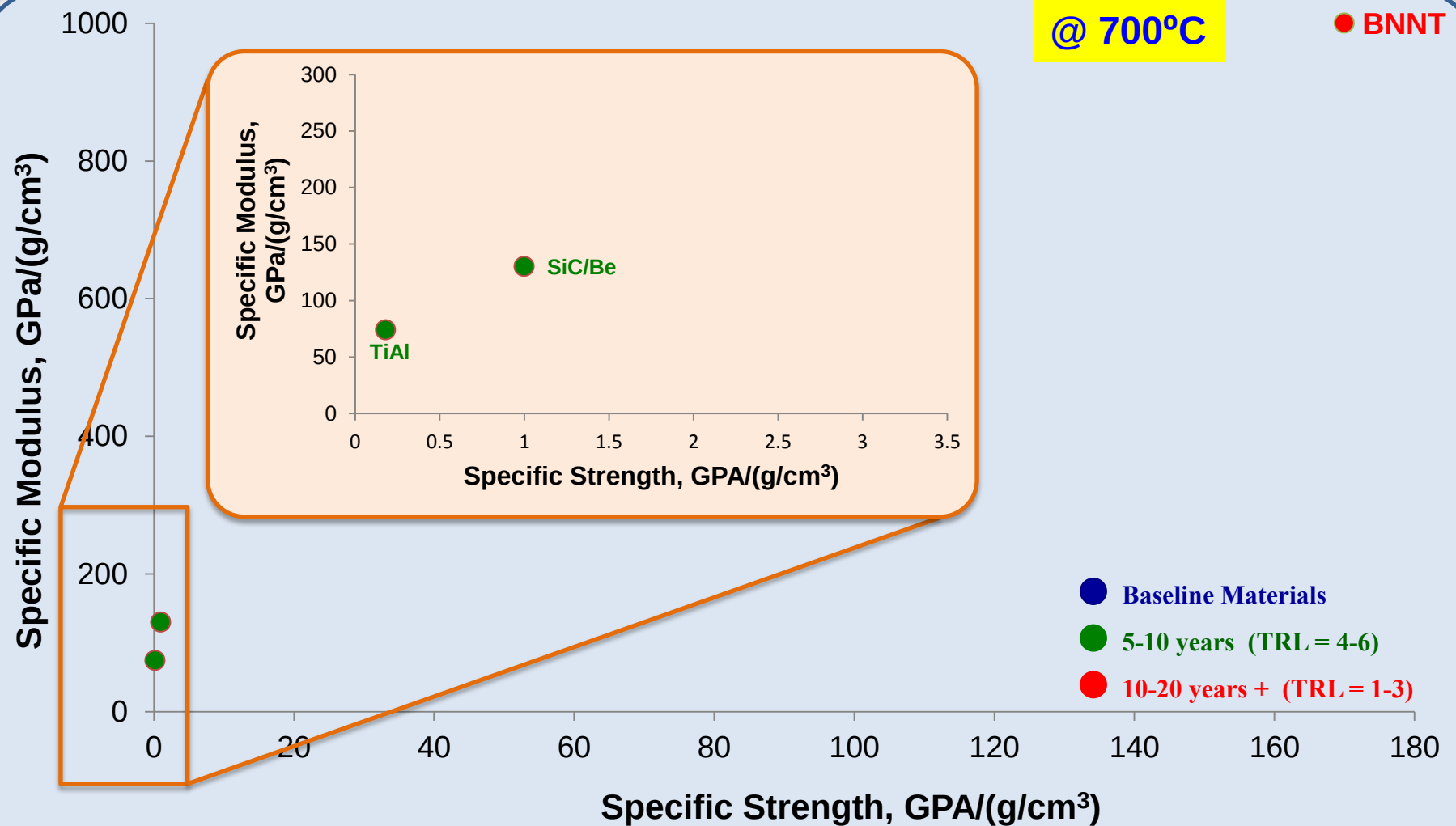


Potential Impact: Produce advanced **lightweight structural BNNT composites** with higher thermal stability, no corrosion, high toughness, sensing/actuation, and radiation shielding effectiveness

Properties of Materials for Vehicle Structure



Properties of Materials for Vehicle Structure





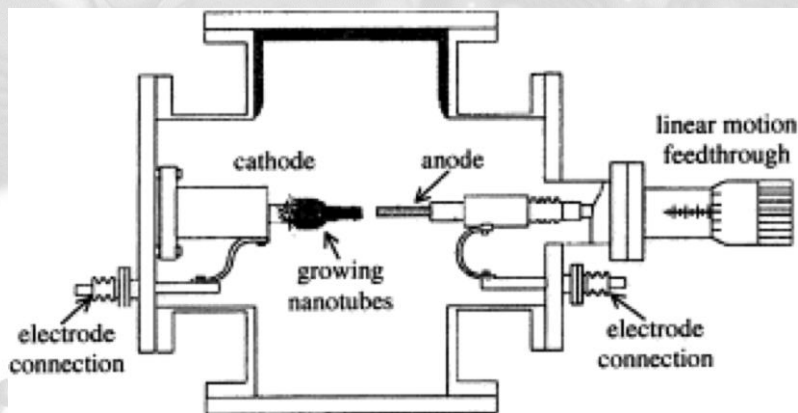
Nanotube Comparison



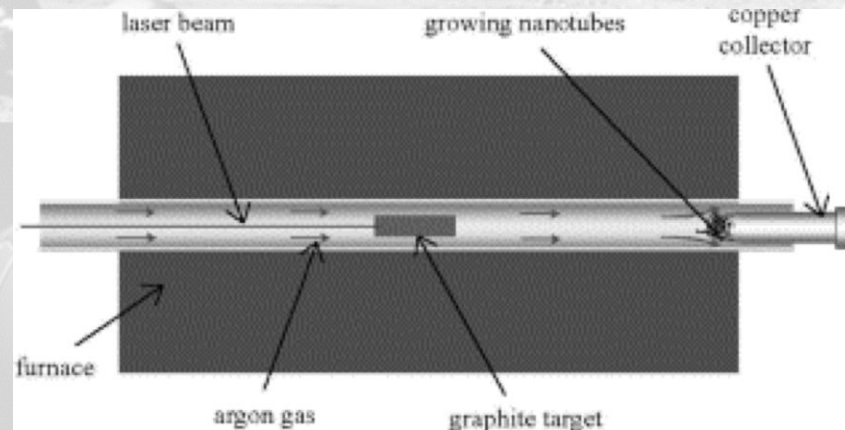
	Carbon Nanotubes	Boron Nitride Nanotubes
Electric Properties	Metallic or semiconducting	Wide band gap (about 6.0 eV band gap)
Mechanical Properties (Young's Modulus)	1.33 TPa (very stiff)	1.18 TPa (very stiff)
Thermal Conductivity	>3000 W/mK (highly conductive)	~300–3000 W/mK (highly conductive)
Thermal Oxidation Resistance	Stable up to 300-400 °C in air	Stable to over 800 °C in air
Neutron Absorption Cross-Section	C = 0.0035 barn	B = 767 barn (B ¹⁰ ~3800 barn) N = 1.9 barn (Excellent radiation shielding)
Polarity	No dipole	Permanent dipole Piezoelectric (0.25-0.4 C/m ²)
Surface Morphology	Smooth	Corrugated (Provides better bonding for composites, ionic bonding)
Color	Black	White (can be dyed to color)
Coefficient of Thermal Expansion	-1 x10 ⁻⁶ K ⁻¹ (very low)	-1 x 10 ⁻⁶ K ⁻¹ (very low)

Synthesis Methods of Carbon Nanotubes

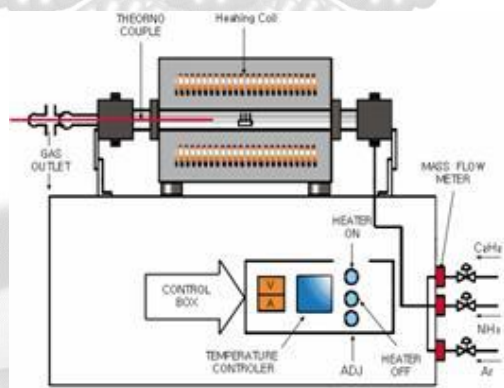
- Arc-discharge: solid state carbon precursor
- Laser ablation: solid state carbon precursor
- Chemical vapor deposition (CVD): gaseous carbon precursor
- High pressure carbon monoxide (HiPco): Smalley (Rice Univ) funded by NASA.
- Free Electron Laser (Jefferson Lab): funded by NASA-LaRC C&I



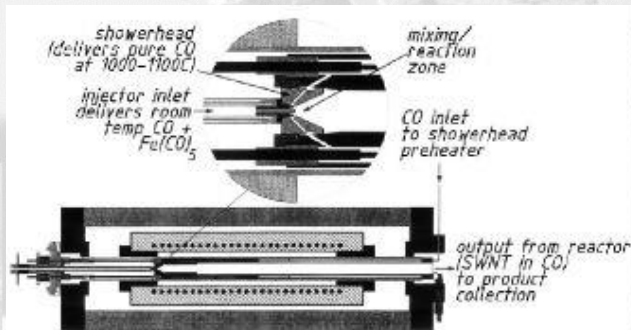
Arc-discharge



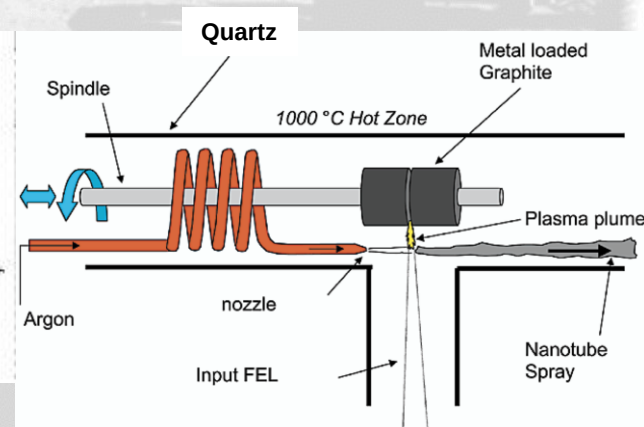
Laser ablation



Chemical vapor deposition (CVD)



HiPco



Free Electron Laser (Jefferson Lab)

BNNT Synthesis History

- First Theoretical prediction: *PRB* **49** 5081–5084 (1994) (Cohen, UC Berkeley), computation
- First Synthesis Arc Discharge: *Science* **269** 966 (1995) (Cohen, Zettl, UC Berkeley) BNNT by Arc Discharge
- Arc Discharge: *PRL* **76** 4737 (1996) (ONERA France, Loiseau) Arc Discharge HfB₂ with N₂ gas
- Laser heating: *APL* **69** 2045 (1996) (NIMS Japan, Golberg, Bando), Diamond Anvil, c-BN target laser heating High pressure
- Laser ablation: *APL* **72** 1966 (1998) (Yu, BN powder with Co/Ni, first laser ablation
- Ball Milling/Thermal Annealing: *CPL* **74** 2782 (1999) (ASU, Australia, Chen) Ball milling of B powder in NH₃ gas
- CVD: *Chem. Mater.* **12** 1808 (2000) (WA Univ, Lourie, Ruoff, Buhro) CVD Borazine (B₃N₃H₆)
- Laser ablation, *PRB* **64** 121405(R) (2001) (ONERA Lee, Loiseau) CO₂ laser, no catalyst
- CVD: *Solid State Comm.* **135** 67 (2005) (NIMS, Zhi. Bando, Golberg) CVD NH₃ B₂O₃ from MgO/B powder
- High Pressure, High Temp, Laser vaporization: *Nanotechnology* **20** 505604 (2009) (NIA/NASA/Jlab) High Temperature, Pressure (HTP) BNNT, Free Electron Laser/CO₂ Laser

High Temperature, Pressure (HTP)-BNNTs

- Free Electron Laser or CO₂ laser
- No Catalyst, only B and N resource
- Very long, small diameter, highly crystalline BNNT

Physics Today, P35, Nov 2010, **Cohen and Zettl** quoted,
“A particularly effective recent production method focuses kilowatt-power laser beams on boron-containing feedstock in a high-pressure nitrogen atmosphere [1]. The development of that and other high-throughput synthesis methods is yielding larger quantities of samples and rapidly changing the landscape of BNNT scientific study.”

Free Electron Laser: Atmosphere



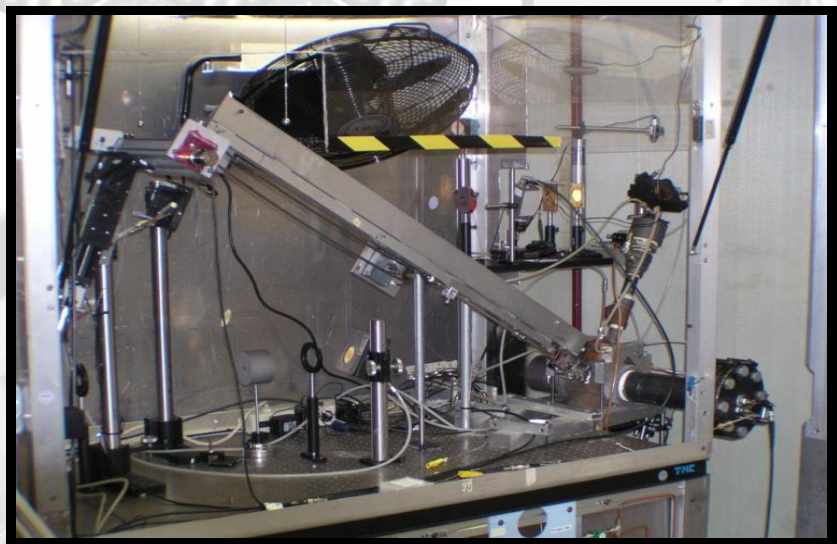
Free Electron Laser: High Pressure



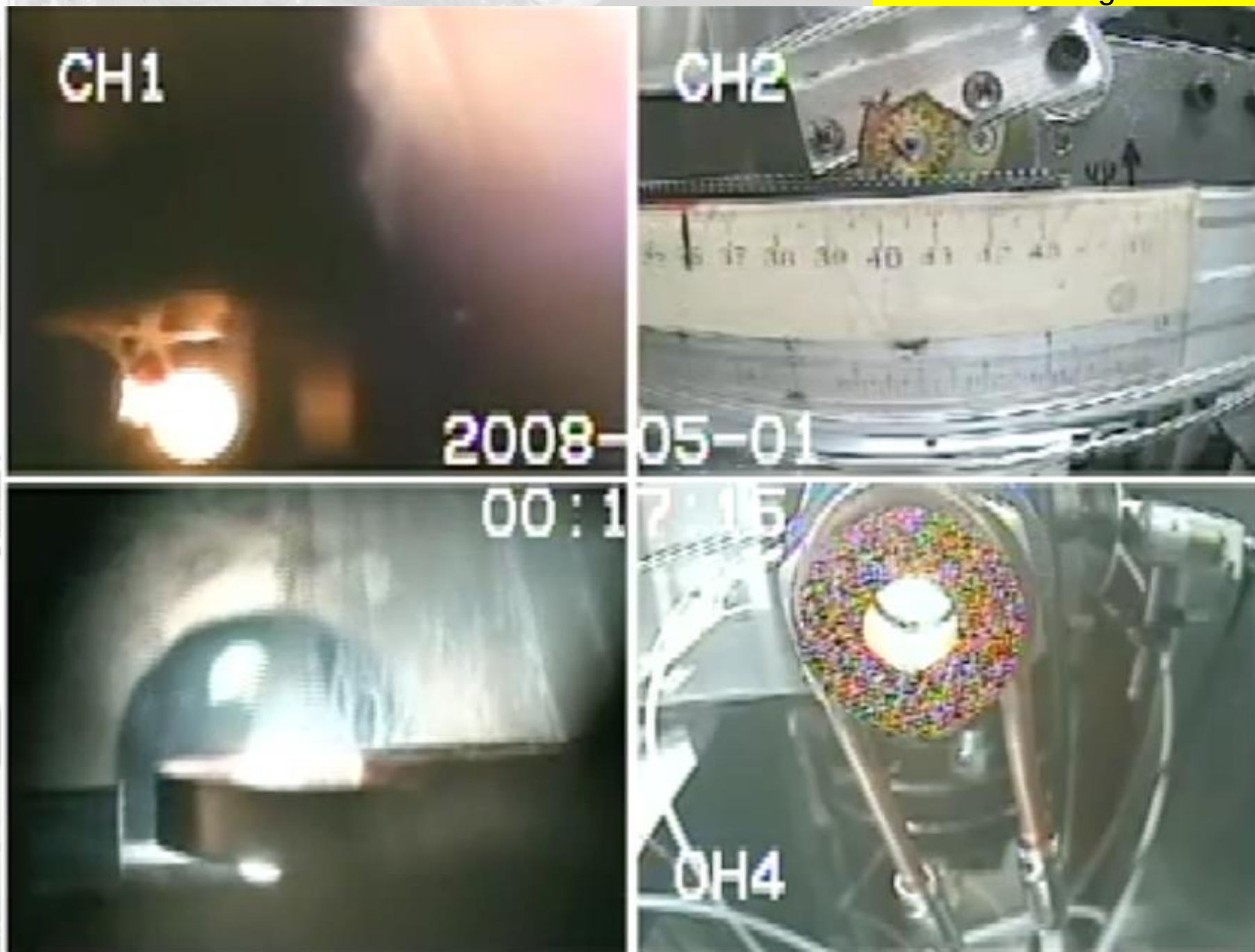
BNNT Synthesis



Production Chamber



- 5 kW of infrared radiation @ $10.6\mu\text{m}$
- Heat source for vaporizing Boron feed stock above 3500°C
- Pressurized with Nitrogen to 200 psi
- LaRC rig operating since May 2012; producing 30 mg/hour of BNNT; monthly production with 25% operation time is 1.2 g.



Cotton-like High Pressure and Temperature (HPT)-BNNT (~ 30 minutes run time)

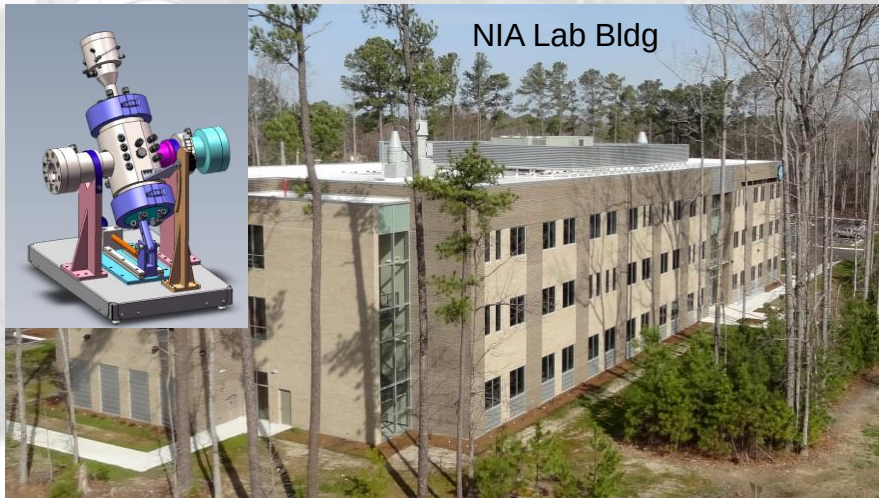


Benefits

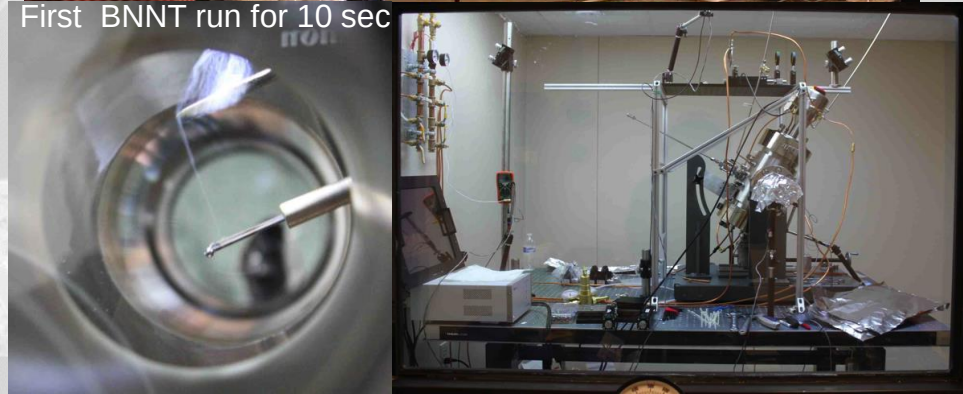
- One-to-few-walled tubes with high crystallinity
- Very long, high-aspect ratio tubes
- High scale-up potential
- No toxic catalysts (only B and N as reactants)
- Standard industrial cutting/welding lasers
- High service temperature (over 800°C)
- Highly electroactive (due to the B-N polar bond)
- Neutron radiation shielding (due to their B content)



NIA Research and Innovation Laboratories



First BNNT run for 10 sec

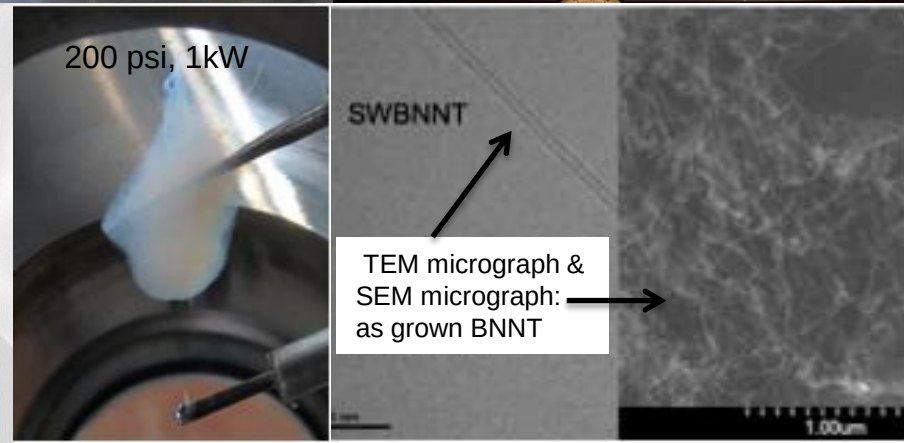


First BNNT run successfully without optimization July 2013; excellent quality (long, thin, highly crystalline BNNT)

Successful pressure test up to **950 psi** (higher pressure leads to better BNNT potentially)

In-situ diagnostic tools installed (planar laser induced fluorescence: PLIF); more tools coming (CARS, pyrography, high speed camera...)

Parallel computational study for nucleation and growth ongoing (both NIA and NASA)

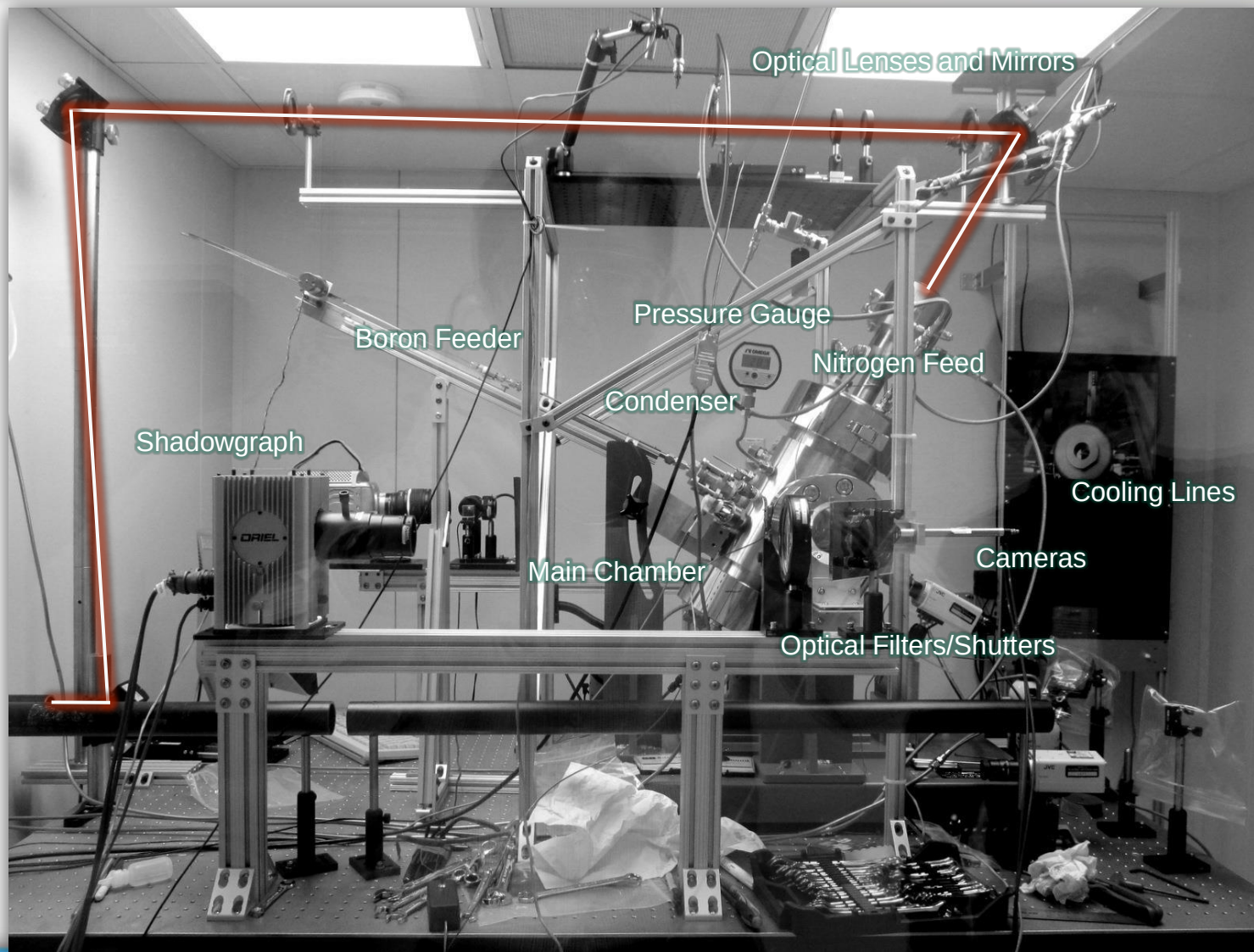


NIA BNNT Chamber

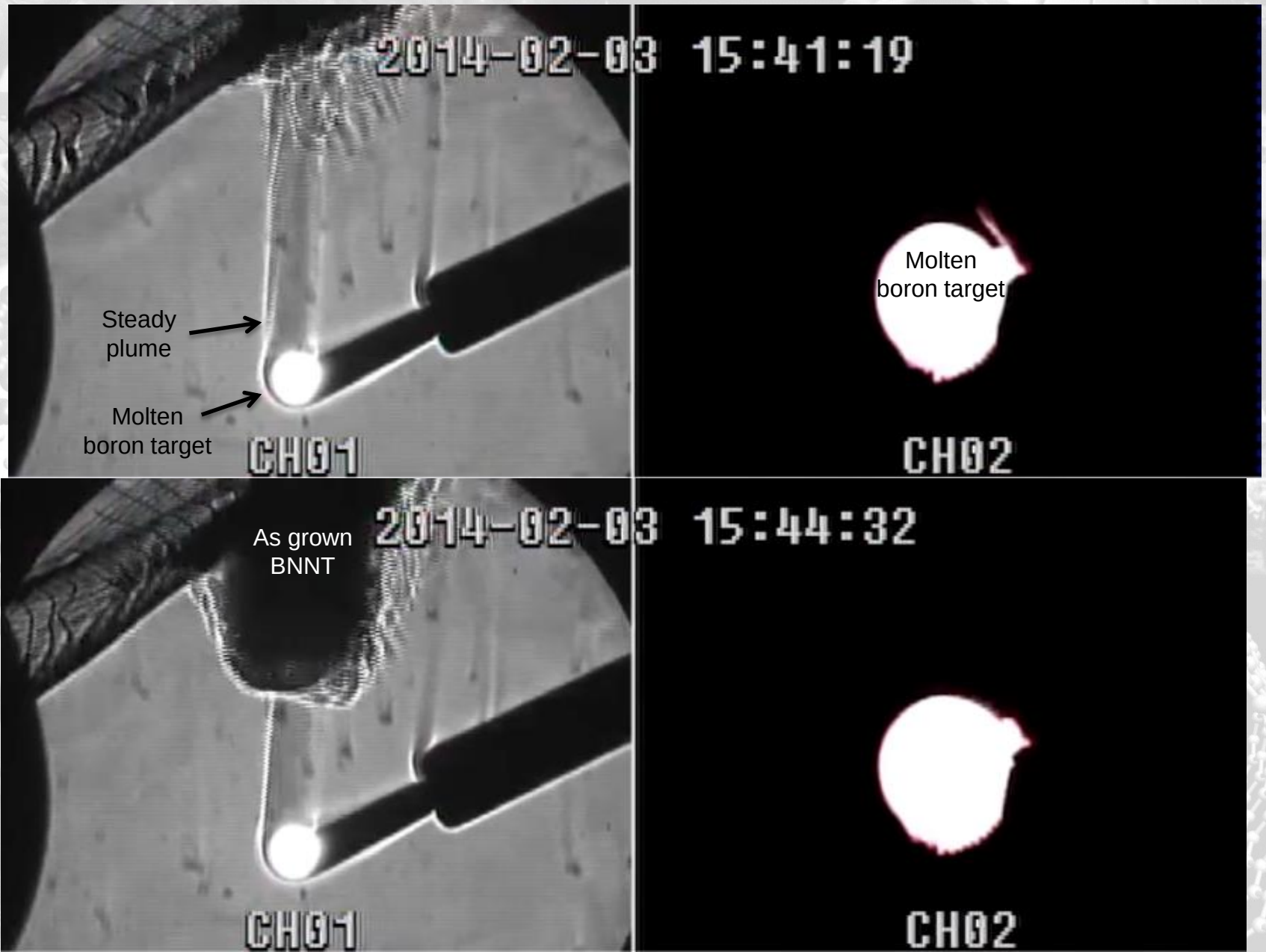
NATIONAL
INSTITUTE OF
AEROSPACE



Sang-Hyon Chu, NIA



NIA BNNT Science Rig HTP Run (Snap Shots)

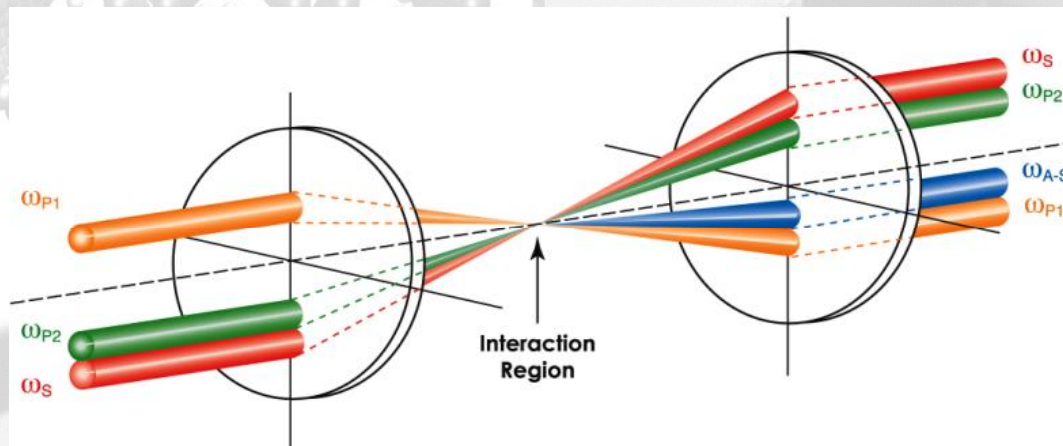
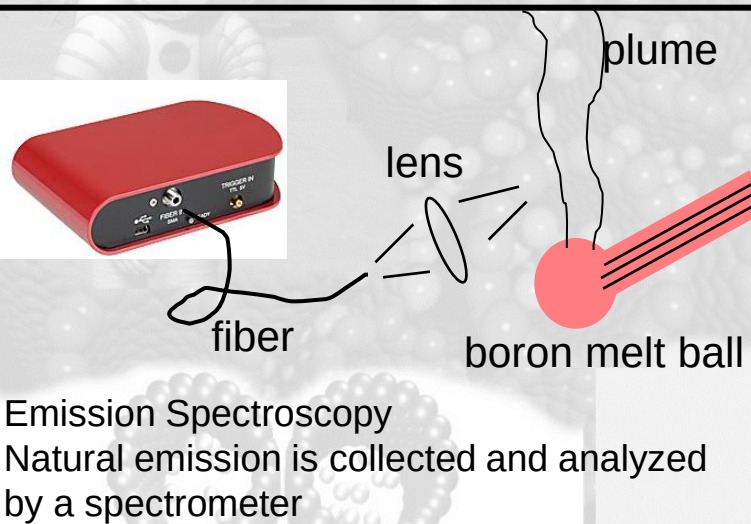


Diagnostics

Paul Danehy/Jennifer Inman/Steve Jones

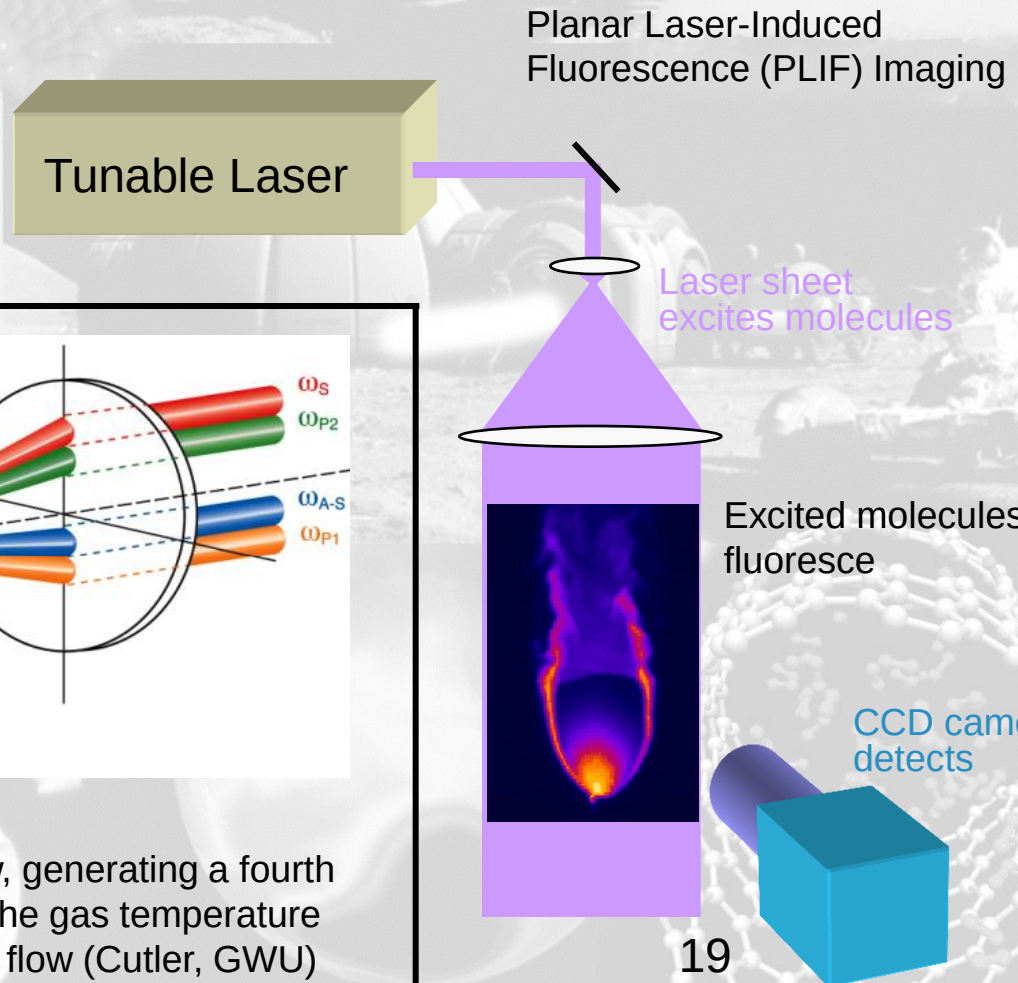


Diagnostics should help explain *how* and *why* as well as providing validation data.



Dual-pump CARS

Three laser beams are focused into the flow, generating a fourth beam which can be analyzed to determine the gas temperature and species concentrations at a point in the flow (Cutler, GWU)



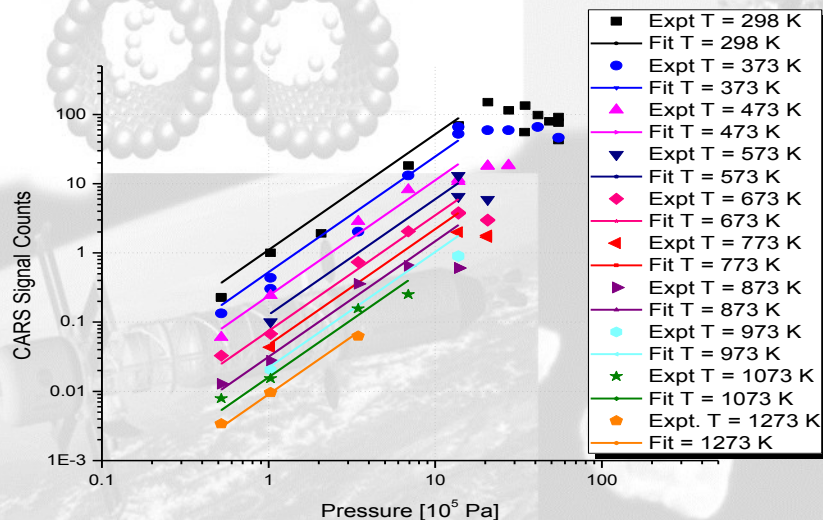
Optical Diagnostics for BNNT

- Provide qualitative and quantitative information about BNNT production process to aid in understanding the fabrication process and to provide data to validate computations.

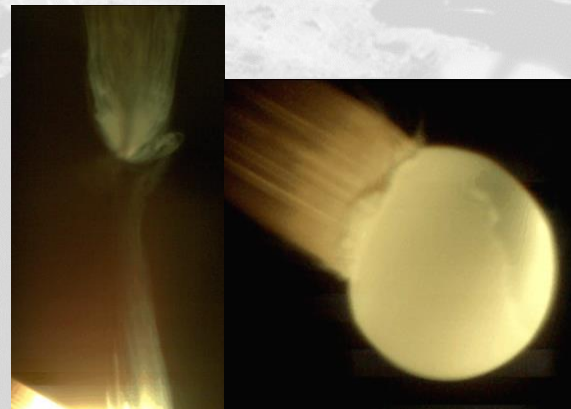
In-situ Diagnostic Systems

- High speed (1 kHz) imagery showed that the nanotube fibrils were being generated before they hit the condenser wire, challenging the conventional view of how the BNNT growth process works.
- Shadowgraph system set up in NIA BNNT rig, allows day-to-day monitoring of BNNT synthesis
- High speed (1 kHz) optical pyrometer being developed to study melt-ball dynamics.
- CARS spectroscopy for temperature and N_2 , B_2 and BN mole fraction tested at high pressure.
- BN planar laser-induced fluorescence (PLIF) imagery capability being developed.

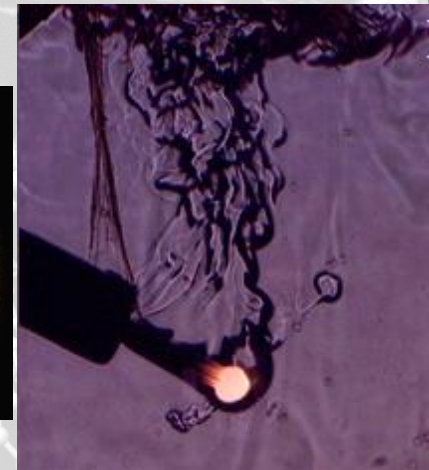
CARS intensity measurements



High speed camera imagery

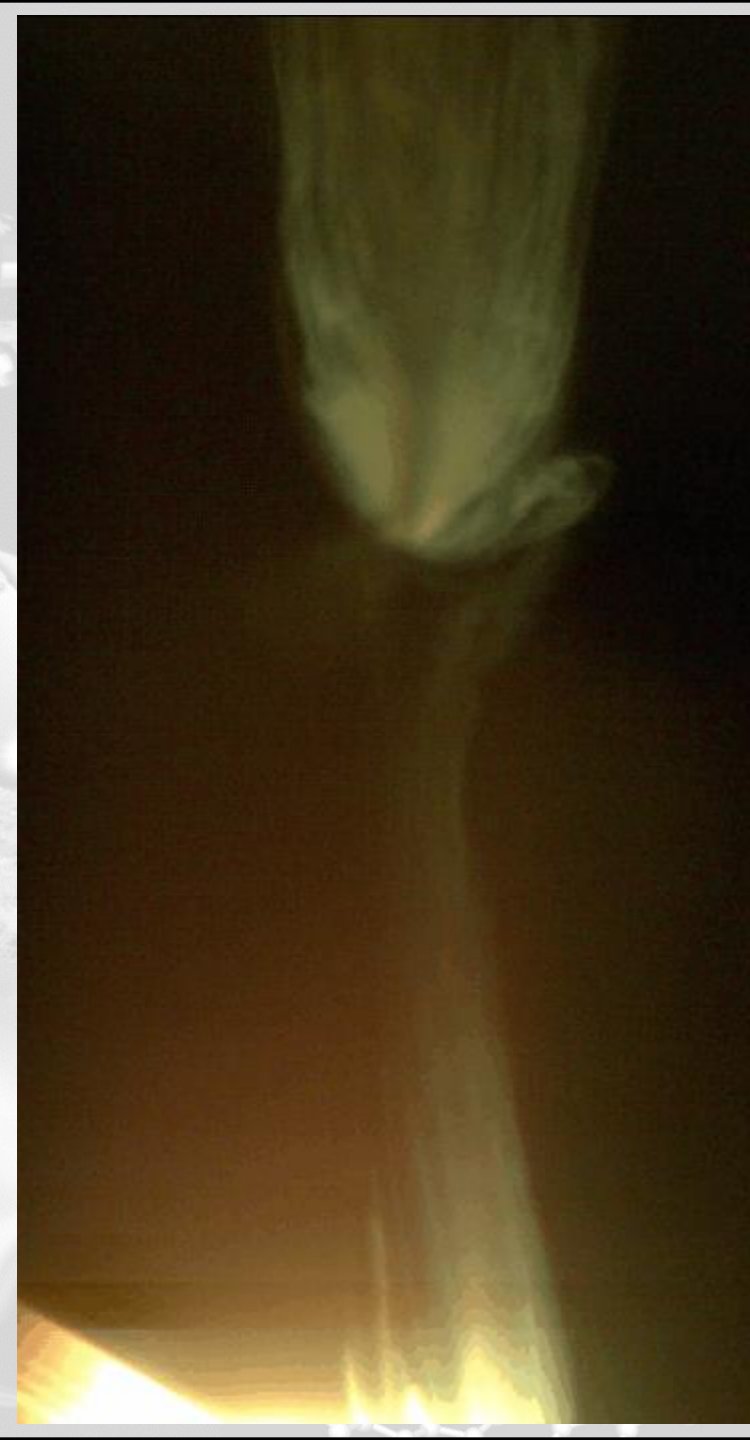


Shadowgraph imagery

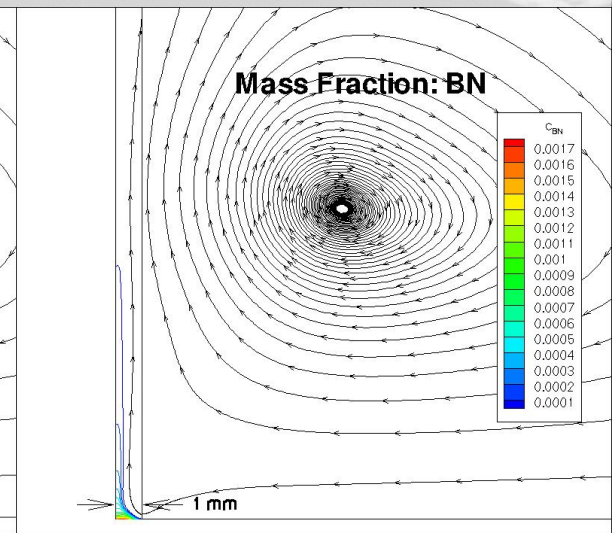
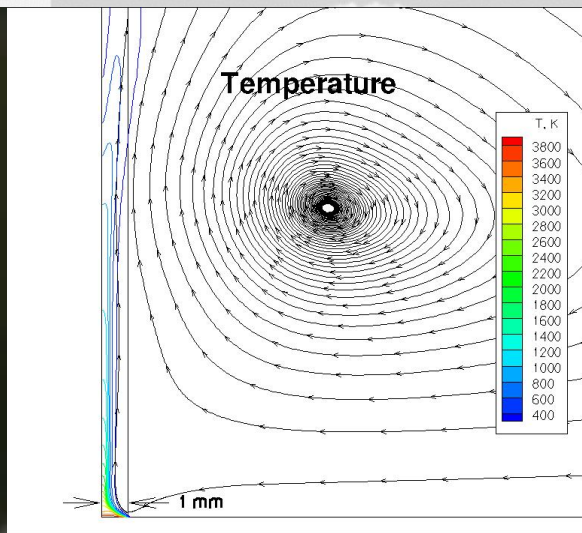


In-situ Optical Diagnostics

- Need a detailed understanding of chemistry and flow physics of nanotube generation and how the process changes under different operating conditions
 - Improve and validate simulation/modeling
 - Optimize material properties, production rate
- Specific Goals:
 - Determine gas and melt-ball temperatures
 - Determine amount of B_2 , B, BN, N and N_2
- In-situ, on-surface measurement:
 - optical pyrometry for surface temperature
- Off-surface, gas phase measurement:
 - High-speed, high-resolution imaging
 - Shadowgraph and visible emission
 - Species sensitive imaging (BN PLIF)
 - Temperature measurements (CARS)



Modeling of Laser Ablation and Plume Chemistry in a Boron Nitride Nanotube Production Rig



Contour lines of temperatures and mass fraction of BN in the plume

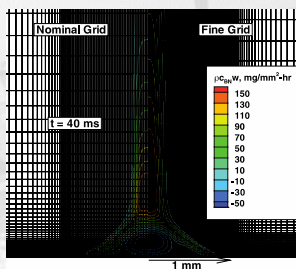


Fig. 5 Contour lines of BN flow rates in the plume.

Mass fraction of B, Plume Base

Pressurized Cylinder

Radius = 5 cm

Height = 10 cm

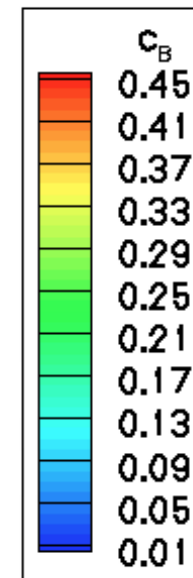
Vertical line on left is cylinder axis.

The second vertical line is offset 1 mm from axis.

The right boundary is a porous wall designed to maintain internal pressure.

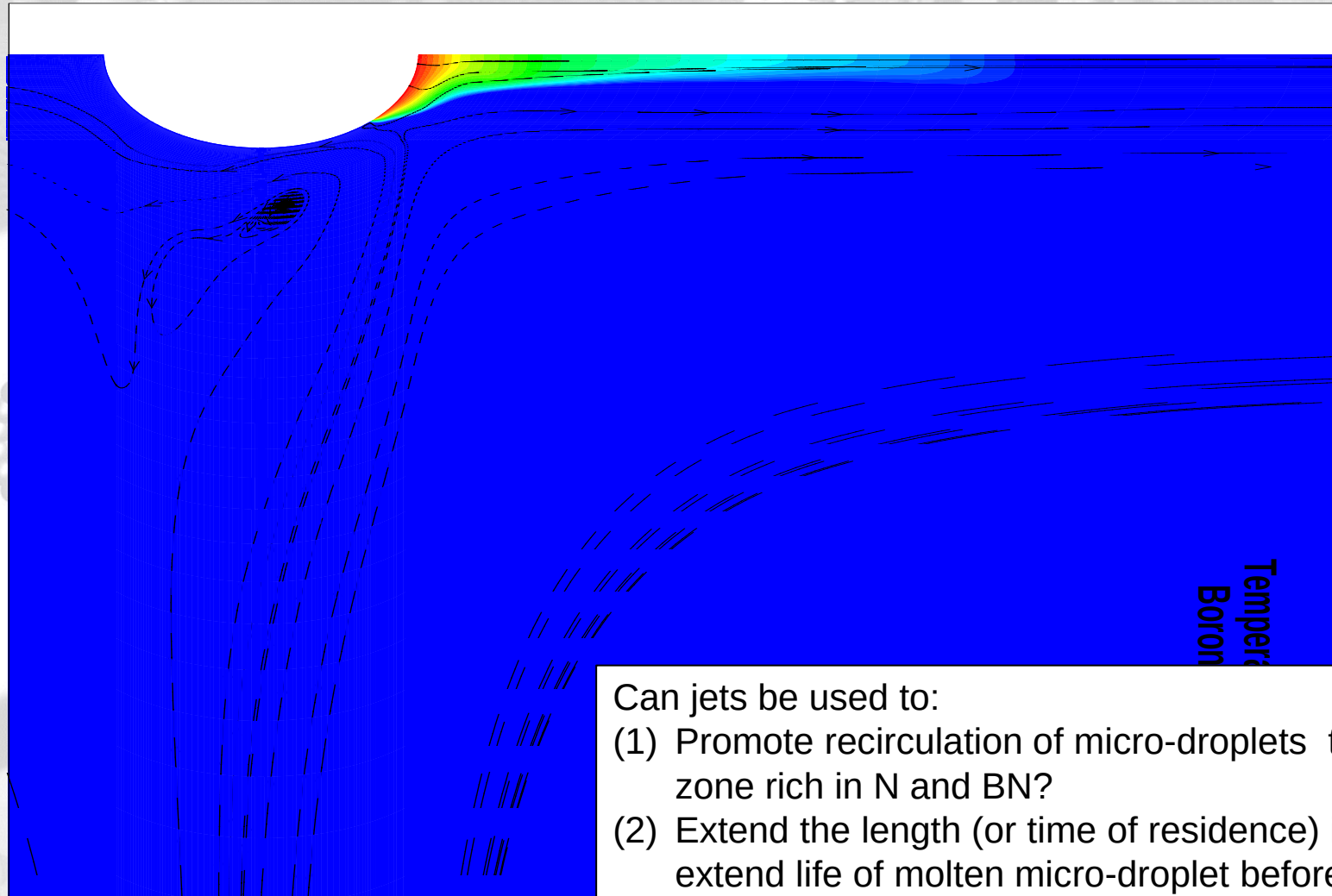
Top and bottom boundaries - except for laser spot on bottom left - are fixed temperature, no-slip, equilibrium catalytic.

At time $t=0$ a laser delivers constant energy flux to the 1 mm radius spot on lower left, initiating vaporization of boron target and buoyancy driven plume to rise from hot spot.



Temperature Contours Around 1 mm Radius Boron Droplet

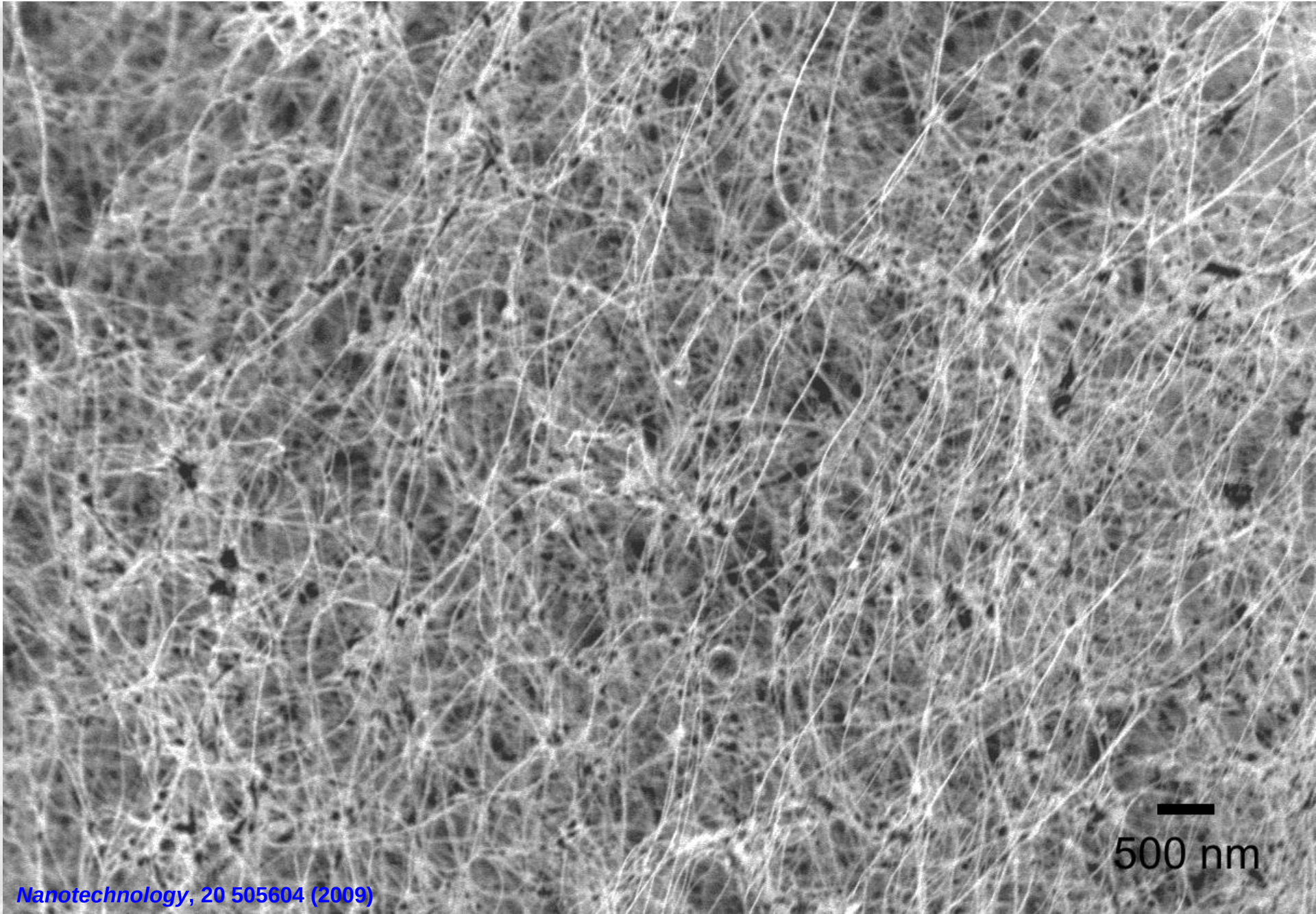
200psi



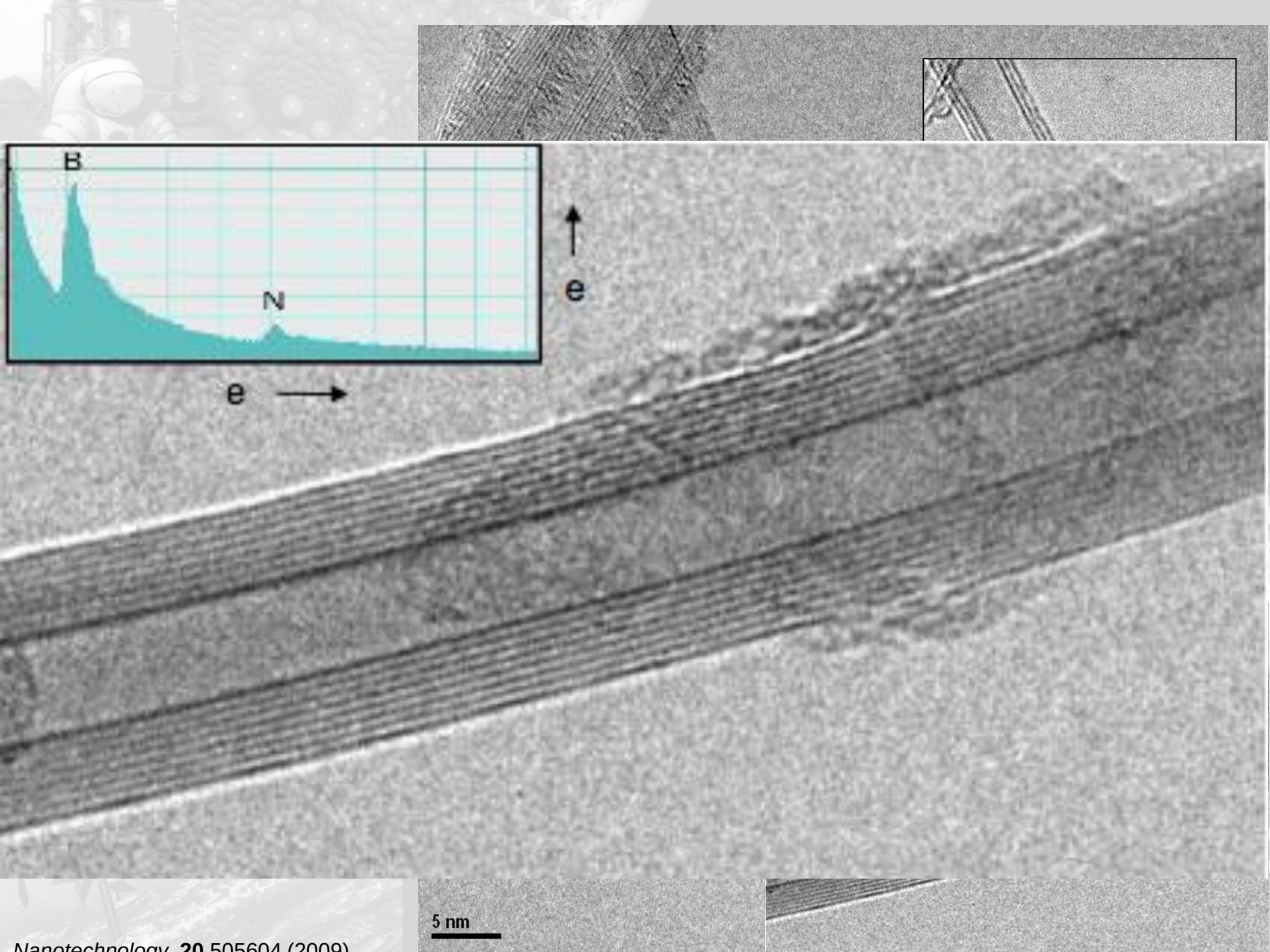
Can jets be used to:

- (1) Promote recirculation of micro-droplets through hot (red) zone rich in N and BN?
- (2) Extend the length (or time of residence) in green zone to extend life of molten micro-droplet before solidification

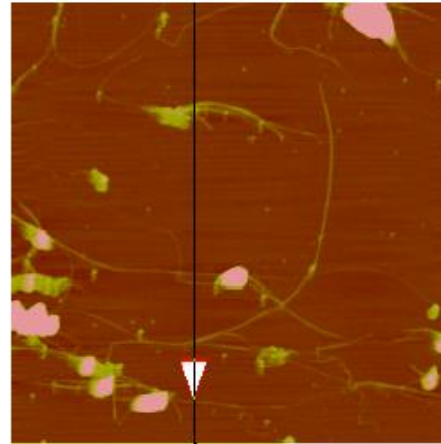
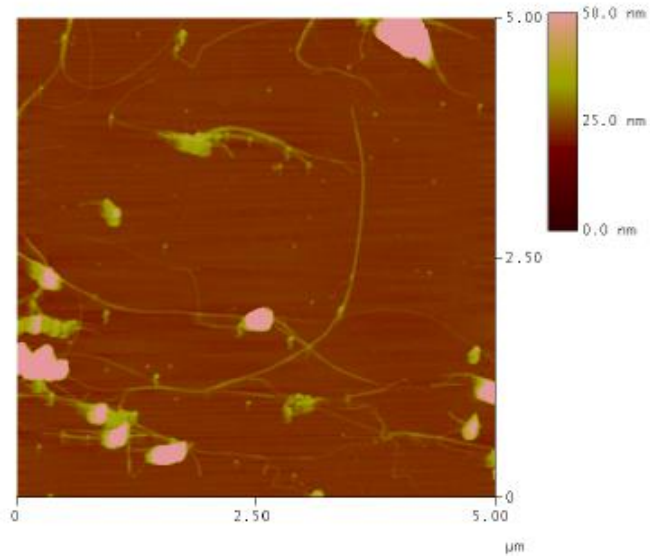
High Resolution Scanning Electron Micrograph: As grown BNNT



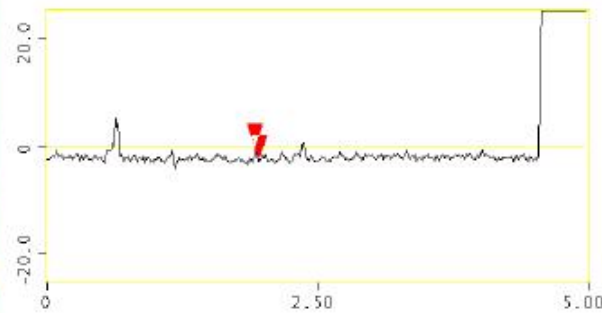
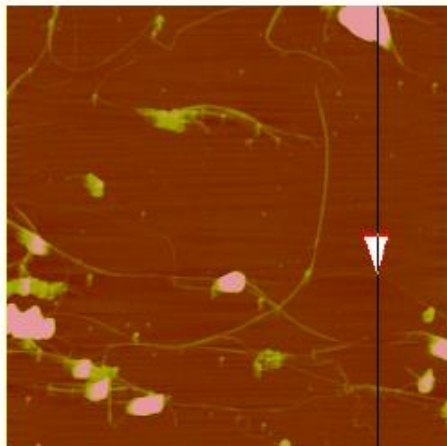
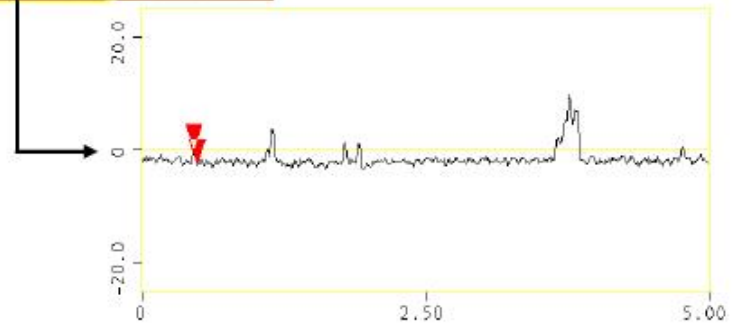
500 nm



AFM of individual BNNTs

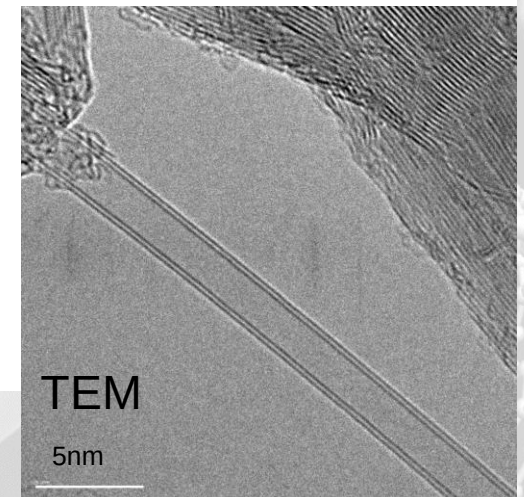


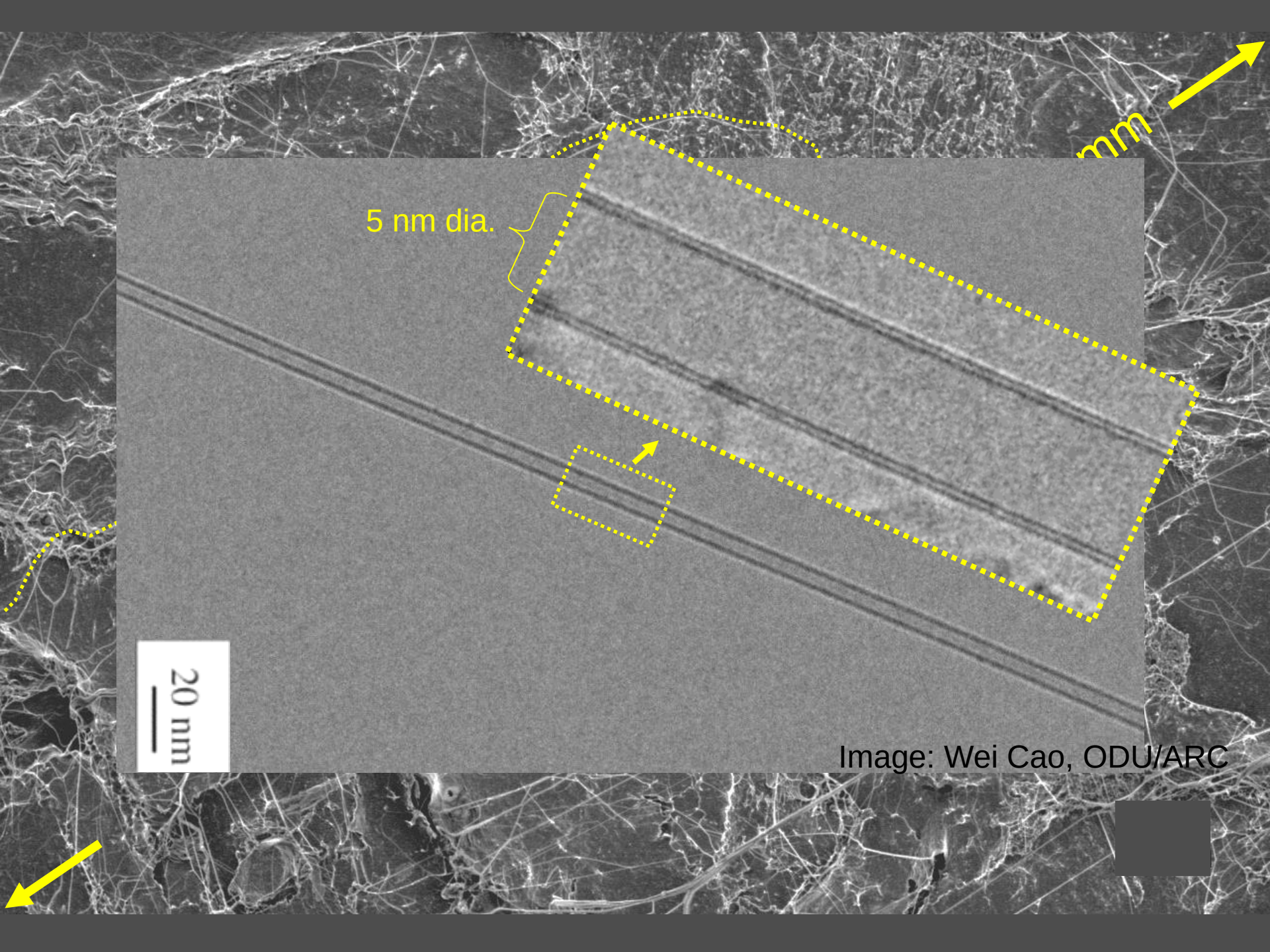
Vertical distance: 2.687 nm



Vertical distance: 2.119 nm

SW-BNNT



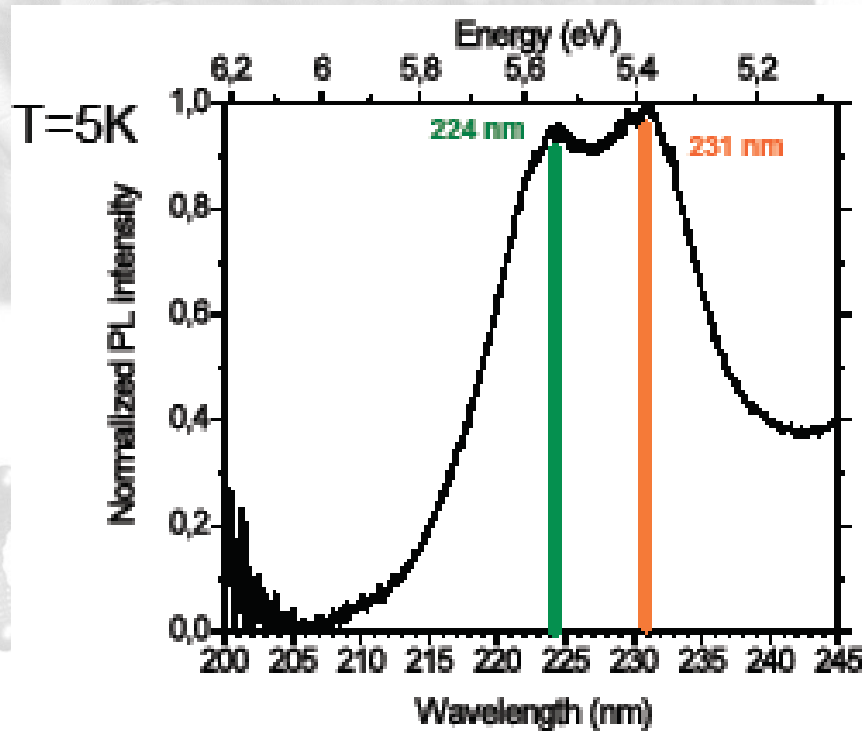


5 nm dia.

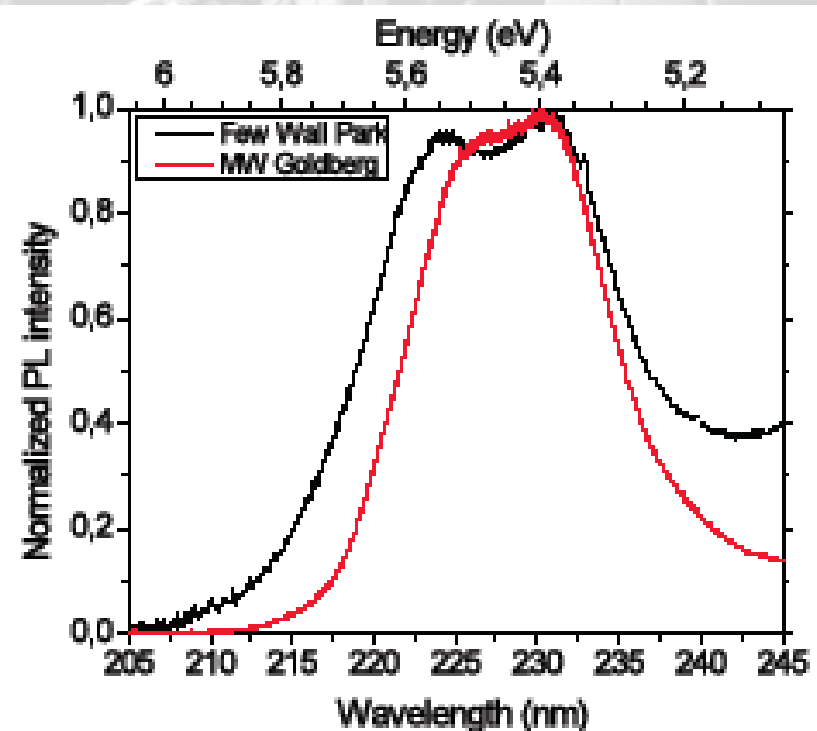
20 nm

Image: Wei Cao, ODU/ARC

Microphotoluminescence of NASA/NIA BNNT



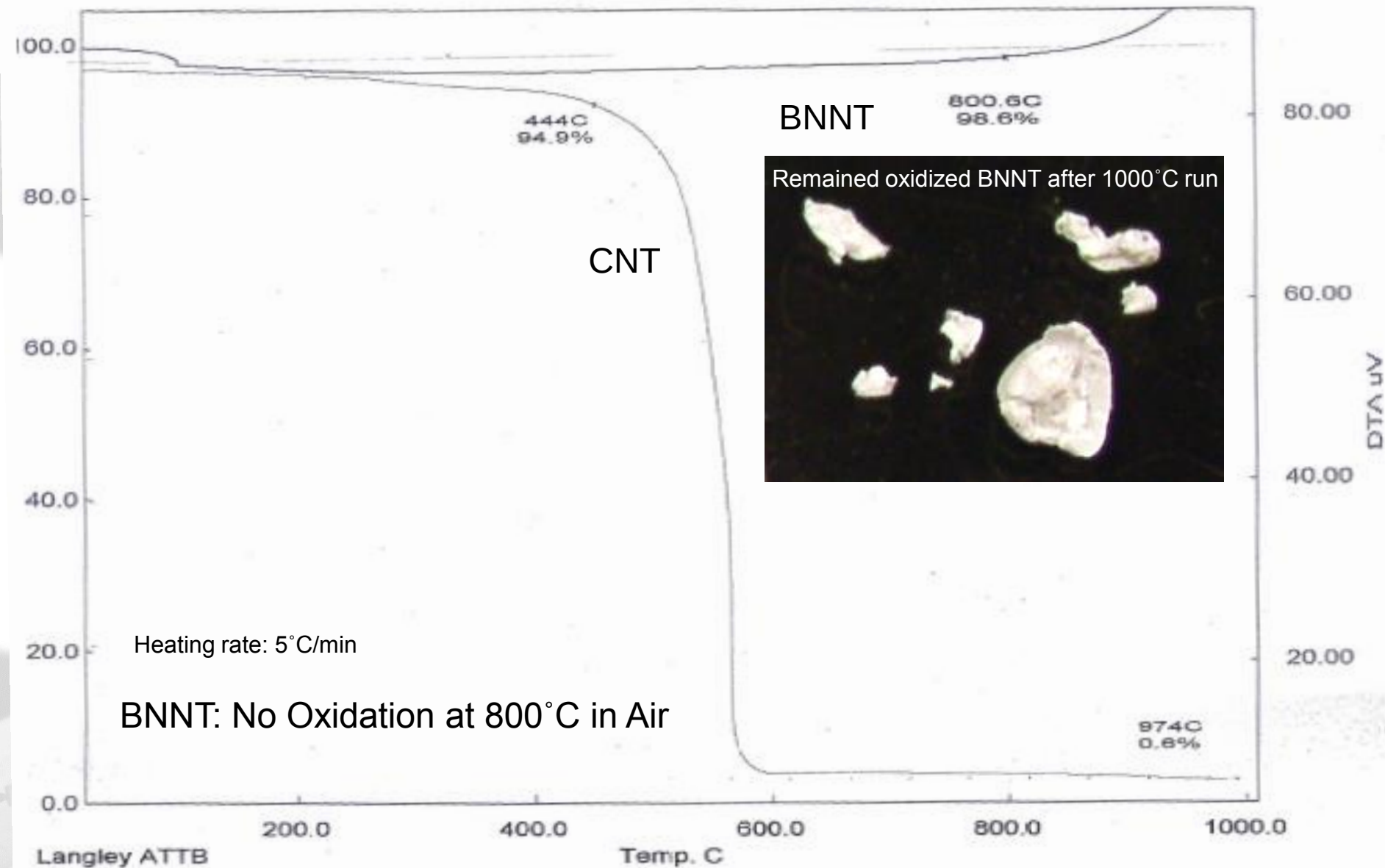
NASA/NIA/Jlab BNNT



NIMS BNNT

Our FW-BNNT exhibited two clearly split peaks at 224 and 231 nm while the NIMS' BNNTs showed one peak at 231nm with a shoulder at around 224nm.

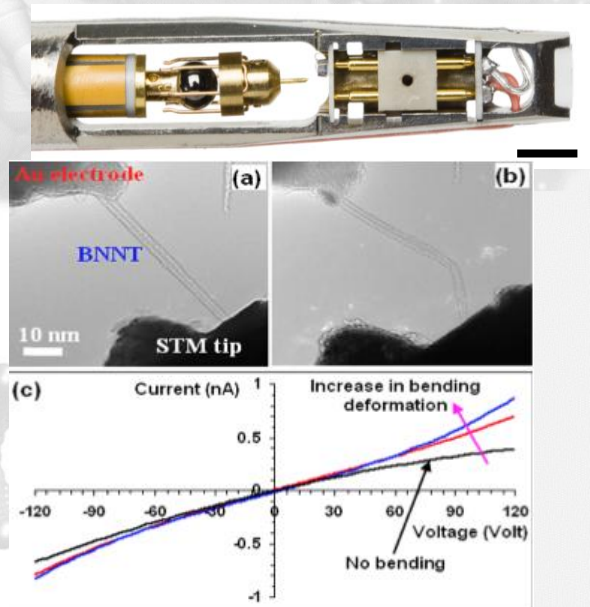
Thermal Stability of BNNT vs. CNT: TGA



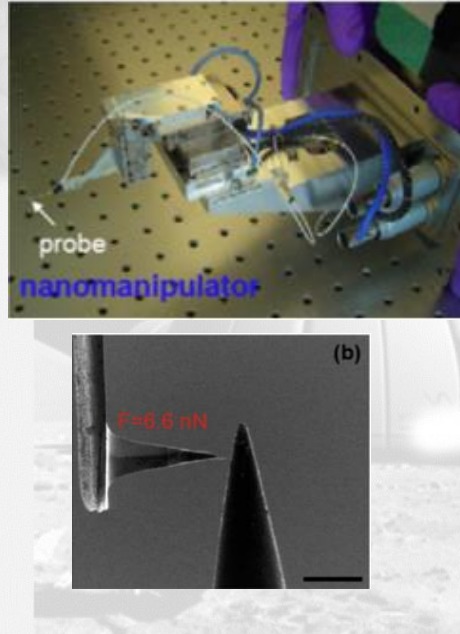
Mechanical Properties of BNNT and BNNT Composites: Processing and Characterization Techniques

Individual BNNT and BNNT Bundles: compressive modulus, tensile modulus and strength, radial modulus

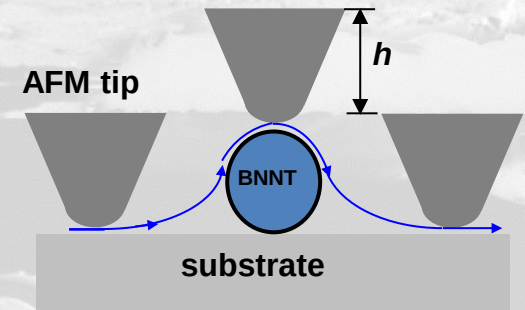
TEM-AFM, TEM-STM Holders
NASA LaRC/NIA/Binghamton



3D Nanomanipulator in SEM/FIB
SUNY Binghamton



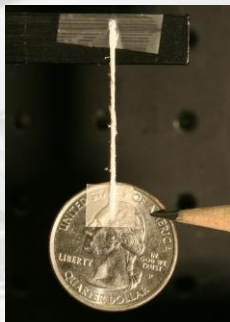
AFM
SUNY Binghamton



Small, 8, 116 (2012)
ACS Nano, 6, 1814 (2012)
Nanotechnology, 23, 095703 (2012)

BNNT composites and BNNT yarns

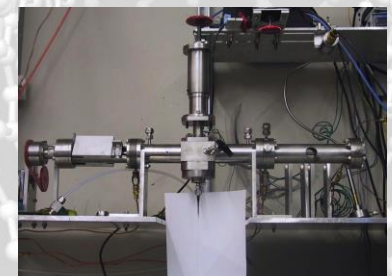
Spun yarns: NASA LaRC/NIA



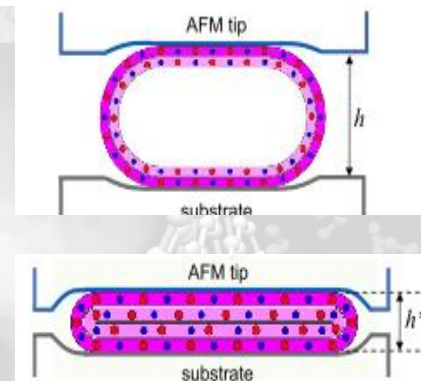
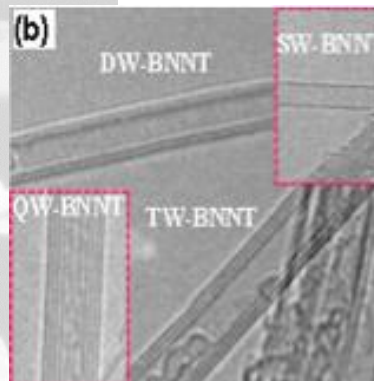
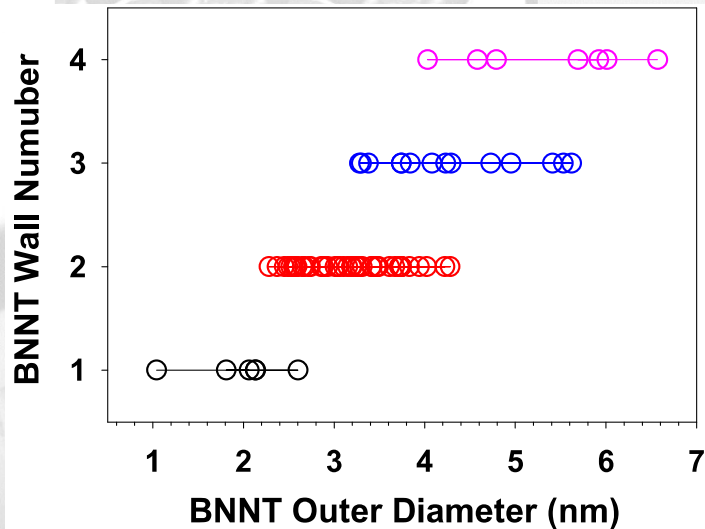
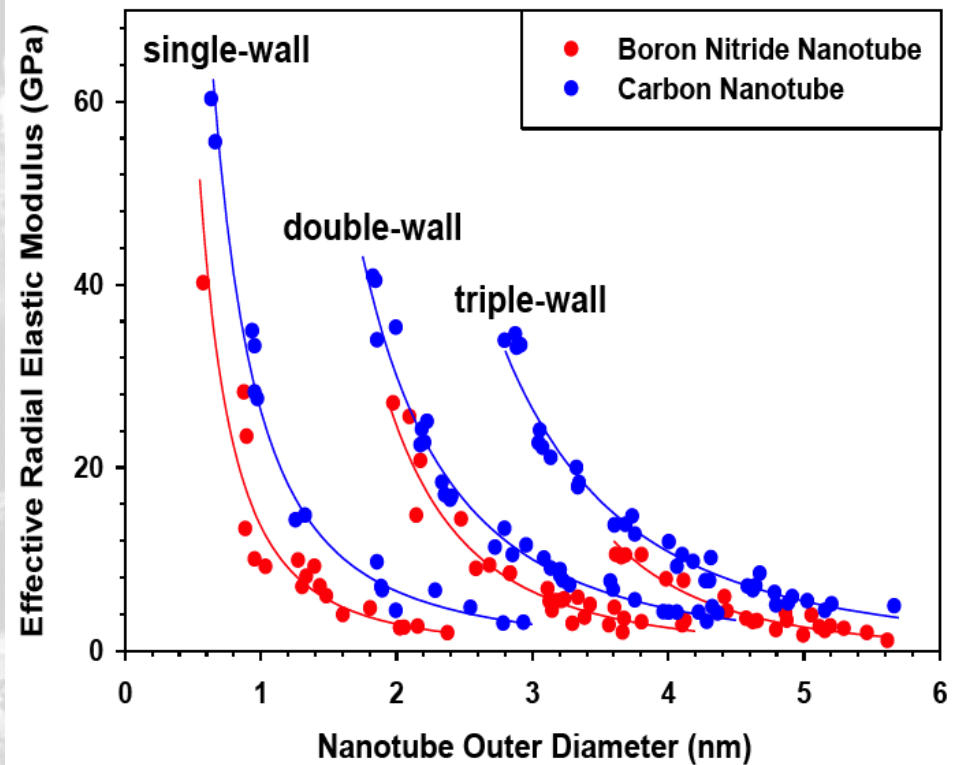
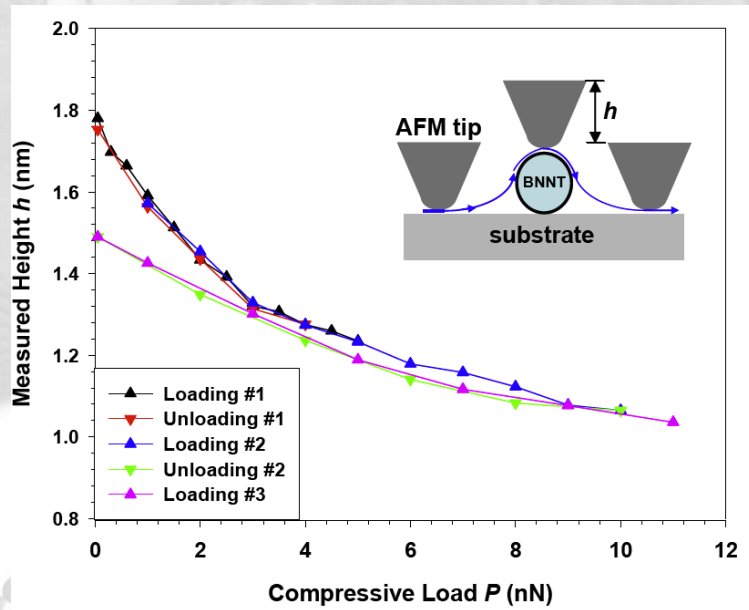
Wet spinning/Electrospinning
NASA LaRC/NIA



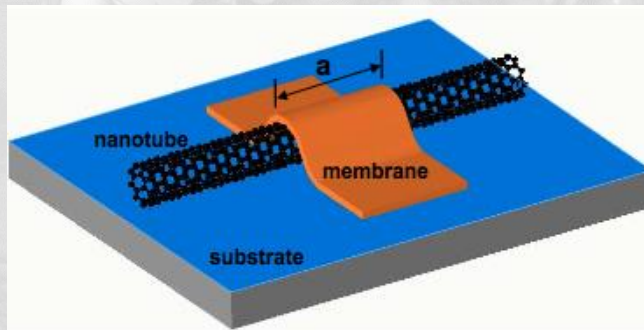
Superacid Spinning
Rice/NIA



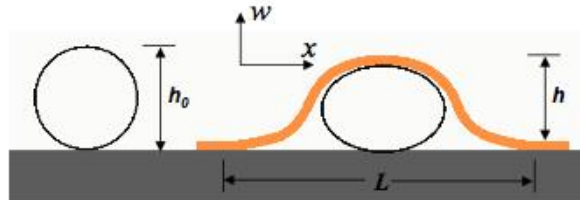
Compression Radial Modulus of BNNTs and SWCNTs



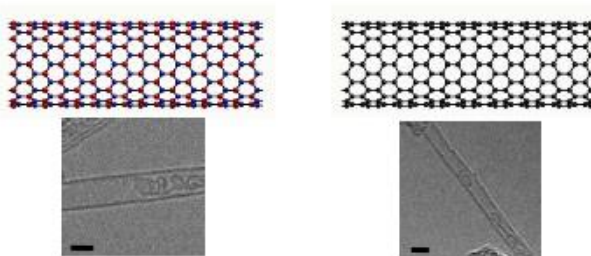
Mechanical Properties of BNNT (continued)



(a)



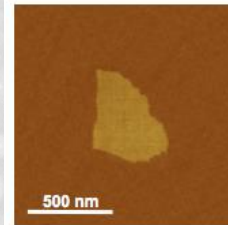
(b)



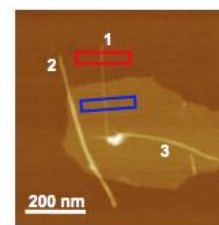
SW-BNNT

SWCNT

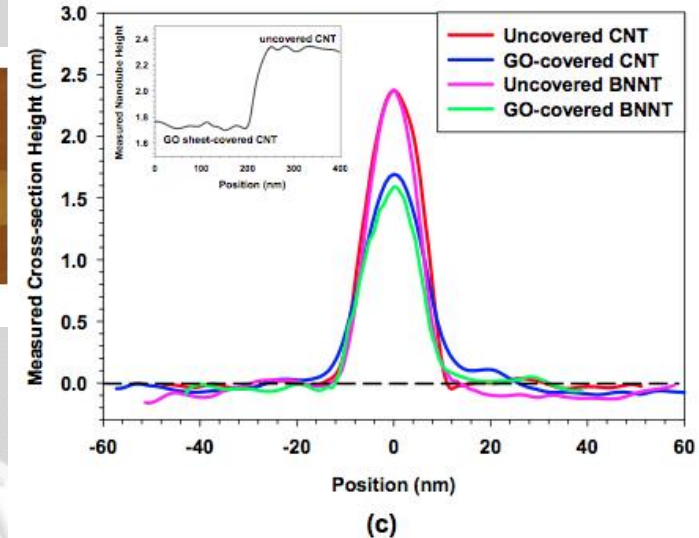
(c)



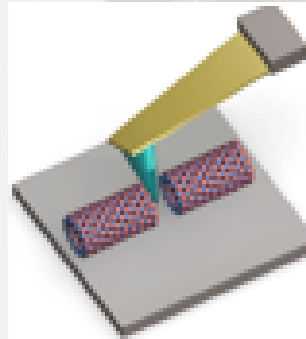
(a)



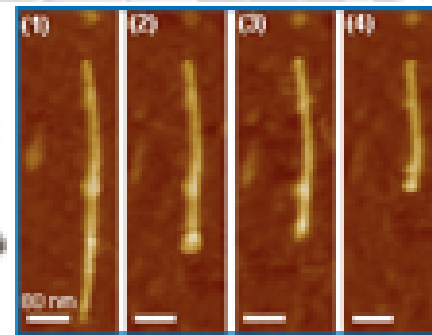
(b)



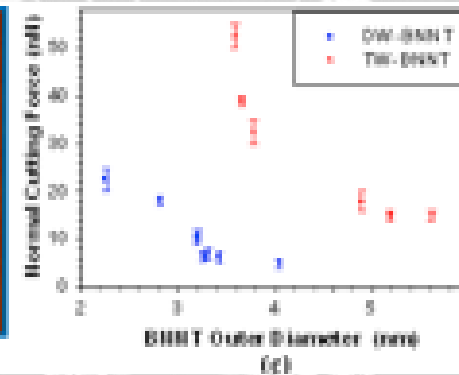
(c)



(a)



(b)



(c)

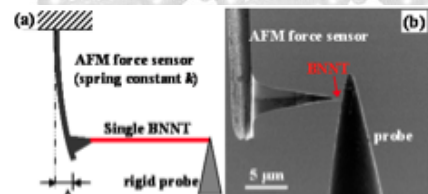
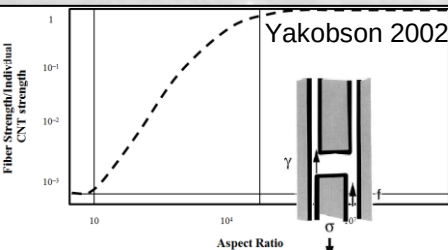
(a) Schematic of cutting a BNNT by lateral force AFM. (b) AFM images of a sequentially shortened BNNT. (c) The dependence of the critical normal cutting force on the BNNT outer diameter for both double and triple walled BNNTs.

How to make strong, stiff, and tough structural BNNT composite?

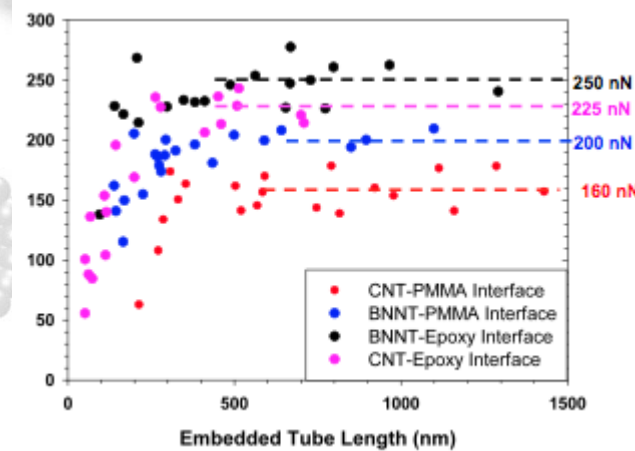
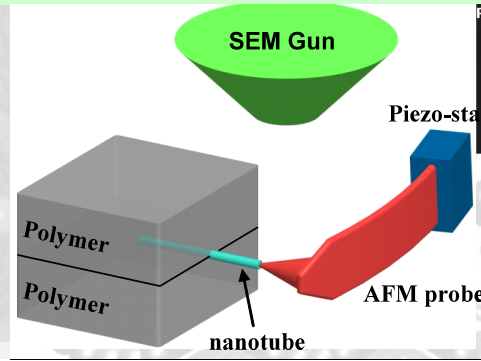
Good tubes:

highly crystalline,
long, thin BNNTs →
Excellent intrinsic
BNNT properties

Longer tube (high aspect ratio)
→ Greater yarn strength



High interfacial strength



BNNT-epoxy and BNNT-PMMA interfacial strength are superior to CNT counterpart (*Small*, 9, 3345 (2013))

High orientation

Solution spinning and extrusion



Science 2013
Pasquali Rice Univ



Hearle's Yarn Equation

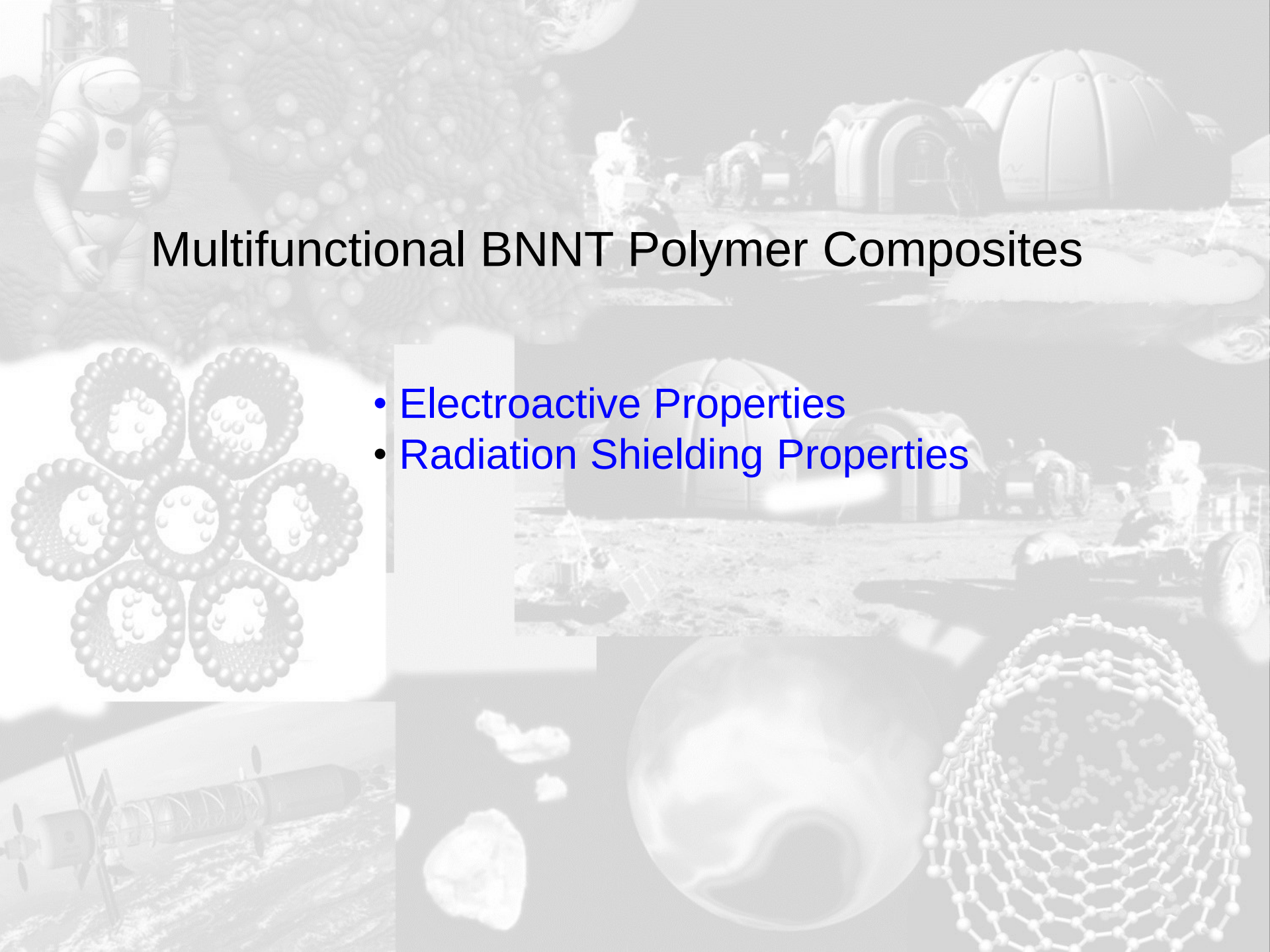
$$\sigma_y \approx \cos^2 \zeta (1 - k \cos \zeta) \cdot \sigma_f$$

σ_y : yarn strength, σ_f : fiber (tube) strength
 ζ : helix angle that fibers make with yarn axis
 k : $(dQ/\mu)^{1/2}/3L$, d : fiber diameter
 μ : coefficient of friction, L : fiber length
 Q : fiber migration length

$$\text{If } \sigma_f \uparrow, d \downarrow, L \uparrow, \mu \uparrow \rightarrow \sigma_y \uparrow$$

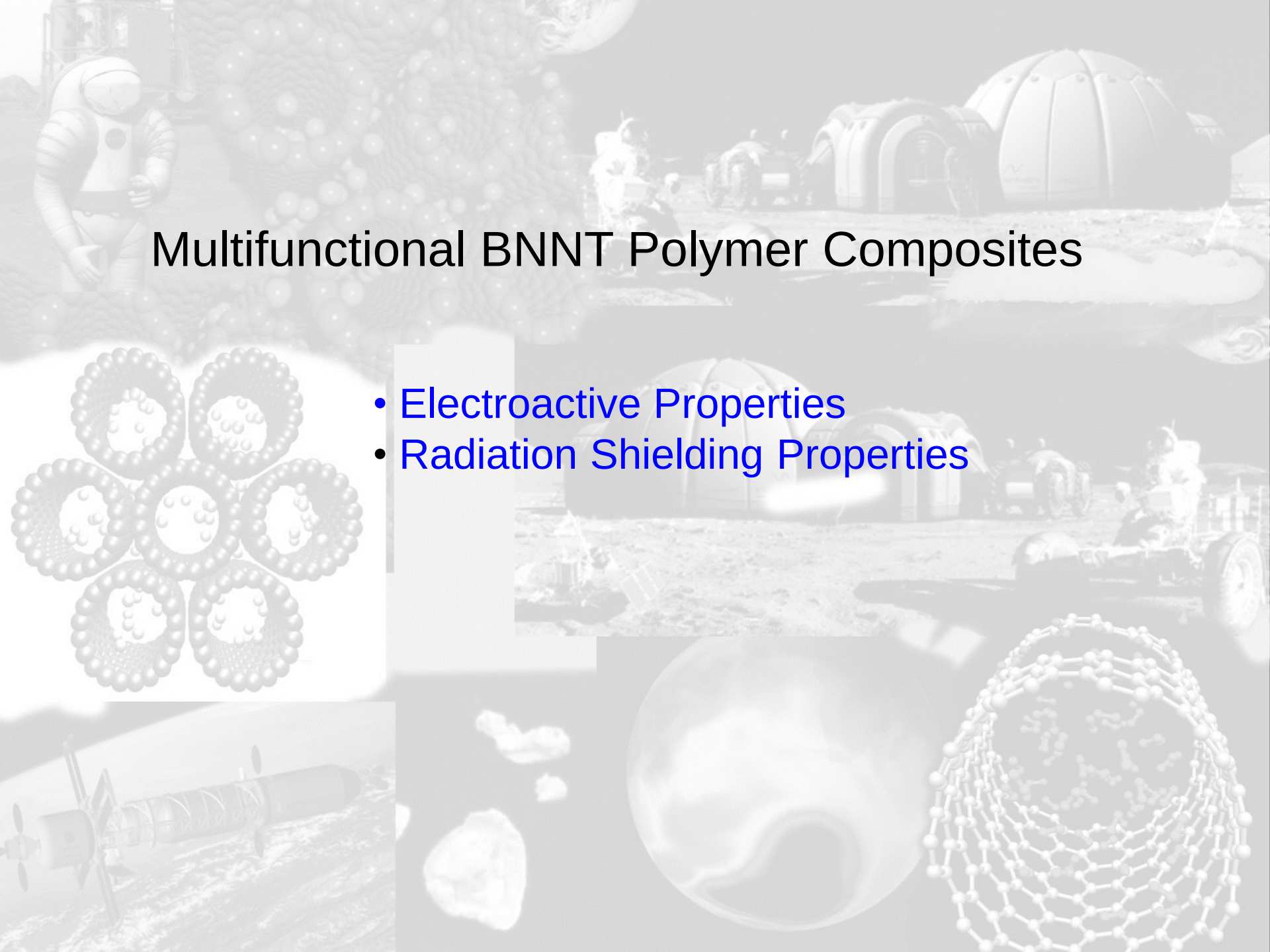
BNNT Tensile Test Results (Only for comparison with CNT)

Diameter	Elastic modulus (GPa)	Breaking Strength (GPa)
D = 2.5 nm	760-960	14-38



Multifunctional BNNT Polymer Composites

- Electroactive Properties
- Radiation Shielding Properties

- 
- # Multifunctional BNNT Polymer Composites
- Electroactive Properties
 - Radiation Shielding Properties

Piezoelectric and Electrostrictive Properties for Sensors/Actuators

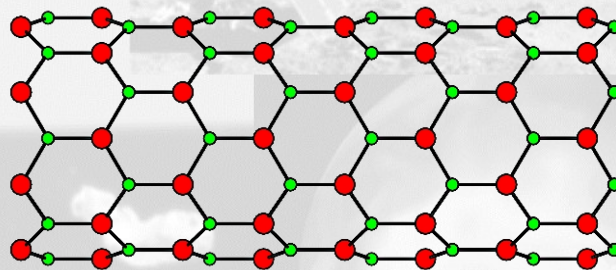


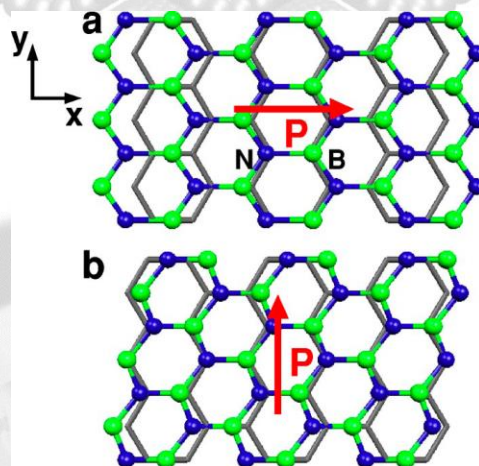
Table 2. Approximate properties of piezoelectric ceramic and nanotube materials.

PVDF: 0.12

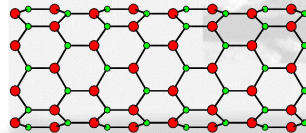
Material	Temperature Limit (°C)	Elastic Modulus Y (GPa)	Band-width (Hz)	Volt. Range	Density (kg/m ³)	Pk Strain (ϵ_m)	Strain/Volt (ϵ_m /volts)	Strain Energy $Y\epsilon_m^2/2$ (J/m ³)	Energy Density $Y\epsilon_m^2/2\rho$ (J/m ³)	Piezo-induced Stress e_{33} (C/m ²)
PZT monolithic Wafer ¹	175	55–69	10 ⁶	+/-200	7700	0.00026	1.3×10^{-6}	2332	0.3	5–10
Active fiber composite ²	~110	35	10 ⁵	+2.8 kV	4250	0.0018	6.4×10^{-6}	56,700	13.34	6.2
Piezoelectric (5,0) BNT ³	~1000	1220	–	–	1370	–	–	–	–	0.4 max
Piezoelectric (5,5) CNT ⁴	600	1000	–	–	1330	–	–	–	–	0.0003 max
Electrochemical CNT ⁵	–	5.5	10 ²	+/-2	1330	0.002	1×10^{-3}	11,000	8.25	–
Electrochemical CNT ⁶	–	640	10 ³	+/-1	1330	0.01	1×10^{-2}	29×10^6	2400	–
Aluminum nitride-ALN ⁷	~1000	–	–	–	–	–	–	–	–	0.58
SiCNT nanotube ⁸	–	–	–	–	–	–	–	–	–	–

References: ¹ PZT 5A (Active Control eXperts, Inc.); ² Testing (Bent, 1997); ³ Theory, M. Nardelli (Nardelli et al., 2001); ⁴ Theory, N. Lebedev (Lebedev et al., 2001); ⁵ Bundled test Q.M. Zhang/R. Baughman (Baughman et al., 1999); ⁶ Nonbundled theory (Baughman et al., 1999); ⁷ Testing (Dubois and Murali, 1999); ⁸ Properties TBD (NASA Glenn Research).

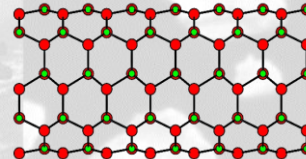
03SPIE5062 629Pammi smart nanocomp



zig-zag

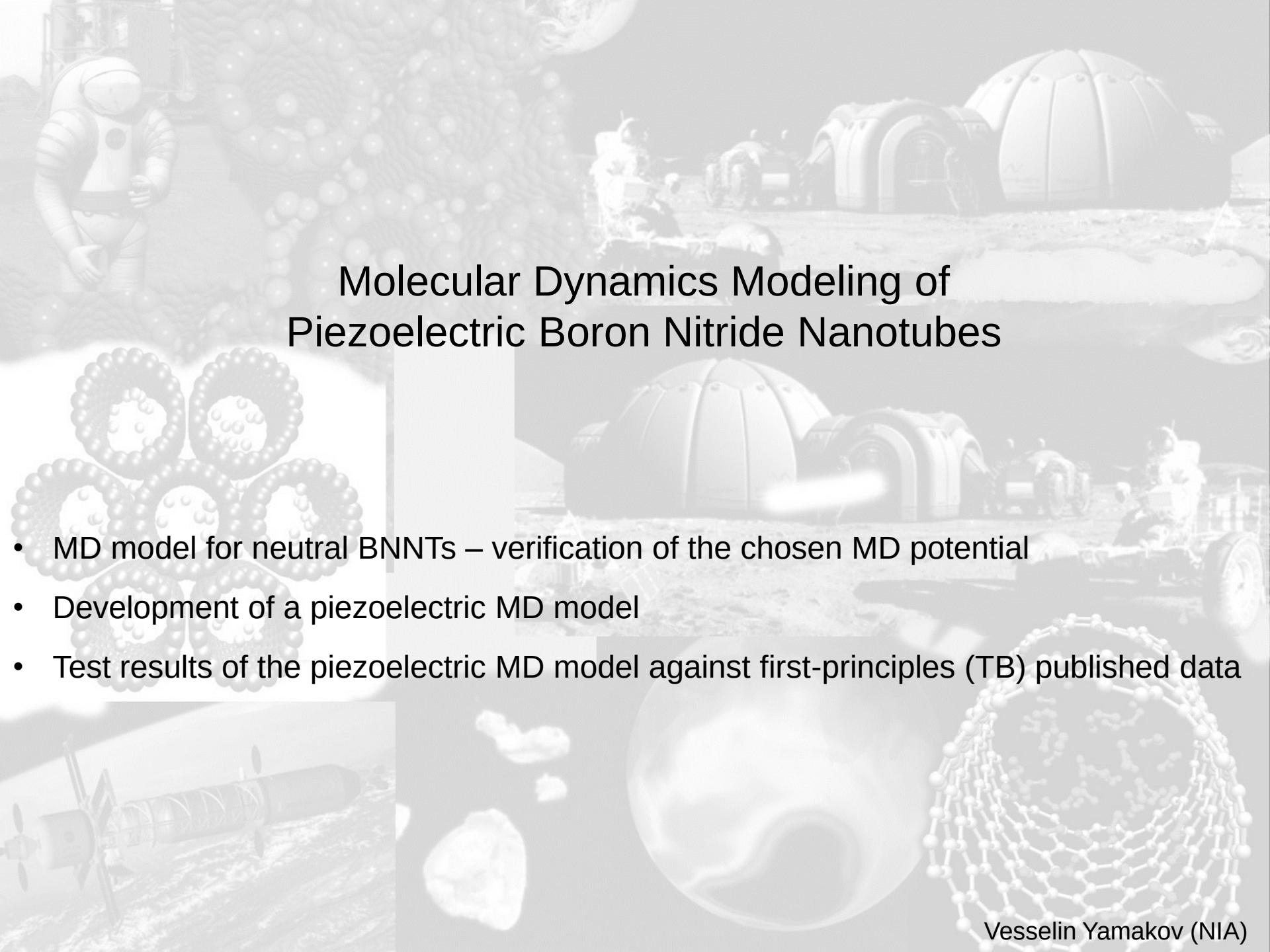


arm chair

**BNNT Piezoelectricity Publications (simulations)**

02PRL88 056803Mele

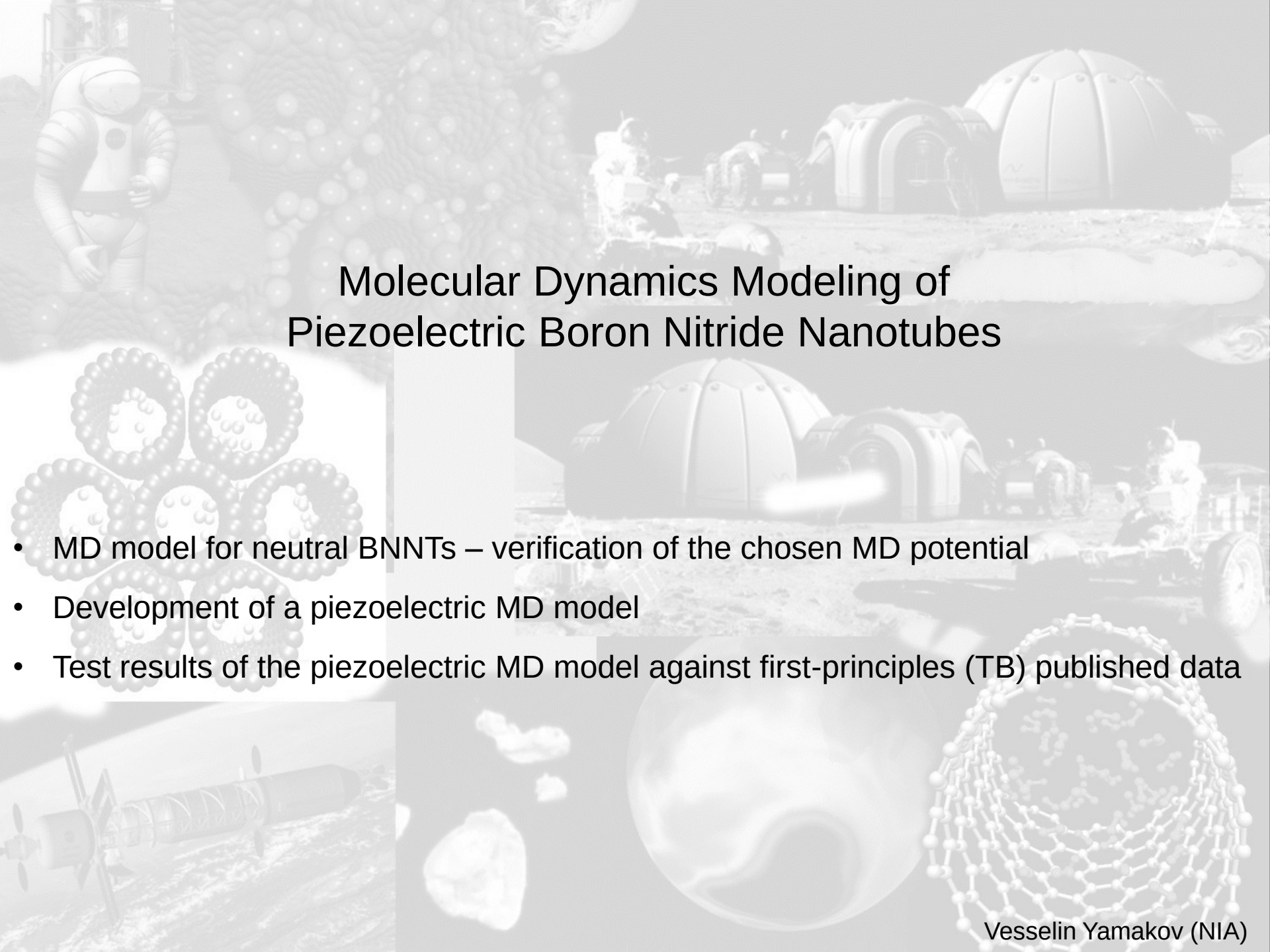
03PRB67235406Nakhmanson Nardelli



Molecular Dynamics Modeling of Piezoelectric Boron Nitride Nanotubes

- MD model for neutral BNNTs – verification of the chosen MD potential
- Development of a piezoelectric MD model
- Test results of the piezoelectric MD model against first-principles (TB) published data

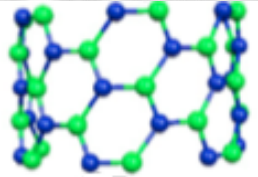
Vesselin Yamakov (NIA)

- 
- # Molecular Dynamics Modeling of Piezoelectric Boron Nitride Nanotubes
- MD model for neutral BNNTs – verification of the chosen MD potential
 - Development of a piezoelectric MD model
 - Test results of the piezoelectric MD model against first-principles (TB) published data
- Vesselin Yamakov (NIA)

Current State-of-the-Art

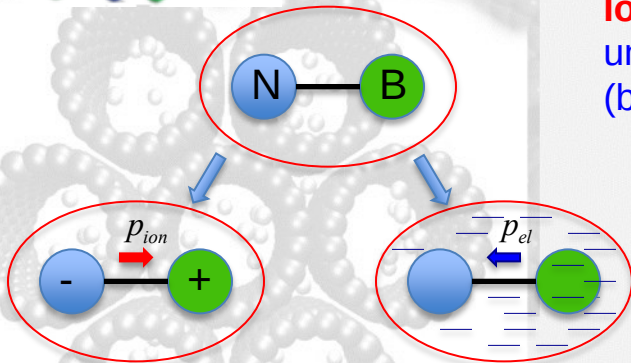
Electronic Properties of BNNTs: QM Approach

- Nakhmanson et al, PRB 67 (2003) 235406
- Sai & Mele, PRB 68 (2003) 241405
- Peng et al., Comp. Mater. Sci. 56 (2012) 11



BNNT: a hexagonal B-N tube

Ionic and electronic polarization cancel exactly,
unless their symmetry is broken
(by deformation or intrinsic interactions)



Ionic Polarization

Electronic Polarization

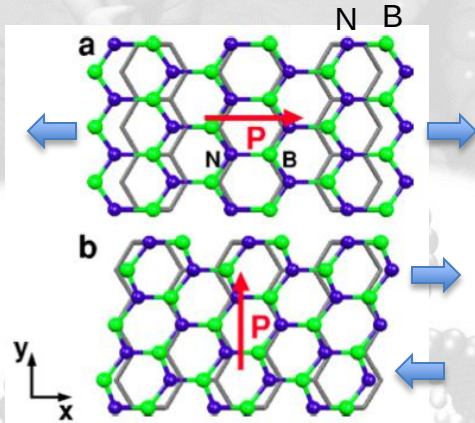
$$\vec{p}_{BN} = \vec{p}_{ion} + \vec{p}_{el} = \begin{cases} 0; & \text{- symmetric state} \\ \propto \mu \text{ strain}; & \text{- deformed state} \\ & \text{(piezoelectricity)} \end{cases}$$

- QM approach predicts quantitatively the polarization of the BN bond
 - QM approach is too exhaustive to be used for large systems (>100 atoms)
 - QM parameterized MD model multiscale approach
 - Parallel with a known piezoelectric MD model: a case study of quartz: $\vec{p}_i = Q_i \vec{r}_i + \vec{m}$ for i -th atom
 $Q_i, \vec{m} = \text{const}$
- Herzbach & Muser, Comp. Phys. Comm. 174 (2006) 17

Piezoelectric Properties of BNNTs

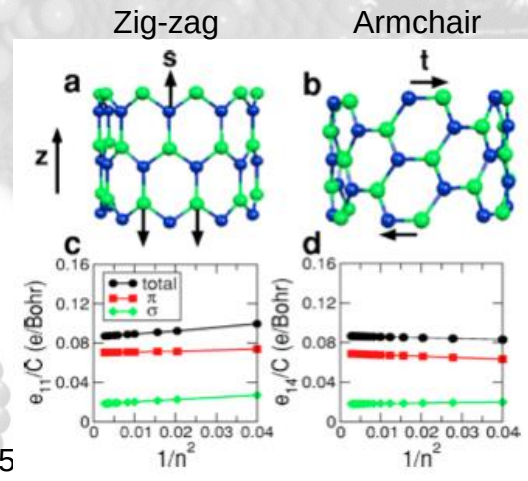
Piezoelectric Effect

h-BN plane



(Sai & Mele, PRB 68, (2003) 241405)

BNNT



Induced polarization, $\vec{p}$, under strain e_{jk} : $p_i = e_{ijk} e_{jk}$

where e_{ijk} - piezoelectric tensor with symmetry:

$$e_{xxx} = -e_{xyy} = -e_{yxy} = -e_{yyx}; \quad e_{xxx} = 0.086 - 0.12 \text{ e/Bohr}$$

The MD model has to reproduce this behavior!

Molecular Dynamics

- Define forces between atoms using a given interatomic potential (energy)

$$U_r = \sum_{i,j} \left[\frac{1}{2} B_{ij} \left(\frac{r_{ij}}{r_0} \right)^{12} - B_{ij} V_A \left(\frac{r_{ij}}{r_0} \right) \right] \quad \vec{F}_i = - \nabla U_r / \nabla \vec{r}_i$$

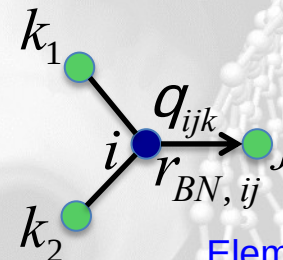
- Evolve atoms according to Newton's law: $\vec{a}_i = \vec{F}_i / m_i$

Piezoelectric MD

- Introduce dipole term to the interatomic potential (energy)

$$U = U_r + U_p; \quad U_p = \sum_{i=\{B\}, j=\{N\}} U(\vec{p}_{BN,ij})$$

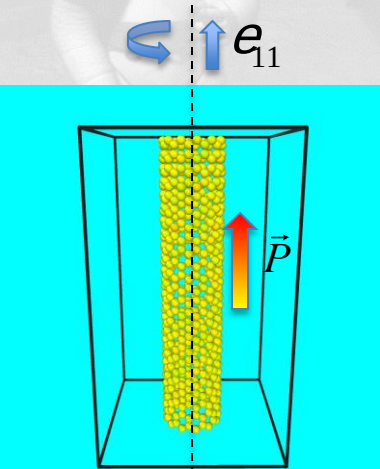
$$\vec{p}_{BN,ij} = p_0 \frac{\vec{e}_{BN,ij} \cdot \vec{r}_0}{r_0} + \sum_{k^1 i, j} \frac{\partial}{\partial \vec{e}} \frac{\partial}{\partial \vec{r}_0} \cos q_{ijk} \frac{\partial}{\partial \vec{r}_0}$$



Elementary dipole unit

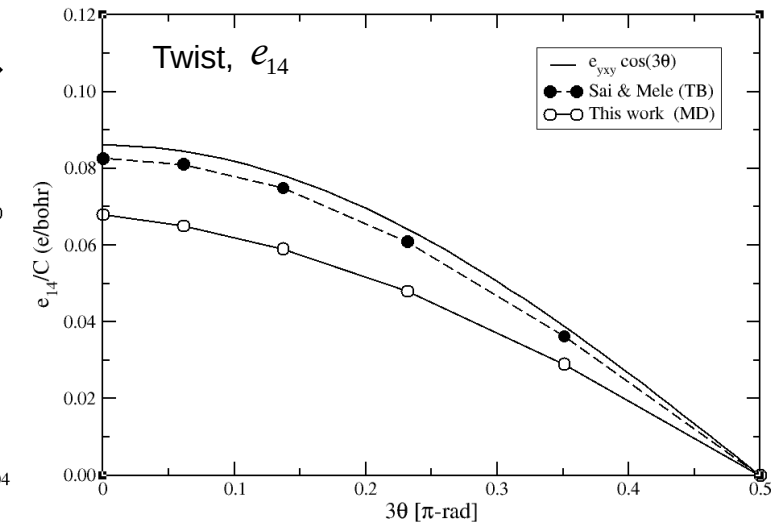
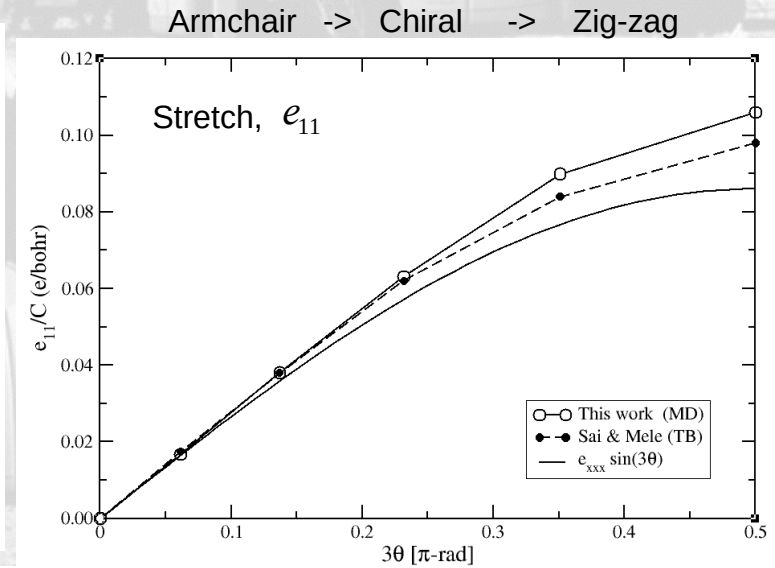
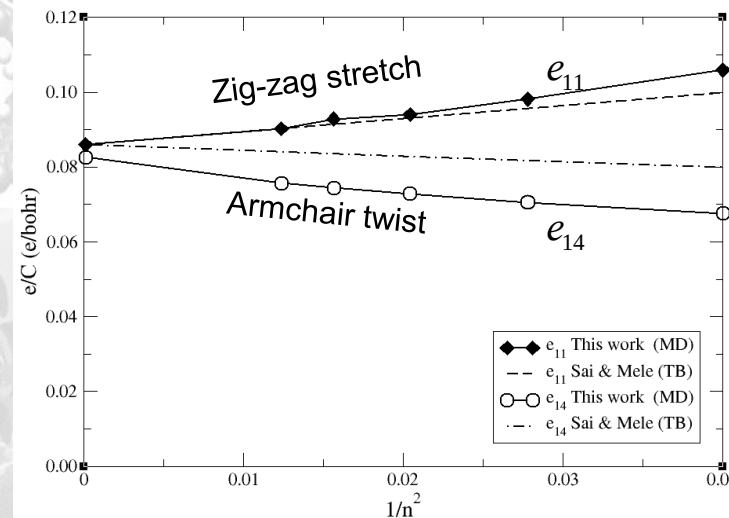
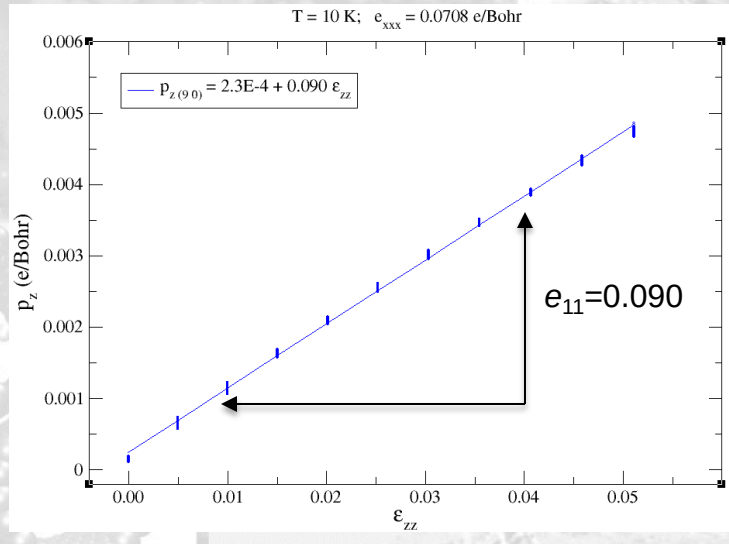
Results: Piezoelectricity under Deformation

The MD model is successful in representing the piezoelectric properties of BNNTs



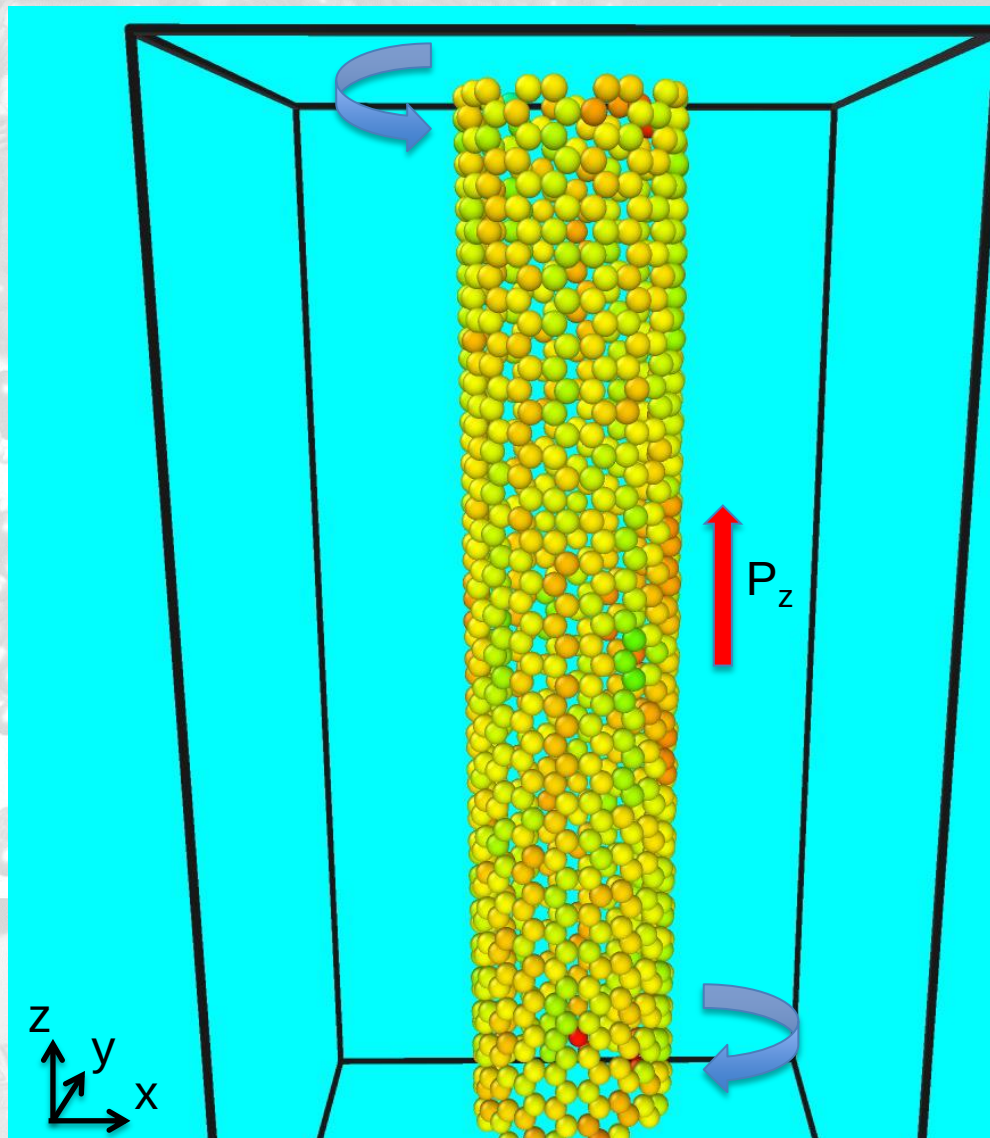
$$p_z(\text{stretch}) = e_{11} \epsilon_z$$

$$p_z(\text{twist}) = e_{14} \epsilon_t$$

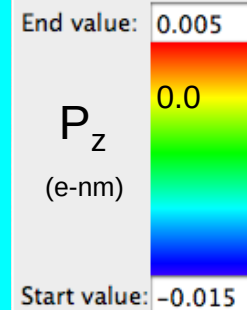


BNNT (9 9) Polarization in Twisting

Dipole moment, P_z



An MD model of an arm-chair single wall BNNT polarizing in the vertical direction under twist going from 0 to 5% and back.



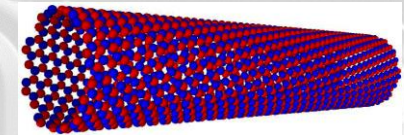
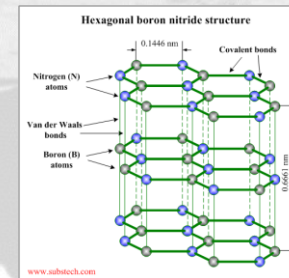
Experiment Displacement Study

Polymer Matrix:

- Polyimides [CP2, (β -CN)AMPB/ODPA (bCNAO), (β -CN)APB/PMDA (bCNAP)]
- Polyurethane
- PMMA
- Nylon 6,10

Inclusions:

- h-BN (hexagonal boron nitride powders)
- BNNT (purchased CVD, large, fat tubes, low quality)
- BNNT (high pressure, high temp, CO₂ laser as grown)



Alignment (stretched)

No alignment (no stretched) and stretched (up to 100%)

Polyimide (CP2)

Polyimide (bCNAO)

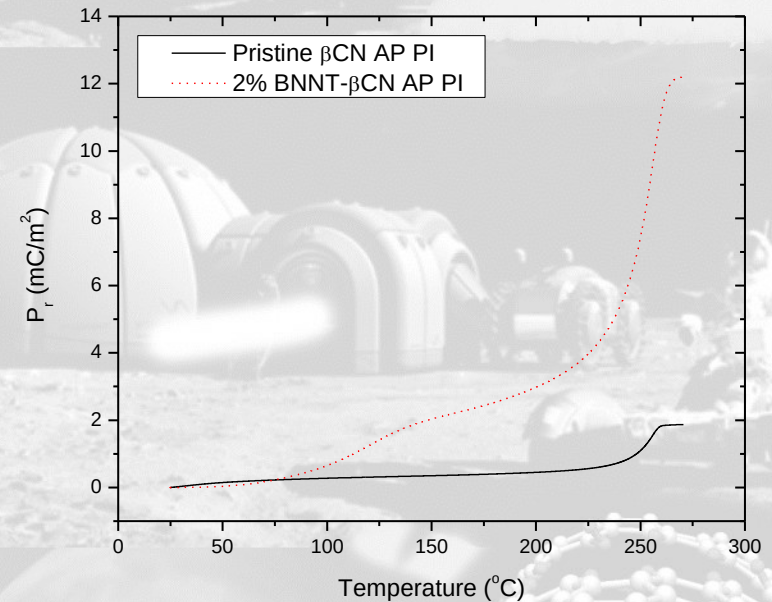
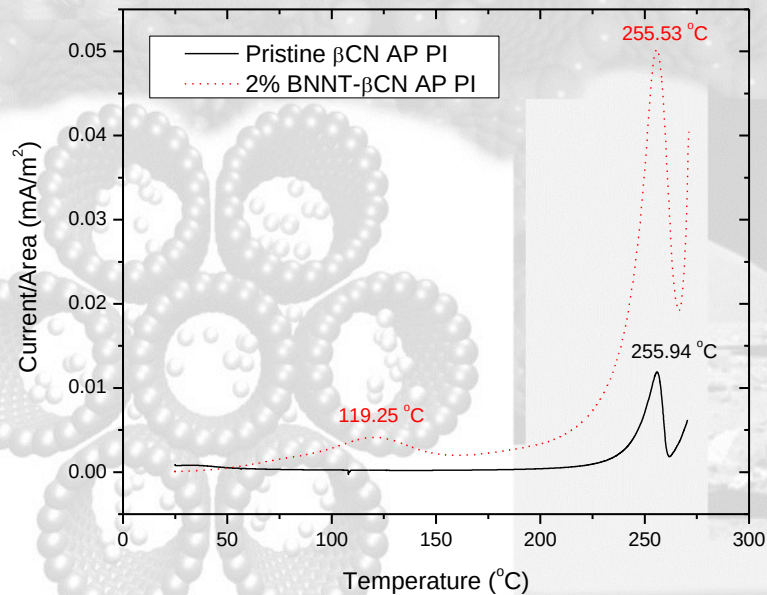
Polyimide (bCNAM) (unstretched and stretched 100%)

5wt%hBN/polyimide (stretched 110%)

5wt%BNNT(CVD)/polyimide

2wt%BNNT(laser)/polyimide (unstretched and stretched 100%)

Thermally Stimulated Current (TSC) Spectra of 2%BNNT-Polyimide Composite, Poling at $T_g-5^{\circ}\text{C}$, 5MV/m



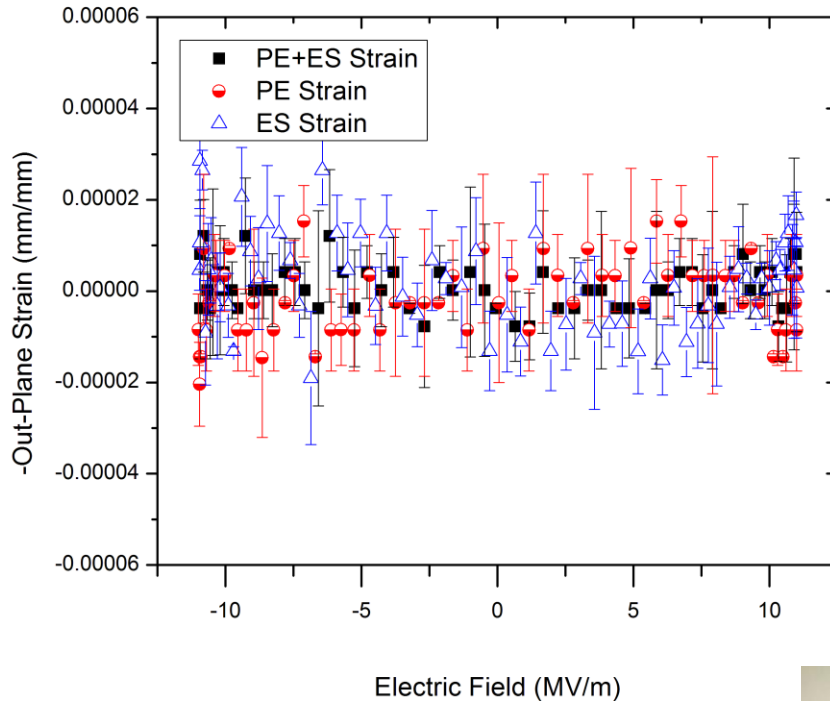
Using SETARAM TSC-II

$$P_r = \Delta\epsilon \cdot \epsilon_0 E_p$$

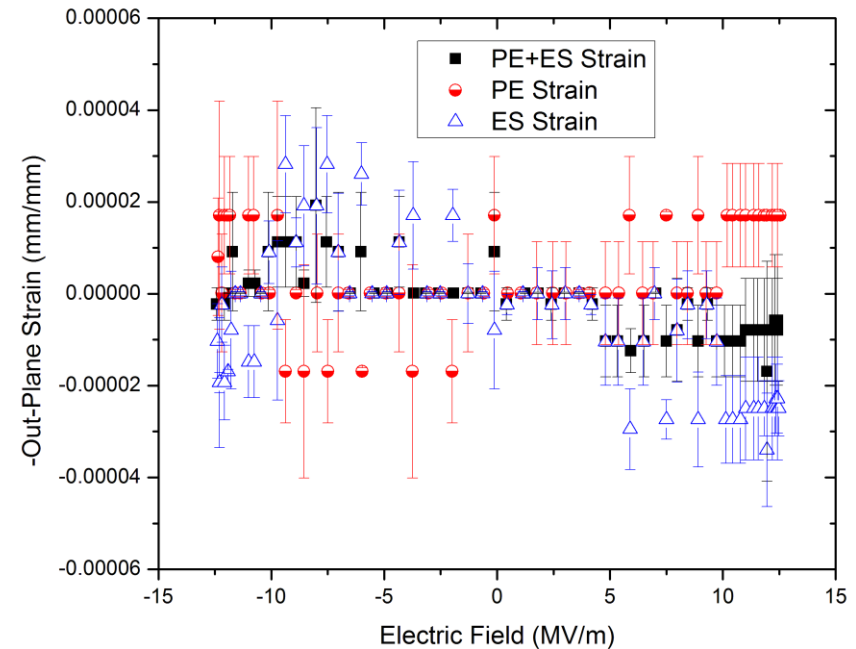
Study of Origin of Actuation: Stretched Films

Actuation of Unstretched/Stretched Pristine Polyimide

Unstretched



100% Stretched
@225°C, Annealing



Field induced strain (ϵ_{33})

$$\epsilon_{33} = d_{33} \cdot \mathbf{E} + M_{33} \cdot \mathbf{E}^2 + \dots$$

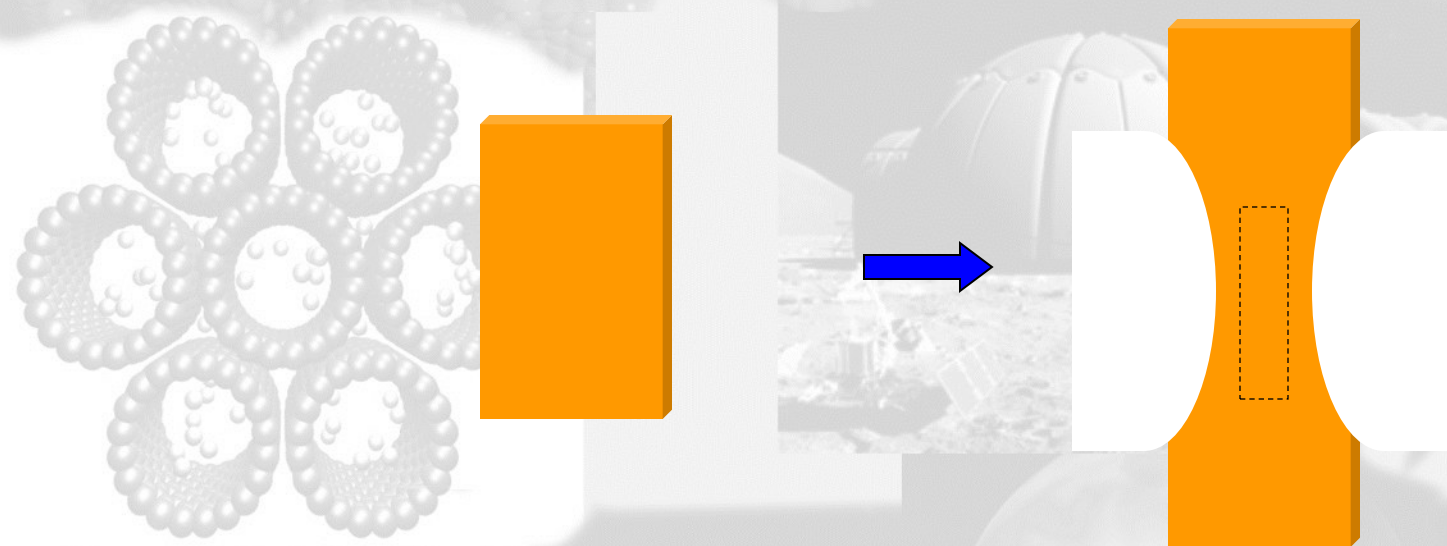
d_{33} : piezoelectric (PE)

M_{33} : mostly electrostrictive (ES)



Pristine and composite films are stretched with a tensile tester (Instron microtest) in an oven at above T_g

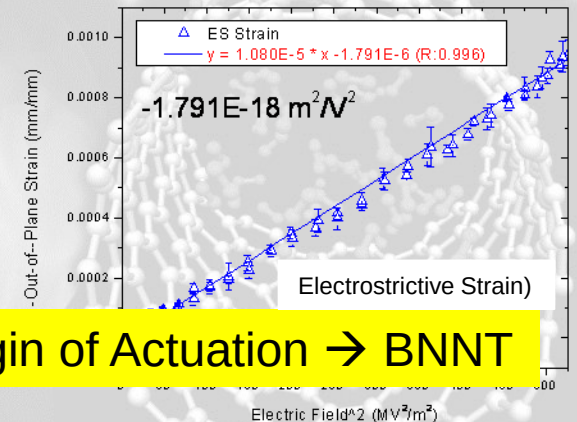
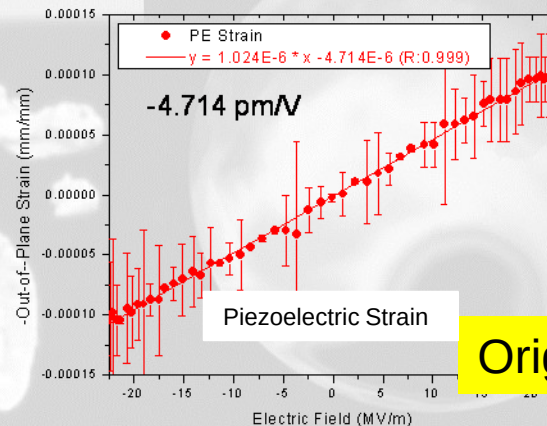
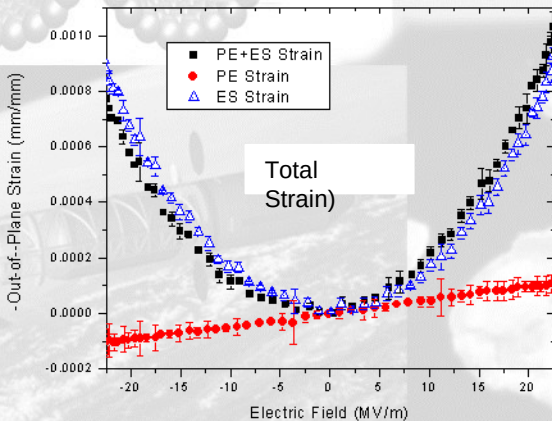
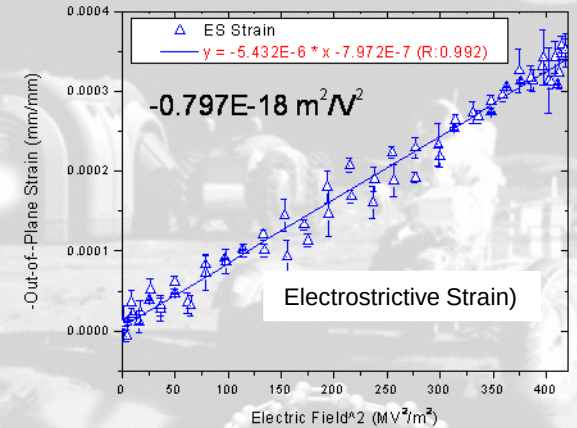
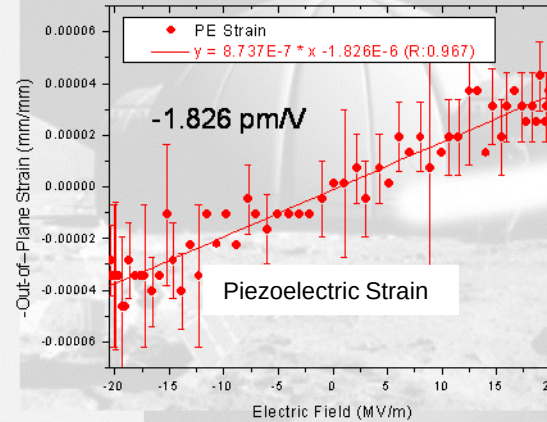
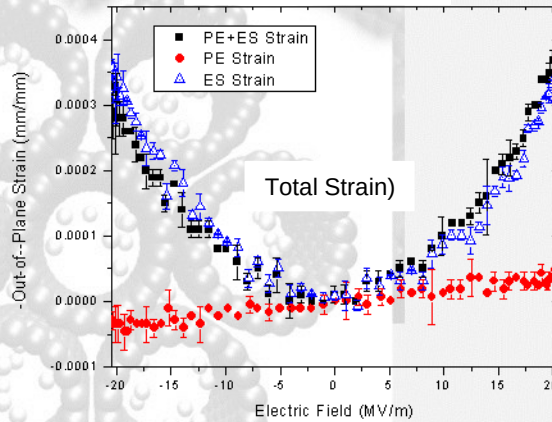
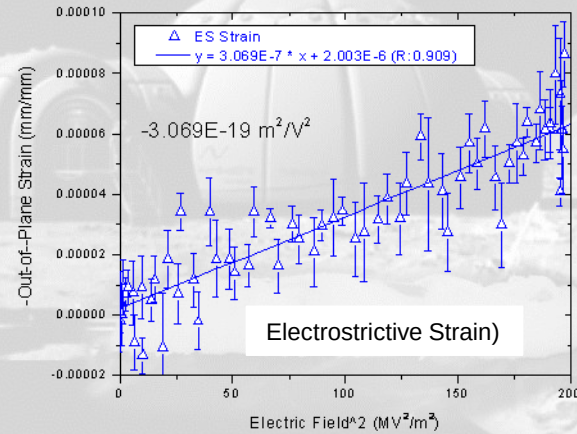
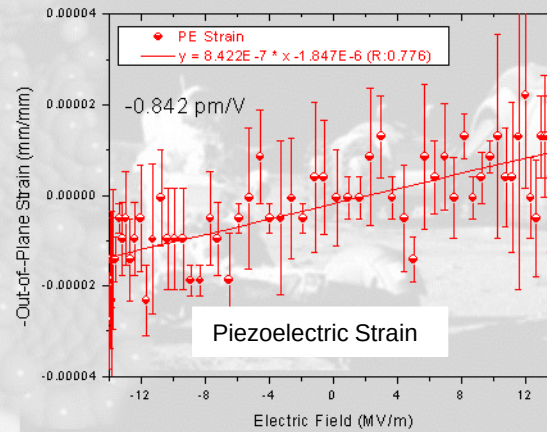
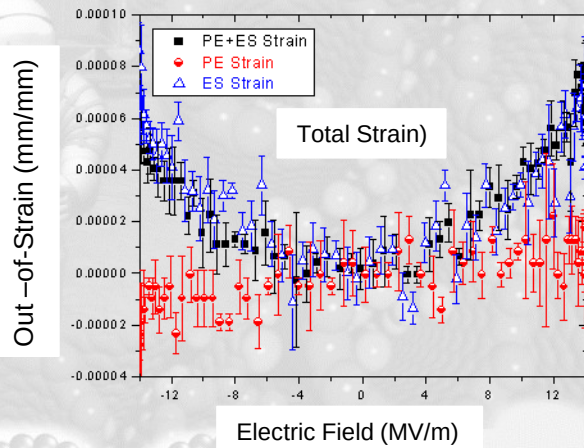
Stretched BNNT-bCN AP PI Composite



100 % Strain,
225°C slightly above T_g

Actuation of Unstretched/Stretched 2% BNNT/Polyimide

Unstretched



Origin of Actuation → BNNT

100% Stretched
@225°C, Quenching

100% Stretched
@225°C, Annealing

Langley All-Nanotubes Actuator/Sensor (LaRC-ANAS) Film

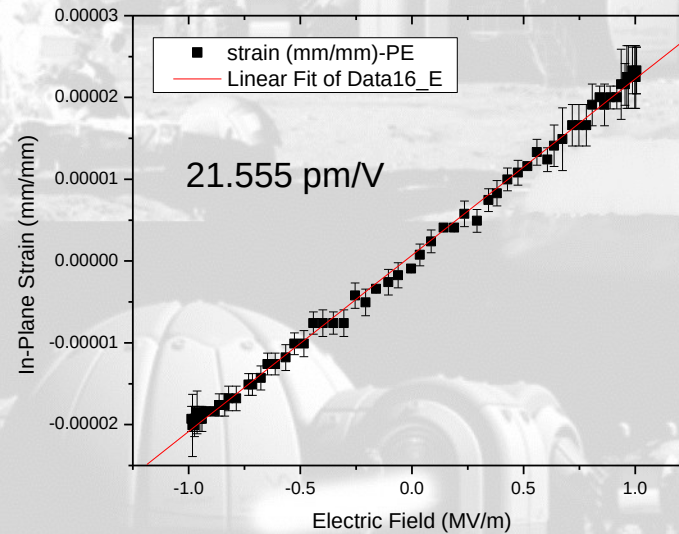
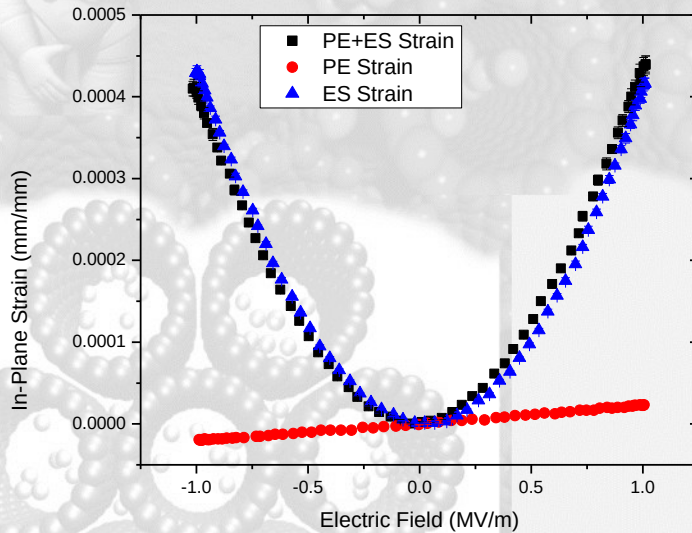
SWCNT film electrode



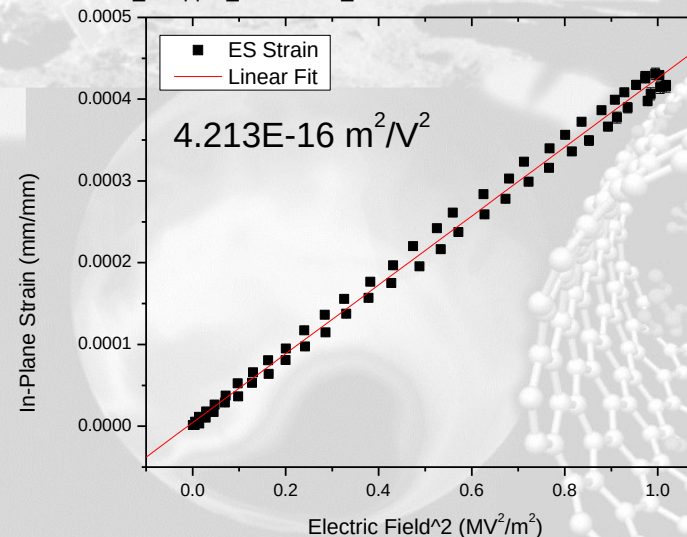
Goal: Flexible, transparent, large actuation, high sensitivity,
Mechanically Durable

Langley All-Nanotubes Actuator/Sensor (LaRC-ANAS-II) film

In-Plane Strain



JK 919-57-04-A-LaRC ANA-CNT-BNNT+PU film-In Plane Strain-1Hz_30Vpp-1_1HzFT & 2_5Hz, 9.51mmL, 11umthick, 2.2mmW



Field induced strain (ϵ_{33})

$$\epsilon_{33} = d_{33} \cdot E + M_{33} \cdot E^2 + \dots$$

d_{33} : piezoelectric coefficient

M_{33} : electrostrictive coefficient

E : applied electric field

Materials	Inclusions	Polymer	Actuation
Polyimide (PI)	None	Polyimide	None
5%hBN/Polyimide (100% stretched)	5%hBN	Polyimide	None
5%BNNT (CVD)/Polyimide	5%BNNT (CVD)	Polyimide	None
Polyimide (100% stretched)	None	Polyimide	None
2%BNNT (laser)/Polyimide	2%BNNT	Polyimide	✓
2% BNNT (laser)/Polyimide (100% stretched)	2%BNNT	Polyimide	✓✓✓
20%BNNT/Polyurethane	>20% BNNT	Polyurethane	✓✓✓✓✓✓✓✓✓✓✓✓✓✓✓✓

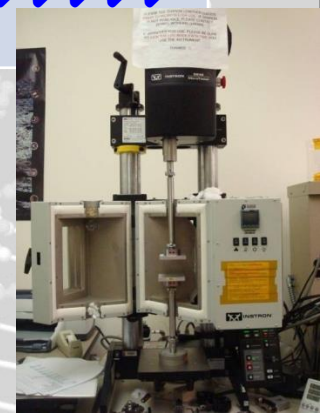
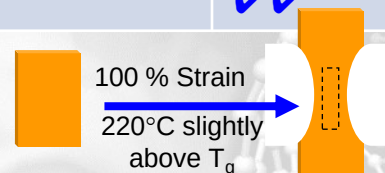
h-BN → No Actuation

Commercial BNNT (CVD) → No Actuation

Polymer → No Actuation

Stretched Polymer → No Actuation

BNNT (high pressure, high temp laser) → Origin of the Actuation



Radiation Shielding Properties

Modeling



Science **340** 1080 (2013)

Measurements of Energetic Particle Radiation in Transit to Mars on the Mars Science Laboratory

C. Zeitlin,^{1*} D. M. Hassler,¹ F. A. Cucinotta,² B. Ehresmann,¹ R. F. Wimmer-Schweingruber,³ D. E. Brinza,⁴ S. Kang,⁴ G. Weigle,⁵ S. Böttcher,³ E. Böhm,³ S. Burmeister,³ J. Guo,² J. Köhler,³ C. Martin,³ A. Posner,⁶ S. Rafkin,¹ G. Reitz⁷

The Mars Science Laboratory spacecraft, containing the Curiosity rover, was launched to Mars on 26 November 2011, and for most of the 253-day, 560-million-kilometer cruise to Mars, the Radiation Assessment Detector made detailed measurements of the energetic particle radiation environment inside the spacecraft. These data provide insights into the radiation hazards that would be associated with a human mission to Mars. We report measurements of the radiation dose, dose equivalent, and linear energy transfer spectra. The dose equivalent for even the shortest round-trip with current propulsion systems and comparable shielding is found to be 0.66 ± 0.12 sievert.

Spacecraft data nails down radiation risk for humans going to Mars

Nature News, May 30, 2013, Ron Cowan

Interviewed Sheila Thibeault at NASA Langley about the study published in *Science*

Mars Science Laboratory (MSL) during its cruise to Mars between 6 December 2011 and 14 July 2012 (253 days)

Mars Round Trip Dose
Equivalent is around 0.66
Sievert

Neutron Radiation Shielding Study

Materials

- Hydrogen, Boron, Nitrogen
- BN, BNNT, Gd
- Low density polyethylene (LDPE), polyimide (Kapton, CP2, (β -CN)APB/ODPA), polyurethane

Radiation Shielding Structural Materials

- In-situ polymerization under simultaneous sonication and shear
- Supercritical Fluid Infusion

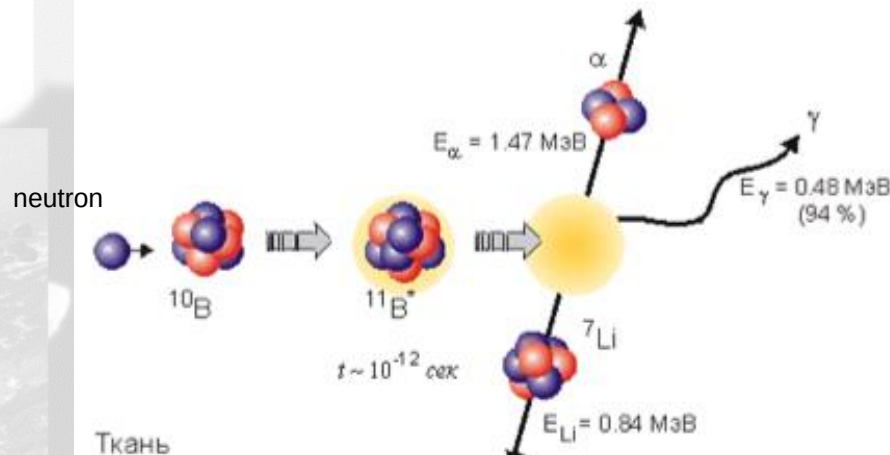
Characterization

- Neutron Radiation Exposure Lab: Source: Am/Be 1Curie
- Moderated by borated polyethylene cylinder block (44mm thick): 45 mrem/hr thermal neutrons
- Sample: 2 x 2" polymer and BN polymer composites
- Detection Foil: 1.25" Indium Foil (0.5mm, 19 barns)
- RSMES: Radiation Shielding Materials Evaluation Software

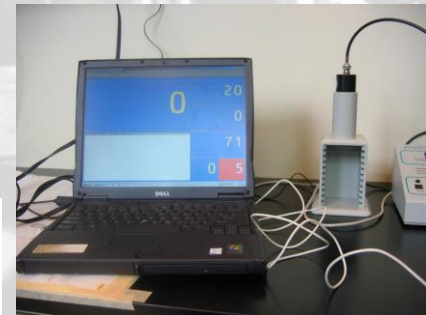
- $^{115}\text{In}(n, \gamma)^{116}\text{In}$

Modeling

- OLTARIS

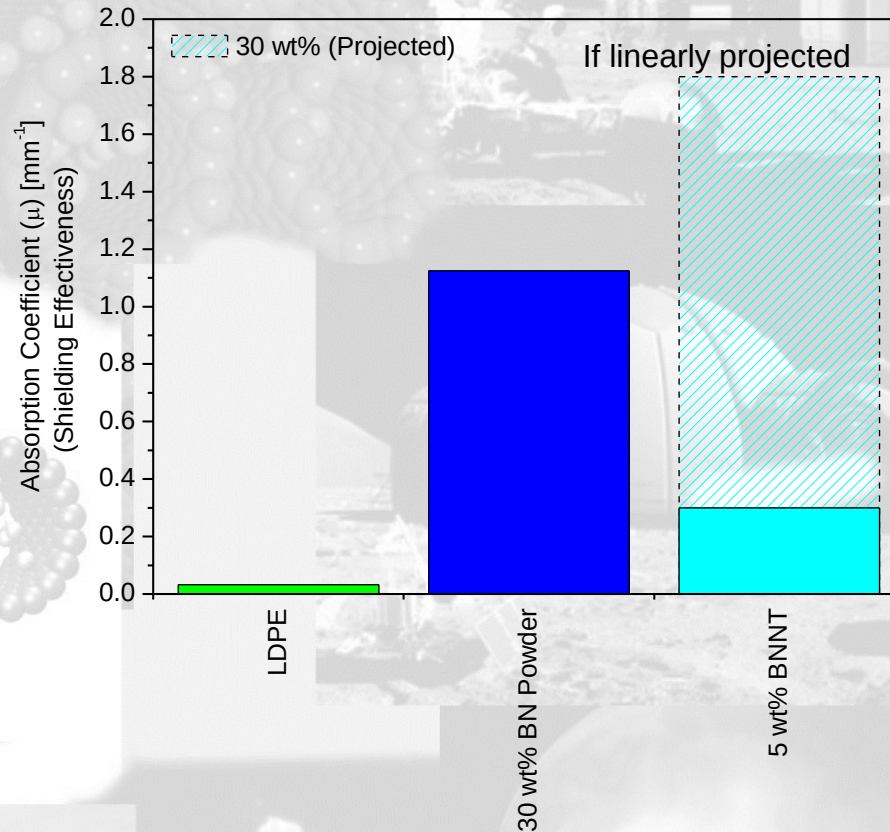


<http://www.inp.nsk.su/bnct/introduction/introduction.en.shtml>



Geiger-Mueller Tube

Advanced Radiation Shielding Materials Containing Hydrogen, Boron, and Nitrogen: Preliminary Results



Nitrogen is effective shielding material.

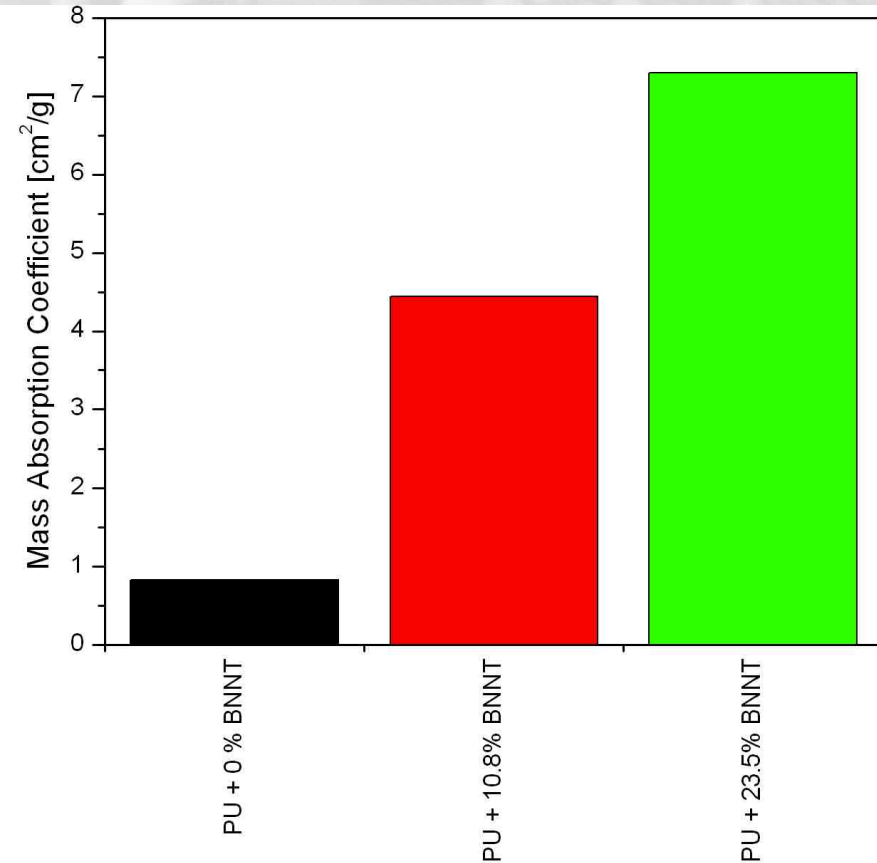
$$\ln\left(\frac{I_s}{I_0}\right) = -\mu x, \Rightarrow \mu = \ln\left(\frac{I_0}{I_s}\right) \cdot \frac{1}{x}$$

BNNT is effective shielding material.

LDPE: Low-density polyethylene.
h-BN: Hexagonal boron nitride platelets.
BNNT: Boron nitride nanotubes.
Considering wt%, BNNT is better than h-BN.

Advanced Radiation Shielding Materials Containing Hydrogen, Boron, and Nitrogen: Preliminary Results

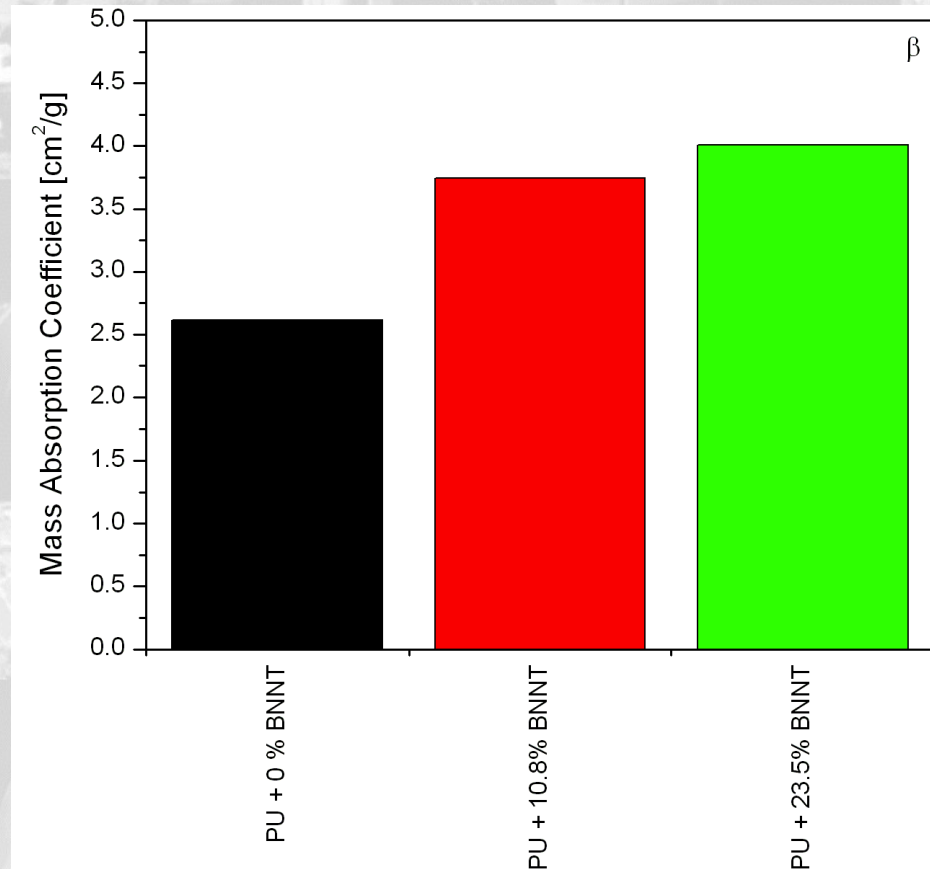
Neutron radiation



Am/Be 1Curie & moderated by borated PE



Beta radiation

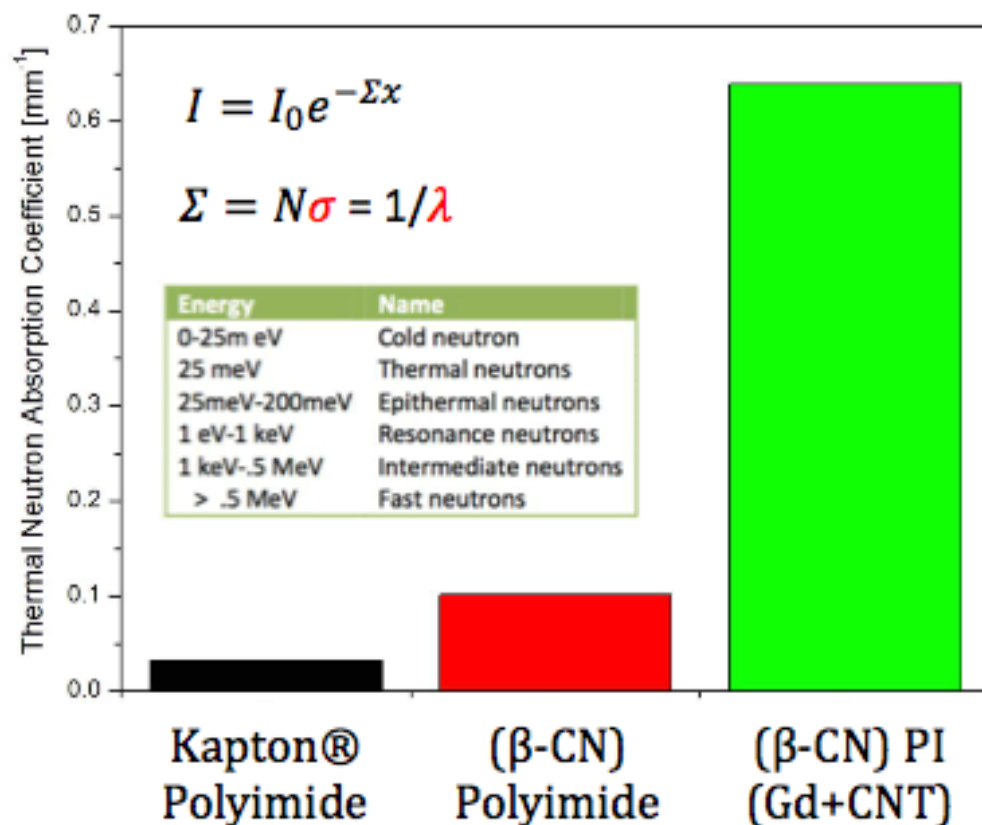


0.1 μCi Sr-90: β (Synthesized Apr 2009)

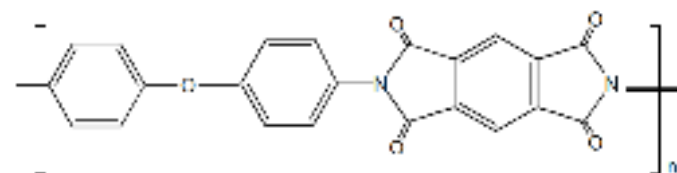


Neutron Exposure Study

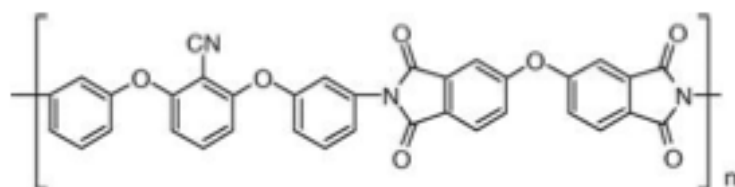
(β -CN)PI Nanocomposite (Gd/CNT)



- Thermal Neutron: 0.025 eV
- The Gd(14%)/CNT(0.1%)/PI exhibited excellent neutron shielding capability with high thermal neutron absorption coefficient compared to control polymers.
- Nitrogen containing polymer also exhibited better shielding properties.



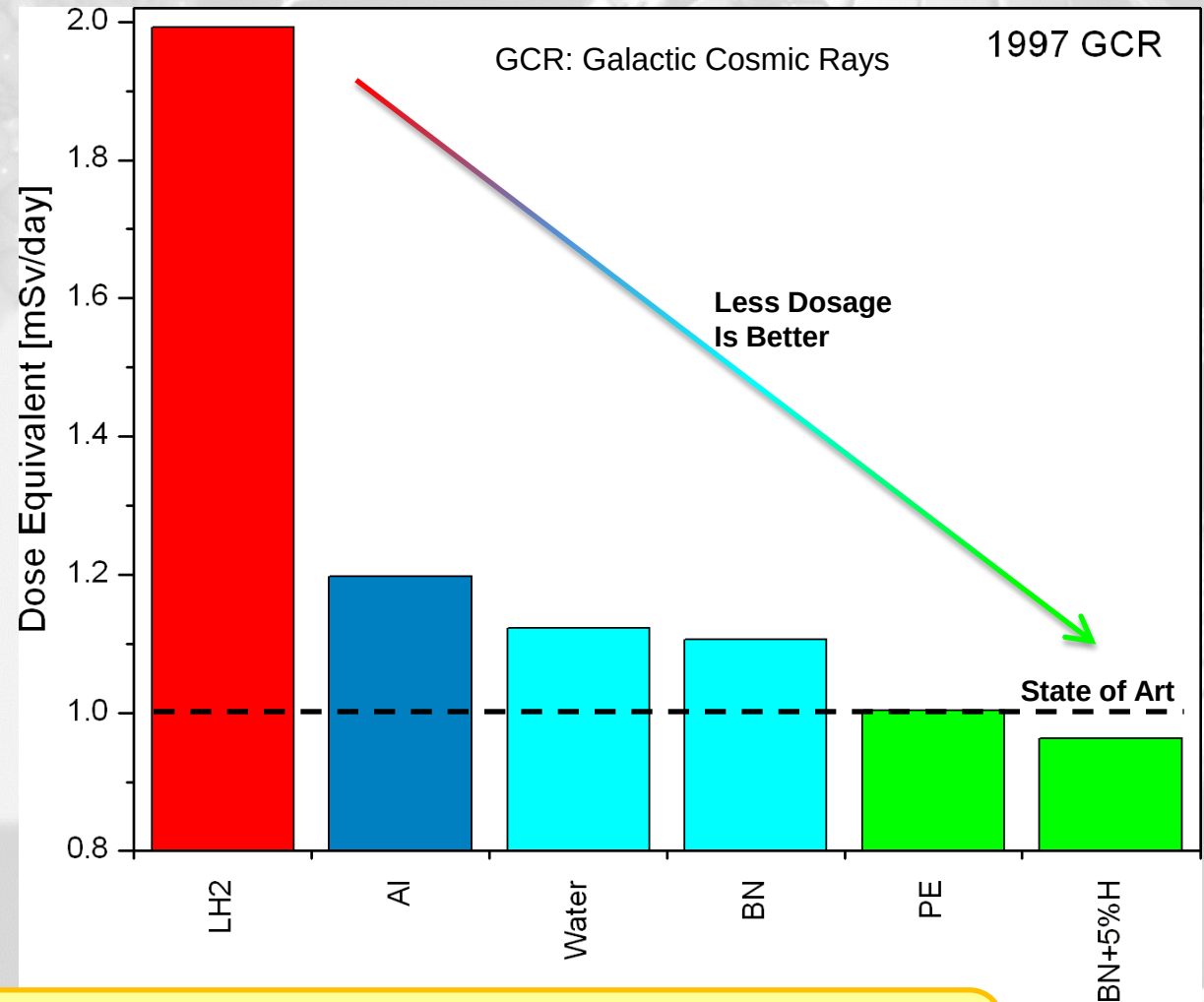
Kapton®



(β -CN)APB/ODPA

Dose Equivalent of Various Shielding Materials: OLTARIS Modeling: GCR 1997

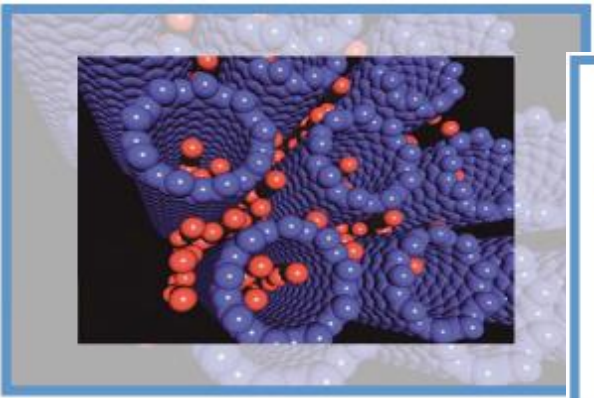
Materials assumed to have common 30 cm thickness.



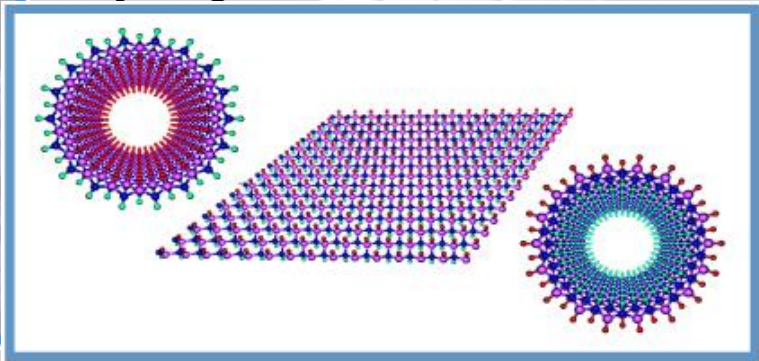
**BN materials perform better than LH2 and water.
BN+5%H performs better than state of art polyethylene.**

BNNT enables.....

Hydrogen Storage
BNNT

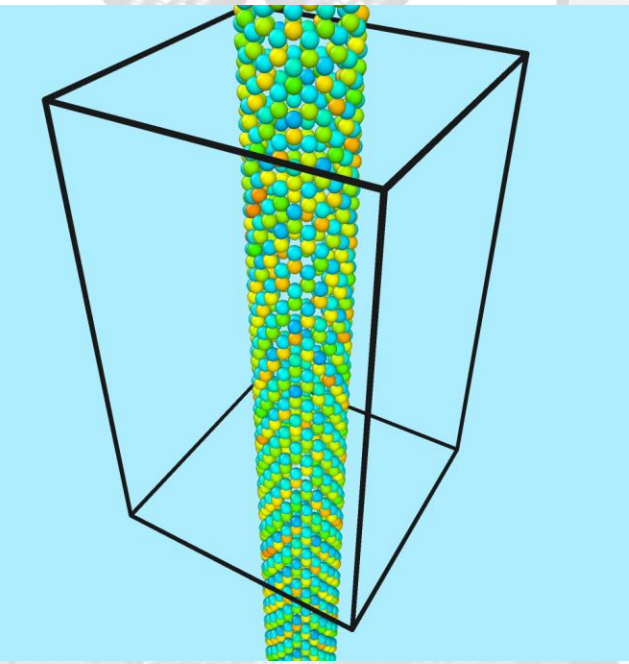


Hydrogenated BNNT

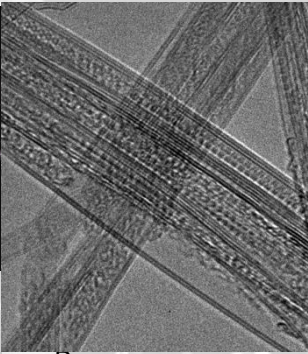
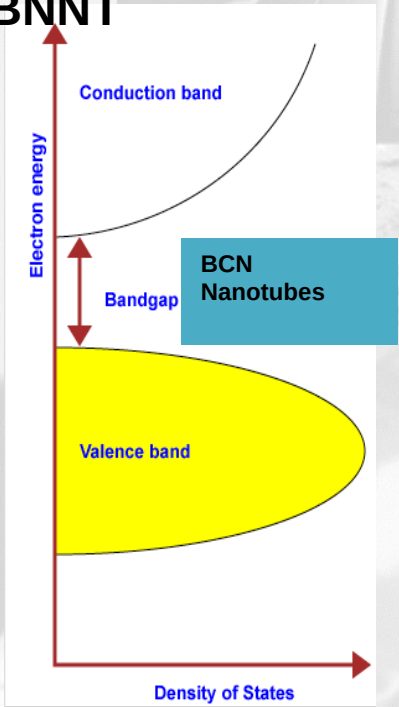


Radiation Shielding Materials Containing Hydrogen, Boron, and Nitrogen: Systematic Computational and Experimental Study

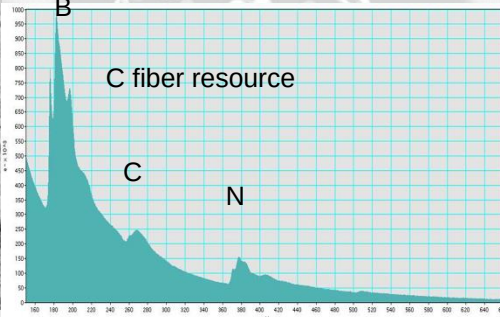
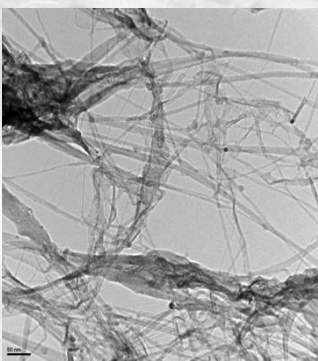
Electroactive properties of BNNT



BNNT (12 0) Polarization in Stretching Induced Electric charge (e)



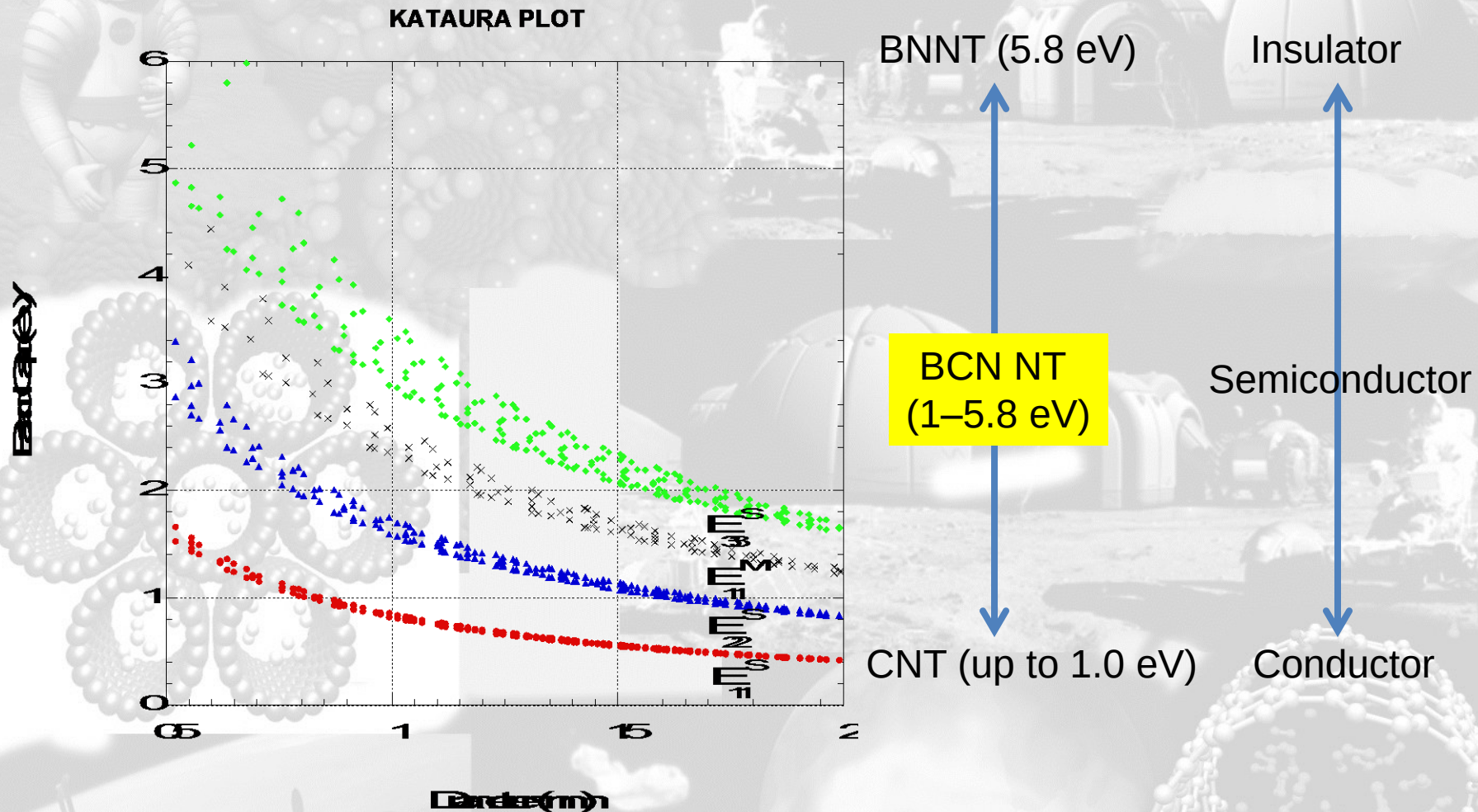
TEM image of C₆₀ BNNT (endo-doped) UC Berkeley



TEM, EELS, and Raman spectra of BCNNT.

$B_xC_yN_z$ Nanotube (BCNNT) Development

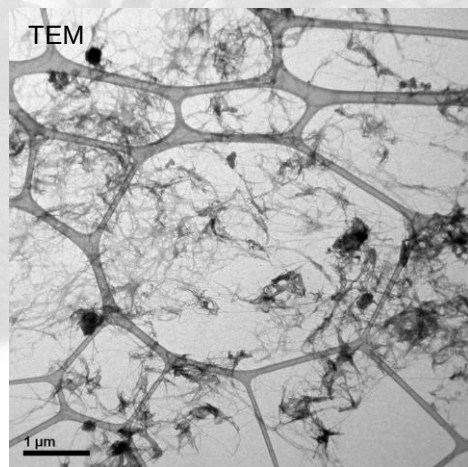
Band Gap Engineering of BCN Nanotubes



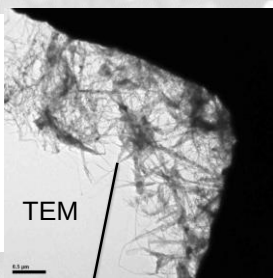
Tailored band gap for a suite of applications requiring specific electronic, electrical, dielectric, optical properties.

- Conductor: electrodes, supercapacitor, fuel cell, batteries, LED
- Semiconductor: actuators, sensors (gas, pressure sensor...), impedance matching materials
- Insulator: insulation cables, high dielectric strength (BN is highest dielectric strength (2×10^5 V/mm))

B_xC_yN_z Nanotube (BCNNT) Synthesis and Characterization

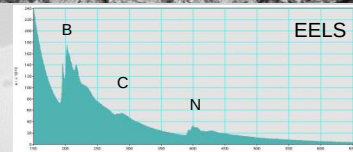
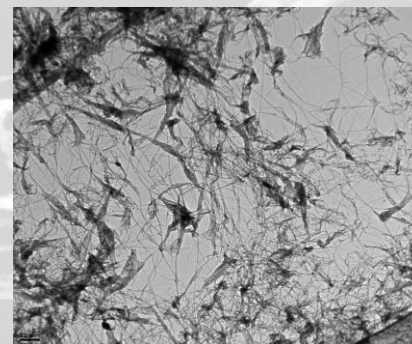
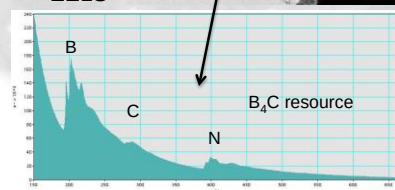


B₄C/B target

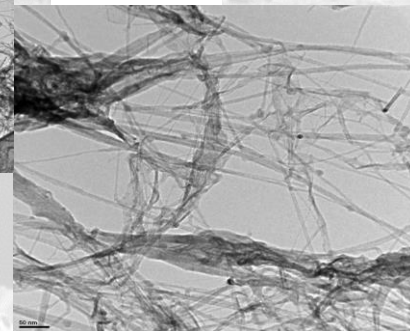


TEM

EELS



Carbon Fiber/B target



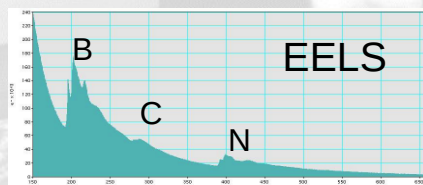
Signal quantification parameters:

Elem.	Signal (counts)	Edge Type	Integration range (eV)	Cross-section (barns)
B	2.20e+007 ± 5790	K	188.0 - 213.0	309 ± 31
C	2.20e+006 ± 3254	K	284.2 - 309.2	118 ± 12
N	3.26e+006 ± 2408	K	401.0 - 426.0	50 ± 5
O	1.32e+005 ± 1662	K	532.0 - 572.2	36 ± 4

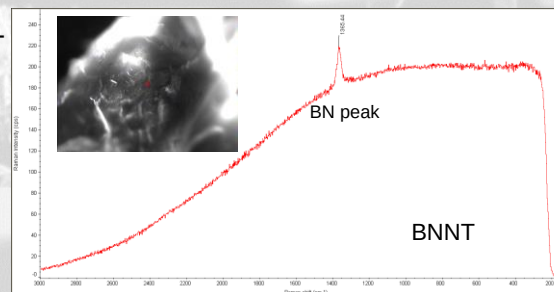
Relative quantification:

Elem. Atomic ratio (/B) Percent content

B	1.00 ± 0.000	44.86
C	0.26 ± 0.037	11.74
N	0.92 ± 0.129	41.07
O	0.05 ± 0.007	2.32

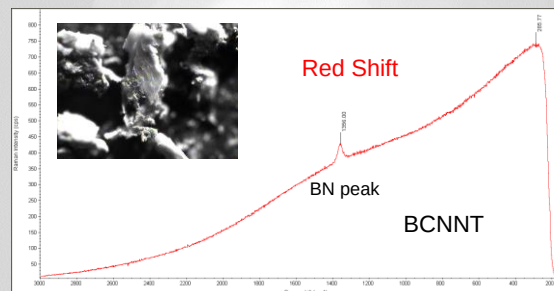
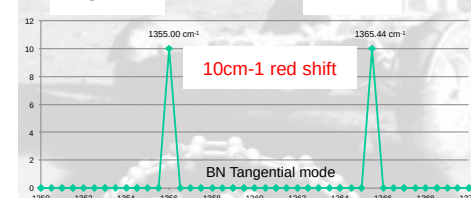


Raman Spectra



BCNNT

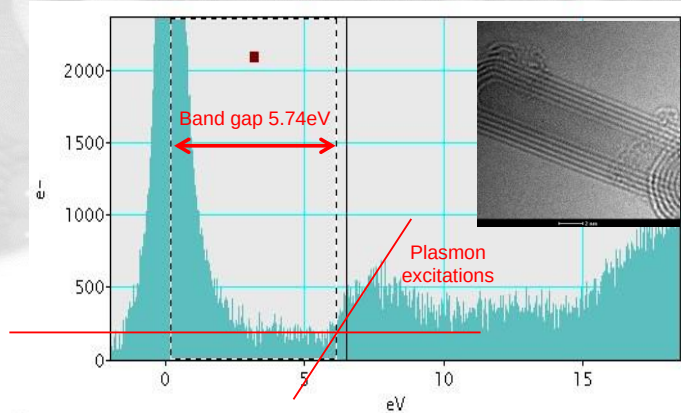
BNNT



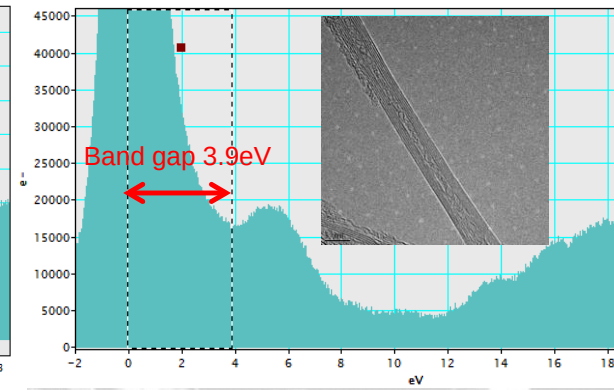
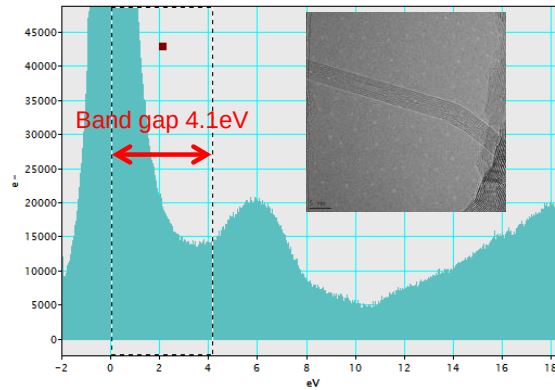
BN peak shift indicates potential optical, electronic, dielectric property change
 → Needs quantitative analysis
 → Band gap measurement by Low energy EELS

Band Gap Measurement: Low Energy EELS (modified BNNT)

Bandgap measurement of BNNT
(Low-loss region)

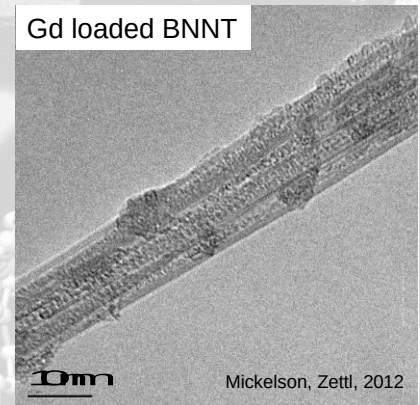
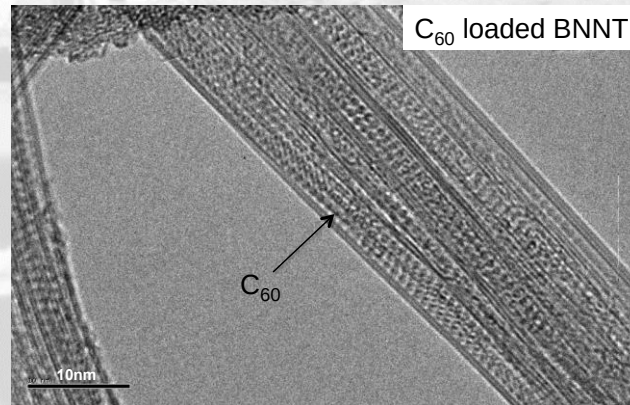
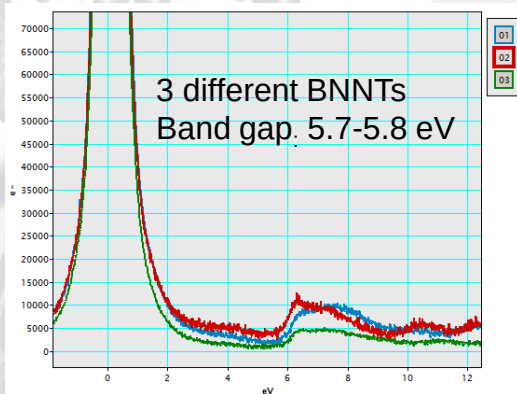


Bandgap measurement of C₆₀/BNNT
(Low-loss region)

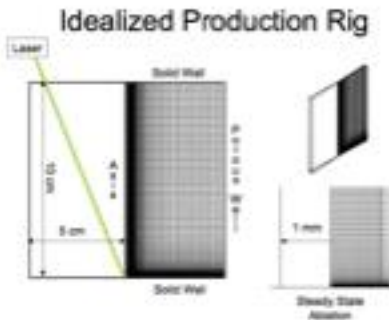


Endo-Doped BNNNT (C₆₀/BNNT, Gd/GNNT) UC Berkeley

Superimposed Low Loss EEL spectra of multi walled Boron nanotubes shown in previous pages



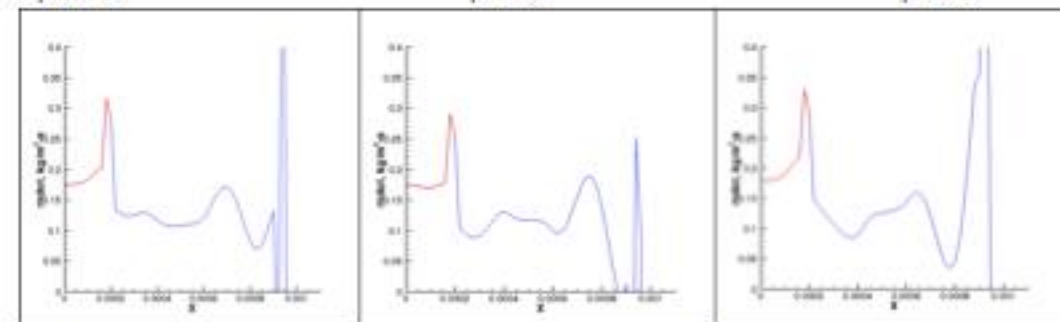
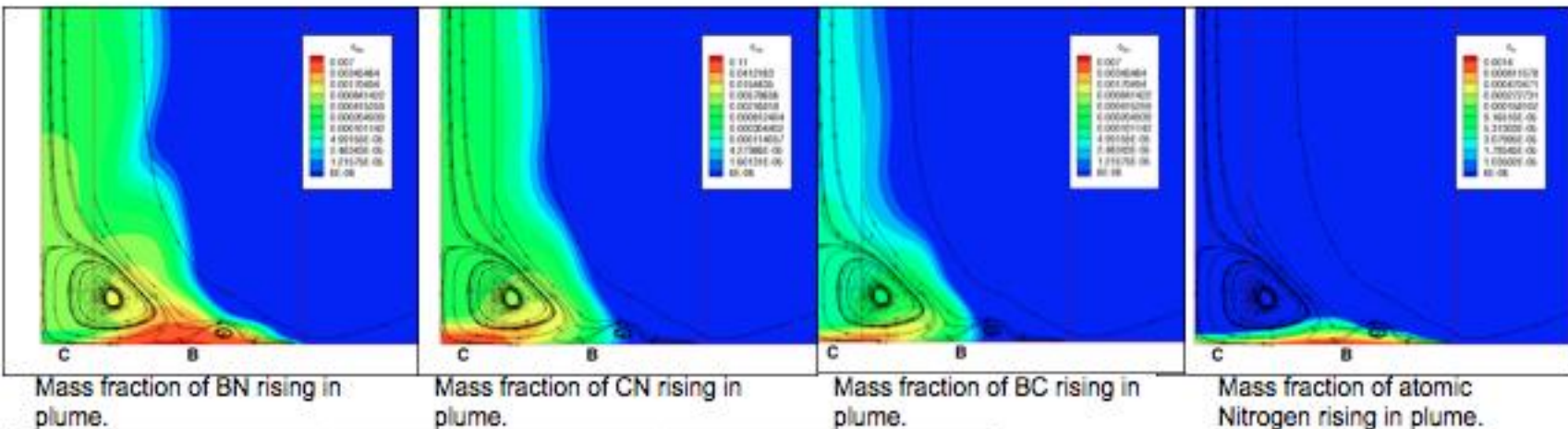
BCNNT Modeling (Peter Gnoffo)



Goals and Objectives: The objective of this study element is to model the gas plume as a function of the vaporizing surface configuration, laser power, and pressure in the pressurized vapor condensation (PVC) rig.

Deliverable(s): Predicted plume environments at the condensation wire from which nucleation of BCNNT occurs.

Progress/Preliminary Results: Simulations have been generated for boron and carbon targets separately as a function of nominal laser power and pressure conditions in an idealized production rig.



Summary

- Highly crystalline, long, small diameter BNNT was successfully synthesized at high pressure, high temperature environments.
- Daily operation of BNNT synthesis (about 4g) enables purification, dispersion, BNNT mat/yarn formation, extend BNNT research to external collaborators.
- Advanced *in-situ* optical diagnostics: verified up to 950 psi/1000°C with a new NIA BNNT science chamber
- BNNT polymer composites exhibited piezoelectric and electrostrictive strain at low electric fields, which originated from the presence of BNNTs. MD modeling study supported the experimental results.
- BNNT polymer composites exhibited excellent neutron and beta radiation shielding properties and both boron and nitrogen contribute to the shielding effectiveness.