Multifunctional Nanomaterials for Aerospace Applications: Overview

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NASA Vision and Mission

NASA Mission

Drive advances in science, technology, aeronautics, and space exploration to enhance knowledge, education, innovation, economic vitality, and stewardship of Earth.

NASA Vision

We reach for new heights and reveal the unknown for the benefit of humankind…

NASA Langley Research Center

NASA Langley Research Center Hampton, Virginia
Founded in 1917 (NACA): first civil aeronautical research laboratory converted to NASA in 1958
Facilities: $4 billion replacement value
People: 2000 Civil Servants ; 1700 Contractors

All images credit: NASA

Langley's Role in NASA

For the Past 99 Years….

Langley has created innovative solutions to the grand challenges of earth science, space exploration and flight in all atmospheres, for the benefit of all humankind.

Langley continues to make significant contributions to all of NASA's missions and strategic goals.

All images credit: NASA

NASA Langley at a Glance (2016)

As of 11/1/15

Langley's Economic Impact (2015)

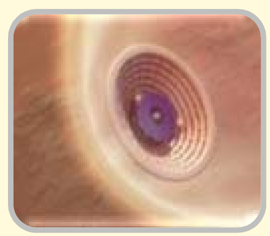
- National economic output of ~$2.3b and generates over 17,400 high-tech jobs
- Virginia economic output of ~$1.1b and generates over 8,800 high-tech jobs

PY2016 Budget Estimate	**~$925m**
NASA Langley Budget	**~$902m**
External Business	~$23m
Workforce	**~3,470**
Civil Servants	~1,840
Contractors (on/near-site)	~1,630
Infrastructure/Facilities	
156 Buildings	764 acres
Replacement Value	~$3.6b

AERONAUTICS
$191m

SCIENCE
$232m

SPACE TECH
$33m



HUMAN EXPLORATION
$41m

EDUCATION
$1m

SAFETY, SECURITY & MISSION SERVICES & CONSTRUCTION/ENVIRONMENTAL COMPLIANCE & RESTORATION

Center Management & Operations
(Facilities, IT, Engineering, Tech Authority, B&P, IRAD, Safety/Mission Assurance, Legal, Finance, Procurement, Human Resources)

Agency Management & Operations
(NASA Engineering & Safety Center, Office of Chief Engineer, Agency IT)

Construction Environmental Compliance & Restoration
(Revitalization Plan)

All images credit: NASA

NASA Langley Core Competencies

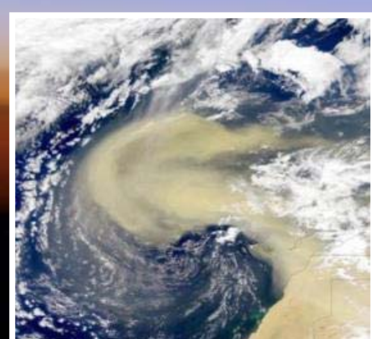
Aerosciences

Research for Flight in All Atmospheres

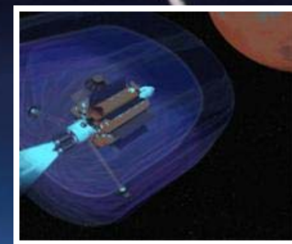


Characterization of all Atmospheres

(Lasers & LIDAR)

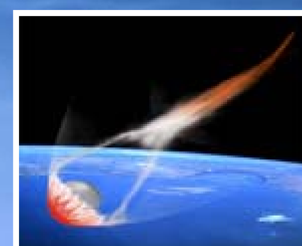



Aerospace Systems Analysis

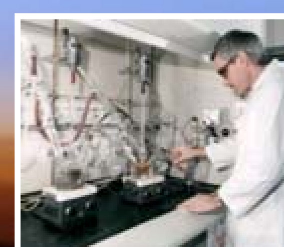


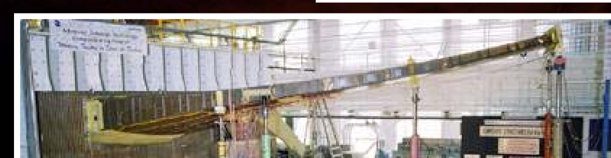

Space Exploration

Entry, Descent & Landing




Aerospace Structures & Materials





All images credit: NASA

Research Directorate Areas of Expertise

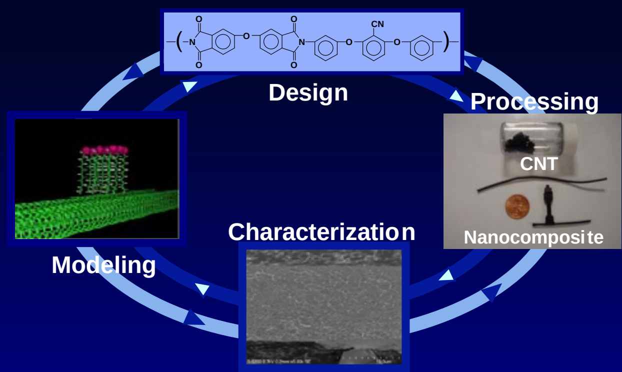
- **Structures** (integrated multifunctional design, damage mechanics, nonlinear mechanics, radiation physics, loads and dynamics)
- **Materials** (lightweight materials, multifunctional materials, computational design, environmental interactions, innovative processing)
- **Measurement Sciences** (noninvasive measurement techniques and physics-based models of measurement methodologies)
- **Acoustics** (source noise, system noise, structural acoustics, and psychoacoustics)
- **Aerodynamics** (subsonic/transonic/supersonic aerodynamics, aeroelasticity & controls, fluid physics & modeling, flow control, computational methods, uncertainty)
- **Hypersonics** (physics & chemistry modeling, aerothermodynamics, air-breathing propulsion)
- **Flight Dynamics and Controls** (flight dynamics, control theory, systems identification, guidance & trajectory optimization, flying qualities)
- **Crew Systems & Aviation Operations** (air traffic operations, flight deck interface, human automation integration, atmospheric hazards and wake turbulence)
- **Safety-Critical Avionics Systems** (high confidence software-intensive systems)
- **Test Technologies** (methods and advanced tools to improve experimental facility data quality and fidelity; and operational processes and automation to improve experimental facility productivity and reduce operation costs)

Advanced Materials and Processing Branch
5+ Facilities : Offices and Laboratories

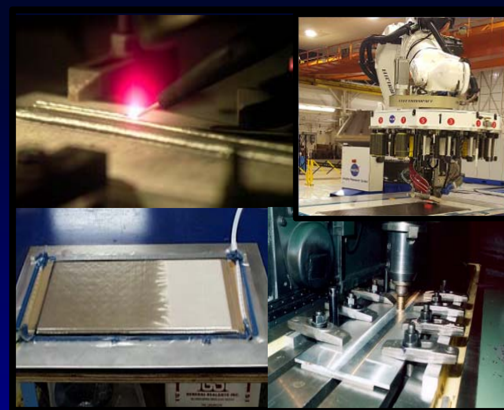
All images credit: NASA

Advanced Materials and Processing Branch

Materials Design

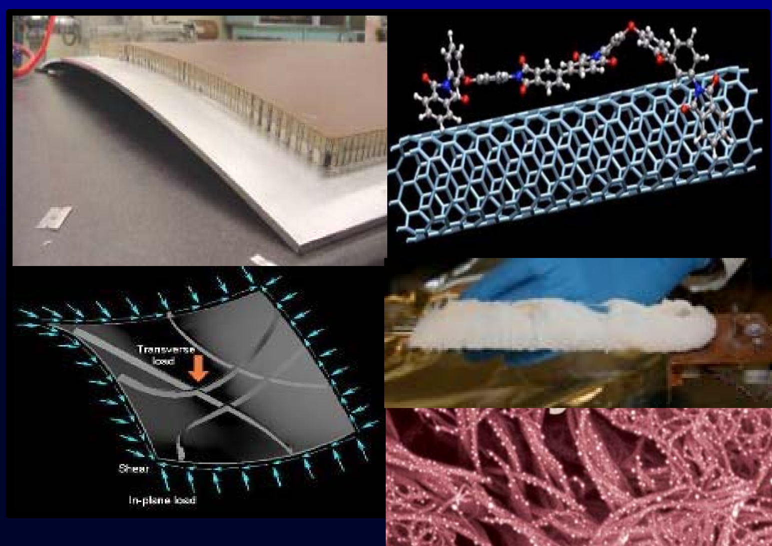


Innovative Materials Processing

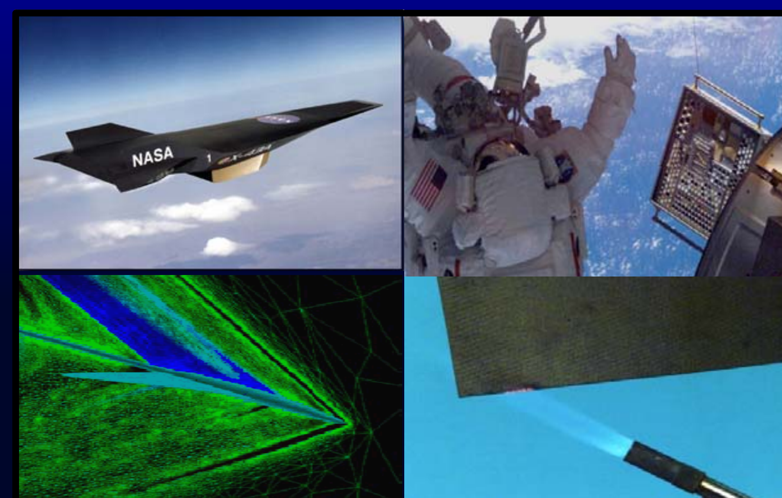


Materials Testing

Advanced Material Systems



Materials for Extreme Environments



All images credit: NASA

Future of Materials for NASA

- **Reduction in areal densities of <u>load bearing structures</u> requires the combination of all three material classes: Polymers, Metals, and Ceramics**
  - Reduce amount and traditional use of mechanical fasteners
  - Make bondlines and welds stronger than the weakest parent material
  - Directly insert the correct material where it is needed
- **The increased efficiency of solid state <u>device technology</u> requires the combination of all three material classes: Polymers, Metals, and Ceramics**
  - Decrease material defects and increase operating temperature ranges
  - Increase control of multifunctional properties
  - Directly insert the correct material where it is needed

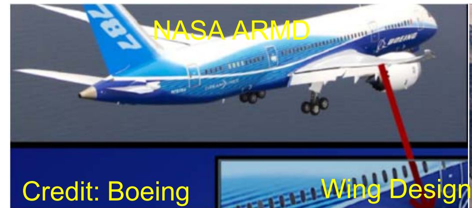
➢ **To achieve this, AMPB needs to continue investing in 4 fundamental core technical areas:**
  - New Materials through **Synthesis** (Composition of Matter)
  - New Materials through **Processing**
  - **Characterization** of Materials
  - **Computational** Modeling and Lifing of Material Interactions

Technical Capabilities/Instrumentation

- **Materials Synthesis**
  - Chemical (small molecule)
  - Polymer (macromolecule)
  - Metallic Alloys
- **Materials Processing**
  - Prepreg and Composite (any resin/fiber)
  - Solution film casting/melt extrusion
  - Vacuum Press, VARTM, Autoclave, Automated Tape Placement (ATP)
  - Plasma Spray
  - EBF3
  - Bonding/Joining
  - Heat treatment Vac. Furnaces
  - Sputtering/PVD
- **Mechanical**
  - Electromagnetic/servo-hydraulic load-frames (Liq. He to 3000F to 10-7T)
  - Small Ball-screw frames w/ E-Chambers
  - Pin-on-disk Tribometer w/ furnace
  - Tabor Abrader
- **Analytical**
  - Microscopy: SEM, TEM, HR-SEM, ESEMs – Variable Pressure Lg chamber (w/ EDX, WDS, μ-probe, load frame, EBSD/AFM tips, EELS, SIMS)
  - Thermal Analysis: DSC, TGA, TGA-MS, DMA, TMA, Laser Flash, Heat Flow, Rheometers
  - Spectroscopy: NMR, IR, near-IR, UV-Vis, RAMAN, XRD, Ellipsometer, XPS, Auger
  - Chromatography: GPC, GC-MS
  - Surface Analysis: Droplet and Insertion instruments for surface tension, Optical profilometer, SPM, Nitrogen Absorption
  - Optical Microscopy: Confocal, Fluorescence, Metallograph, X-Polarized

*Technical acronyms were used for space limit.

Critical Concerns for Aerospace Systems



Weight
- Reduced fuel consumption & emissions
- Reduced launch costs
- Enabler for many new vehicles designs

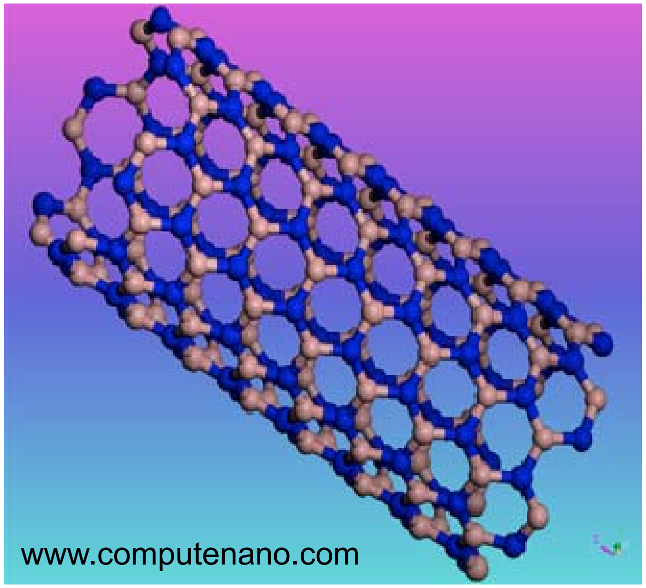
Functionality/Performance
- Reduced fuel or power consumption
- Multifunctionality: additional weight reduction

Durability
- Safety and reliability
- Maintenance down-time and costs
- Extreme environments

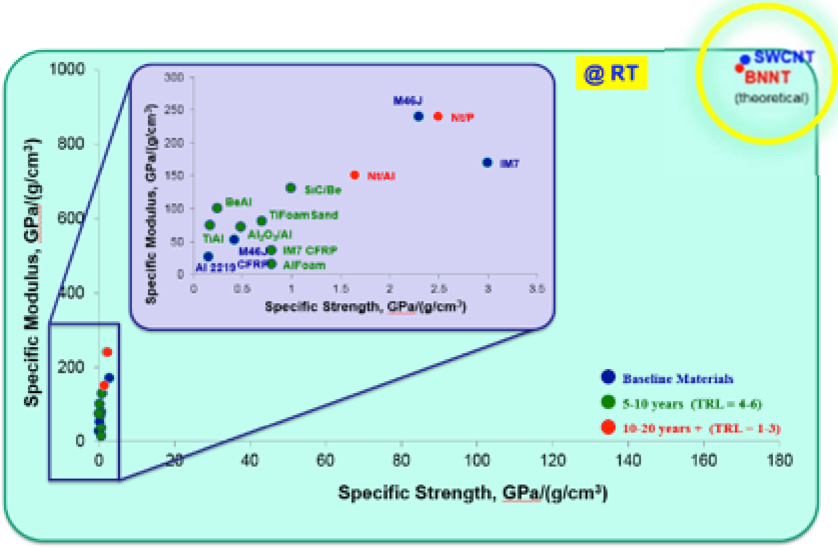
All images credit: NASA

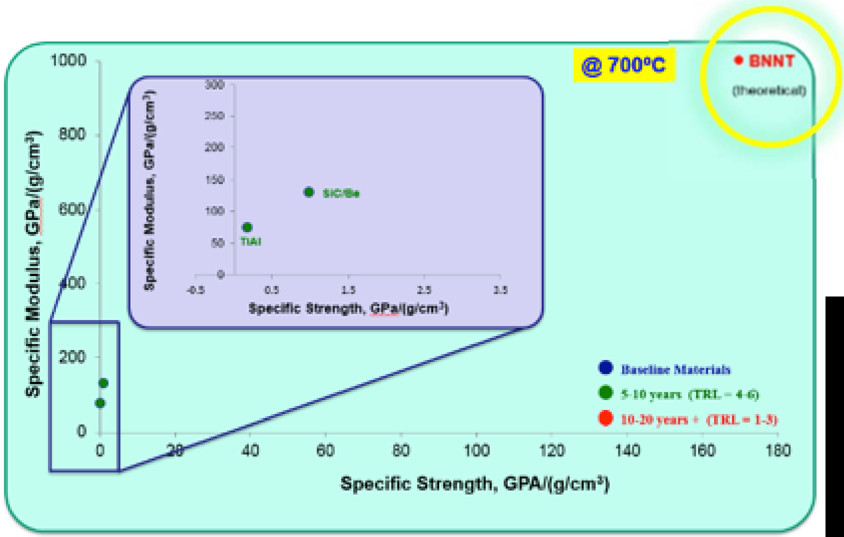
Outline

- Nanotube Synthesis
  - High Temperature-Pressure (HTP) Boron Nitride Nanotube (BNNT) Synthesis
- Interfacial Strength/Fracture Energy of BNNT Polymer Composites
- Dispersion
- Sensors/Actuators
- Radiation Shielding
- Summary



Properties of Materials for Vehicle Structure





	Carbon Nanotubes	Boron Nitride Nanotubes
Electric Properties	Metallic or semiconducting	Insulating: Wide 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 Emissivity	> 0.95 (very high)	0.92 (very high, measured)
Thermal Oxidation Resistance	Up to 300-400 °C in air	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 ($0.25\text{-}0.4\ C/m^2$)
Surface Morphology	Smooth	Corrugated (better bonding for composites, ionic bonding)
Color	Black	White (can be dyed to color)
Coefficient of Thermal Expansion	$-1 \times 10^{-6}\ K^{-1}$ (very low)	$-1 \times 10^{-6}\ K^{-1}$ (very low)

Catharine Fay: CIF Interview (YouTube)

Click Above

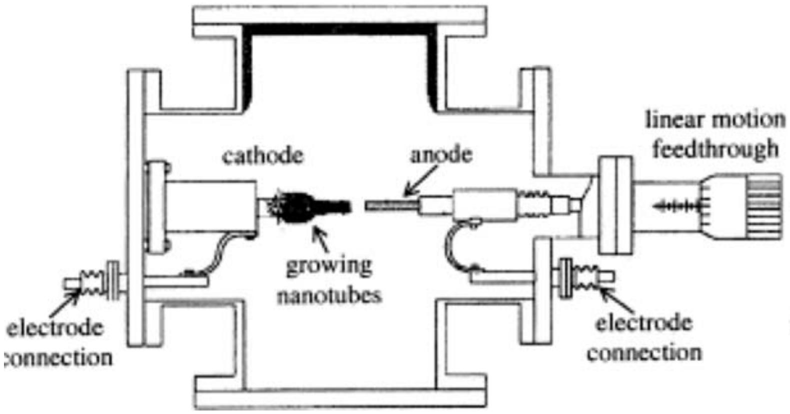
Sheila Thibeault: CIF Interview (YouTube)

Click Above

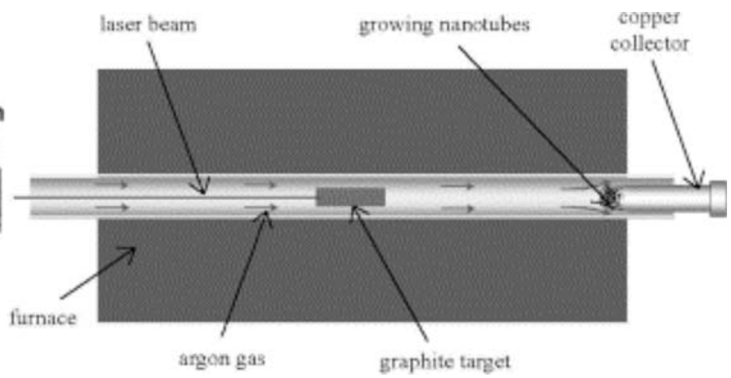
Charlie E. Harris, M. J. Shuart, H. Gray, NASA/TM-2002-211664
http://www.youtube.com/watch?v=r25RMceegKM (Fay)
http://www.youtube.com/watch?v=ADA-FtQ_Vno (Thibeault)

Synthesis Methods of Carbon Nanotubes

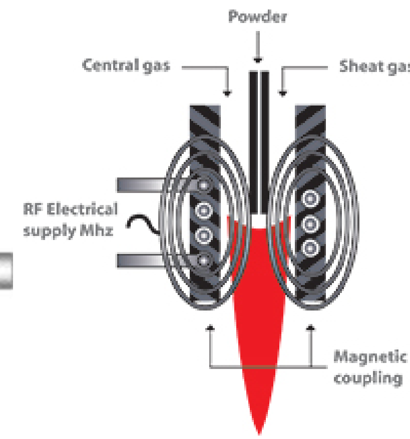
- Arc-discharge: solid state carbon precursor
- Laser ablation: solid state carbon precursor
- Chemical vapor deposition (CVD): gaseous carbon precursor/ HiPco (High pressure CO)
- Free Electron Laser (Jefferson Lab): funded by NASA-LaRC C&I
- RF Induction Thermal Plasma (Canadian NRC)



Arc-discharge

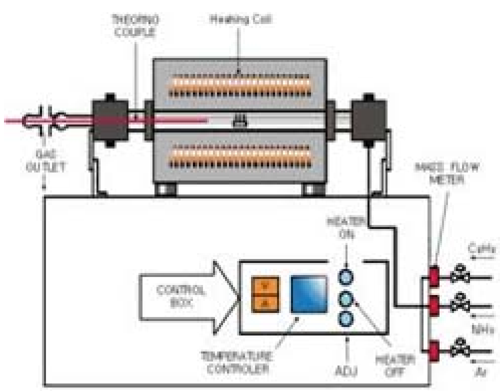


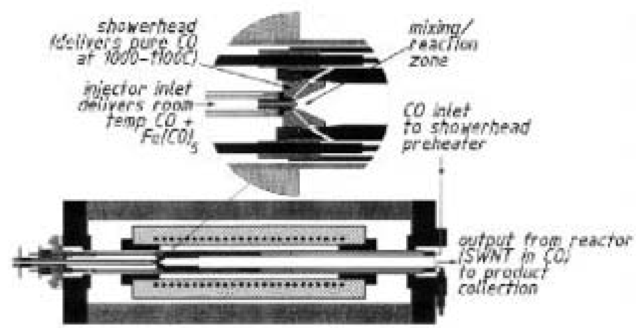
Laser ablation



Credit: www.tekna.com

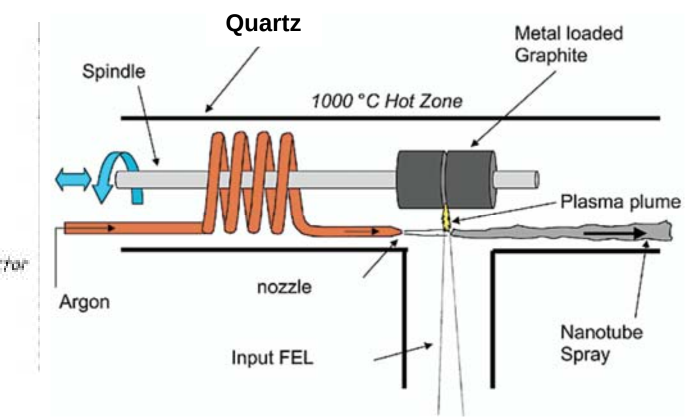
Induction Plasma





HiPco

Chemical vapor deposition (CVD)



Laser ablation (Free electron laser)

Credit: http://students.chem.tue.nl/ifp03/synthesis.html

Nano Lett **2**, 56 (2002)

BNNT Synthesis History

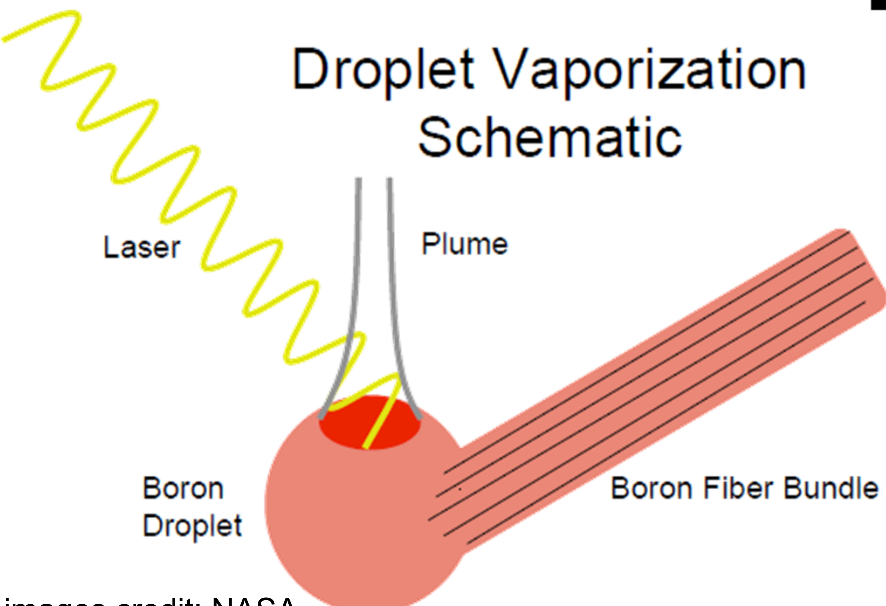
- First Theoretical prediction: *PRB* **49** 5081–5084 (1994) (UC Berkeley, Cohen), computation
- First Synthesis Arc Discharge: *Science* **269** 966 (1995) (UC Berkeley, Cohen/Zettl) BNNT by Arc Discharge
- Arc Discharge: *PRL* **76** 4737 (1996) (ONERA France, Loiseau) Arc Discharge HfB2 with N2 gas
- 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 Temp, High Pressure, Laser vaporization: *Nanotechnology* **20** 505604 (2009) (NIA/NASA/Jlab) High Temperature, Pressure (HTP) BNNT, Free Electron Laser/CO2 Laser
- High Temp Induction Thermal Plasma: *ACS Nano* **8** 6211 (2014) (NRC Canada, Kim, Kingston, Simard): 20g/hr, need H2
- High Temp, High Press Induction Thermal Plasma: NL 14 4881 (2014) (UC Berkeley, Zettl): 35g/hr

High Temperature-Pressure (HTP) BNNT and BCNNT

- Free Electron Laser or CO_2 laser
- No Catalyst, only B and N resources (and C for BCNNT)
- Very long, small diameter, highly crystalline BNNT, BCNNT

Nanotechnology, **20** 505604 (2009)
US Patent Appl US20120171487 A1 (2012) BCNNT

BNNT Synthesis Lab: NASA Langley (1st Gen)

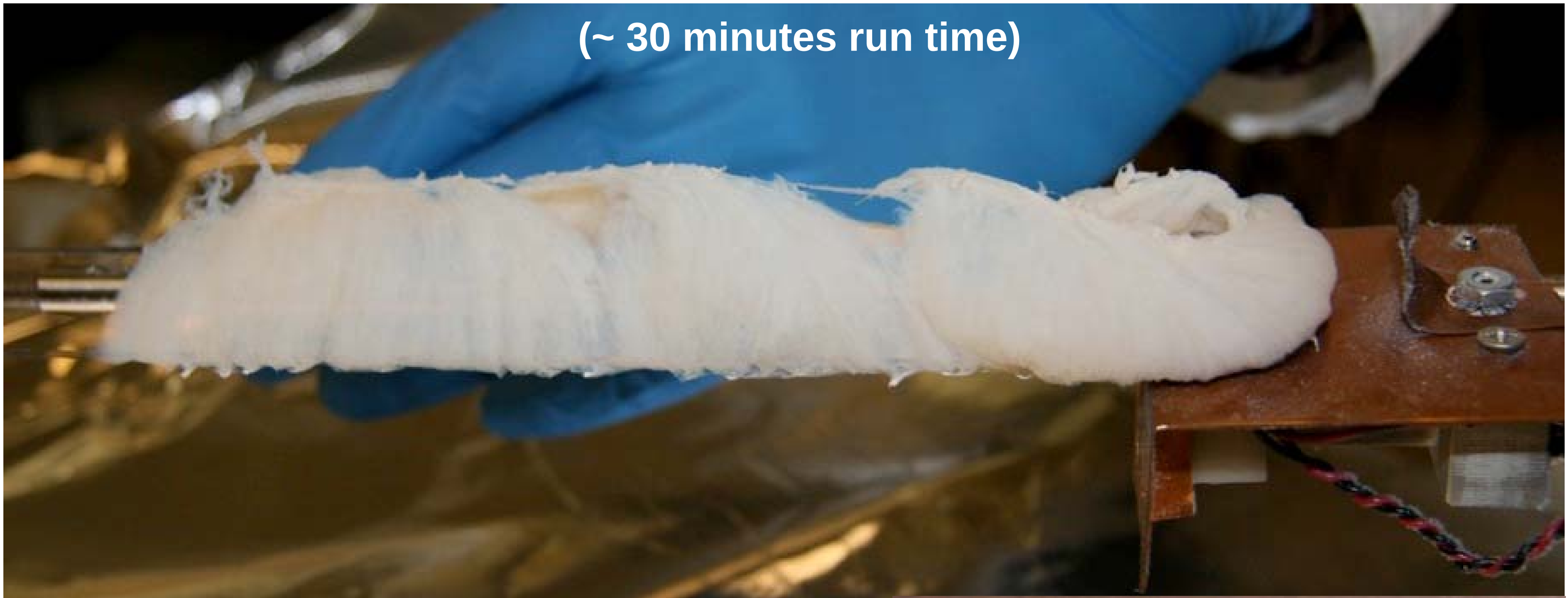


All images credit: NASA

- 5 kW of infrared radiation @ 10.6µm Heat source for vaporizing Boron feed stock above 3500ºC
- Pressurized with Nitrogen to 200 psi
- LaRC rig operating since May 2012 daily with two operators for 1 shift

Nanotechnology, **20** 505604 (2009)
J. Thermophysics and Heat Transfer **27** 369 (2013)
Proc. SPIE **9060** 906006 (2014)

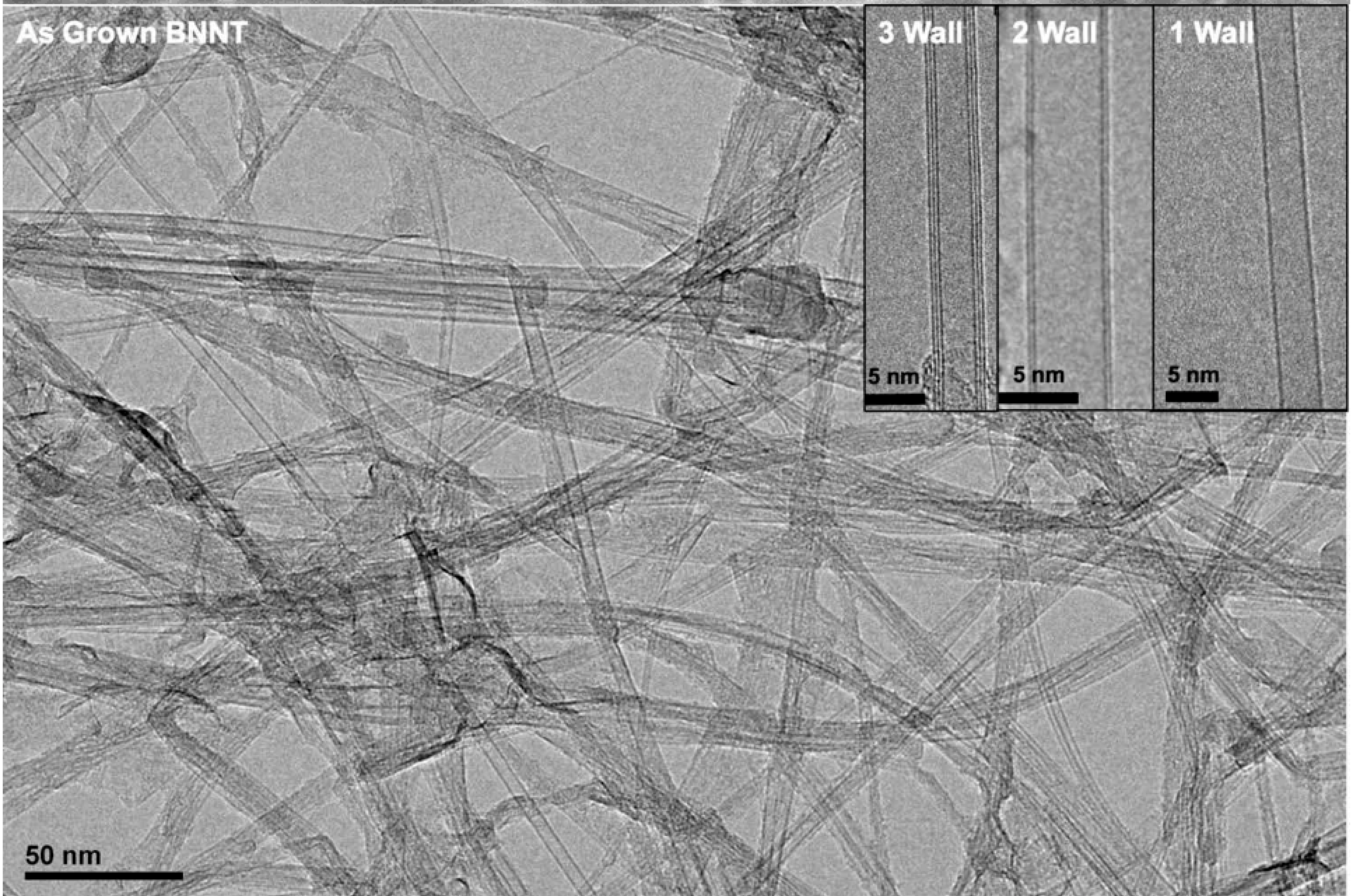
Cotton-like High Pressure and Temperature (HPT)-BNNT



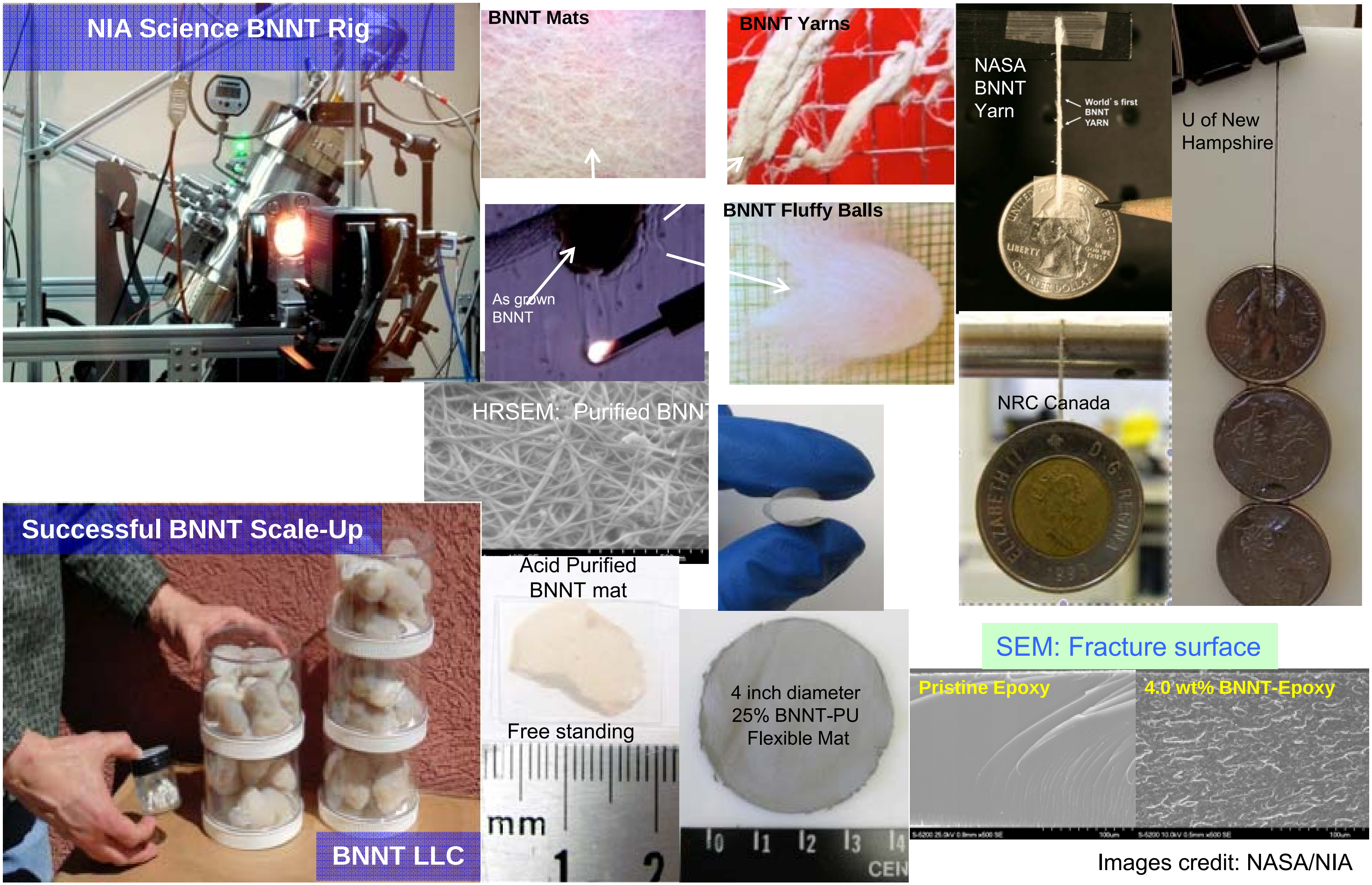
Benefits

- 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 800ºC)
- Highly electroactive (due to the B-N polar bond)
- Neutron radiation shielding (due to their B content)

All images credit: NASA

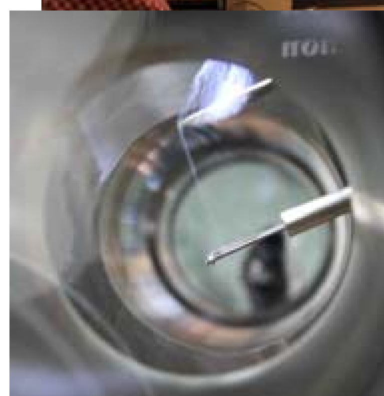

As Grown BNNT
3 Wall
2 Wall
1 Wall
5 nm
5 nm
5 nm
50 nm

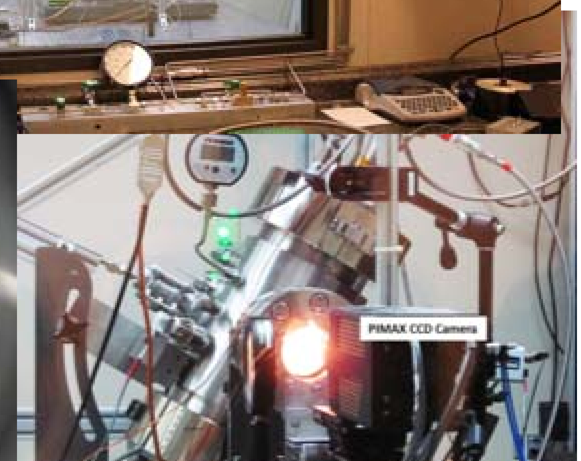
BNNT Scale-Up and Various Forms of BNNT (BNNT Fluffy Balls, BNNT Mats, BNNT Yarns)

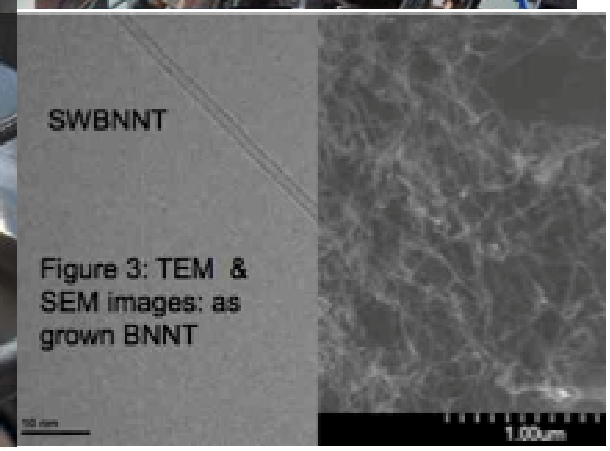


Images credit: NASA/NIA

NIA BNNT Science Rig: 2^{nd} Gen







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

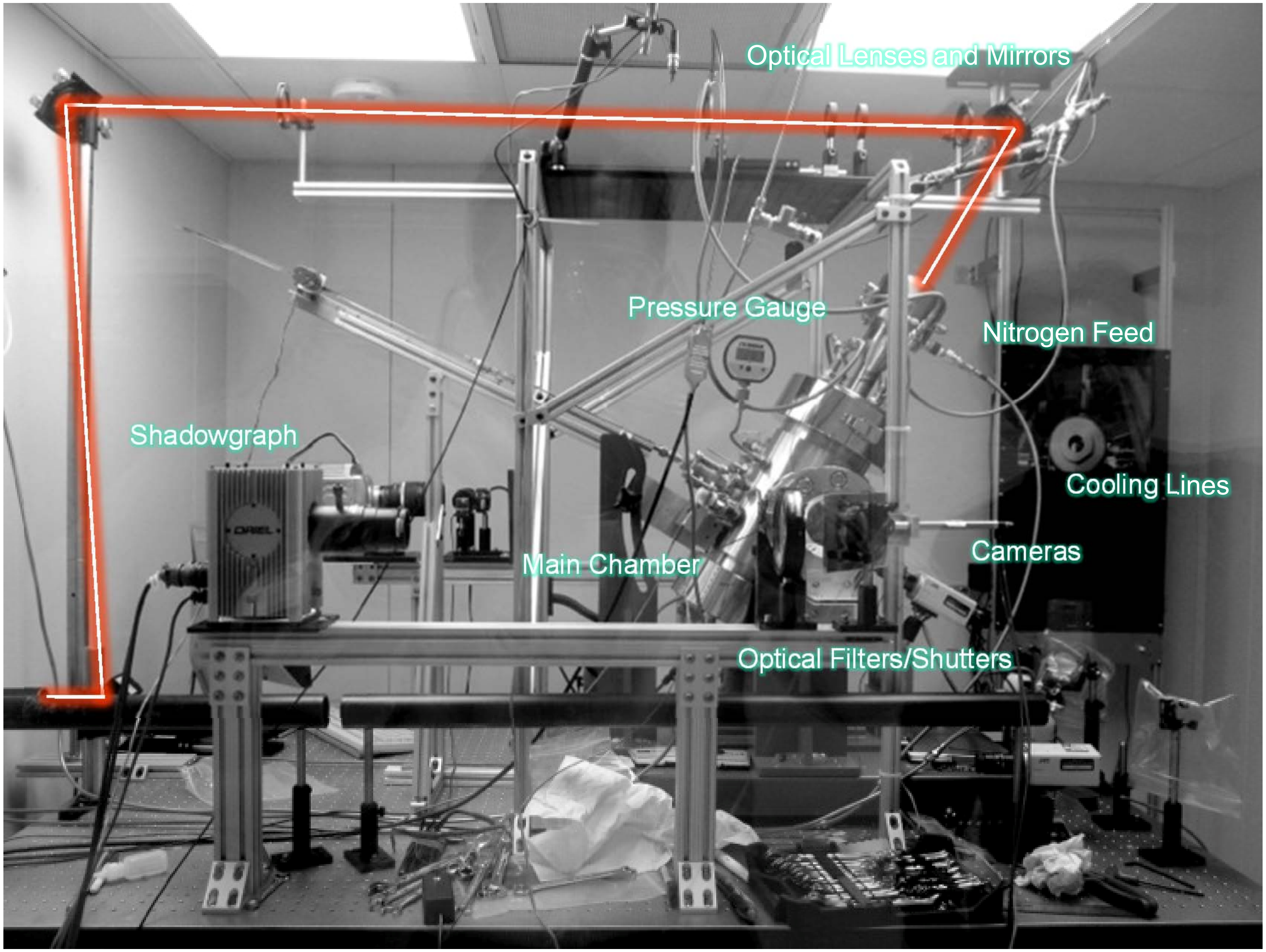
Successful pressure test up to 950 psi (higher pressure leads to better BNNT potentially)

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

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

All images credit: NASA/NIA

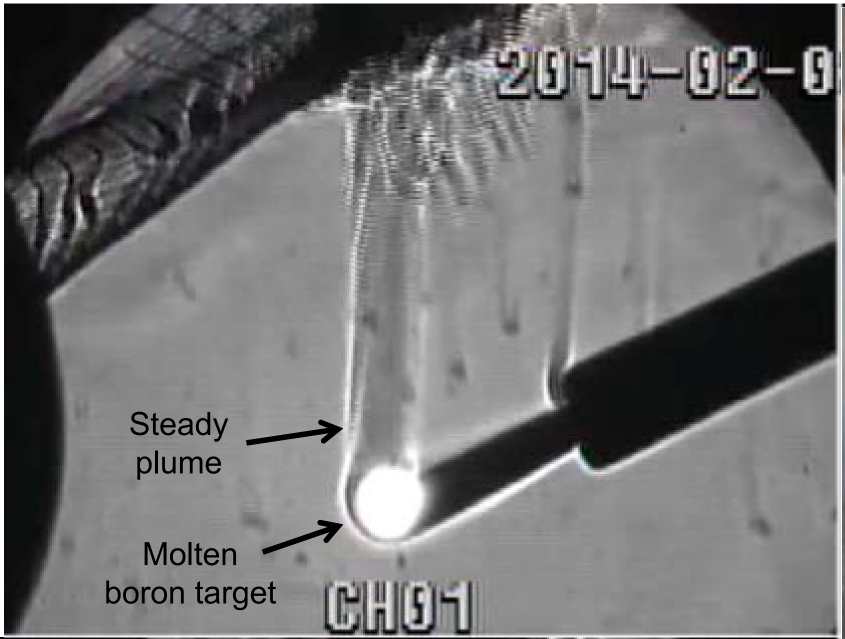
NIA BNNT Science Chamber

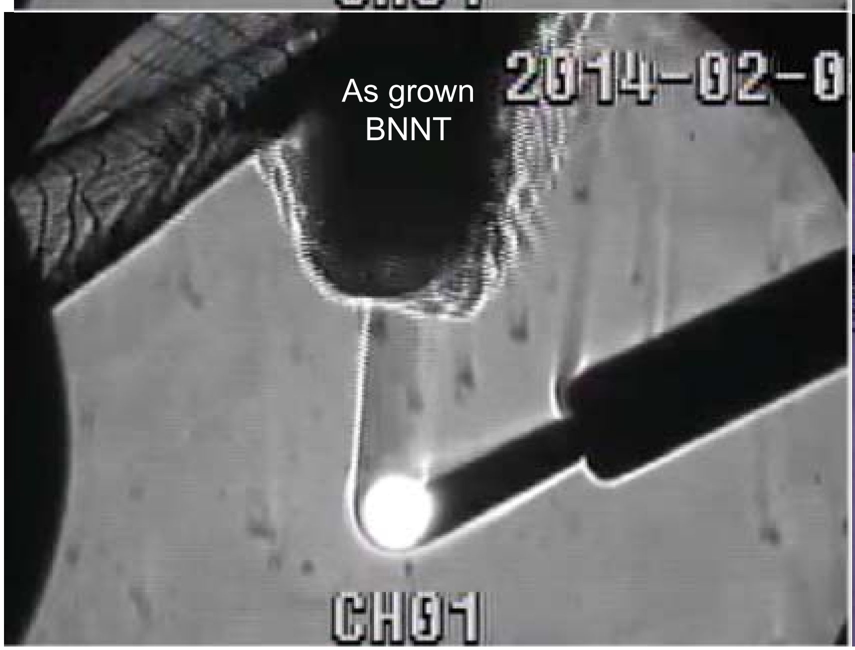


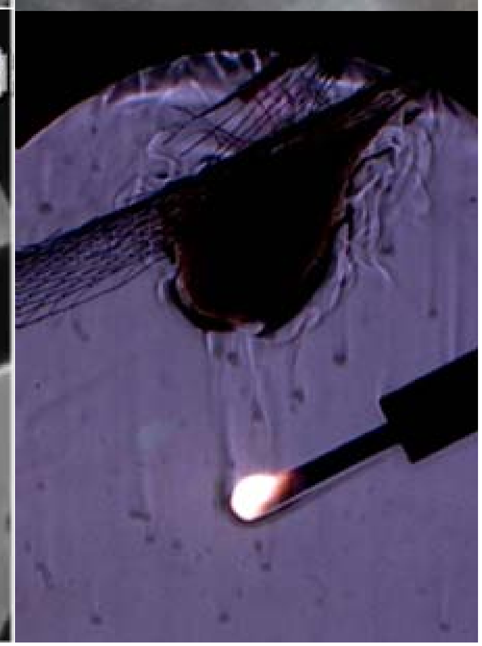
All images credit: NASA/NIA

NIA Science Rig HTP BNNT Run (Snapshots)

All images credit: NASA/NIA



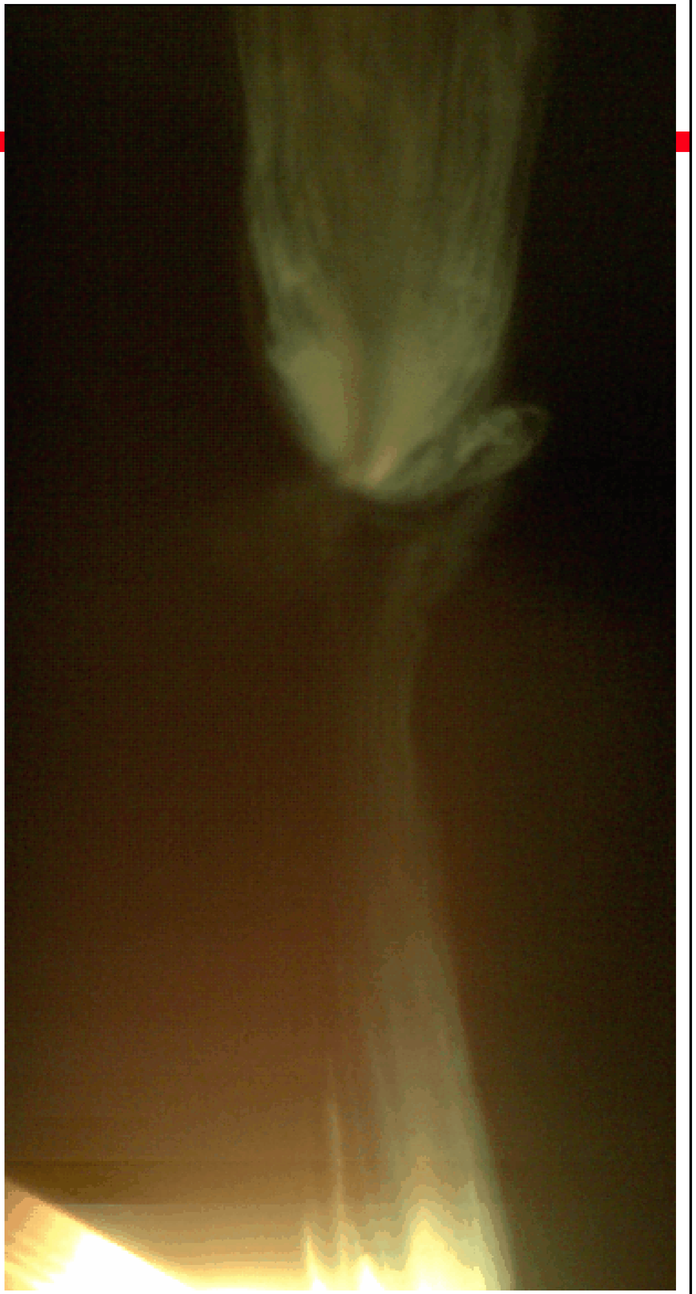




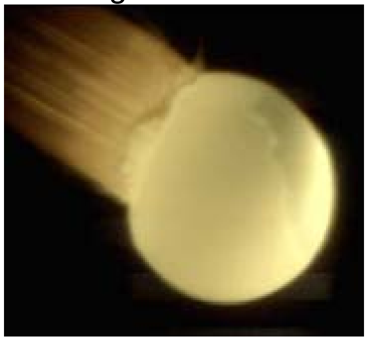
Proc. SPIE **9060** 906006 (2014)

In-situ Optical Diagnostics

- Understand chemistry and flow physics of nanotube generation
- 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:
  - High speed imaging; high speed (1 kHz) optical pyrometer being developed to study melt-ball dynamics
- Off-surface, gas phase measurement:
  - High-speed, high-resolution imaging
    - Shadowgraph and visible emission
  - Species sensitive imaging (BN PLIF)
  - Temperature measurements (CARS)

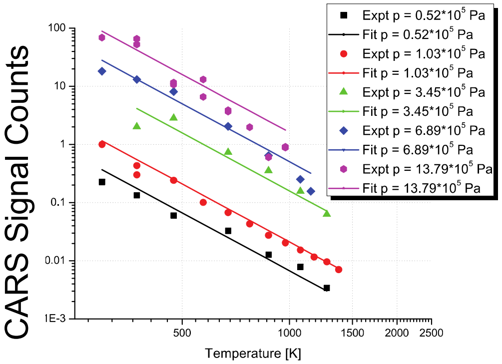


All images credit: NASA/NIA



High Speed Camera

Shadowgraph

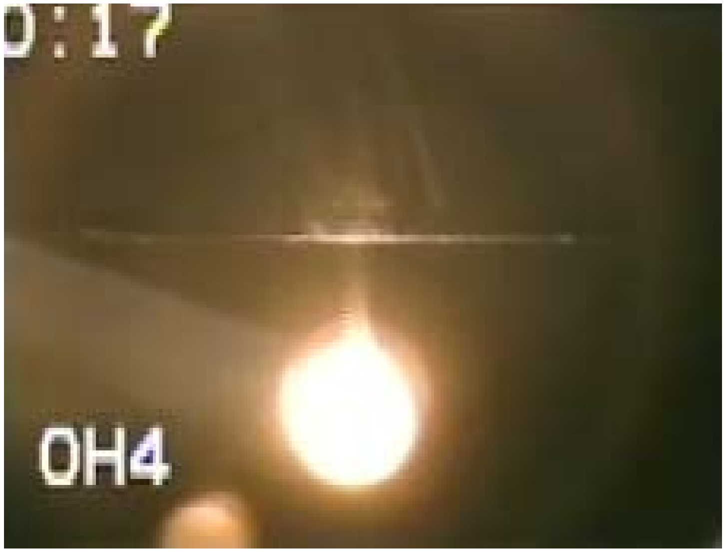


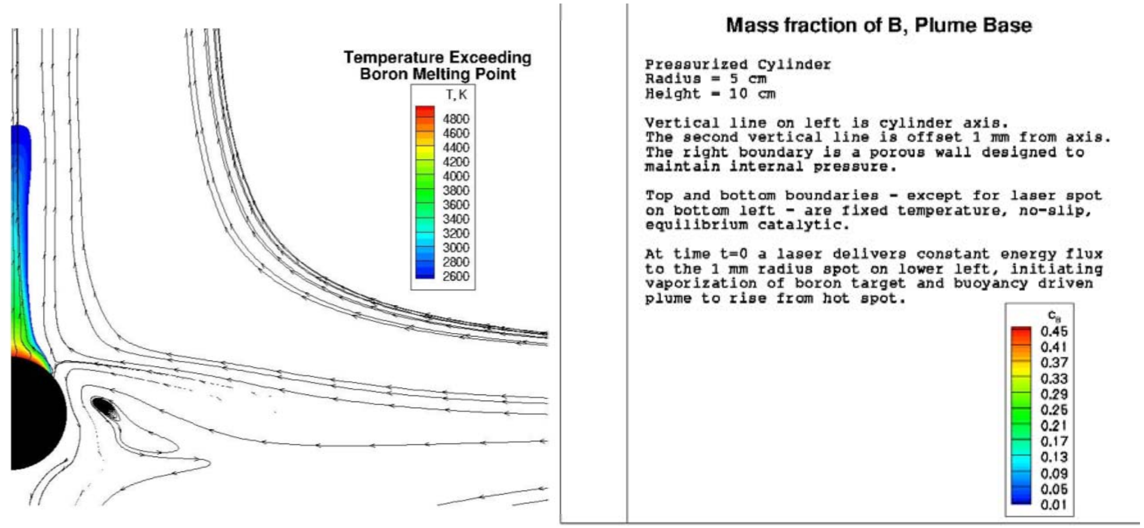
CARS Intensity Measurement

Jennifer Inman, Paul Danehy, Steve Jones, Joe Lee (NASA LaRC), Andrew Cutler (GWU)

AIAA SciTech2014-1098 (2014)
Proc. SPIE **9060** 906006 (2014)

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

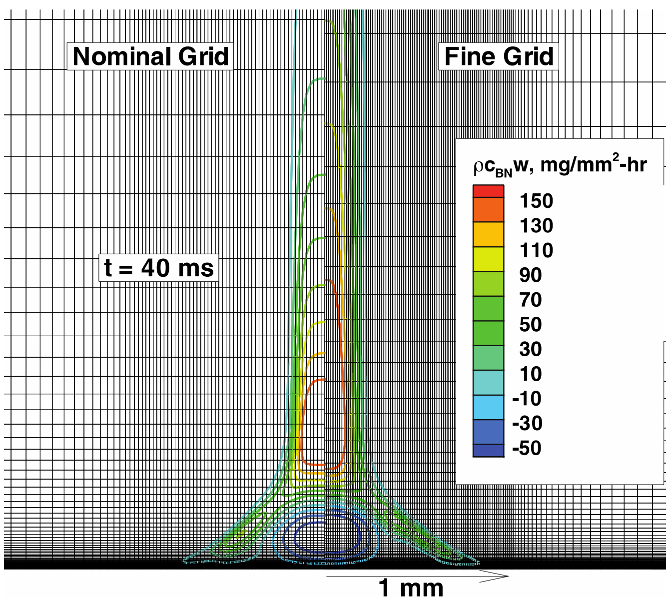
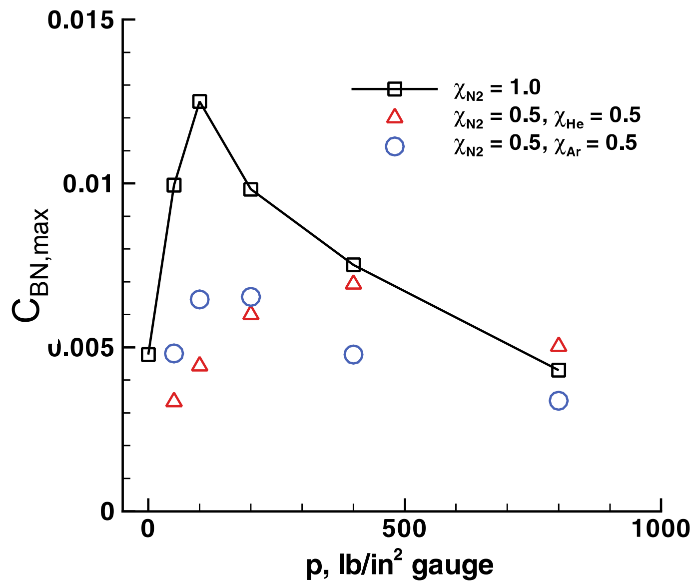


Fig. 5 Contour lines of BN flow rates in the plume.



a) Total chamber pressure

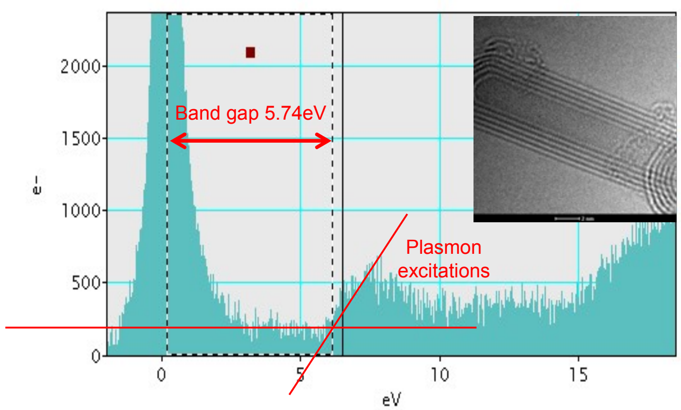
All images credit: NASA

Proc. SPIE **9060** 906006 (2014)

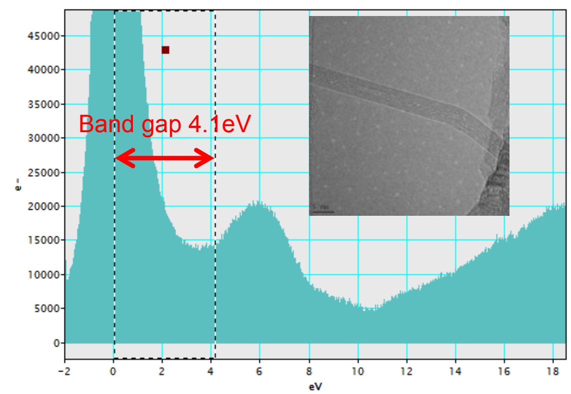
J. Thermophysics and Heat Transfer **27** 369 (2013)

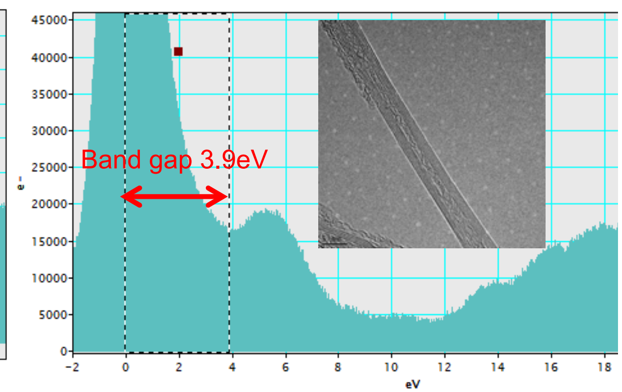
Low Energy EELS Band Gap Measurement (modified BNNT)

Bandgap measurement of BNNT
(Low-loss region)

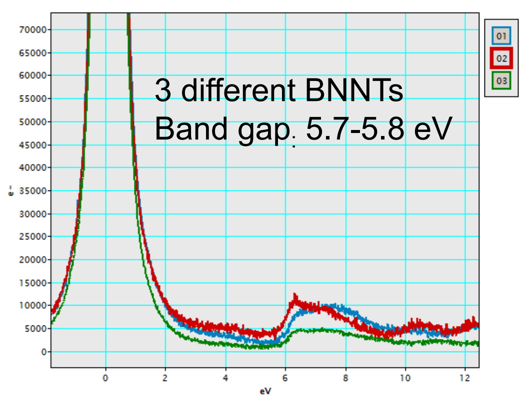


Bandgap measurement of C_{60}/BNNT
(Low-loss region)

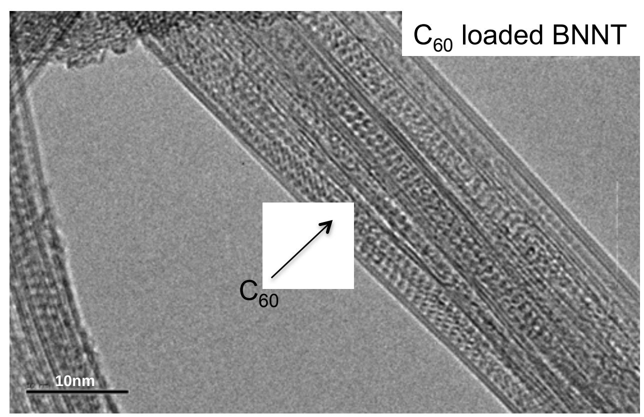


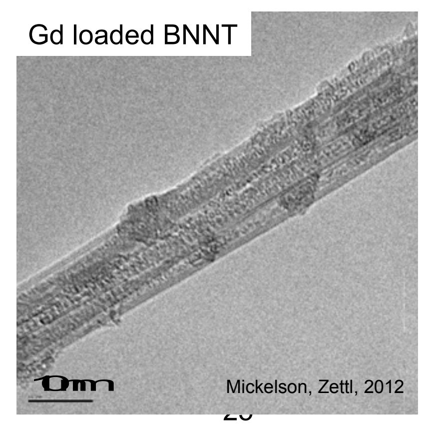


Superimposed Low Loss EEL spectra of multi walled Boron nanotubes shown in previous pages



Endo-Doped BNNNT (C_{60}/BNNT, Gd/GNNT) UC Berkeley



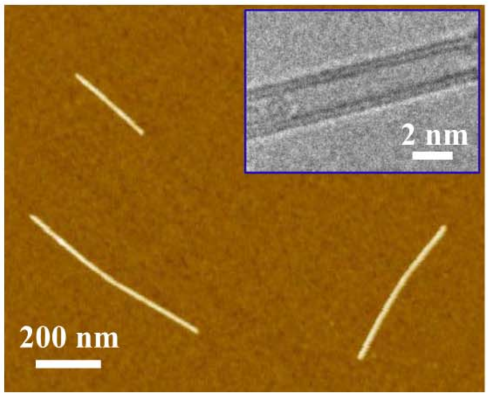


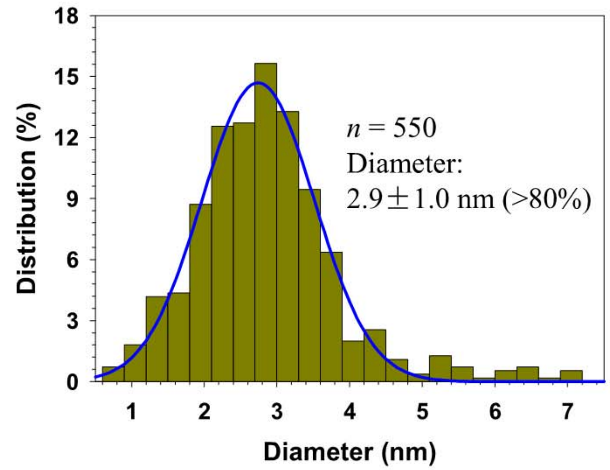
Credit: UC Berkeley; Zettl

All images credit: NASA

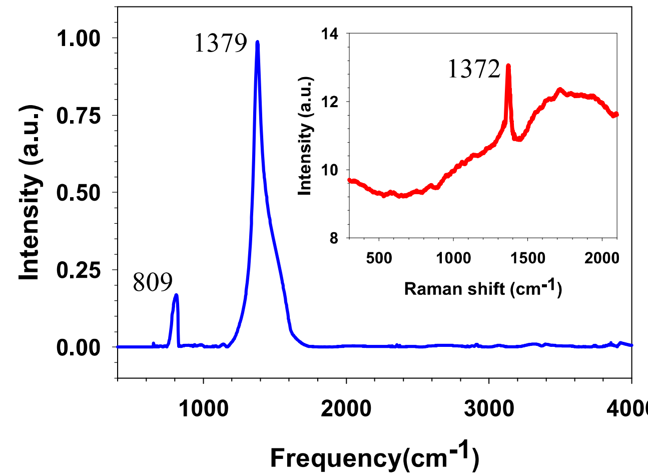
In-situ Single Nanotube Pull-Out Test inside of an SEM

AFM

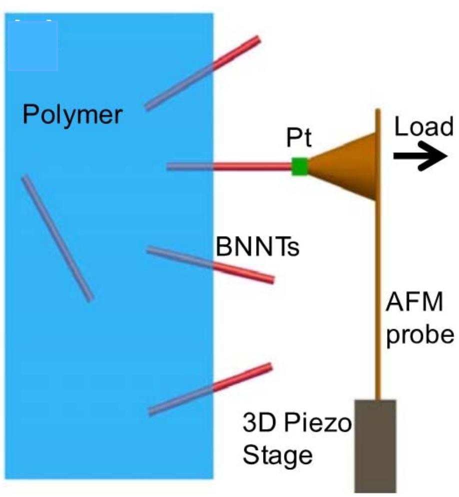


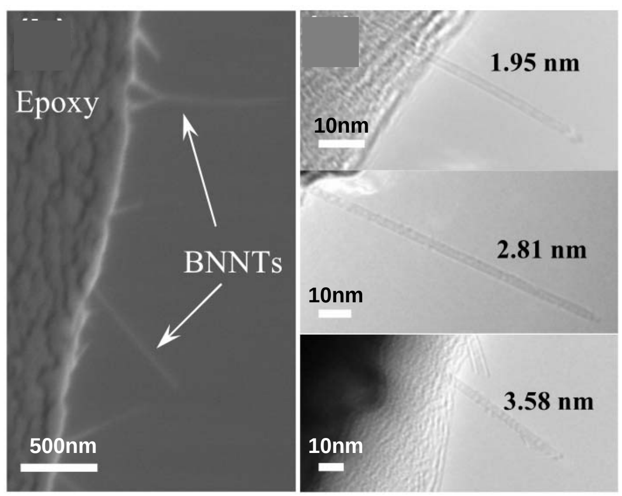


FTIR and Raman

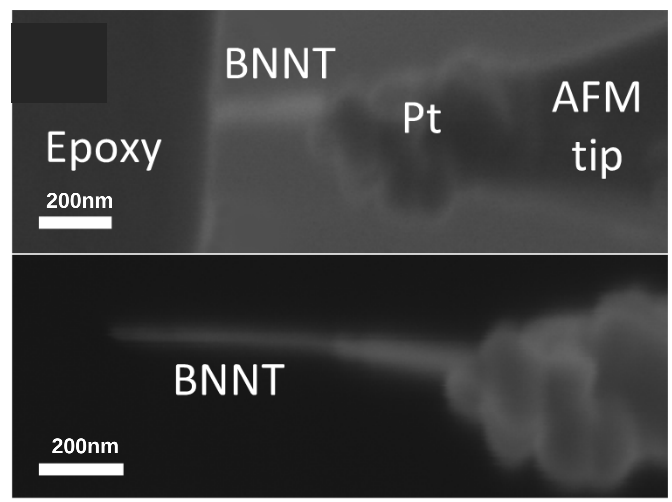


SEM





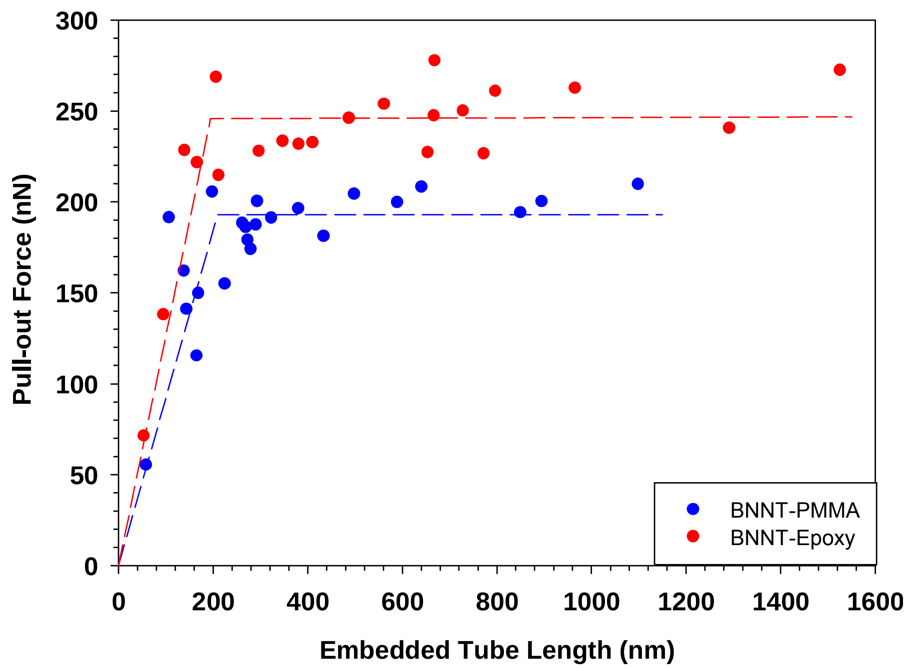
SEM

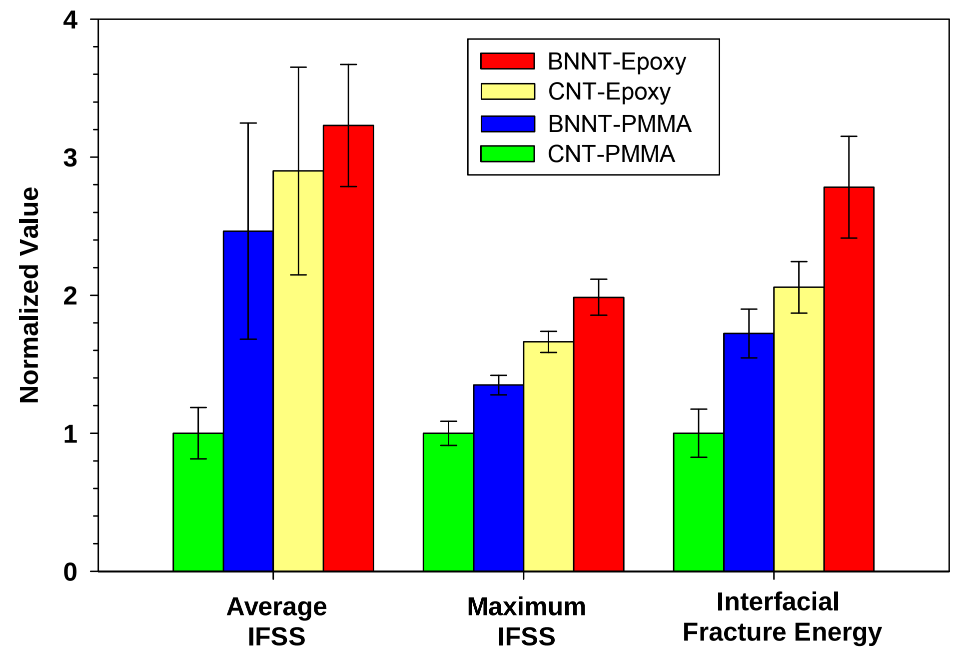


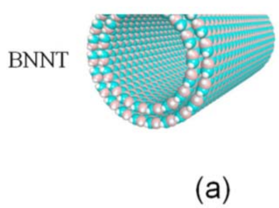
Credit: Prof Ke (SUNY Binghamton)

Small **9** 3345 (2013), Carbon **82** 214 (2015), *APL* **107** 253105 (2015)

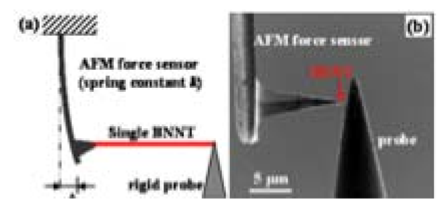
Interfacial Strength: *In-situ* Single Nanotube Pull-Out Test







BNNT Tensile Test Results

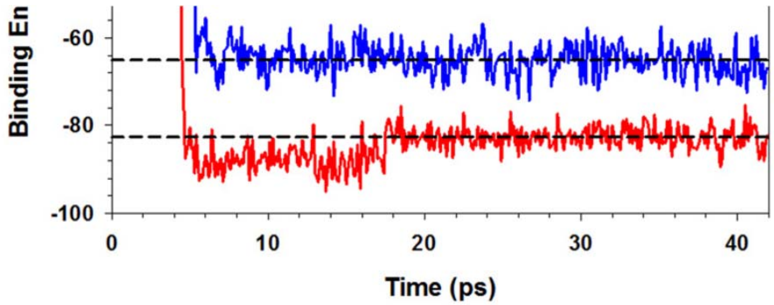


Diameter	Elastic modulus (GPa)	Breaking Strength (GPa)
D = 2.5 nm	760-960	14-38

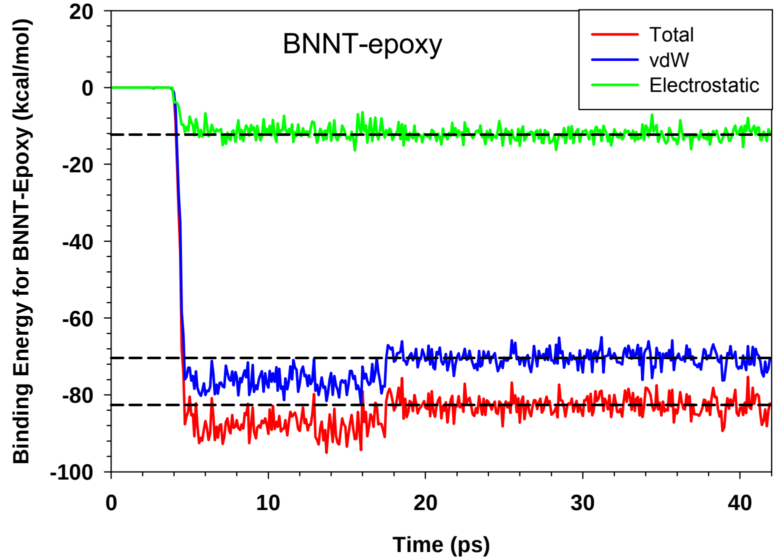
Small **9** 3345 (2013), Carbon **82** 214 (2015), *APL* **107** 253105 (2015)

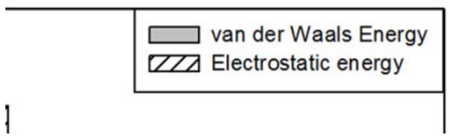
Credit: Prof Ke (SUNY Binghamton)

Interfacial Strength: *In-situ* Single Nanotube Pull-Out Test



(b)



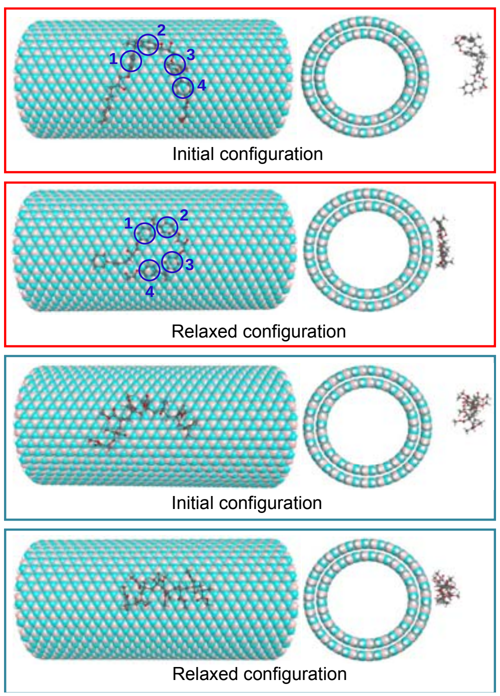


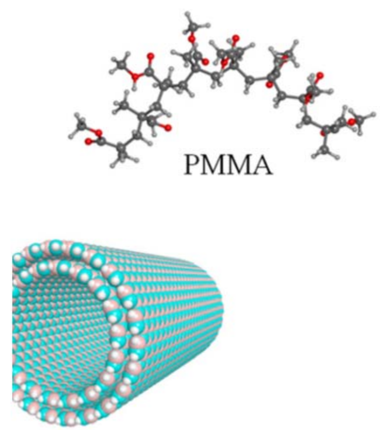
BNNT/Epoxy

BNNT/Epoxy

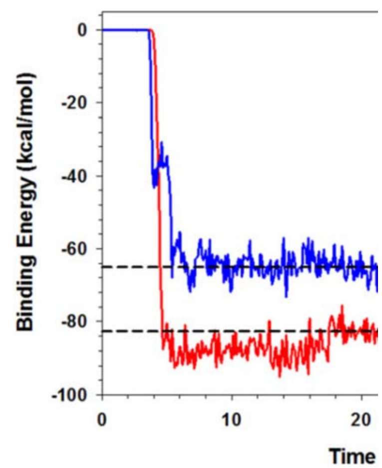
BNNT/PMMA

BNNT/PMMA





(a)

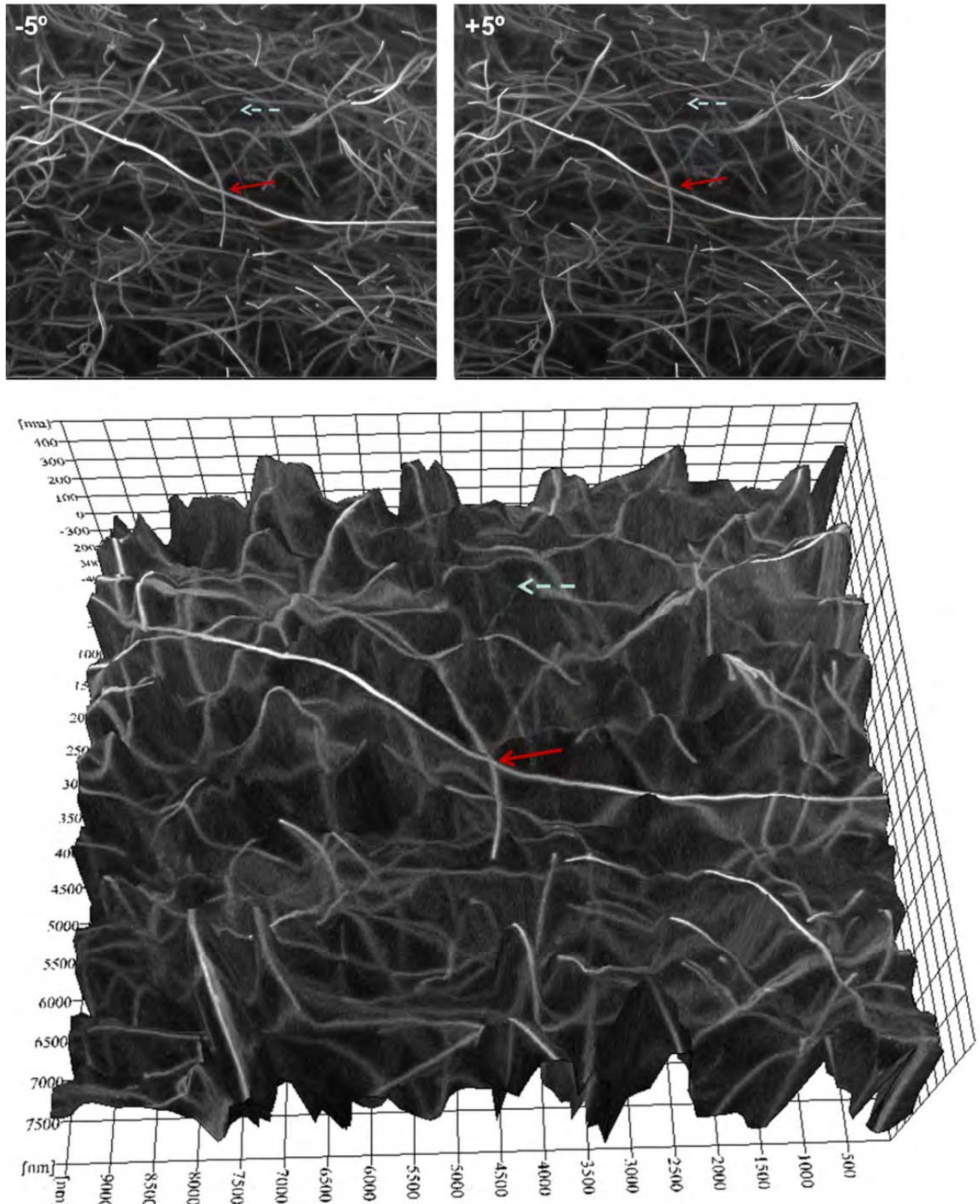


(b

Credit: Prof Ke (SUNY Binghamton)

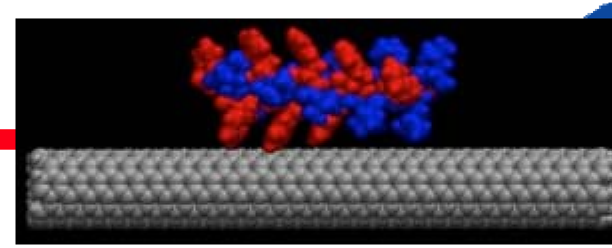
Small **9** 3345 (2013), Carbon **82** 214 (2015), *APL* **107** 253105 (2015)

Dispersion



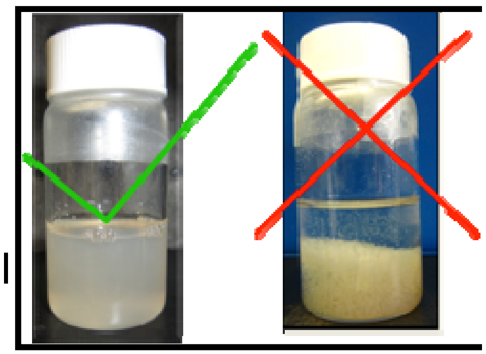
Credit: Zhao, Park et al, *Nanotechnology* **36** 085703 (2015)

How to disperse Nanotubes?



1) Kinetic Approach

High shear (stirring, homogenization, speedmix)
Sonication (cavitation force)
Melt mixing (twin screw mixer, extruder, calendering, capillary rheometer, fiber spinning)
In-situ polymerization
In-situ polymerization under simultaneous sonication & high shear (*Chem. Phys. Lett.* 364, 303 (2002))



2) Thermodynamic Approach (Minimizing free energy of mixing)

Covalent bonding

Acid etching
Stirring, reflux, and soxhlet extraction with H_2SO_4, HNO_3, and HCl
Functionalization
Fluorination, reflux with amine, electrochemical (diazonium compound)

Non-covalent bonding

Amphiphilic (surfactant), hydrophobic interaction: Water soluble polymers
Wrapping: PmPV, Polyvinyl pyrrolidone, Polystyrene sulfonate, PPE
Charge Transfer (Donor-acceptor) (*Chem. Phys. Lett.* 391, 207 (2004))
Dispersion Interaction (London force, Permittivity matching)
Solvent or Co-solvent selection (Hansen solubility parameter, surface energy)
Similar size/structure to SWCNT
Zwitterion
Complex formation
Nonspecific interaction

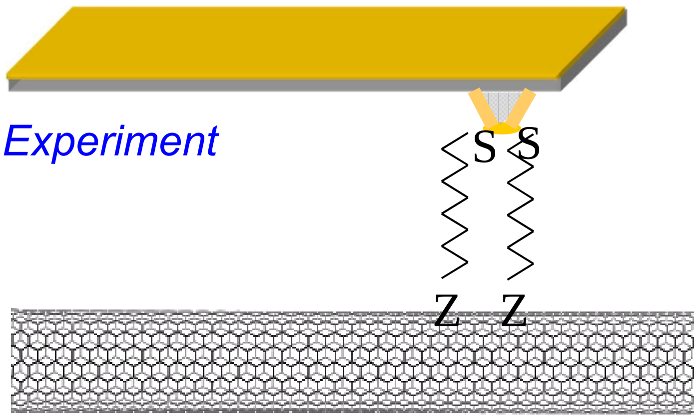
$$\Delta G_{mix} = \Delta H_{mix} - T^{*}\Delta S_{mix}$$

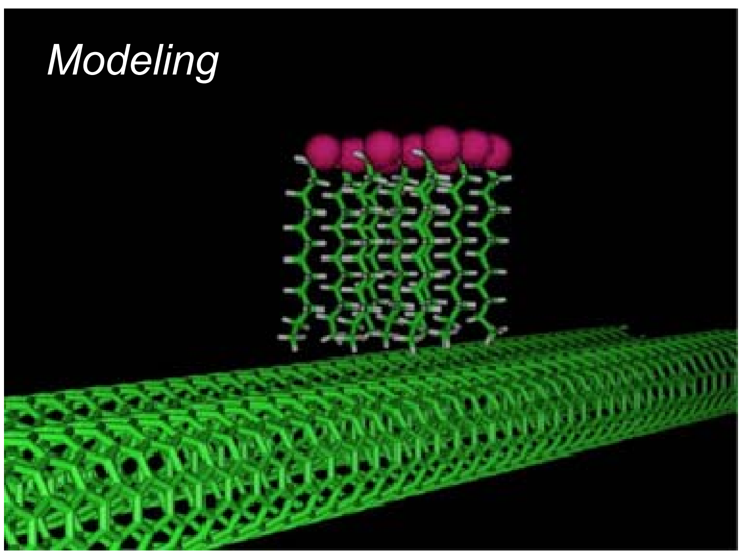
Encyclopedia of Nanoscience and Nanotechnology, 2nd Ed, Chapter: Polymer Nanocomposites and Functionalities, American Scientific Publishers, vol 21 171-218 (2011) (www.aspbs.com/enn)

Adhesion Between Nanotubes & Various Functional Groups

- Using Functionalized AFM tips interaction forces can be directly probed.

Experiment





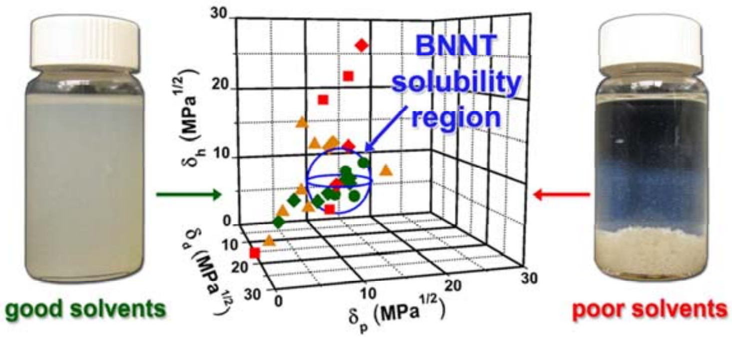
Alkyl-thiol Endgroup	Experiment Force/Molecule (pN)	Modeling (pN)
–OH	9.6 ± 2	
–perfluoro	8.7 ± 3	
–SH	9.2 ± 3	
$–CH=CH_2$	8.1 ± 2	
$–CH_3$	7.6 ± 2	1.92
–COOH	12.2 ± 3	
$–NH_2$	23.4 ± 4	2.98
Aryl-thiol Endgroup		
4-methylbenzene	18.9 ± 5.7	
4-nitrobenzene	21.8 ± 5.3	
4-aminebenzene	22.6 ± 4.7	
4-bromobenzene	26.9 ± 3.6	
4-hydroxybenzene	32.0 ± 8.4	
4-fluorobenzene	39.5 ± 8.8	
4-methoxybenzene	41.5 ± 10.9	
H-benzene	46.8 ± 11.8	
4-Nitrilebenzene	56.9 ±15.5	

Proceedings of 31st Adhesion Society Meeting, p39, Ed. by G. Anderson, Austin TX, Feb (2008)

Thermodynamic Approach: Minimizing Free Energy of Mixing

Gibbs Free Energy of Mixing

$$\Delta G_{mix} = \Delta H_{mix} - T^*\Delta S_{mix}$$



If ΔG_{mix} is negative, spontaneous mixing happens to form a homogeneous solution

Hansen Solubility Parameters (δ_d, δ_p, δ_h): "like dissolves like"

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$$

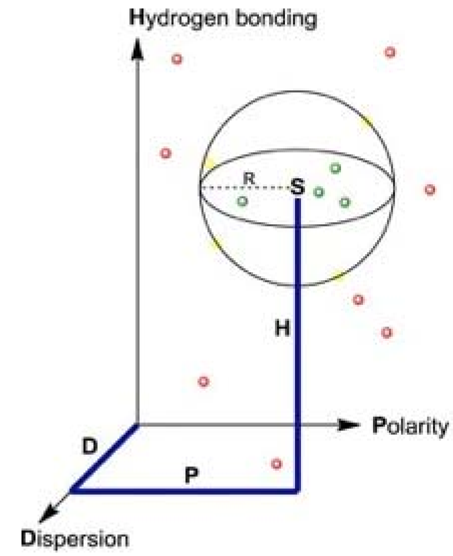
δ_t^2: Hildebrand parameter
δ_d: dispersion component
δ_p: polar
δ_h: hydrogen bond

Match Hansen Solubility Parameters (HSPs) of the solvent to the solute of interest

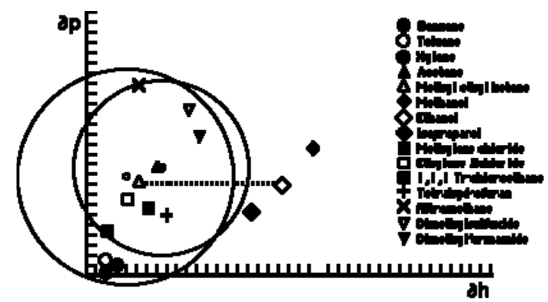
C.M. Hansen "Hansen Solubility Parameters: A User's Handbook" Taylor & Francis, 2007

Dispersion State of Single Solvents for BNNT

Solvent	δ_d, MPa$^{1/2}$	δ_p, MPa$^{1/2}$	δ_h, MPa$^{1/2}$	δ_t, MPa$^{1/2}$	Structure	Dispersion state (stirring only)	Dispersion state (stirring + 30 mins sonication)	Dispersion state (after 1 week settling time)	R_a[e]	RED[f]
N,N'-dimethylacetamide (DMAc)	16.8	11.5	10.2	22.5	$CH_3C(O)N(CH_3)_2$	sediment	dispersed	dispersed	1.44	0.34
N,N'-dimethylformamide (DMF)	17.4	13.7	11.3	24.9	$HC(O)N(CH_3)_2$	swollen	dispersed/swollen	dispersed/swollen	3.97	0.92
acetone	15.5	10.4	7.0	19.9	CH_3COCH_3	sediment	dispersed/swollen	dispersed/swollen	3.29	0.77
methanol	15.1	12.3	22.3	29.6	CH_3OH	swollen	dispersed/swollen[b]	swollen	13.82	3.21
isopropyl alcohol (IPA)	15.8	6.1	16.4	23.6	$(CH_3)_2CHOH$	swollen	dispersed/swollen[b]	sediment	8.94	2.08
tetrahydrofuran (THF)	16.8	5.7	8.0	19.4	$(CH_2)_4O$, cyclo	swollen	dispersed/swollen	swollen	5.10	1.19
N-methyl-2-pyrrolidone (NMP)	18.0	12.3	7.2	23.0	$HN((CH_2)_3CO)$, cyclo	swollen	dispersed/swollen[a]	dispersed/swollen	3.40	0.79
chloroform	17.8	3.1	5.7	19.0	$CHCl_3$	sediment	swollen[a]	swollen	8.52	1.98
dichloromethane	18.2	6.3	6.1	20.0	CH_2Cl_2	swollen	swollen[a]	swollen	5.97	1.39
acetic acid	14.5	8.0	13.5	21.4	CH_3COOH	swollen[*]	swollen[a,b,d]	swollen	6.98	1.62
dimethylsulfoxide (DMSO)	18.4	16.4	10.2	26.7	$(CH_3)_2SO$	swollen	swollen	swollen	6.65	1.55
toluene	18.0	1.4	2.0	18.2	$C_6H_5CH_3$, cyclo	sediment	swollen[a]	swollen	11.88	2.76
pyridine	19.0	8.8	5.9	21.8	C_5H_5N, cyclo	sediment	sediment[c]	sediment	5.71	1.33
ethanol	15.8	8.8	19.4	26.5	C_2H_5OH	swollen	sediment	sediment	10.76	2.50
hexane	15.3	0.0	0.0	15.3	$CH_3(CH_2)_4CH_3$	sediment[a]	sediment	sediment	14.30	3.33
water	15.6	16.0	42.3	47.8	H_2O	n/a[d]	n/a[d]	n/a[d]	33.80	7.86



An example of 3D Hansen space.[1]



Choosing solvent blends for a solute.[2]

Nanoscale 8 4348 (2016)

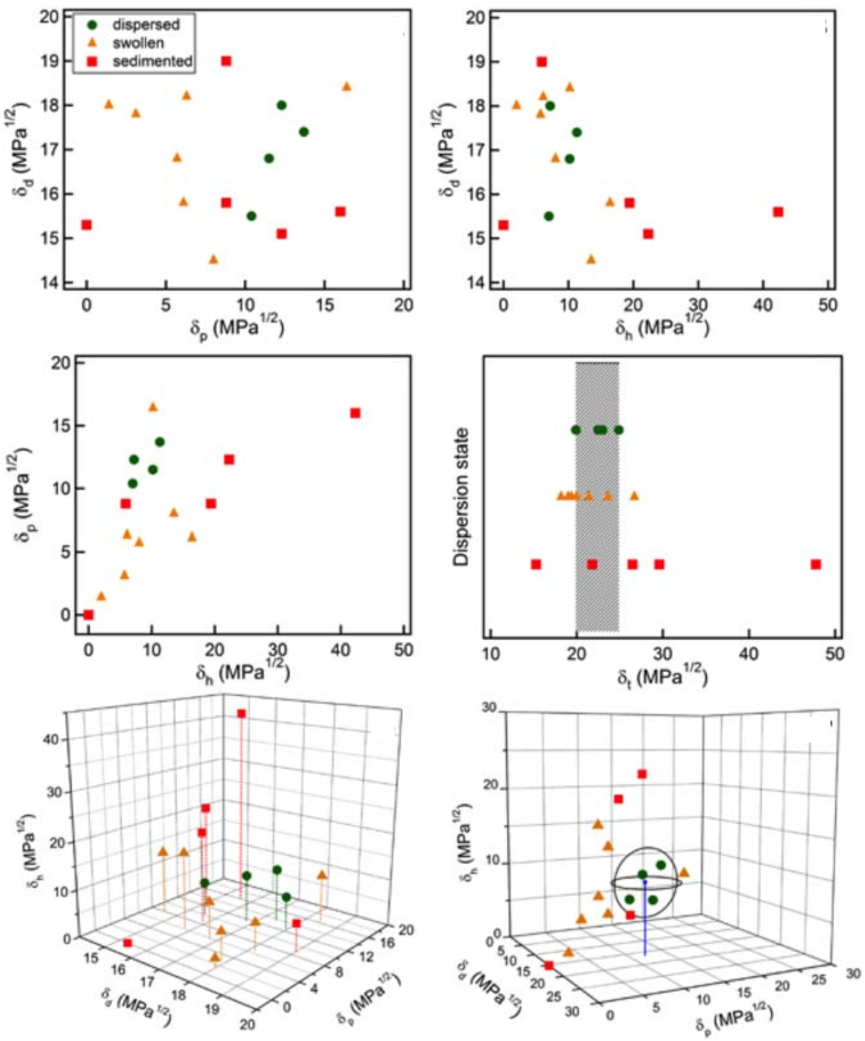
1. http://confidentsolventselection.com/about/solubility-parameters.html
2. http://cool.conservation-us.org/coolaic/sg/bpg/annual/v03/bp03-04.html

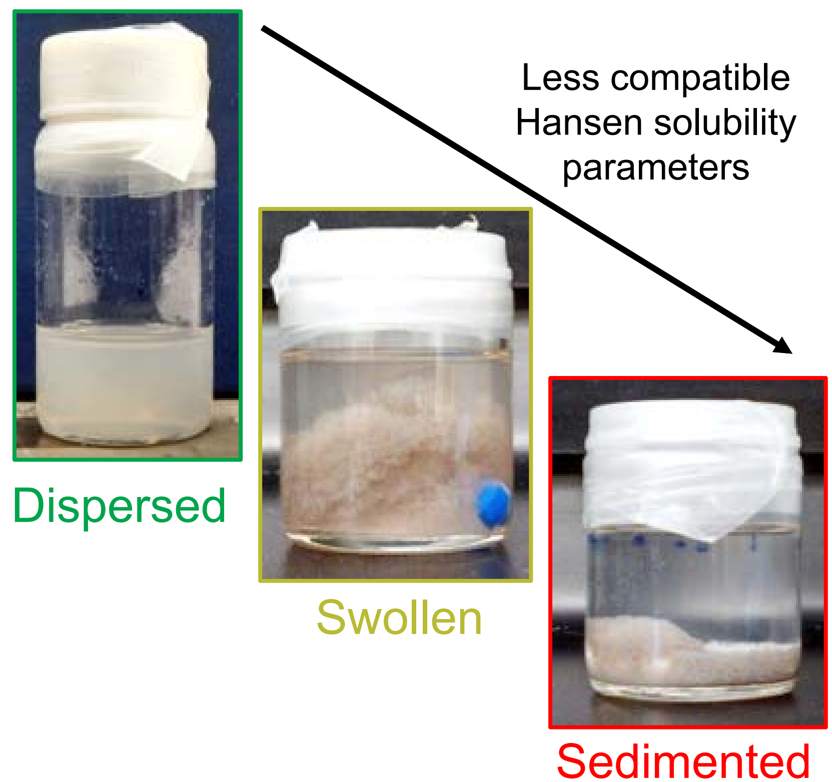
2&3D Plots of HSPs of Single Solvents vs. Dispersion State

The dispersion state is characterized in one of three ways:

J. Colloid. Int. Sci. **286** 216 (2005)

1. Dispersed: maintains a uniform color without aggregation or precipitation
2. Swollen: aggregated nanotubes and phase separation are observed
3. Sedimented: large aggregations; material rapidly precipitates after agitation

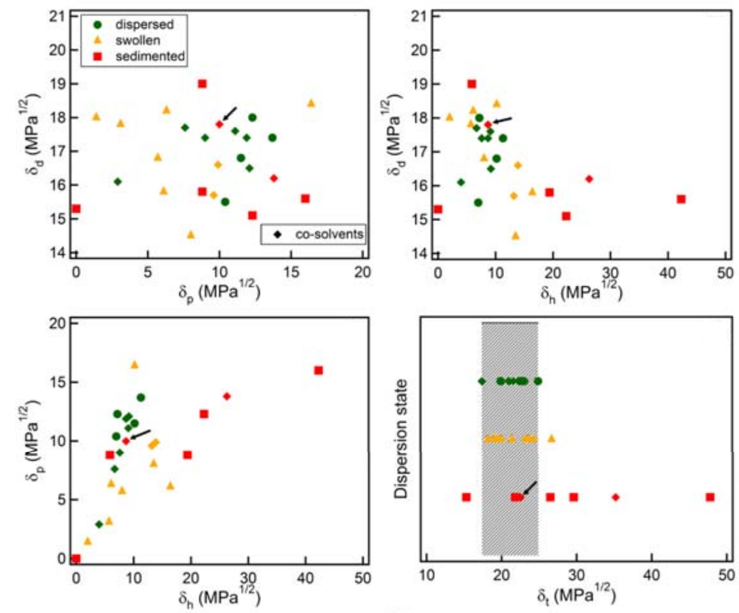


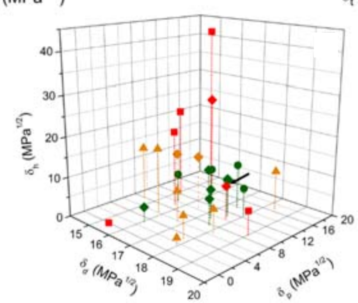


Nanoscale 8 4348 (2016)

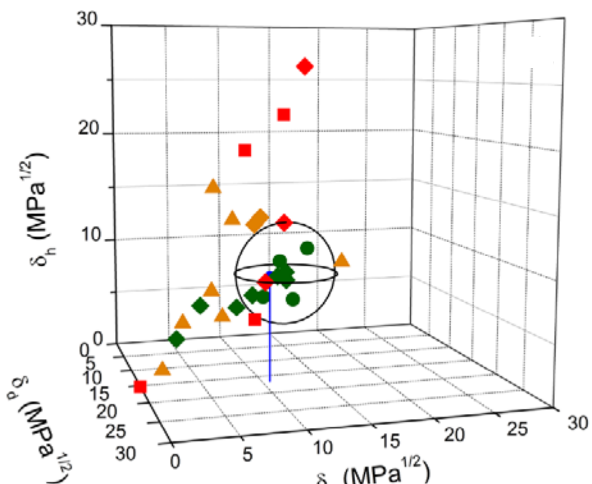
Dispersion: Dispersion State of Co-solvents (1:1) for BNNT

Co-solvent	δ_d, MPa$^{1/2}$	δ_p, MPa$^{1/2}$	δ_h, MPa$^{1/2}$	δ_t, MPa$^{1/2}$	Dispersion state (stirring only)	Dispersion state (stirring + 30 mins sonication)	R_a[c]	RED[d]
THF-NMP	17.4	9.0	7.6	21.0	swollen	dispersed/swollen[b]	2.51	0.58
DMF-acetone	16.5	12.1	9.2	22.4	swollen[a]	dispersed/swollen[b]	1.54	0.36
DMAc-NMP	17.4	11.9	8.7	22.8	swollen[a]	dispersed/swollen	1.72	0.40
DMSO-THF	17.6	11.1	9.1	23.1	swollen	dispersed/swollen[b]	1.65	0.38
DMF-toluene	17.7	7.6	6.7	21.6	swollen	dispersed	4.26	0.99
IPA-DMF	16.6	9.9	13.9	24.3	sediment	dispersed/swollen[b]	4.98	1.16
ethanol-acetone	15.7	9.6	13.2	23.2	swollen	dispersed/swollen[b]	4.87	1.13
DMF-DCM	17.8	10.0	8.7	22.5	swollen	dispersed/swollen[b]	2.14	0.50
THF-hexane	16.1	2.9	4.0	17.4	sediment	dispersed/swollen	9.37	2.18
DMAc-water	16.2	13.8	26.3	35.2	swollen	sediment	17.62	4.10

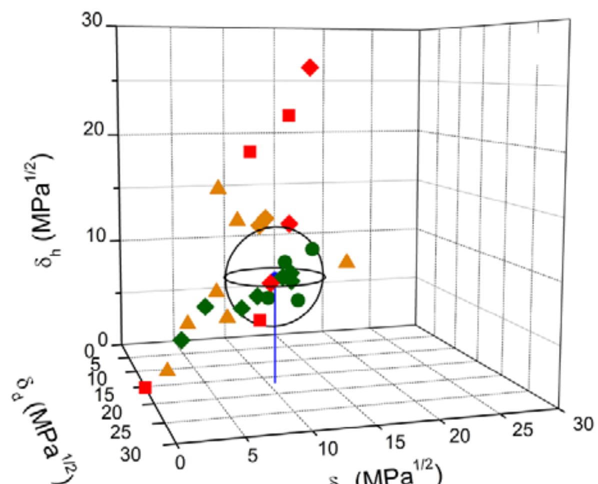




Single Solvent



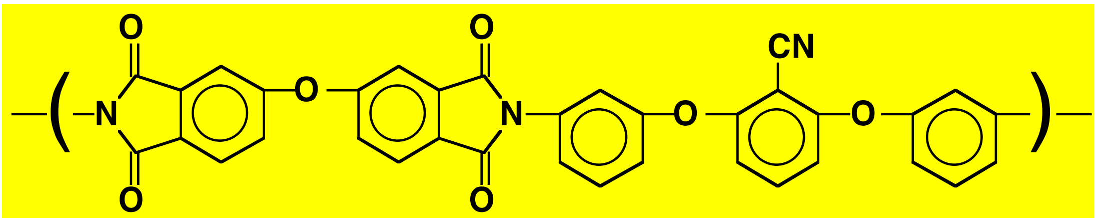
Co-solvent



BNNT HSP
δ_d, δ_p, δ_h = 16.8, 10.7, 9.0 MPa$^{1/2}$
δ_t = 21.8 MPa$^{1/2}$

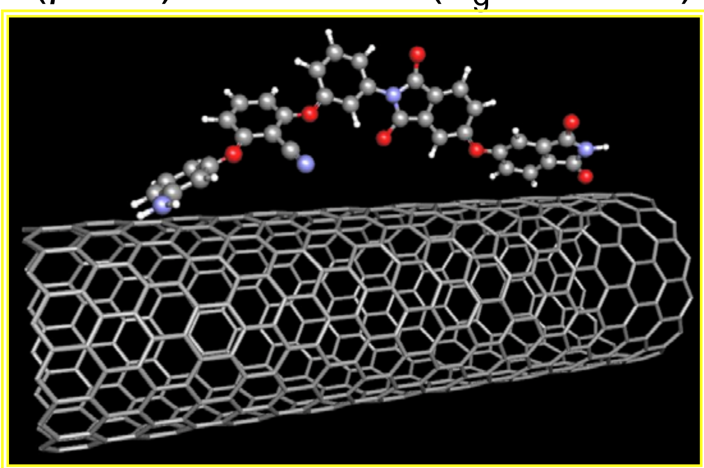
Building Blocks: SWCNT/Polymer Nanocomposites

Electroactive High Performance Polyimide

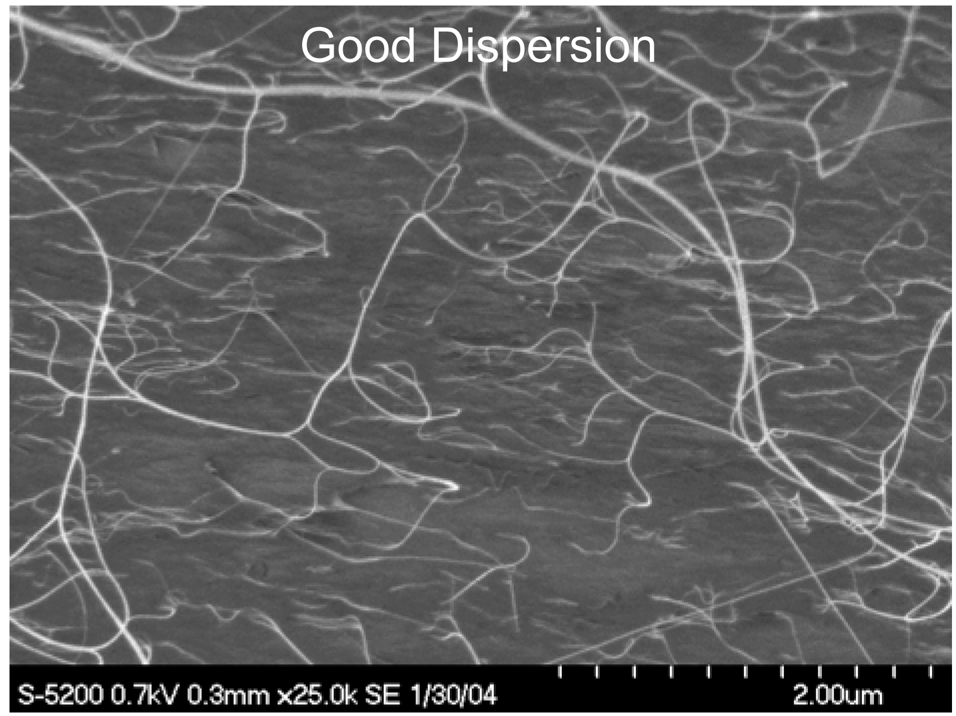


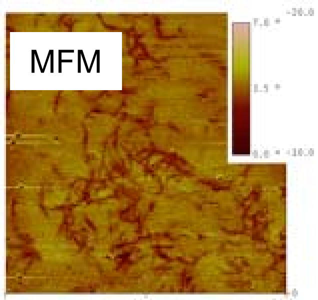
(β-CN)APB/ODPA (T_g = 220°C)

- Dispersion Interaction
- Donor-Acceptor interaction
- In-situ Polymerization under sonication and shear

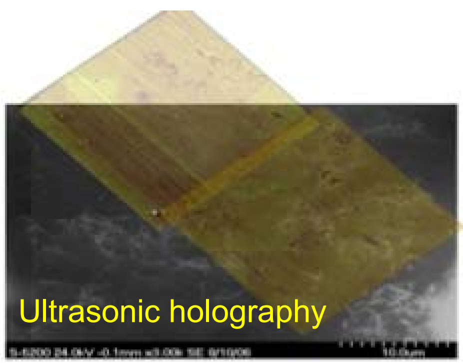


Polyimide + SWNT



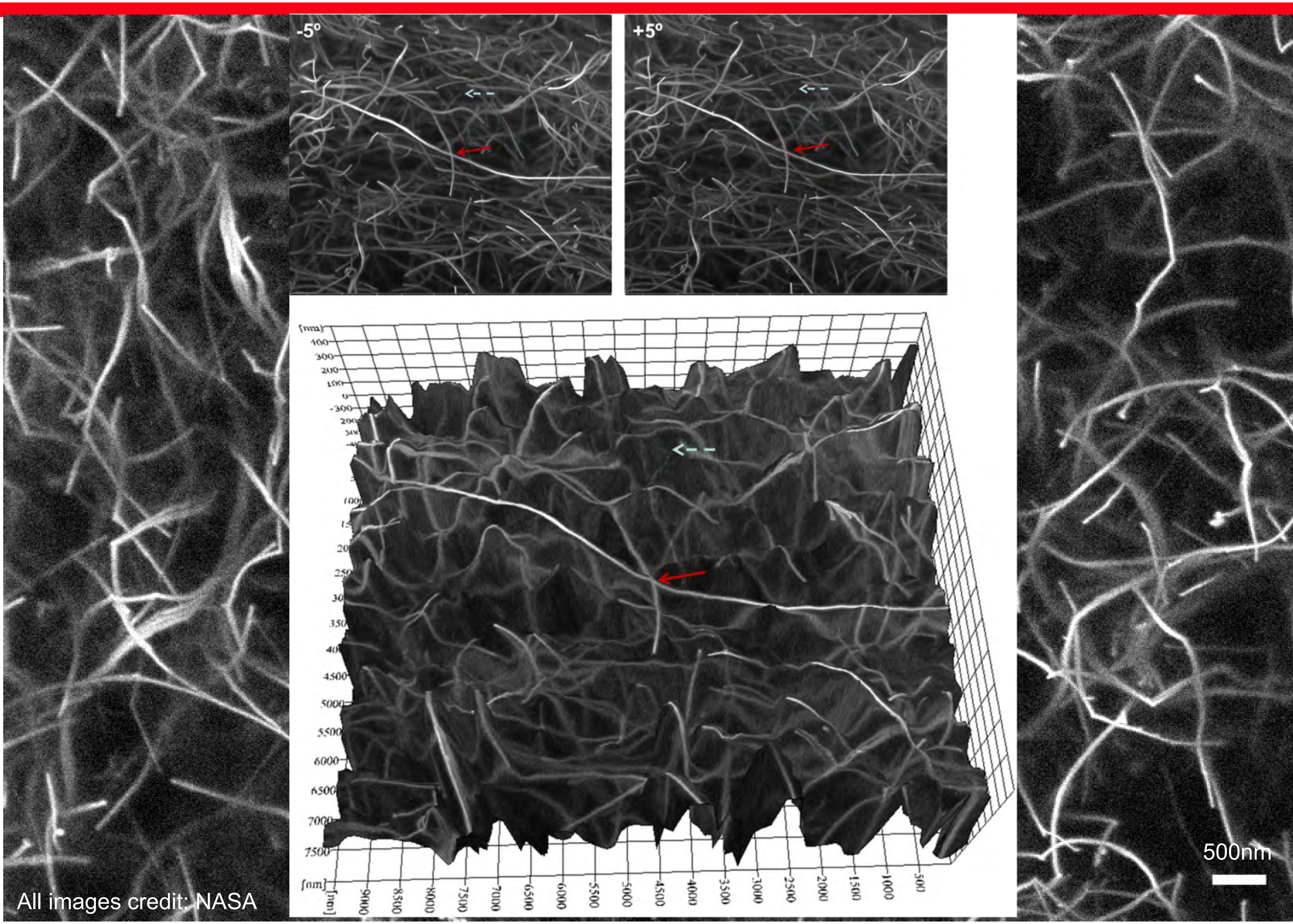


All images credit: NASA



Park et al, *Chem. Phys. Lett.,* 364 303 (2002)
Wise et al, *Chem. Phys. Lett.* 391 207 (2004)

HRSEM: Well Dispersed SWCNT in Polyimide (2D & 3D)



Hypersonic Materials Experiment Test System (HYMETS) Test & Analysis

Sample: BNNT Mat (as grown, nonwoven)

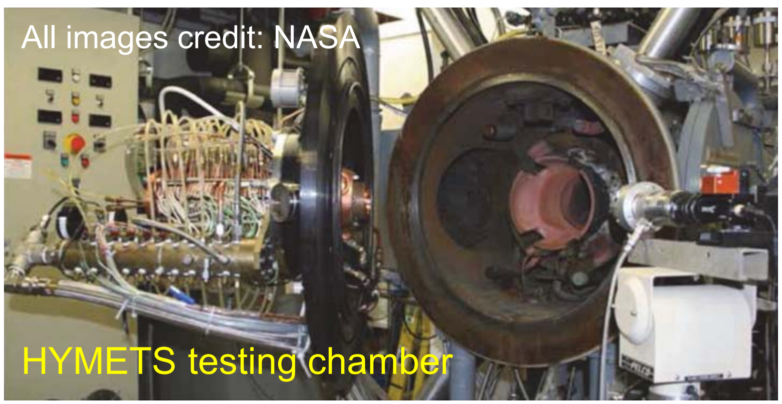
- Diameter: 26.1 mm
- Thickness: 2.1 mm
- Mass: 251.5 mg
- Density: 0.23 g/cm^3

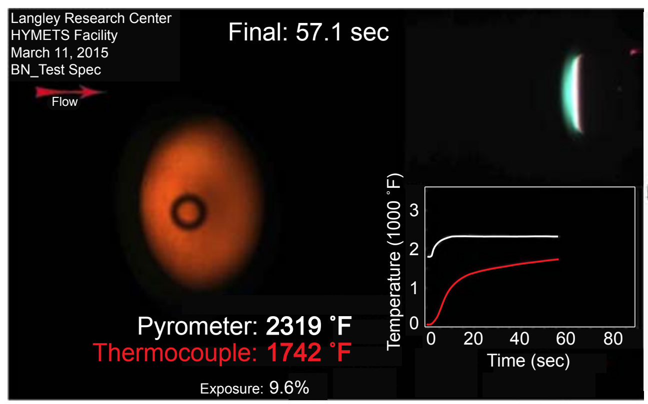
HYMETS TEST Info

- Heat flux: Set at 46.7 W/cm^2
- Duration: 1 min (57.1 sec)
- Temperature: 2343F (1284˚C)
- Atmosphere: Air (with 5% Ar)
- Cooled under vacuum down to 156F

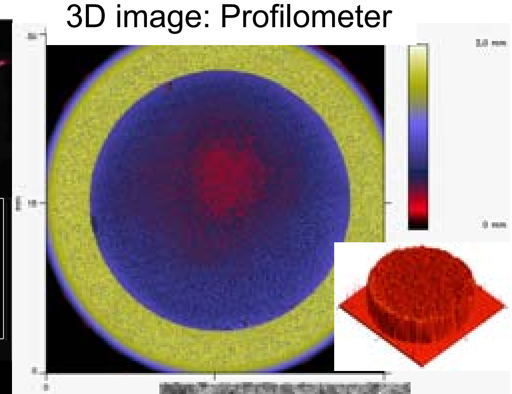
Preliminary Test Result Summary

- The BNNT mat sample **survived** through the hypersonic heat flux (46.7W/cm^2) for 60 sec run with a minimal loss.
- The front (purplish) side formed a thin boron oxide layer after the heat exposure, but the back side remained intact BNNT without noticeable damage, which was confirmed by FTIR spectra and energy dispersive X-ray (EDX) analysis under an environmental scanning electron microscope (ESEM).
- The mechanical integrity of the BNNT mat was preserved even after the hypersonic thermal flux exposure.

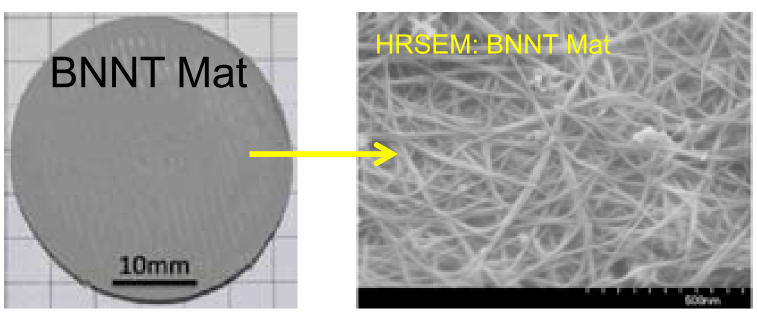




3D image: Profilometer

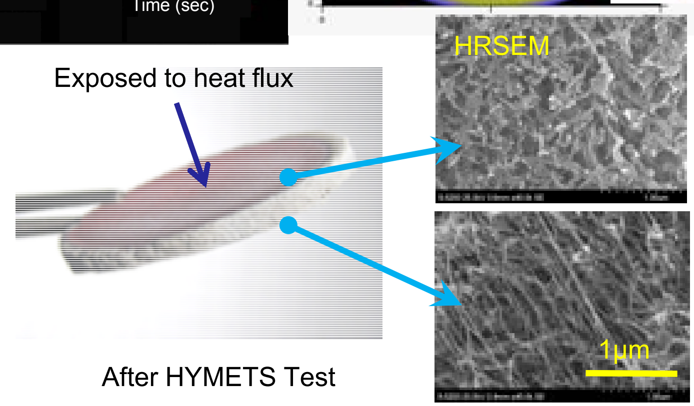


Before HYMETS Test



Exposed side

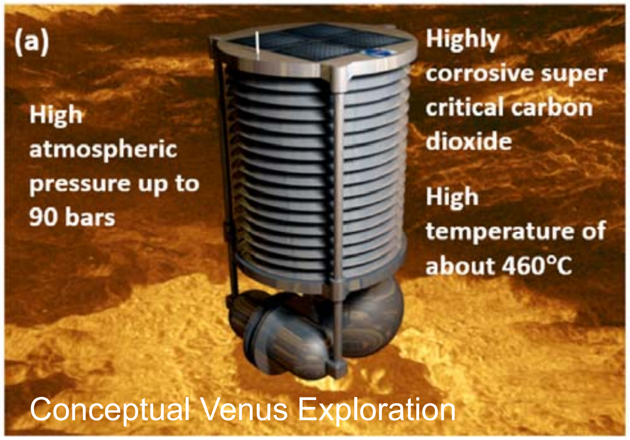
After HYMETS Test

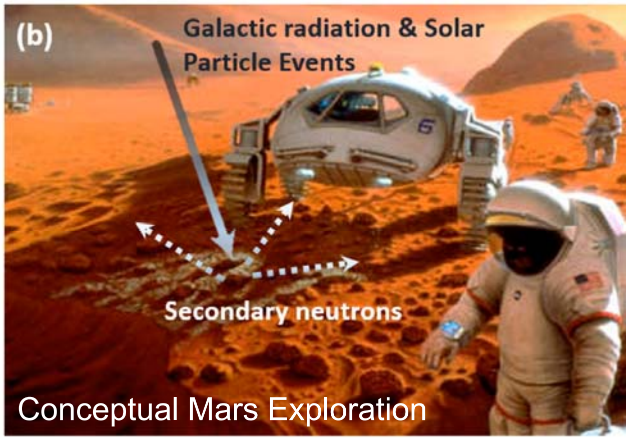


After HYMETS Test

Multifunctional BNNT Polymer Composites

- Electroactive Properties
- Radiation Shielding Properties





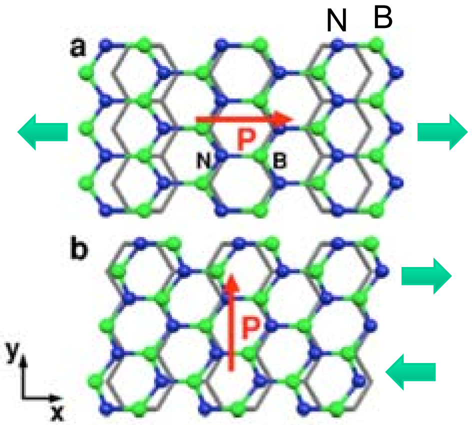
All images credit: NASA

ACS Nano **9** 11942 (2015)

Piezoelectric Properties of BNNTs

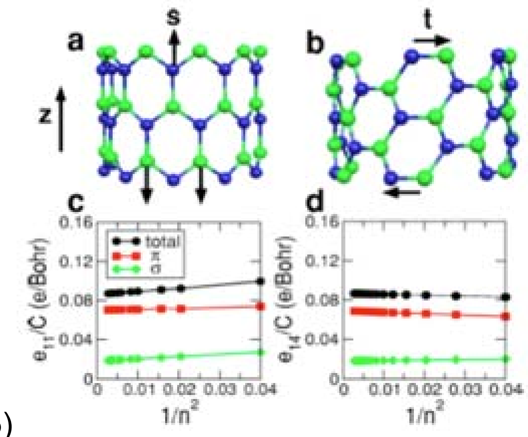
Piezoelectric Effect

h-BN plane



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

BNNT



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

where e_{ijk} - piezoelectric tensor with symmetry:

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

The MD model has to reproduce this behavior!

Molecular Dynamics

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

$$U_r = \sum_{i,j}\left[V_R(r_{ij}) - B_{ij}V_A(r_{ij})\right]; \quad \vec{F}_i = -\partial U_r / \partial \vec{r}_i$$

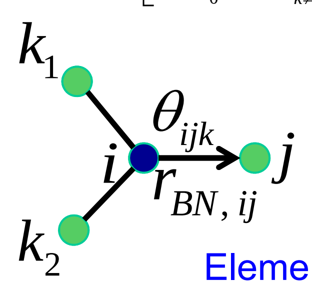
- Evolve atoms according to Newton's law: $\vec{a}_i = \vec{F}_i / m_i$

Piezoelectric MD

- Introduce dipole term to the interatomic potential (energy)

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

$$\vec{p}_{BN,ij} = p_0\left[\frac{r_{BN,ij} - r_0}{r_0} + \sum_{k\neq i,j}\left(\frac{1}{2} + \cos\theta_{ijk}\right)\right]$$

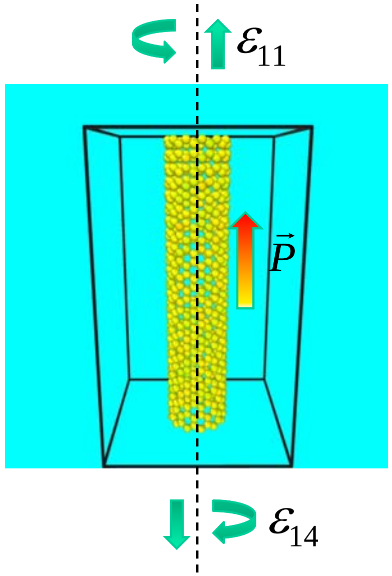


Elementary dipole unit

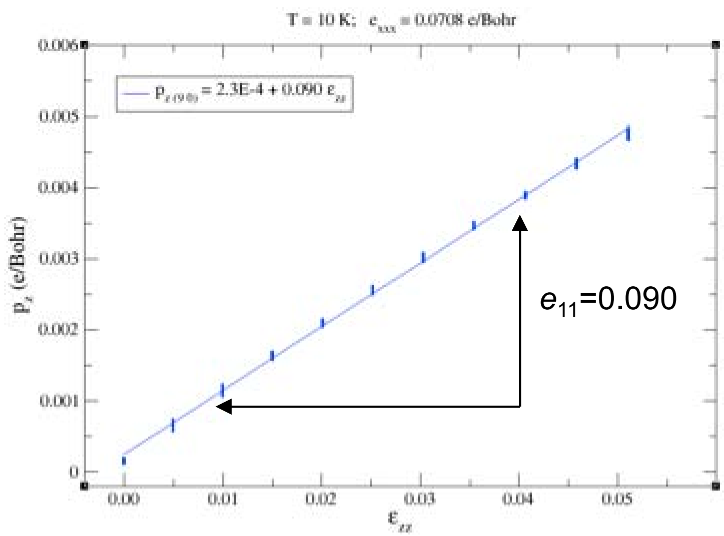
Comp. Mater. Sci., **95** 362 (2014)

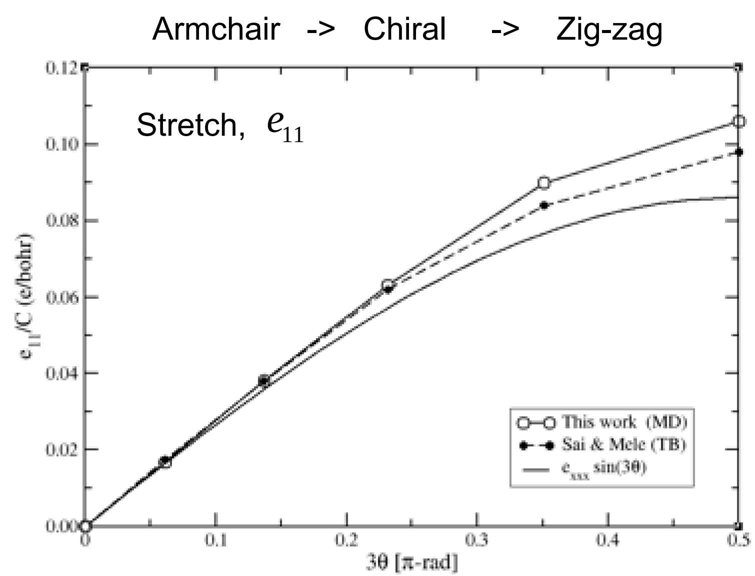
Results: Piezoelectricity under Deformation

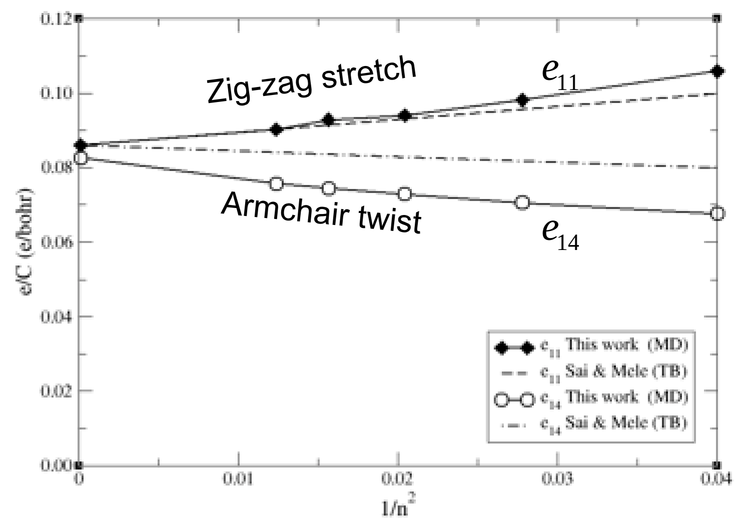
The MD model is successful in representing the piezoelectric properties of BNNTs

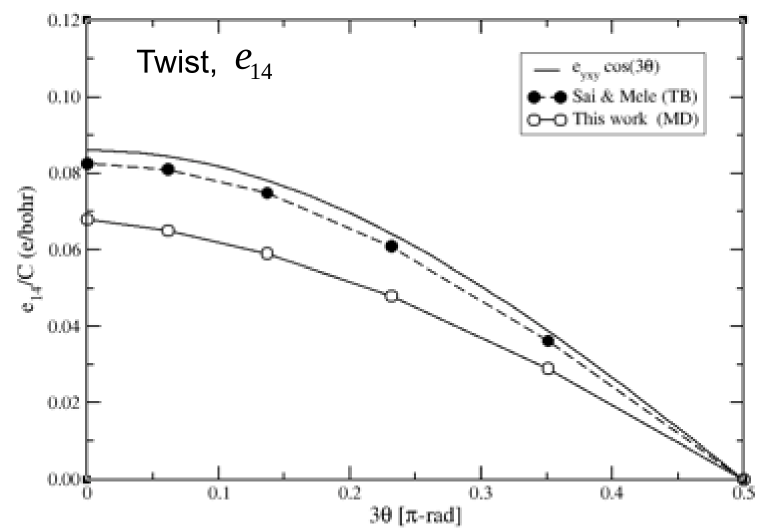


$$p_z(stretch) = e_{11}\varepsilon_s$$
$$p_z(twist) = e_{14}\varepsilon_t$$







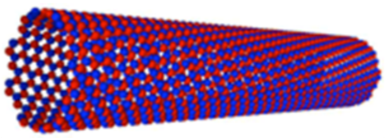


Comp. Mater. Sci., **95** 362 (2014)

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)



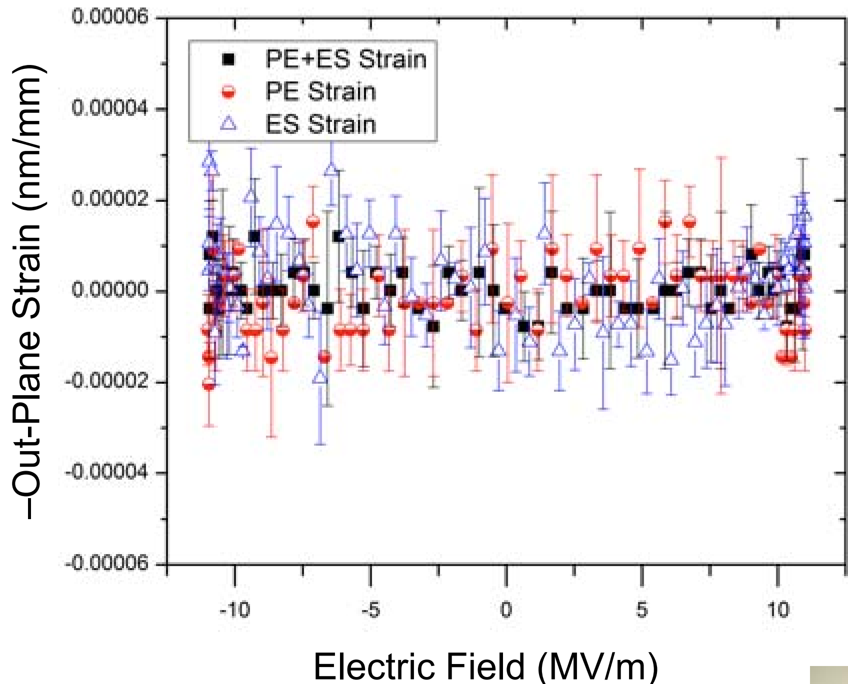
Alignment (stretched)
No alignment (not stretched) and stretched (up to 100%)

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%)

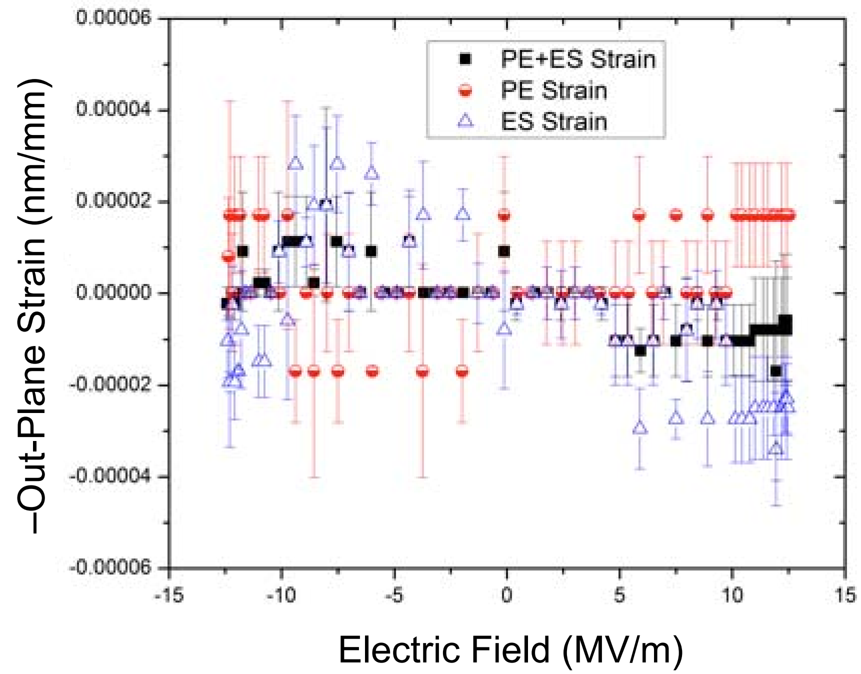
ACS Nano **9** 11942 (2015)

Study of Origin of Actuation: Stretched Films
Actuation of Unstretched/Stretched Pristine Polyimide

Unstretched



100% Stretched
@225°C, Annealing



Field induced strain (ε_{33})

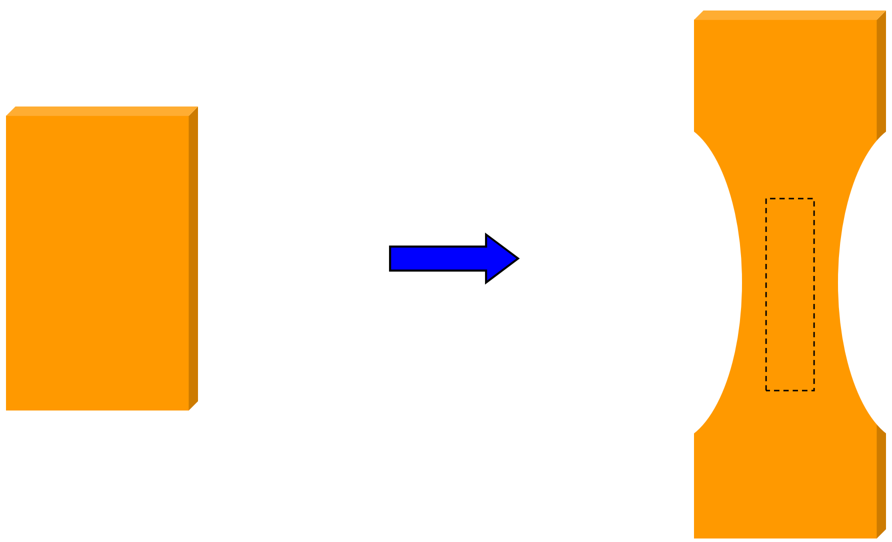
$$\varepsilon_{33} = d_{33}\cdot\boldsymbol{E} + M_{33}\cdot\boldsymbol{E}^2 + \ldots$$

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 Tg

All images credit: NASA

Stretched BNNT-Polyimide Nanocomposite



100 % Strain,
225°C slightly above Tg

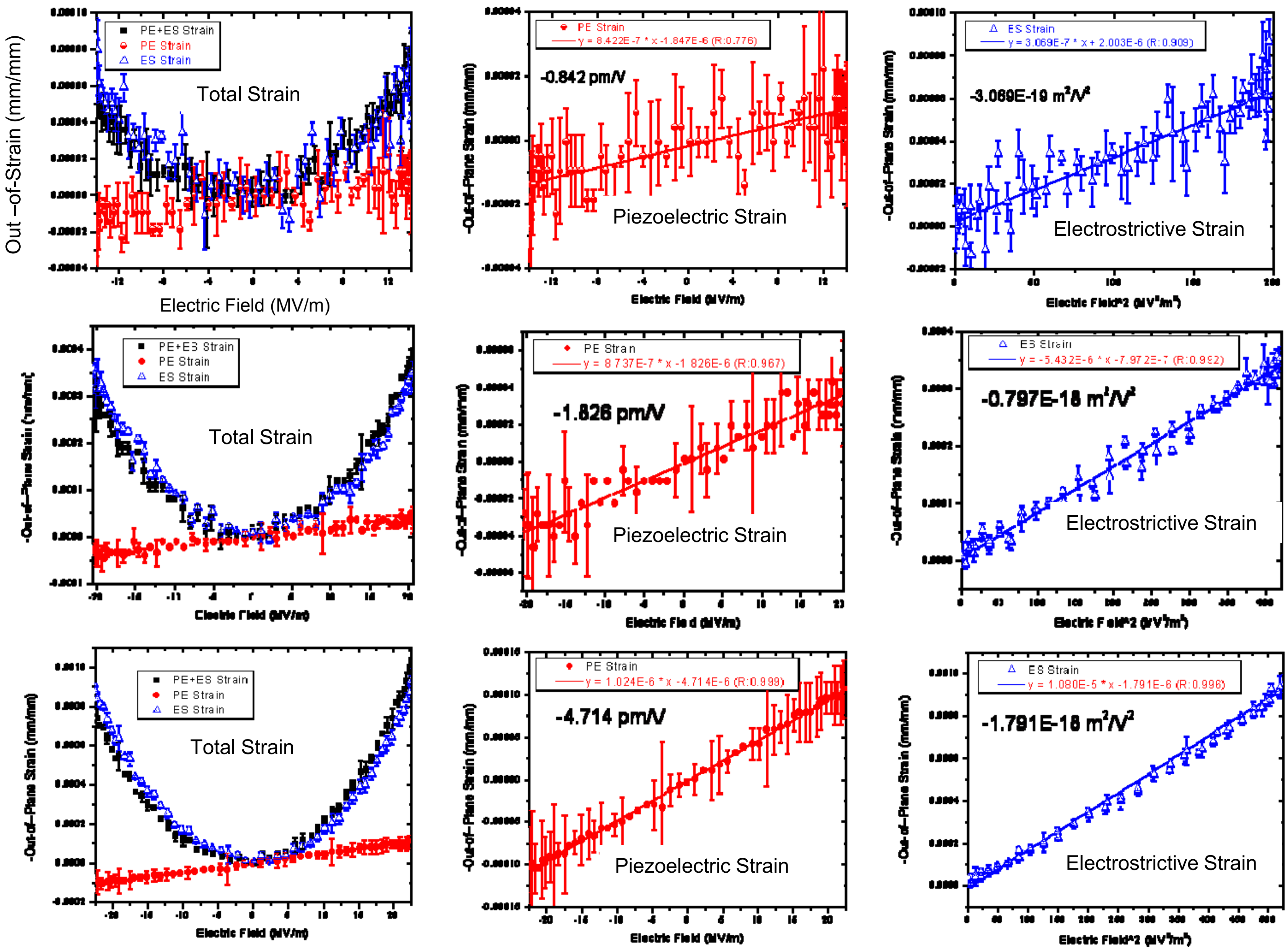
Actuation of Unstretched/Stretched 2% BNNT/Polyimide

Origin of Actuation → BNNT

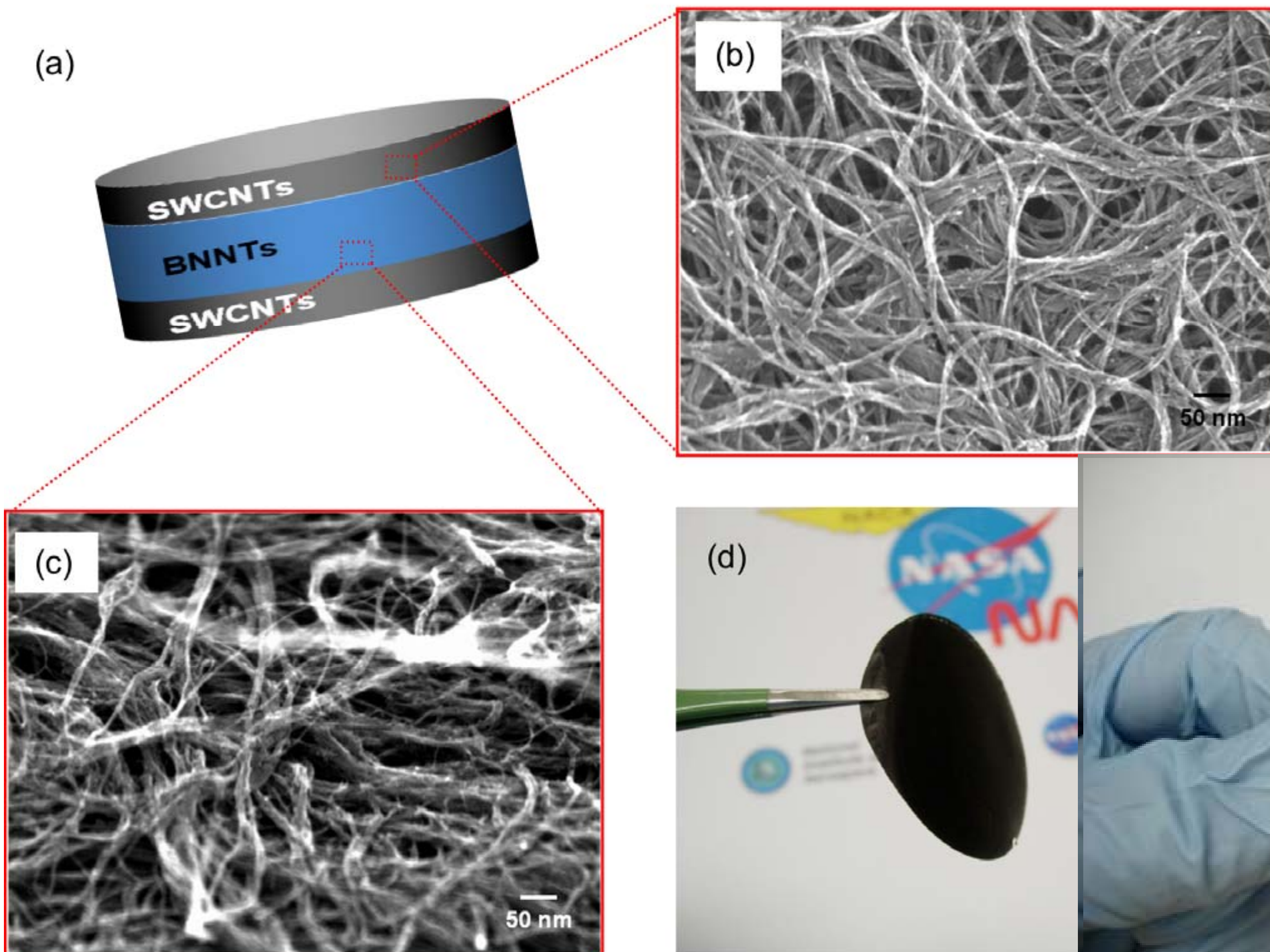
Unstretched

100% Stretched @225ºC, Quenching

100% Stretched @225ºC, Annealing



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

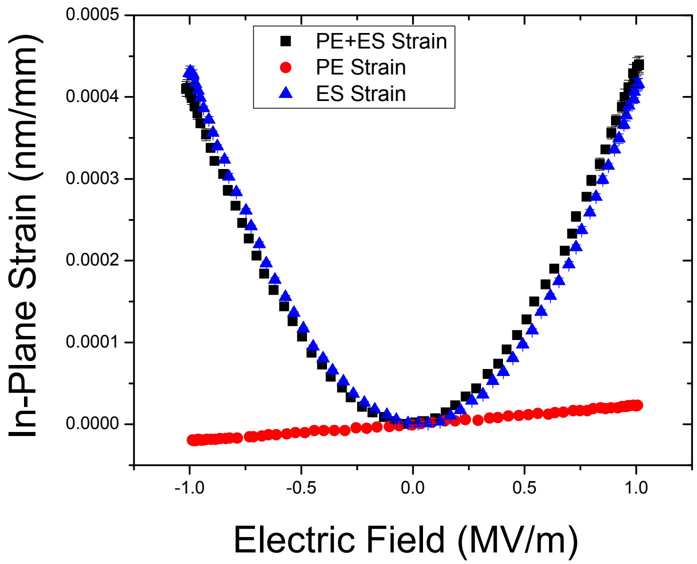


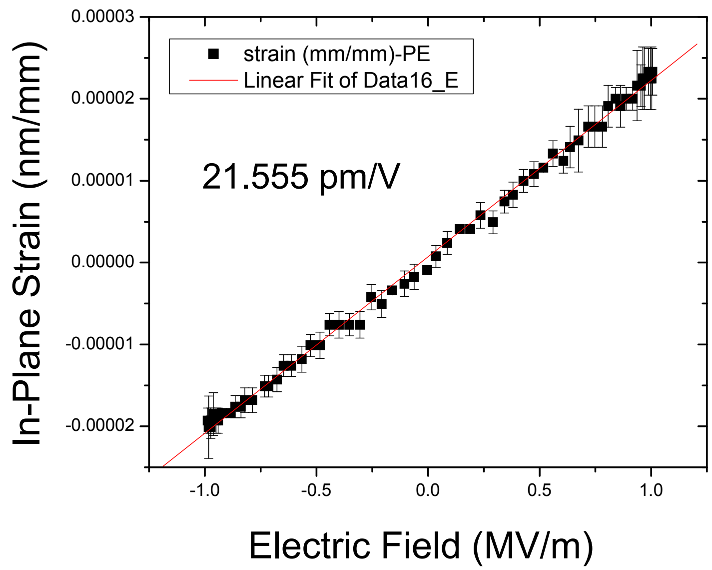
Goal: Flexible, transparent, large actuation, high sensitivity, Mechanically Durable

All images credit: NASA

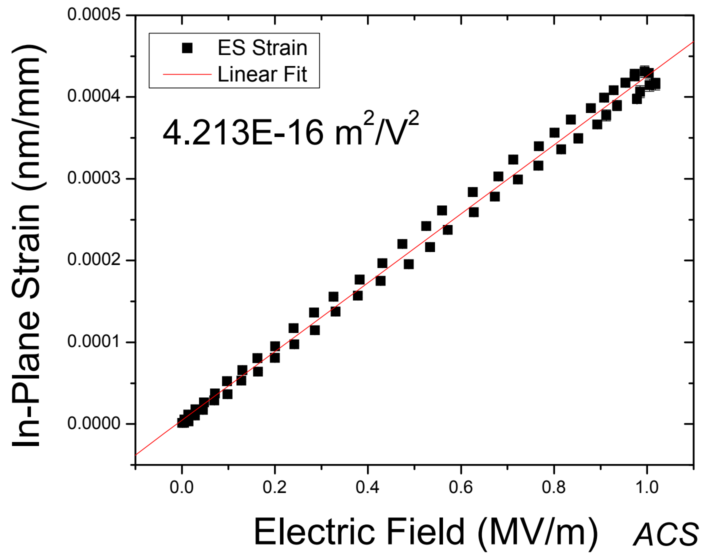
ACS Nano **9** 11942 (2015)

All-Nanotubes Actuator/Sensor 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})

$$\varepsilon_{33} = d_{33} \cdot \boldsymbol{E} + M_{33} \cdot \boldsymbol{E}^2 + \ldots$$

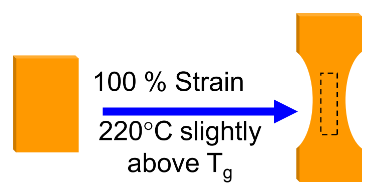
d_{33}: piezoelectric coefficient
M_{33}: electrostrictive coefficient
E: applied electric field

ACS Nano **9** 11942 (2015)

Actuation of Unstretched/Stretched h-BN/BNNT Materials

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	✓✓✓✓✓✓✓✓✓✓✓✓

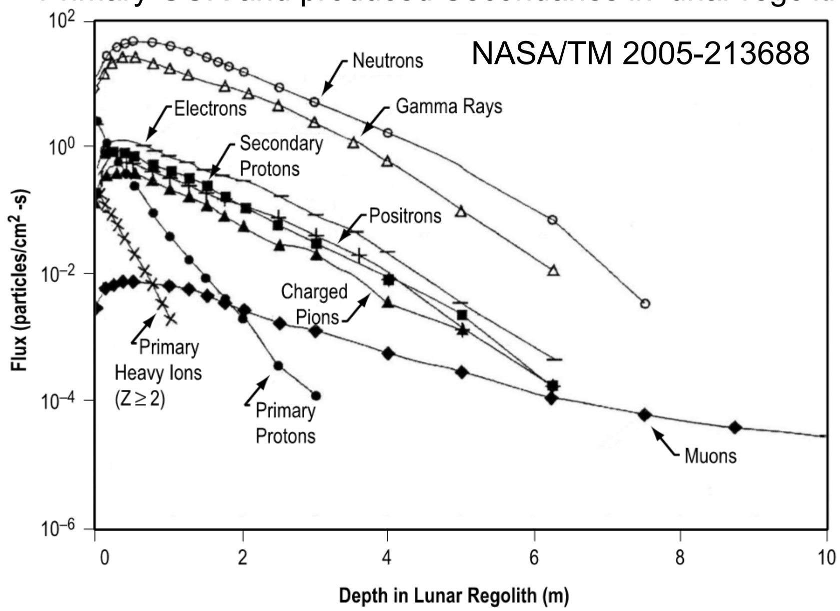
h-BN → No Actuation
Commercial BNNT (CVD) → No Actuation
Polymer → No Actuation
Stretched Polymer → No Actuation
BNNT (high pressure, high temp laser) → Origin of the Actuation



All images credit: NASA

Radiation Shielding Properties

Primary GCR and produced Secondaries in lunar regolith



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. Reitz[7]

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

Image credit: NASA

Neutron Radiation Shielding Study

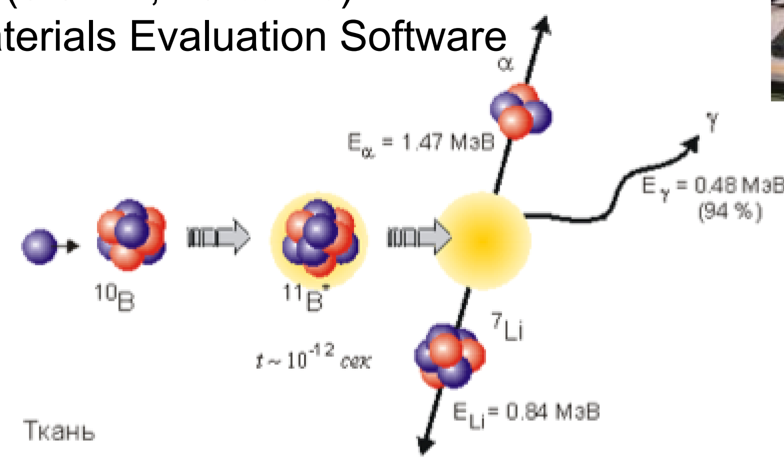
Materials
- Hydrogen, Boron, Nitrogen
- BN, BNNT, Gd
- Low density polyethylene (LDPE), polyimide (Kapton, CP2, (β-CN)APB/ODPA), polyurethane

Radiation Shielding Structural Materials
- In-situ polymerization under simultaneous sonication and shear
- Supercritical Fluid Infusion

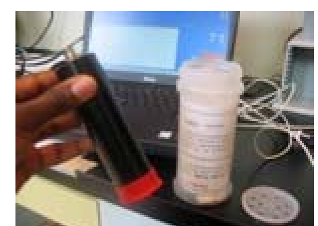
Characterization
- Neutron Radiation Exposure Lab: Source: Am/Be 1Curie
- Moderated by borated polyethylene cylinder block (44mm thick): 45 mrem/hr thermal neutrons
- Sample: 2 x 2” polymer and BN polymer composites
- Detection Foil: 1.25” Indium Foil (0.5mm, 19 barns)
- RSMES: Radiation Shielding Materials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

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

neutron



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



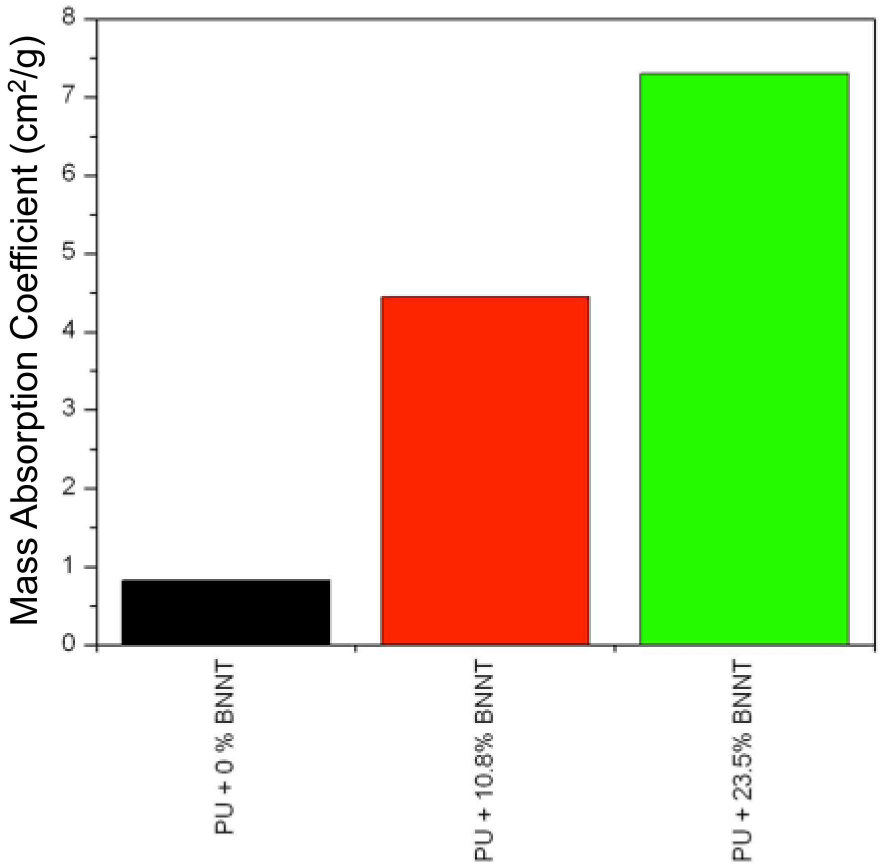
Geiger-Mueller Tube

Modeling
- OLTARIS

All images credit: NASA

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

Neutron radiation

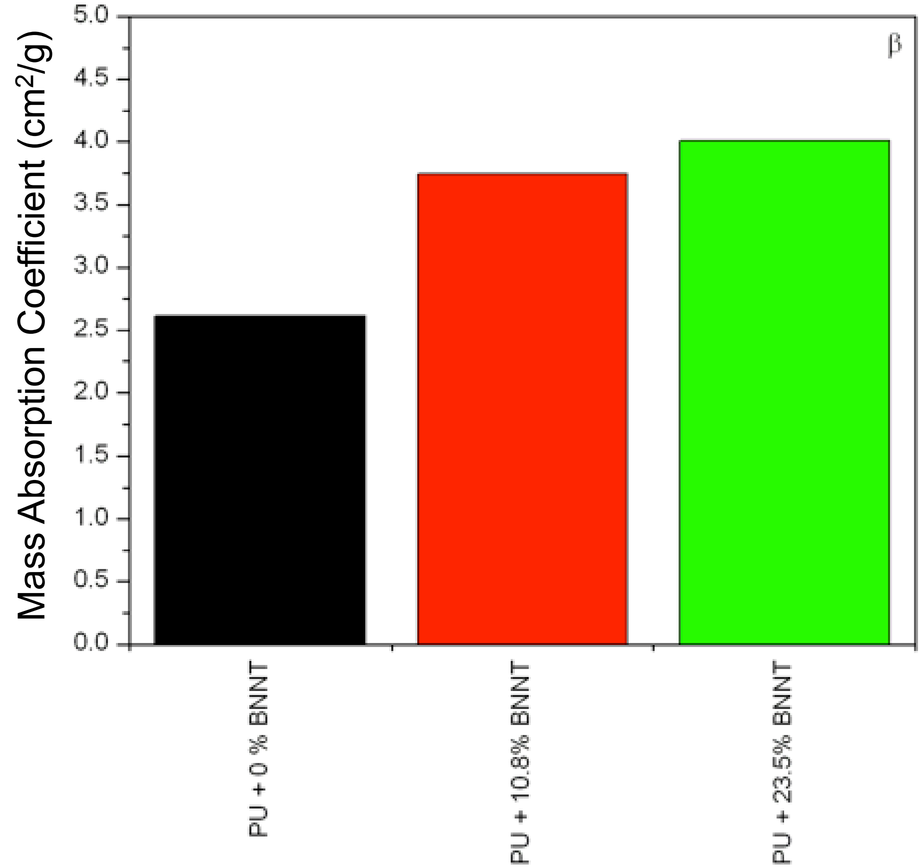


Am/Be 1Curie & moderated by borated PE

$$^{241}_{95}Am \rightarrow ^{237}_{93}Np \div ^{4}_{2}He(\alpha)$$

$$^{4}_{2}He \div ^{9}_{4}Be \rightarrow ^{12}_{6}C \div ^{1}_{0}n \div \gamma(5.71MeV)$$

Beta radiation



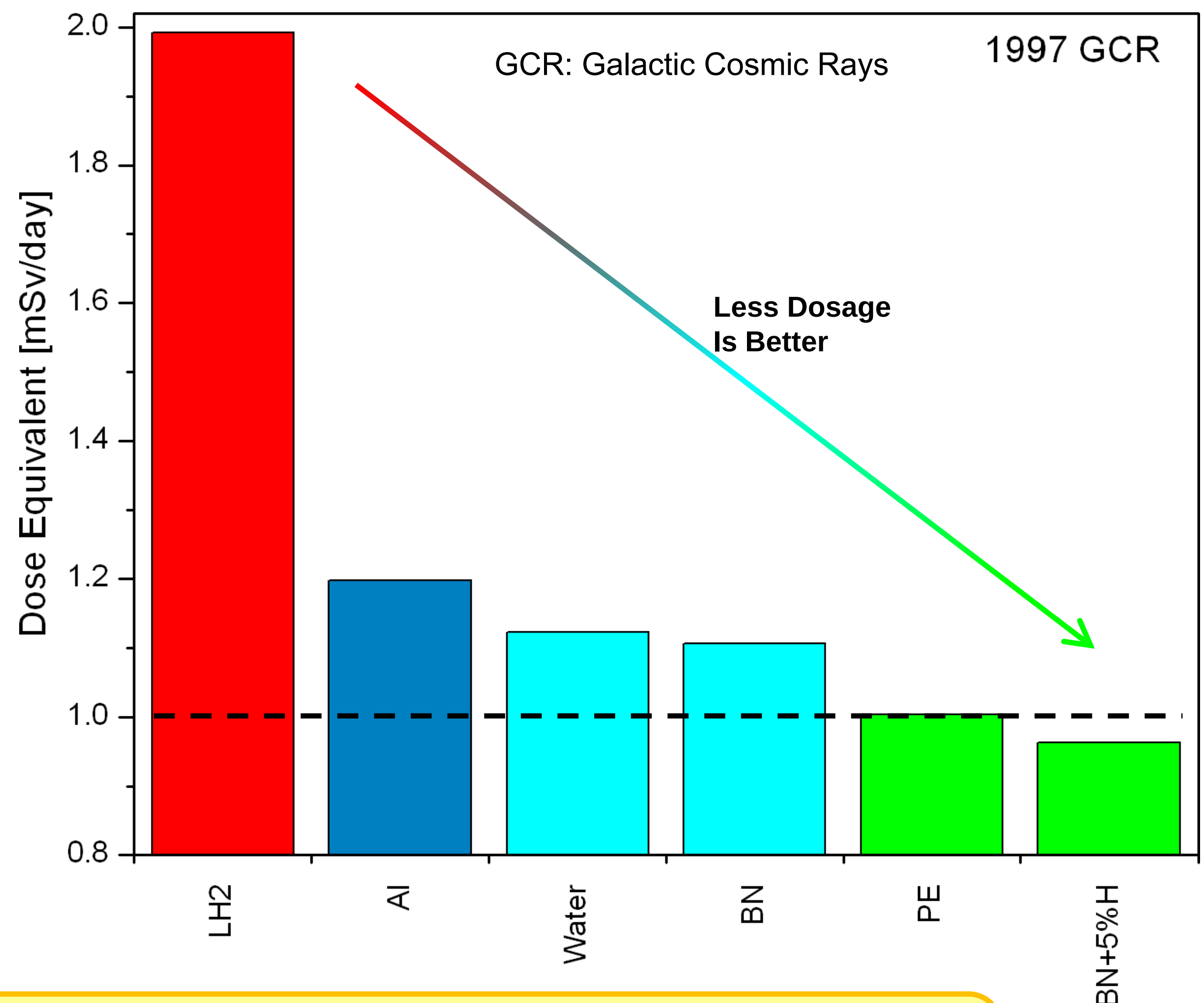
0.1 μCi Sr-90: β (Synthesized Apr 2009)

$$^{90}_{38}Sr \rightarrow ^{90}_{39}Y \div \beta^{-}; t_{half} = 28.8y$$

ACS Nano **9** 11942 (2015)

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.

MRS Bulletin **40** 836 (2015)

Summary

- High Temperature-Pressure BNNT synthesis method was introduced.
- Interfacial shear strength and fracture energy of BNNT with polymers were superior to those of CNT.
- BNNT dispersion was successfully achieved by thermodynamic approach using Hansen solubility parameters for single and co-solvent systems.
- BNNT polymer composites exhibited excellent piezoelectricity as well as electrostrictive behavior even without poling.
- BNNT exhibited excellent neutron radiation shielding effectiveness and hydrogen containing BNNT showed superb shielding effectiveness against GCR and SPE.

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NASA C&I, B&P, GCD, IRAD, NIAC

Thank You

Image credit: NASA