Multifunctional Nanocomposites for Aerospace Applications: Overview

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NASA Langley Research Center

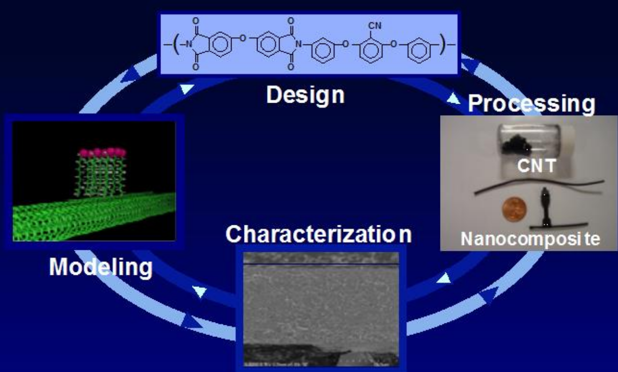
NASA Langley Research Center Hampton, Virginia
Founded in 1917: first civil aeronautical research laboratory
Facilities: $4 billion replacement value

People: 2000 Civil Servants ; 1700 Contractors

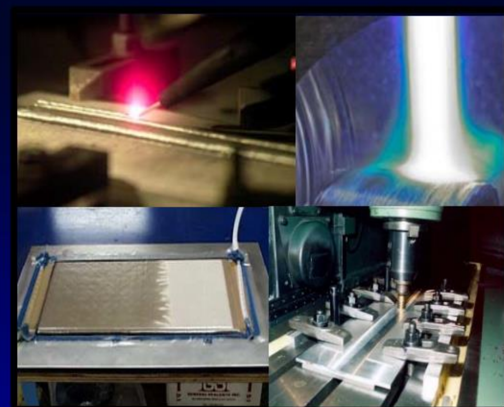
All images credit: NASA

Advanced Materials and Processing Branch

Materials Design

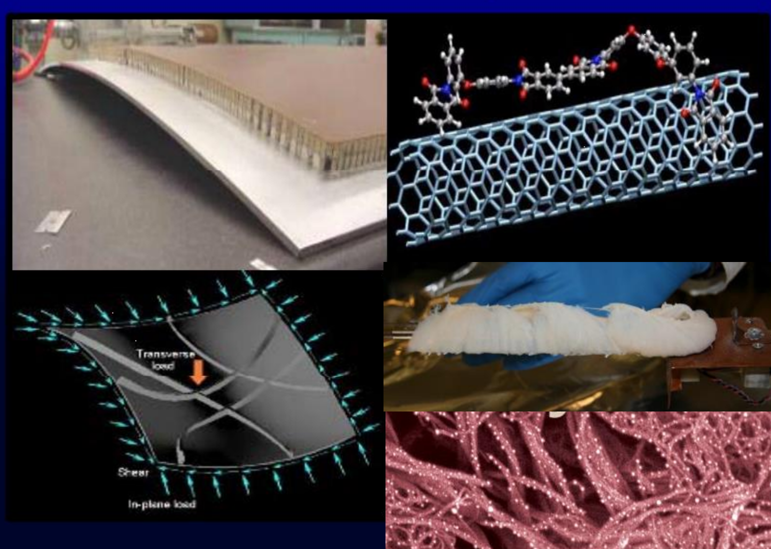


Innovative Materials Processing

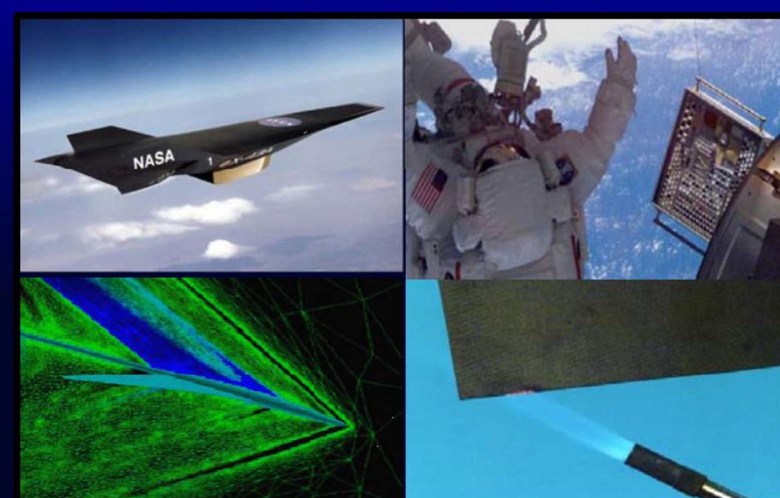


Materials Testing

Advanced Material Systems



Materials for Extreme Environments



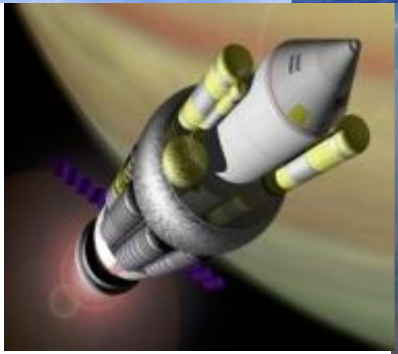
All images credit: NASA

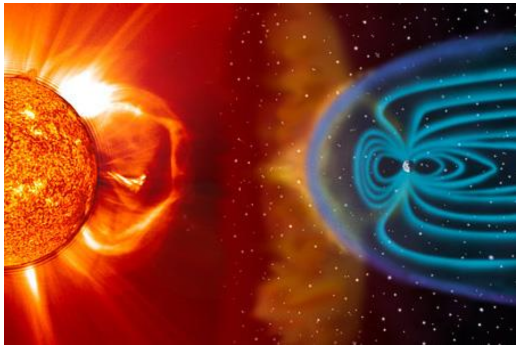
Critical Concerns for Aerospace Systems

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

Functionality/Performance
- Reduced fuel or power consumption
- Multifunctionality – additional reduced weight

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





All images credit: NASA

Design Materials Properties

Materials Properties to be Tailored
- Electrical Conductivity
- Dielectric Permittivity
- Magnetic Permeability
- Thermal Conductivity/expansion coefficient
- Radiation Shielding
- Mechanical (modulus, strength, toughness…)
- Solar Absorptivity/Thermal Emissivity
- Band gap engineering
- Optical property (transparency, refractive index…)
- Piezoelectricity/Pyroelectricity/Electrostrictive
- Gas/Liquid Permeability
- Anisotropy/orientation

Design Parameters
- Nano Inclusion type and combination (CNT, BNNT, BCNNT, GP, hBN, NP…)
- Matrix type
- Composition
- Dispersion
- Orientation
- Geometry, Fabrication, Processing…

Specific Applications
- R2R Printing of Electroactive Polymer Composites: NSF/NASA
- Electroactive properties & Radiation Shielding of BNNT Composites: AFOSR/NASA C&I
- Radiation Detection and Conductivity Control: DOE (ORNL)/NASA
- Solar Absorption and Thermal Emission Control: NASA C&I
- Structural BNNT composites, BNNT fibers and mats: Rice Univ/NASA GCD, B&P, IRAD
- Multiple Metal Infusion for Multifunctionality (S2M2N): NASA IRAD
- Bandgap Engineering of nanotubes: NASA IRAD
- Doped Chiral Polymer Metamaterials (DCPM): NASA IRAD
- Radiation Shielding and Thermal Conduction (Electronic Packaging): NASA IRAD
- Ultralight Flexible Shielding Tension Shell: NASA IRAD

Outline

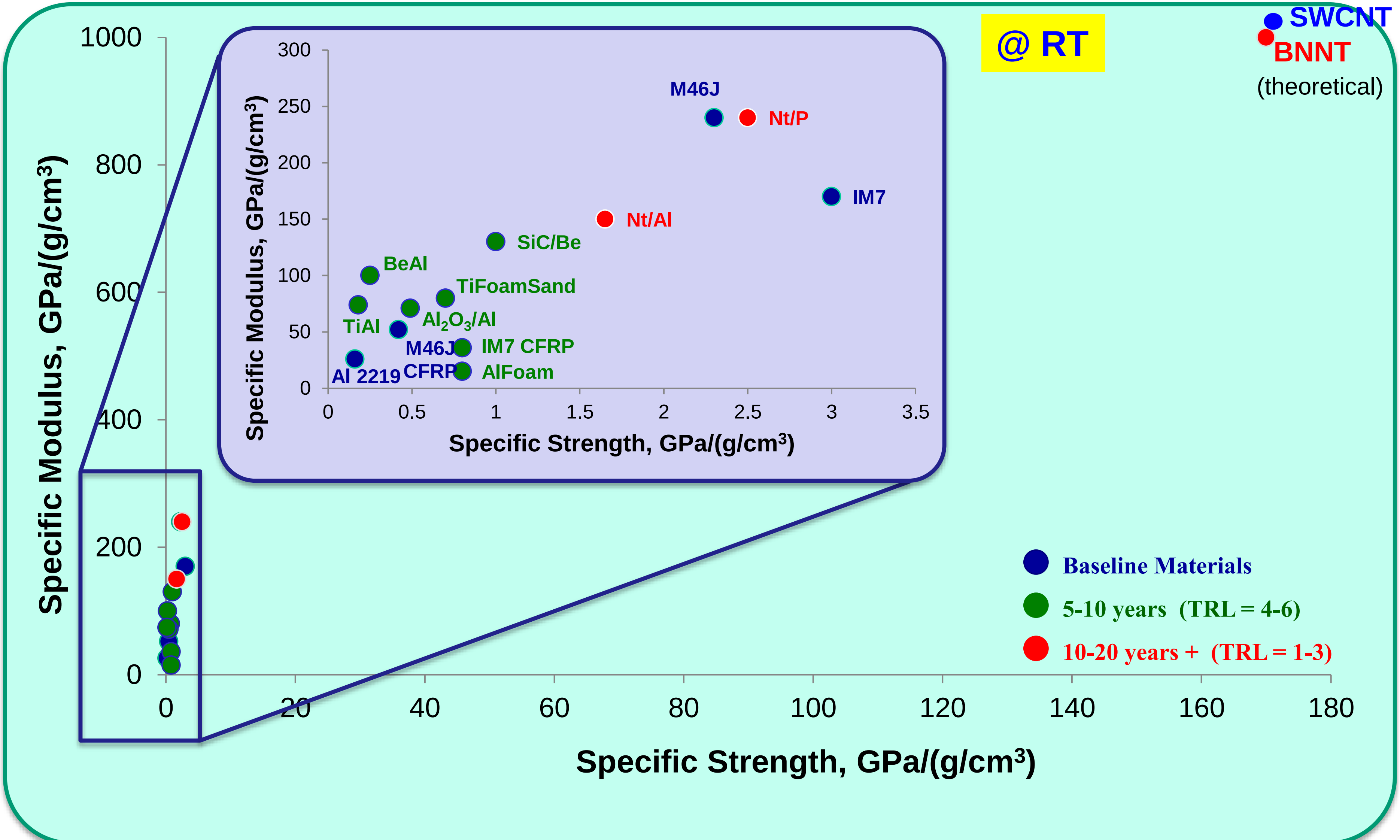
- Multifunctional Nanocomposites
  - Nanotube Synthesis: High Temperature-Pressure (HTP) BNNT and BCNNT Synthesis
  - Dispersion
  - Tailoring physical properties of nanocomposites for multifunctions
  - Metallized Nanotube Polymer Composites (MNPC)
  - Doped Chiral Polymer Metamaterials (DCPM)
  - Band Gap Engineering ($B_xC_yN_z$ Nanotubes)

- Sensors/Actuators

- Radiation Shielding

- Summary

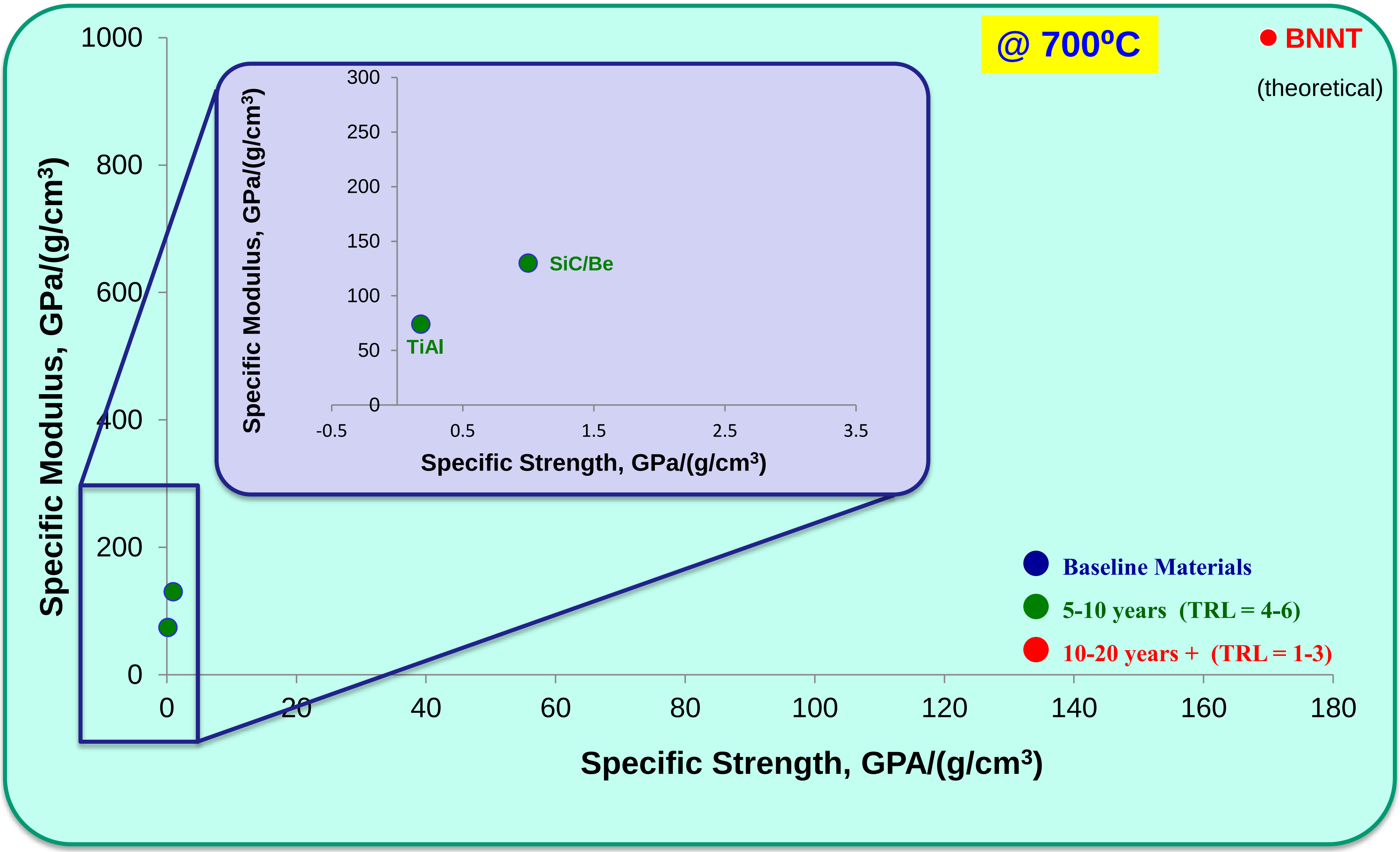
Properties of Materials for Vehicle Structure



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

Nanotube values are theoretical.

Properties of Materials for Vehicle Structure



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

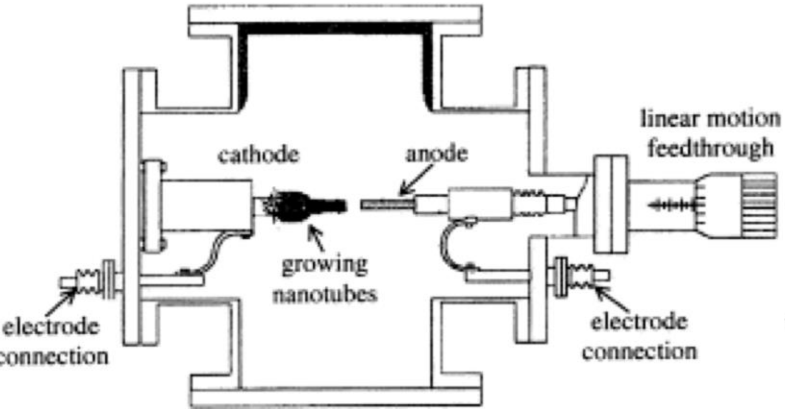
Nanotube values are theoretical.

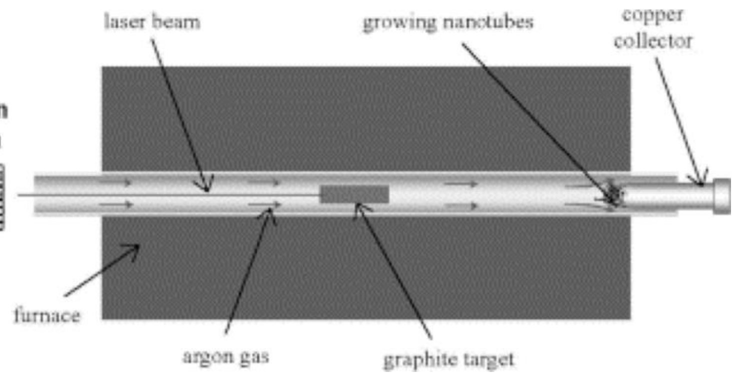
Nanotube Comparison (Theoretical)

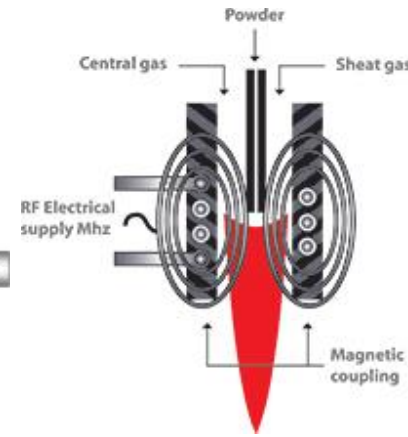
	Carbon Nanotubes	Boron Nitride Nanotubes
Electric Properties	Metallic or semiconducting	Wide band gap (about 6.0 eV band gap)
Mechanical Properties (Young's Modulus)	1.33 TPa (very stiff)	1.18 TPa (very stiff)
Thermal Conductivity	>3000 W/mK (highly conductive)	~300–3000 W/mK (highly conductive)
Thermal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

Synthesis Methods of Carbon Nanotubes

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





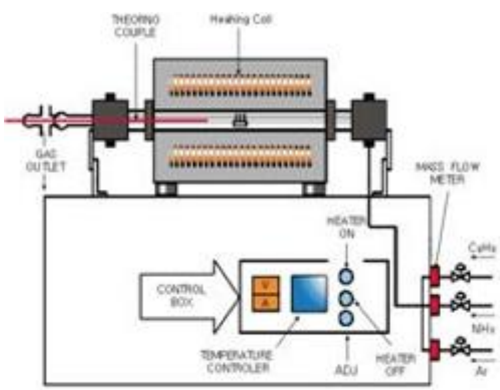


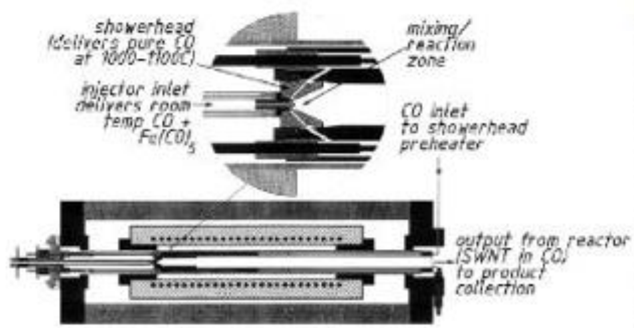
Credit: www.tekna.com

Arc-discharge

Laser ablation

Induction Plasma





HiPco

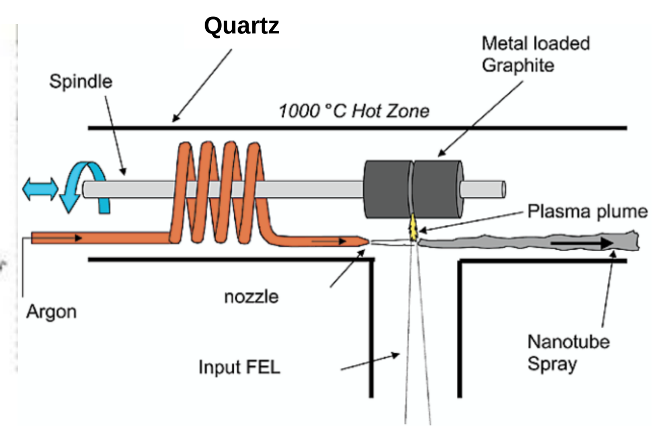


Image credit: NASA

Chemical vapor deposition (CVD)

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

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

BNNT Synthesis History

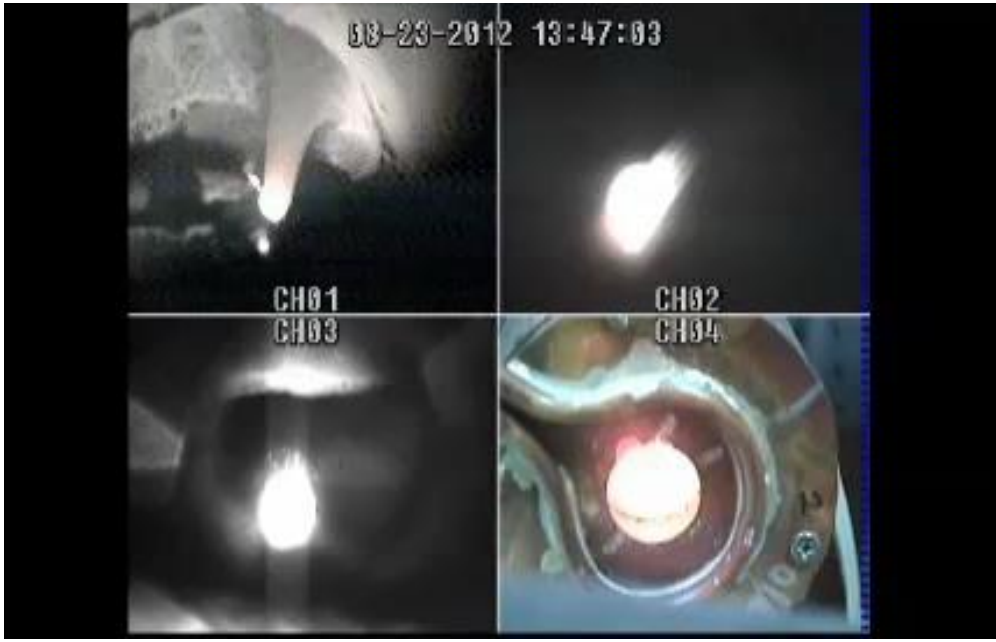
- First Theoretical prediction: *PRB* **49** 5081–5084 (1994) (UC Berkeley, Cohen), computation
- First Synthesis Arc Discharge: *Science* **269** 966 (1995) (UC Berkeley, Cohen/Zettl) BNNT by Arc Discharge
- Arc Discharge: *PRL* **76** 4737 (1996) (ONERA France, Loiseau) Arc Discharge HfB2 with N2 gas
- 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

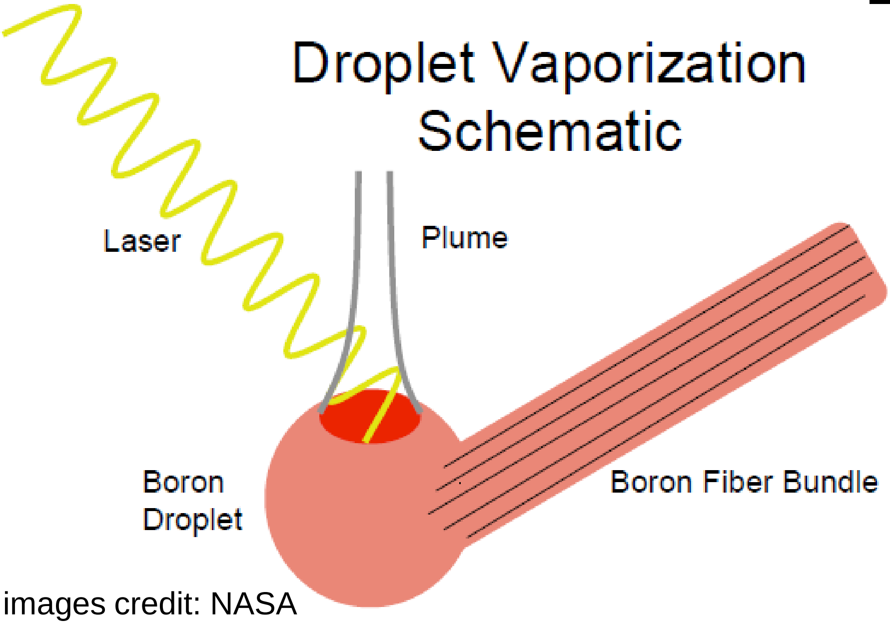
High Temperature-Pressure (HTP) BNNT and BCNNT

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

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

NASA LaRC BNNT Synthesis Lab





- 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)

All images credit: NASA

Free Electron Laser: Atmosphere: Spark

All images credit: NASA

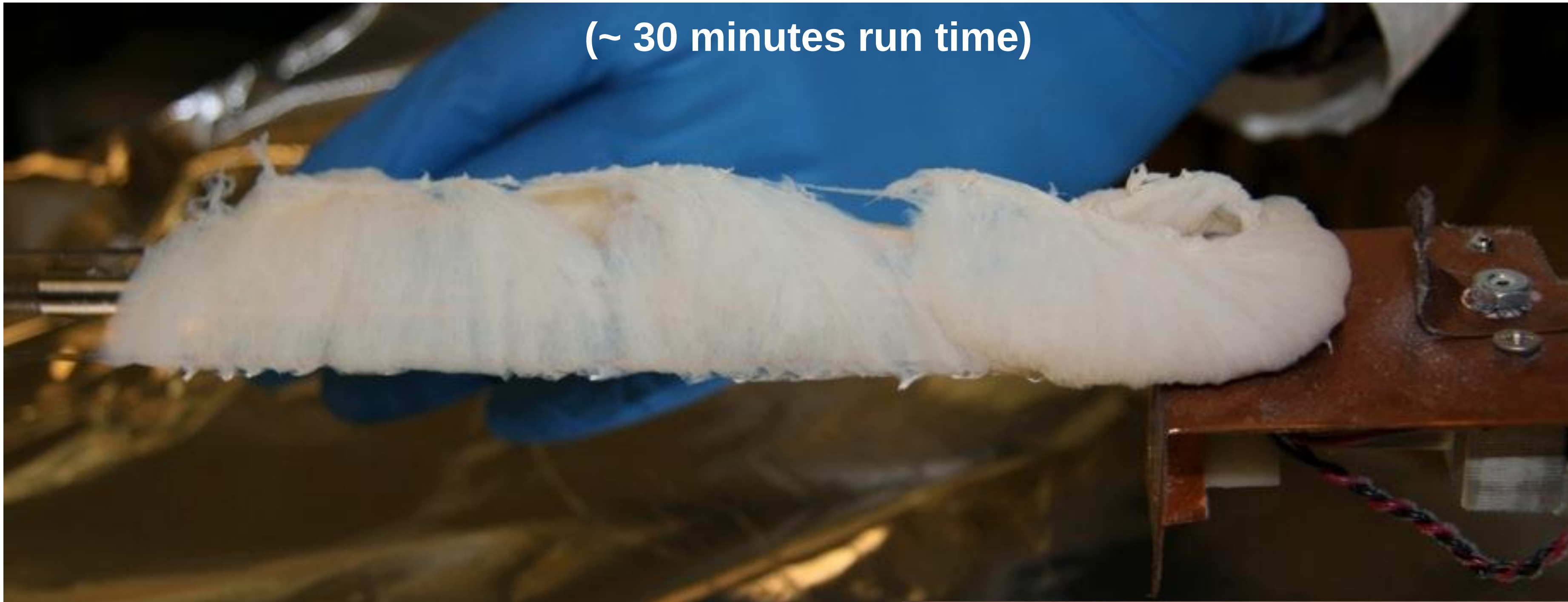
Free Electron Laser: High Pressure: BNNT Streamer

All images credit: NASA

CO_2 Laser: High Pressure

All images credit: NASA

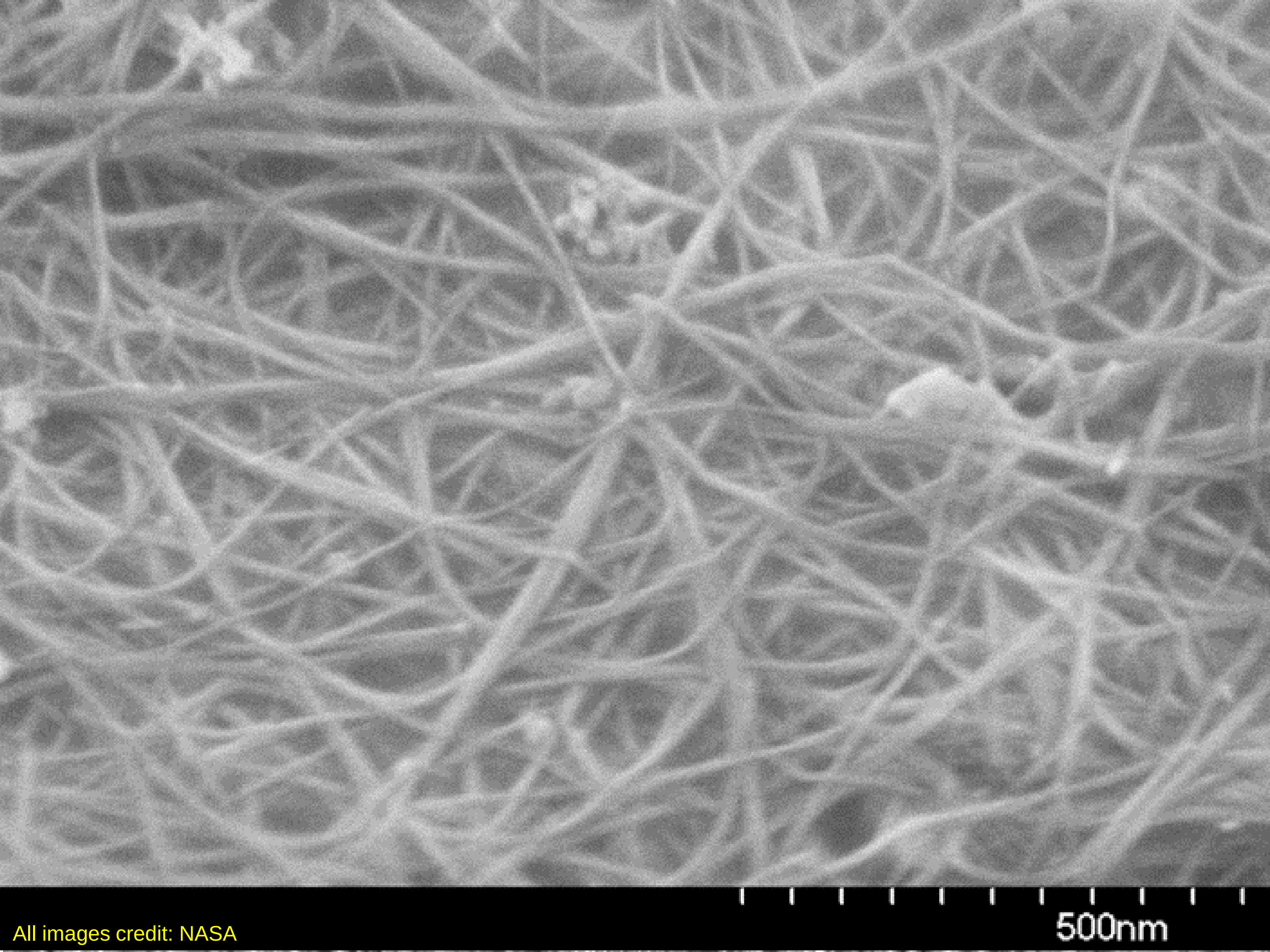
Cotton-like High Pressure and Temperature (HPT)-BNNT



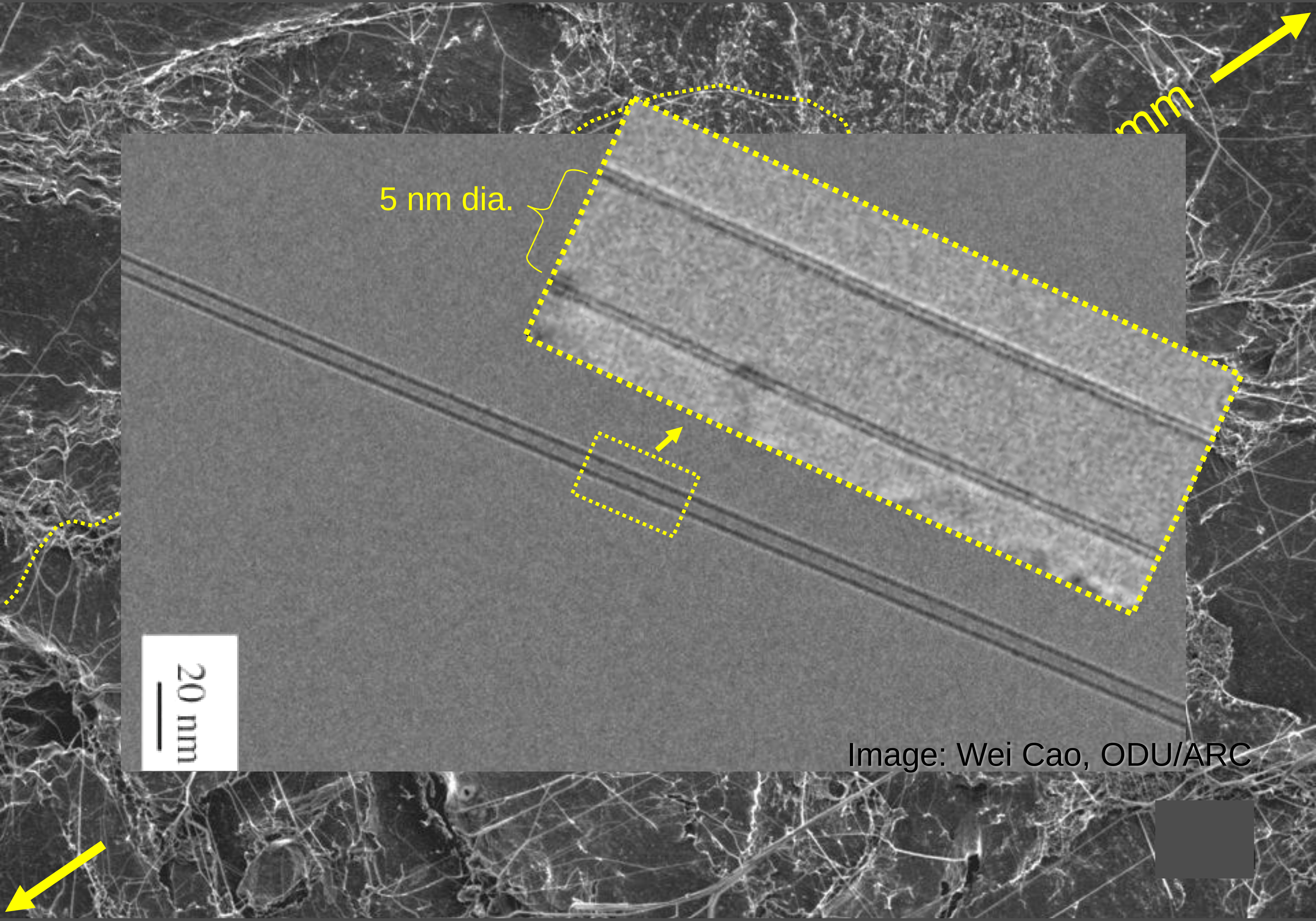
Benefits

- 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

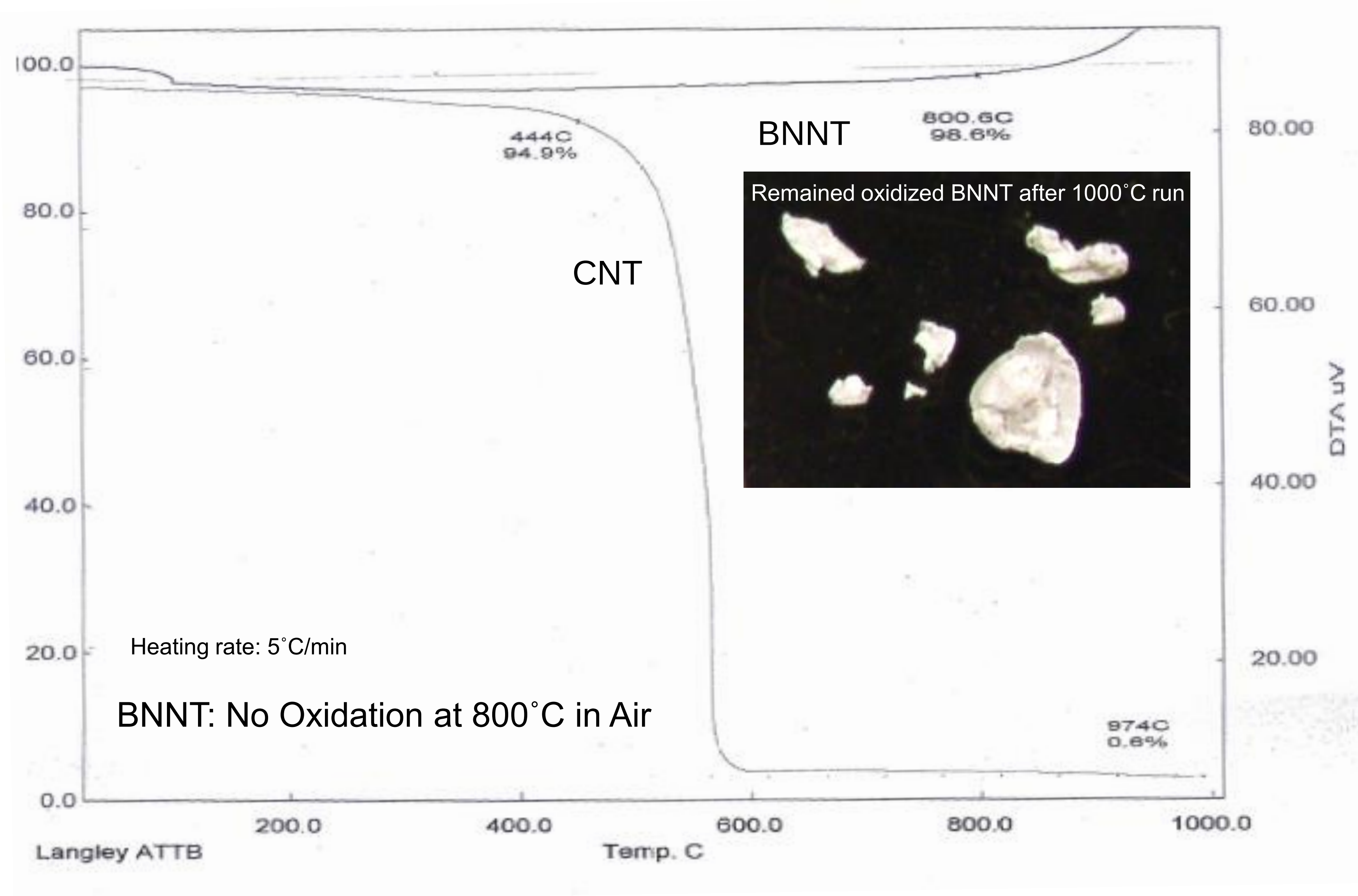


All images credit: NASA



All images credit: NASA

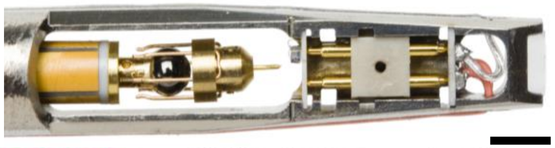
Thermal Stability of BNNT vs. CNT: TGA

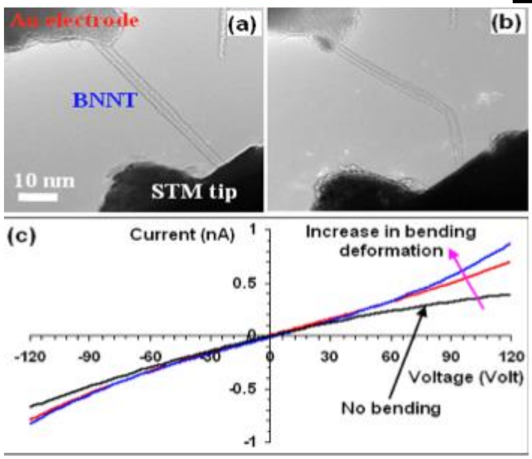


Mechanical Properties of BNNT and BNNT Composites: Processing and Characterization Techniques

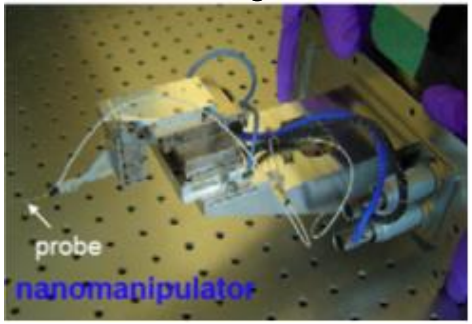
Individual BNNT and BNNT Bundles: compressive modulus, tensile modulus and strength, radial modulus

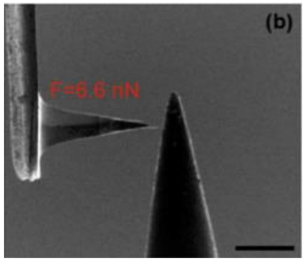
TEM-AFM, TEM-STM Holders
Credit: NASA LaRC/NIA/Binghamton



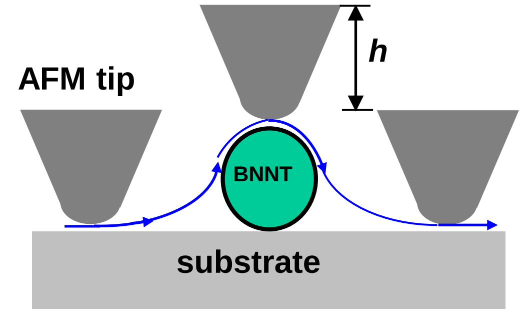


3D Nanomanipulator in SEM/FIB
Credit: SUNY Binghamton





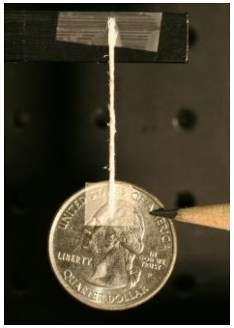
AFM
Credit: SUNY Binghamton



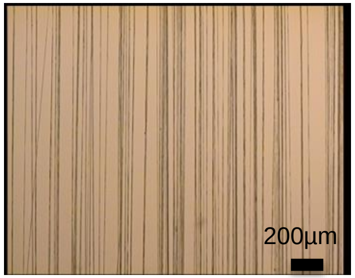
Small, 8, 116 (2012)
ACS Nano, 6, 1814 (2012)
Nanotechnology, 23, 095703 (2012)

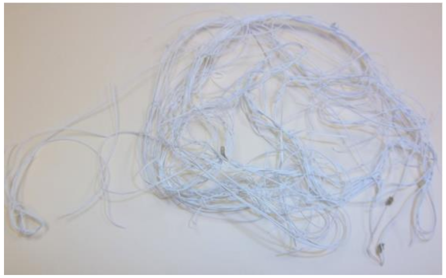
BNNT composites and BNNT yarns

Spun yarns: NASA LaRC/NIA (credit)

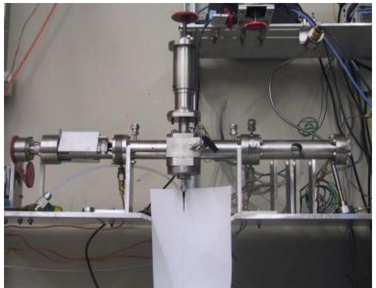


Wet spinning/Electrospinning
Credit: NASA LaRC/NIA





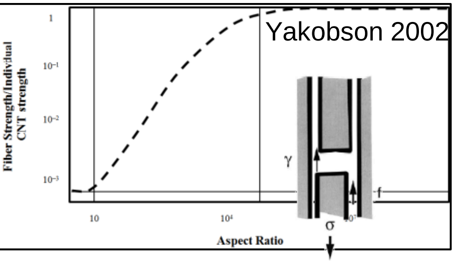
Superacid Spinning
Credit: Rice U

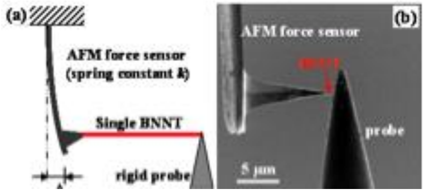


How to make strong, stiff, tough structural BNNT composite?

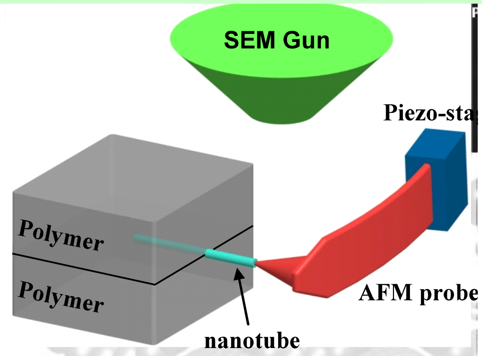
Good tubes:
highly crystalline, long, thin BNNTs → Excellent intrinsic BNNT properties

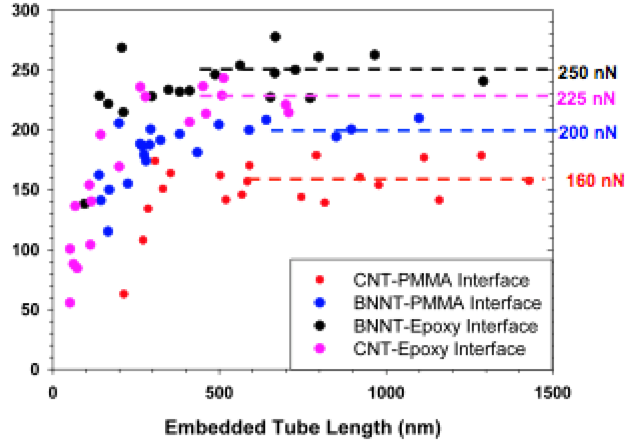
Longer tube (high aspect ratio)
→ Greater yarn strength





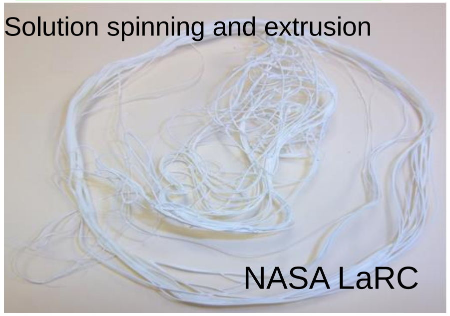
High interfacial strength

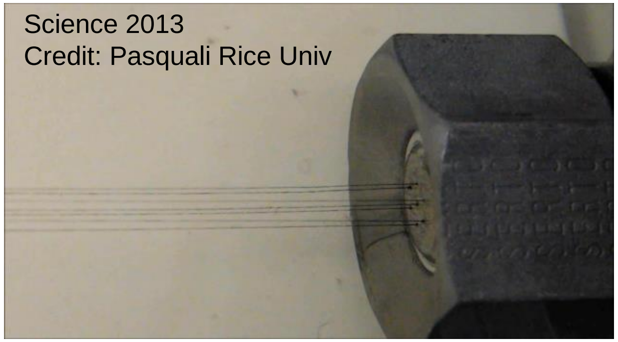




BNNT-epoxy and BNNT-PMMA interfacial strength are superior to CNT counterpart (*Small*, **9**, 3345 (2013)

High orientation





BNNT Tensile Test Results (Only for comparison with CNT)

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

Credit: Prof Ke (SUNY Binghamton)

Hearle's Yarn Equation

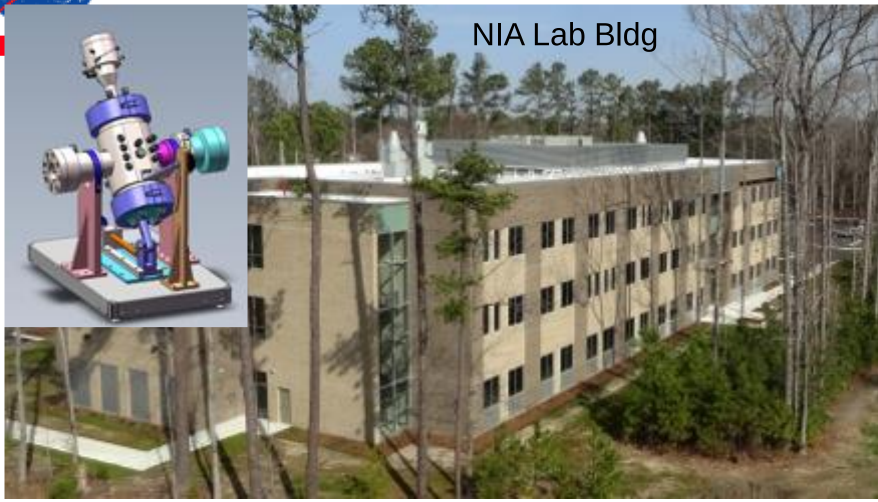
$\sigma_y \approx \cos 2\theta(1 - k\,\mathrm{cosec}\,\theta) \cdot \sigma_f$

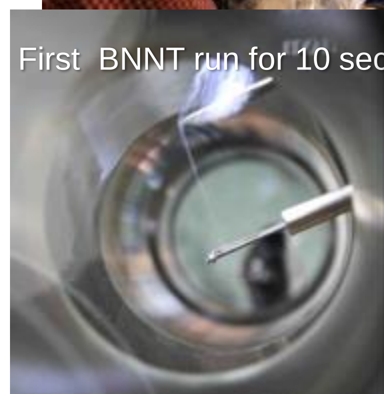
σ_y: yarn strength, σ_f: fiber (tube) strength
θ: helix angle that fibers make with yarn axis
k: $(dQ/\mu)^{1/2}/3L$, d: fiber diameter
μ: coefficient of friction , L: fiber length
Q: fiber migration length

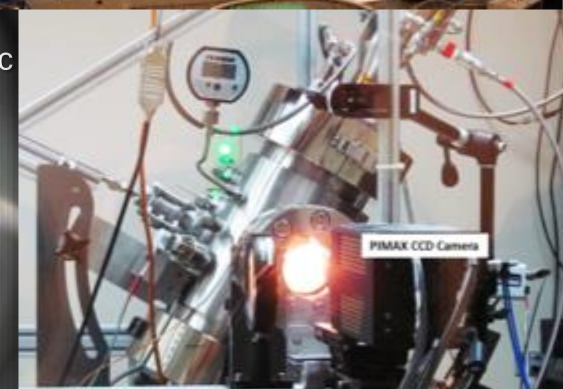
If $\sigma_f\uparrow$, $d\downarrow$, $L\uparrow$, $\mu\uparrow$ → $\sigma_y\uparrow$

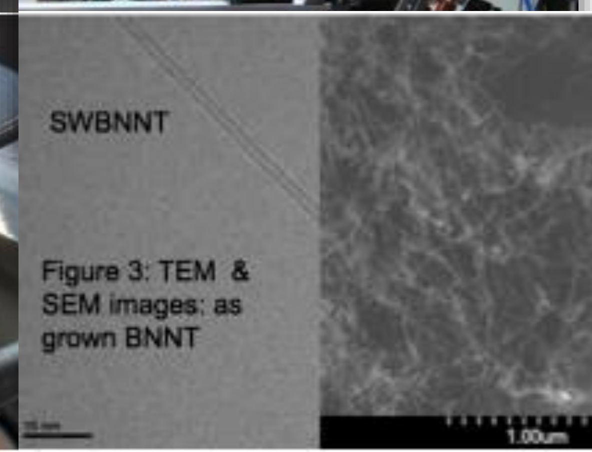
Credit: Hearle, Structural mechanics of fibers, yarns, & fabrics, (1969)

NIA Research and Innovation Laboratories









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

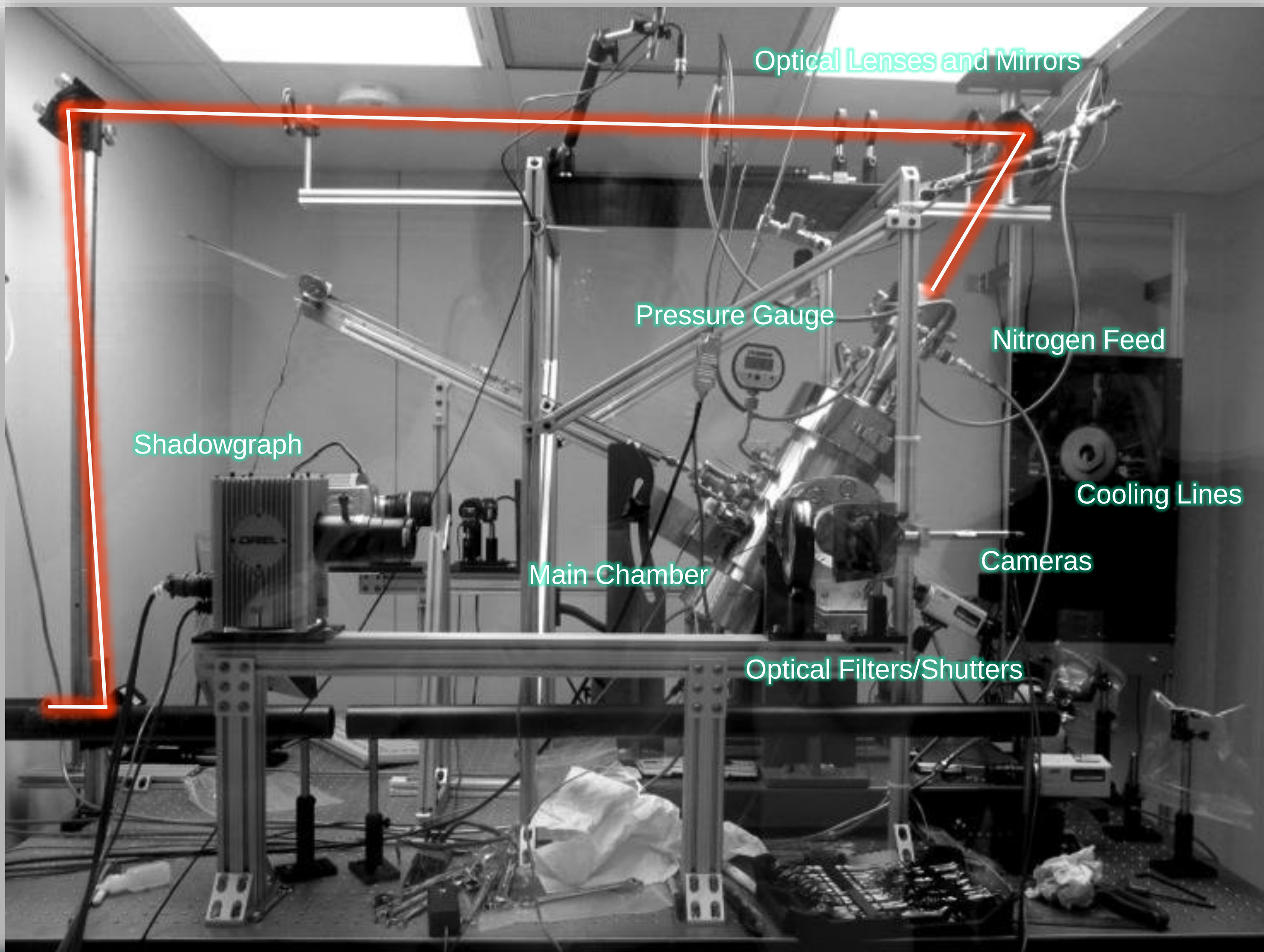
Successful pressure test up to 950 psi (higher pressure leads to better BNNT potentially)

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

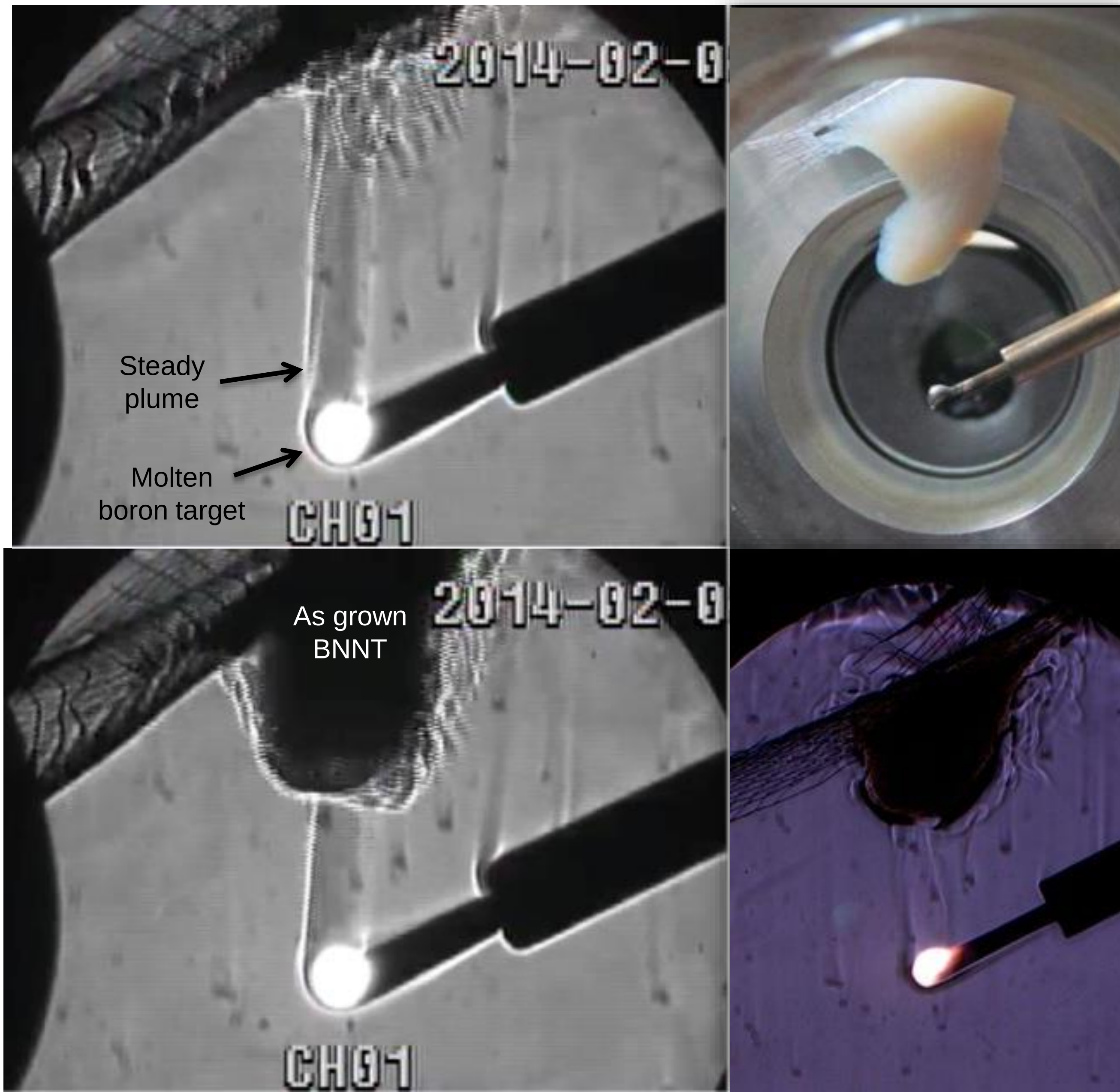
Parallel computational study for nucleation and growth ongoing (both NIA and NASA)

All images credit: NASA/NIA

NIA BNNT Science Chamber



NIA Science Rig HTP BNNT Run (Snapshots)



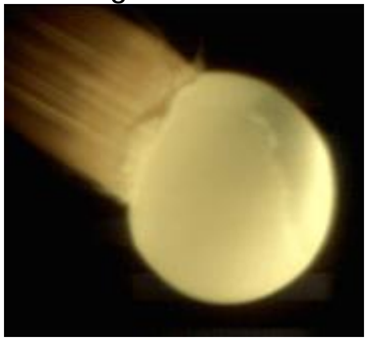
All images credit: NASA/NIA

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

In-situ Optical Diagnostics

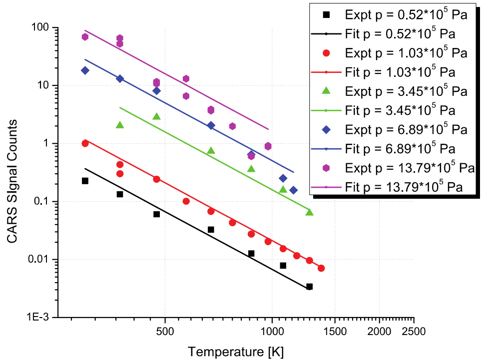
- Understand chemistry and flow physics of nanotube generation
- Improve and validate simulation/modeling
- Optimize material properties, production rate
- Specific Goals:
  - Determine gas and melt-ball temperatures
  - Determine amount of B_2, B, BN, N and N_2
- In-situ, on-surface measurement:
  -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

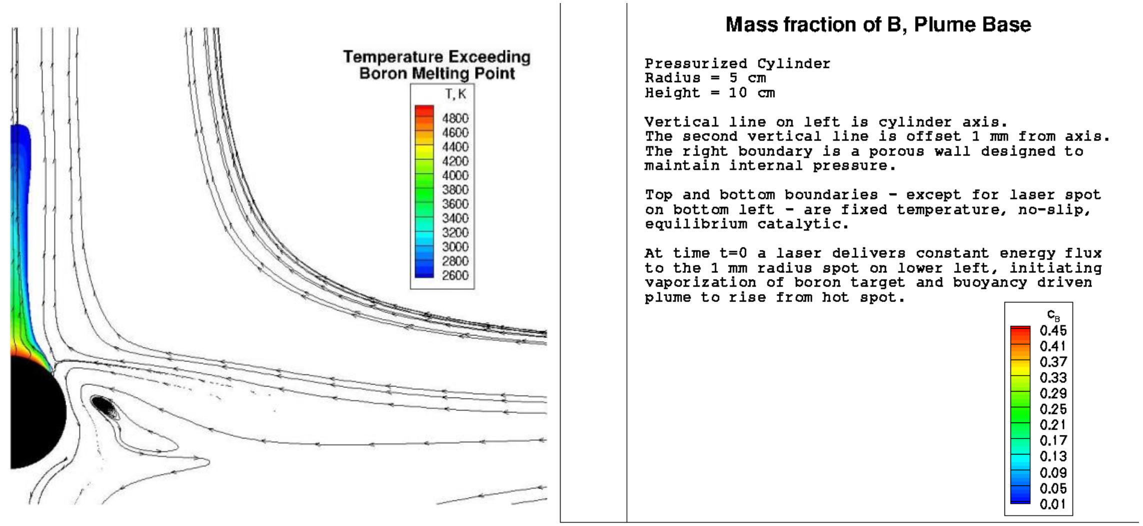


CARS Intensity Measurement

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

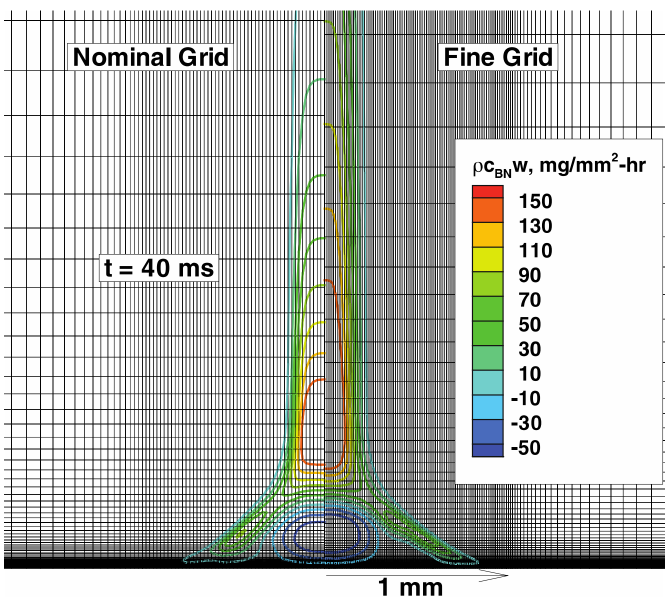
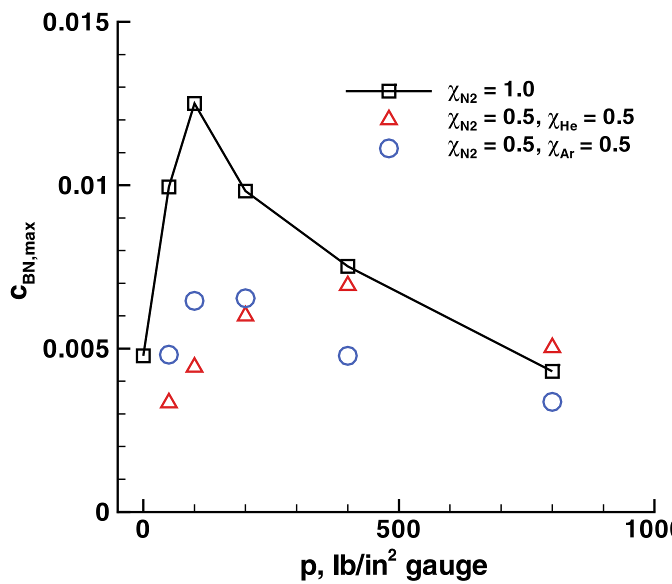


Fig. 5 Contour lines of BN flow rates in the plume.



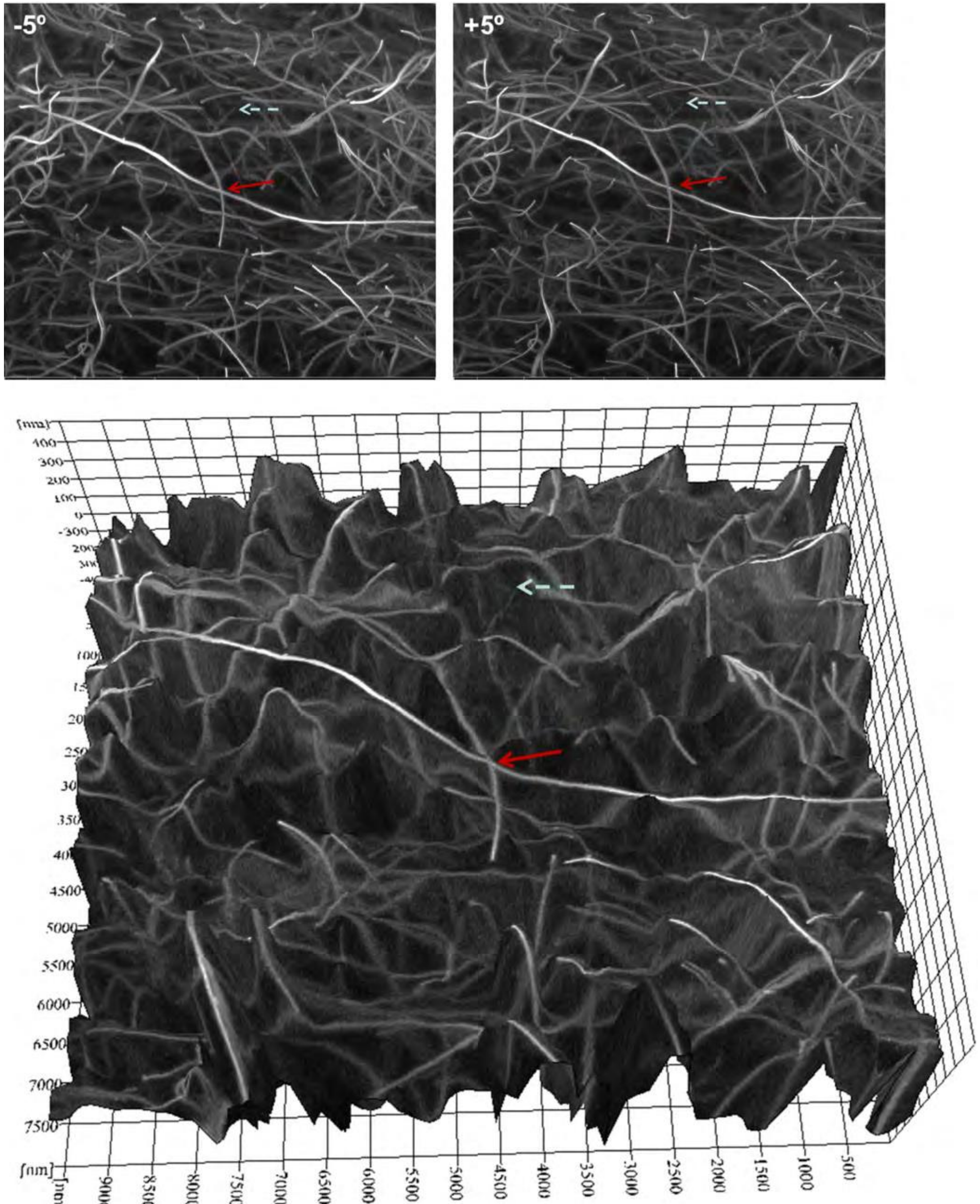
a) Total chamber pressure

All images credit: NASA

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

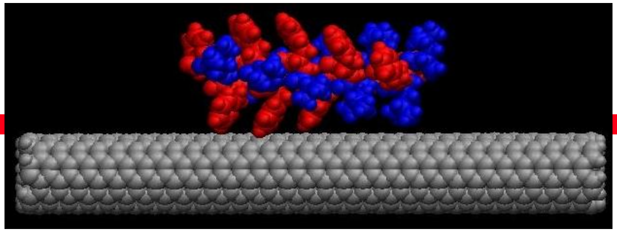
J. Thermophysics and Heat Transfer **27** 369 (2013)

Dispersion



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

How to disperse Nanotubes?



1) Kinetic Approach

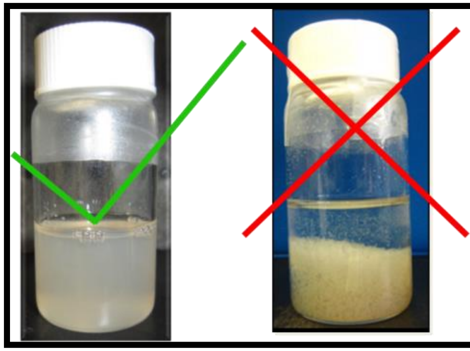
High shear (stirring, homogenization, speedmix)

Sonication (cavitational 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

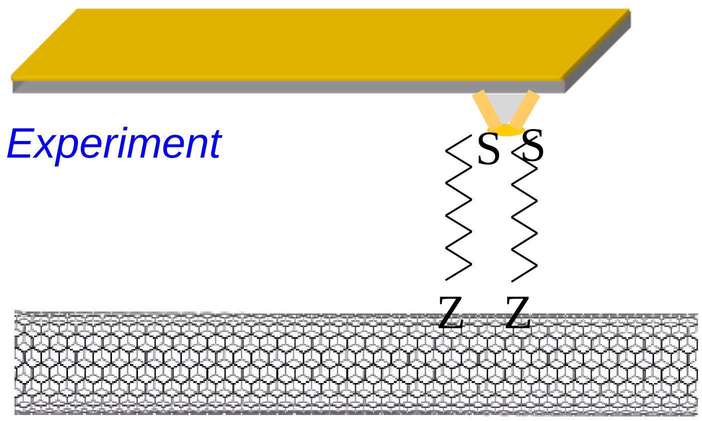
Nonspecific interaction

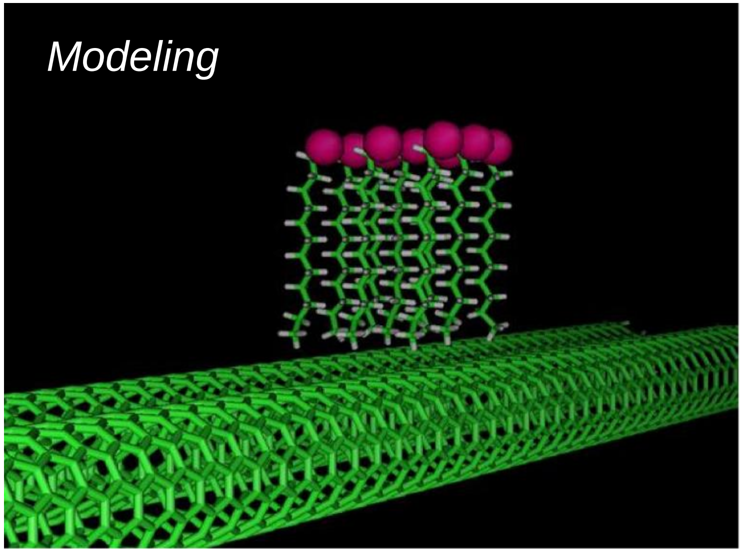
$$\Delta G_{mix} = \Delta H_{mix} - T^*\Delta S_{mix}$$

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.





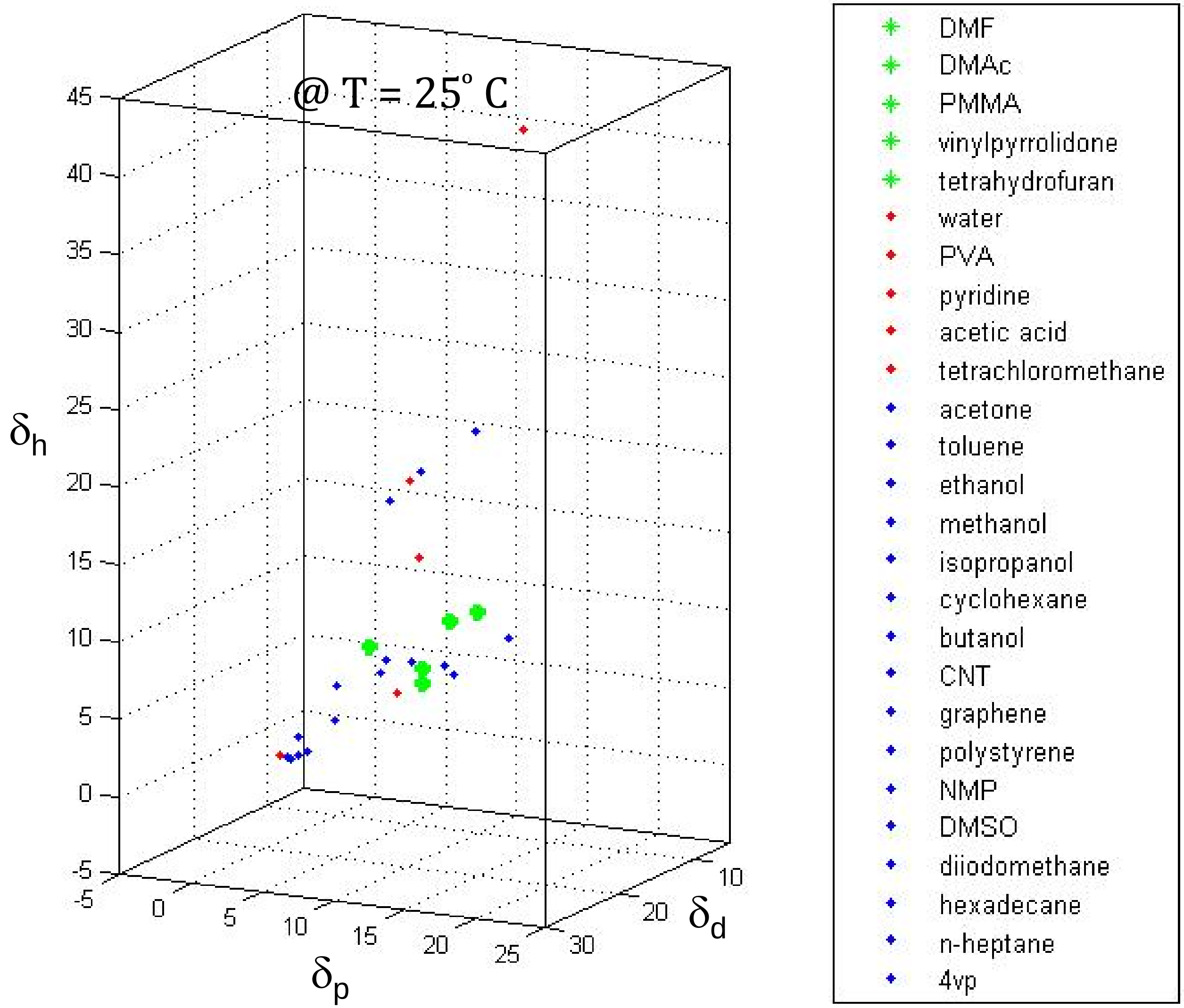
Alkyl-thiol Endgroup	Experiment Force/Molecule (pN)	Modeling (pN)
–OH	9.6 ± 2	
–perfluoro	8.7 ± 3	
–SH	9.2 ± 3	
$–CH=CH_2$	8.1 ± 2	
$–CH_3$	7.6 ± 2	1.92
–COOH	12.2 ± 3	
$–NH_2$	23.4 ± 4	2.98
Aryl-thiol Endgroup		
4-methylbenzene	18.9 ± 5.7	
4-nitrobenzene	21.8 ± 5.3	
4-aminebenzene	22.6 ± 4.7	
4-bromobenzene	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	

Hansen and Hilderbrand Solubility 3D Plot for BNNT

Hanson and Hilderbrand Solubility: $\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$

δ_d: dispersion component
δ_p: polar
δ_h: hydrogen bond

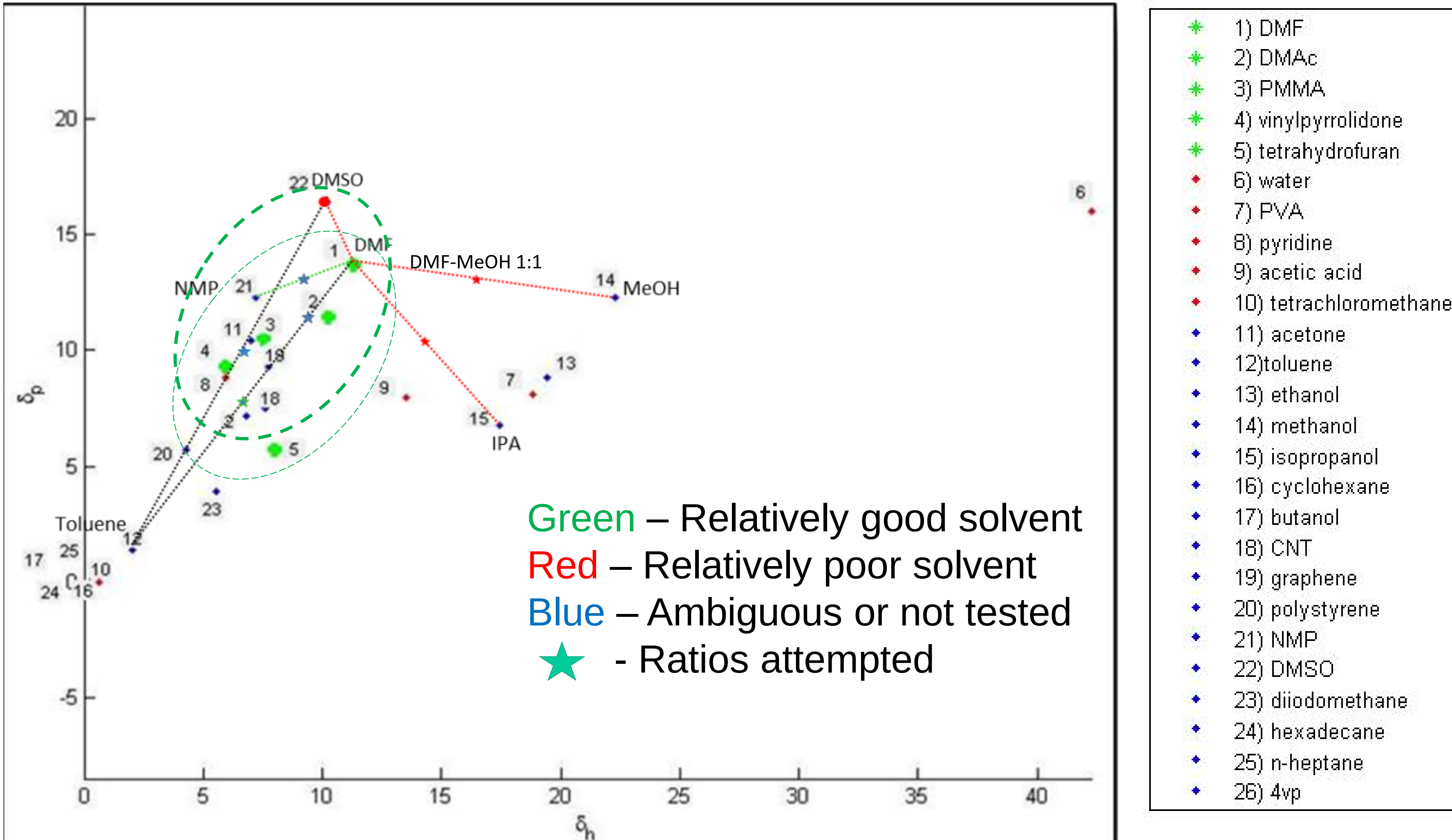
Code written to plot coordinates (δ_d, δ_p, δ_h) for each solvent and solute and color code good, poor, and unknown solvents



Michelle Tsui (UC Berkeley, LARSS)

2-D Hansen Plot (δ_p, δ_h only): Select Good Solvents/Co-Solvents

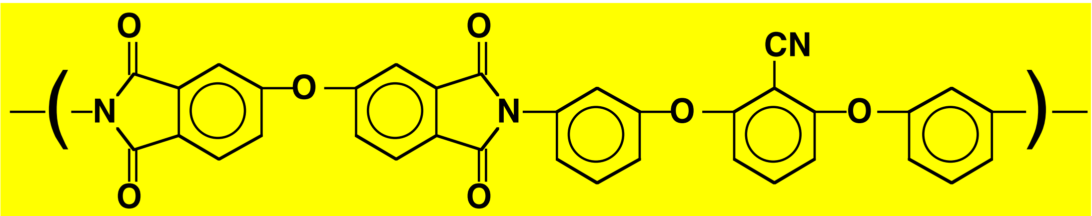
Hanson and Hilderbrand Solubility: $$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$$



Michelle Tsui (UC Berkeley, LARSS)

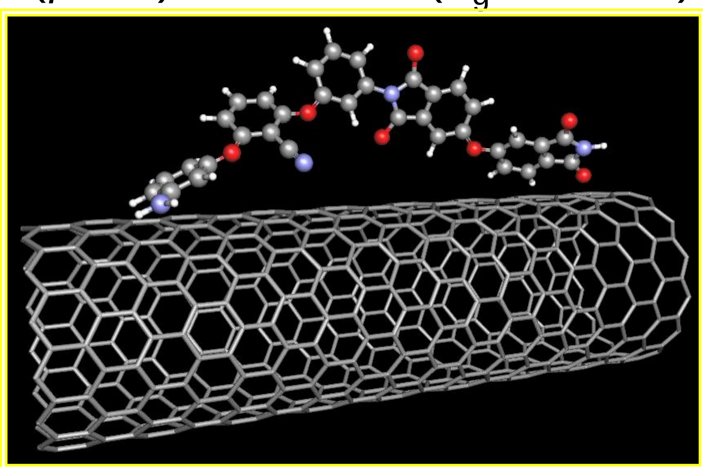
Building Blocks: SWCNT/Polymer Nanocomposites

Electroactive High Performance Polyimide

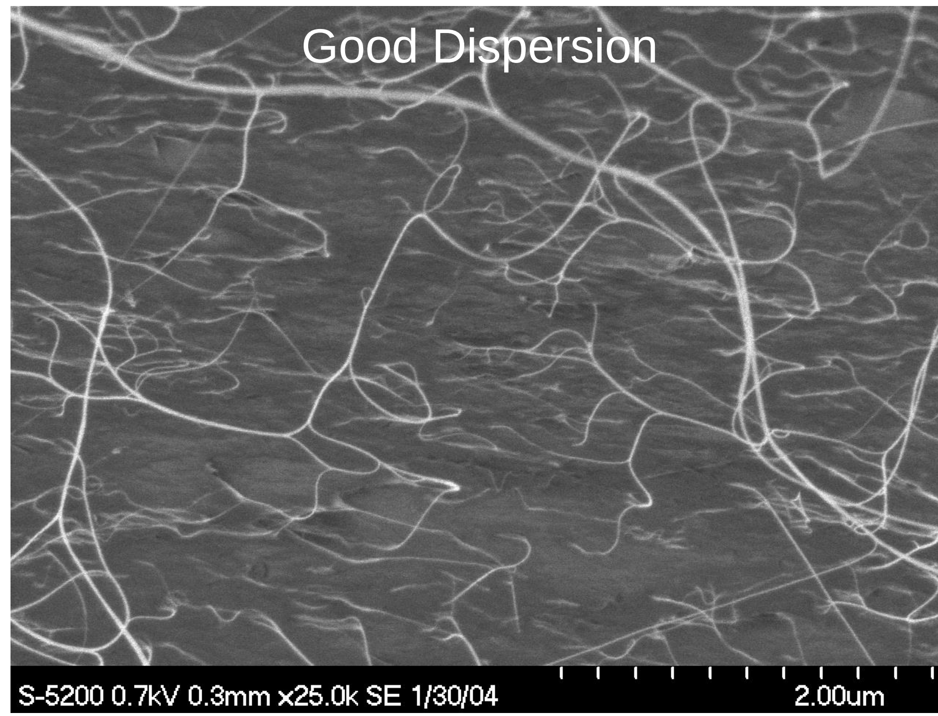


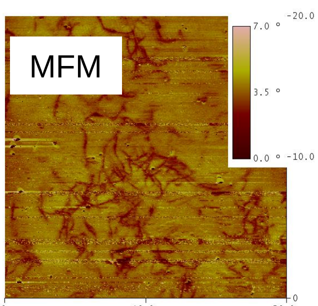
- Dispersion Interaction
- Donor-Acceptor interaction
- In-situ Polymerization under sonication and shear

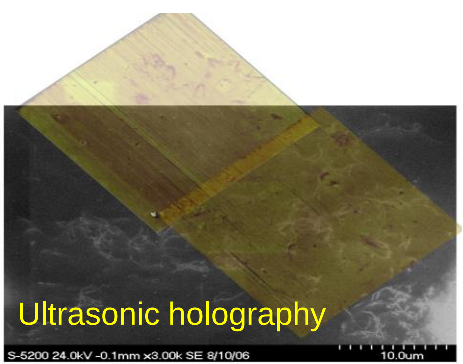
(β-CN)APB/ODPA (T_g = 220°C)



Polyimide + SWNT



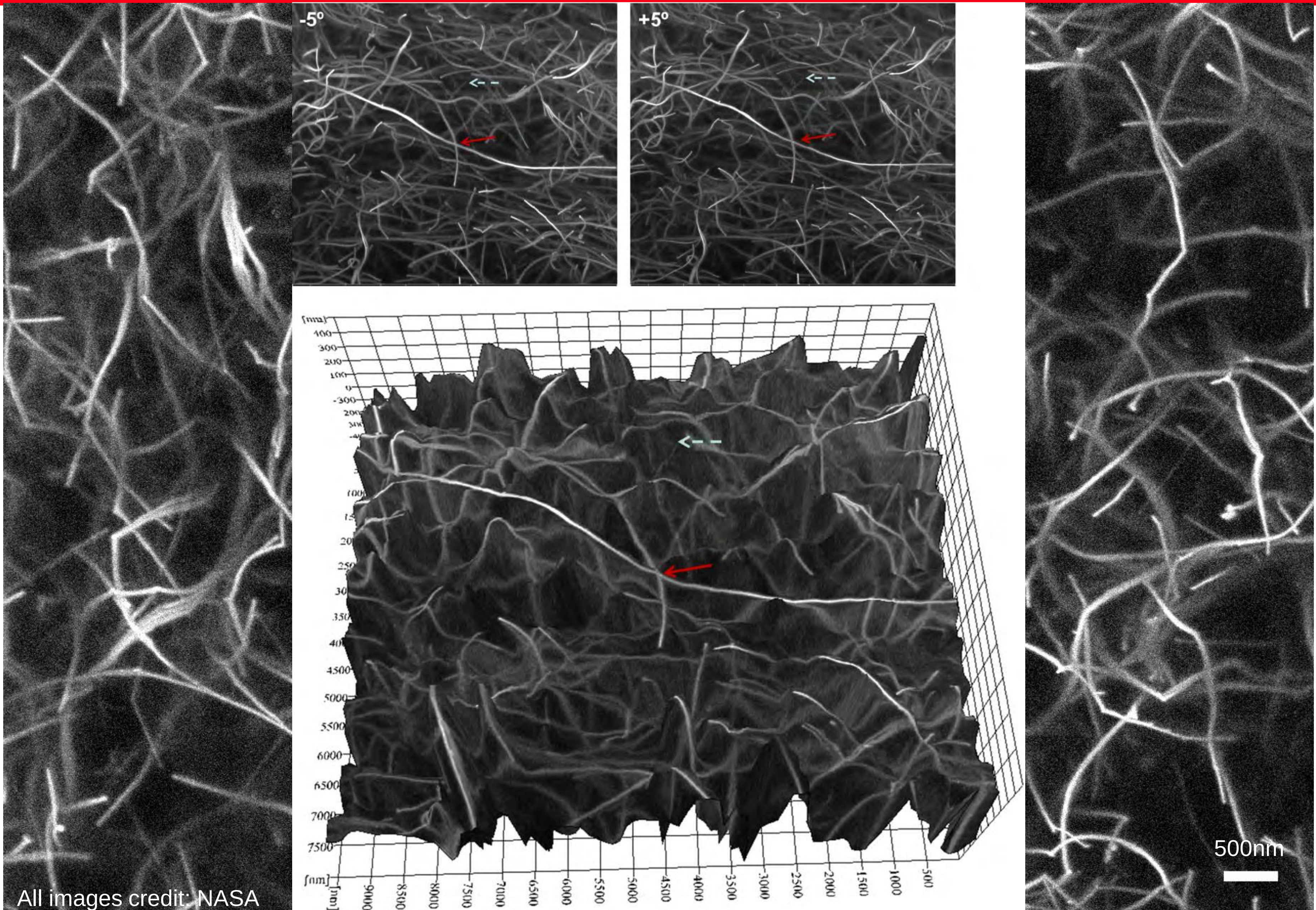




All images credit: NASA

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)



Tailoring Physical Property for Multifunctions

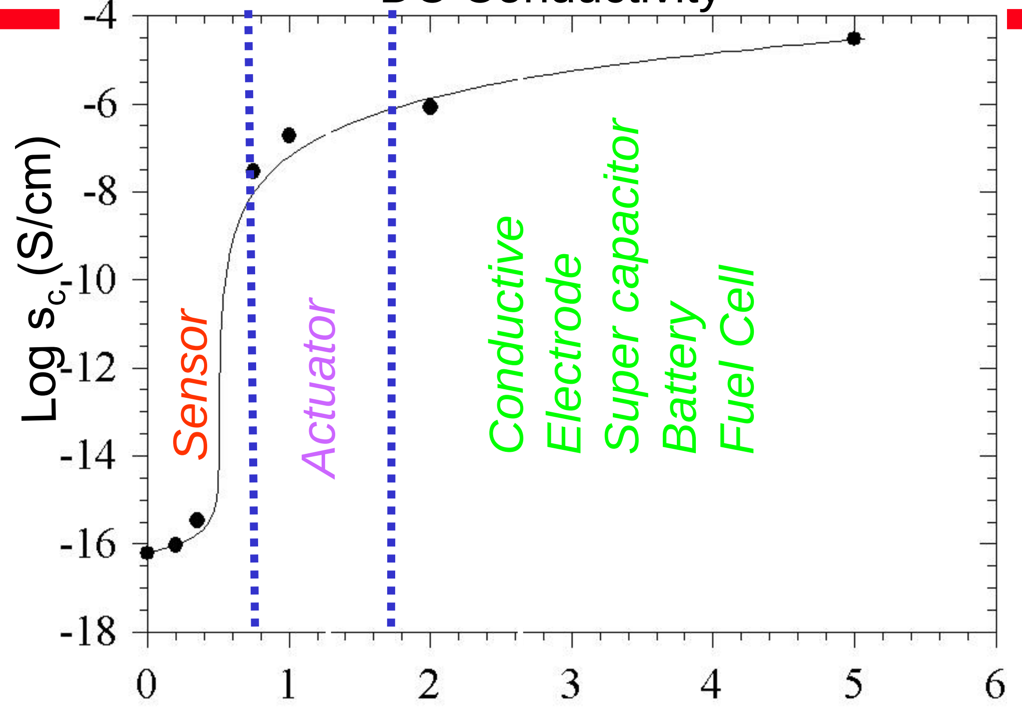
Materials Properties to be Tailored

- Electrical Conductivity
- Dielectric Permittivity
- Magnetic Permeability
- Thermal Conductivity/expansion coefficient
- Radiation Shielding
- Mechanical (modulus, strength, toughness…)
- Solar Absorptivity
- Thermal Emissivity
- Band gap engineering
- Optical property (transparency, refractive index…)
- Piezoelectricity/Pyroelectricity/Electrostrictive
- Gas/Liquid Permeability
- Anisotropy/orientation

Design Parameters

- Nano Inclusion type and combination (CNT, BNNT, BCNNT, GP, hBN, NP…)
- Matrix type
- Composition
- Dispersion
- Orientation
- Geometry, Fabrication, Processing…

Versatility of SWCNT Electroactive Polymer Nanocomposites



$$(1-f)(\sigma_i^{1/s}-\sigma_m^{1/s})/(\sigma_i^{1/s}+A\sigma_m^{1/s})+f(\sigma_c^{1/t}-\sigma_m^{1/t})/(\sigma_c^{1/t}+A\sigma_m^{1/t})=0$$

$$A=(1-f)/f_c$$

McLachlan et al, *J. Phys. C* 20 865 (1987), *PRB* 56 1236 (1998)

- In the vicinity of percolation, the composite acts as a dielectric material and yields an enhanced sensor response
- Above percolation, the composite is conductive (anti-static) and can be used as an electrostatic actuator
- Well above percolation, the composite is very conductive

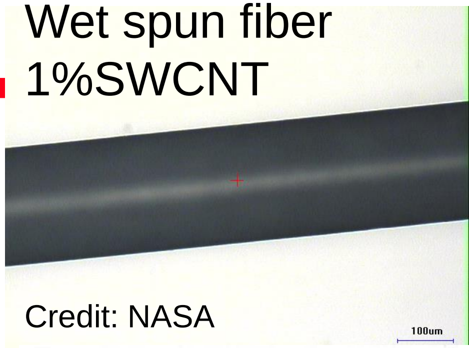
McLachlan at al, *J. Poly. Sci.: Poly. Phys.* 43 3273(2005)

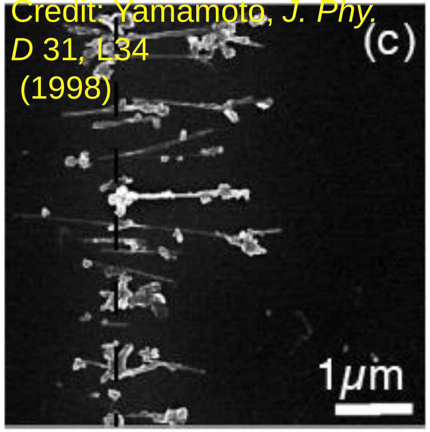
Alignment Approach

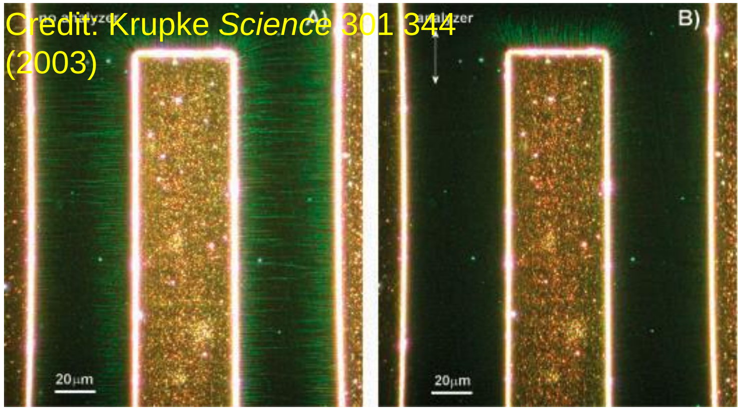
- *SWCNT Reinforced Functional Polymer Composites*

- *Alignment*
  - *High Shear Alignment (Passive)*
    - Extrusion, Pultrusion, Calendering
    - Fiber spinning (melt and wet spinning)
    - Electrospinning

  - *Electric Field Alignment (Active)*
    - AC & DC in a solvent
    - *CNT growth w/* EF
  - *Magnetic Field Alignment (Active)*
    - MF in a solvent

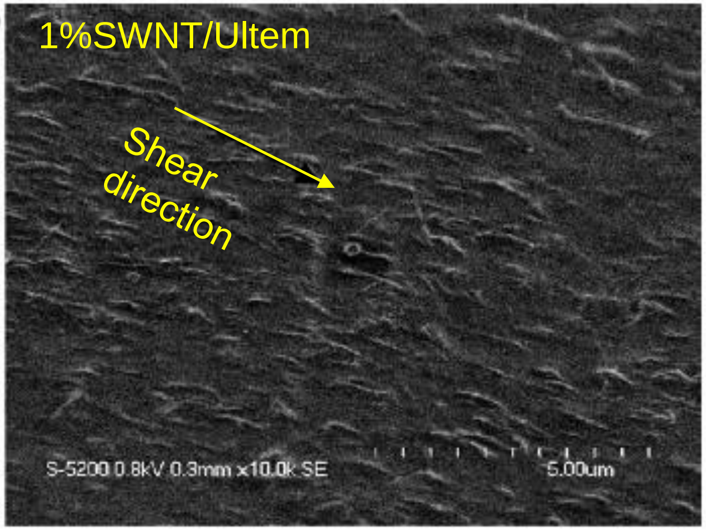


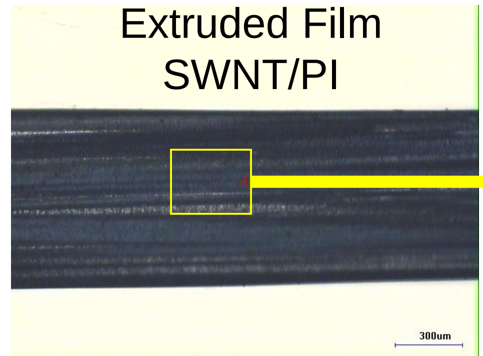


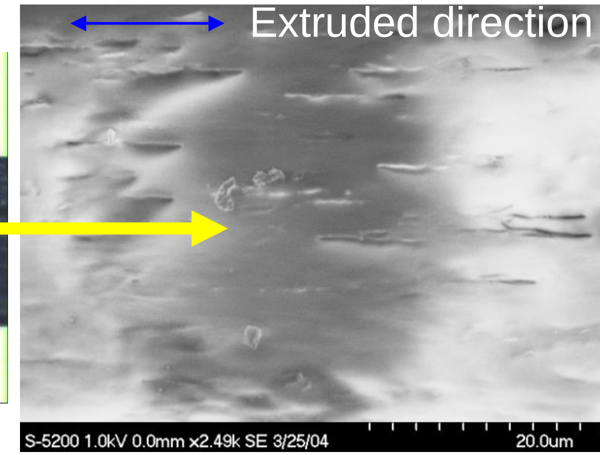


- *Aligned SWCNT-Functional Polymer Composites Using Dielectrophoresis*
  Tailoring Physical Properties (Mechanical, Electrical, Dielectric, Thermal…)

Shear Alignment: Extruded Fibers and Films

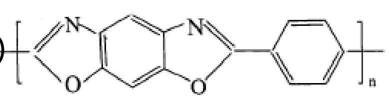






Composites: B, 35 439 (2004)

Poly(*p*-phenylene benzobisoxazole)



Dry-jet wet spinning

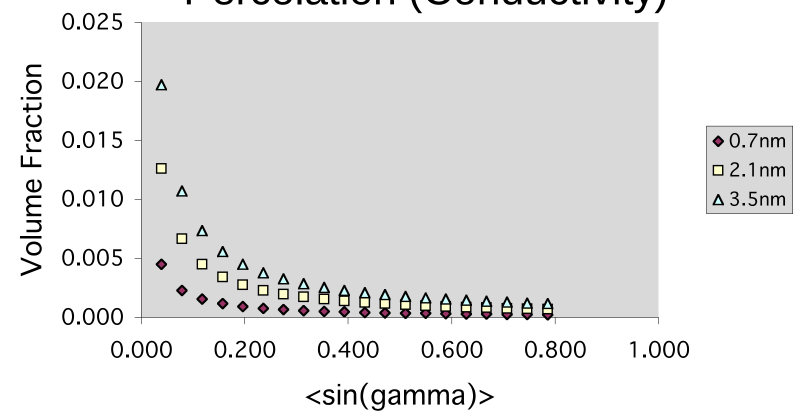
Georgia Tech Fiber	Yield strength (GPa)	Tensile mod (GPa)	Elongation (%)	Conductivity (S/cm)
PBO	2.6	138	2.0	insulating
5wt% SWCNT/PBO	3.2	156	2.3	insulating
10wt% SWCNT/PBO	4.2	167	2.8	insulating

Macromolecules 35 9039 (2002)

Percolation concentration of well dispersed SWCNT in a polyimide ≈ 0.05vol%

Comp. Sci. Tech. 63 (2003) 1637

Chem. Phys. Lett., 364 (2002) 303.

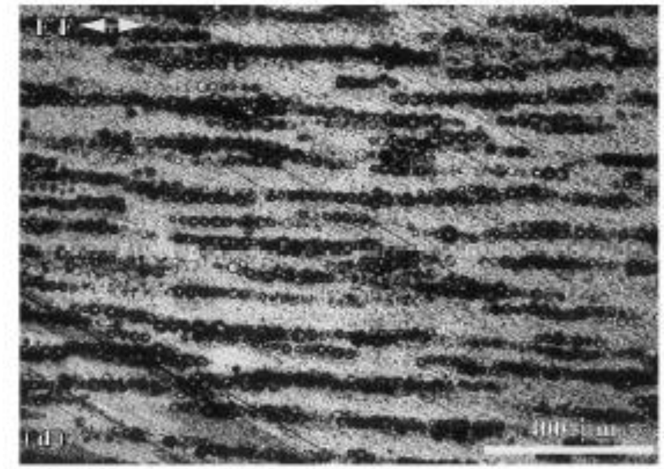


Orientation increase

All images credit: NASA

Dielectrophoretic Alignment: Spheres, Platelets, Fibers… AC Electric Field Alignment

Spheres



Fibers

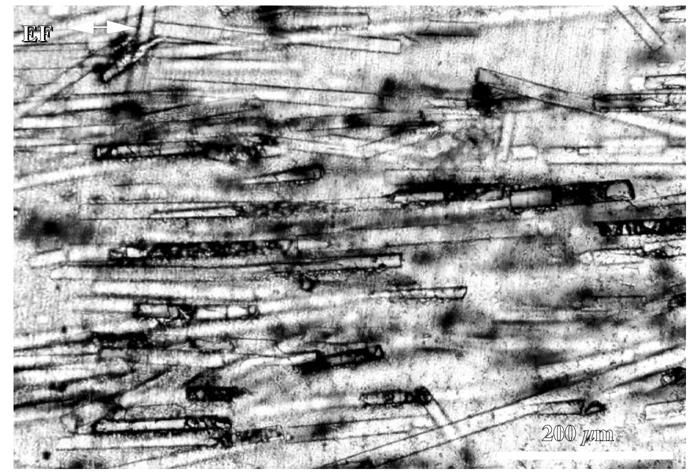
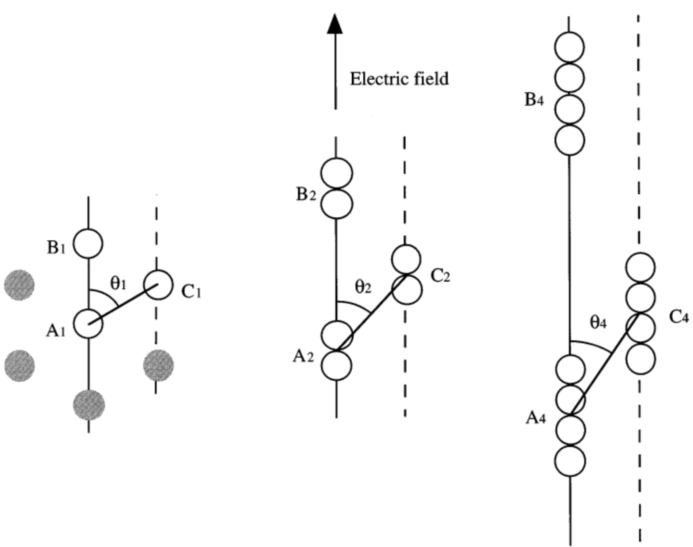


Figure 14. Optical micrograph of thin section of aligned glass fibers (4.5 vol%). Polymerized after 30 s under 0.81 kV/mm AC.

Model for longitudinal and lateral aggregation of inclusions

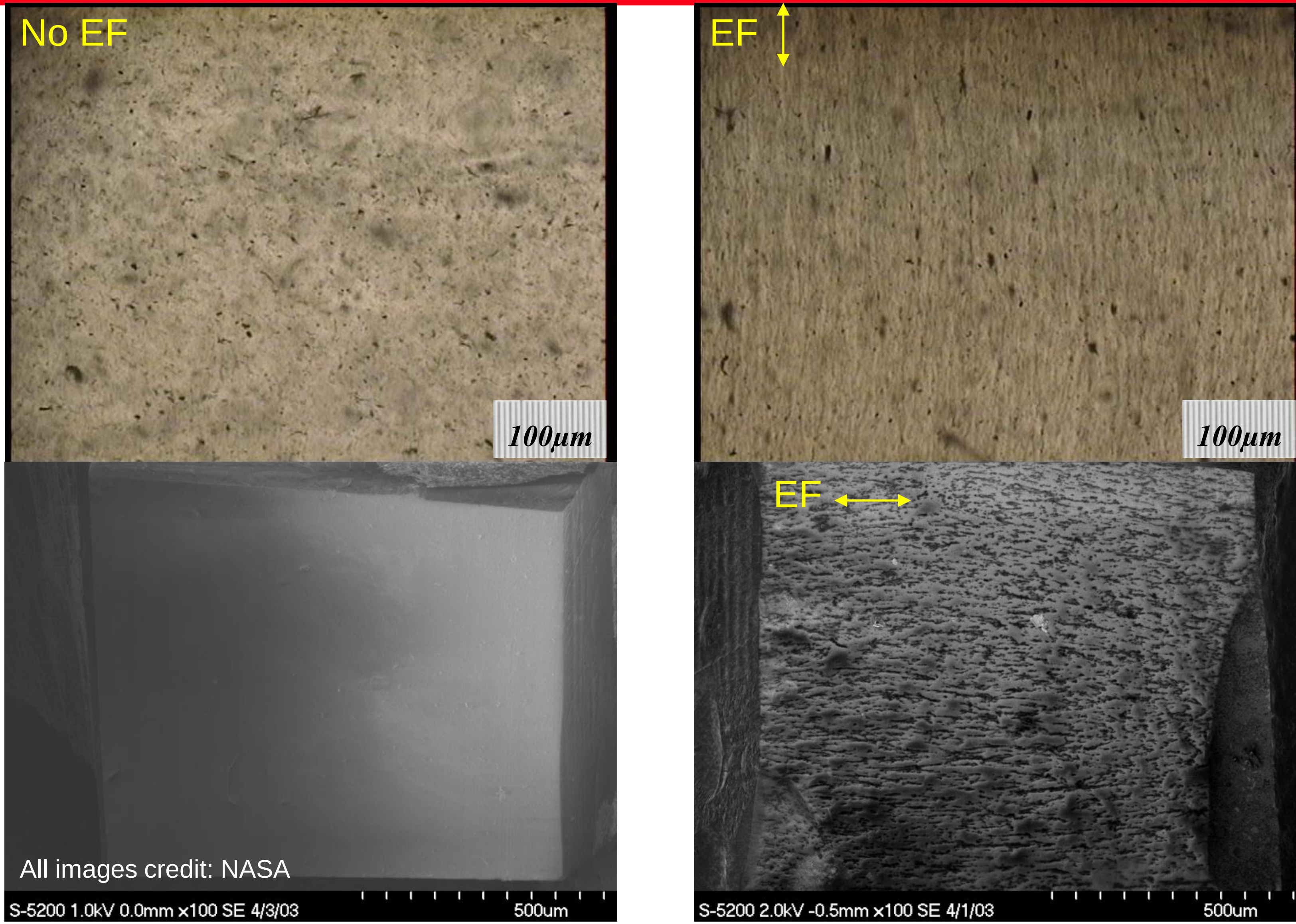


$$\lambda = \frac{\pi\varepsilon_0\varepsilon_1 a^3(\beta E)^2}{k_B T} > 1 \text{ for Alignment}$$

$$\beta = (\varepsilon_2 - \varepsilon_1)/(\varepsilon_2 + 2\varepsilon_1) \text{ or } (\sigma_2 - \sigma_1)/(\sigma_2 + 2\sigma_1)$$

Davis, *J. Appl. Phys.* 72, 1334 (1992)
Park and Robertson, *J. Mater. Sci.,* 33, 3541 (1998)
Images Credit: Park and Robertson, *Mater. Sci. Eng.,* A257, 295 (1998)

Aligned SWCNT/Polymer Composites: OM and SEM



Cured without electric field

Cured with electric field ($200V_{p\text{-}p}$, 10Hz, 10min)

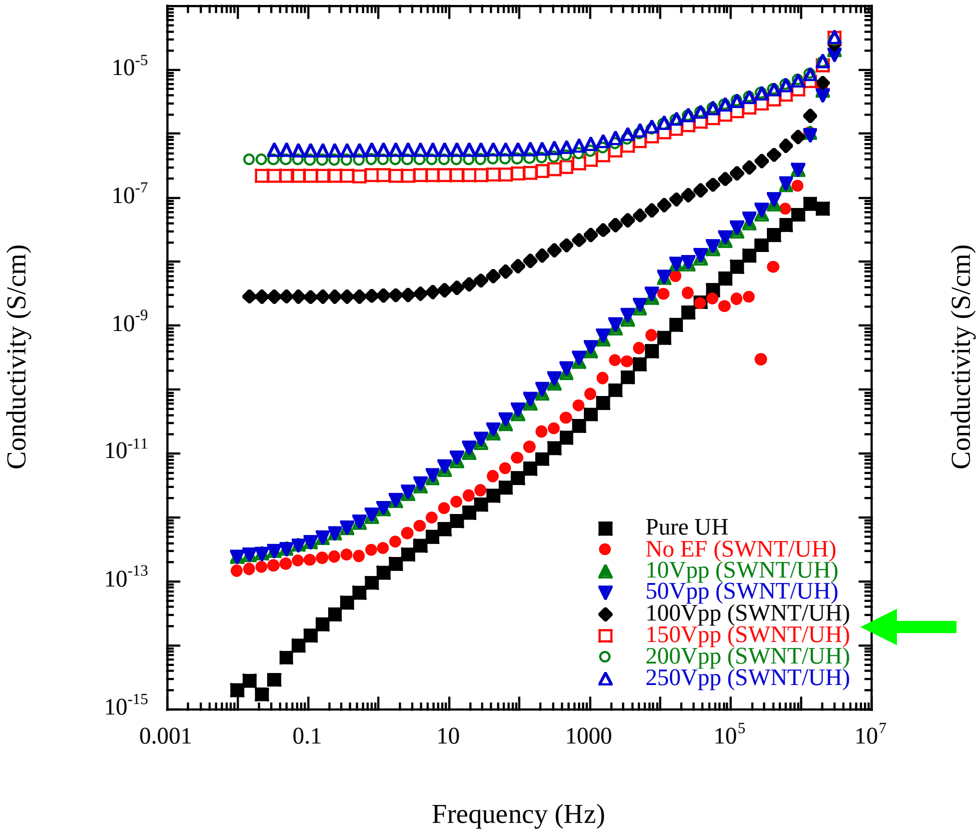
SWCNT loading: 0.03wt%

Park et al, *J. Poly. Sci: Poly. Phys.* 44 1751 (2006)

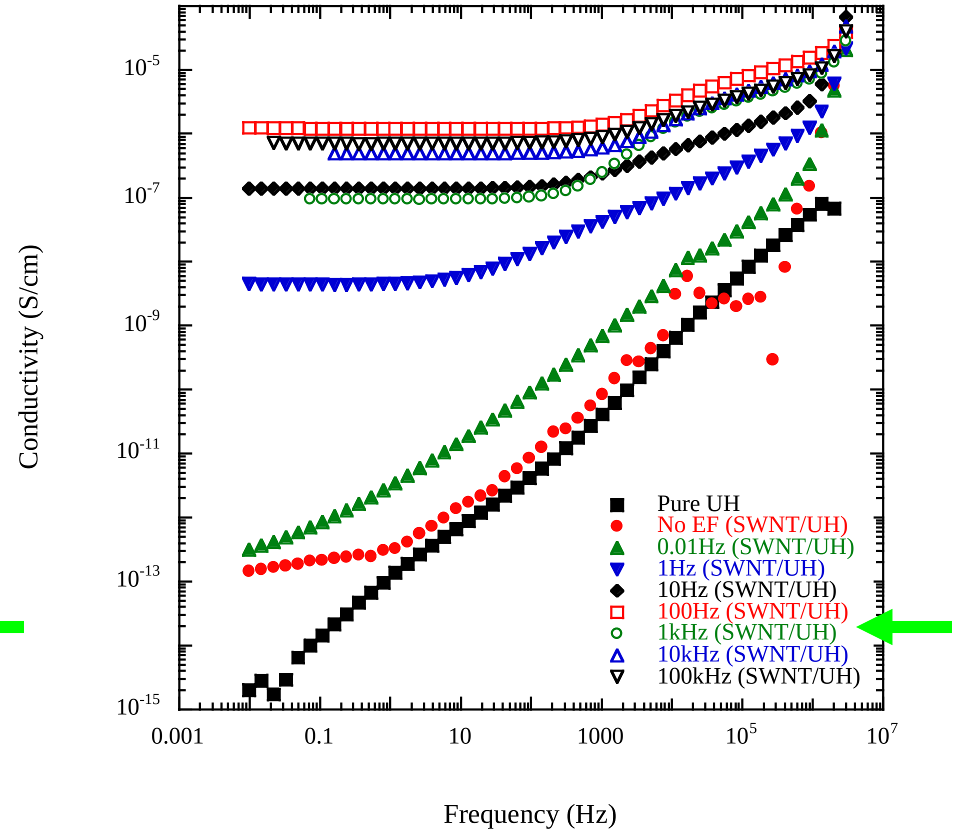
Effect of Alignment of 0.03%SWCNT/Polymer Composites

$0.03\% < \phi_c$

Applied Voltage



Frequency

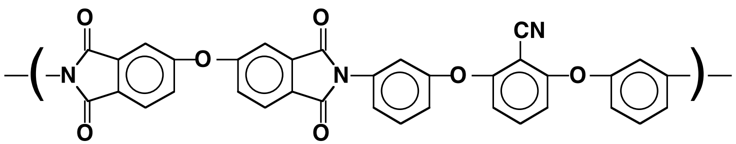


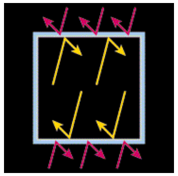
Degree of SWCNT Alignment ==>> Tailor Physical Properties

Park et al, *J. Poly. Sci: Poly. Phys.* 44 1751 (2006)

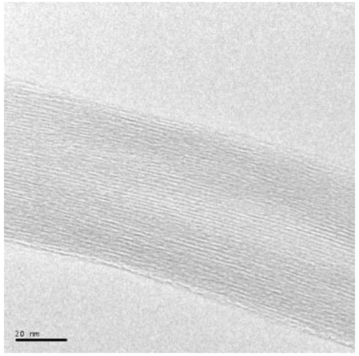
Metallized Nanotube Polymer Composite (MNPC) Metal Infusion Process into SWCNT/Polyimide Film

SWCNT/polyimide film formation: good dispersion

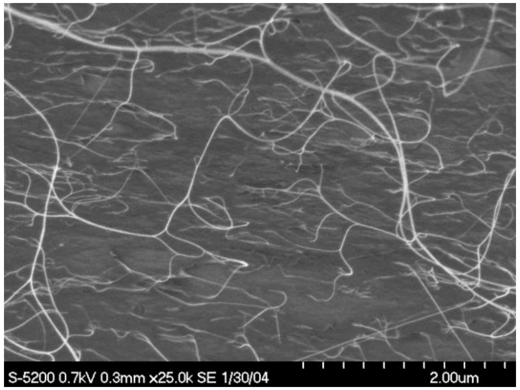




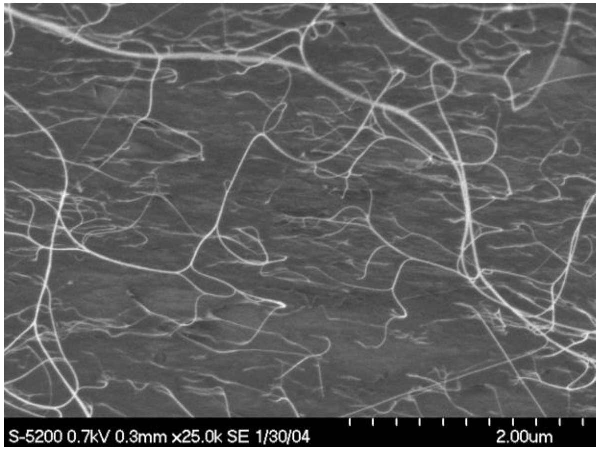
+



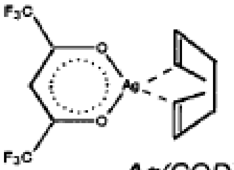
→



Metal-MNPC (Metal/SWCNT/polyimide) film formation: SCF Metal impregnation



+

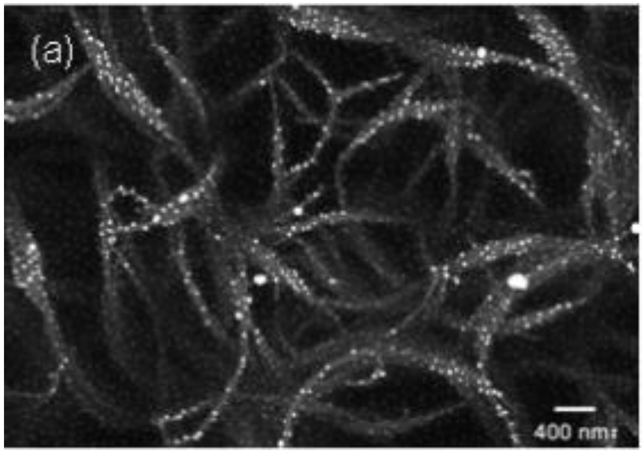


Ag(COD)(HFA)

> 200 atm
> 100˚C
1–6 hr

→

250˚C
1hr



All images credit: NASA

Park et al, *J. Poly. Sci.: Poly. Phys.*, 50, 394 (2012)

Ag-MNPC Films with various SWCNT Concentration

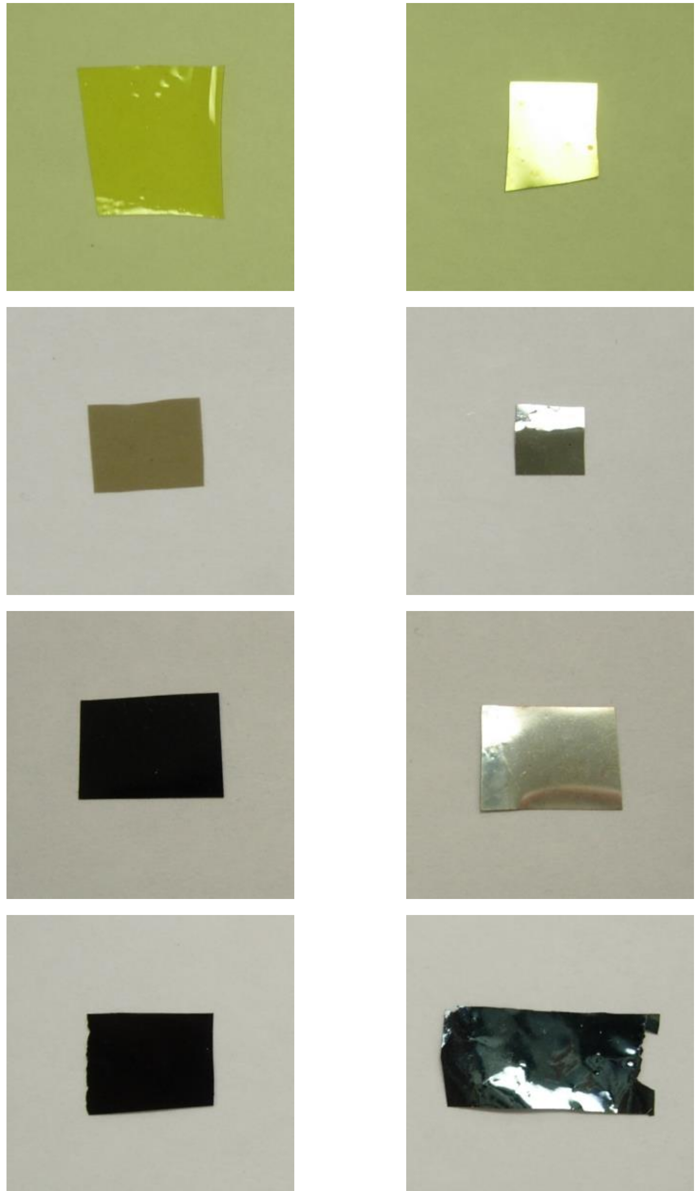
Control | Ag-MNPC

0%SWCNT

0.1%SWCNT

2%SWCNT

10%SWCNT

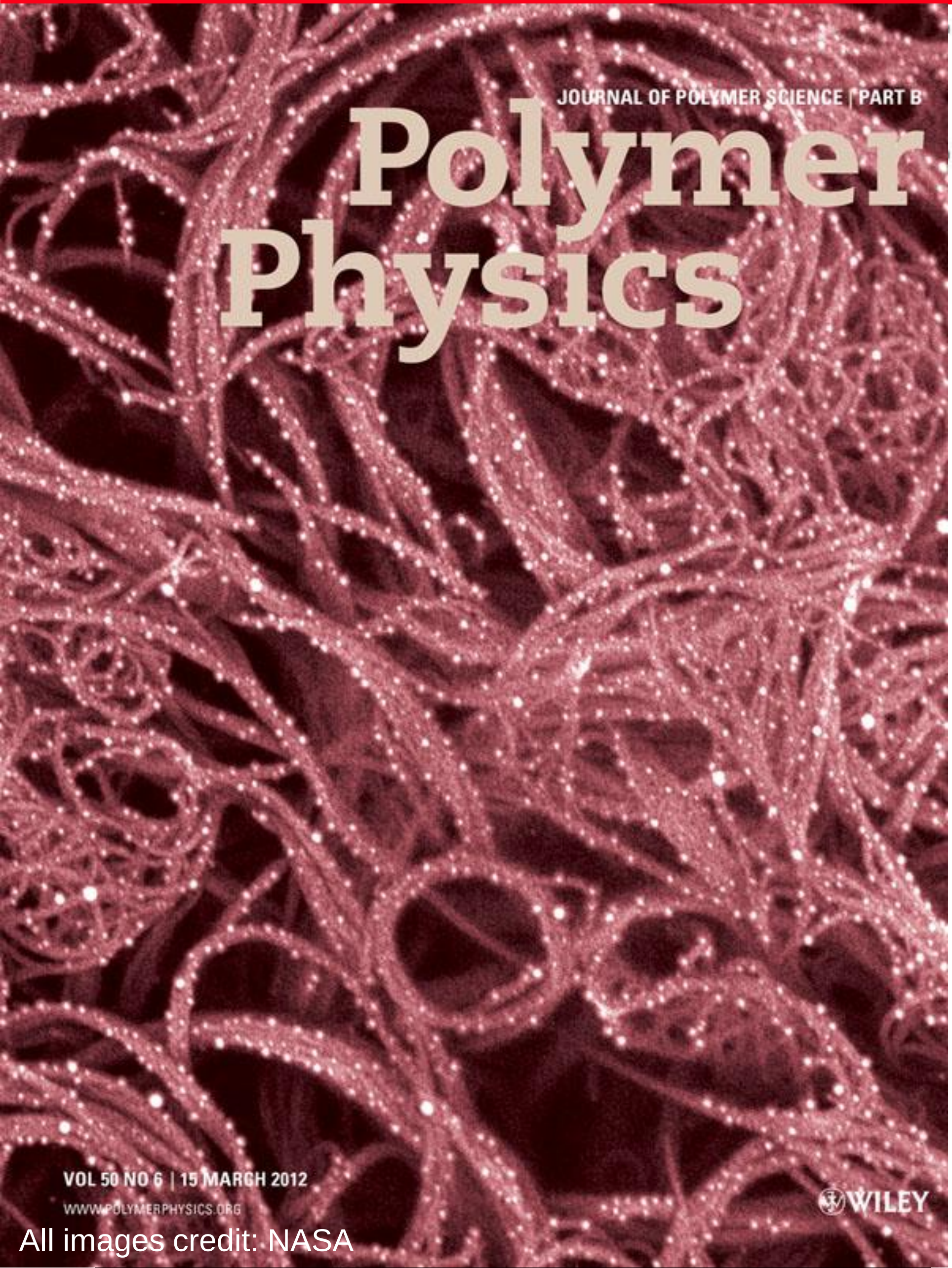


Shiny surfaces
Reflection shielding

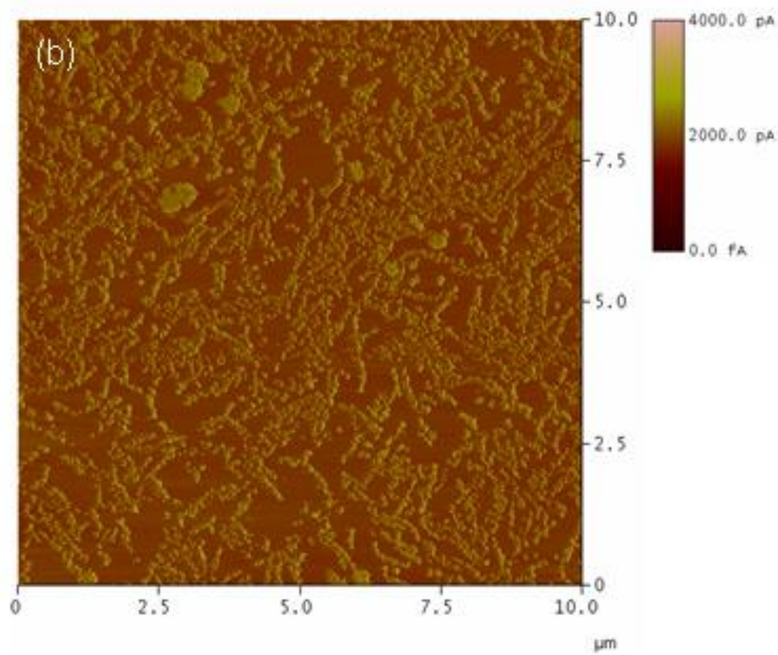
All images credit: NASA

Park et al, *J. Poly. Sci.: Poly. Phys.*, 50, 394 (2012)

Tunneling AFM & HRSEM: Ag-MNPC: Ag/10%SWNT/βCN AO



All images credit: NASA



Above: Topograph and tunneling AFM images of 10 wt.% SWNT/□-CN AO/Ag prepared by 20 % metallization solution.

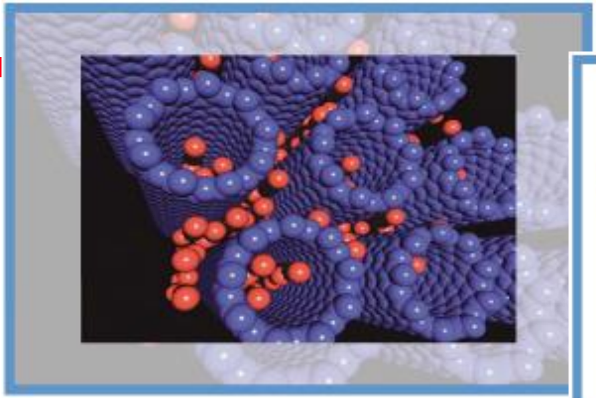
Conductivity & Toughness increased

Left: HRSEM micrograph of 10 wt.% SWNT/□-CN AO/Ag prepared by 20 % metallization solution.

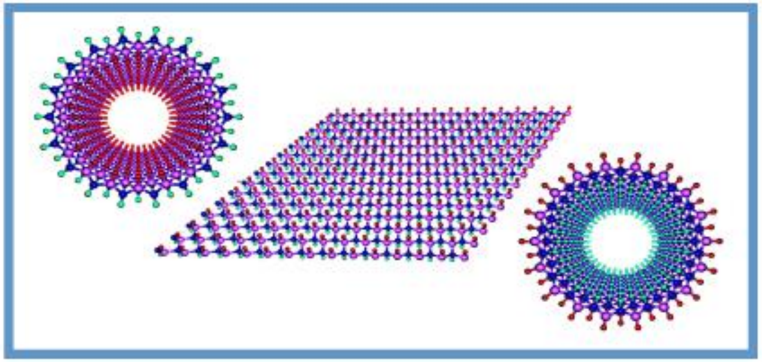
Credit: *J. Poly. Sci.: Poly. Phys.*, 50, 394 (2012)

BNNT enables……………………

Hydrogen Storage BNNT

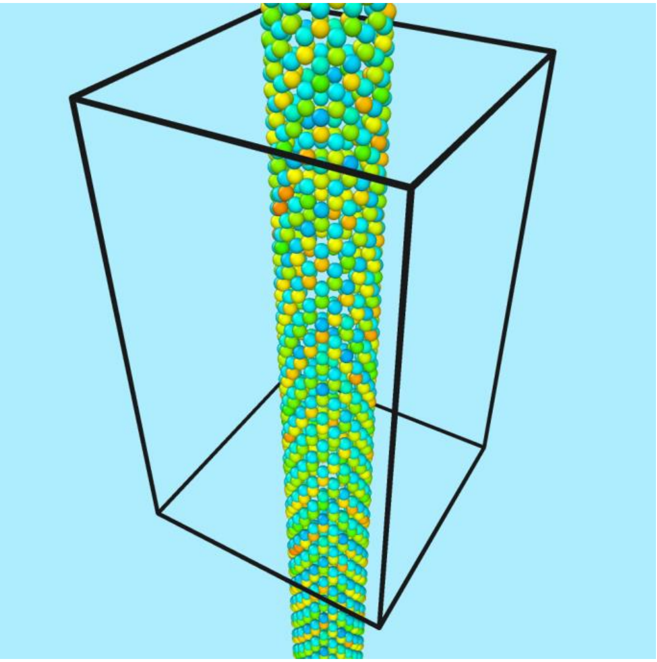


Hydrogenated BNNT

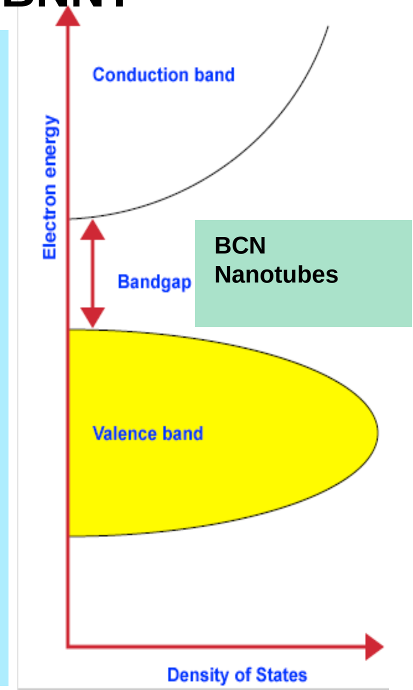


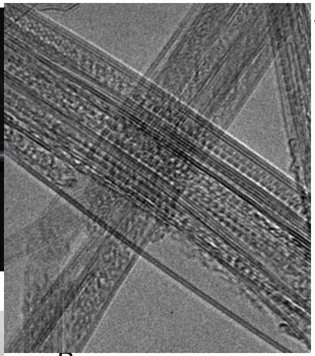
Radiation Shielding Materials Containing Hydrogen, Boron, and Nitrogen: Systematic Computational and Experimental Study

Electroactive properties of BNNT

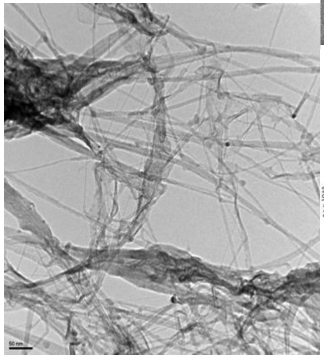


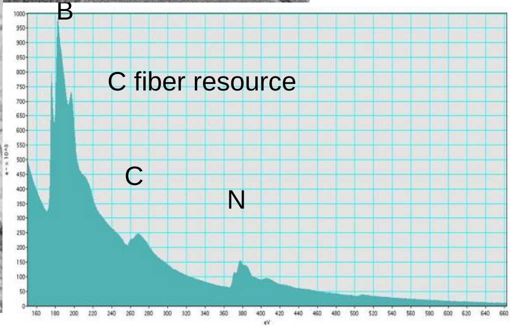
BNNT (12 0) Polarization in Stretching Induced Electric charge (e)





TEM image of C_{60}-BNNT (endo-doped) UC Berkeley





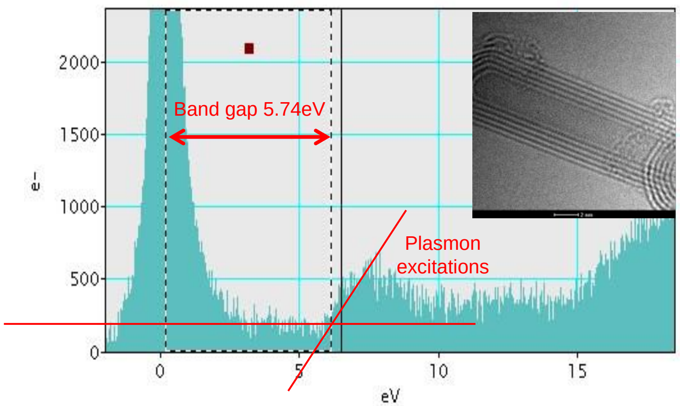
TEM, EELS, and Raman spectra of BCNNT.

$B_xC_yN_z$ Nanotube (BCNNT) Development

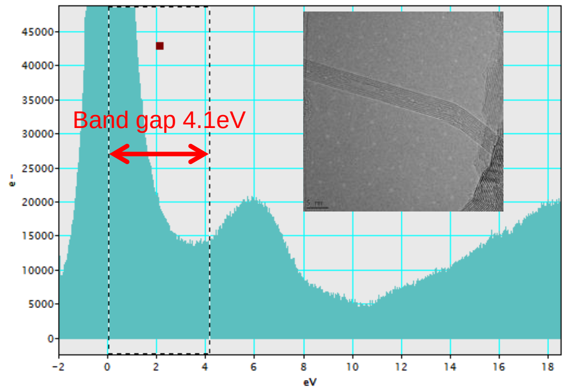
All images credit: NASA

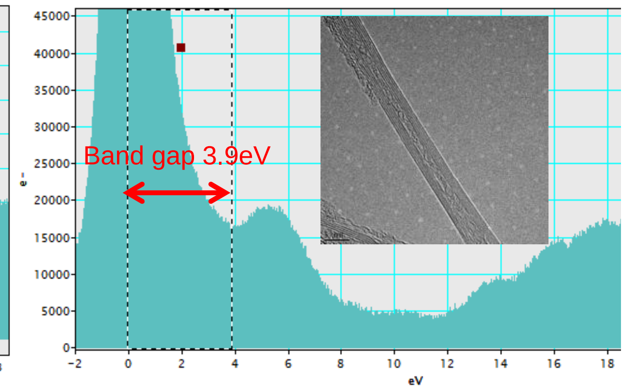
Band Gap Measurement: Low Energy EELS (modified BNNT)

Bandgap measurement of BNNT
(Low-loss region)

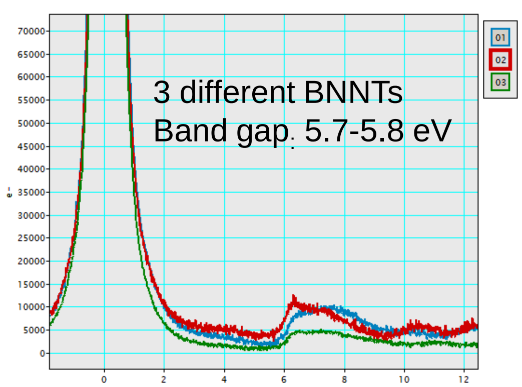


Bandgap measurement of C_{60}/BNNT
(Low-loss region)

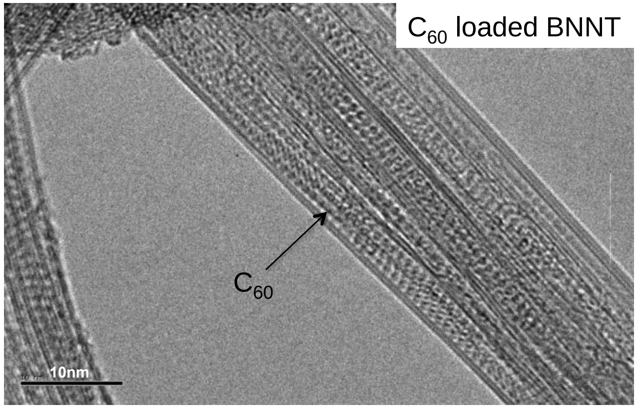


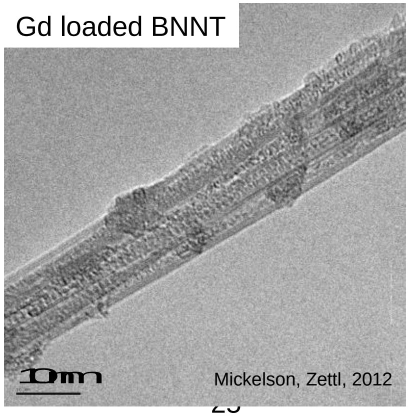


Superimposed Low Loss EEL spectra of multi walled Boron nanotubes shown in previous pages



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



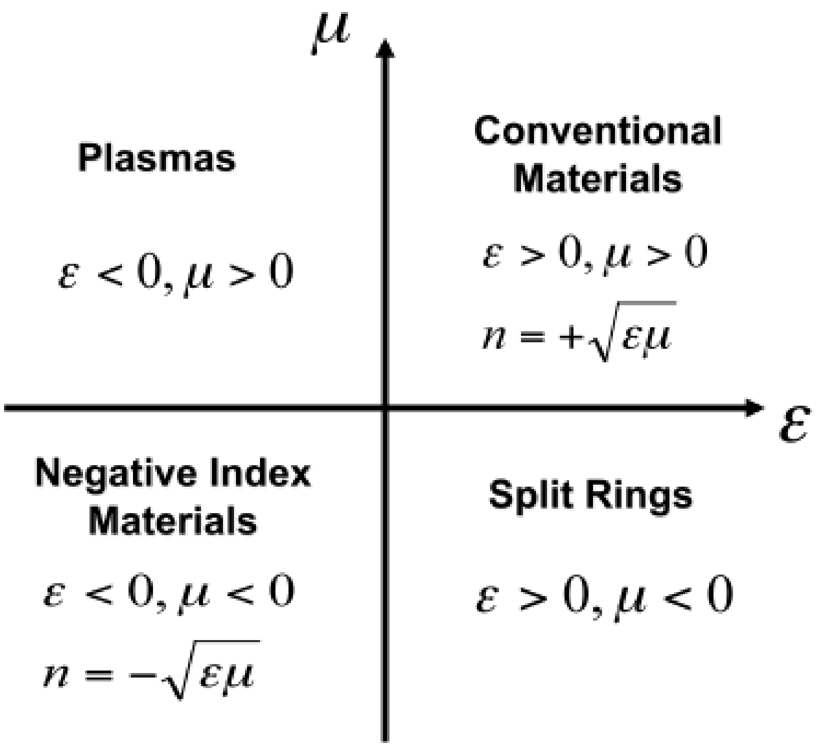


Credit: UC Berkeley; Zettl

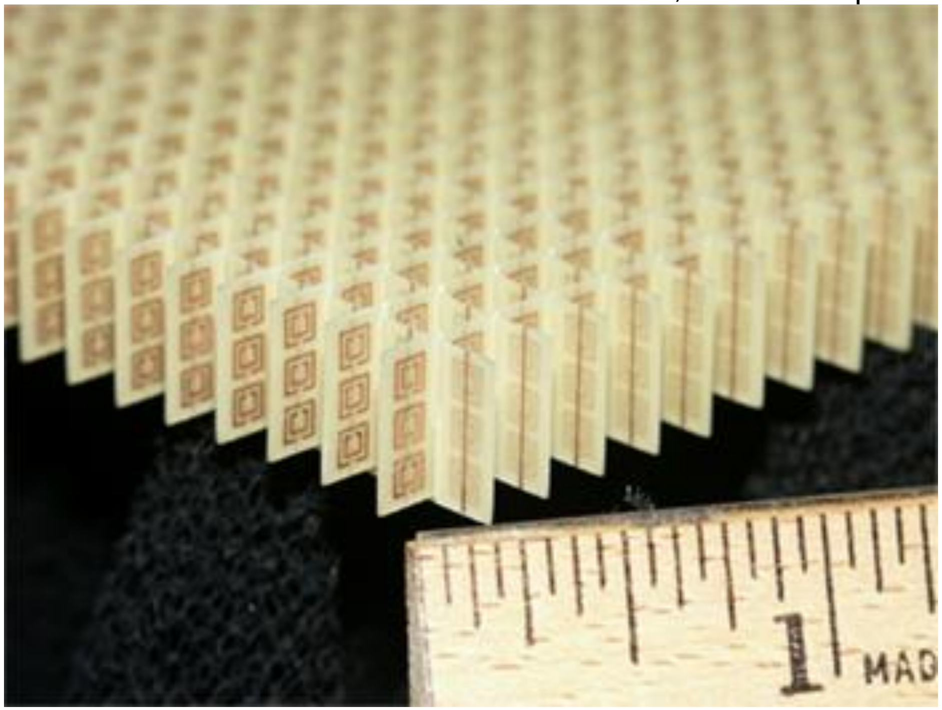
All images credit: NASA

Doped Chiral Polymer Metamaterials (DCPM)

What is Metamaterial? & Challenges



Metamaterials, Credit: Wikipedia



Credit: *APL* **78** 489 (2001)

$n < 1$ → **Metamaterials**

Approaches

Problems of SOA Split Resonance Ring (SRR)

- Special architecture and complex design required
- Difficult to build SRR crystalline structures
- Difficult to scale-up
- Not flexible and difficult to apply for complex structures
- Difficult to reach optical ranges
- Lack of resonance frequency tunability

Metamaterials without special architecture or design (negative permeability) possible for optical ranges?

$$n_{eff} = \sqrt{\varepsilon\mu - \kappa}$$

Novel Approach: Metamaterial without special architecture and negative permeability

Chiral Metamaterials

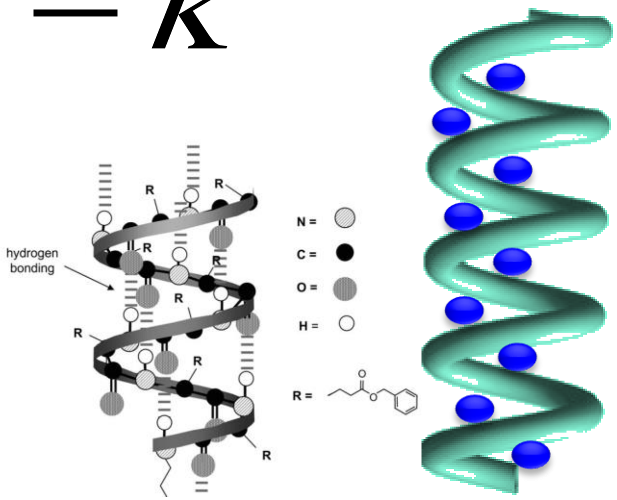
$$k = \frac{c}{v L_v} \frac{j}{d}$$

$$n_{eff} = \sqrt{\varepsilon\mu} - \kappa$$

Our Novel Approach

$$n_{\text{eff}} = n_{\text{composite}} - \kappa_{\text{composite}}$$

$$n_{\text{composite}} = n_{\text{host}} - \Delta n_{\text{plasmonic}}$$

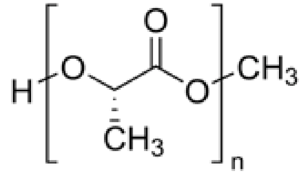


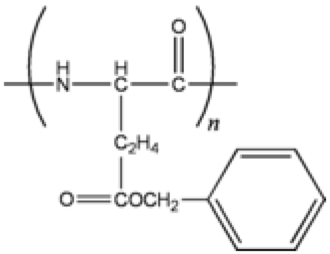
Credit: *IEEE Journal of selected topics in quantum electronics*, **10** 1154 (2004)

- The size of the **helical chiral polymer** is of the order of wavelengths in the optical range
- Self-organization of helical polymer chains
- Incorporating **plasmonic inclusions** lowers the permittivity
- Electronic coupling between plasmonic particles and helical polymer chains enhances chirality

Plasmon NP infusion: *in situ* Direct Mixing & SCF infusion

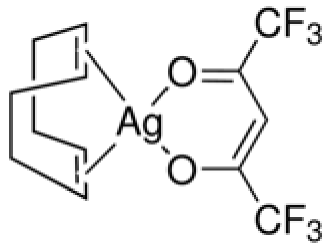
<u>In-situ Direct mixing</u>

Or  **Poly(L-lactide)**



PBLG

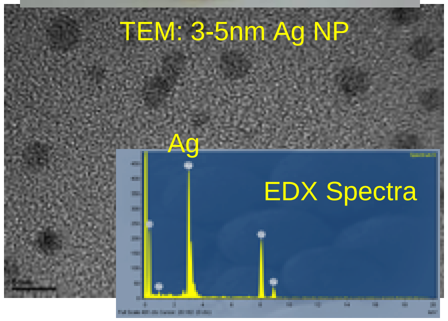
+



Ag salt

$CHCl_3$ → Direct mixing cast

Ag/PBLG Film



<u>Supercritical fluid (SCF) CO_2 Ag impregnation</u>

PBLG Film

+

SCF CO_2

> 345.4 atm
> 70˚C
1–6 hr
→
200˚C
1hr
reduction

Ag/PBLG Film

All images credit: NASA

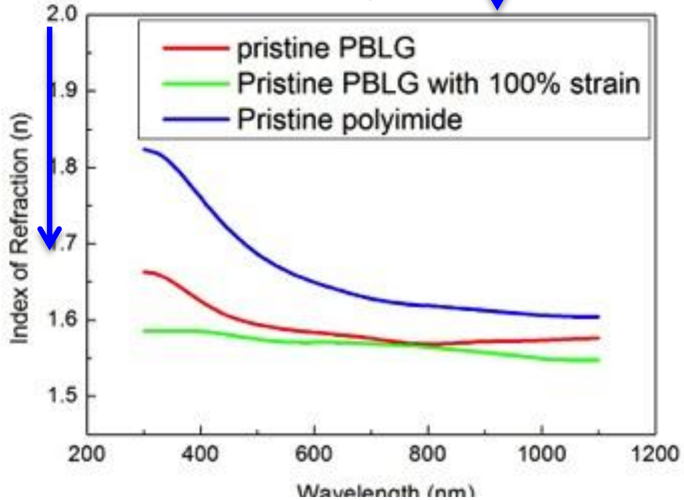
Ellipsometry (Index of Refraction): PBLG, DCPM

Drawing of chiral polymer → Reduction of index of refraction

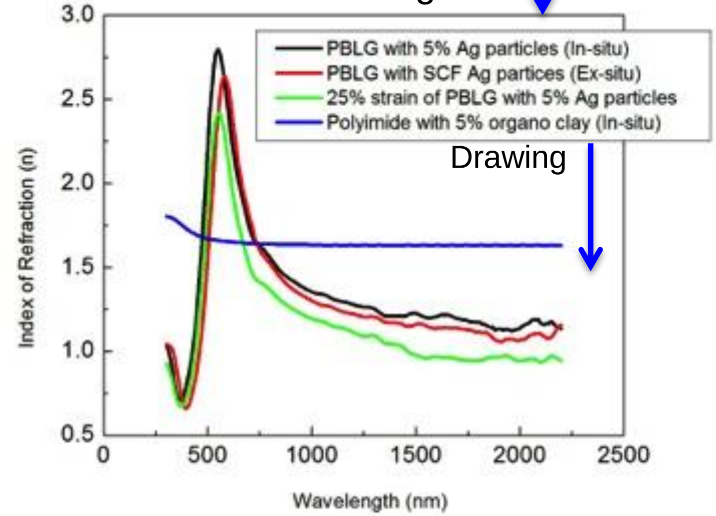
n_{PBLG} ≈ 1.55 in visible range

Addition of Ag or Au plasmonic nanoparticles → Reduction of index of refraction

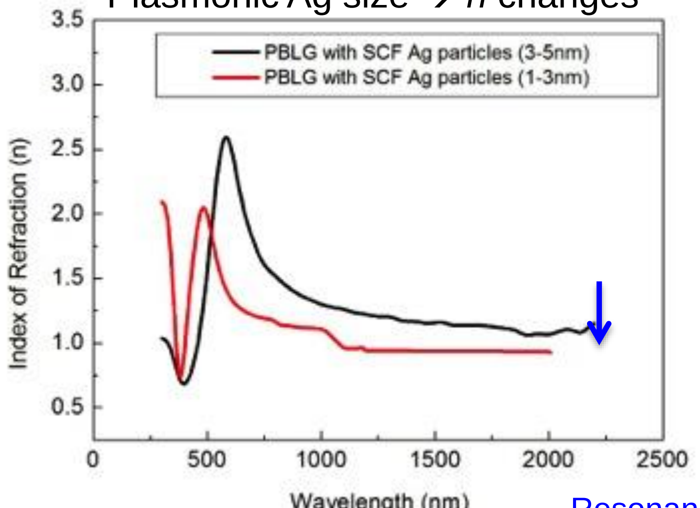
Drawing → *n*



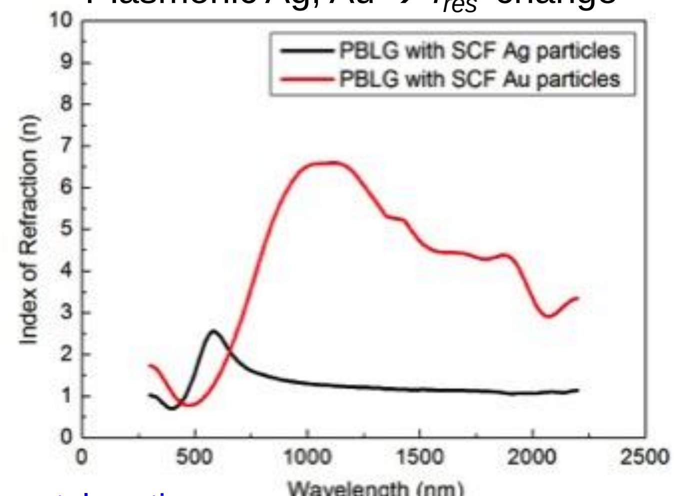
Plasmonic Ag → *n*



Plasmonic Ag size → *n* changes

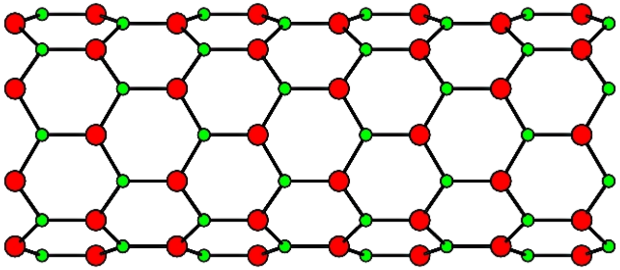


Plasmonic Ag, Au → f_{res} change



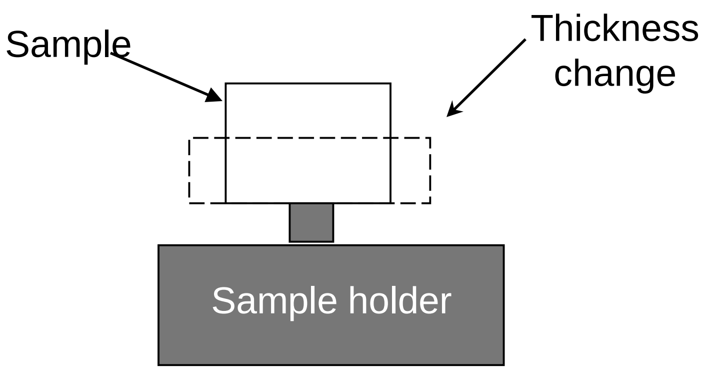
Resonance peak is not from metal coating

Piezoelectric and Electrostrictive Properties for Sensors/Actuators (SWCNT and BNNT Composites)

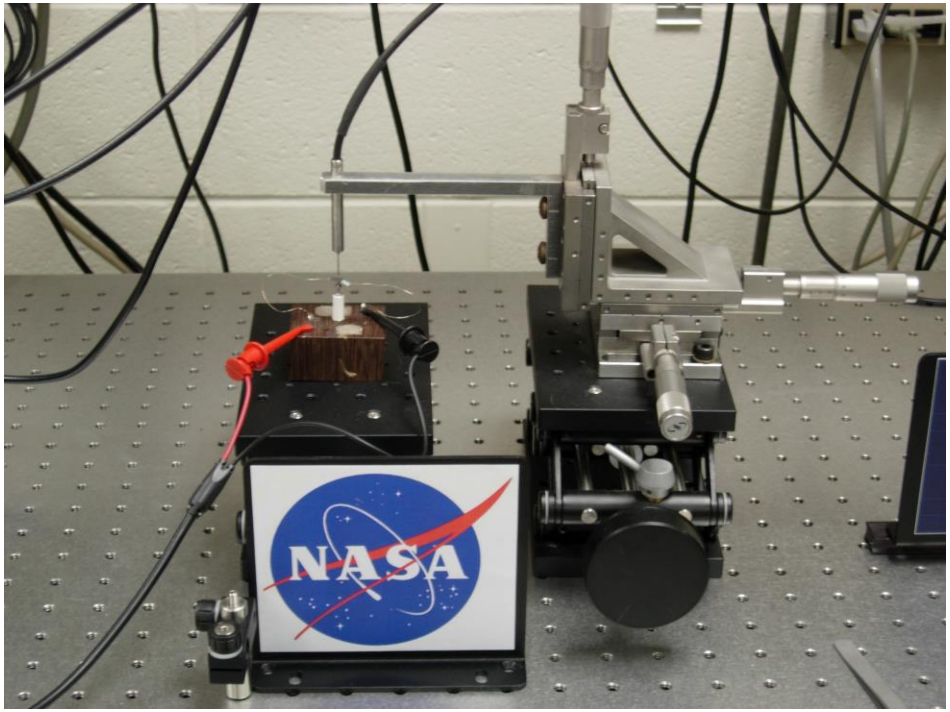


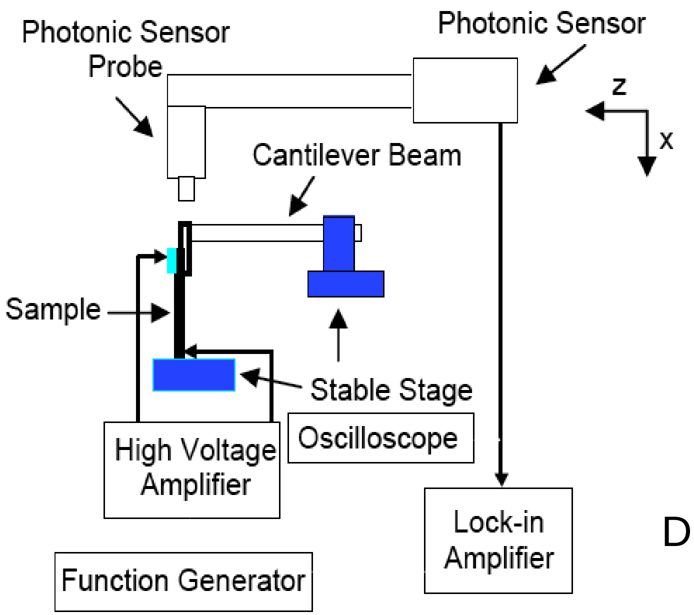
Actuation Response: SWCNT/Polyimide Composite

Out-of-plane strain



Using Fiber Optic Displacement Measurement



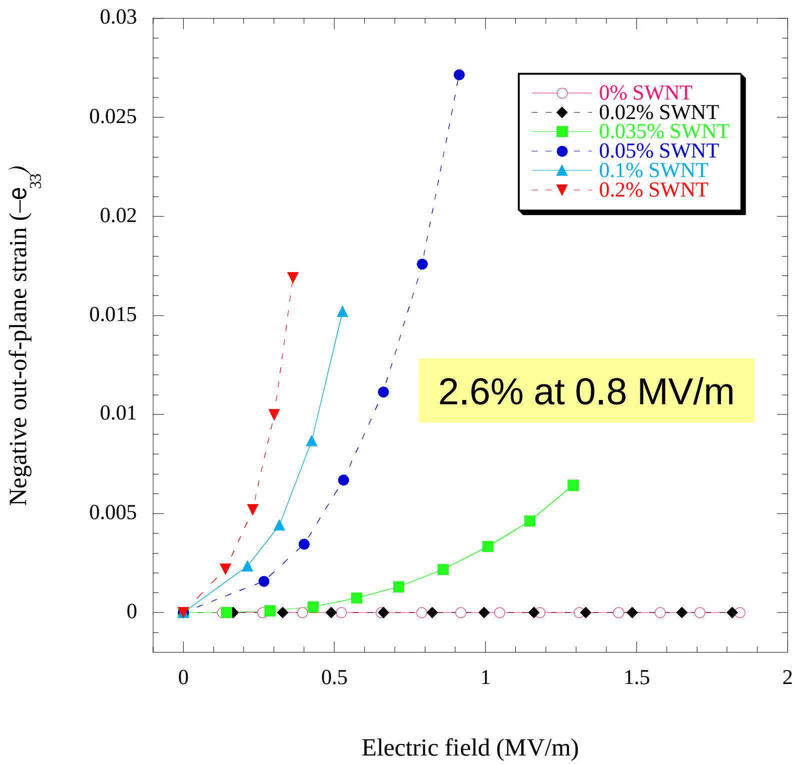


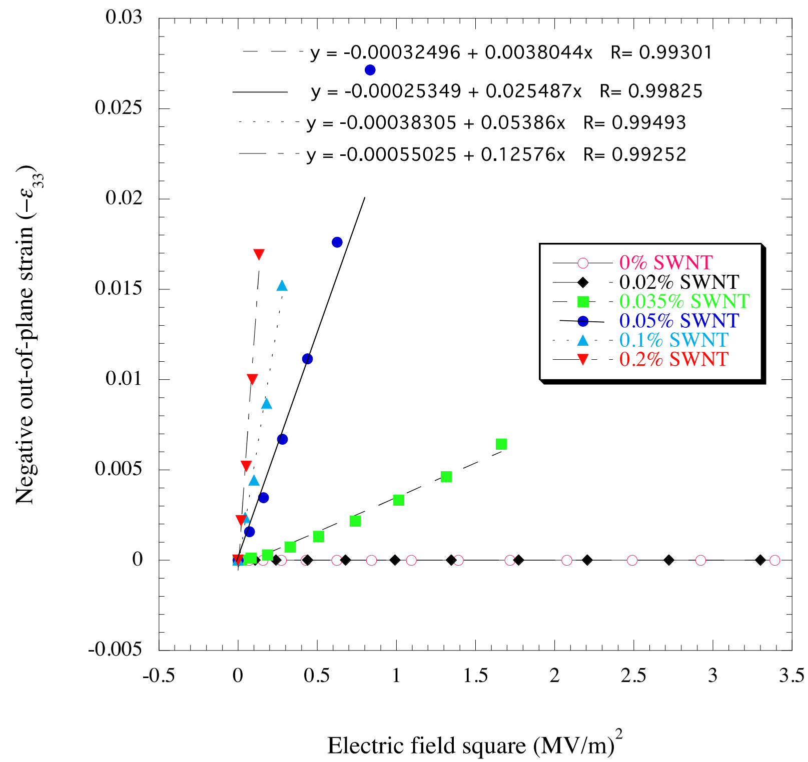
Acousto-Optic Sensors model 201 Angstrom Resolver™

Dilatometer with cantilever

All images credit: NASA

Actuation: Out-of Plane Strain: SWCNT Polymer Composite





$10^3 - 10^4$ times higher

<u>Electrostrictive coefficient</u>

SWCNT/Polyimide $M_{33} = -3.6 \times 10^{-15} \sim -1.2 \times 10^{-13}$ m²/V²

Polyurethane $M_{33} = -4.6 \times 10^{-18} \sim -1.6 \times 10^{-17}$ m²/V²

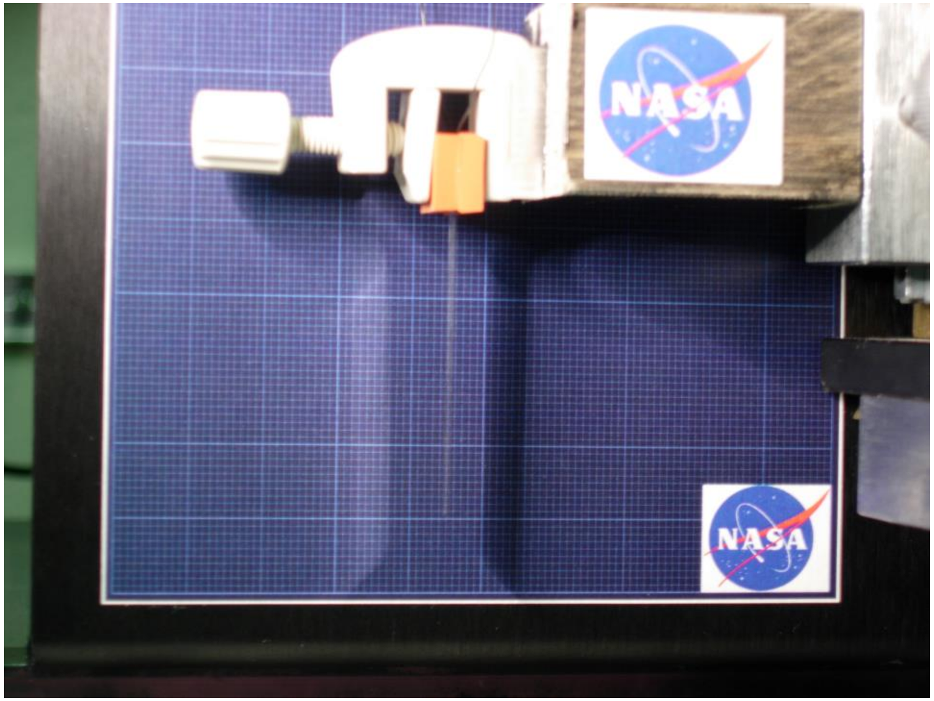
$S_{33} = S_E$ *(Electrostriction)*
$+ S_M$ *(Maxwell effect)*

$$S_M = -\frac{1}{2Y} e_0 e_r E^2 (1 + 2n) < 0.01\%$$

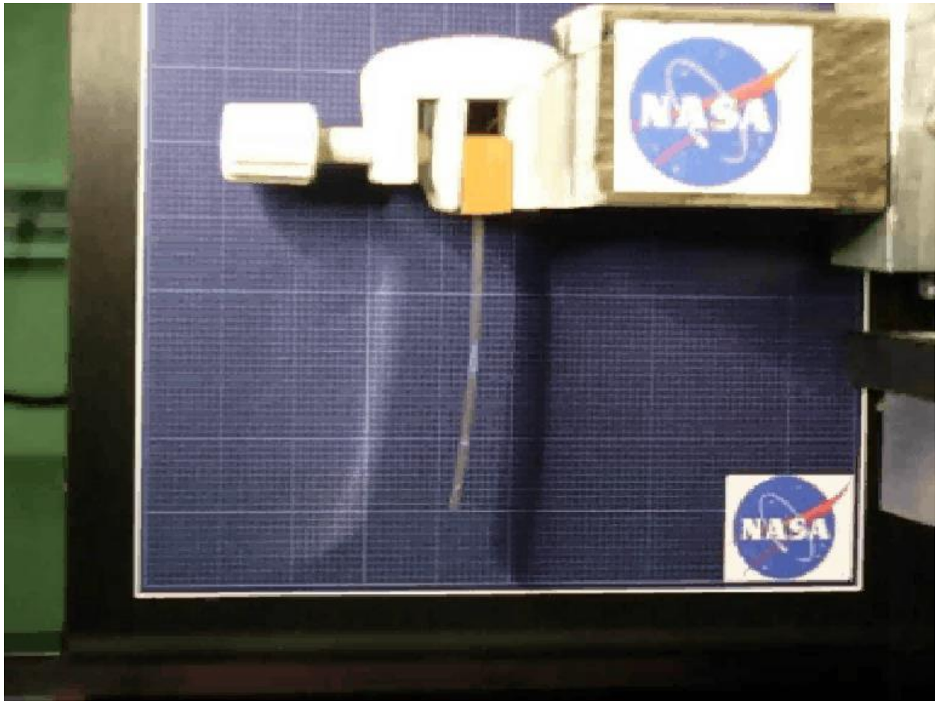
Park et al, *Adv Mater*, 20 2074 (2008)

Bending Actuation of SWNT Polymer Nanocomposite

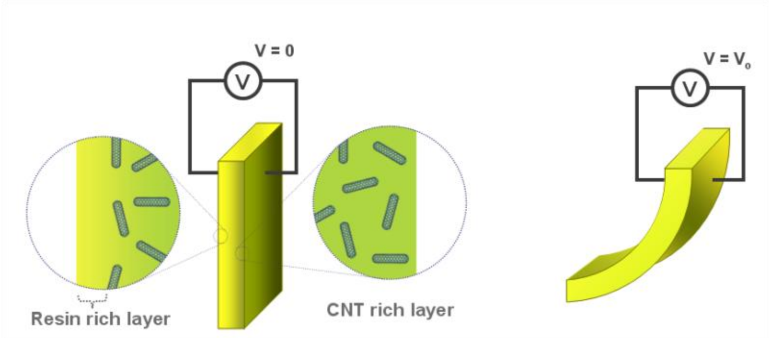
No EF



EF = 0.8 MV/m



$M_{31} = 2.86 \times 10^{-15}\ (m^2/V^2)$



Sonic fatigue abatement
Noise transmission attenuation
Wing and panel flutter control
Tail buffet alleviation control
Surface shape control

All images credit: NASA

Park et al, *Adv Mater*, 20 2074 (2008)

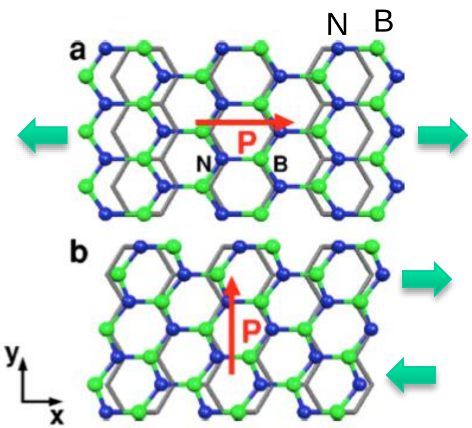
Multifunctional BNNT Polymer Composites

- Electroactive Properties
- Radiation Shielding Properties

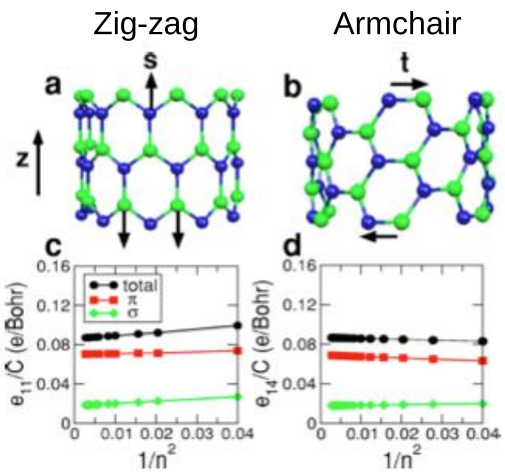
Piezoelectric Properties of BNNTs

Piezoelectric Effect

h-BN plane



BNNT



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

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)

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

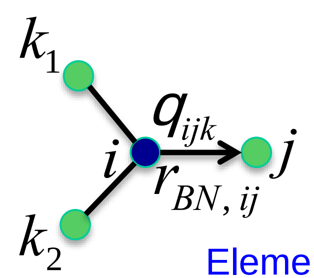
- Evolve atoms according to Newton's law: $\vec{a}_i = \vec{F}_i / m_i$

Piezoelectric MD

- Introduce dipole term to the interatomic potential (energy)

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

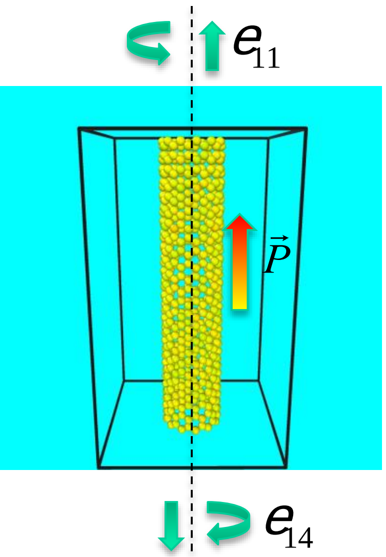
$$\vec{p}_{BN,ij} = p_0 \left[\frac{r_{BN,ij} - r_0}{r_0} + \sum_{k \neq i,j} \left(\frac{1}{2} + \cos\theta_{ijk} \right) \right]$$



Elementary dipole unit

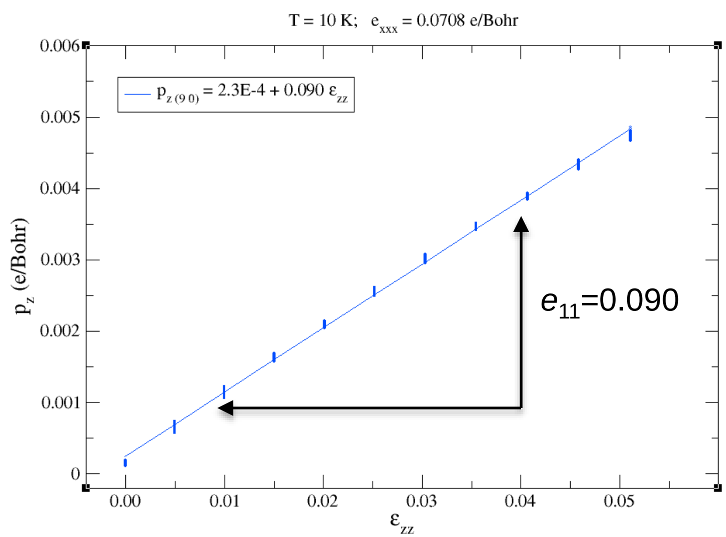
Results: Piezoelectricity under Deformation

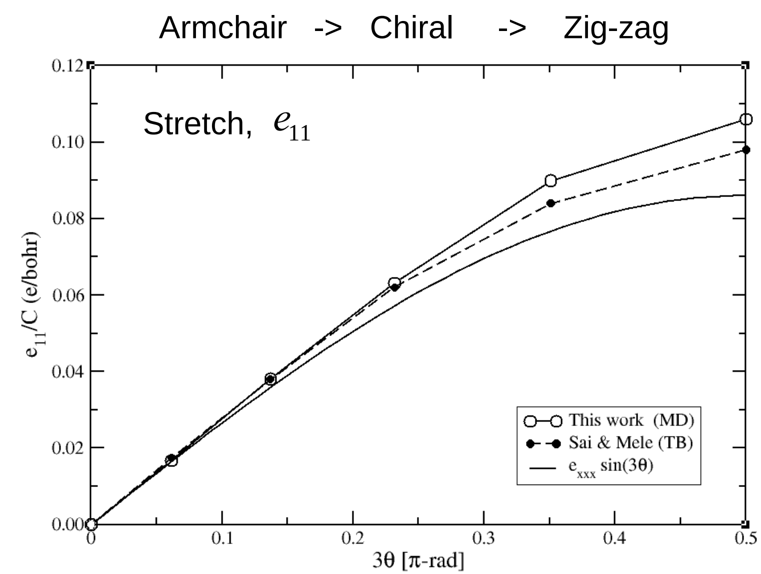
The MD model is successful in representing the piezoelectric properties of BNNTs

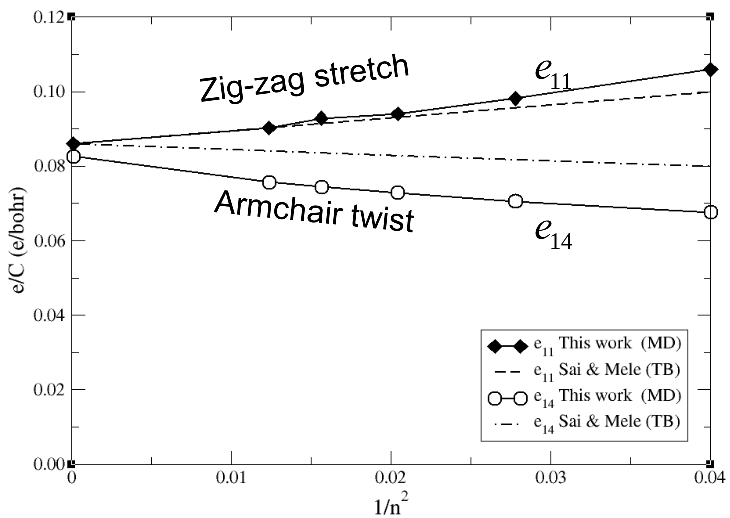


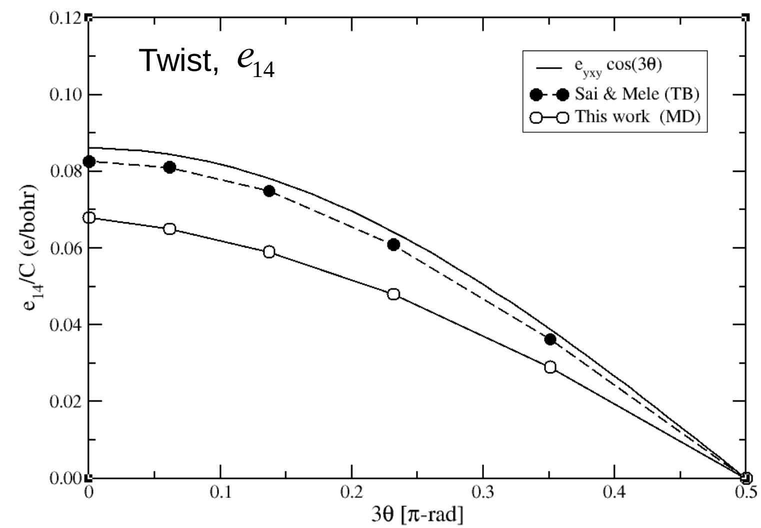
$p_z(stretch) = e_{11}e_s$

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







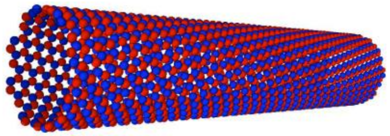


Yamakov, Park et al., *Comp. Mater. Sci.*, **95** 362 (2014)

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, CO_2 laser as grown)



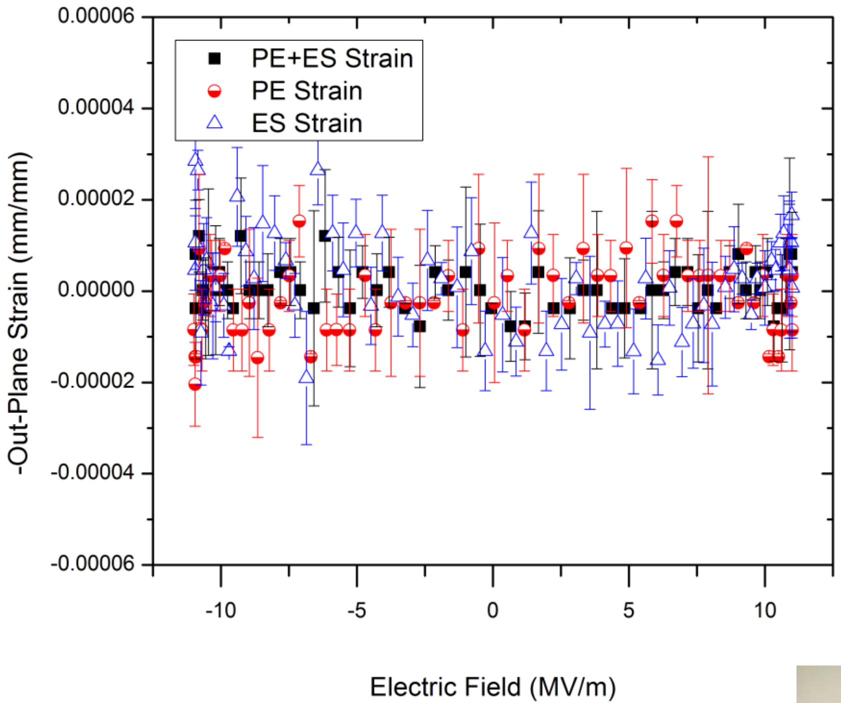
Alignment (stretched)
No alignment (no stretched) and stretched (up to 100%)

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

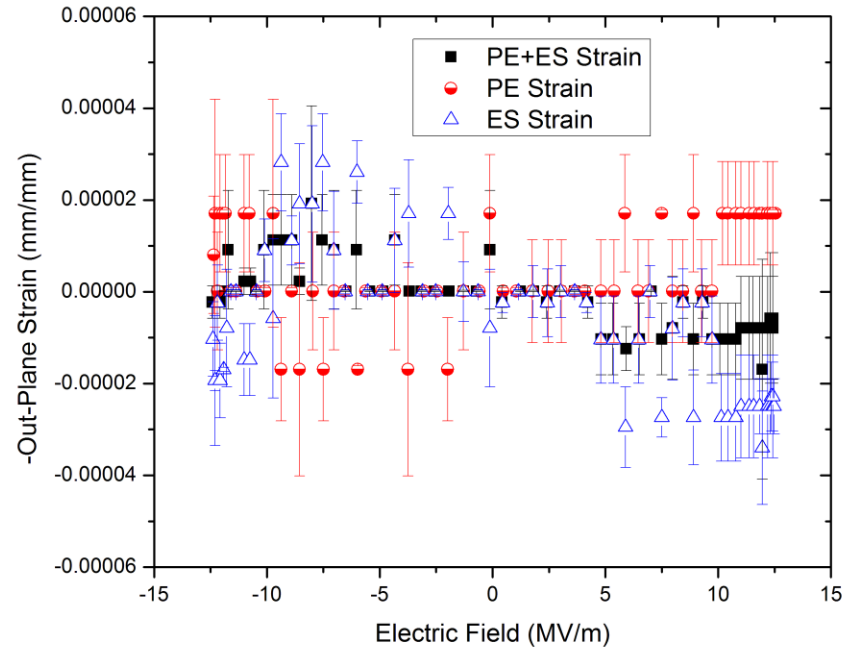
All images credit: NASA

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

Unstretched



100% Stretched
@225^{o}C, Annealing



Field induced strain (ε_{33})

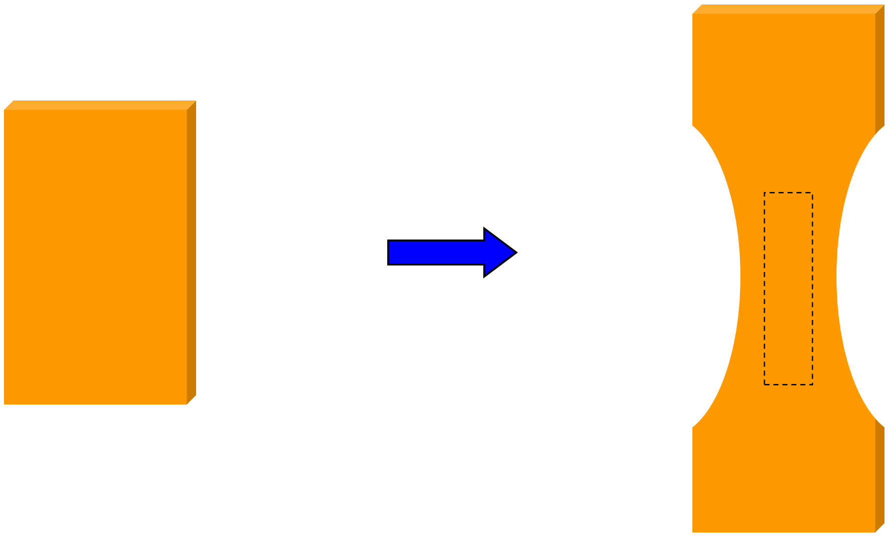
$$\varepsilon_{33} = d_{33}\cdot\boldsymbol{E} + M_{33}\cdot\boldsymbol{E}^2 + \ldots$$

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

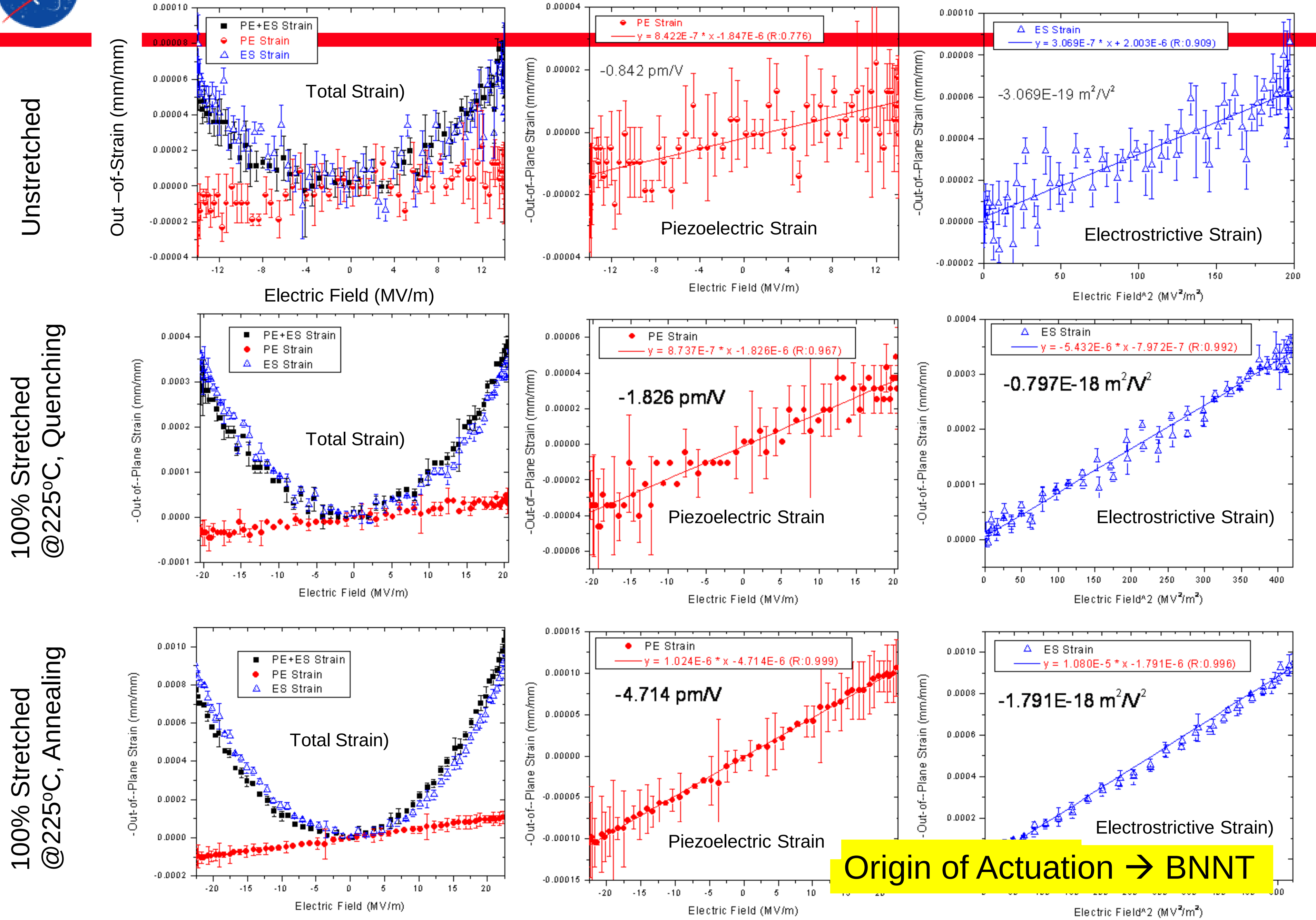
All images credit: NASA

Stretched BNNT-Polyimide Nanocomposite



100 % Strain,
225°C slightly above Tg

Actuation of Unstretched/Stretched 2% BNNT/Polyimide



Origin of Actuation → BNNT

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

SWCNT film electrode

NT/

CN

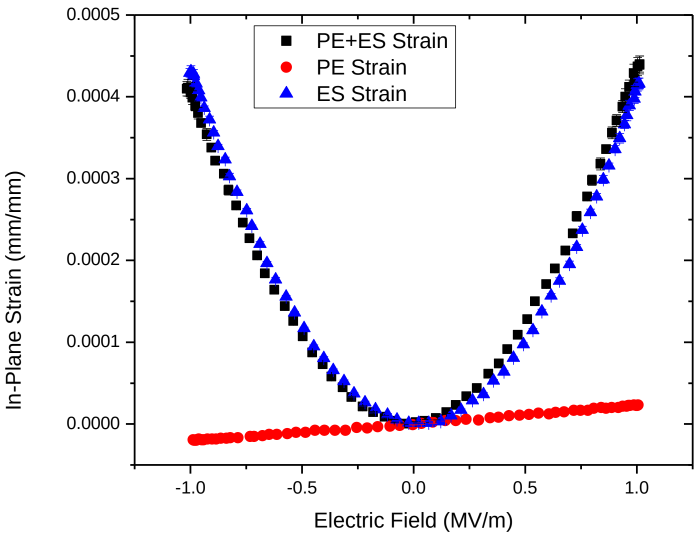
du

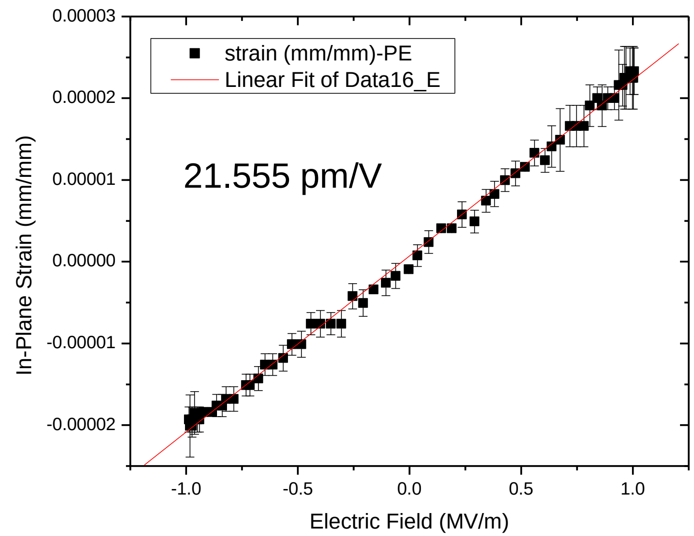
esi

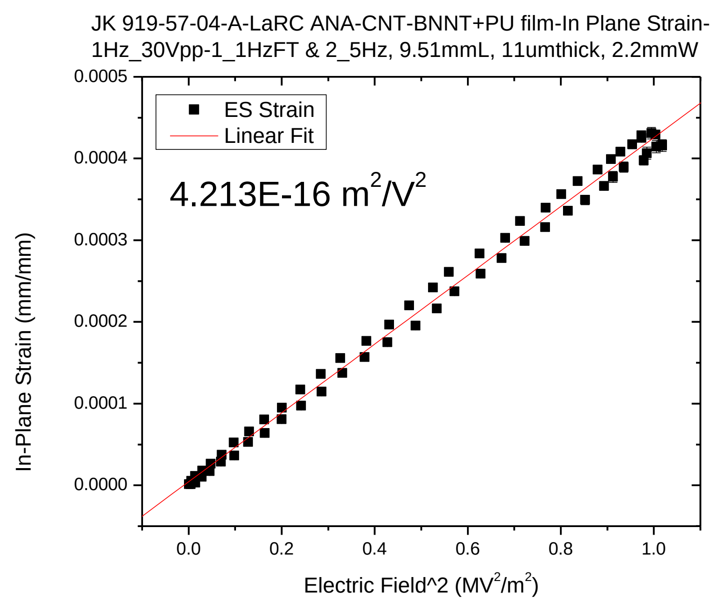
Goal: Flexible, transparent, large actuation, high sensitivity,
Mechanically Durable

All images credit: NASA

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







Field induced strain (ε_{33})

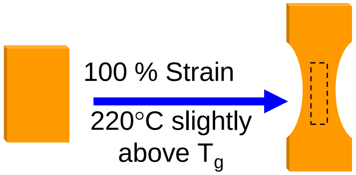
$$\varepsilon_{33} = d_{33}\cdot\boldsymbol{E} + M_{33}\cdot\boldsymbol{E}^2 + \ldots$$

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

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

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,[3] 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)

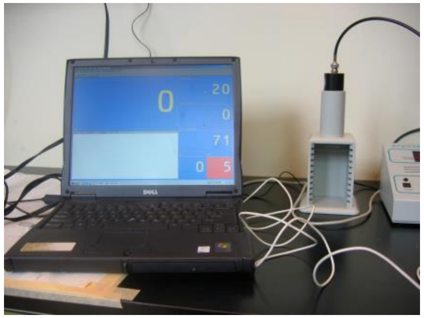
Mars Round Trip Dose Equivalent is around 0.66 Sievert

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

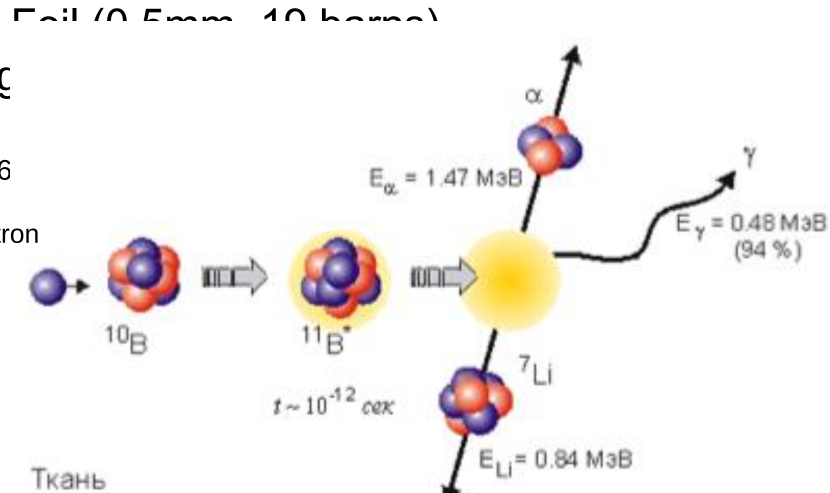
Radiation Shielding Structural Materials
- In-situ polymerization under simultaneous sonication and shear
- Supercritical Fluid Infusion



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
- RSMES: Radiation Shielding
- $^{115}In(n, \gamma)^{116}$

Geiger-Mueller Tube

neutron



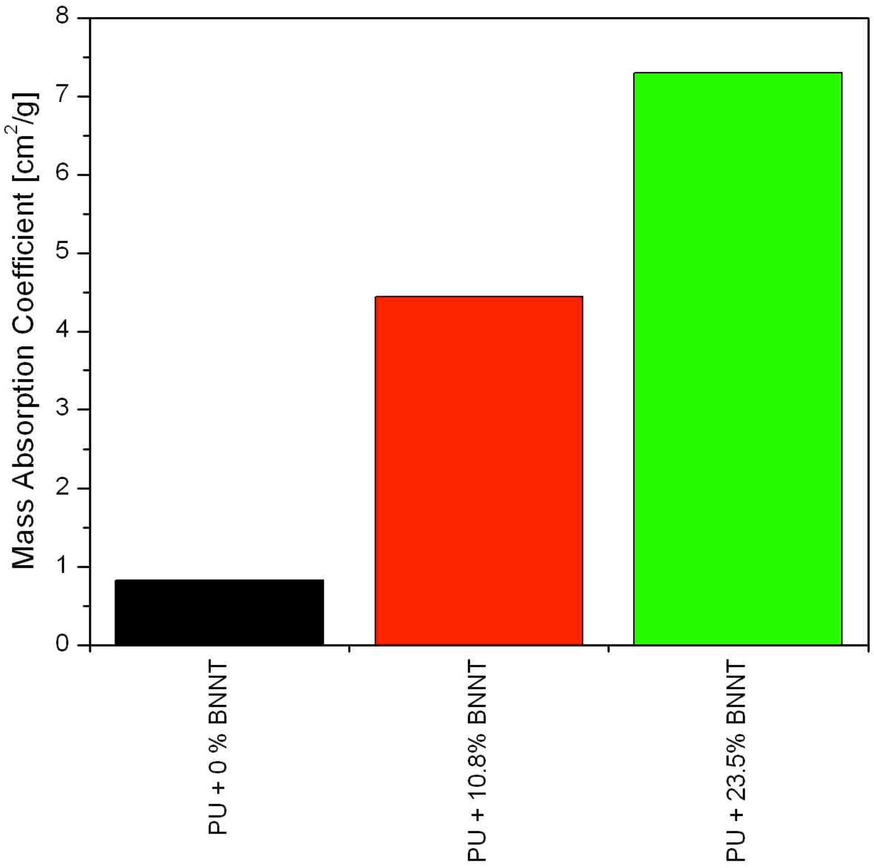
http://www.inp.nsk.su/bnct/introduction/introduction.en.shtml

Modeling
- OLTARIS

All images credit: NASA

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

Neutron radiation

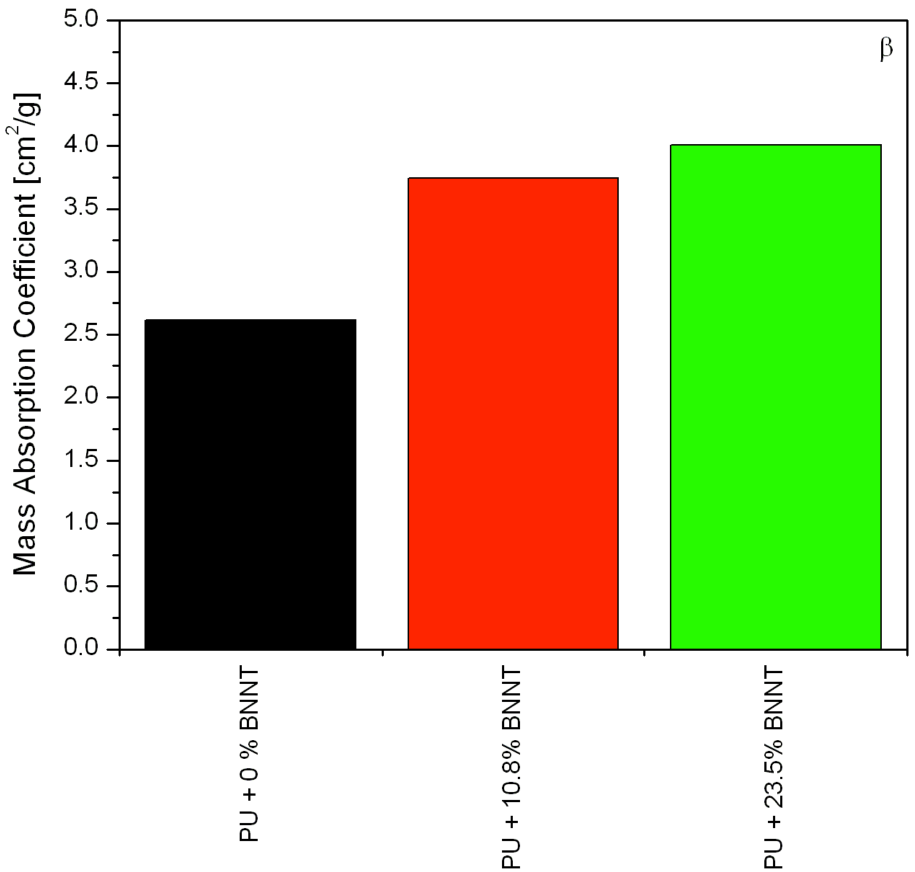


Am/Be 1Curie & moderated by borated PE

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

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

Beta radiation

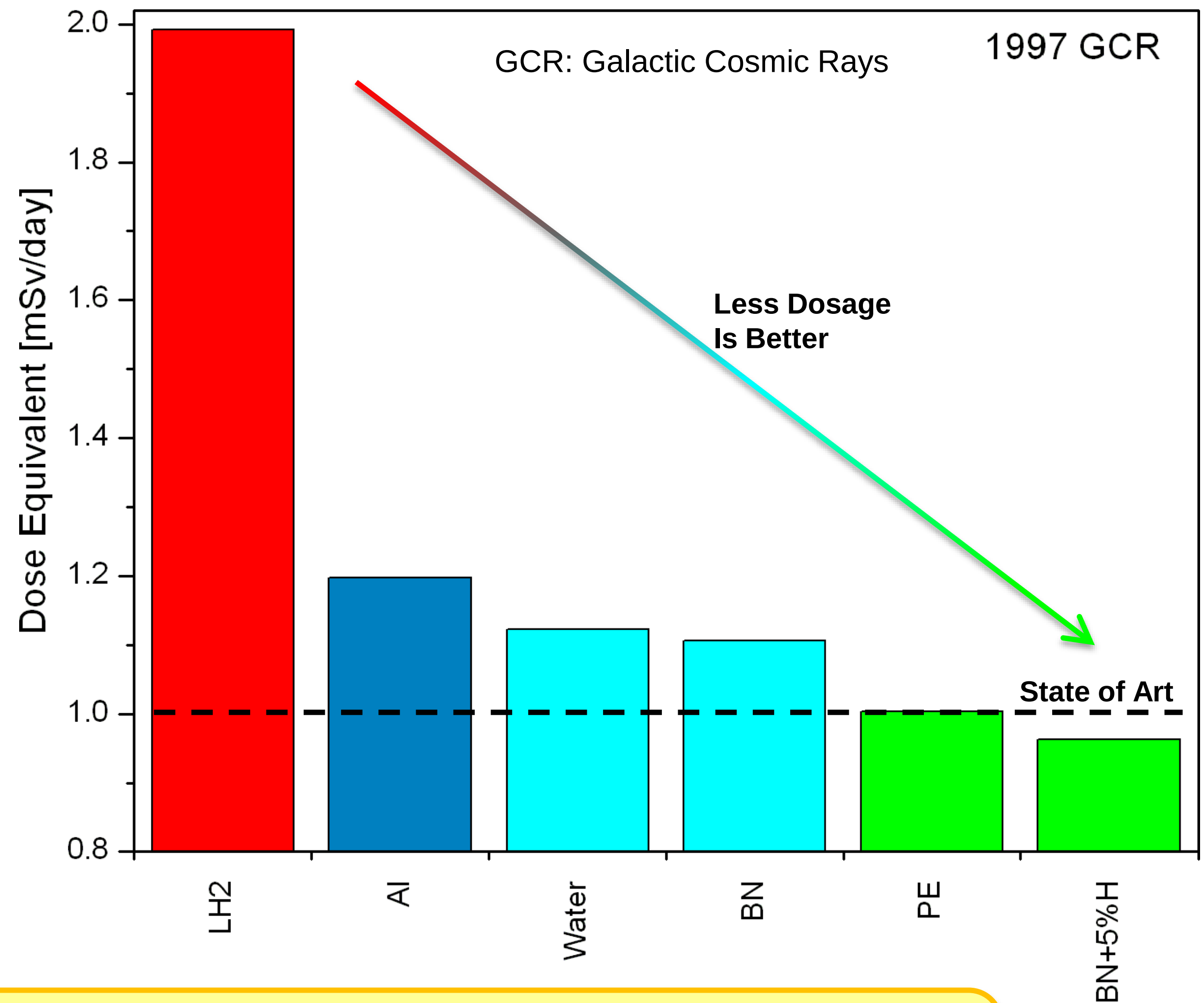


0.1 μCi Sr-90: β (Synthesized Apr 2009)

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

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.

Summary

- $B_xC_yN_z$ Nanotubes (BNNT, BCNNT) were successfully synthesized with High Temperature-Pressure Laser Synthesis method.
- Development of multifunctional nanotube polymer nanocomposites with uniform dispersion.
- Ne Physical properties of nanocomposites can be tailored over a wide range by fine tuning the type of tubes, concentration, and degree of the alignment of nanotubes.
- In-situ diagnostics and modeling were implemented to support study of the BNNT and BCNNT nucleation and growth mechanism.
- Multifunctional Nanocomposites can sense strain, stress, pressure, damage, temperature.
- Multifunctional Nanocomposites can actuate through piezoelectrical and electrostrictive phenomena and generate large strain at low electric fields.
- Multifunctional Nanocomposites can shield radiation and high heat flux.

Thank You