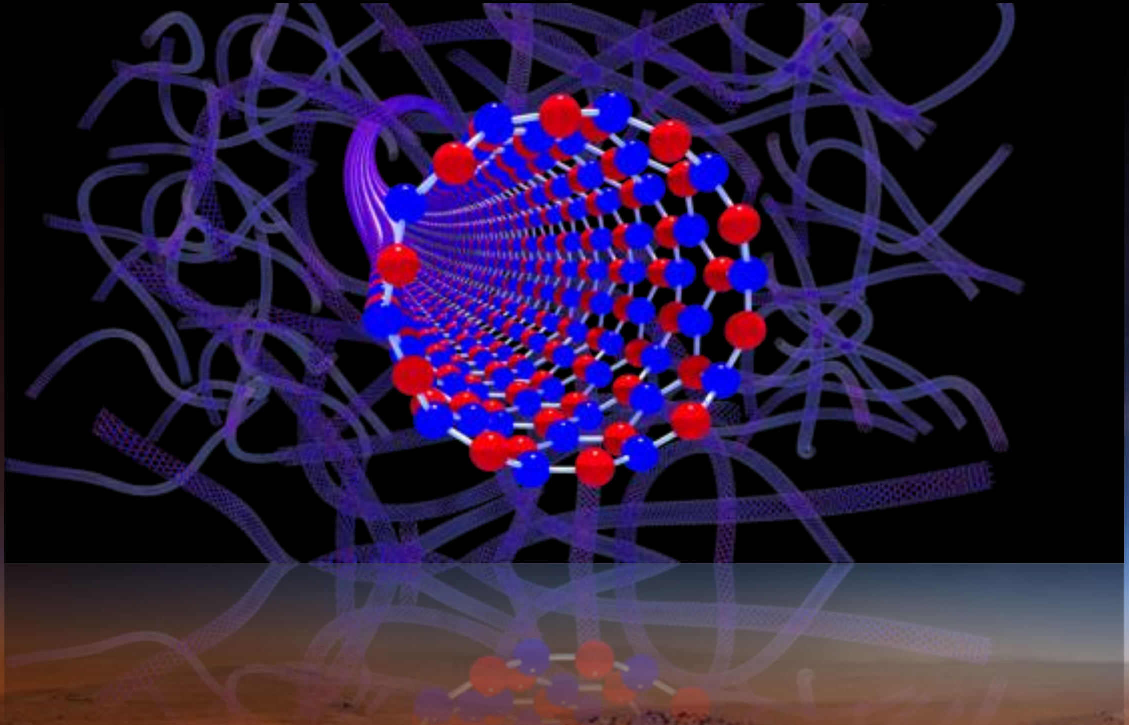
Boron Nitride Nanotube (BNNT) and BNNT Composites: Overview

Cheol Park, Sang-Hyon Chu*, and Catharine Fay



Advanced Materials and Processing Branch, NASA Langley Research Center
**National Institute of Aerospace, Hampton VA USA*

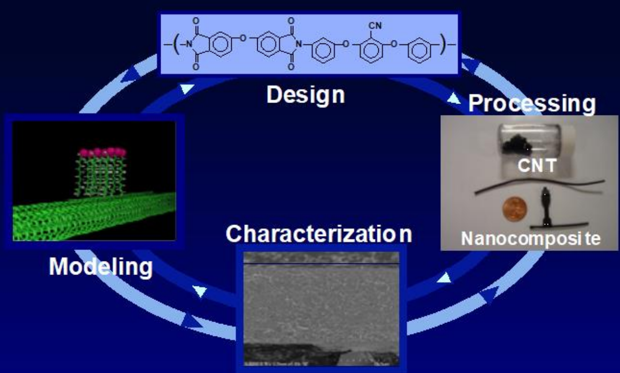
NASA Langley Research Center

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

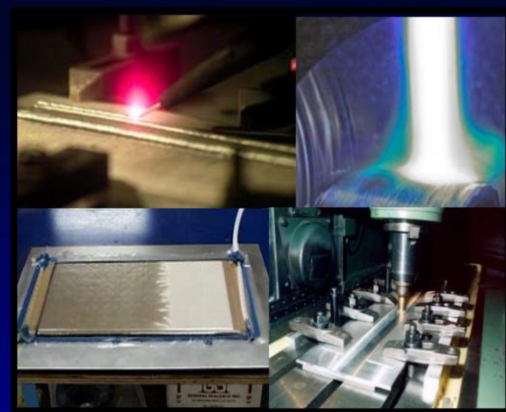
All images credit: NASA

Advanced Materials and Processing Branch

Materials Design

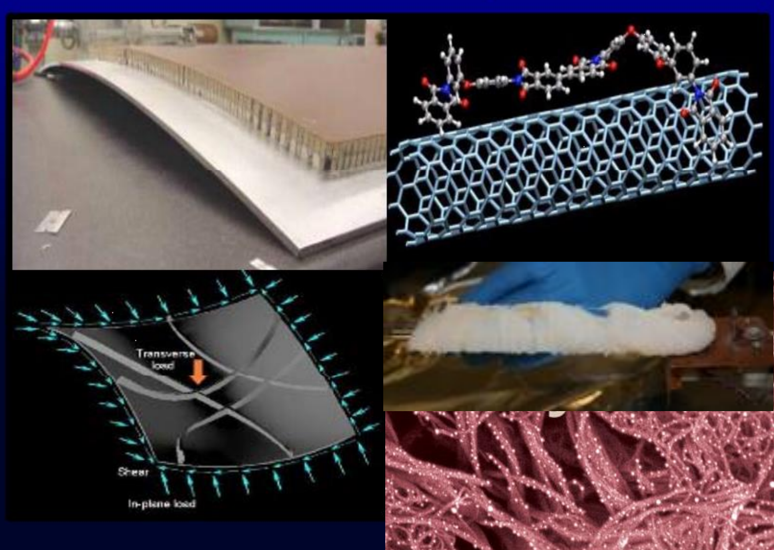


Innovative Materials Processing

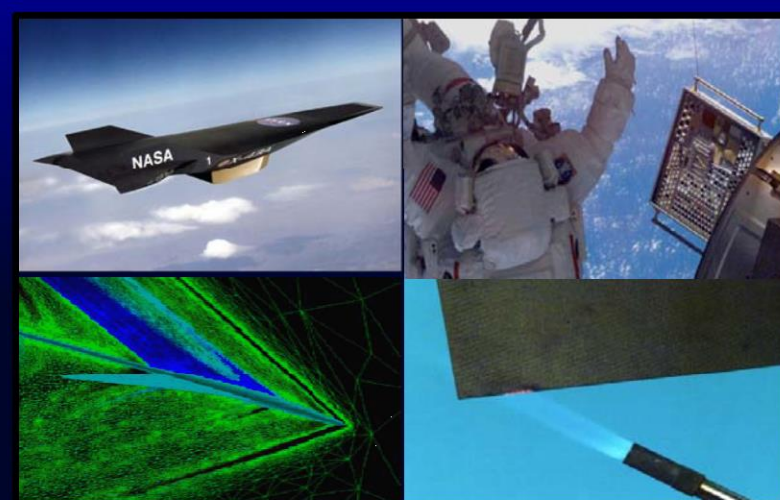


Materials Testing

Advanced Material Systems



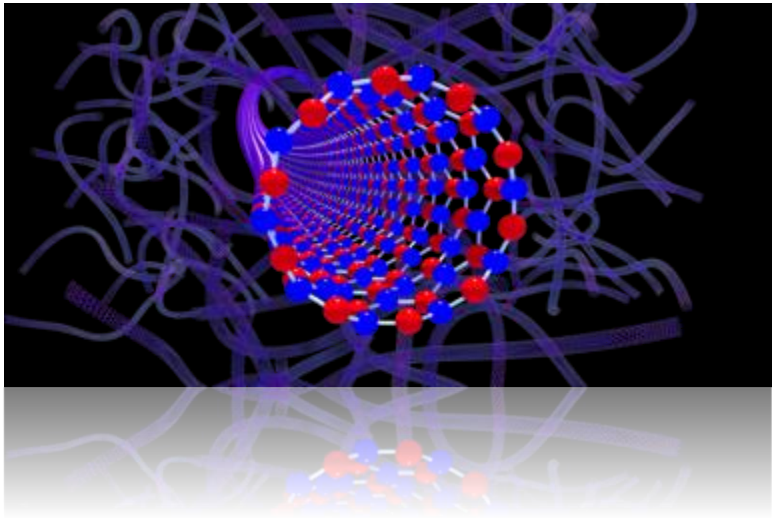
Materials for Extreme Environments



All images credit: NASA

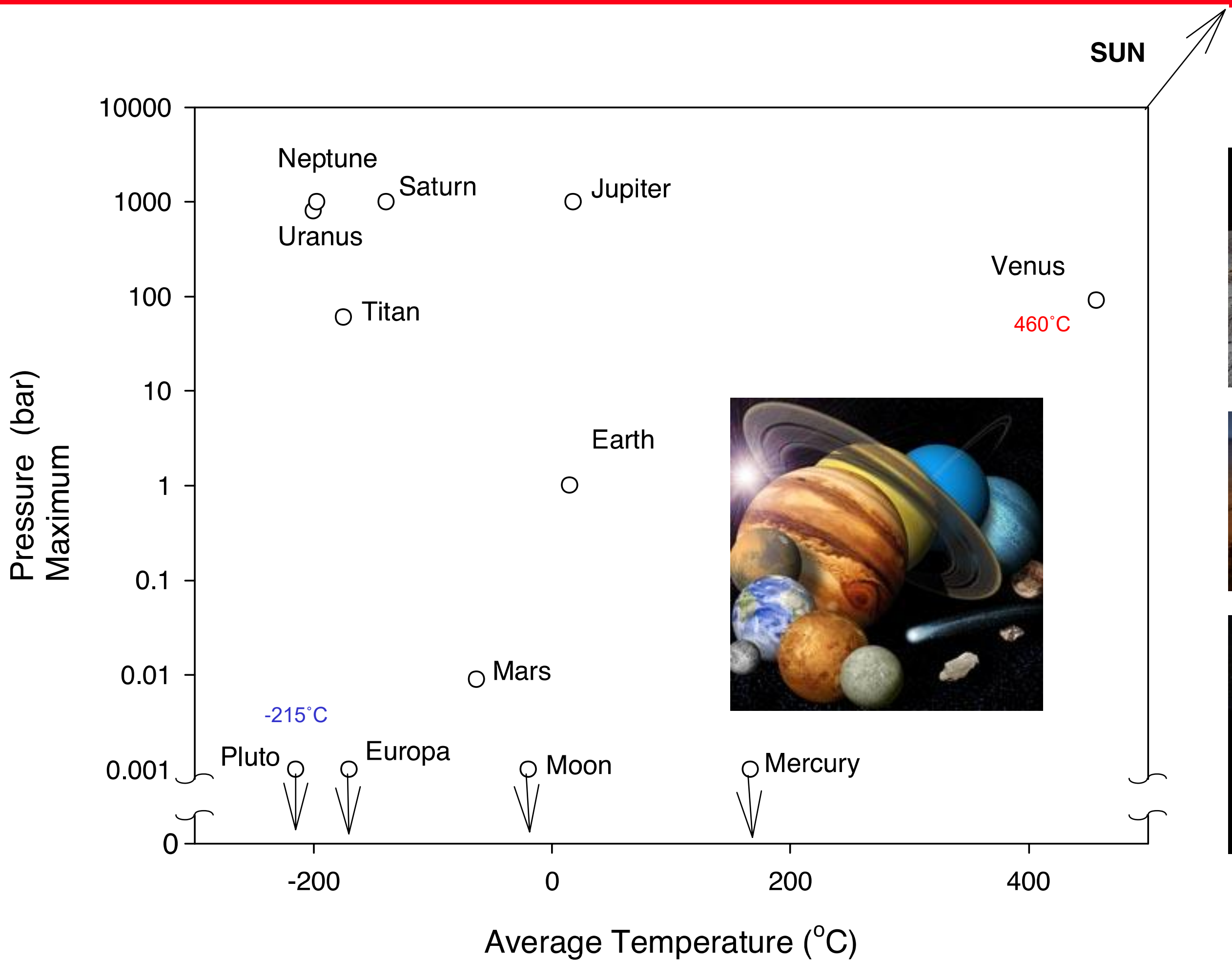
Outline

- Motivation
- BNNT Synthesis (High Temperature Pressure (HTP) Method)
- BNNT and BNNT Composite Application
- Dispersion and Purification
- Mechanical Properties
- Thermal Properties
- Multifunctional Properties in Extreme Environments
    - Sensor/Actuator/Energy Harvester
    - Radiation Shielding
- Summary

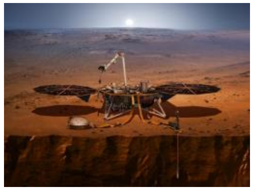


Extreme Environments in Space Exploration

http://www.jpl.nasa.gov/solar_system/
17NASA Extreme Environments Tech Space missions Report FINAL



Lunar surface
-173 to 127˚C
-247˚C (25K) at pole
Sharp abrasive edge dust
Radiation

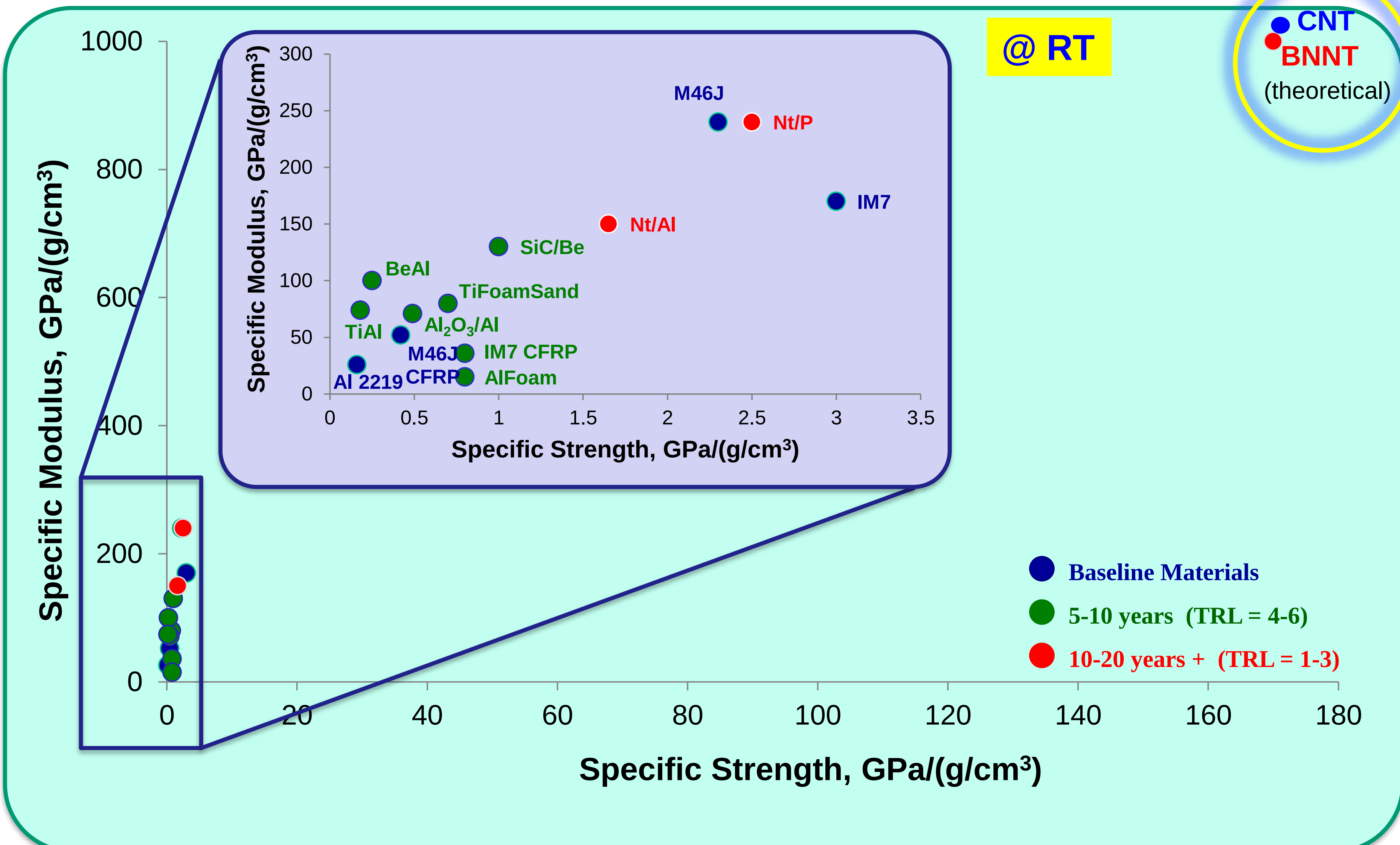


Mars surface
-126 to 21˚C
Sand storm
Radiation
Entry, Descent, & Landing

Deep space
2.7K
Radiation
Microgravity

Heat flux at atmospheric entry: Heat fluxes often exceeding 10's W/cm^2
Hypervelocity impact: Higher than 3 km/sec
Low and high temperature: Lower than −55˚C and Exceeding +460˚C
Thermal cycling: Cycling between temperature extremes outside of the military standard range of −55˚C to +125˚C
High pressures: Exceeding 20 bars
High radiation: Total ionizing dose (TID) exceeding 300 krad (Si), GCR, SPE, Neutron
Low and High gravity: microgravity on comets, 2.5g on Jupiter, launch, entry, descent

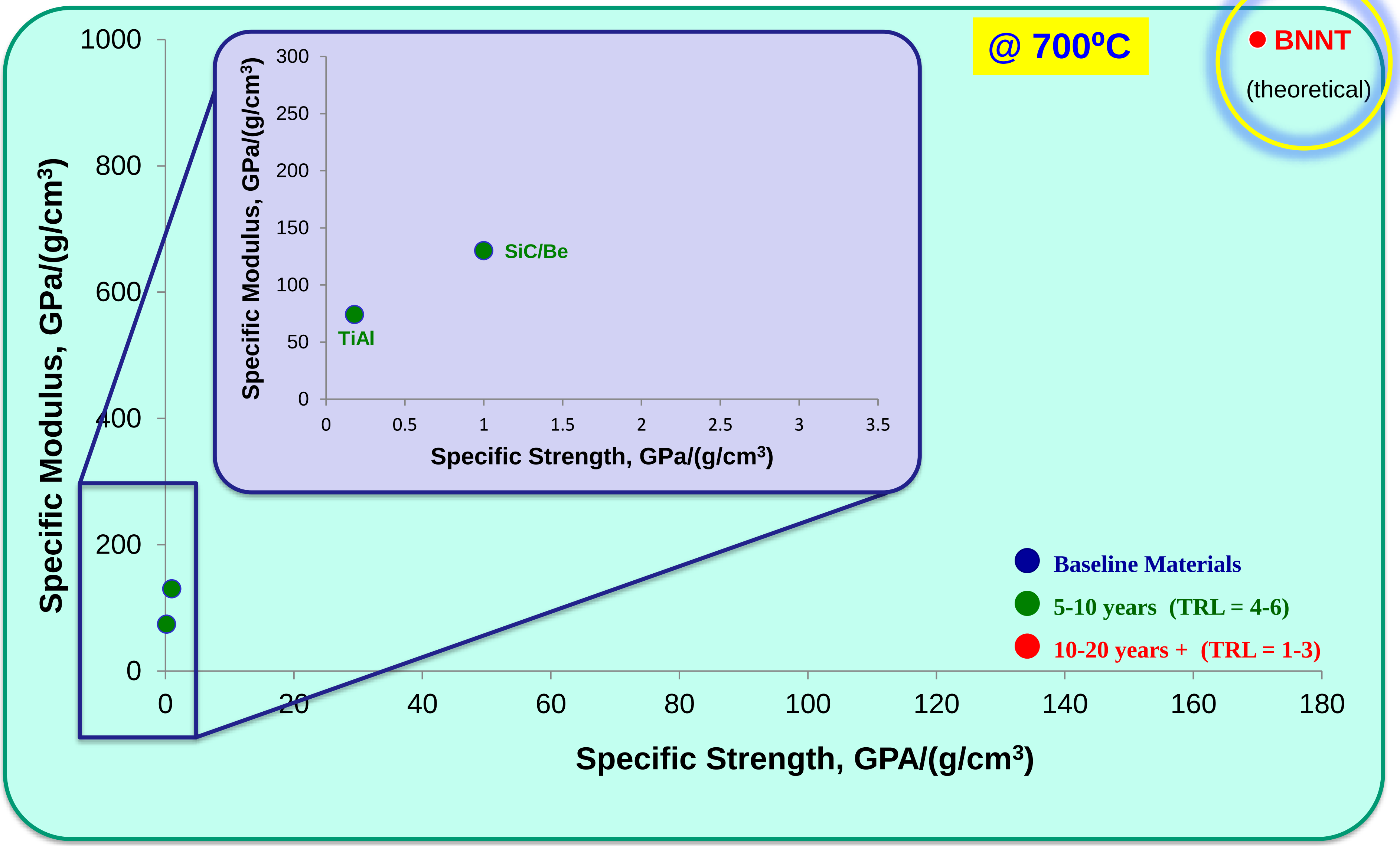
Motivation: Properties of Materials for Vehicle Structure



Charlie E. Harris, M. J. Shuart, H. Gray, NASA/TM-2002-211664

Nanotube values are theoretical.

Motivation: Properties of Materials for Vehicle Structure



Charlie E. Harris, M. J. Shuart, H. Gray, NASA/TM-2002-211664

Nanotube values are theoretical.

Nanotube Comparison (Theoretical)

	Carbon Nanotubes	Boron Nitride Nanotubes
Electric Properties	Metallic or semiconducting	Wide band gap (about 6.0 eV) Insulation, corrosion resistant
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 900 °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 Better interfacial strength for composites, ionic bonding
Color	Black	White (can be colored)
Coefficient of Thermal Expansion	-1×10^{-6} K^{-1} (very low)	-1×10^{-6} K^{-1} (very low)

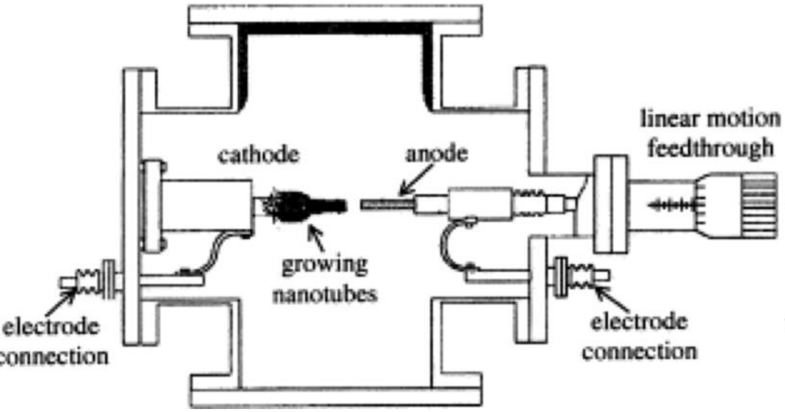
Significance of the BNNT Innovation

- **Structural/Mechanical**: **lightweight** composite armor, thermal protection, engine components, and radiation shielding materials for **extreme environments**.
- **High stiffness as well as high toughness** for spacecraft and space suits, ultrastrong tethers, meteorite impact protection layers, protective gear for astronauts.
- **Space lubricants** without moisture.
- **High temperature** thermal protection systems (**TPS**) used in the **nose cap**, wing **leading edges**, **engine parts**, lubricants, and planetary **Entry, Descent, & Landing** (**EDL)** TPS.
- **Fire resistant and retardant.**
- **High temperature sensor, actuator, energy harvesting devices** in extreme environments.
- **Radiation shielding, UV (ultraviolet) protection,** and electromagnetic transparency while decreasing aircraft weight.
- **Radar transparency** mitigates Electromagnetic Interference (EMI) and Radio Frequency (RF) blackout.
- **Efficient zero-energy water filter and desalination membrane in microgravity**.

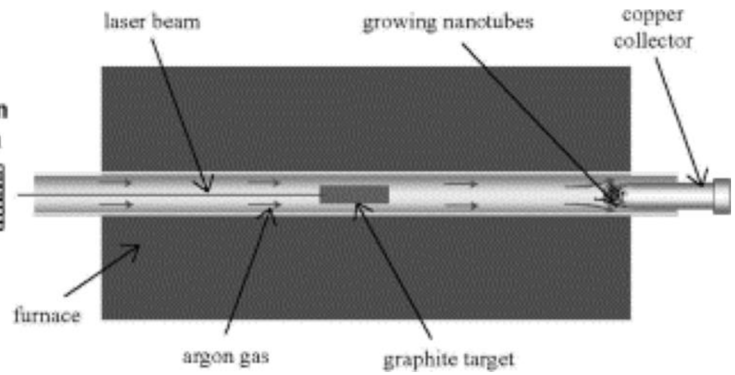
All Images Credit: NASA

Synthesis Methods of Carbon Nanotubes

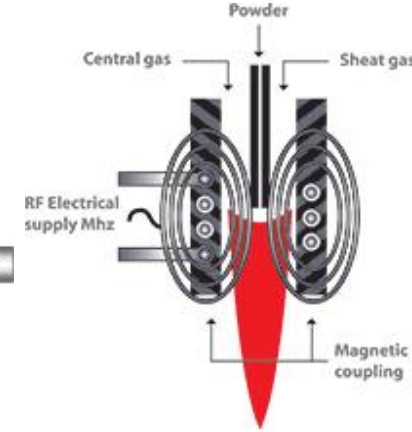
- Arc-discharge: solid state carbon precursor
- Laser ablation: solid state carbon precursor
- Chemical vapor deposition (CVD): gaseous carbon precursor/ HiPco (High pressure CO)
- Free Electron Laser (Jefferson Lab): funded by NASA-LaRC C&I
- RF Induction Thermal Plasma (Canadian NRC)



Arc-discharge

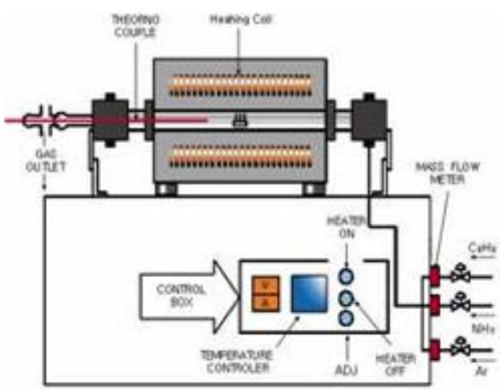


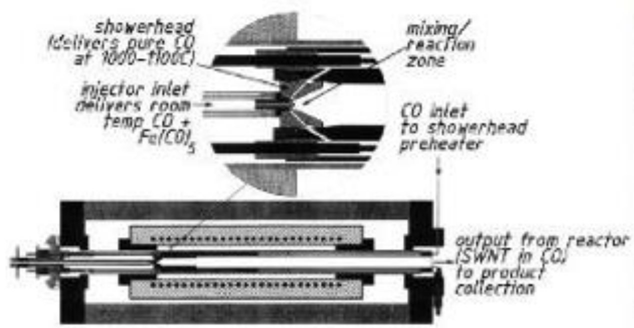
Laser ablation



Credit: www.tekna.com

Induction Plasma





HiPco

Chemical vapor deposition (CVD)

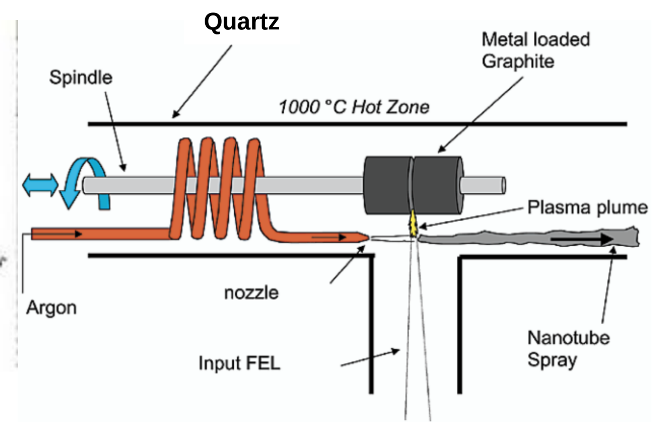


Image credit: NASA

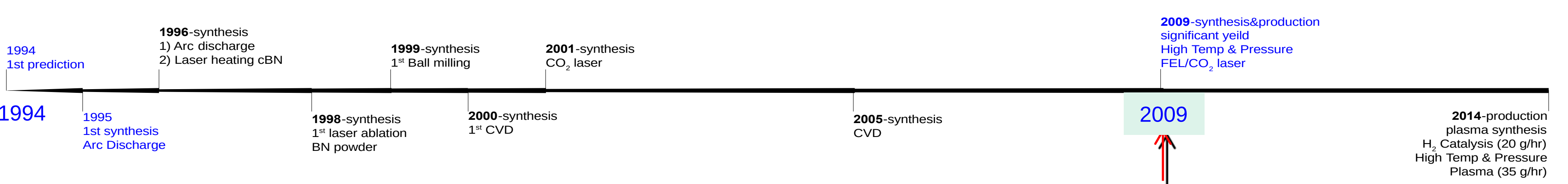
Credit: http://students.chem.tue.nl/ifp03/synthesis.html

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

BNNT Synthesis History

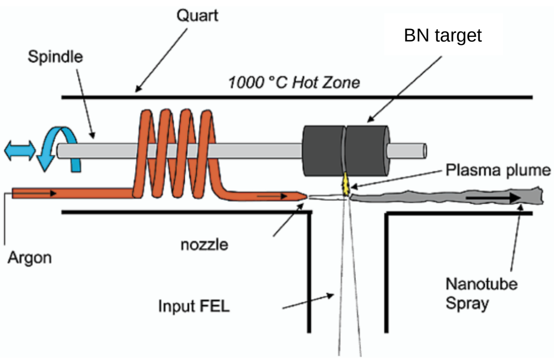
- *First Theoretical prediction: PRB **49** 5081–5084 (1994) (UC Berkeley, Cohen), computation*
- *First Synthesis Arc Discharge: Science **269** 966 (1995) (UC Berkeley, Cohen/Zettl) BNNT by Arc Discharge*
- Arc Discharge: *PRL* **76** 4737 (1996) (ONERA France, Loiseau) Arc Discharge HfB2 with N2 gas
- 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 H_2
- High Temp, High Press Induction Thermal Plasma: NL 14 4881 (2014) (UC Berkeley, Zettl): 35g/hr



High Temperature-Pressure (HTP) BNNT

- Free Electron Laser (FEL) or CO_2 laser
- ***No Catalyst, only B and N resource***
- Very long, small diameter, highly crystalline BNNT



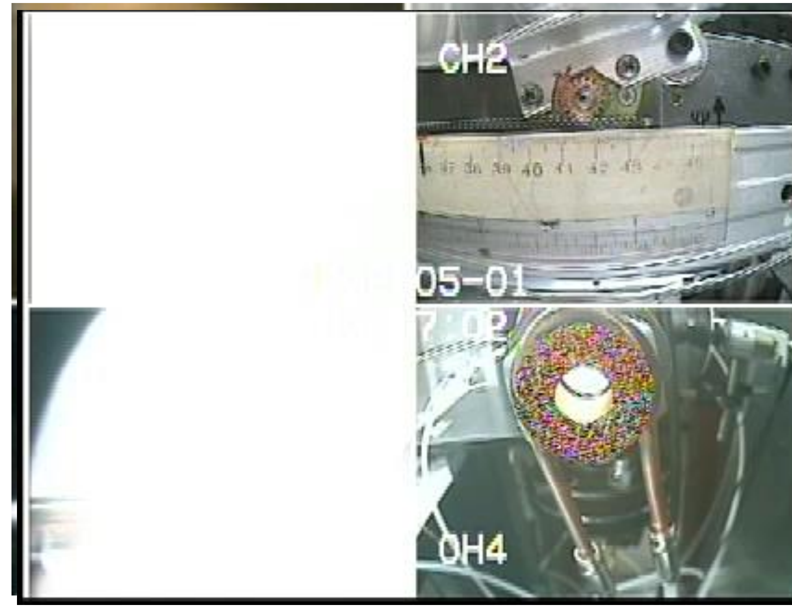
Nanotechnology, **20** 505604 (2009)
US Patent 8206674 B2 (2012)

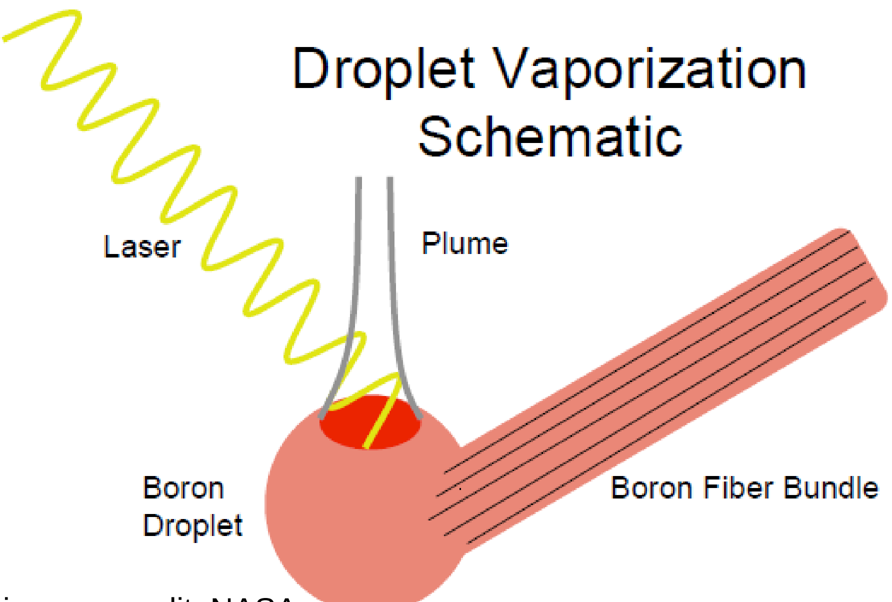
Free Electron Laser: Atmosphere: Spark

All images credit: NASA

Free Electron Laser: High Pressure: BNNT Streamer

BNNT Synthesis Lab: NASA Langley (1st Gen)



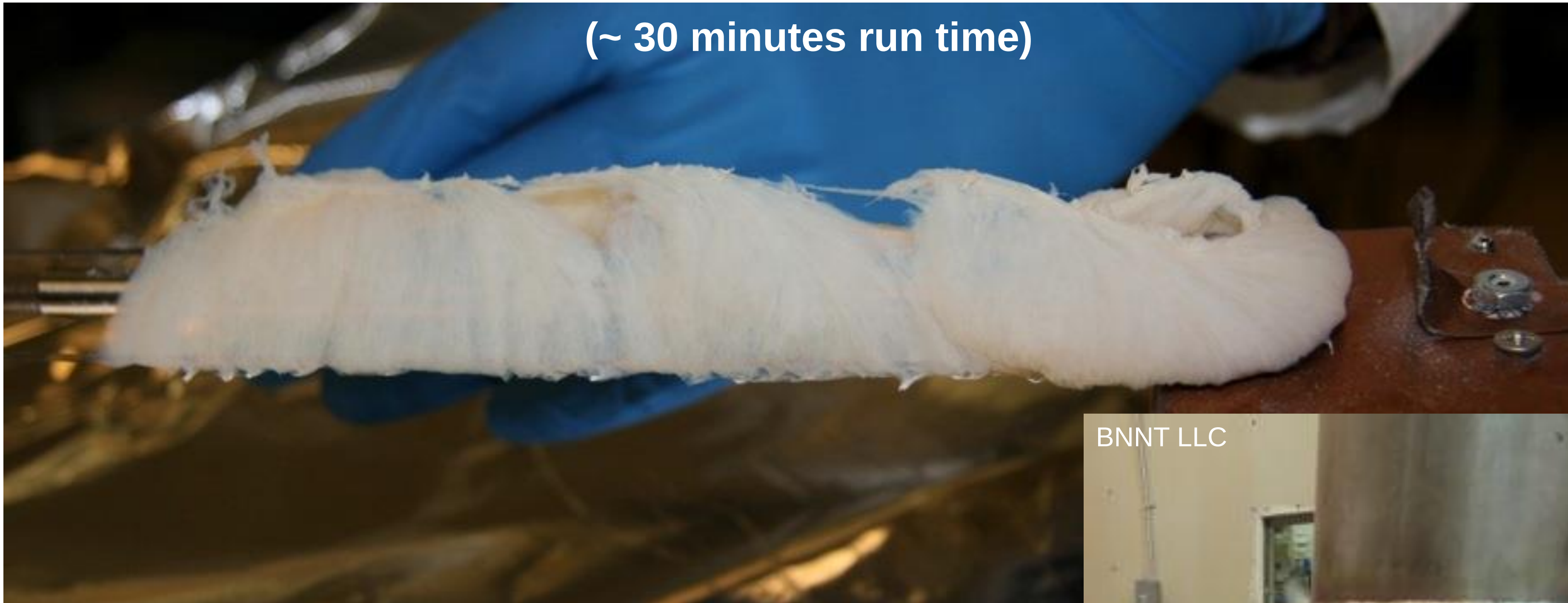


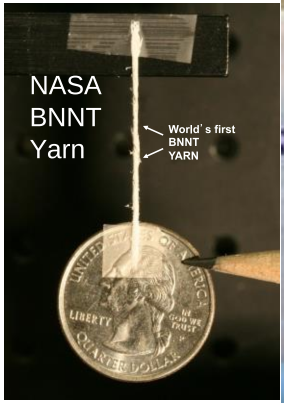
- 5 kW of infrared radiation @ 10.6μm
- Heat source for vaporizing Boron feed stock above 3500ºC
- Pressurized with Nitrogen to 13.6 atm (200 psi)

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

All images credit: NASA

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

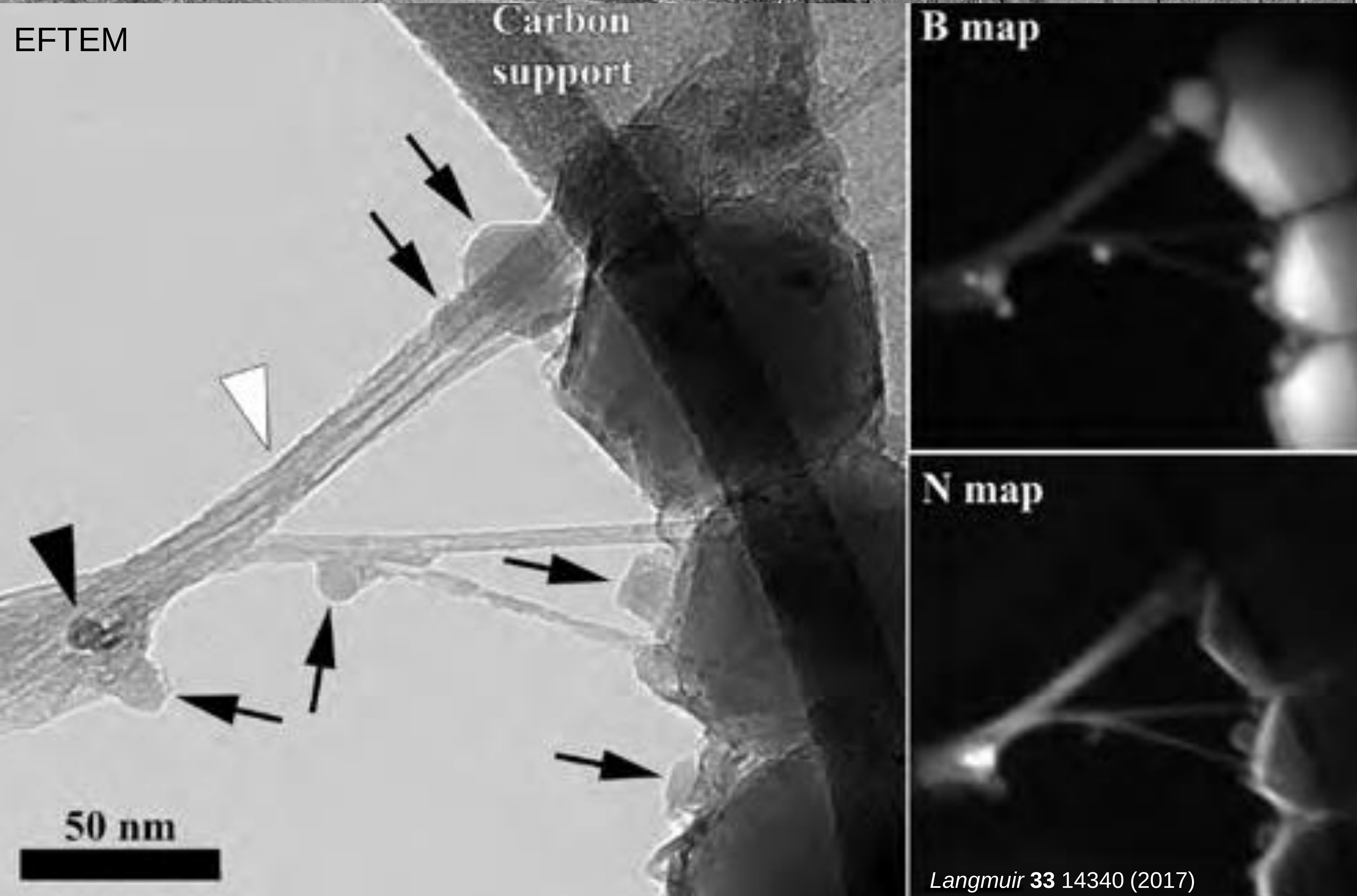




Benefits

- 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)

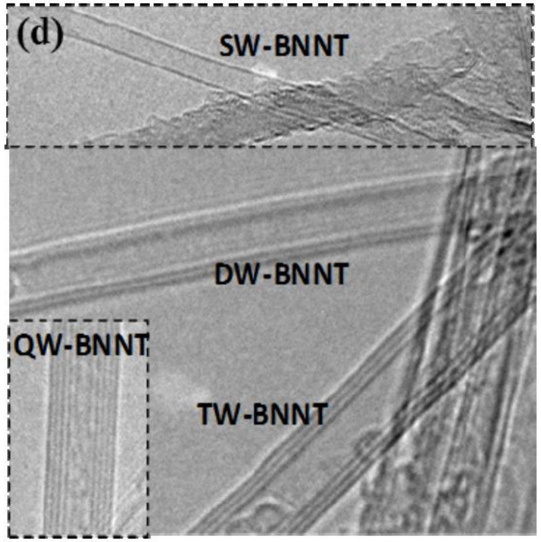
EFTEM

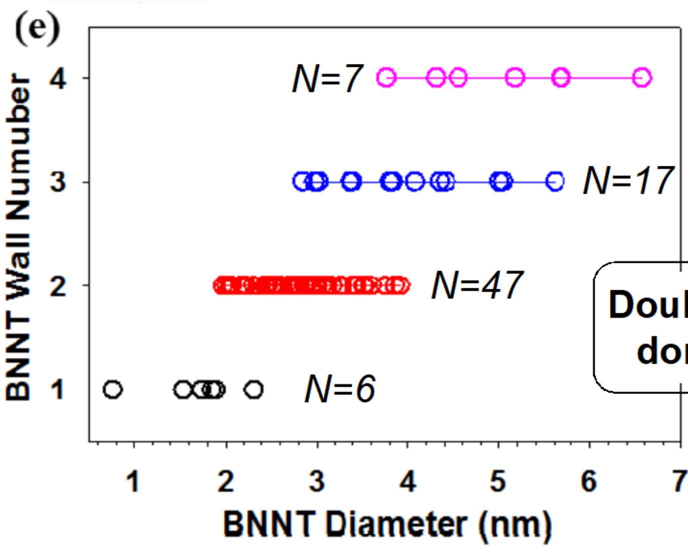


Langmuir **33** 14340 (2017)

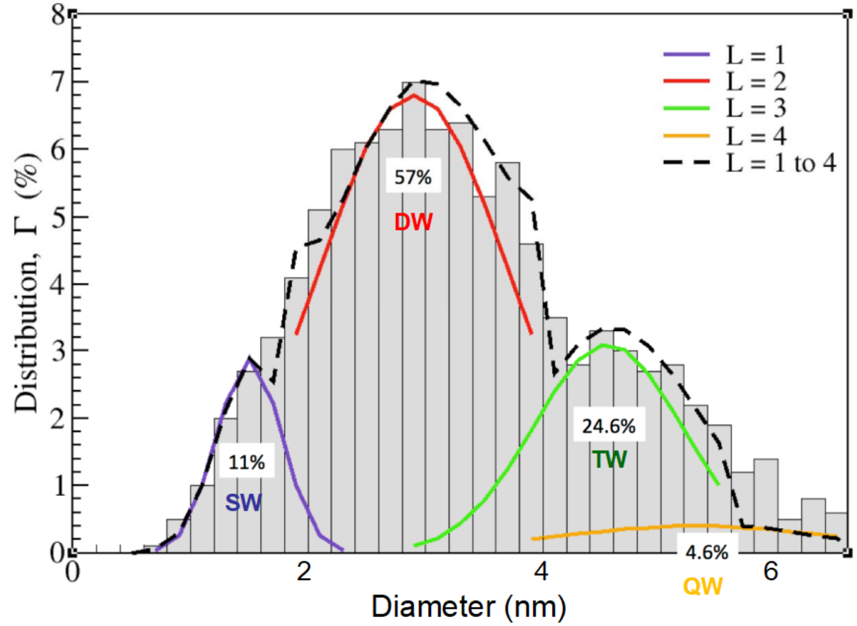
Nanotube Wall Number and Distribution of HTP-BNNTs

TEM Micrographs



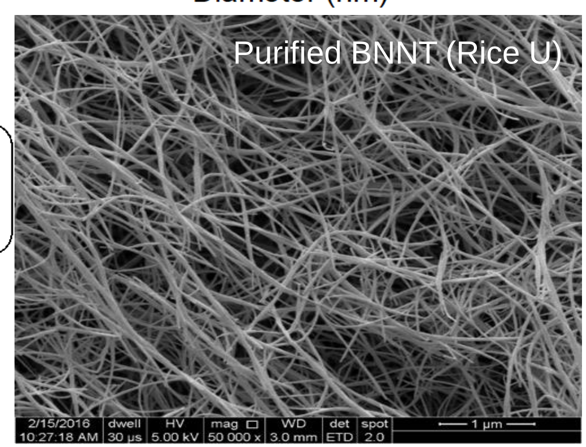


Based on AFM measurements of 1,000 randomly selected individual BNNTs



SW: 11%
DW: 57%
TW: 24.6%
QW: 4.6%
Total: 97.2%

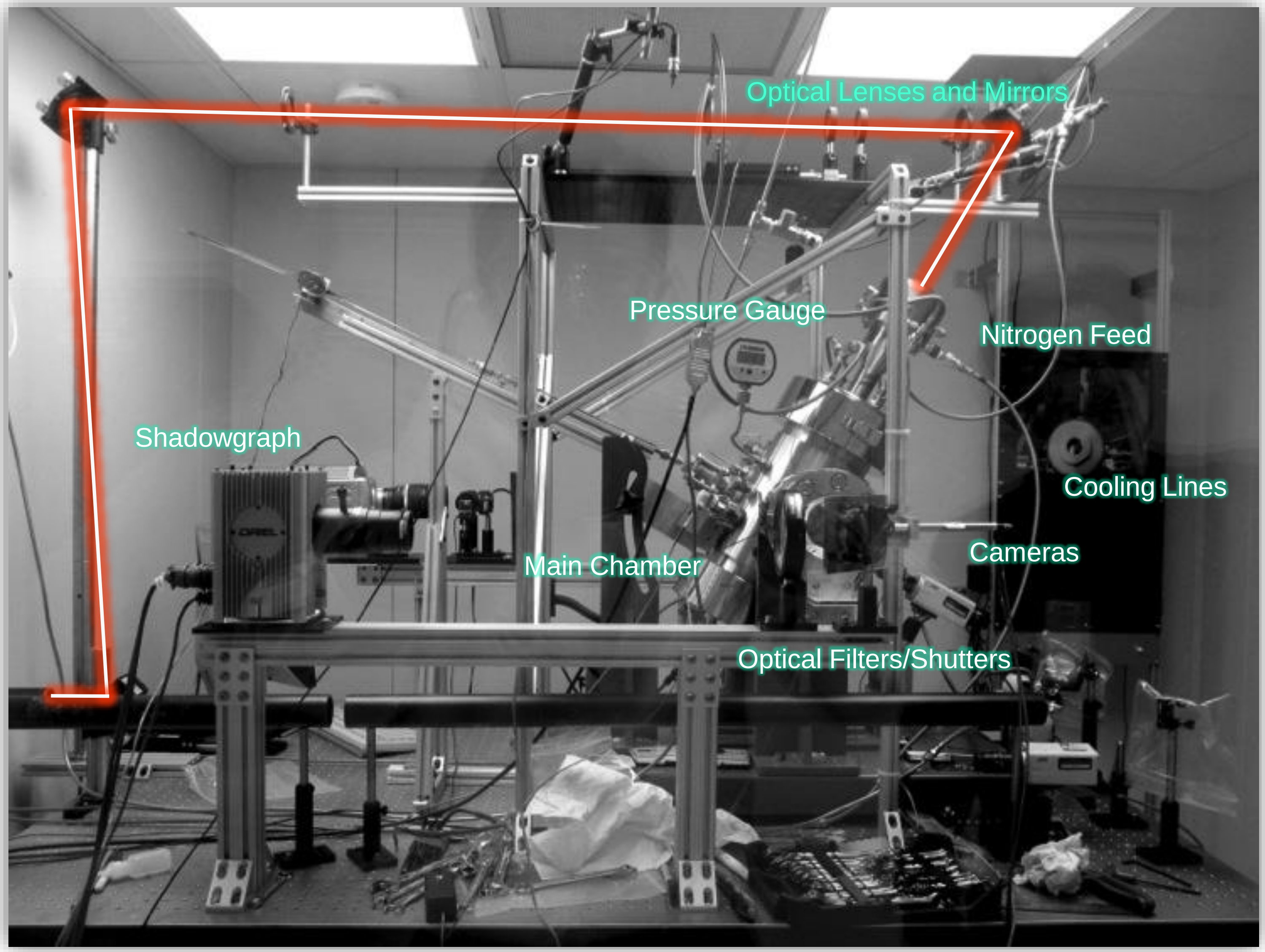
Double-walled dominance



Nanotechnology, **23** 095703 (2012)

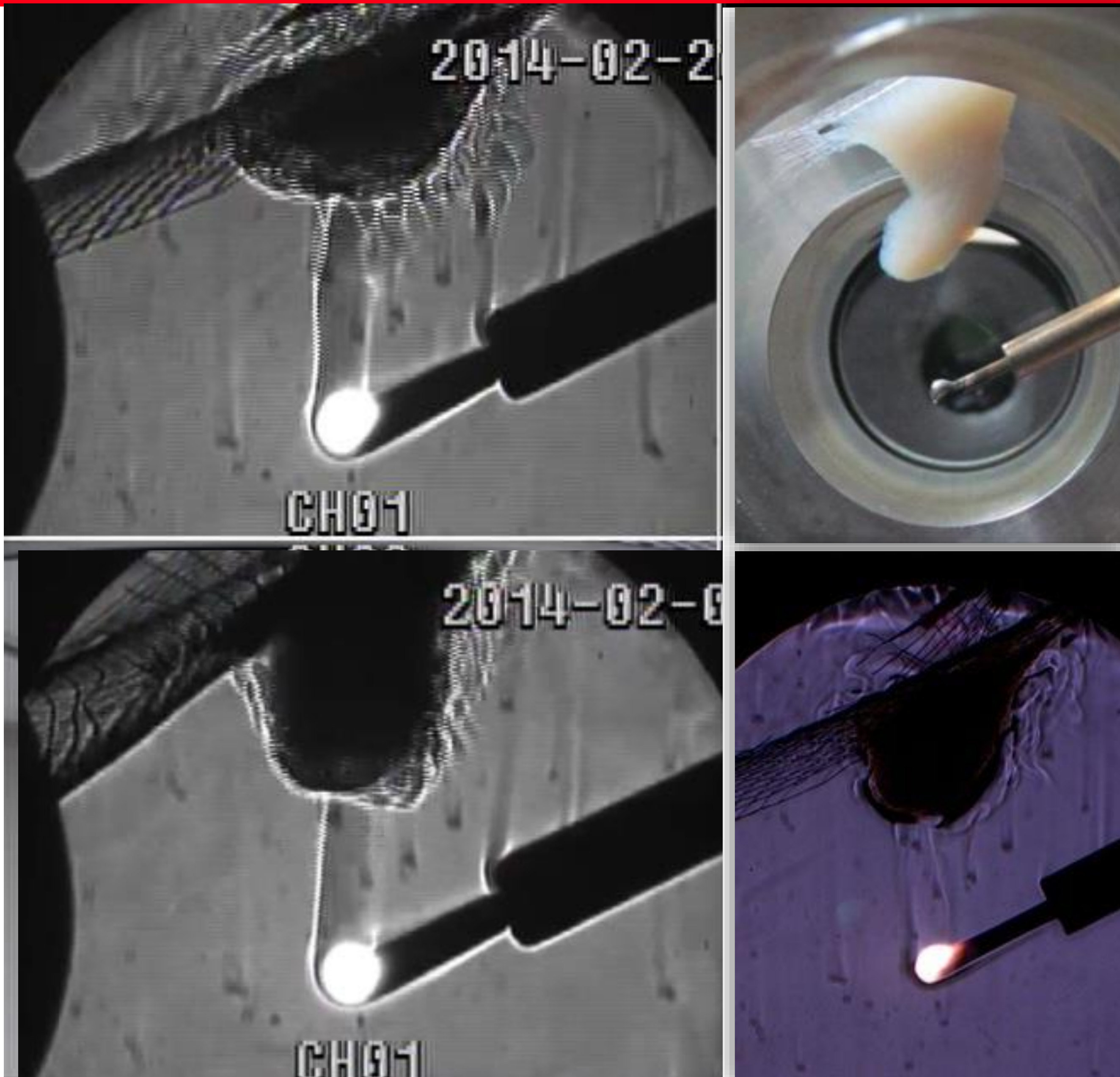
Comp. Mater. Sci., **135** 29 (2017)

National Institute of Aerospace (NIA) BNNT Science Chamber



All images credit: NASA/NIA

NIA Science Rig HTP BNNT Run (Snapshots)



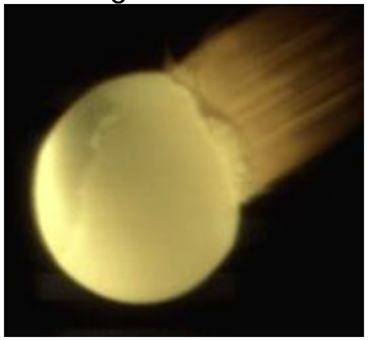
All images credit: NASA/NIA

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

In-situ Optical Diagnostics

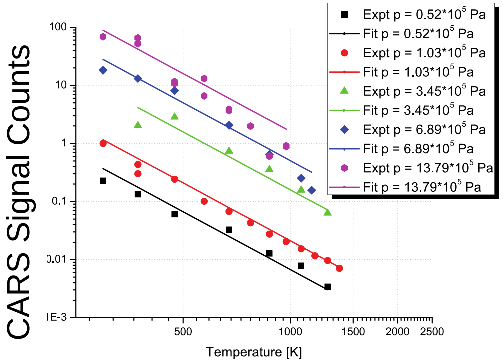
- Understand chemistry and flow physics of nanotube generation
- Improve and validate simulation/modeling
- Optimize material properties, production rate
- Specific Goals:
  - Determine gas and melt-ball temperatures
  - Determine amount of B_2, B, BN, N and N_2
- In-situ, on-surface measurement:
  - 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

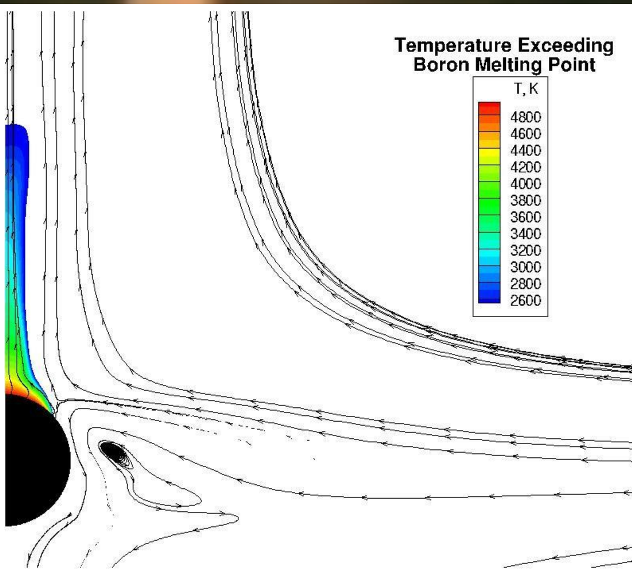


CARS Intensity Measurement

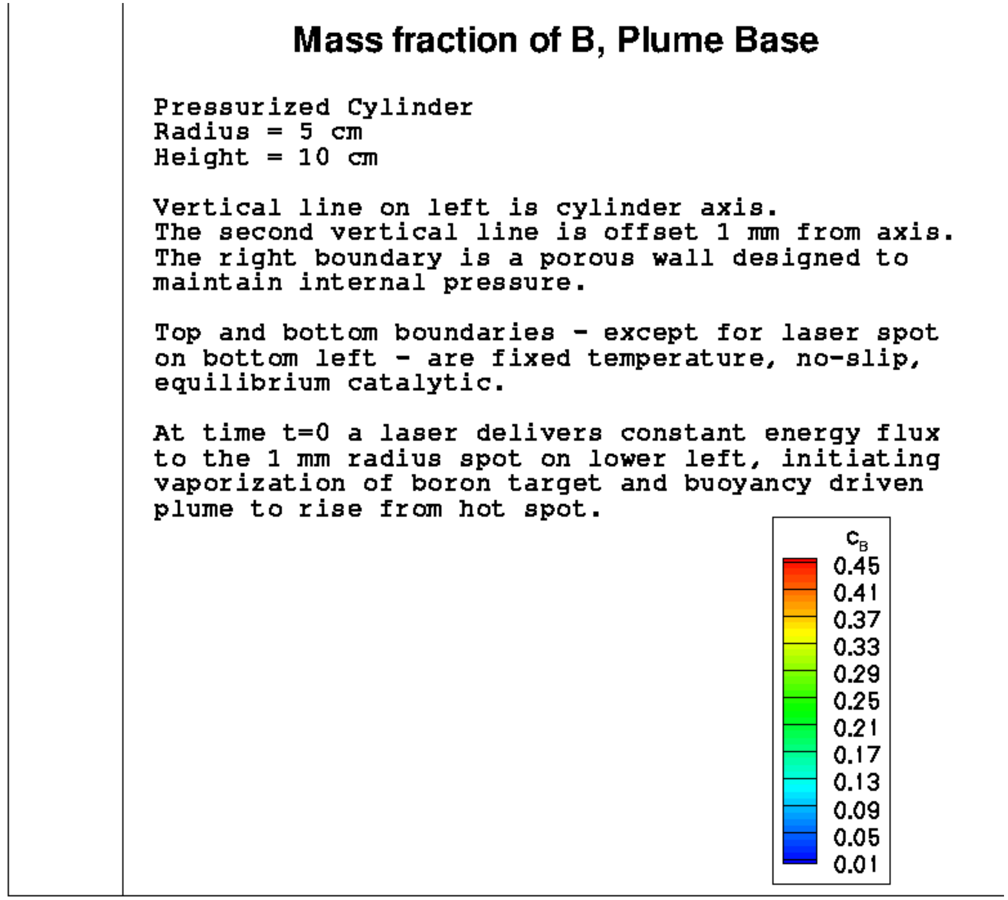
Jennifer Inman, Paul Danehy, Steve Jones, Joe Lee (D304), Andrew Cuttler (GWU)

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

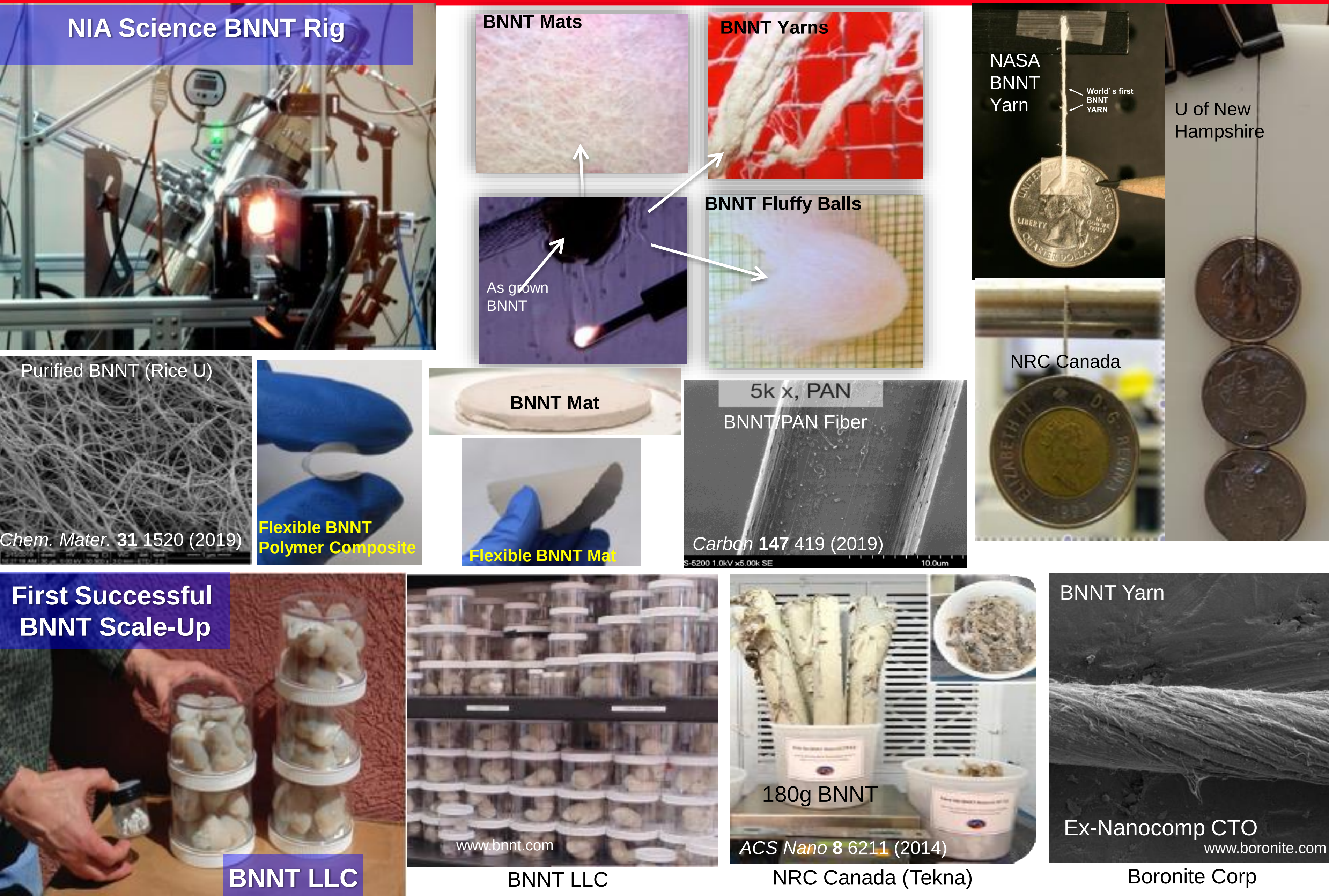


Peter Gnoffo (D305)
Aerothermodynamics Branch
LAURA Code

Proc. SPIE **9060** 906006 (2014)
J. Thermophysics and Heat Transfer **27** 369 (2013)

All images credit: NASA

BNNT Scale-Up and Various Forms of BNNT



Dispersion and Purification

Thermodynamic Approach: Effective BNNT Dispersion

Essential for Quality Yarn, Fabric, and Composite Formation

Thermodynamic Approach:
Gibbs Free Energy of Mixing

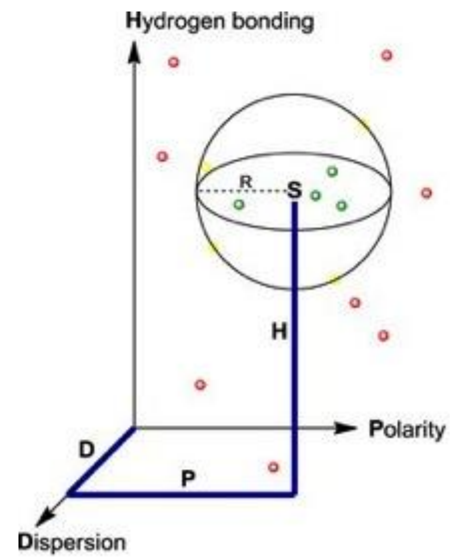
$$\Delta G_{mix} = \Delta H_{mix} - T^*\Delta S_{mix}$$

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

Hansen Solubility Parameters (HSP)
($\delta_d, \delta_p, \delta_h$): "like dissolves like"

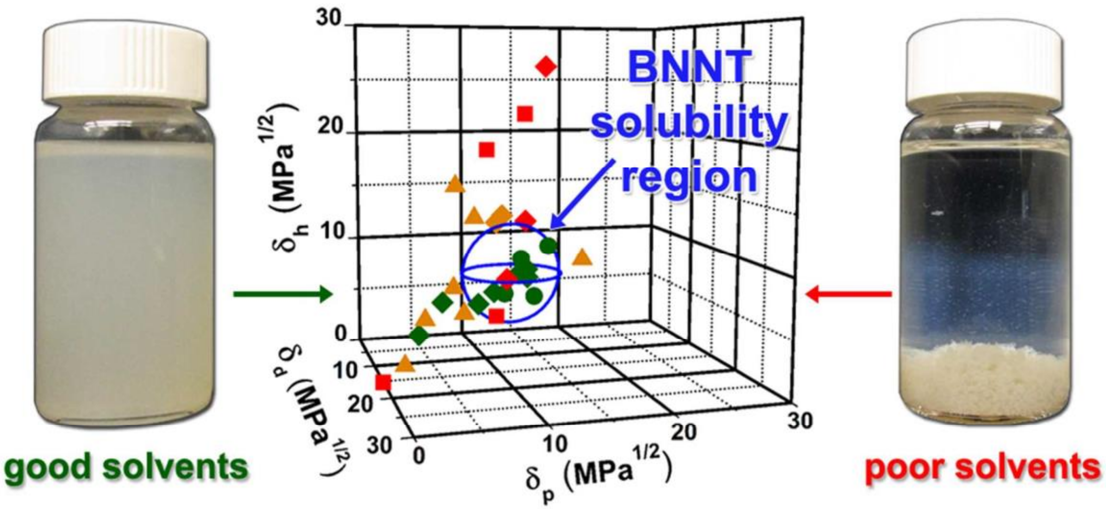
$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$$

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



Example of 3D Hansen space*

Single and Co-solvents



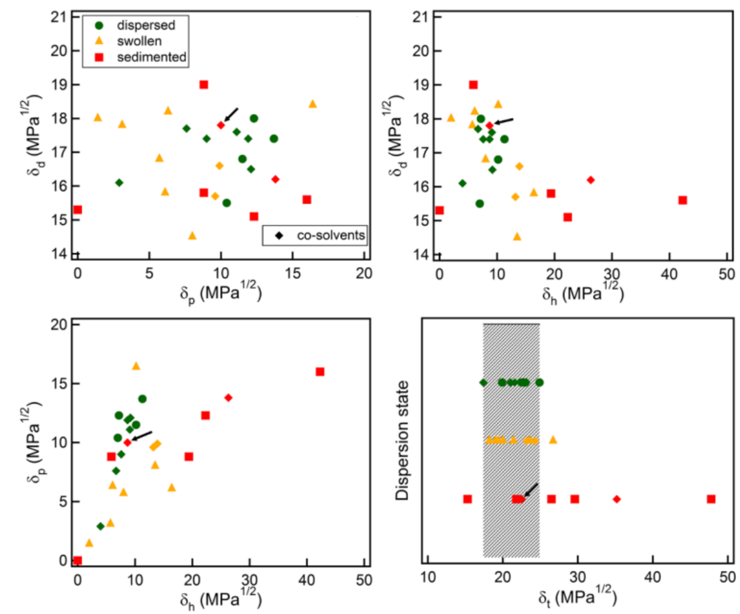
BNNT Hansen Solubility Parameters
$\delta_d, \delta_p, \delta_h$ = 16.8, 10.7, 9.0 MPa$^{1/2}$
δ_t = 21.8 MPa$^{1/2}$

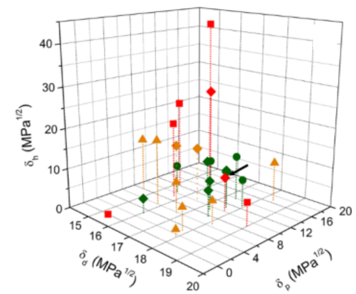
Nanoscale **8** 4348 (2016)

*http://confidentsolventselection.com/about/solubility-parameters.html

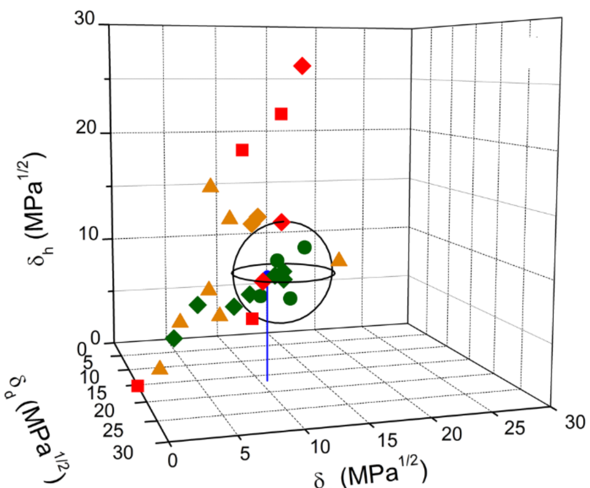
Dispersion: Dispersion State of Single and Co-solvents

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

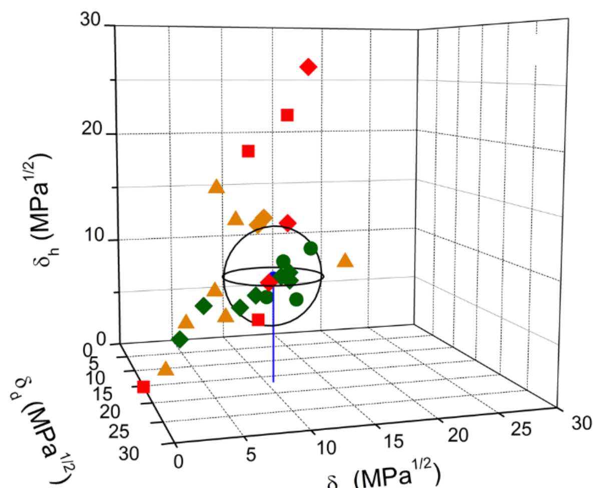




Single Solvent Sphere



Co-solvent Sphere

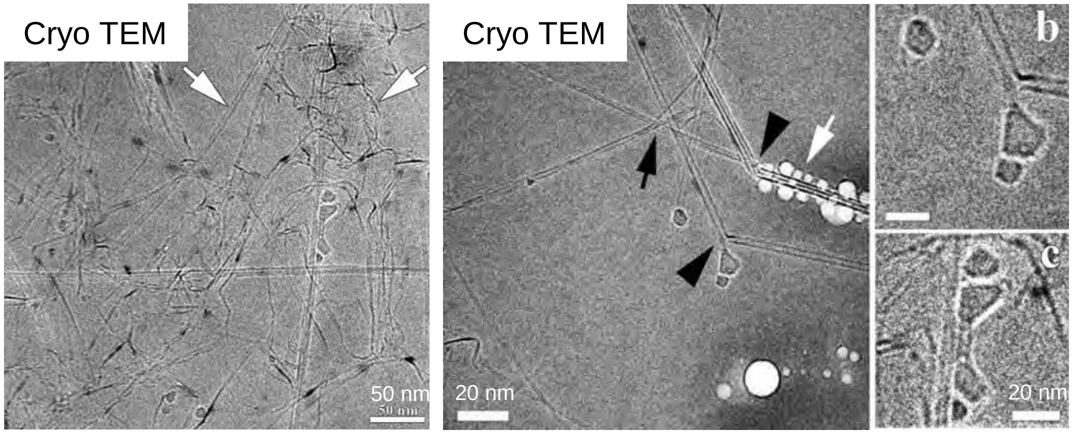


BNNT HSP
δ_d, δ_p, δ_h = 16.8, 10.7, 9.0 $MPa^{1/2}$
δ_t = 21.8 $MPa^{1/2}$

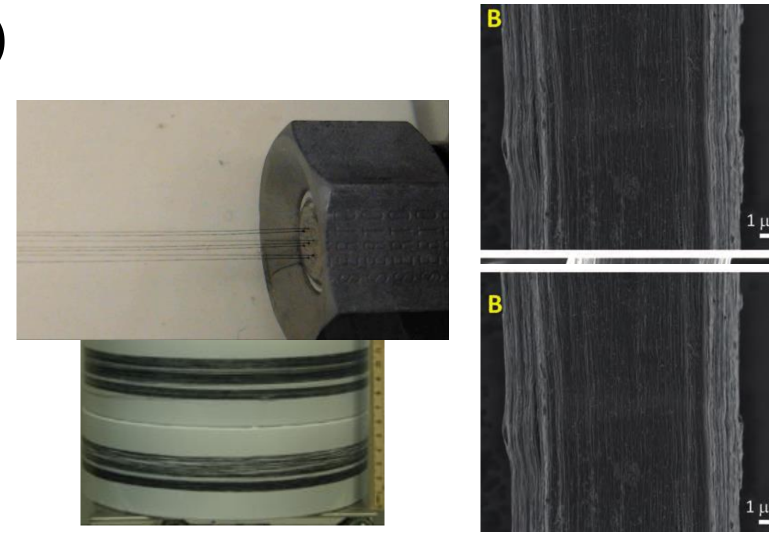
Nanoscale **8** 4348 (2016)

Dispersion and Purification

Dispersion in a Superacid (Chlorosulfuric acid)



BNNT in Chlorosulfuric acid (HSO_3Cl)

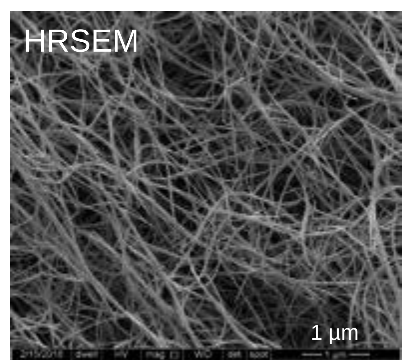


Rice U Nanotube Spinning (*Science* **339** 182 (2013))

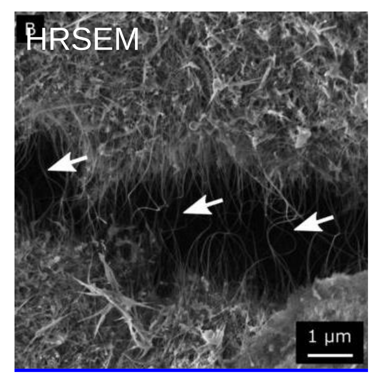
Purification: Wet Thermal Oxidation

As grown BNNT

Purified BNNT



Purified BNNT



BNNT Film (superacid)

Flexible BNNT Mat

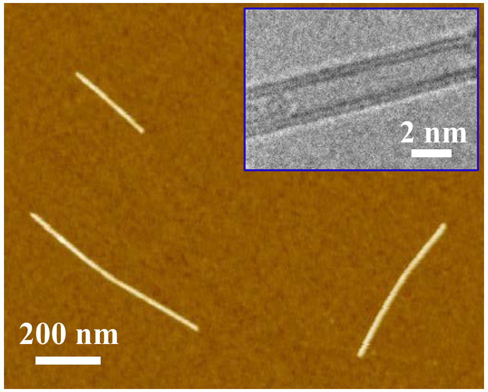
Credit: Prof Pasquali Group at Rice University

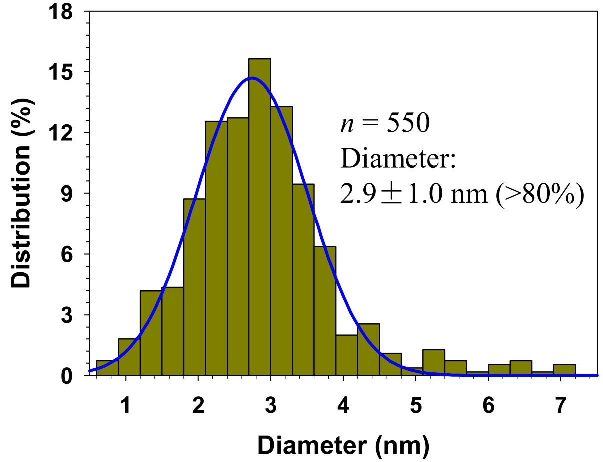
Langmuir **33** 14340 (2017), *Nano Lett* **18** 1615 (2018), *Chem. Mater.* **31** 1520 (2019)

Mechanical and Thermal Properties

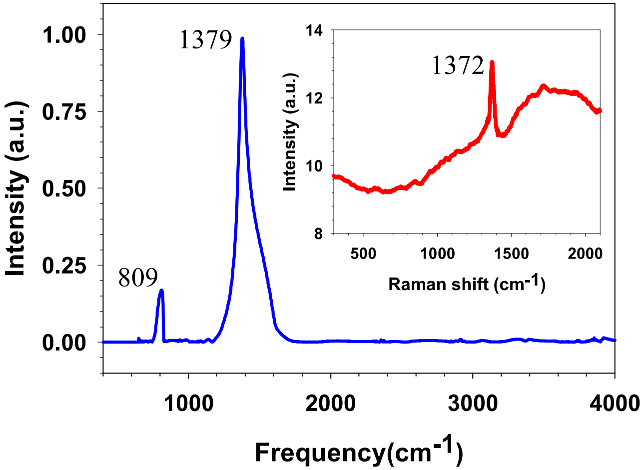
In-situ Single BNNT Test inside of an SEM

AFM

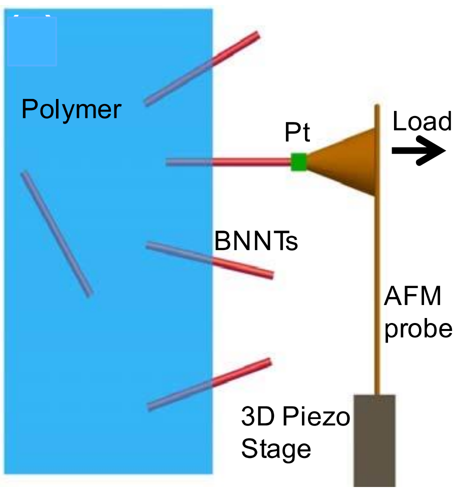




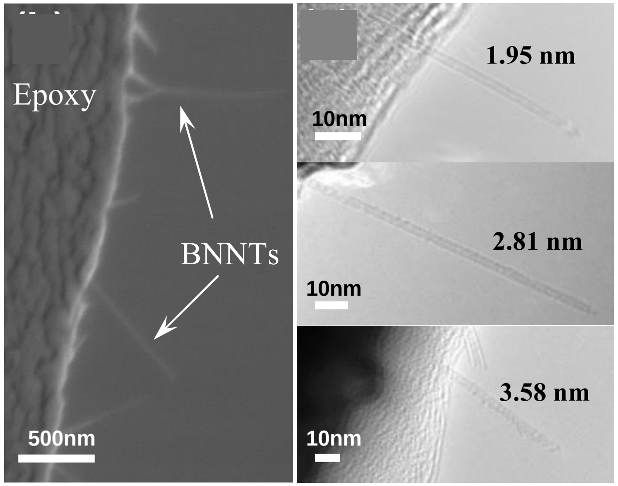
FTIR and Raman



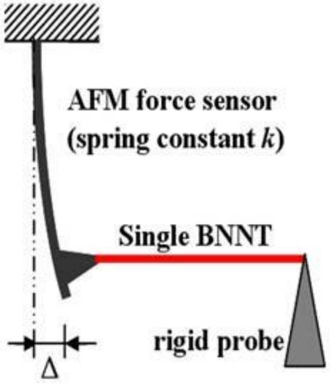
Pull-Out Test

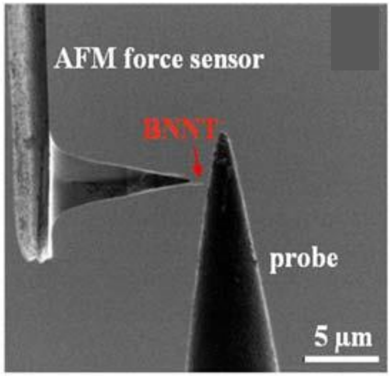


SEM



Tensile Test



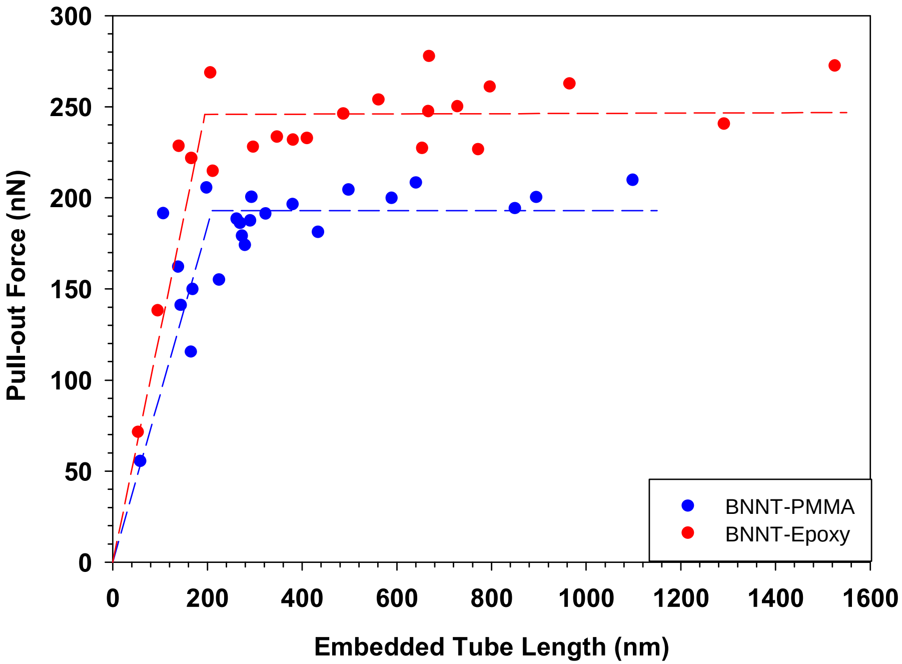


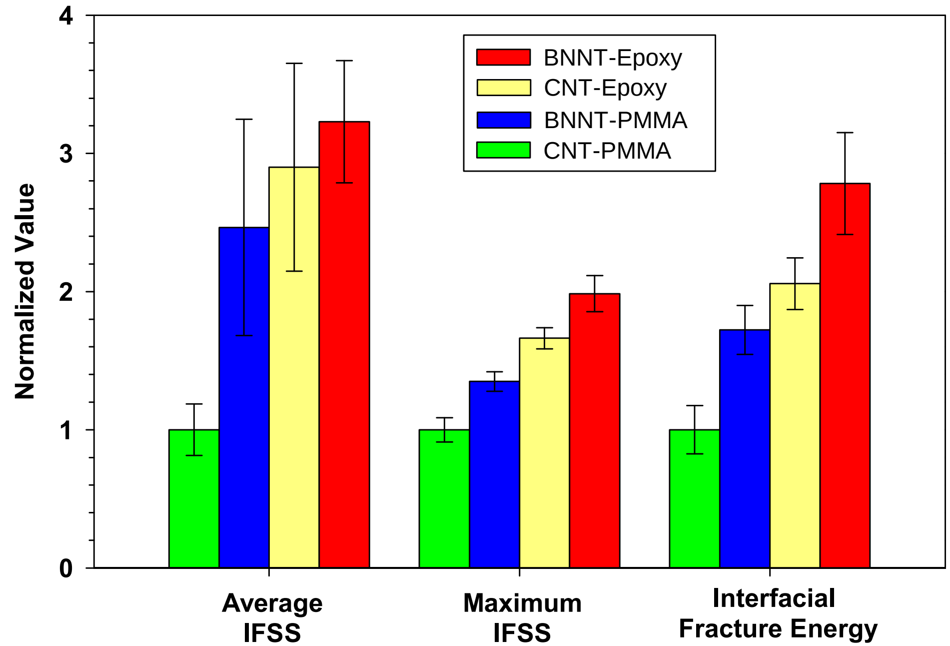
Credit: Prof Ke (SUNY Binghamton)

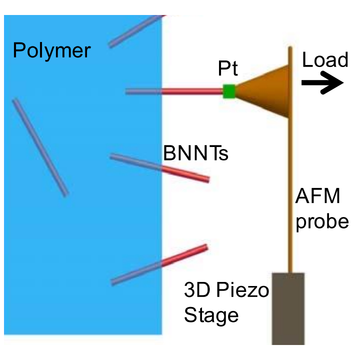
FEI Nanolab 600

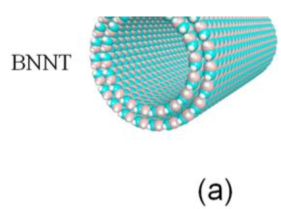
Small **9** 3345 (2013), Carbon **82** 214 (2015), *APL* **107** 253105 (2015)
Carbon **25** 93 (2017), *Carbon* **132** 548 (2018)

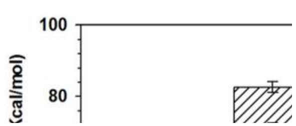
Interfacial Strength: *In-situ* Single Nanotube Pull-Out Test

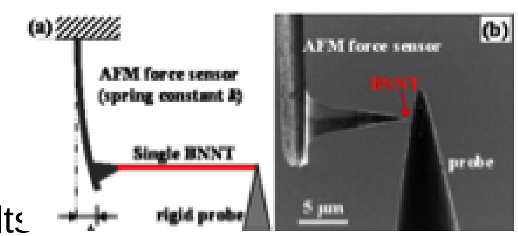












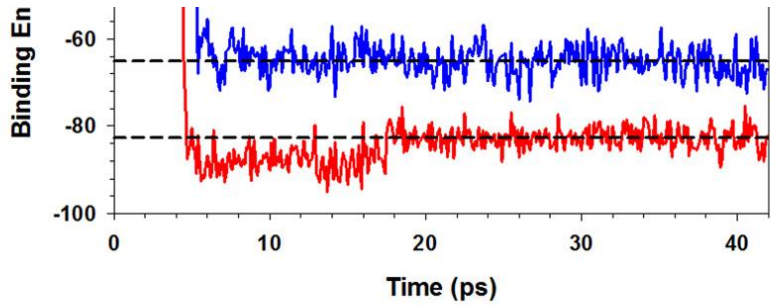
BNNT Tensile Test Results

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

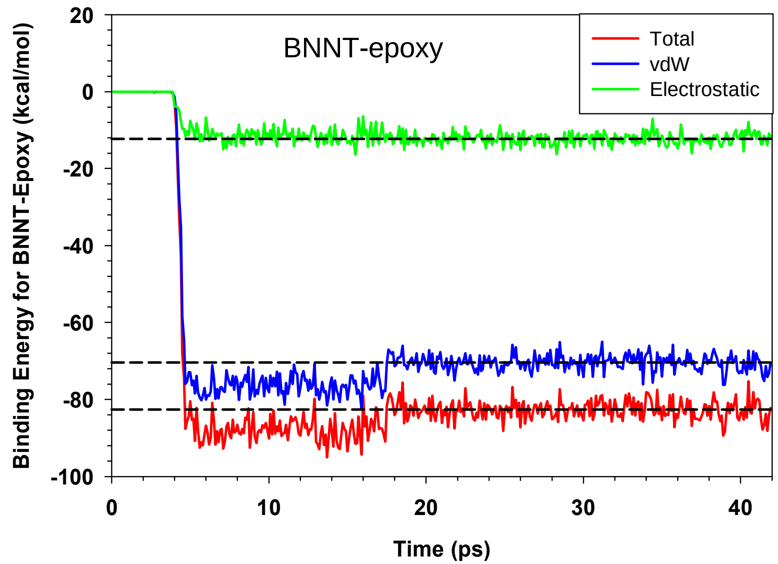
Small **9** 3345 (2013), Carbon **82** 214 (2015), *APL* **107** 253105 (2015)

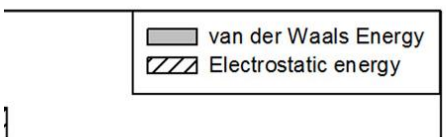
Credit: Prof Ke (SUNY Binghamton)

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



(b)



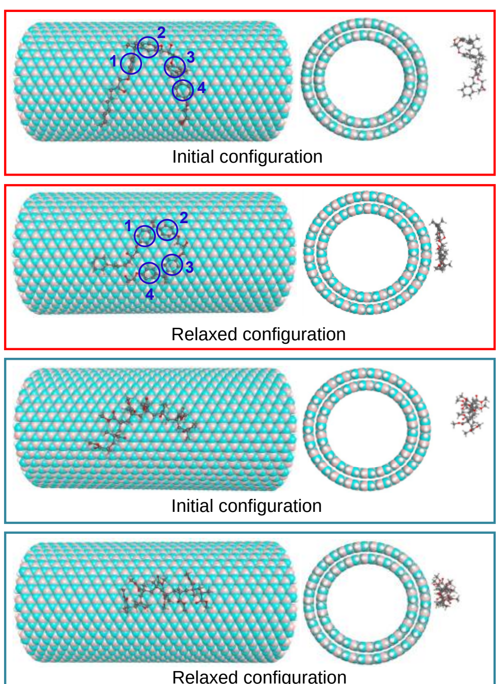


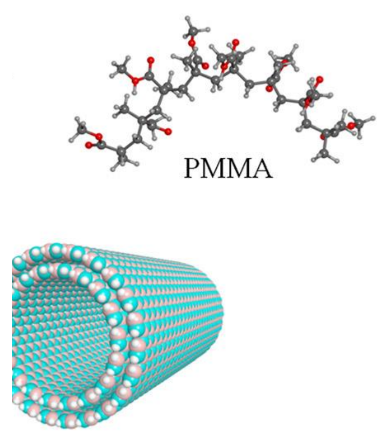
BNNT/Epoxy

BNNT/Epoxy

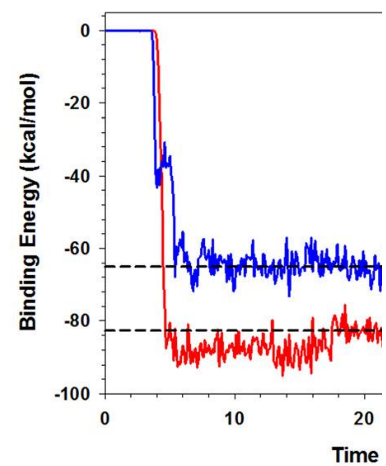
BNNT/PMMA

BNNT/PMMA





(a)

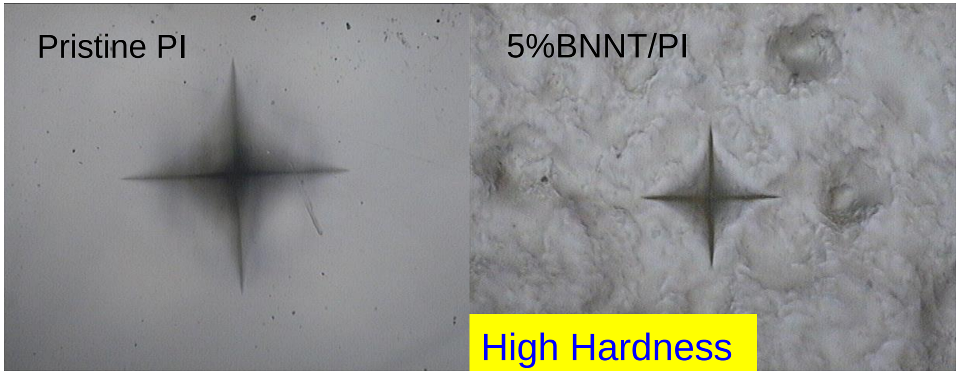


(b

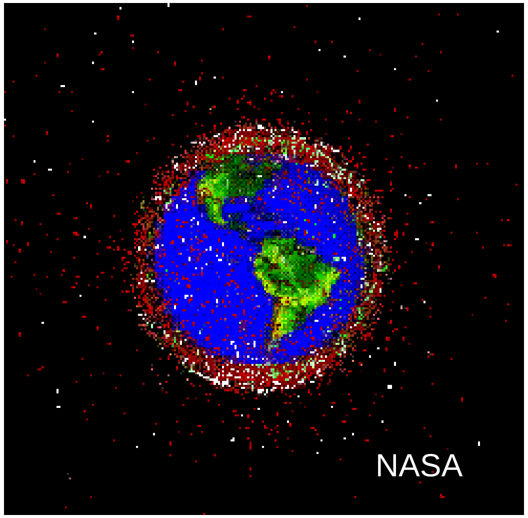
Credit: Prof Ke (SUNY Binghamton)

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

High Velocity Laser Induced Micro-Bullet Impact Test: BNNT Nonwoven Mat (Micro-Ballistics)

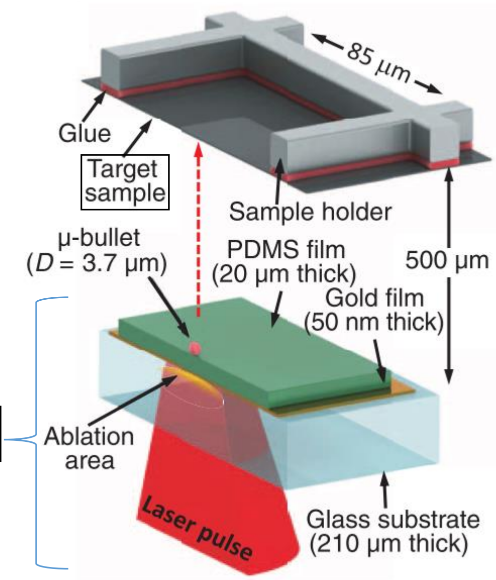


Simulated Micrometeorite Impact Test

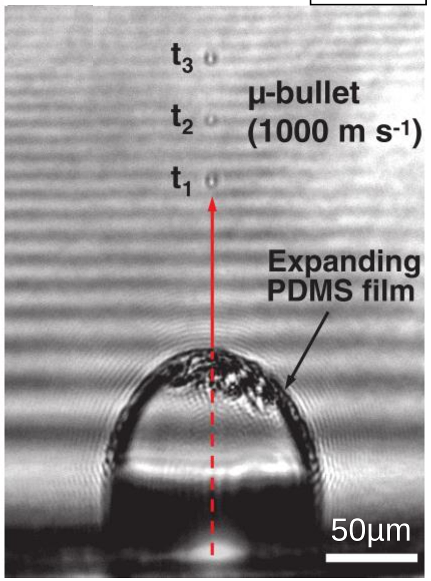


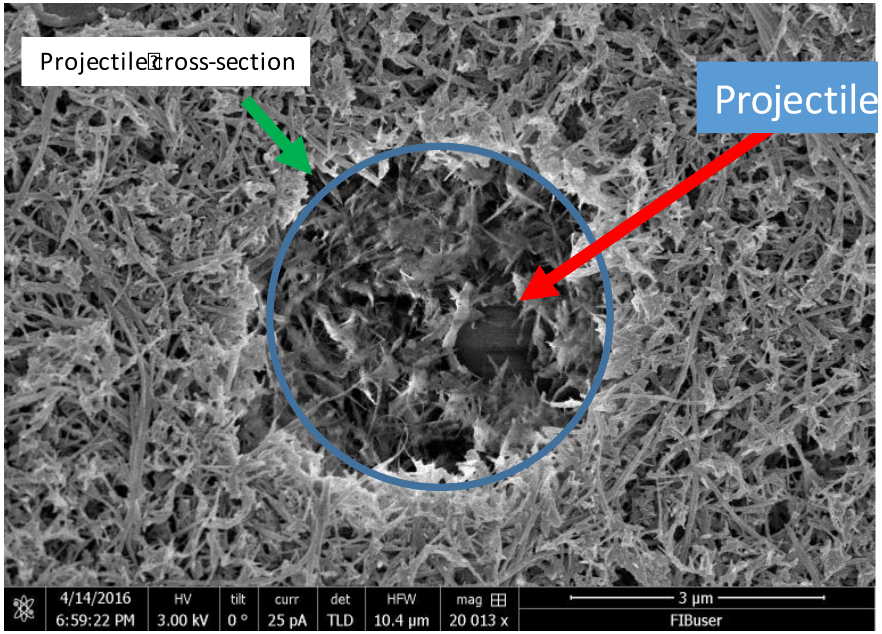
Ballistic Velocities: 100-1500 m/s

Laser Induced Projectile Impact Test (LIPIT)



Imaging Technique

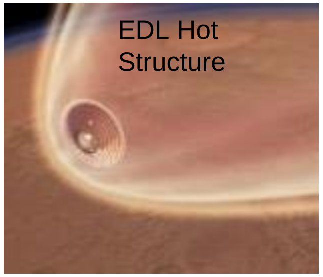


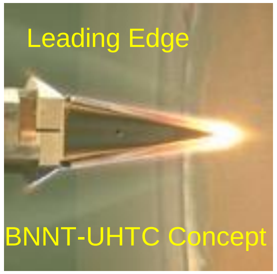


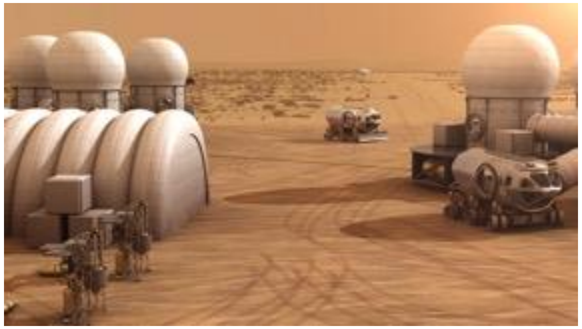
Lee, J.-H et. al. *Science* 346, 1092 (2014)

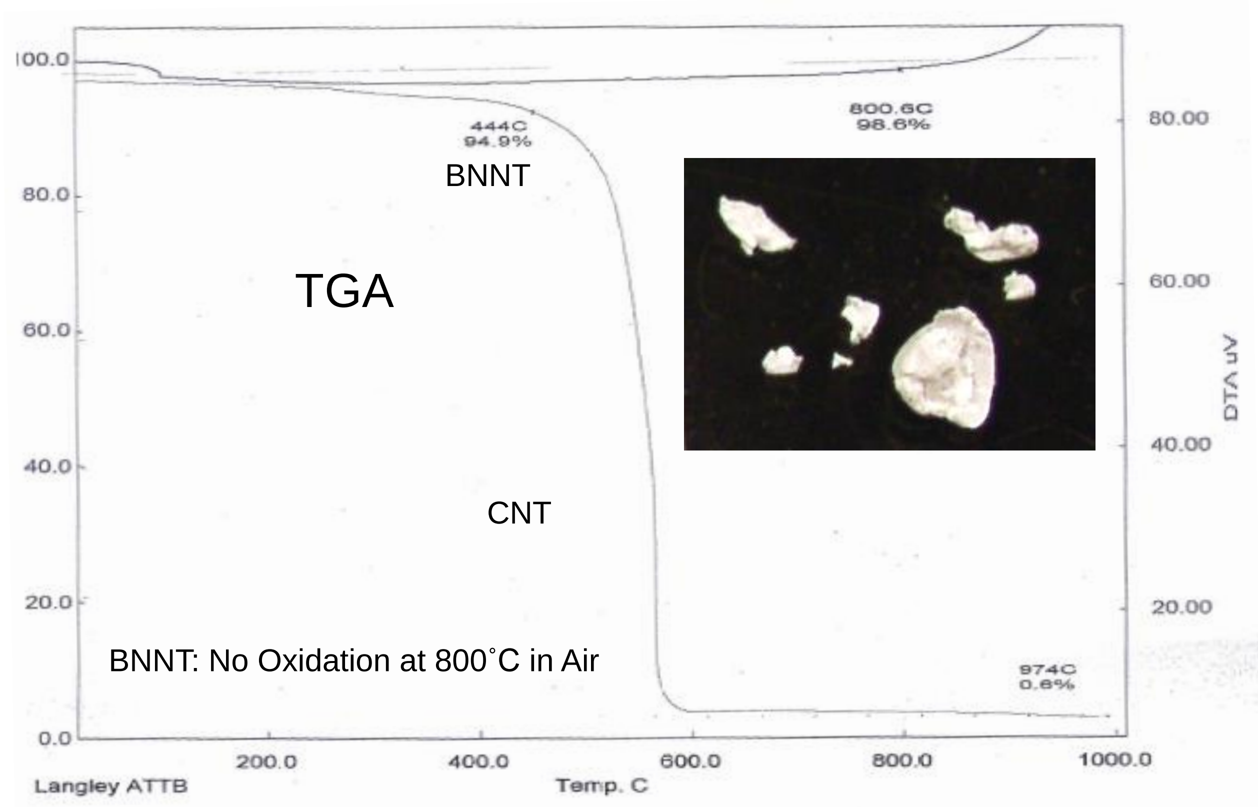
Rice University: Prof Ned Thomas group

Thermal Properties of BNNT









Nanotechnology, **20** 505604 (2009)

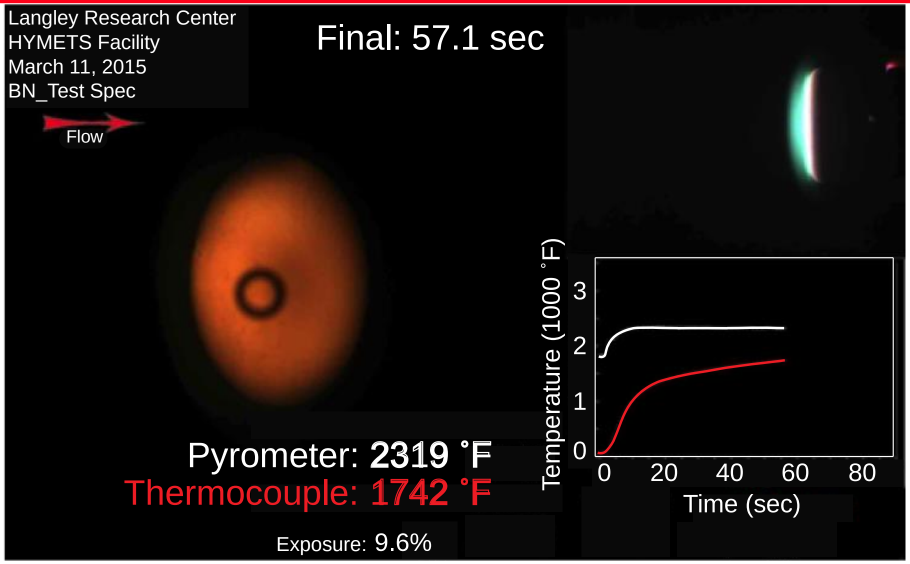
Hypersonic Materials Experiment Test System (HYMETS)

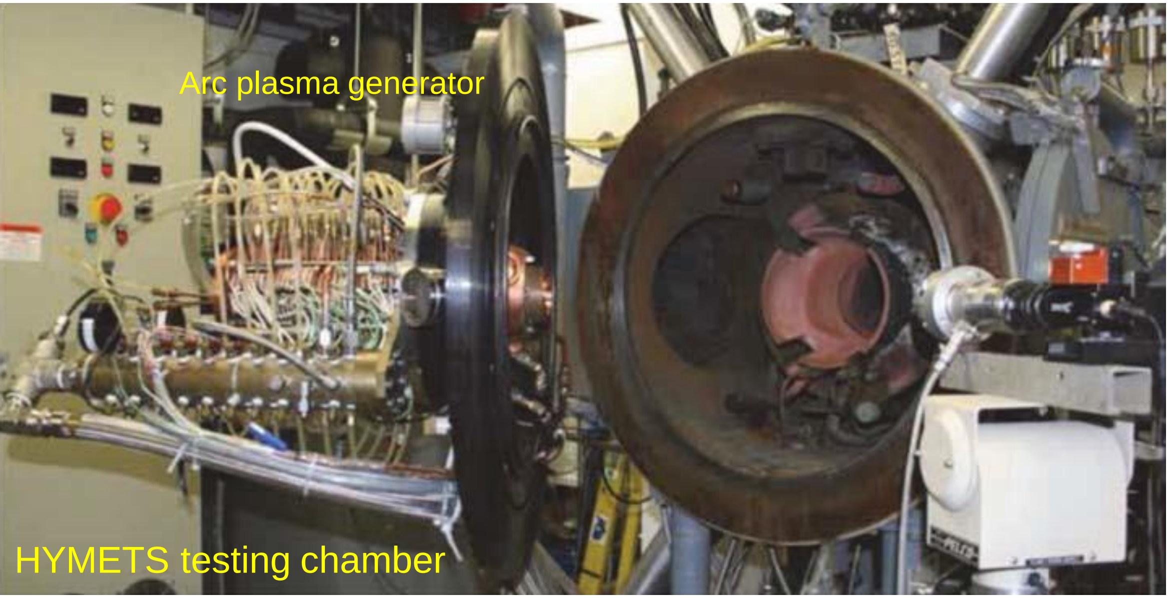
LaRC HYMETS Test Conditions

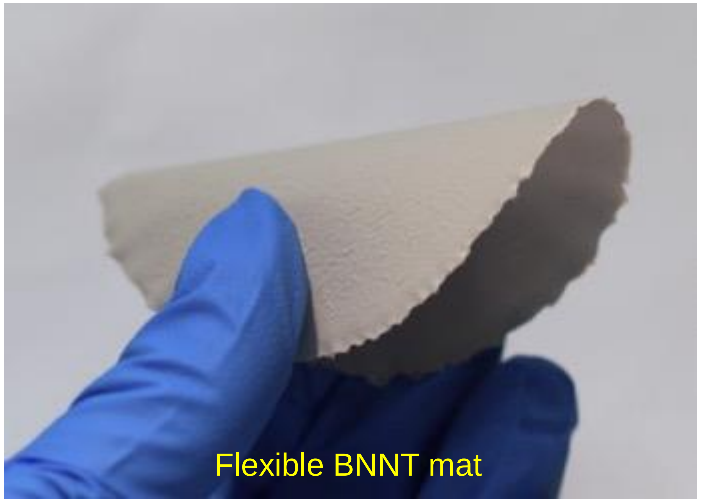
- Specimen Surface Temperature (ºC): 1260-2482
- Specimen Stagnation Pressure (atm): 0.013-0.079
- Free Stream Mach Number: 5.0
- Free Stream Enthalpy (kJ/kg): 5350-26749

HYMETS TEST for BNNT Mats

- Heat flux: Set at **50 W/cm²** (2nd Gen Mars EDL)
- Duration: 1 min - 5 min
- Atmosphere: Air (with 5% Ar)
- Cooled under Vacuum







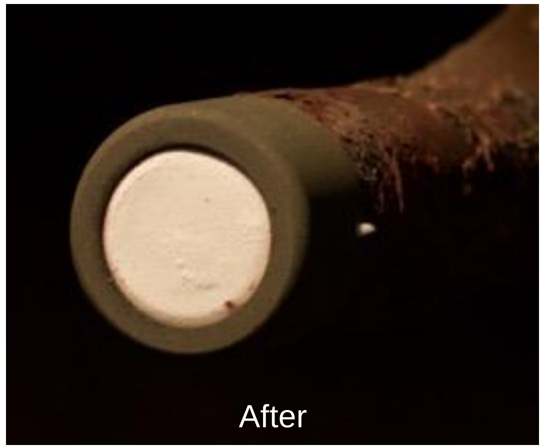
All images credit: NASA

Collaborators: Scott Splinter, Jeff Gragg, Kamran Daryabeigi (AIAA, 2011)

Hypersonic Materials Experiment Test System (HYMETS)

Sample: BNNT Mat (as grown, nonwoven)

- Fabricated by a vacuum filtration process
- Diameter: 25 mm, Thickness: 2 mm, Density: ~ 0.3 g/cm^3

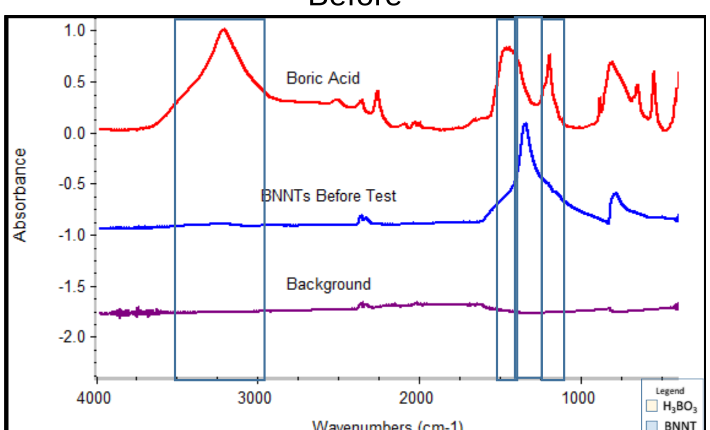


HYMETS Test Conditions

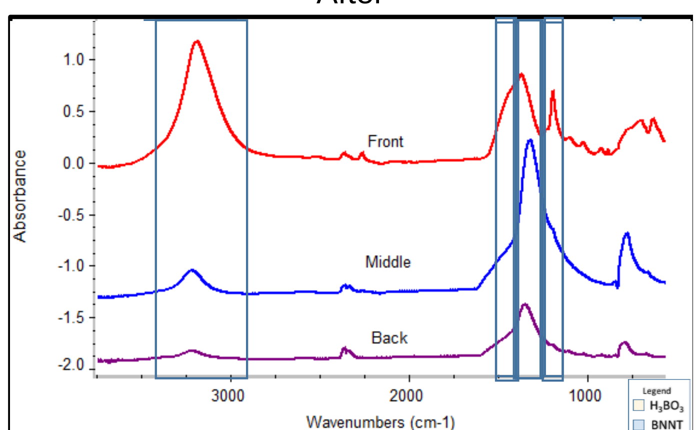
- Test duration: 1 min
- Surface temperature: 2400 ^oF (1315 ^oC)

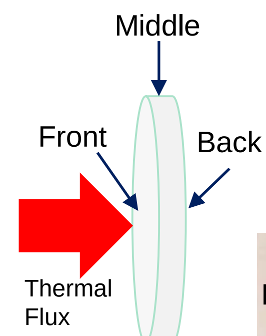
FT-IR Analysis of BNNT mat

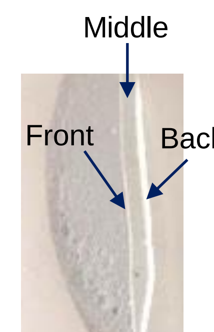
Before



After

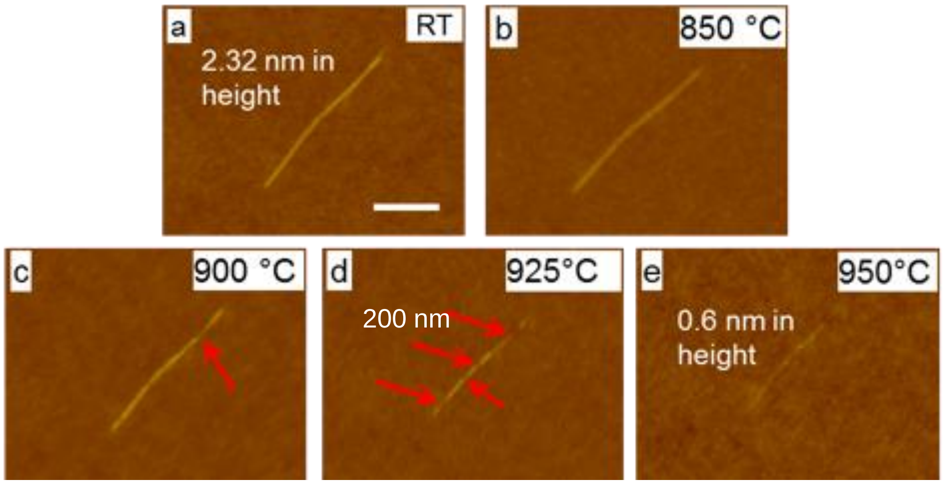




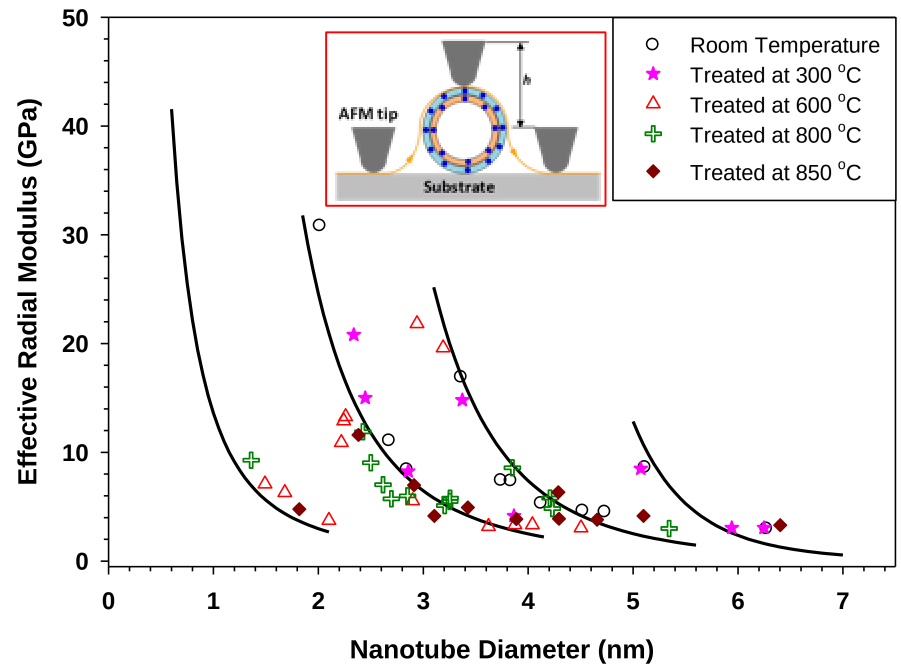


Superior Structural and Mechanical Properties of BNNTs in High Temperature Environments

Credit: Binghamton U (Prof. Ke)



AFM studies show that individual BNNTs can survive at up to 850 ˚C in air and captures the sign of their structural degradation at 900 ˚C and above. (the red arrows mark the positions of the oxidation-induced tube broken sites).

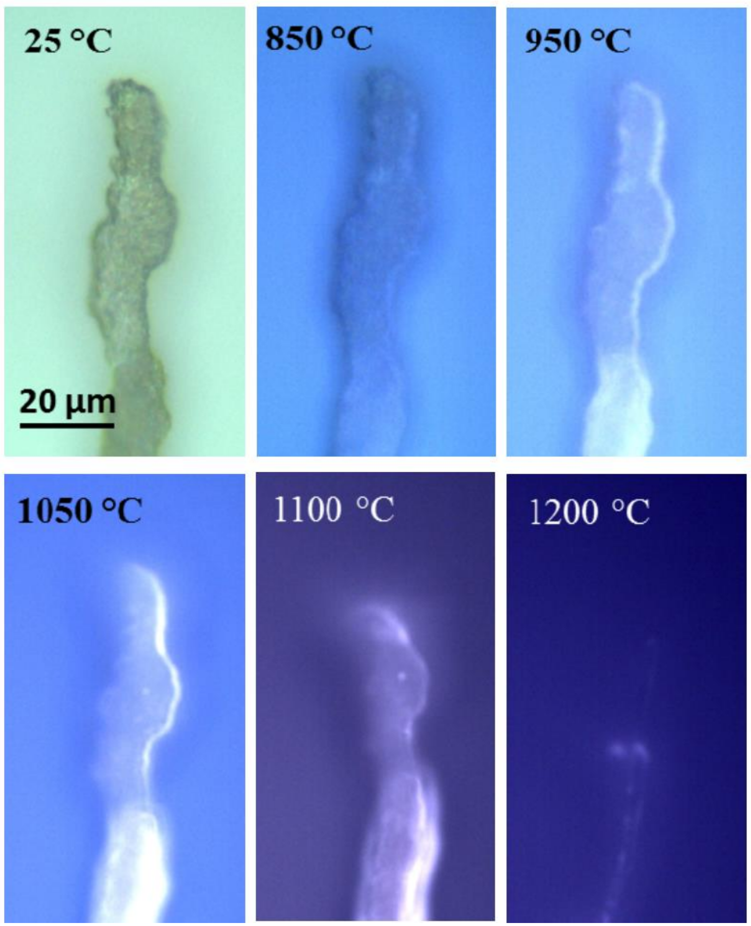


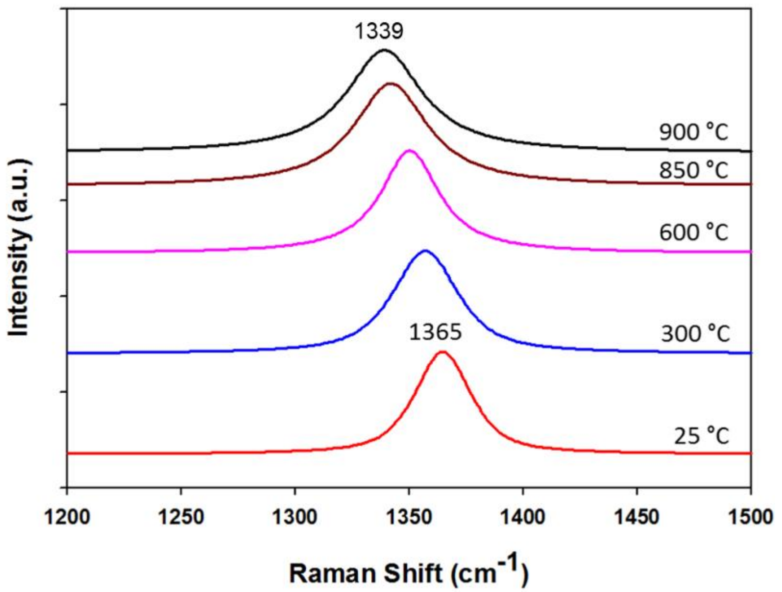
AFM-based nanomechanical compression tests (illustrated in inset drawing) show that the mechanical properties of individual BNNTs remain intact after thermally baked at up to 850 ˚C in air.

Xiaoming Chen, Christopher M Dmuchowski, Cheol Park, Catharine C. Fay and Changhong Ke, "Quantitative Characterization of Structural and Mechanical Properties of Boron Nitride Nanotubes in High Temperature Environments," *Scientific Reports,* **7**, 1138 (2017).

In-situ Optical and Raman Spectroscopy of BNNT

In Air



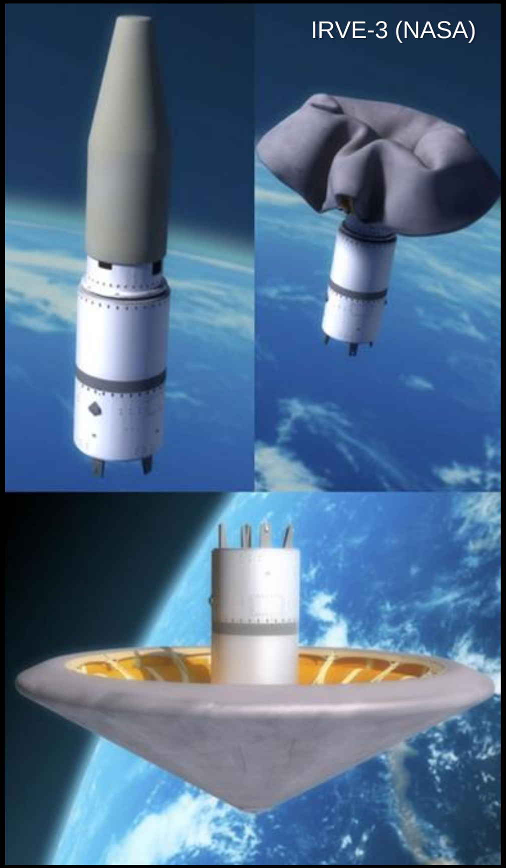


Noticeable structural damage to BNNT occurs at ~1050 ^{o}C in Air

Xiaoming Chen, Christopher M Dmuchowski, Cheol Park, Catharine C. Fay and Changhong Ke, "Quantitative Characterization of Structural and Mechanical Properties of Boron Nitride Nanotubes in High Temperature Environments," *Scientific Reports,* **7**, 1138 (2017).

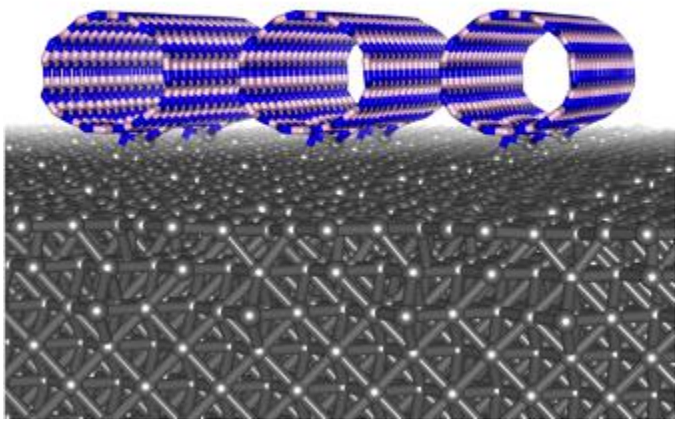
NASA Missions for Extreme Environment

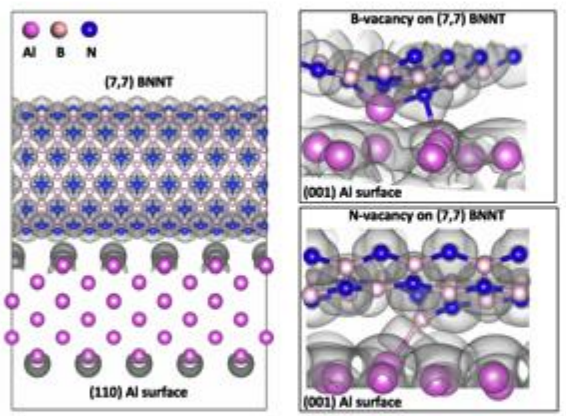
- Ultralight, flexible, shielding materials for extreme environment conditions (thermal, mechanical, chemical, and radiation)
- NASA applications:
  - Materials for space vehicles and structures.
  - Flexible TPS (FTPS) for hypersonic inflatable aerodynamic decelerator (HIAD).



All image credit: NASA

BNNT Metal Matrix Composite (MMC)



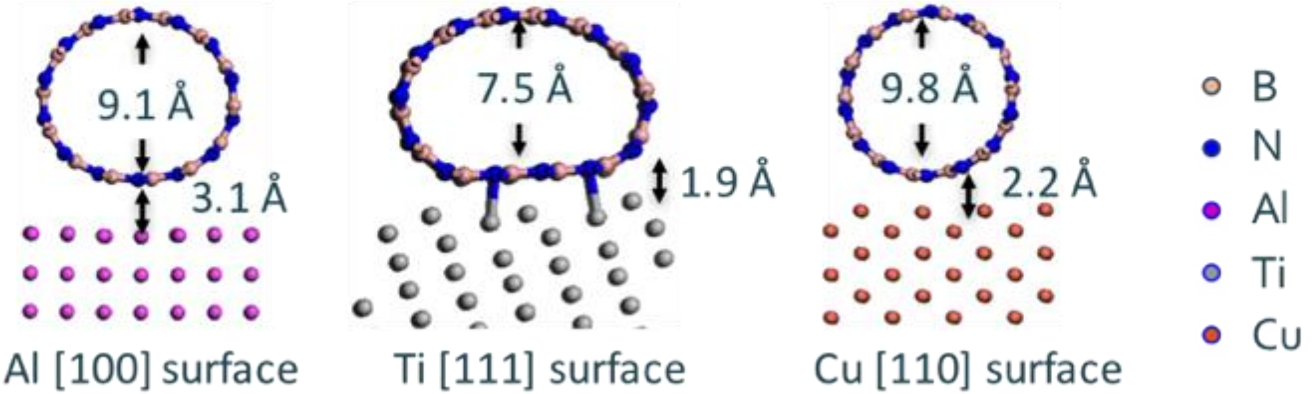


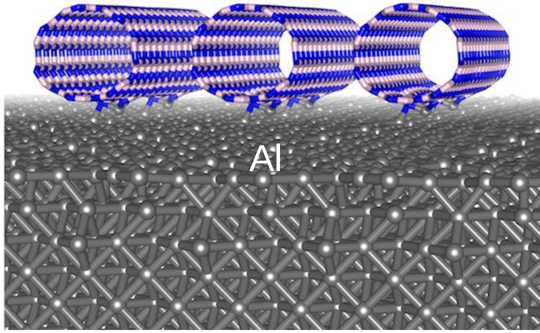
J. Phys. Chem. C **120** 3509 (2016)
J. Phys. Chem. C **122** 15266 (2018)

BNNT Metal Matrix Composite (BNNT-MMC)

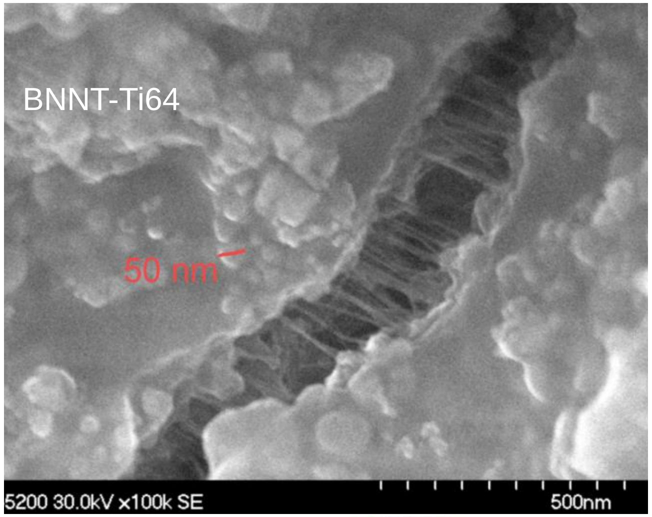
U Queensland: Prof Bernhardt & Dr. Rhomann (AFOSR/AOARD)

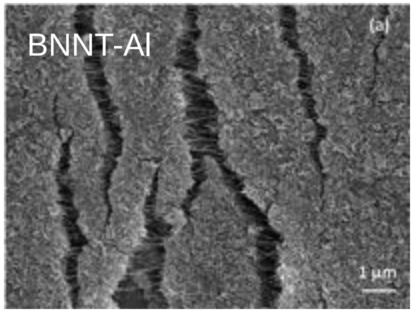
Pristine BNNT (7, 7)

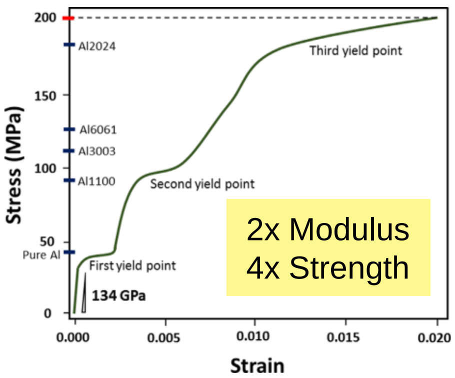


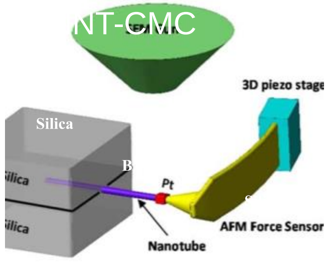


Binding Energies**	Al[100] Surface	Ti[111] Surface	Cu[110] Surface
Pristine	-0.41	-1.77	-0.95
N-vacancy	-0.69	-2.00	-1.23
B-vacancy	-1.26	-3.30	n/a
C sub N	-0.64	-2.17	-1.26
C sub B	-0.51	-1.41	-1.00







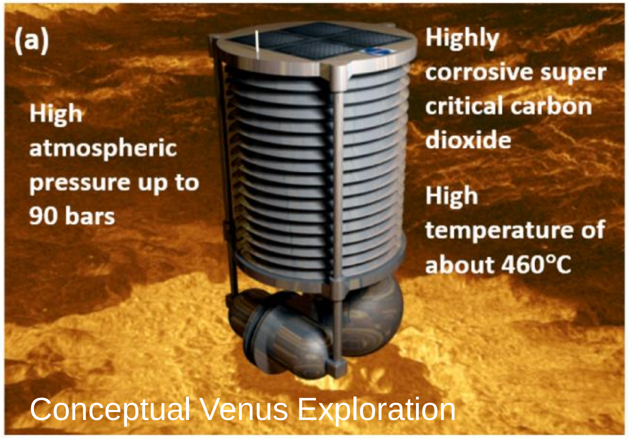


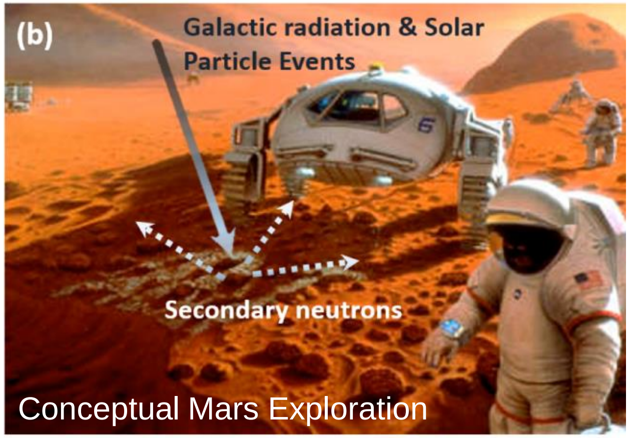
J. Phys. Chem. C **120** 3509 (2016)
J. Phys. Chem. C **122** 15266 (2018)
Nanotechnology, **30** 25706 (2019) BNNT-ceramic interfacial strength
J. Am. Cer. Soc. Early view, BNNT-PDC composite (κ: 2000% increase)

Adv. Eng. Mater. **18** 1747 (2016)
Agarwal Group FIT

Multifunctional BNNT Polymer Composites

- Electroactive Properties
- Radiation Shielding Properties





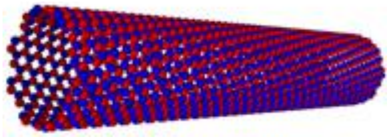
All images credit: NASA

MRS Bulletin **40** 836 (2015)
Comp. Mater. Sci., **95** 362 (2014)
ACS Nano **9** 11942 (2015)

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, large diameter tubes)
- BNNT (high pressure, high temp, CO_2 laser as grown)



Alignment (stretched)
No alignment (unstretched) and stretched (up to 100%)

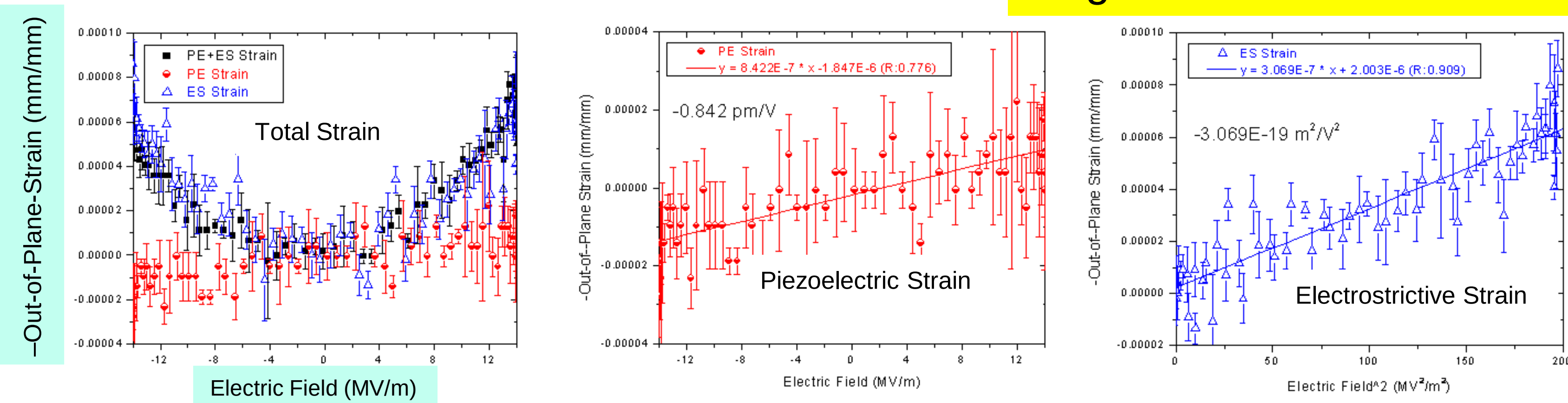
Polyimide (CP2)
Polyimide (bCNAO)
Polyimide (bCNAM) (unstretched and stretched 100%)
5wt%hBN/polyimide (stretched 110%)
5wt%BNNT(CVD)/polyimide
2wt%BNNT(laser)/polyimide (unstretched and stretched 100%)

ACS Nano **9** 11942 (2015)

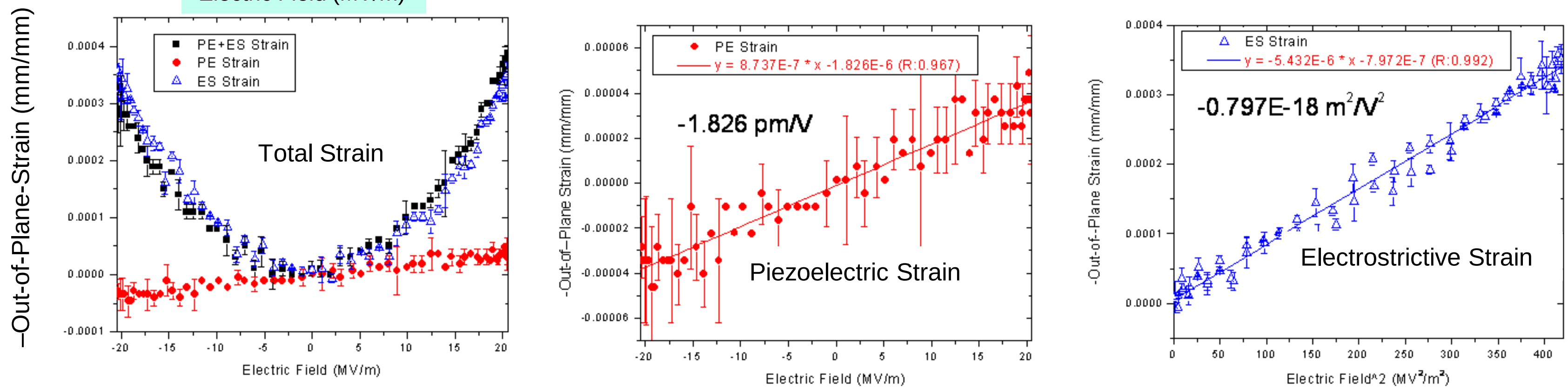
Actuation of Unstretched/Stretched 2% BNNT/Polyimide

Origin of Actuation → BNNT

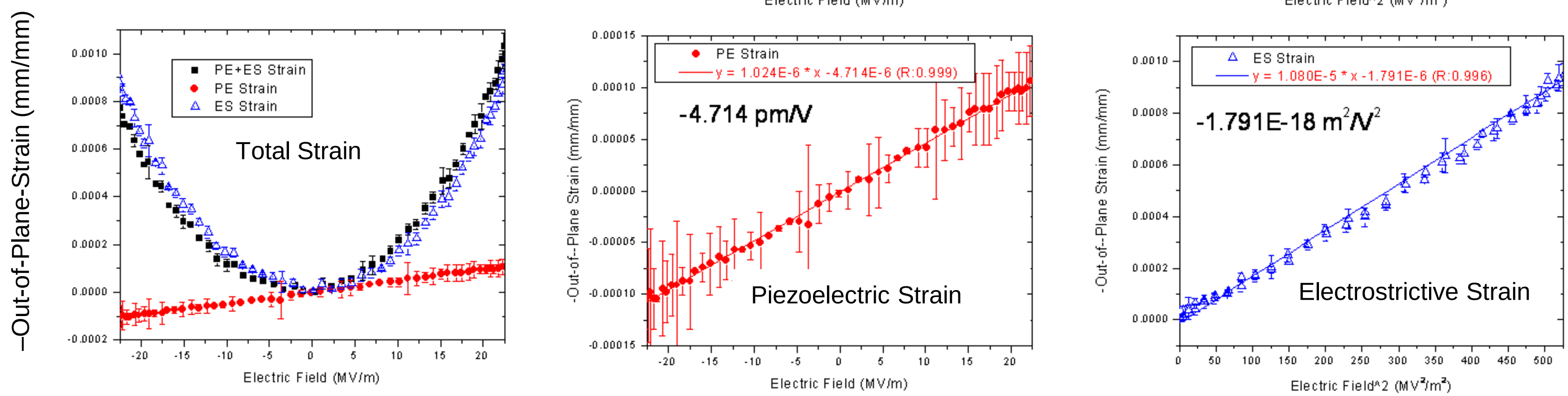
Unstretched



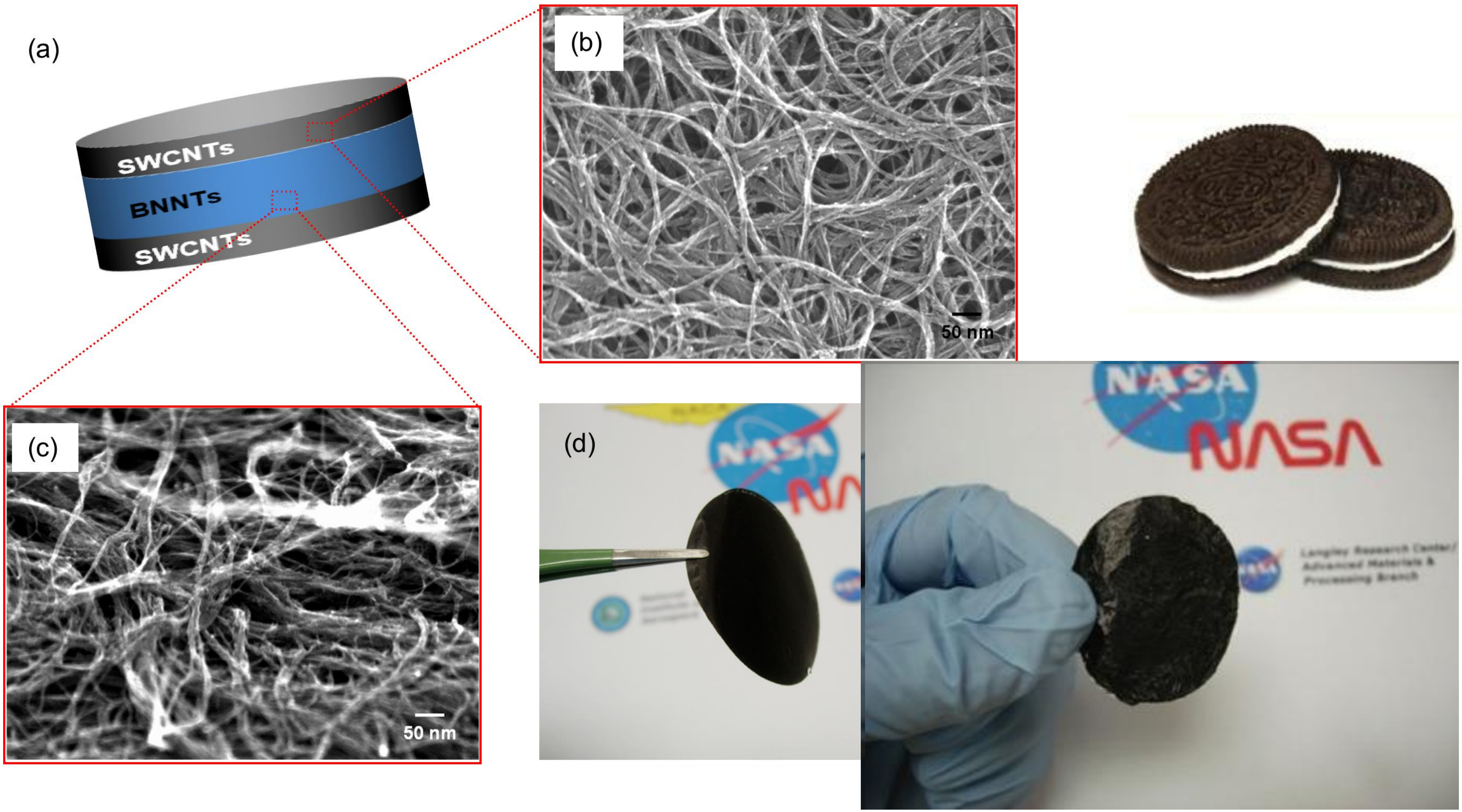
100% Stretched @225ºC, Quenching



100% Stretched @225ºC, Annealing



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

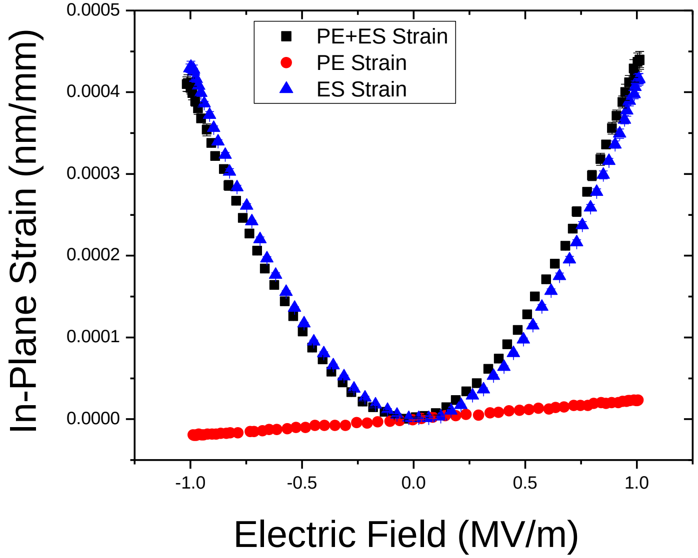


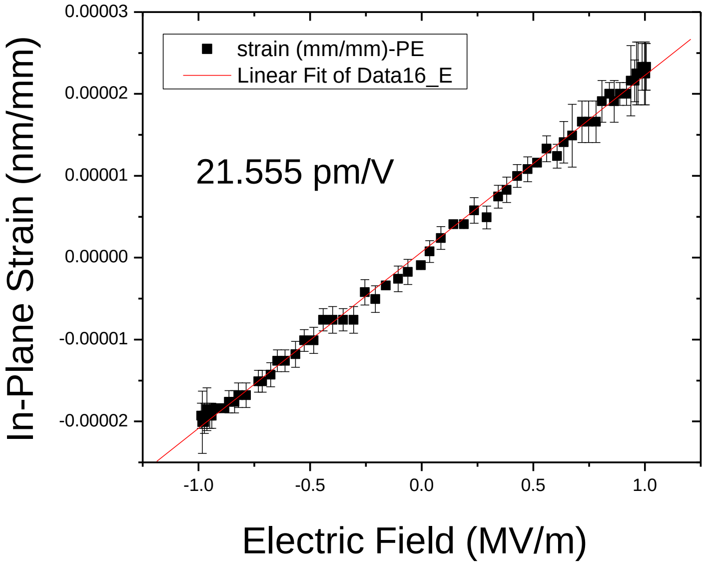
Goal: Flexible, transparent, large actuation, high sensitivity, mechanically durable

All images credit: NASA

ACS Nano **9** 11942 (2015)

All-Nanotubes Actuator/Sensor Film: In-Plane Strain

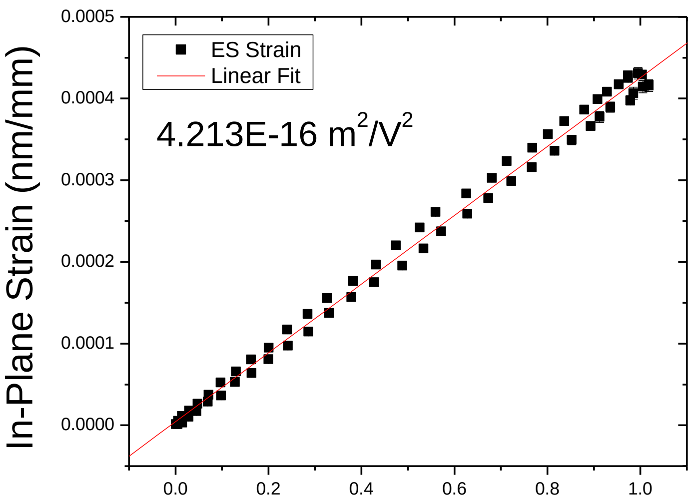




Field induced strain (ε_{33})

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

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

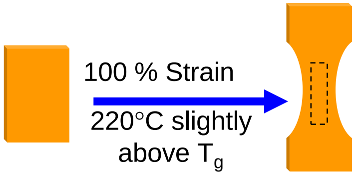


ACS Nano **9** 11942 (2015)

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	✓✓✓✓✓✓✓✓✓✓✓✓

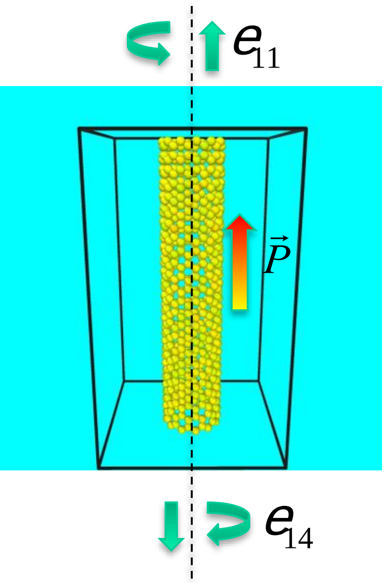
h-BN → No Actuation
Commercial BNNT (CVD) → No Actuation
Polymer → No Actuation
Stretched Polymer → No Actuation
BNNT (high pressure, high temp laser) → Origin of the Actuation



All images credit: NASA

Results: Piezoelectricity under Deformation

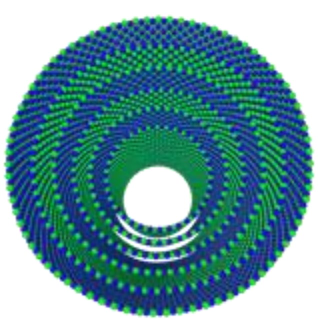
The Molecular Dynamics (MD) model is successful in representing the piezoelectric properties of BNNTs

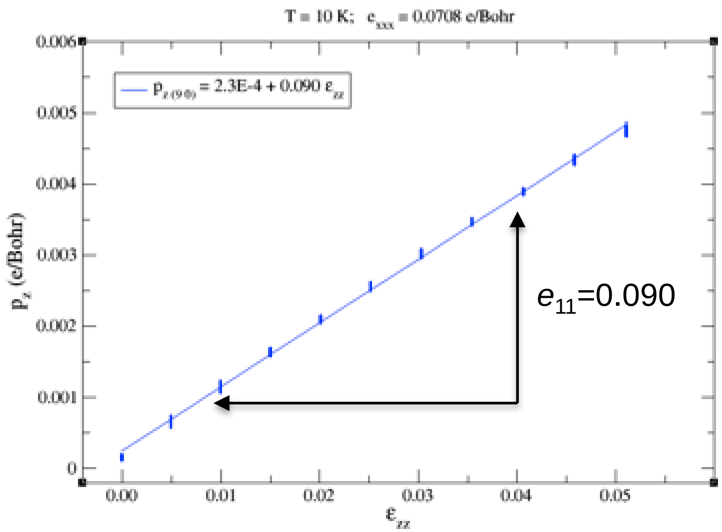


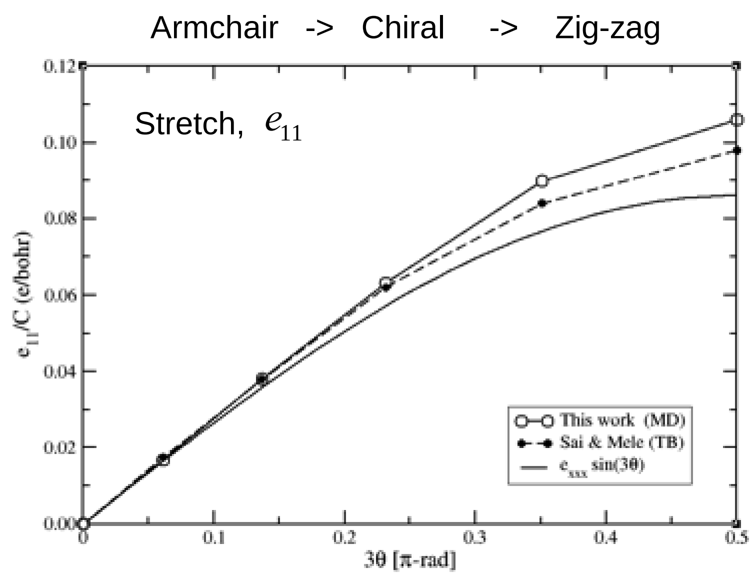
$p_z(stretch) = e_{11} e_s$

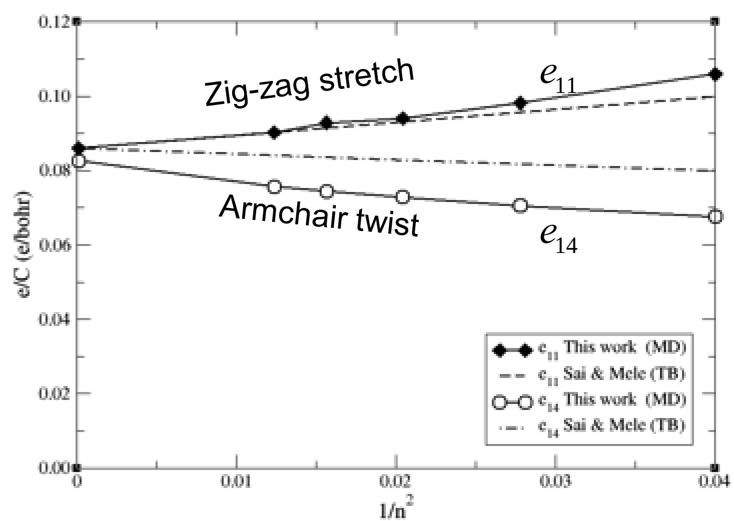
$p_z(twist) = e_{14} e_t$

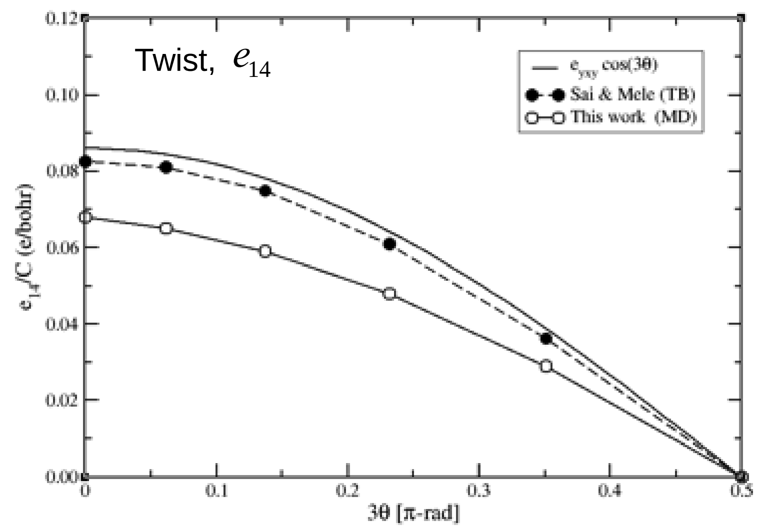
MWBNNT











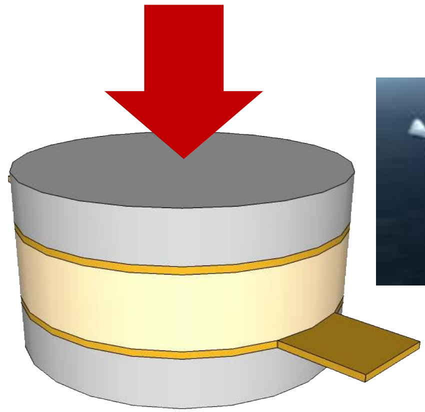
Comp. Mater. Sci., **135** 29 (2017)

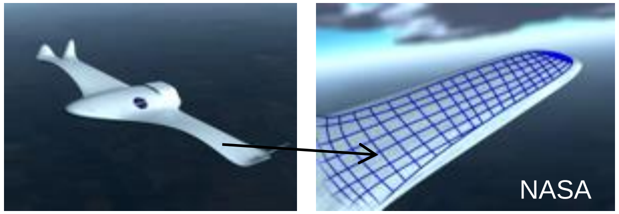
Comp. Mater. Sci., **95** 362 (2014)

2D Printed Electronics as Sensory Applications: BNNT Composites Capacitive Sensors

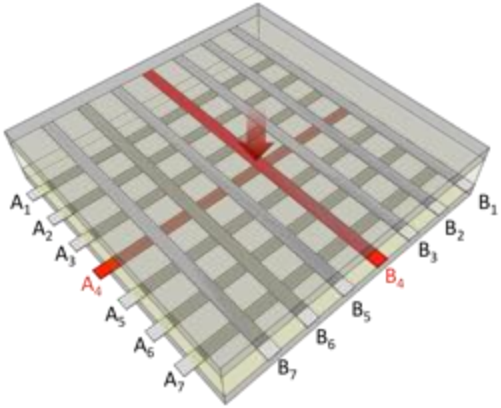
Touch Sensitive Sensor

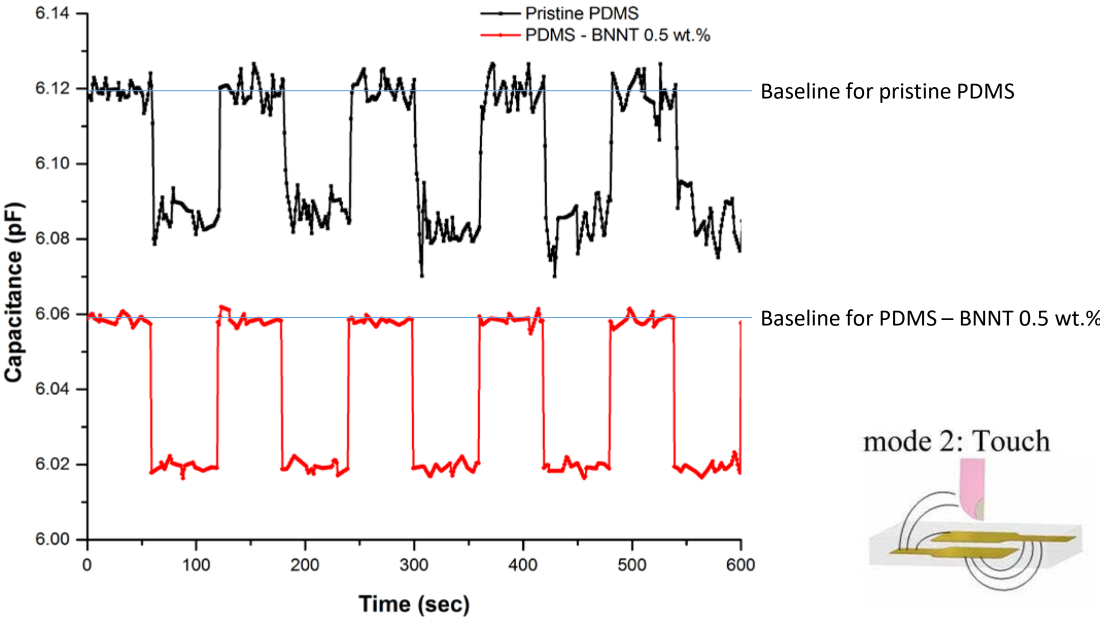
By touch

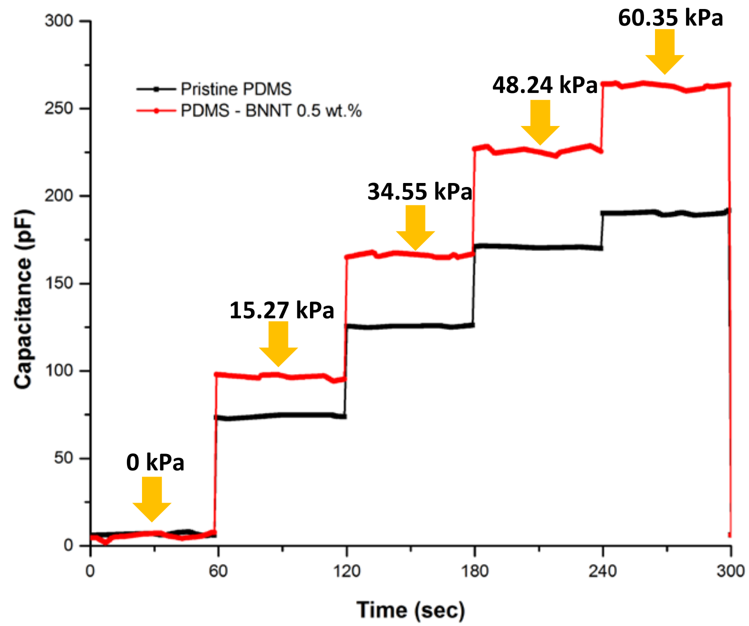




Pressure Sensitive Sensor







GIT : Prof Chuck Zhang/Ben Wang Group

BNNT Applications for Nuclear Medicine
Boron Neutron Capture Technology

Credit: NIA (Dr. Sang-Hyon Chu)
NSF

BNCT (Boron Neutron Capture Technology) - Therapy

- ^{10}B is delivered to encapsulate the tumor and is irradiated with low energy thermal neutrons (< 0.5 eV) to yield high linear energy transfer (LET) alpha particles (^{4}He) and recoiling ^{7}Li nuclei. ($^{10}B(n,\alpha)^{7}Li$)
- Damage to healthy cells is minimized by a short stopping distance (< 10 um) of the alpha particles.
- ^{10}B enriched BNNT has been produced

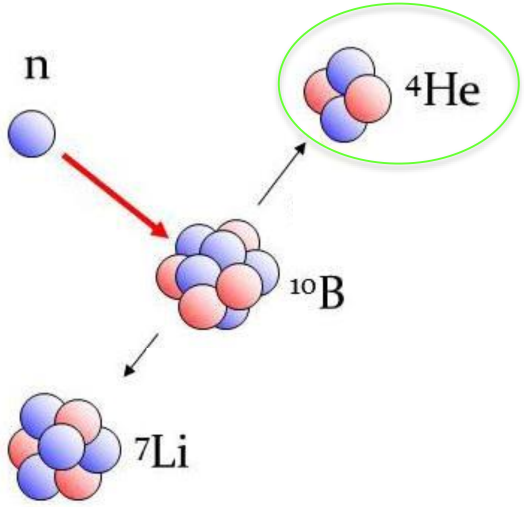
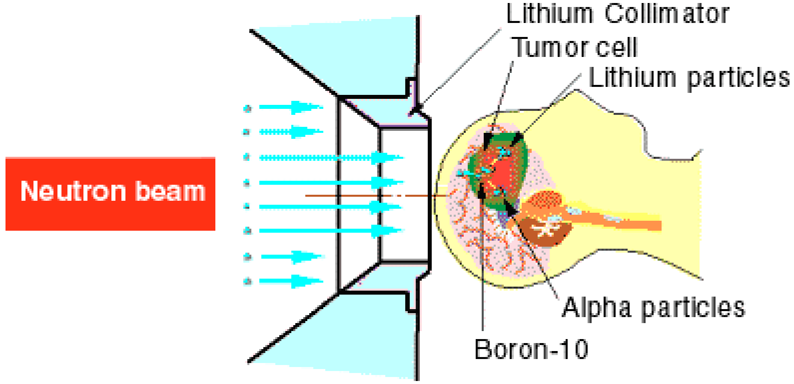


Image from Kyoto Univ.



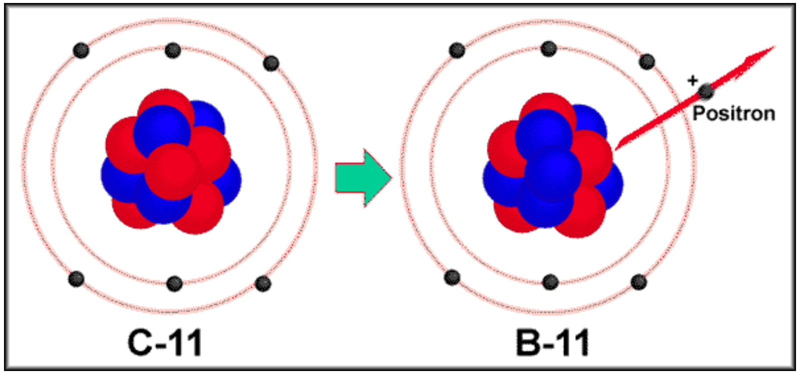
The Boron Neutron Capture Therapy (BNCT) consists of the injection of boron compounds into the human body, collecting them in tumor cells and then irradiating them with thermal neutrons in order to destroy these cells.

Image from Japan Atomic Energy Research Institute (JAERI)

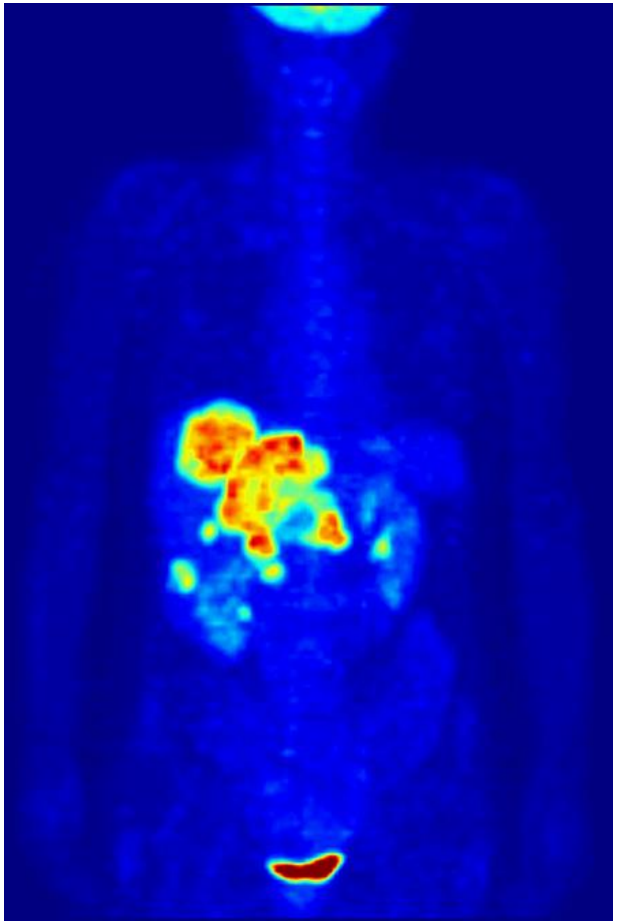
BNNT Applications for Nuclear Medicine
BNNT Targets for PET/CT

Credit: NIA (Dr. Sang-Hyon Chu)
NSF

- **Goal** - To develop ^{11}C biomarker radiopharmaceuticals for PET/CT metabolic imaging using BNNT cyclotron targets.
- NSF-SBIR program phase 1 (2015) and phase 2 (2016-present).
- Collaborators: BTI Targetry (PI) and Lawrence Berkeley National Lab (LBNL).
- Demonstrated boron nitride nanotube cyclotron target for recoil-escape production of ^{11}C through a nuclear reaction of **$^{11}B(p,n)^{11}C$** using low energy proton beam (7-11 MeV).



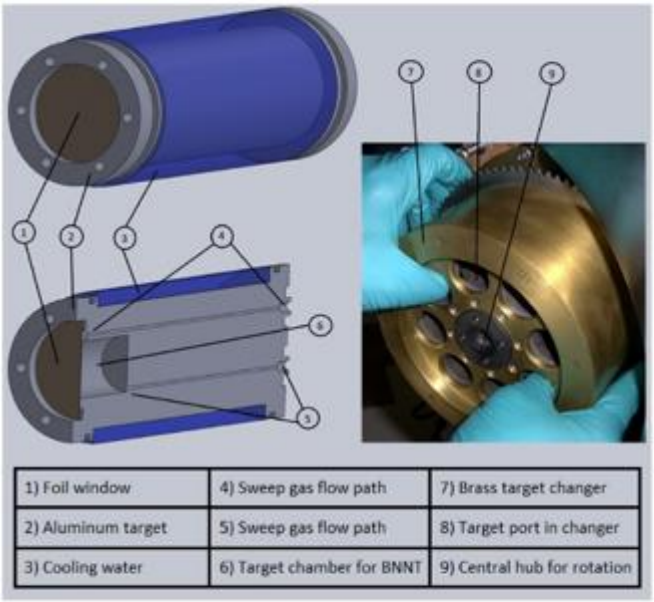
Proton -> Neutron + Positron (positive electron)



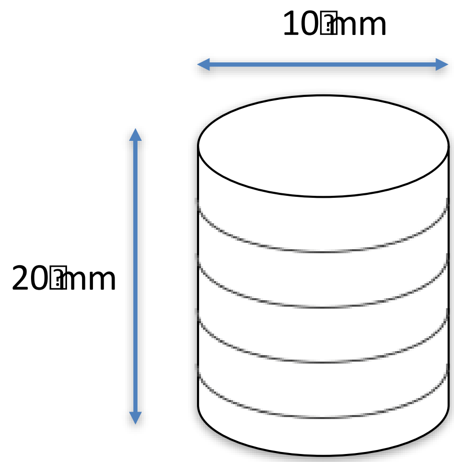
Cancer Diagnosis using PET/CT
(from Wikipedia)

Proton Beam Tests at Lawrence Berkeley National Lab

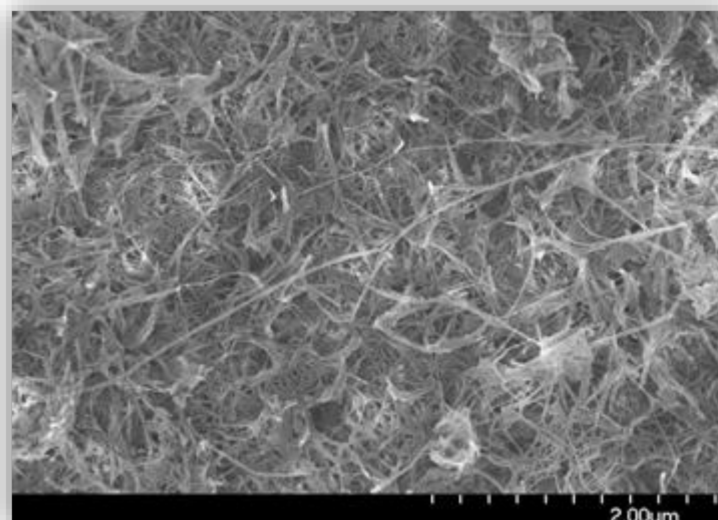
Credit: NIA (Dr. Sang-Hyon Chu)
NSF



The target chamber filled with BNNT
(Image credit: Dr. James O'Neal, LBNL)



Density (average) = 0.27 g/cm^3

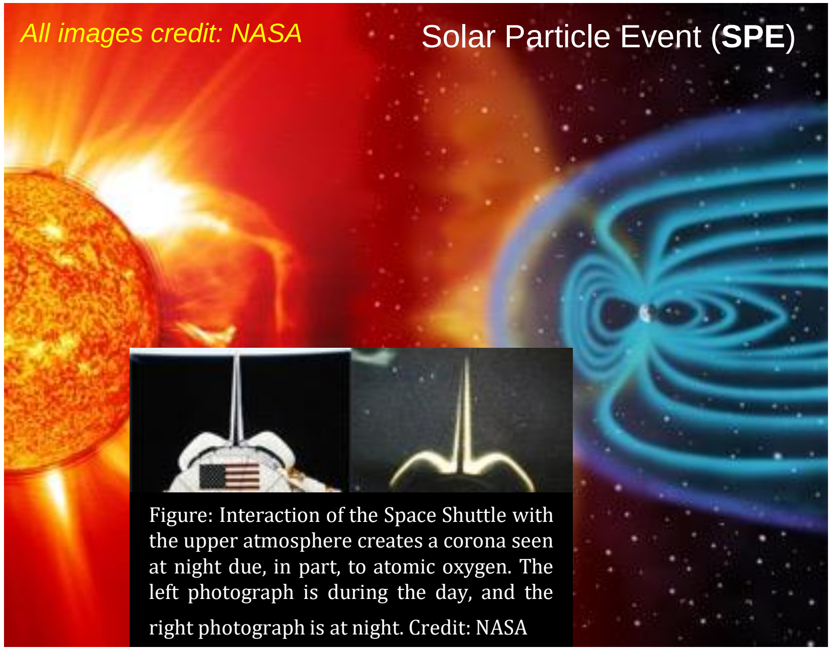


- Fabricated and characterized natural-enrichment BNNT target media with sufficient density: Multi-stack of BNNT discs to meet the size requirement.

- Successfully demonstrated the feasibility goal: recovery of **25%** theoretical yield of $^{11}CO_2$ at 7 MeV and 11 MeV incident energies at 20 μA beam current.

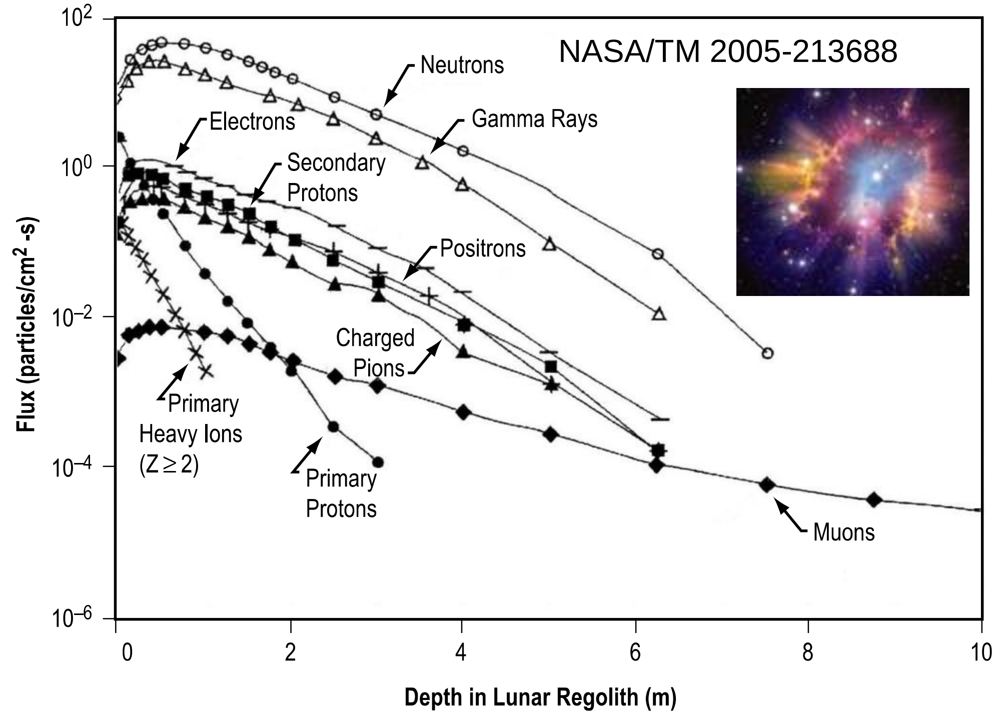
Instruments, 3, 8 (2019), Peeples, Chu et al.

Radiation Shielding Properties



Science **340** 1080 (2013)

Galactic Cosmic Ray (**GCR**) and produced Secondaries in lunar regolith



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

MRS Bulletin **40** 836 (2015)

Neutron Radiation Shielding Study

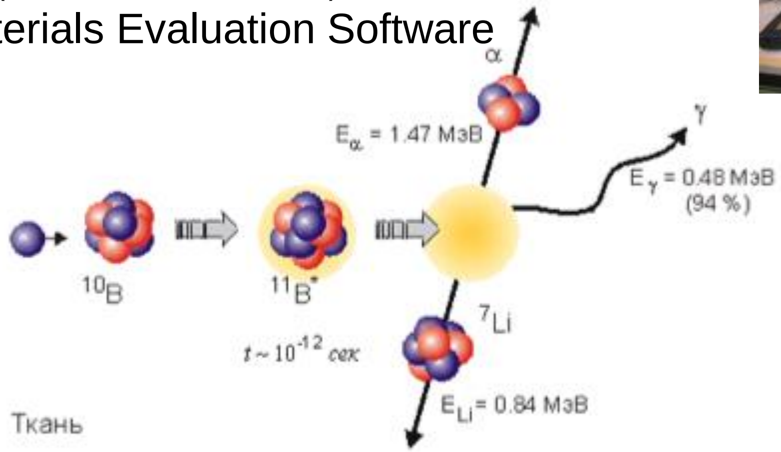
Materials
- Hydrogen, Boron, Nitrogen
- BN, BNNT, Gd
- Low density polyethylene (LDPE), polyimide (Kapton, CP2, (β-CN)APB/ODPA), polyurethane

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



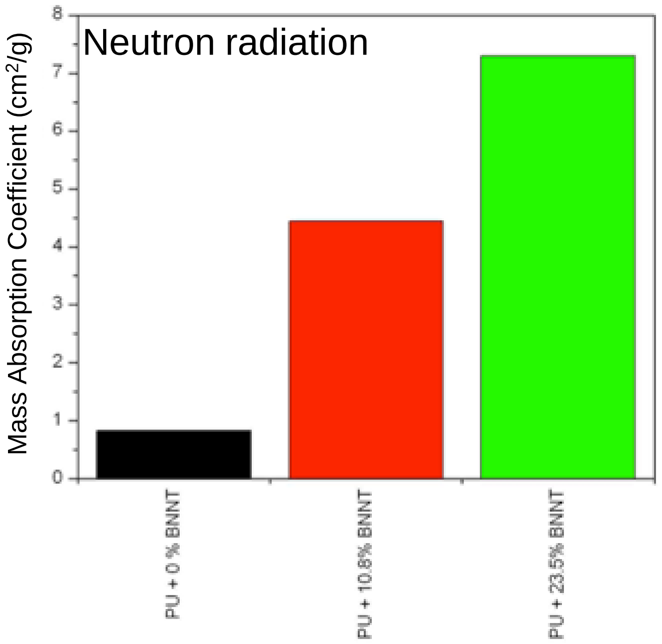
http://www.inp.nsk.su/bnct/introduction/introduction.en.shtml

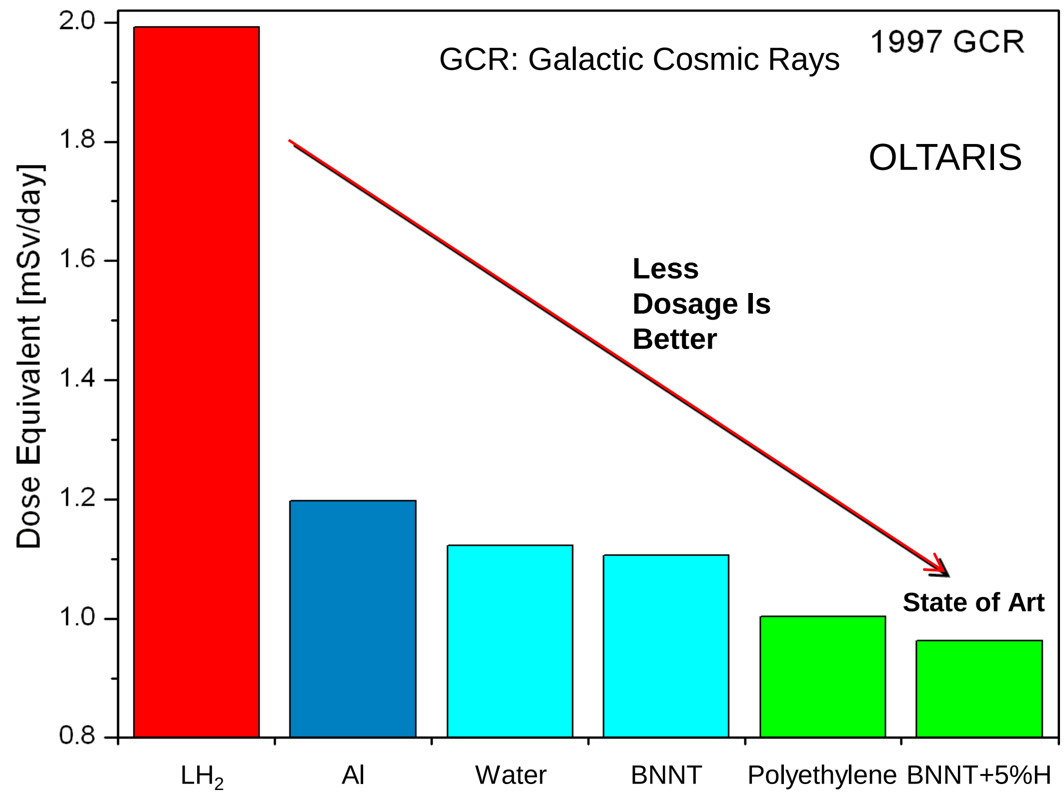
Geiger-Mueller Tube

Modeling
- OLTARIS

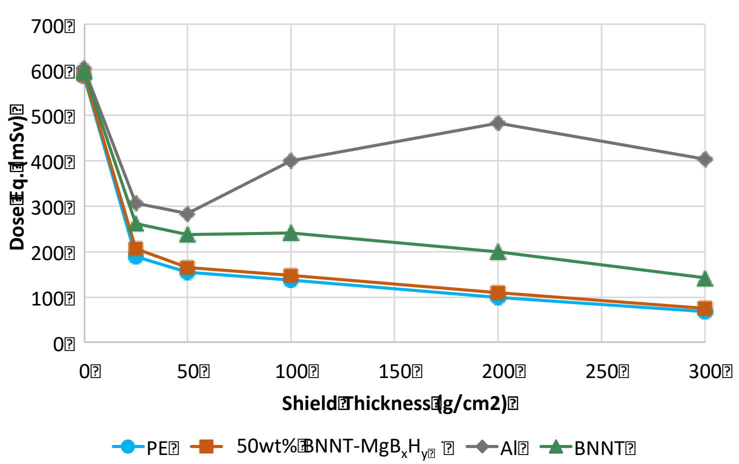
All images credit: NASA

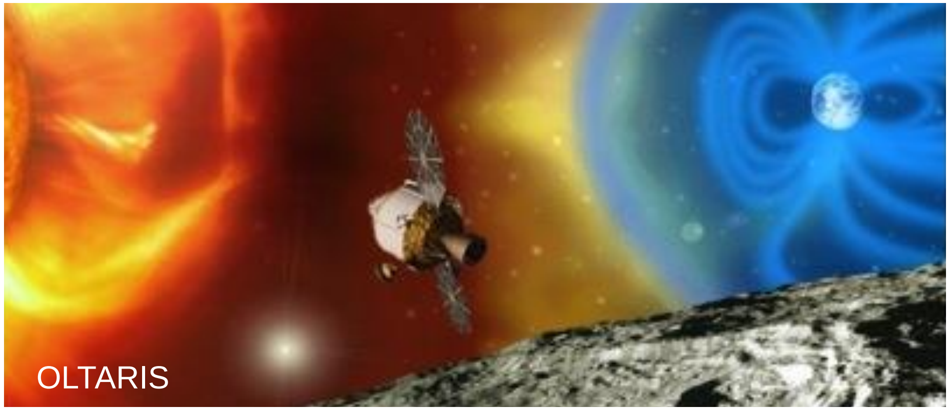
Radiation Shielding Effectiveness of BNNT Composites





BON-14 GCR Model in Free Space with 1977 Solar Min. incident on Vehicles with varying thicknesses





http://www.nasa.gov/pdf/716082main_ Thibeault_2011_PhI_Radiation_Protection.pdf (NASA NAIC Phase I Report)

Summary

- High Temperature-Pressure BNNT synthesis method was introduced.
- BNNT dispersion was successfully achieved by thermodynamic approach using Hansen solubility parameters for single and co-solvent systems.
- Interfacial shear strength and fracture energy of BNNT with polymers were superior to those of CNT.
- BNNT exhibited excellent thermal stability under a simulated planetary entry environment along with flame resistance and retardation properties
- BNNT and 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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Chuck Zhang, Ben Wang

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Thank you

Image credit: NASA

NASA Langley Research Center: 100 Years

https://www.youtube.com/user/nasalangley