Structural Boron Nitride Nanotube Composite Development

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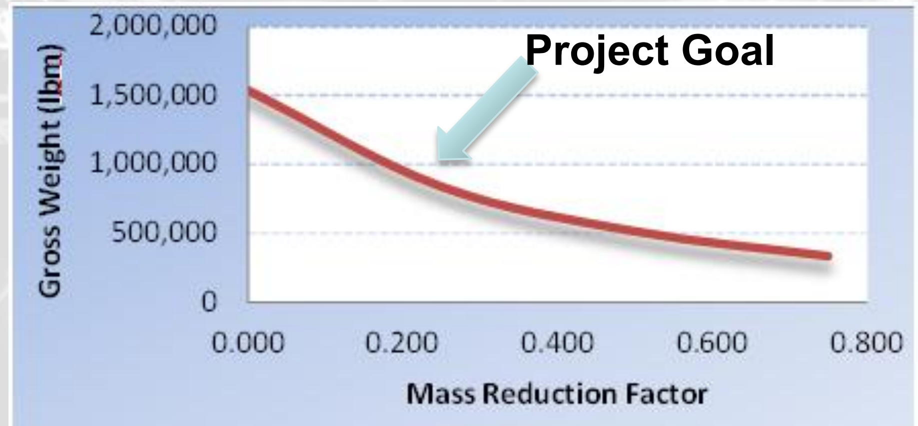
Strategic Partner:

National Institute of Aerospace

Strategic Overview

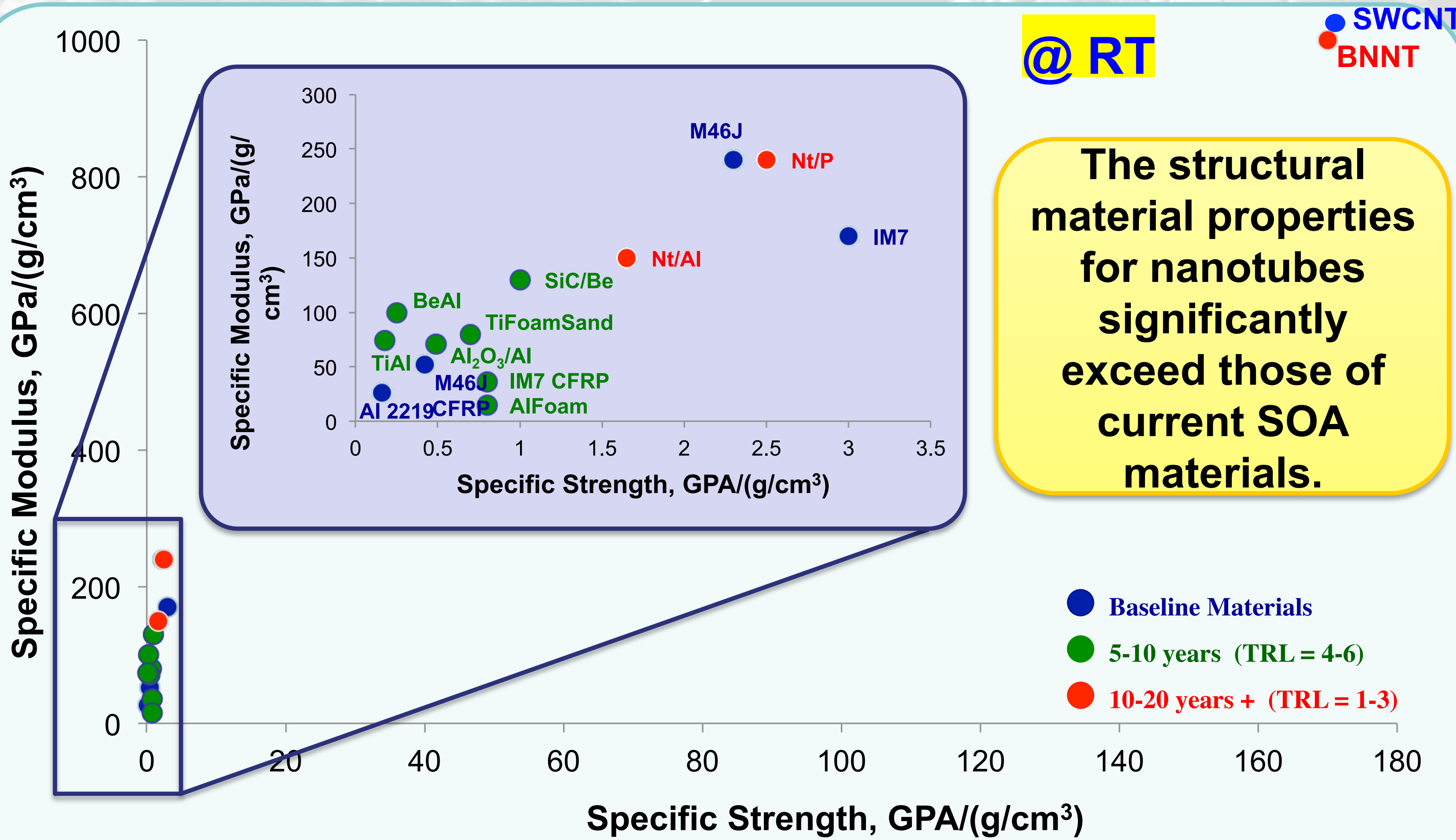
- Vehicle weight is a primary driver for most NASA missions.
  Reducing vehicle weight can:
  - Expand mission capability
  - Reduce launch costs
  - Reduce fuel consumption
  - Systems analysis shows that reducing materials mass by 20% leads to a 30% reduction in launch vehicle gross weight
  - Same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

Effect of Materials Mass Reduction on Launch Vehicle Gross Weight



Potential Impact: Produce advanced BNNT composites with higher thermal stability, lightweight, no corrosion, tough, and radiation shielding effectiveness

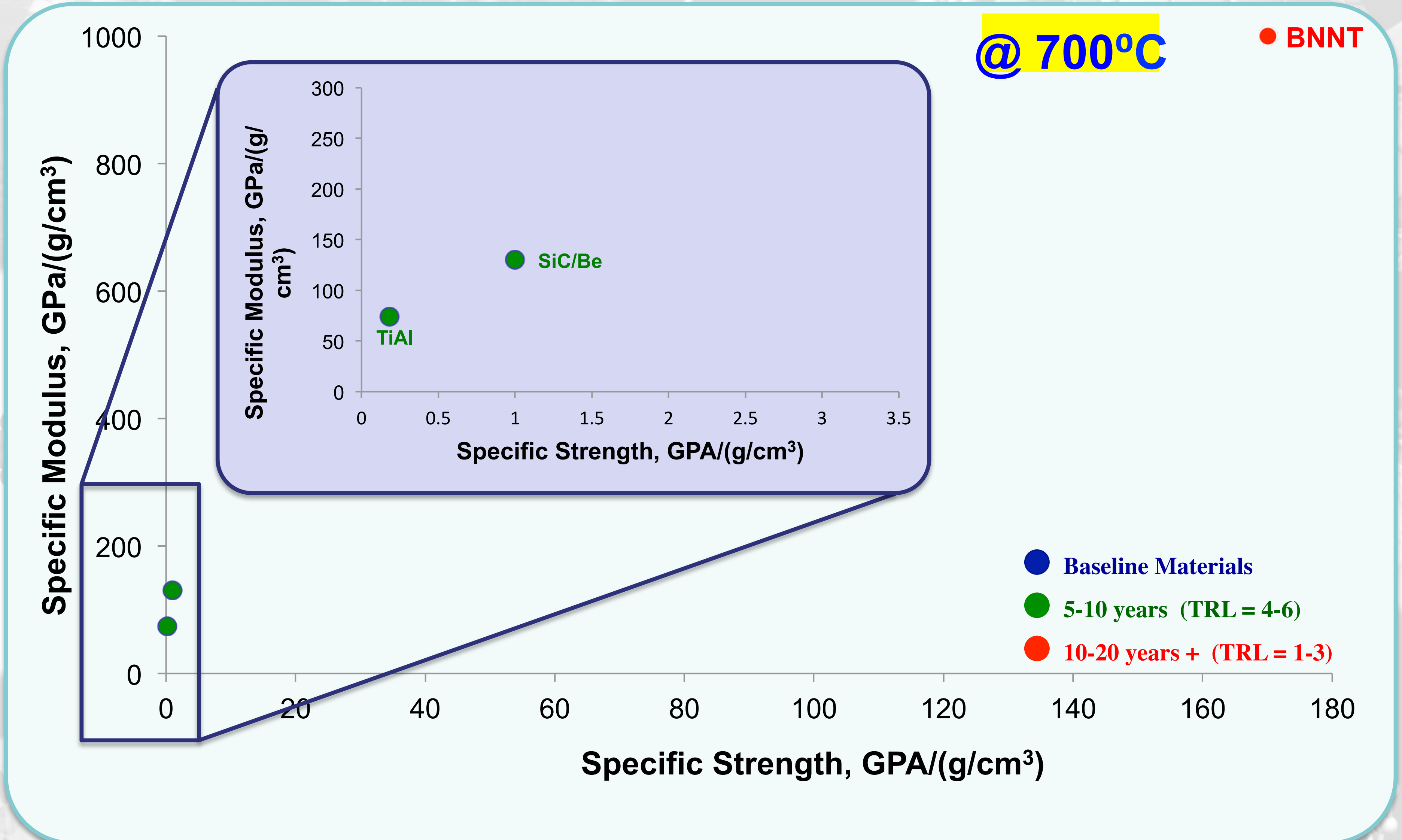
Properties of Materials for Vehicle Structure



The structural material properties for nanotubes significantly exceed those of current SOA materials.

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

Properties of Materials for Vehicle Structure



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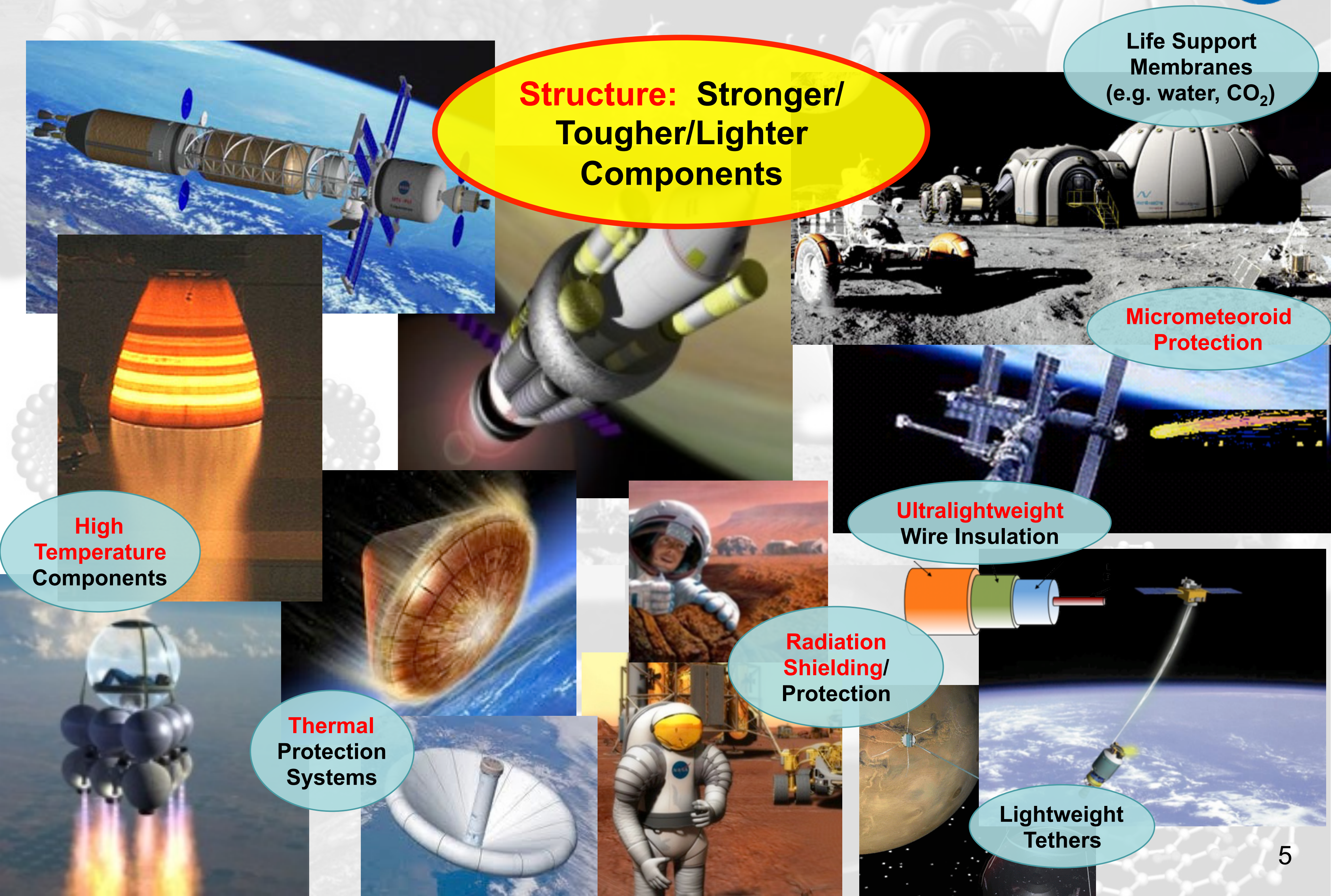
Technology Areas TA 6 7, 10 and 12



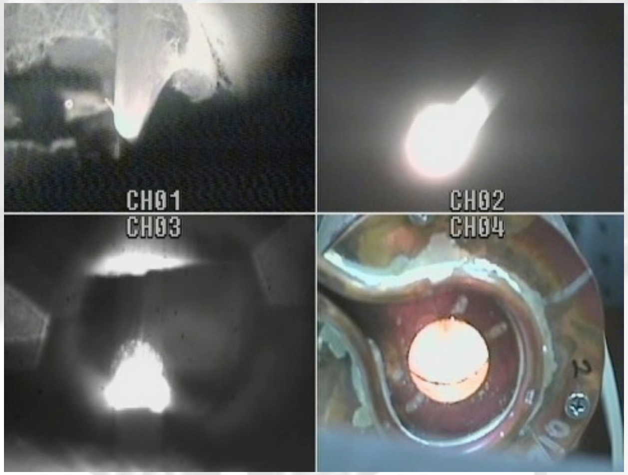
Team

BNNT Team

- **Technical Group Lead** — Catharine Fay[1]
- **Synthesis & Production** — Joseph Lee[2]
  - Hoa Luong[3]
- **Diagnostics** — Paul Danehy[2]
  - Jennifer Inman[2]
  - Stephen Jones[2]
- **Modeling** — Peter Gnoffo[4]
  - Derek Liechty[4]
  - Vesselin Yamakov[6]
- **Radiation** — Sheila Thibeault[1]
  - Godfrey Sauti[6]
- **Systems Analysis** — Kevin Earle[5]
- **Characterization & Processing** — Cheol Park[6]
  - Glen King[1]
  - Sharon Lowther[1]
  - Sang-Hyon Chu[6]
  - Luke Gibbons[6]
  - Jin Ho Kang[6]
  - Amanda Tiano[6]
  - Samantha Applin[6]
  - Wanda Gresham[3]
  - Hyunjung Kim[6]

[1] **Advanced Materials and Processing Branch, LaRC Research Directorate**
[2] **Advanced Sensing and Optical Measurements Branch, LaRC Research Directorate**
[3] **Materials Experiments Branch, LaRC Research Directorate**
[4] **Aerothermodynamics Branch, LaRC Research Directorate**
[5] **Space Mission and Analysis Branch, LaRC Systems Analysis & Concept Directorate**
[6] **National Institute of Aerospace**

NASA BNNT Product Strategy Steps



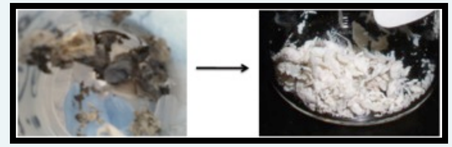
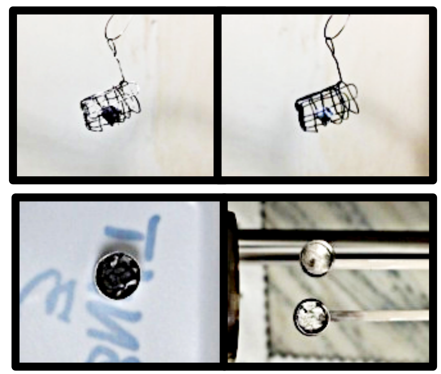
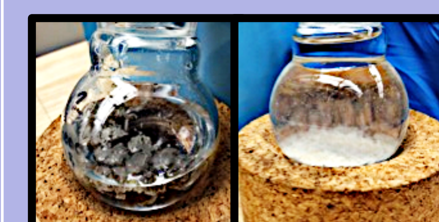
Synthesis

Production

BN Nanotubes

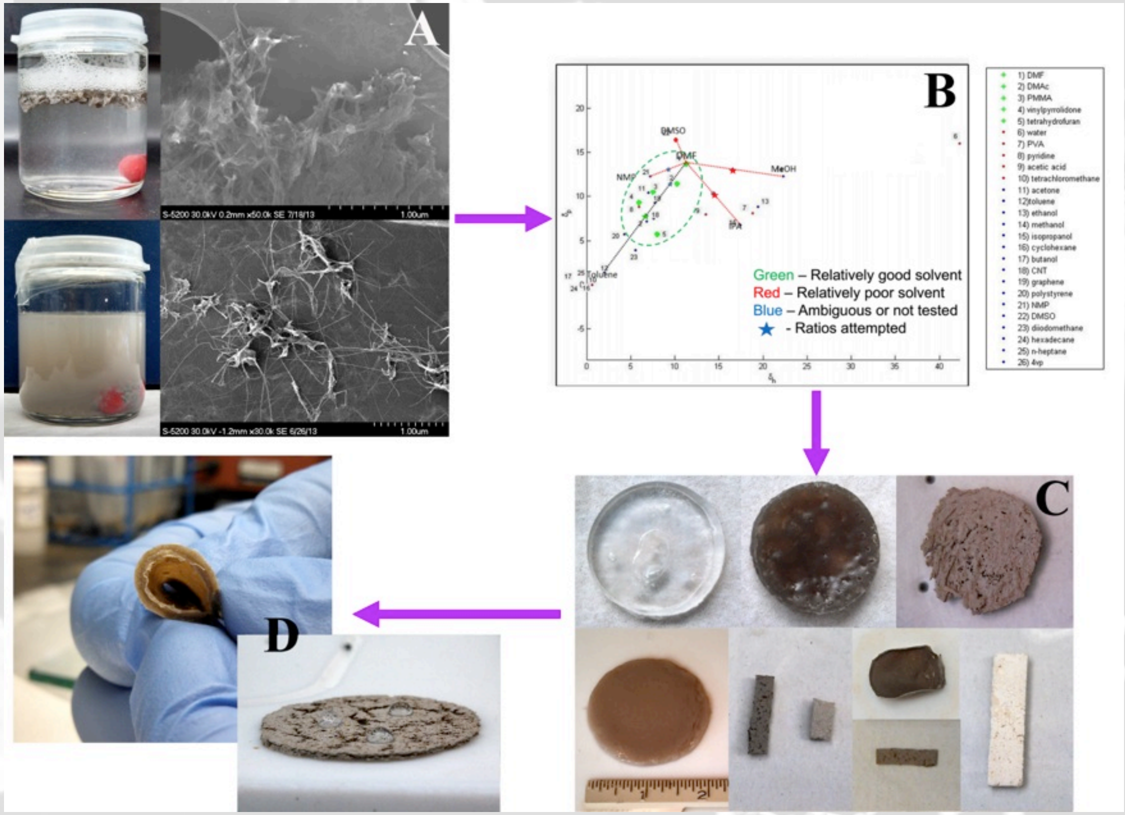
- **Two trained operators.**
- **Runs on average 3 days a week 4 hours per day. (not including startup and shutdown/harvesting)**
- **To date has produced approximately 9 grams of material.**
- **Production rate between 15 and 20 mg per hour.**
- **Enables purification and dispersion studies.**
- **Enables fabrication of yarns mats and other structural components.**
- **Enables Material Transfer Agreements to NIA and Universities.**

BNNT Purification Progress

Acid Treatment Purification	Using nitric acid, remove boron nanoparticles (an impurity) from sample.	 	• Boron nanoparticles removed • Noticeable damage to the nanotubes resulting in poor quality of the acid-treated sample • Acid-treated structural mats have no integrity
Thermal Purification	Use heat to remove boron nanoparticles and potentially remove boron oxides (i.e. <u>water soluble</u> impurities).		• Boron nanoparticle removal alternative • Assumption: the darker the BNNT, the higher the boron content/impurity content; visible color change from a darker to a lighter-colored material • Further analysis and investigation in progress
Surfactant Purification	Using surfactants, remove all impurities, which includes boron nanoparticles and amorphous and crystalline BN.		• Least harmful method to purifying the nanotubes • Potential removal of crystalline BN (which cannot be removed via other listed purification methods) • Further analysis and investigation in progress; will include sonication and centrifugation as well*

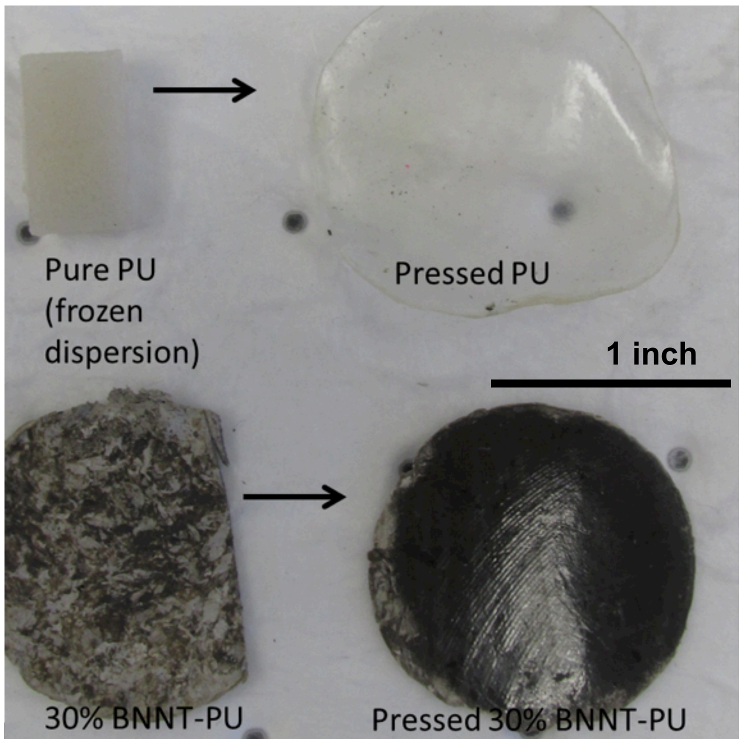
Dispersion studies

- By surveying a variety of solvents/co-solvents, surfactants, and polymers (A), *a solubility region for BNNTs was established* (B) using Hansen solubility theory.
- Extending this knowledge, we generated BNNT structural composites (C) with a plethora of interesting properties (D).



Frozen dispersion fabrication method

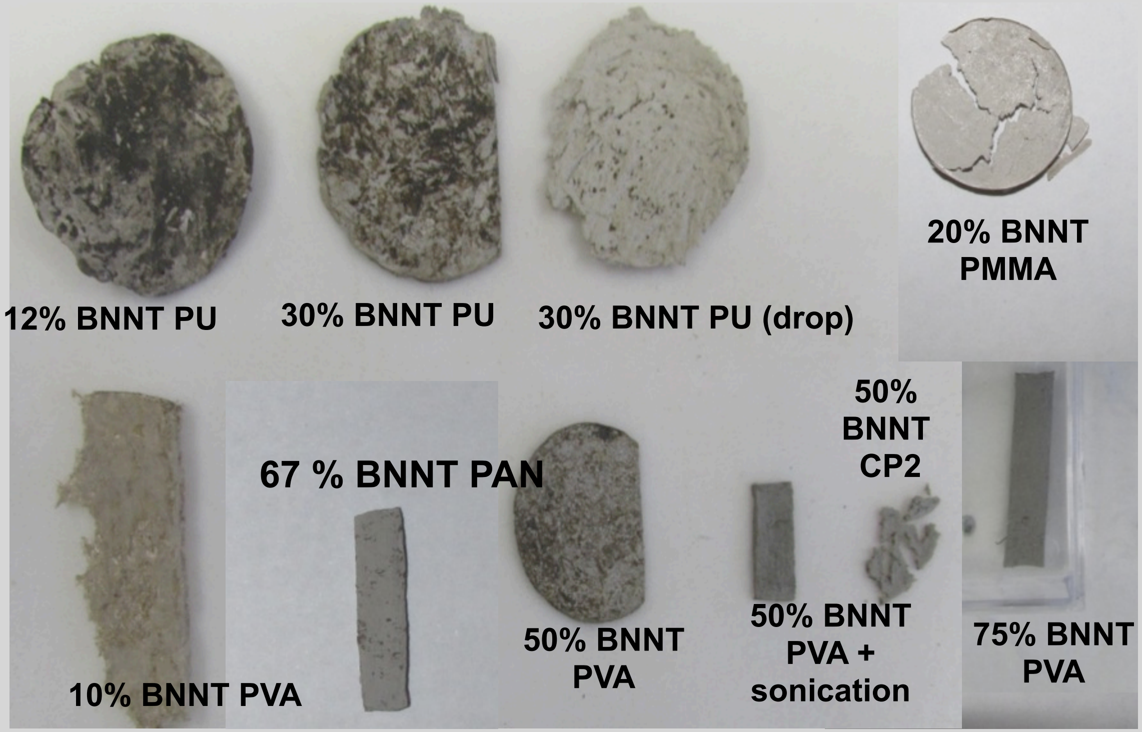
After hot-press



67% BNNT-PU

Pressed 67% BNNT-PU

Before hot-press



New fabrication method simplifies processing for high weight nanocomposites

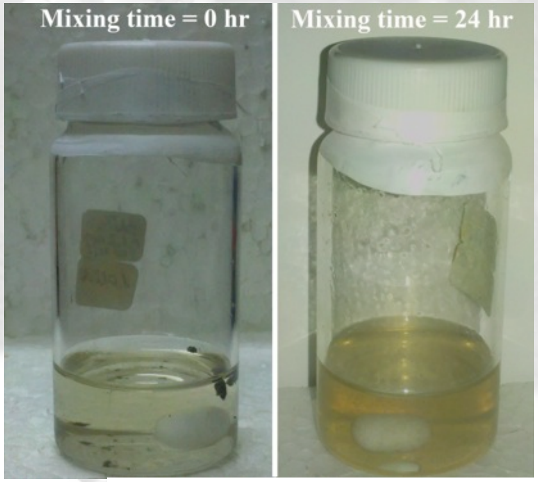
This approach can be used to fabricate BNNT + polymers/ epoxies and lock in the dispersion conditions

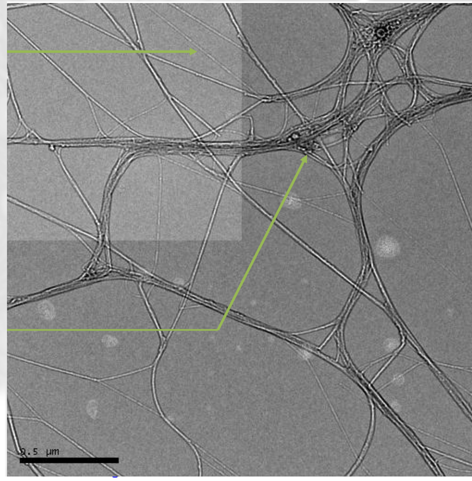
The "frozen dispersion" step is intermediate - the sample is consolidated during hot-pressing

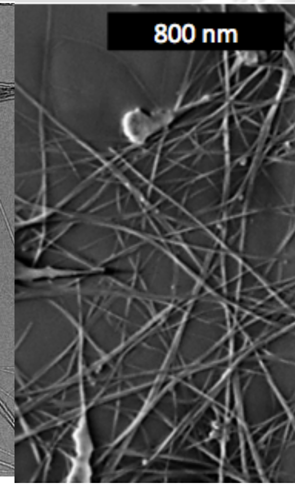
PU - Polyurethane
PMMA - Poly(methyl methacrylate)
PVA - Polyvinyl alcohol
PAN - Polyacrylonitrile
CP2 – LaRC CP2 Polyimide

BNNT Purification, Dispersion, & Spinning

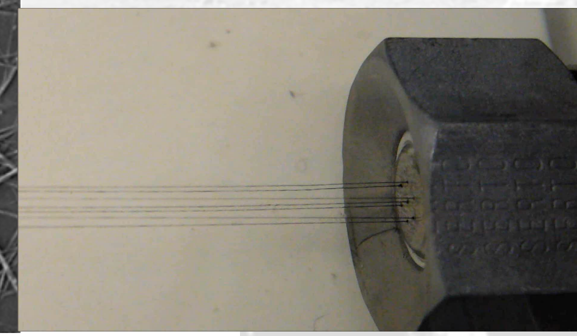
BNNT in Chlorosulfonic (CSF) Acid (Superacid): Spontaneous dispersion and debundling

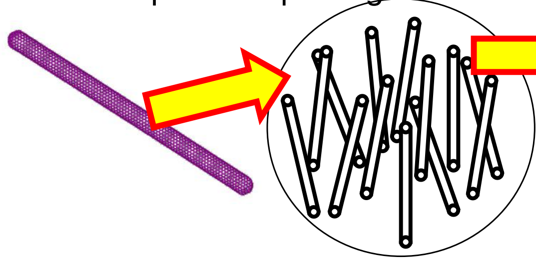


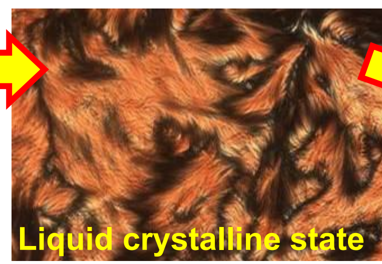




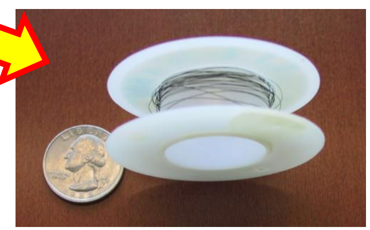
Need purified BNNT for spinning

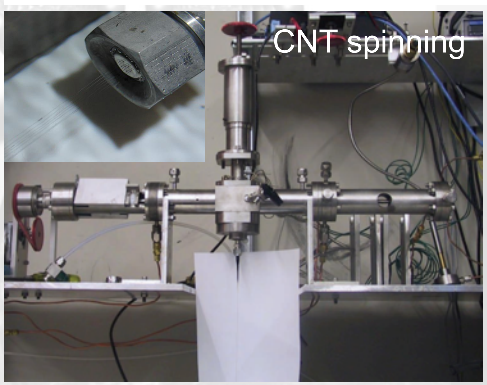




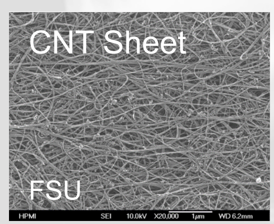


CNT spun fibers

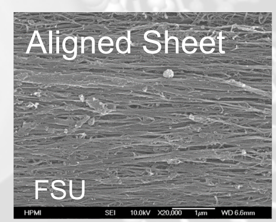




- BNNT Superacid Spinning in collaboration with Rice University
- BNNT Mat/Sheet Formation (filtering) → Stretching BNNT Sheet → Composite Tape → Mechanical Tests



Stretching



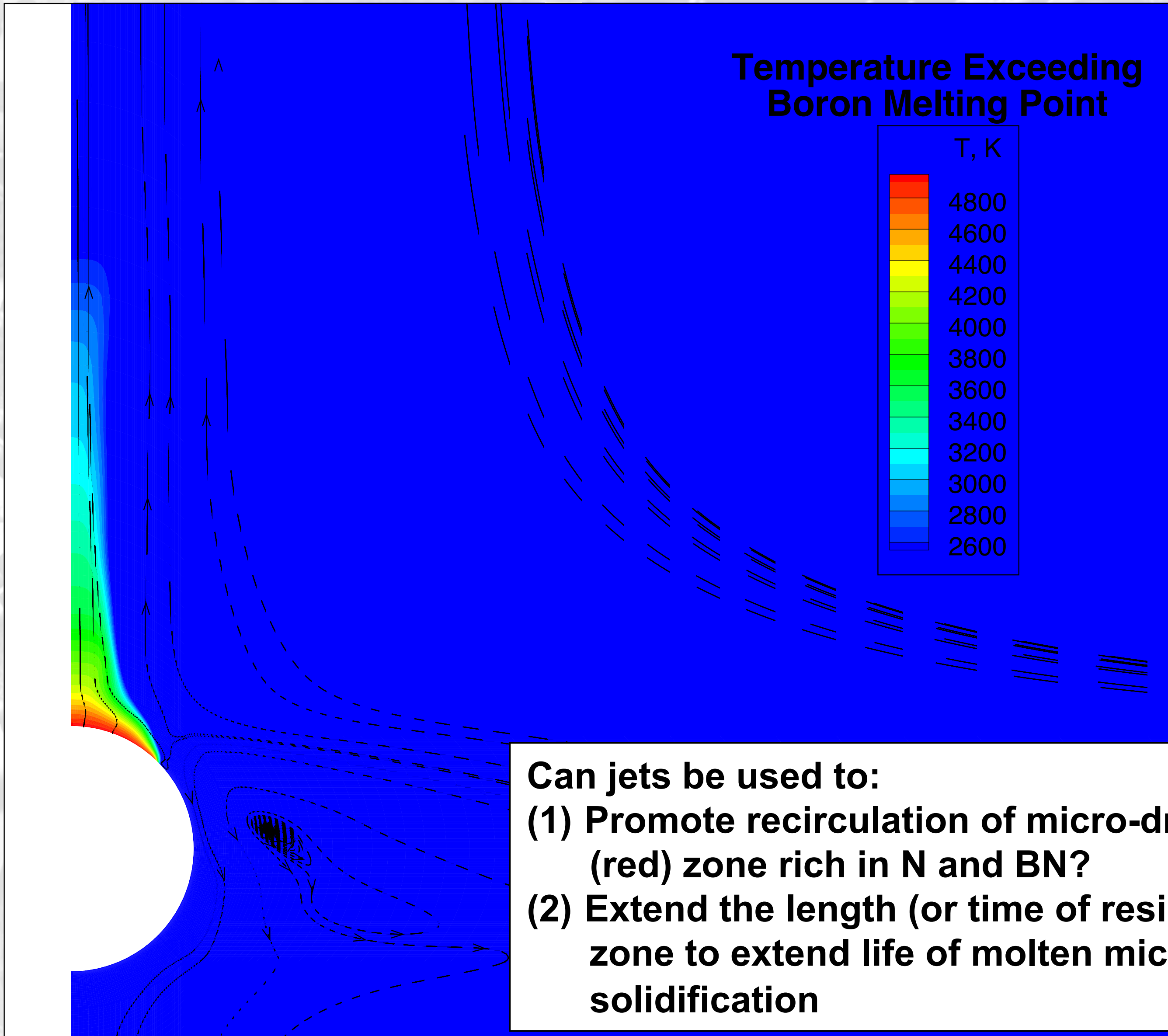
Rice University (Prof Matteo Pasquali)

Florida State University (Wang/Liang)

Three Goals for BNNT Modeling

- Define the environment in which tubes now grow.
  - "Laser Vaporization and Plume Chemistry in a Boron Nitride Nanotube Production Rig", JTHT, Vol. 27, No. 3, 2013
  - Simulate domain for irradiated droplet suspended in space to better model convection currents – key to understanding nucleation site environment
- Define the optimum environment for growing BNNTs.
  - Observations suggest significant formation of tubes at nucleation sites rising from heated surface, even before condensation wire is encountered
  - If tip growth mechanism: need to simulate nucleation of supersaturated BN from rising plume on nucleation site(s)
  - If root growth mechanism: need to simulate micro-droplets of liquid Boron ejected from heated surface
    - Melts at ~ 2600 K, Boils at ~ 5000 K at 200 psi
    - Simulate evolution of absorbed N_2, N, and BN in micro-droplet as it rises in plume and cools
  - Plan to explore molecular dynamics approach of Violi et al. (A multi-scale computational approach for nanoparticle growth in combustion environments)
- Explore modifications to rig by simulation to promote optimum environment.
  - Directed jets may be used to speed or slow the plume dynamics, possibly inducing recirculation through the hot zone rich in BN, to promote BNNT growth.

Temperature Contours Around 1 mm Radius Boron Droplet



Can jets be used to:

(1) Promote recirculation of micro-droplets through hot (red) zone rich in N and BN?

(2) Extend the length (or time of residence) in green zone to extend life of molten micro-droplet before solidification

Optical Diagnostic Techniques for BNNT

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

Partnerships & Collaborations

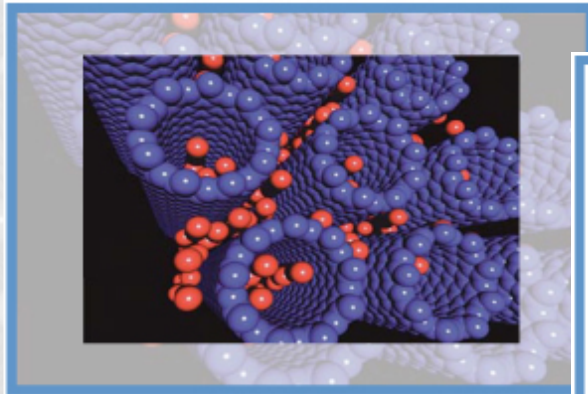
Strategic Partner

National Institute of Aerospace

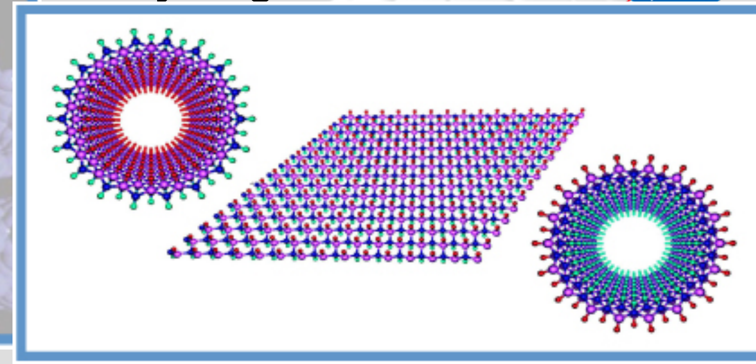
- **NASA LaRC Center (5 branches)**
  - Glenn Research Center
  - Goddard Space Flight Center
  - Johnson Space Center
  - Ames Research Center
- **Other Government**
  - Air Force Office of Scientific Research
  - NIST
- **Commercial**
  - BNNT, LLC
  - Momentive
- **Universities**
  - UC-Berkeley
  - Rice University
  - SUNY-Binghamton
  - VA Commonwealth University
  - University of North Texas
  - University of New Hampshire
  - NC State
  - Hampton University
- **International**
  - ONERA (France)
  - Institutode Nanociencia de Aragon (Universidad de Zaragoza, Spain)

BNNT enables……………………

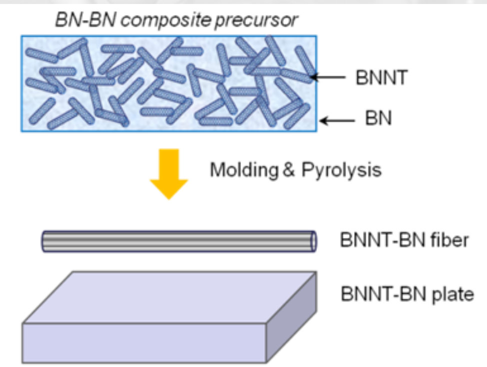
Hydrogen Storage BNNT



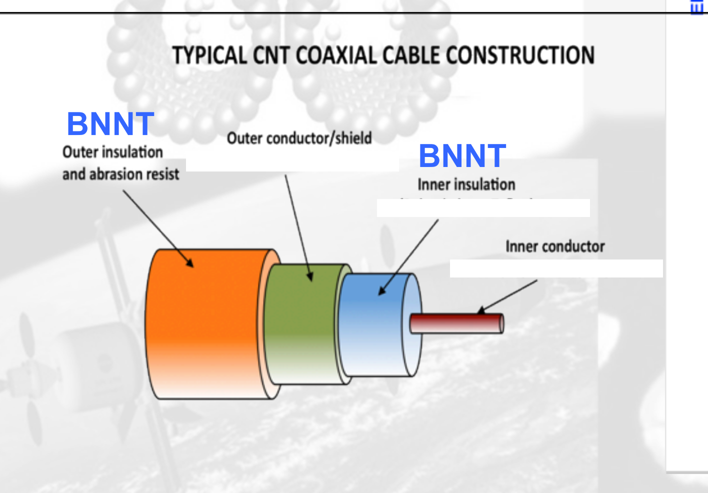
Hydrogenated BNNT



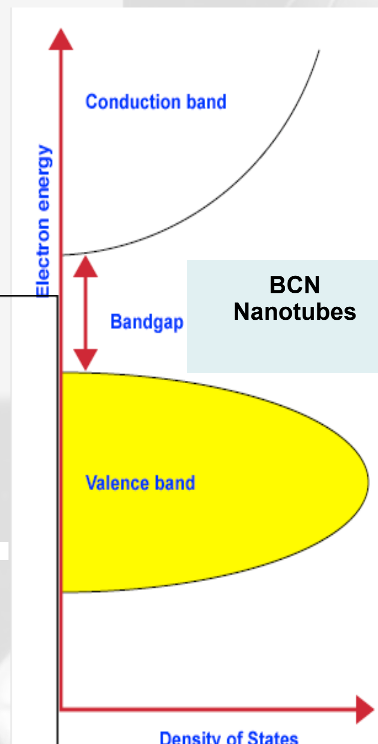
Multi-Functional All BN-BN Composite



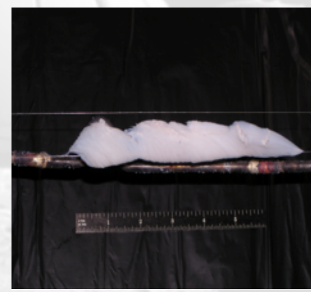
The fabrication processes of BN-BN composite precursor and different BN-BN composite structures (fiber, plate composite).



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



BCN Nanotubes



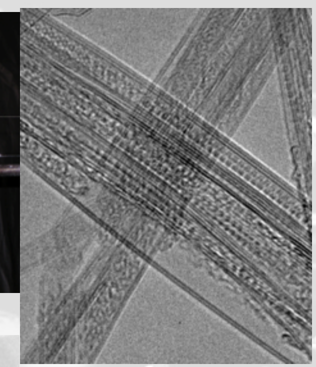
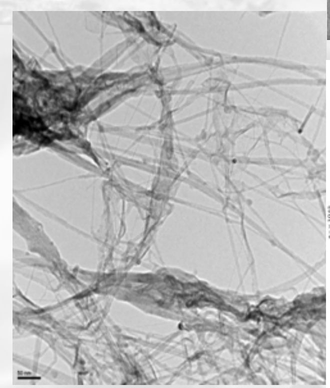


Fig 2. TEM image of C_{60}-BNNT (endo-doped) UC Berkeley



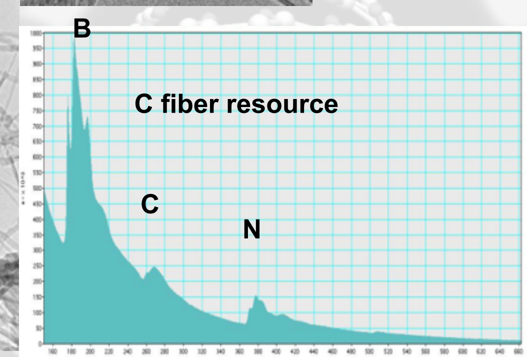


Fig 3. TEM, EELS, and Raman spectra of BCNNT.

$B_xC_yN_z$ Nanotube (BCNNT) Development