Quantifiable Assessment of SWNT Dispersion in Polymer Composites

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Lord Kelvin (Sir William Thomson)

- "In physical science the first essential step in the direction of learning any subject is to find principles of numerical reckoning and practicable methods for measuring some quality connected with it. I often say that when you can measure what you are speaking about, and express it in numbers, you know something about it; but when you cannot measure it, when you cannot express it in numbers, your knowledge is of a meager and unsatisfactory kind; it may be the beginning of knowledge, but you have scarcely in your thoughts advanced to the state of Science, whatever the matter may be." [PLA, vol. 1, "Electrical Units of Measurement", 1883-05-03]

- Chad Snyder, NIST, at the Institute for Defense and Government Advancement, 03-29-2007, Washington D.C.

Subsonic Fixed Wing

http://www.dfrc.nasa.gov/Gallery/Photo/X-48B/index.html

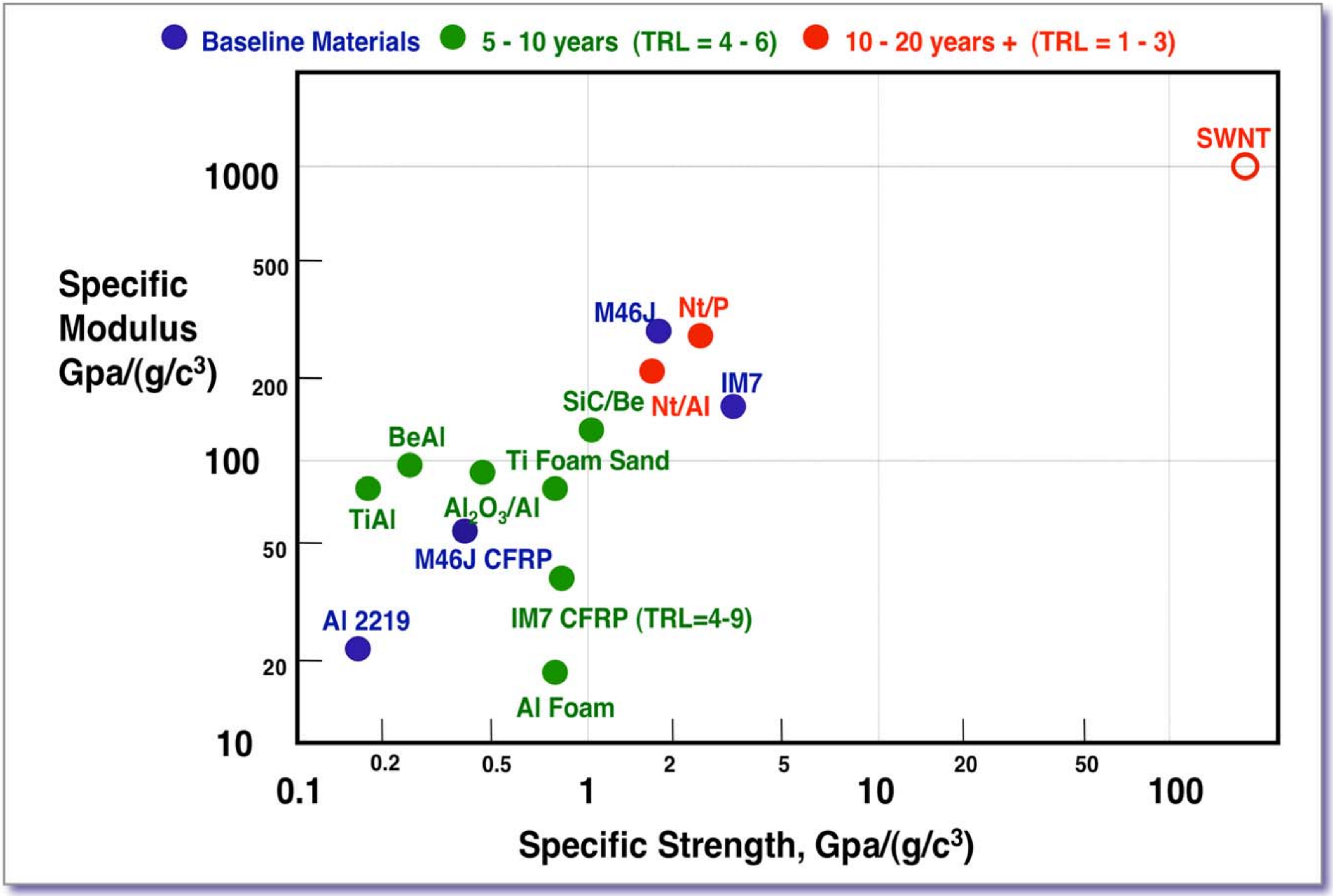
Why Nano?

- Offers the potential to dramatically improve the system, and add functionality to eliminate subsystems.

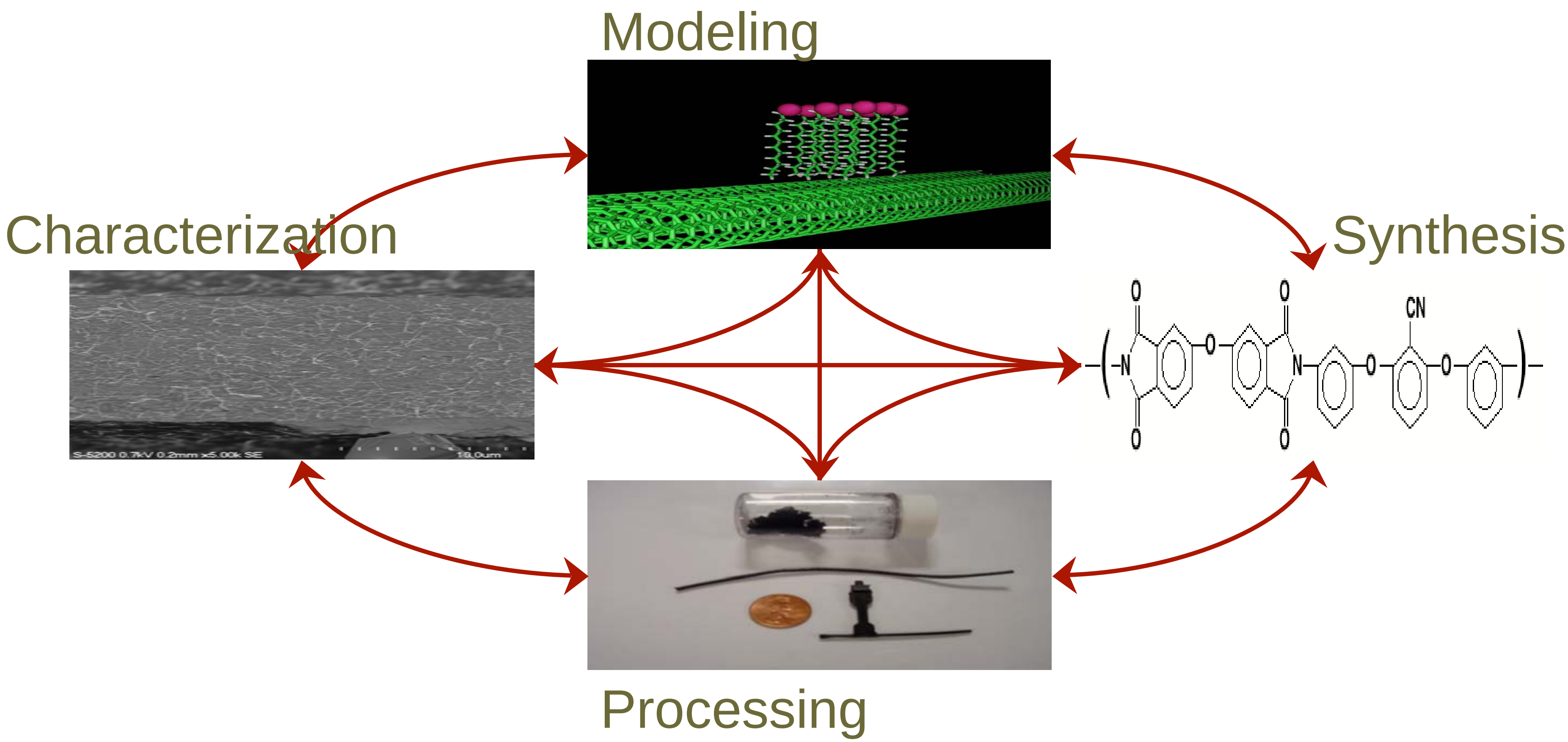
$$\text{Aircraft Range} = \frac{\text{Velocity}}{\text{TSFC}}\left(\frac{\text{Lift}}{\text{Drag}}\right)\ln\left(1 + \frac{W_{fuel}}{W_{PL} + W_{O}}\right)$$

- Engine Fuel Consumption (TSFC)
- Aerodynamics (Lift/Drag)
- Empty Weight (W_O)

Properties of materials for vehicle structure



Moving beyond the beginning of knowledge



Without the loop

http://en.wikipedia.org/wiki/Damascus_steel

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By empirically optimizing their blade-treatment procedure, craftsmen ended up making nanotubes more than 400 years ago.

The diminishing supply of some of these ores during the eighteenth century may have prevented bladesmiths, who would not have been aware of the importance of these alloying elements, from practicing their ancient recipes.

As the nanoscale structure of Damascus steel emerges, a refined interpretation of its remarkable mechanical properties should become possible.

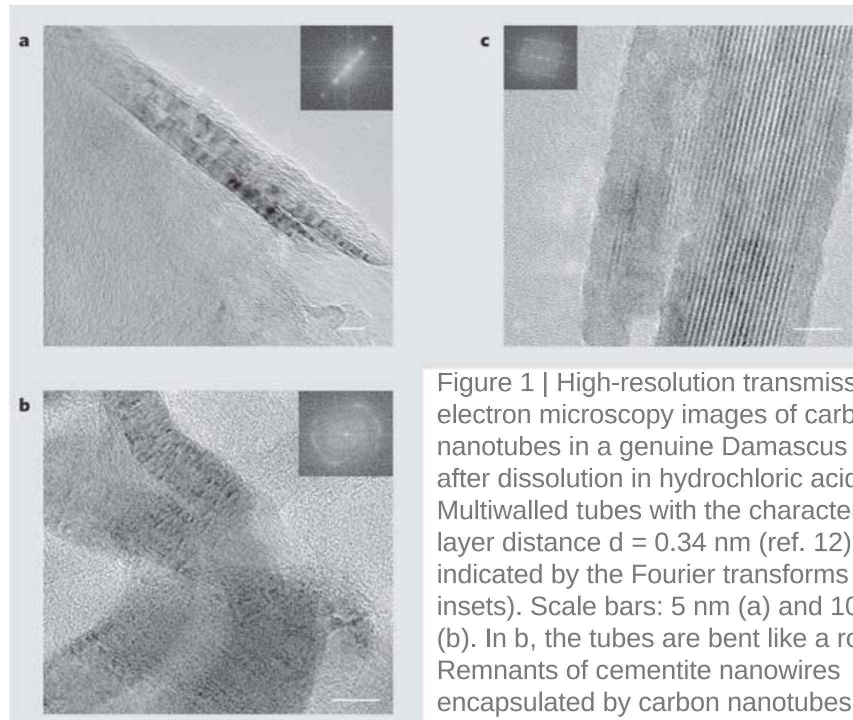


Figure 1 | High-resolution transmission electron microscopy images of carbon nanotubes in a genuine Damascus sabre after dissolution in hydrochloric acid. a, b, Multiwalled tubes with the characteristic layer distance d = 0.34 nm (ref. 12), as indicated by the Fourier transforms (see insets). Scale bars: 5 nm (a) and 10 nm (b). In b, the tubes are bent like a rope. c, Remnants of cementite nanowires encapsulated by carbon nanotubes, which prevent the wires from dissolving in acid. Scale bar, 5 nm. The fringe spacing of the wire is 0.635 nm, taken from the Fourier transform (inset), and is attributed to the (010) lattice planes of cementite. **NATURE|Vol 444|16 November 2006**

Challenges of carbon nanotubes

- Translating the excellent combination of CNT properties on the nanoscale to structural, multifunctional properties on the macroscale requires a fundamental understanding of the underlying physics
  - How is the macroscale property affected by things like:
    - » Dispersion, interfacial phenomena
    - » Primary, secondary, tertiary structure
    - » Defects, purity, functionalization, diameter, aspect ratio, number of walls
    - » Alignment, orientation

- Quality Assurance / Quality Control tools and methods not yet been developed
  - Need to start with a **quantifiable** metric for **dispersion**
  - **Tertiary structure and orientation** also needs to be quantified

EASTON
PLAY WITH IT. OR AGAINST IT.

MORE MUSCLE TO FLEX

From handle to ConneXion™ to barrel, Easton's all new Stealth CNT d
perform. It outperforms. Sixteen times stronger than steel and one
a meter in size, CNT is possibly the strongest fiber that will ever
It enhances the strength of our resins to unprecedented levels,
in revolutionary design and unparalleled performance.

NEW CNT CARBON NANOTUBE ENHANCED OPTI-FLEX COMPOSITE HANDL

The addition of CNT, made possible by Zyvex NanoSolve™ materials and exclusive to Easton, strengthens composite structures to provide improved handle designs with optimized flex, responsiveness, and more "kick" through the hitting zone for maximum performance within the legal limits of the game. zyvex

THINK FAST

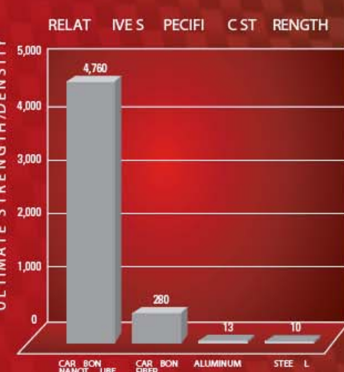
The addition of CNT to ultra lightweight materials makes Synergy CNT Fastpitch the highest performing, most durable bat on the market.

NEW CNT CARBON NANOTUBE ENHANCED ALL-COMPOSITE DESIGN zyvex

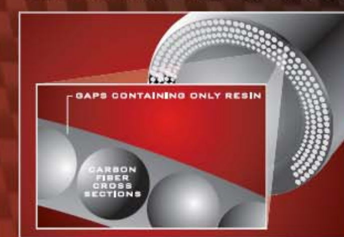
The addition of CNT, made possible by Zyvex NanoSolve™ materials and exclusive to Easton, strengthens composite structures to allow for longer barrels, bigger sweet spots and improved bat designs with optimized flex, responsiveness, and more "kick" through the hitting zone for maximum performance within the legal limits of the game

SUPER HIGH STRENGTH MATERIALS

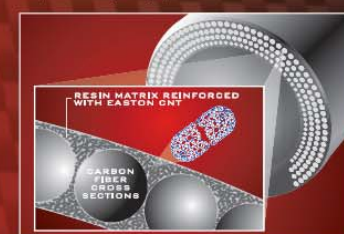
Aerospace grade fibers and high toughness resins create an ultra lightweight, super high strength bat that delivers maximum performance in every swing



The CNT Difference



Cross section of one ply of carbon fiber material with only resin filling the gaps between fibers.



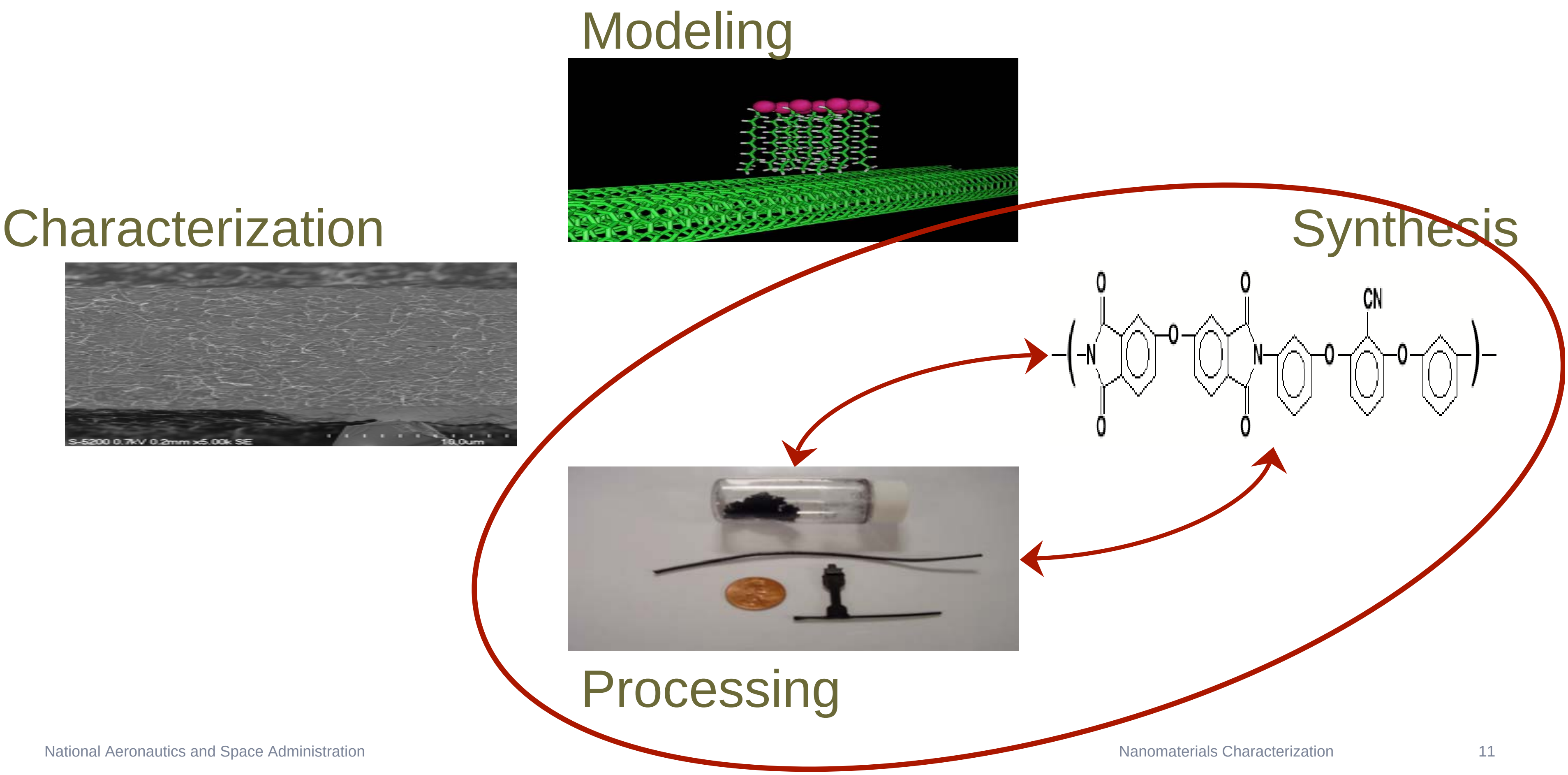
The same ply with Easton's Enhanced Resin System.™ Carbon Nanotubes (CNT) strengthen and toughen the matrix.

SLOW-PITCH FASTPITCH BATS

However, before any “nano” makes it on my plane, the materials…

- Must be demonstrated to a sufficient technology readiness level (TRL level / Production ready)
- Must have a verifiable distribution and orientation of the nano component.
- Must have quality assurance and quality control (QA/QC) tools and methods.
- Must be certifiable and have a certification plan.

Current state of the industry



Field ready QA/QC?

- For Quality Assurance and Quality Control (i.e. an electrical percolation network sufficient for lightning strike protection) the underlying property most responsible for the bulk scale function needs to be **quantified**.

- To quantify the property a means of **measuring** it must be available.

- To measure the property a means of “**seeing**” it must be available.

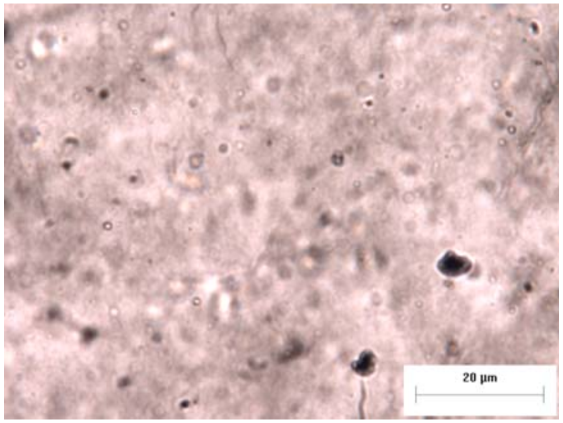
The problem

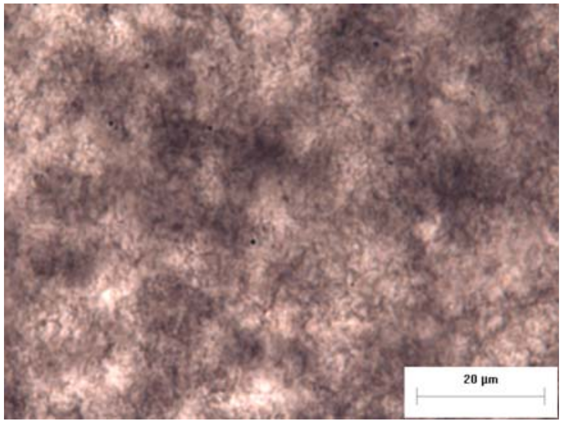
Kinetically stable, weeks

Thermodynamically stable, years

0.02%SWNT-CP2

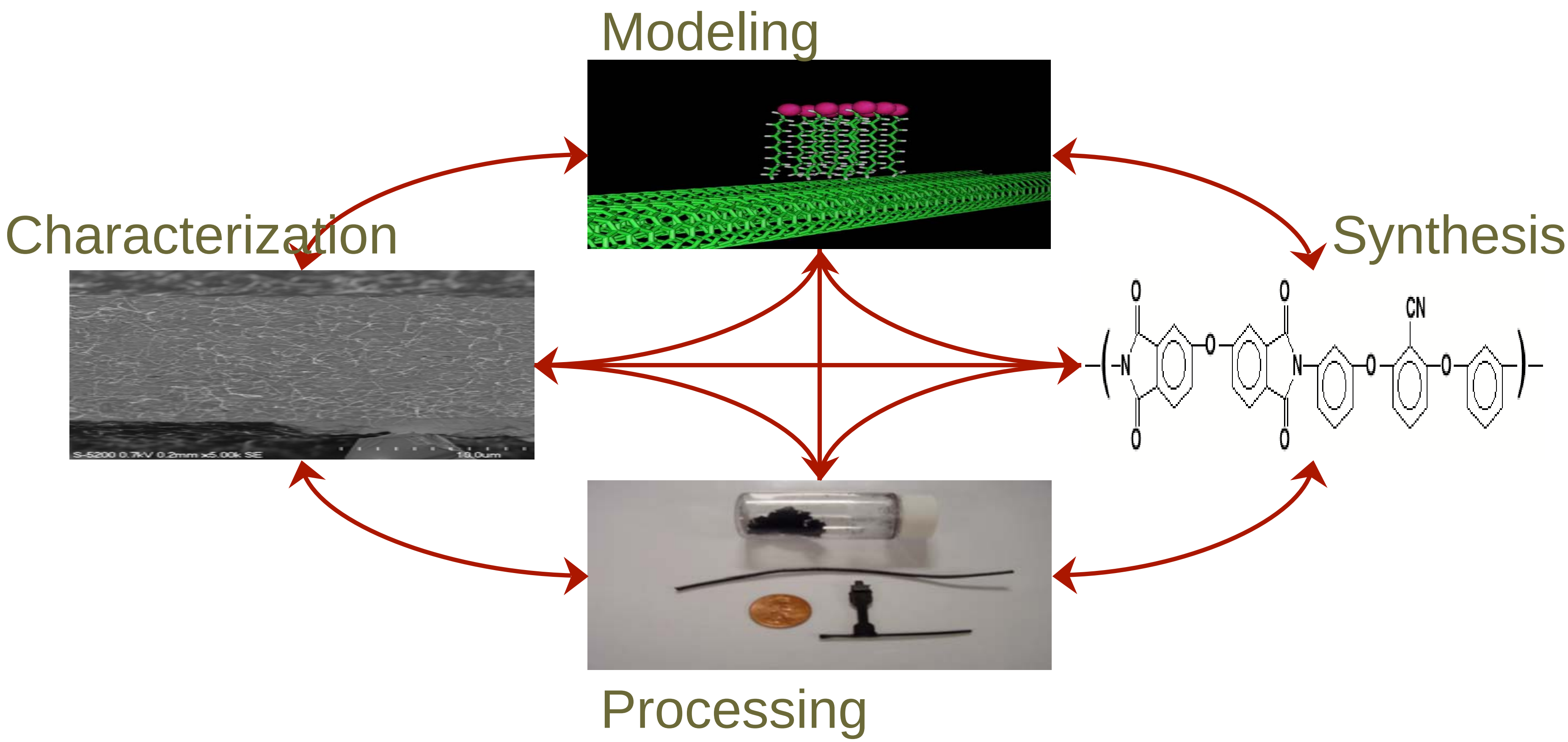
0.02%SWNT-(β-CN)A/O



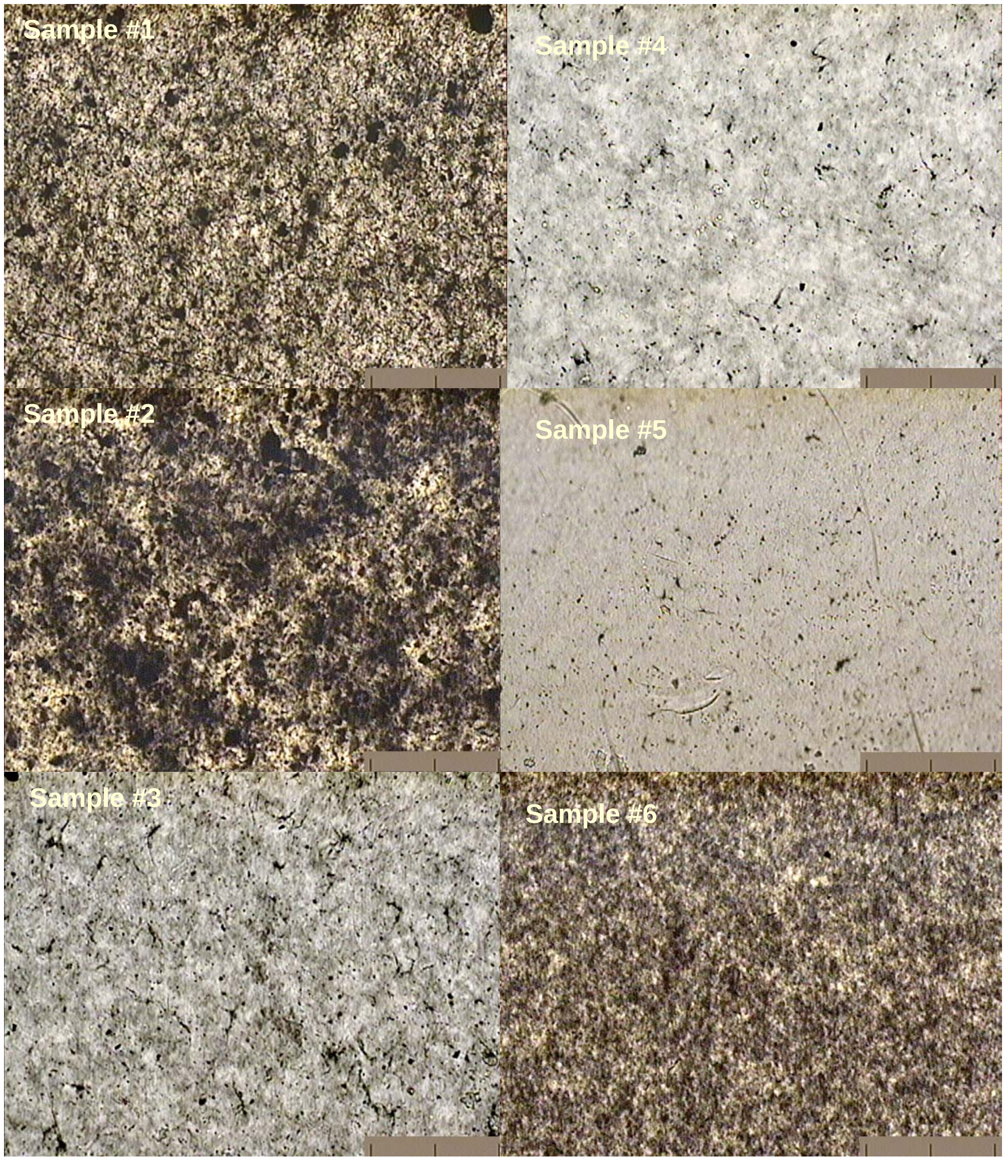


Both samples are indistinguishable by conventional optical characterization techniques

How do we attack the problem



Optical microscopy (OM)

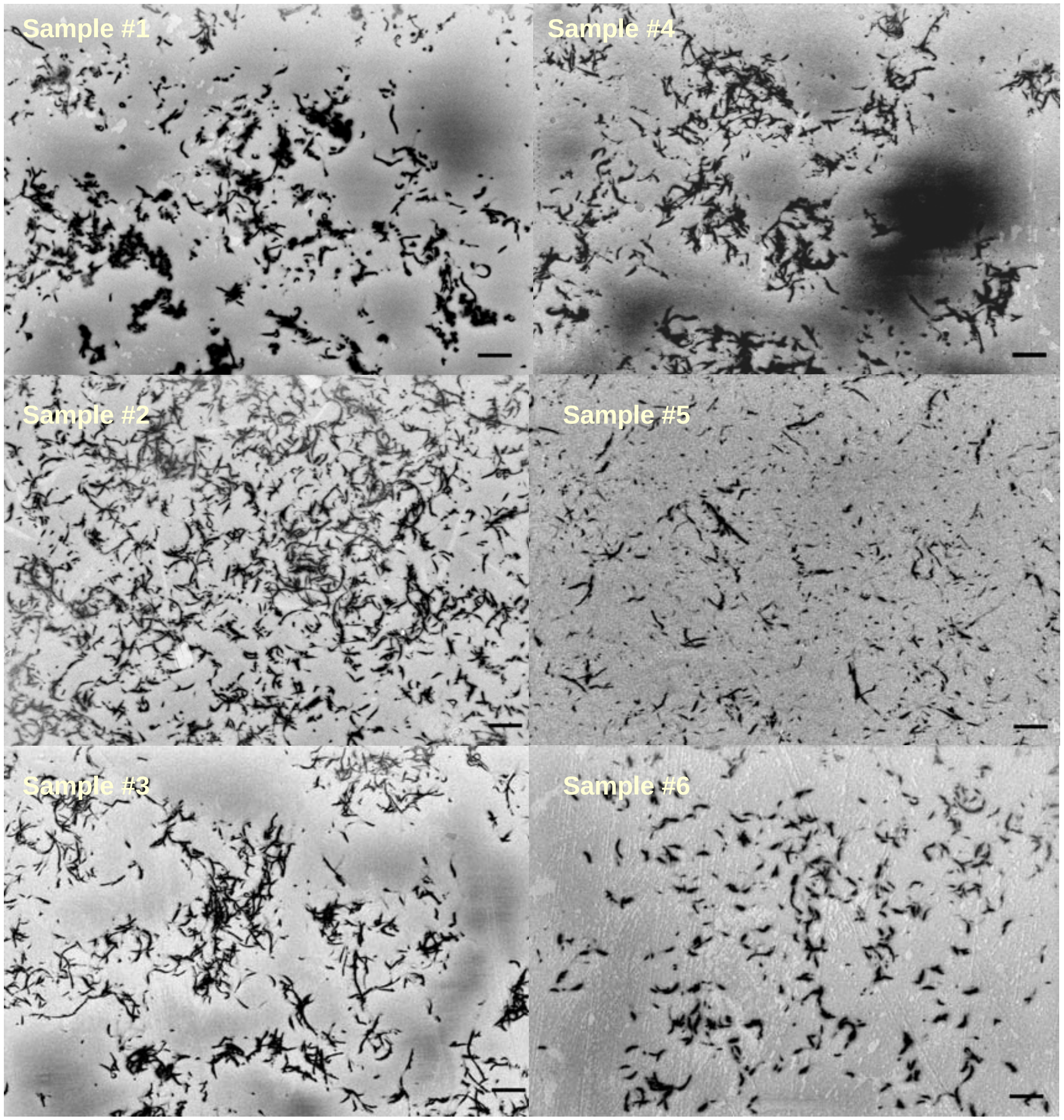


- Sample 1: direct mixing of 1.0% LA-SWNT in CP2
- Sample 2: *in-situ* polymerization of 1.0% LA-SWNT in CP2
- Sample 3: *in-situ* polymerization under sonication of 1.0% LA-SWNT in CP2
- Sample 4: *in-situ* polymerization under sonication of 0.5% LA-SWNT in CP2
- Sample 5: *in-situ* polymerization under sonication of 0.5% LA-SWNT in β-CN
- Sample 6: *in-situ* polymerization under sonication of 0.5% HiPCO-SWNT in β-CN

- Samples 1 and 2 are different fabrication methods which results in different dispersion quality.
- Samples 2 and 3 are fabricated using the same procedure but sample 3 adds sonication.
- Samples 3 and 4 are different concentrations of LA-SWNT.
- Samples 4 and 5 are different polymer compositions.
- Samples 5 and 6 are different SWNT compositions.

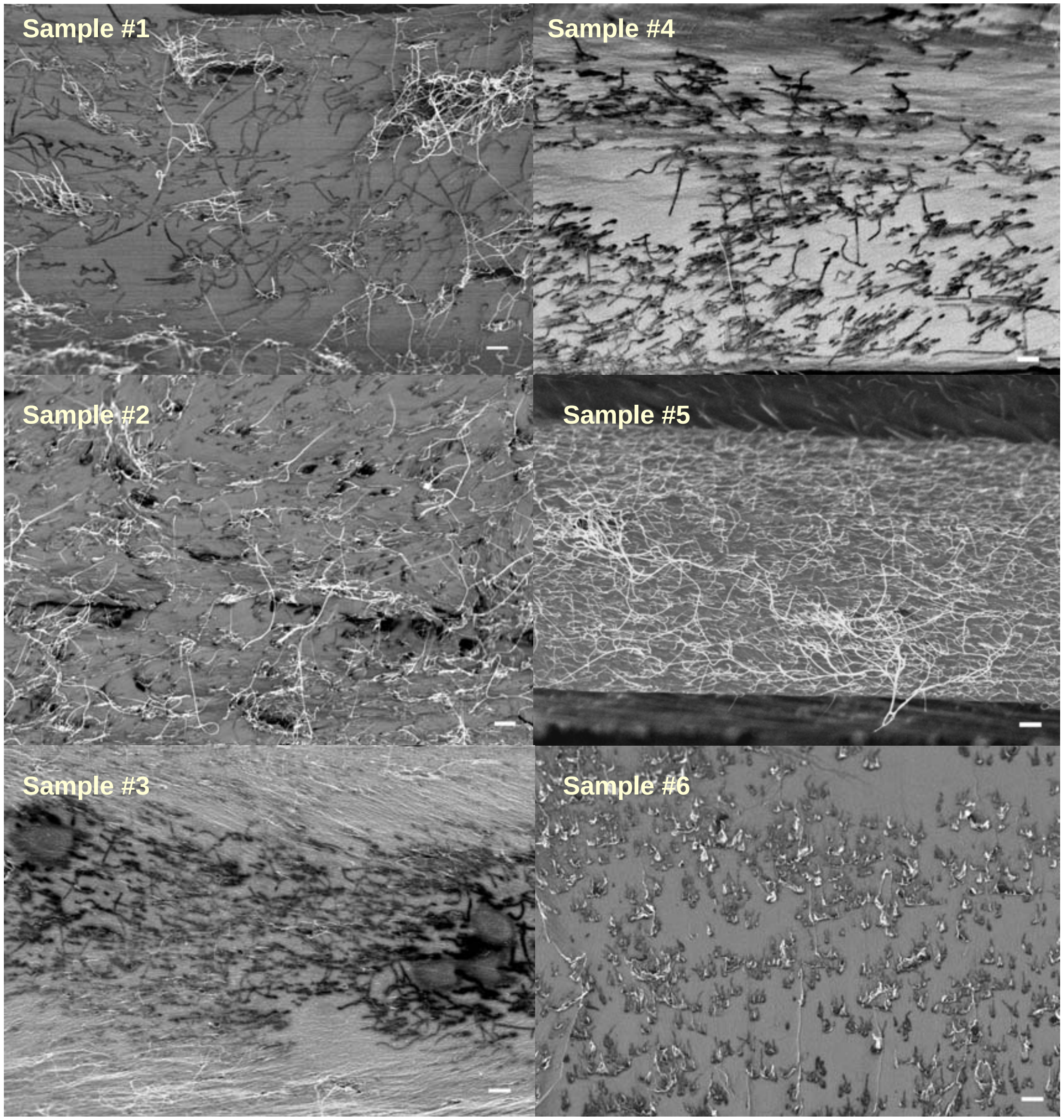
- Samples 3-5 which show no visible aggregation are labeled as “optically dispersed”. Scale bar is 10 μm.

Electron Microscopy (EM)



- HR-FESEM surface and cross-section images on the dispersion quality of Samples 1-6. Sample 1 shows a poor dispersion quality. Sample 2 shows an improved dispersion over the direct mixing technique. Samples 2, 3, 4 and 6 had a dispersion quality that cannot be distinguished from each other using these images. Sample 5 shows an improved dispersion over the other samples from using the β-CN polymer. In Sample 5 contains no visible aggregates, very small bundles and no resin rich areas. Scale bar is 4 μm.

Electron Microscopy (EM)



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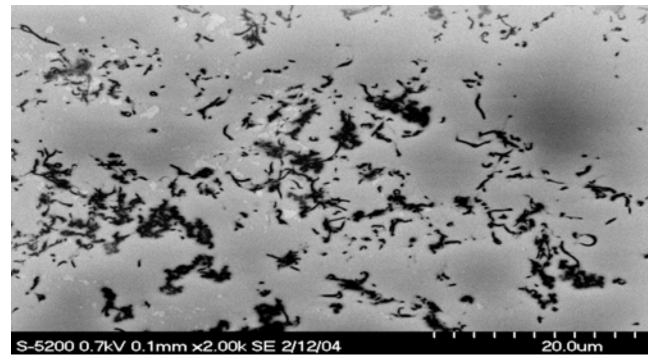
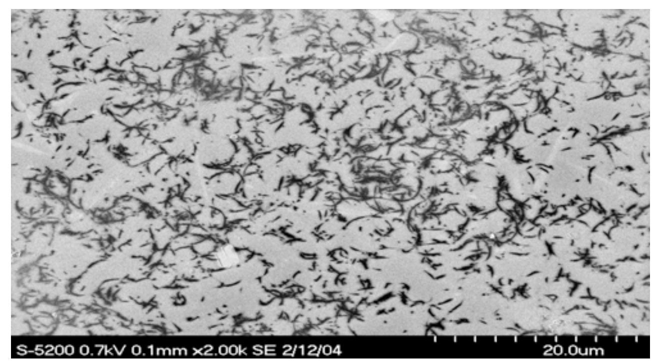
Quantifiable metric for dispersion?

- NIST/NASA workshop on Measurement Issues in Single Wall Carbon Nanotubes: Purity and Dispersion
  - http://www.msel.nist.gov/Nanotube2/Carbon_Nanotubes.htm

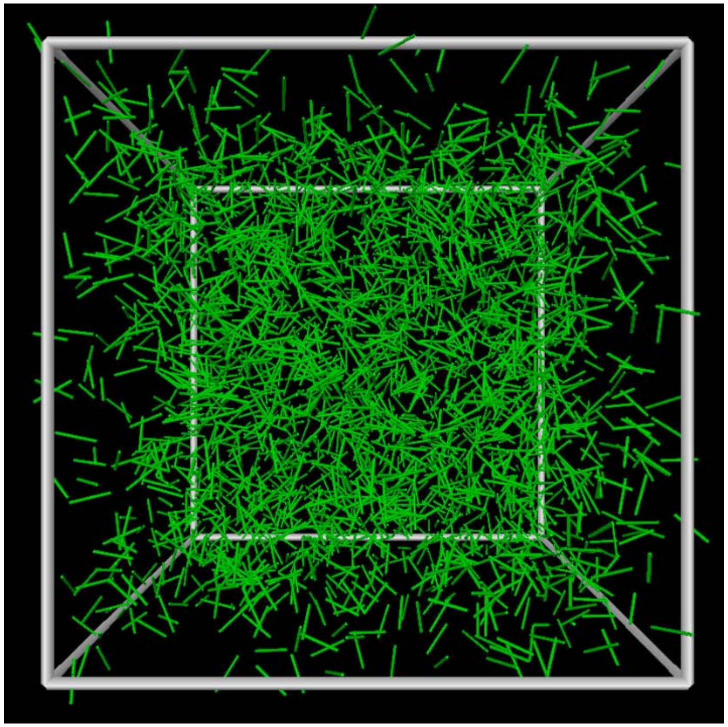
- Using SEM photos, operating conditions, concentration of nanotubes, etc. begin to develop a quantifiable metric.
  - A "gold standard" will be tested fully and shared to allow for tool verification / calibration



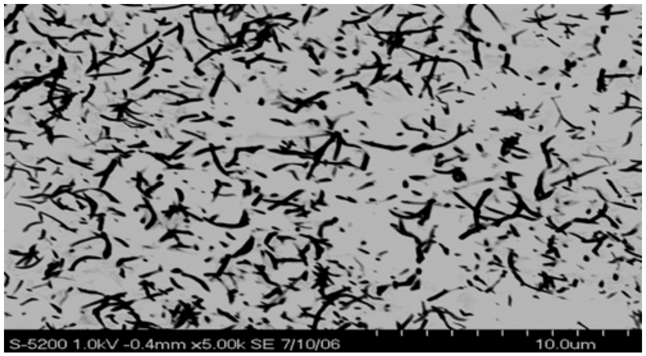


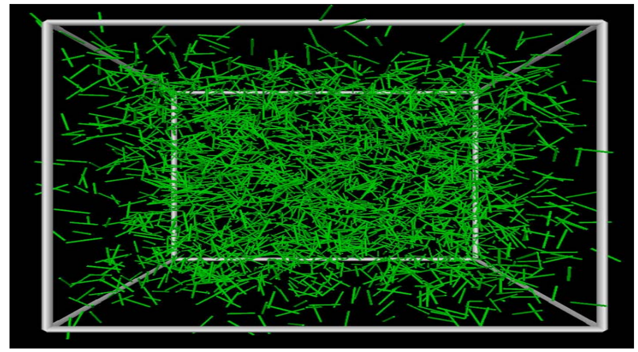
The challenge

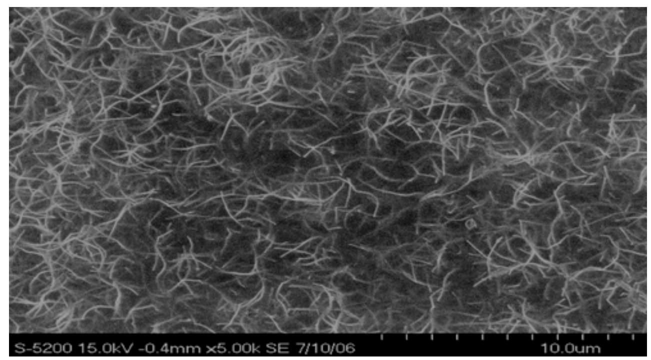
- The data was insufficient to develop a quantifiable measure of the dispersion. What was needed was a measure of the 3D distribution of the tubes not just a 2D projection of where the tubes intersect the surface or the cross-section.
- This was important to make the data meaningful and it would also help refine the models.



Voltage progression



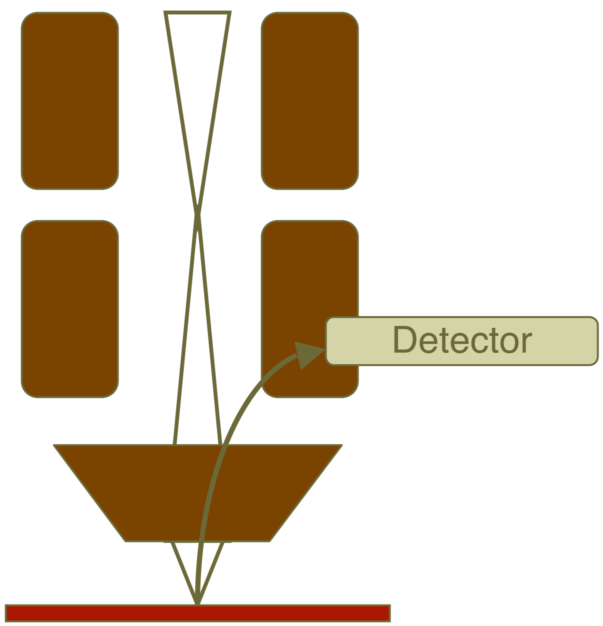


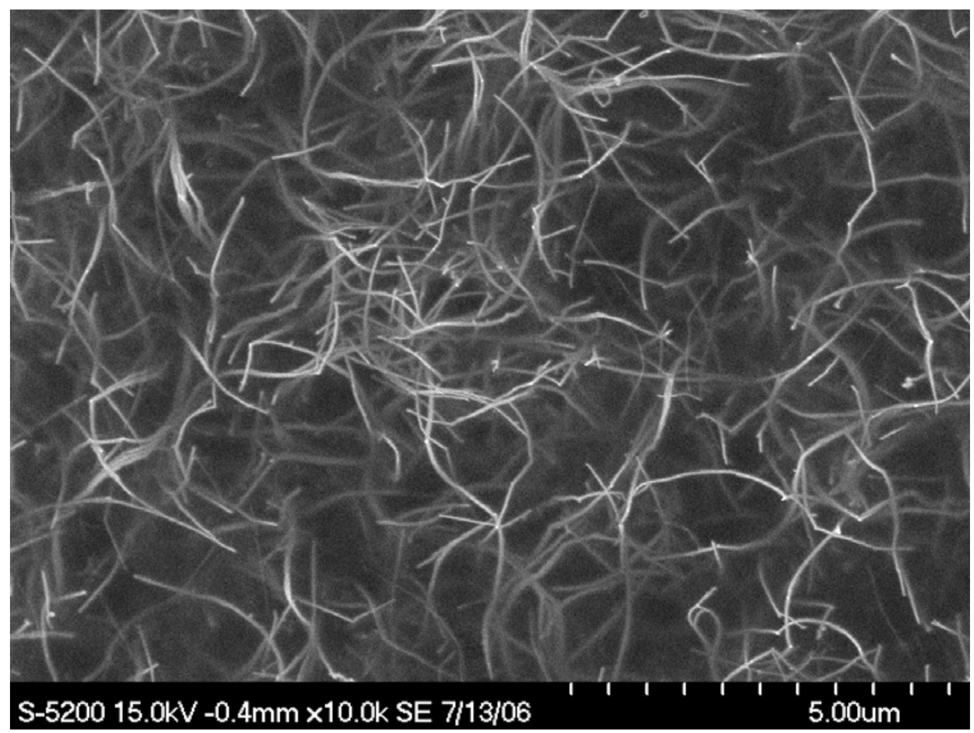


- We developed new tools to allow for the collection of data that was useful to help begin to refine the models and our understanding.

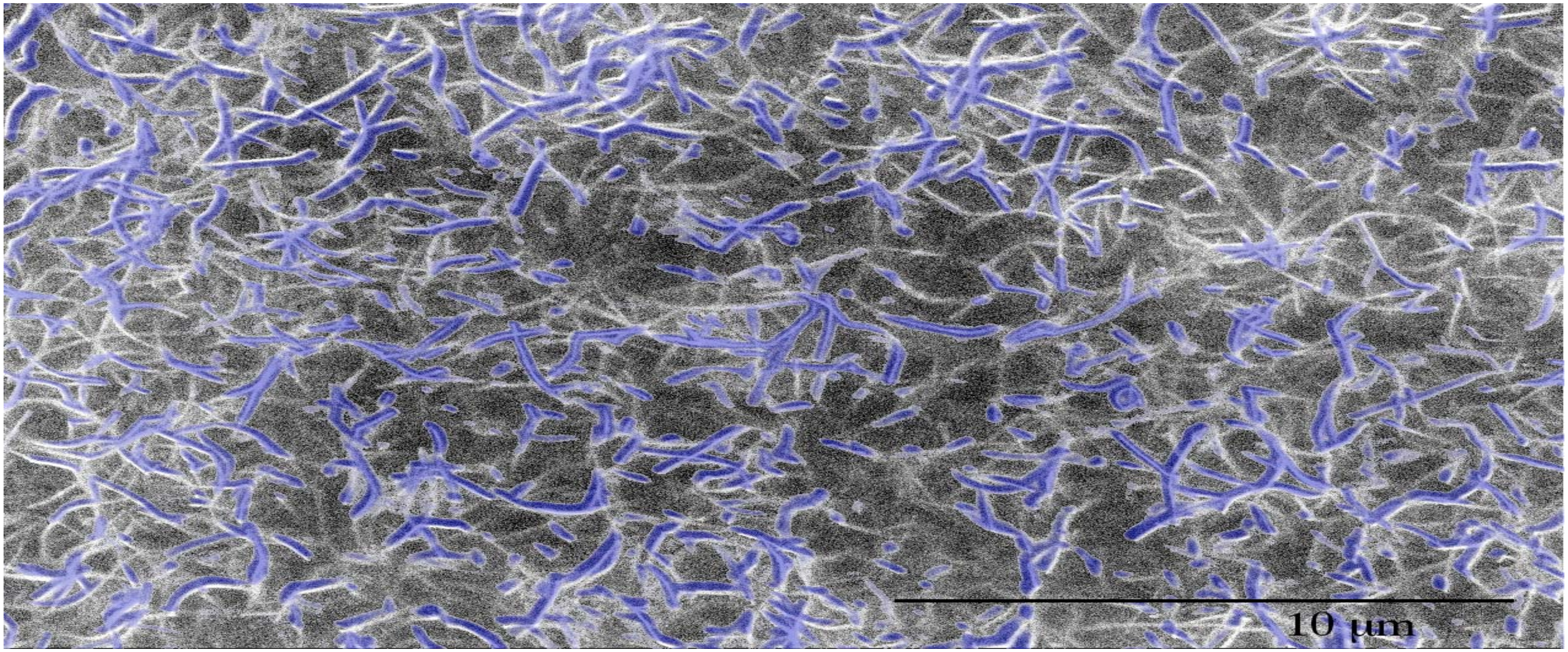
“Poly-transparent” imaging

- “Poly-transparent” imaging allows one to see through the polymer as if it was invisible. The nanotube network is then visible deep within the sample. The contrast mechanism is not well understood, but it now allows us a means of “seeing” the nanomaterial dispersion.



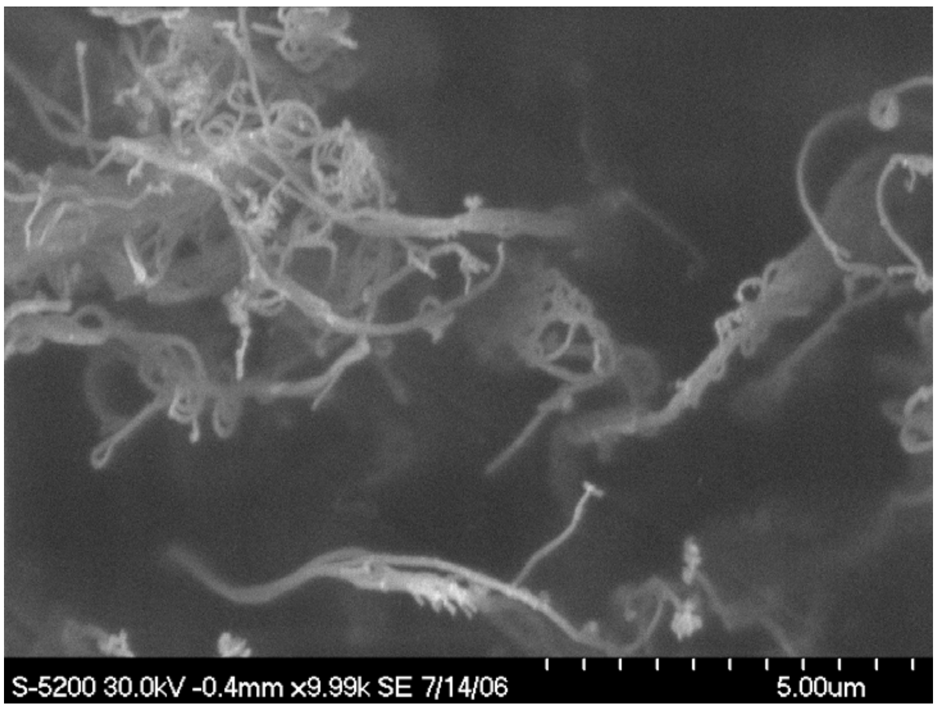


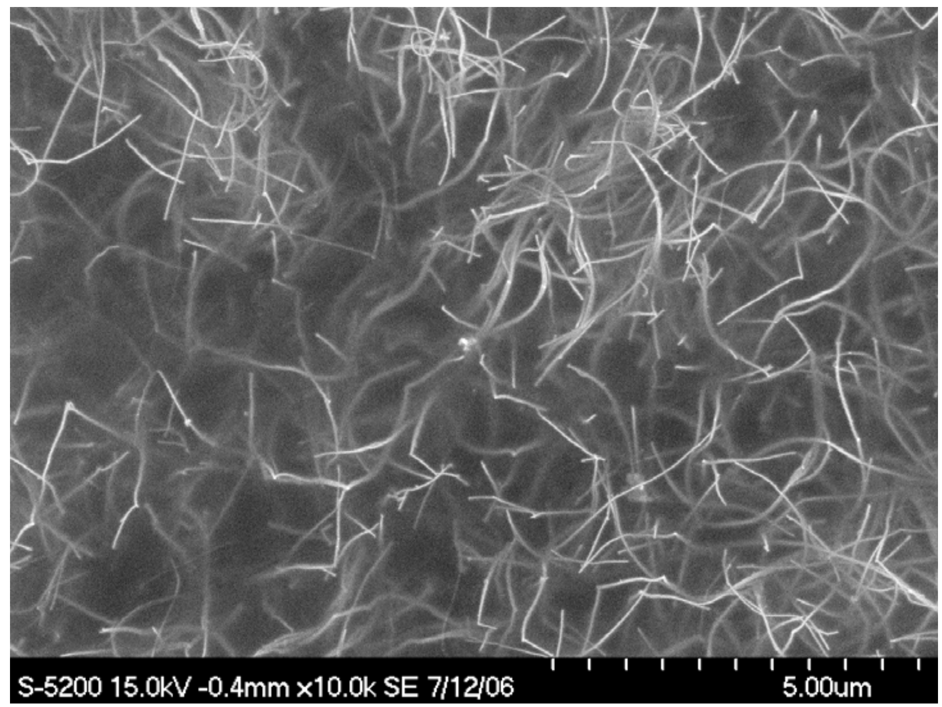
Comparison



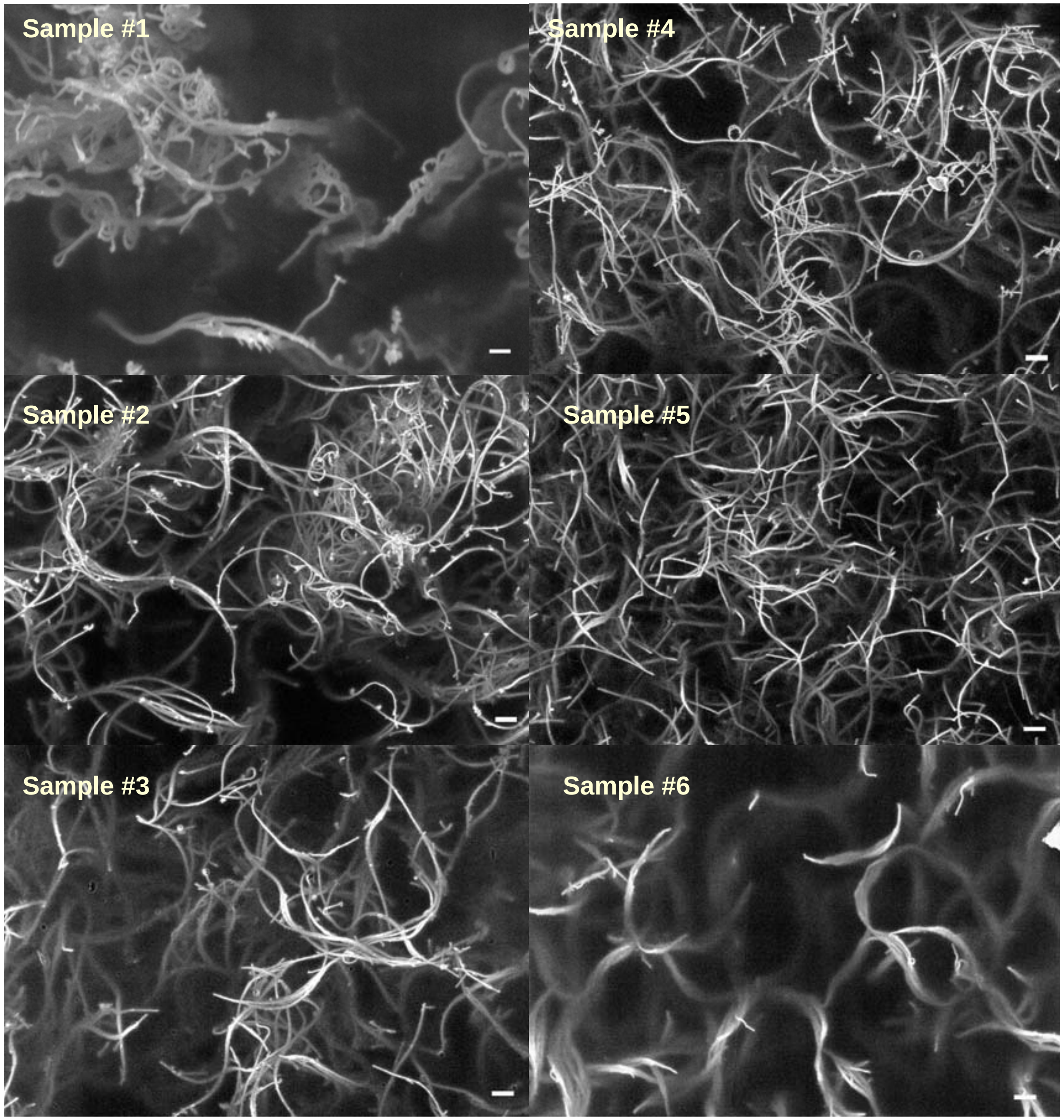
Good verses bad dispersion

- It is now easy to see the difference between the poorly dispersed sample on the left and the well dispersed sample on the right





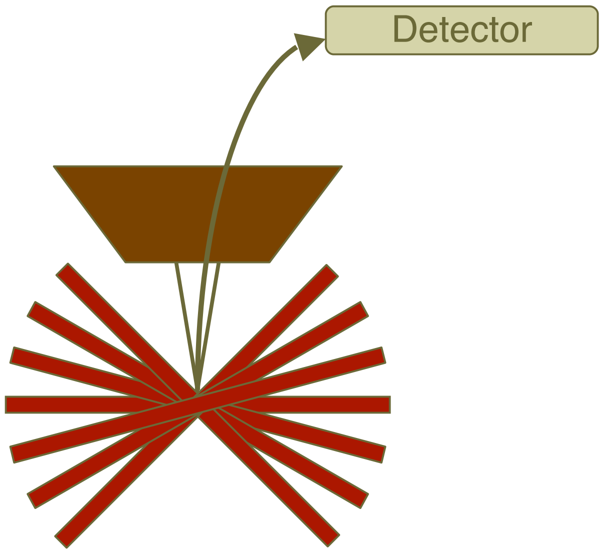
EM (high kV)

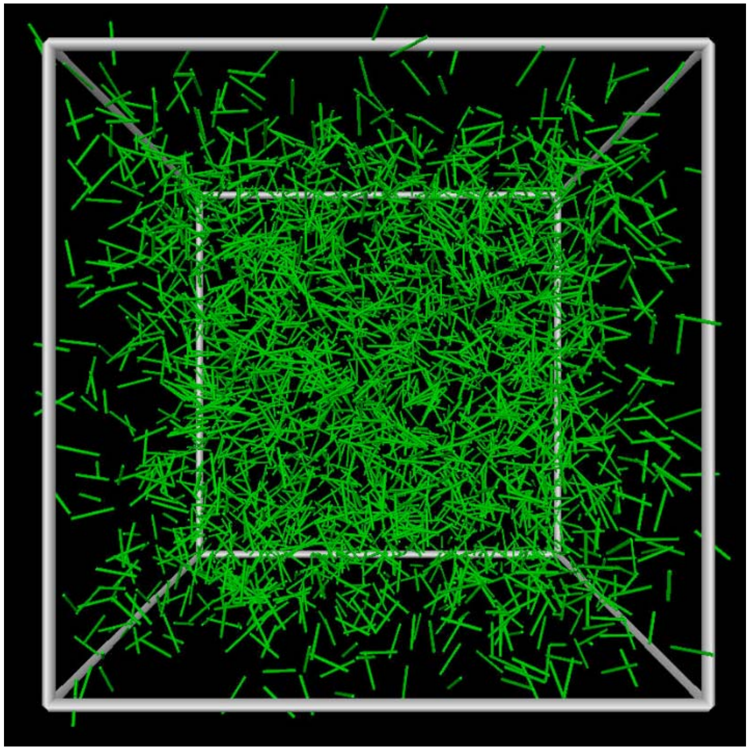


- "Poly-Transparent" images of Samples 1-6. This procedure provides sufficient detail to assess the dispersion quantitatively. Accurate details about the bundle diameter, bundle length, and the spacing between bundles is clearly evident. Sample 1 showing poor dispersion quality, large bundle sizes, twisted and looped tubes due to the direct mixing procedure. Samples 2-6 show longer, straighter tubes and smaller bundle sizes than seen in Sample 1 due to the *in-situ* polymerization procedure, but now there is enough detail to quantify the effects of sonication, SWNT concentration, polymer chemistry and SWNT composition. Scale bar is 500 nm.

Electron tomography now possible

- Through a series of images taken at different angles of incidence, a 3-dimensional reconstruction can be performed from the 2 dimensional images. Analogous to computed tomography (CT) scans of the body.



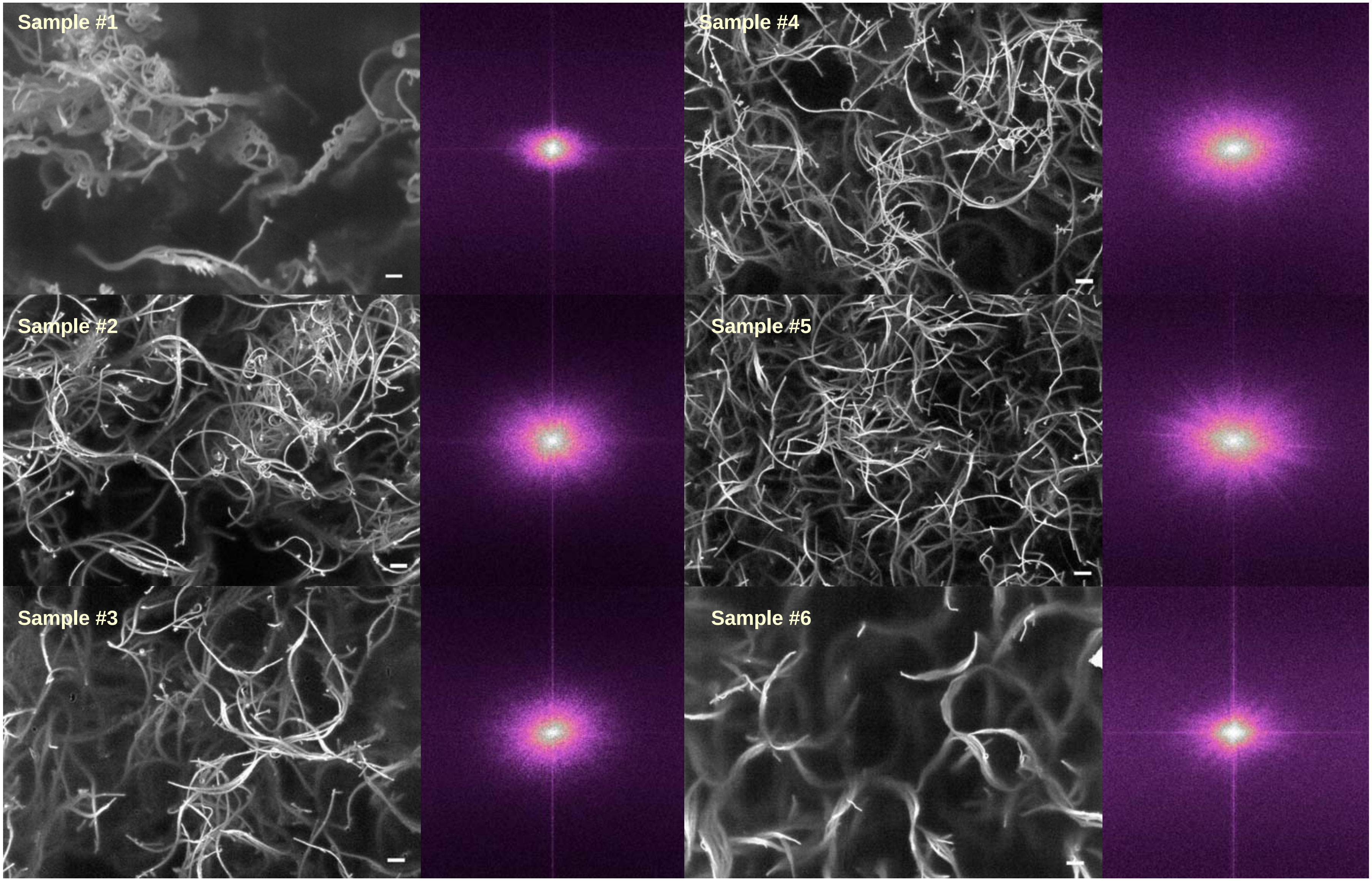


EM Tomography (Sample 3)

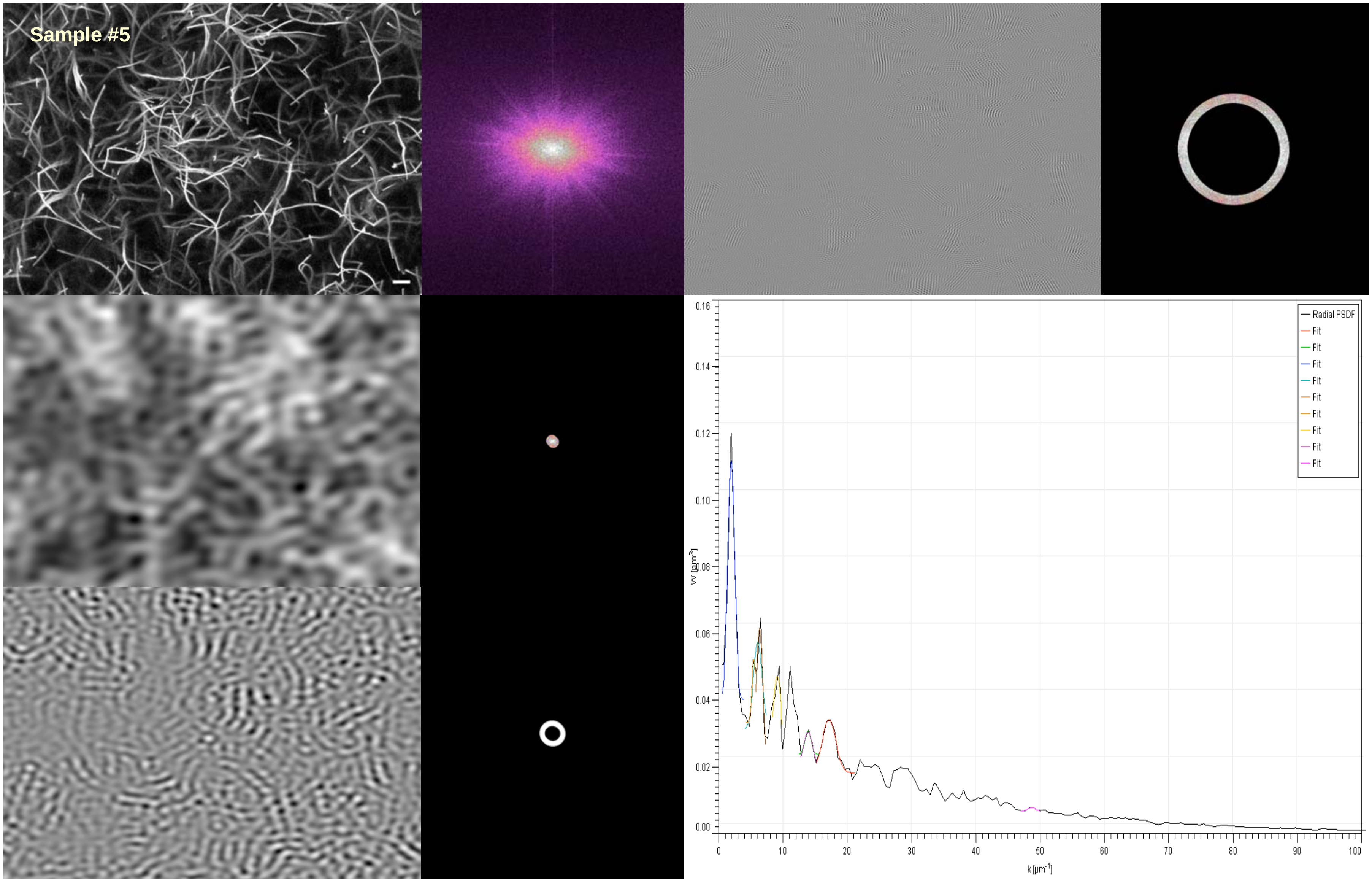
Metric of Dispersion

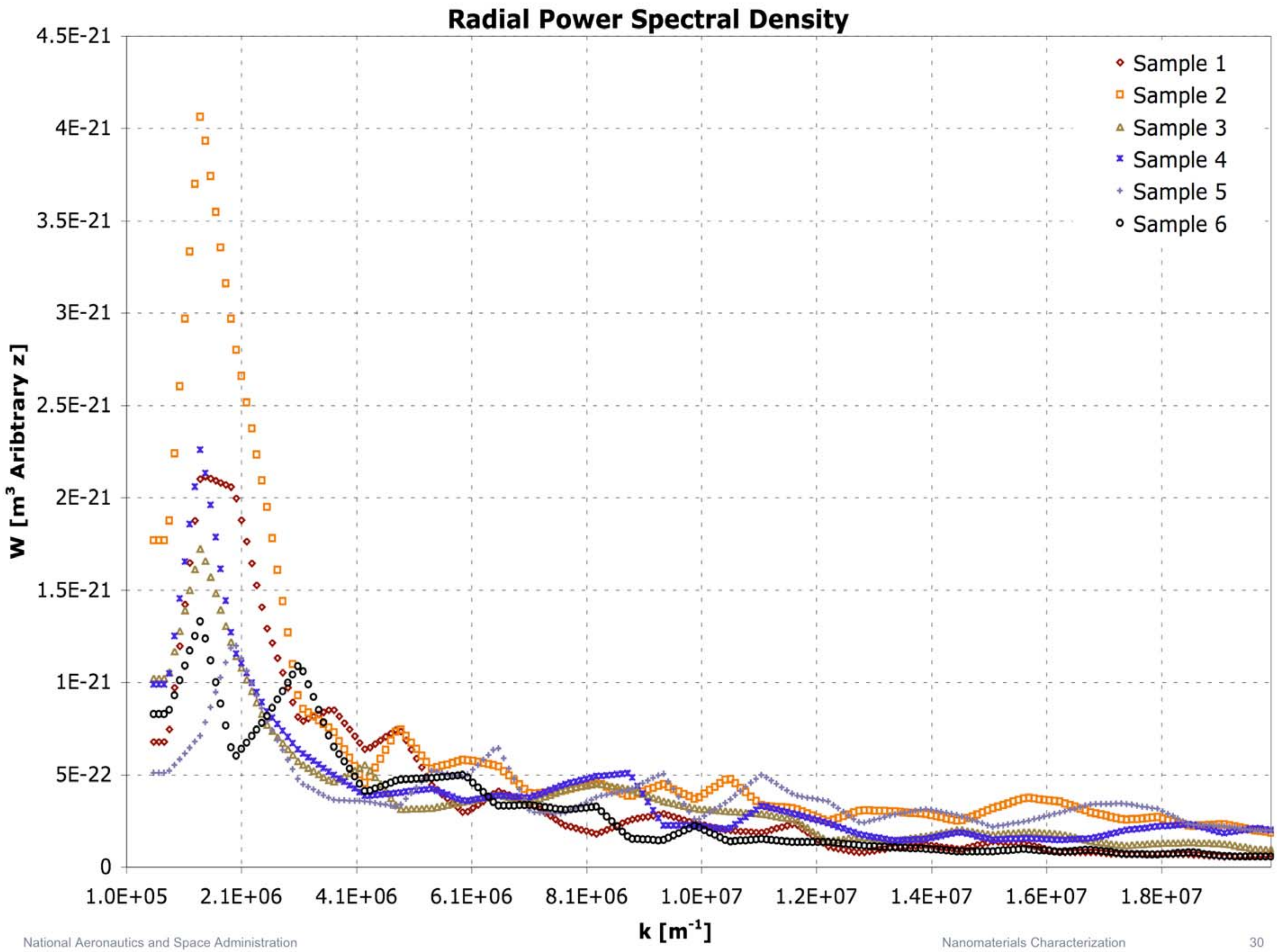
- To measure the distribution, a 2 Dimensional Fourier Transform is performed on the image. Information about the relative size of the features (i.e. bundles), and the ordering is immediately available.

FFT

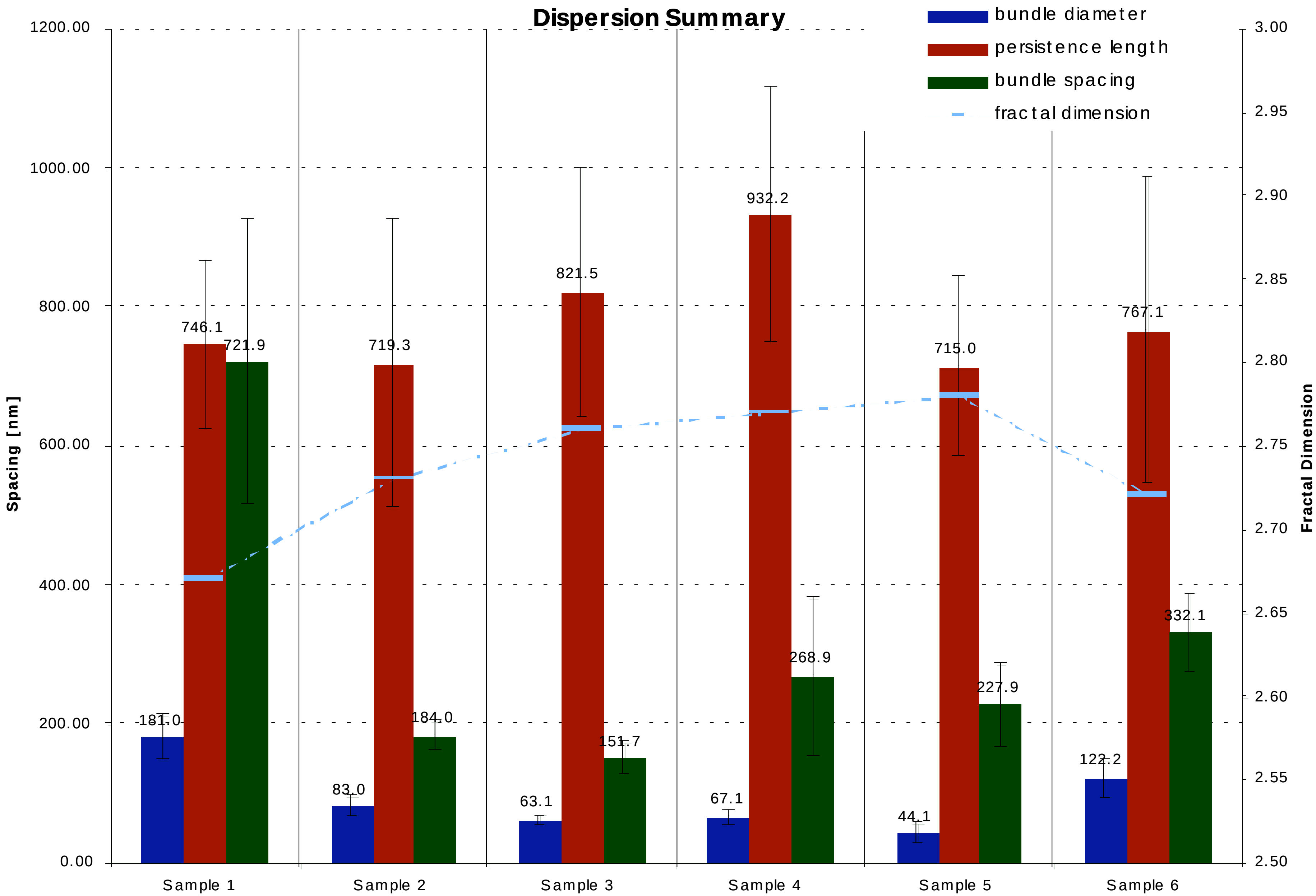


Radial Power Spectral Density





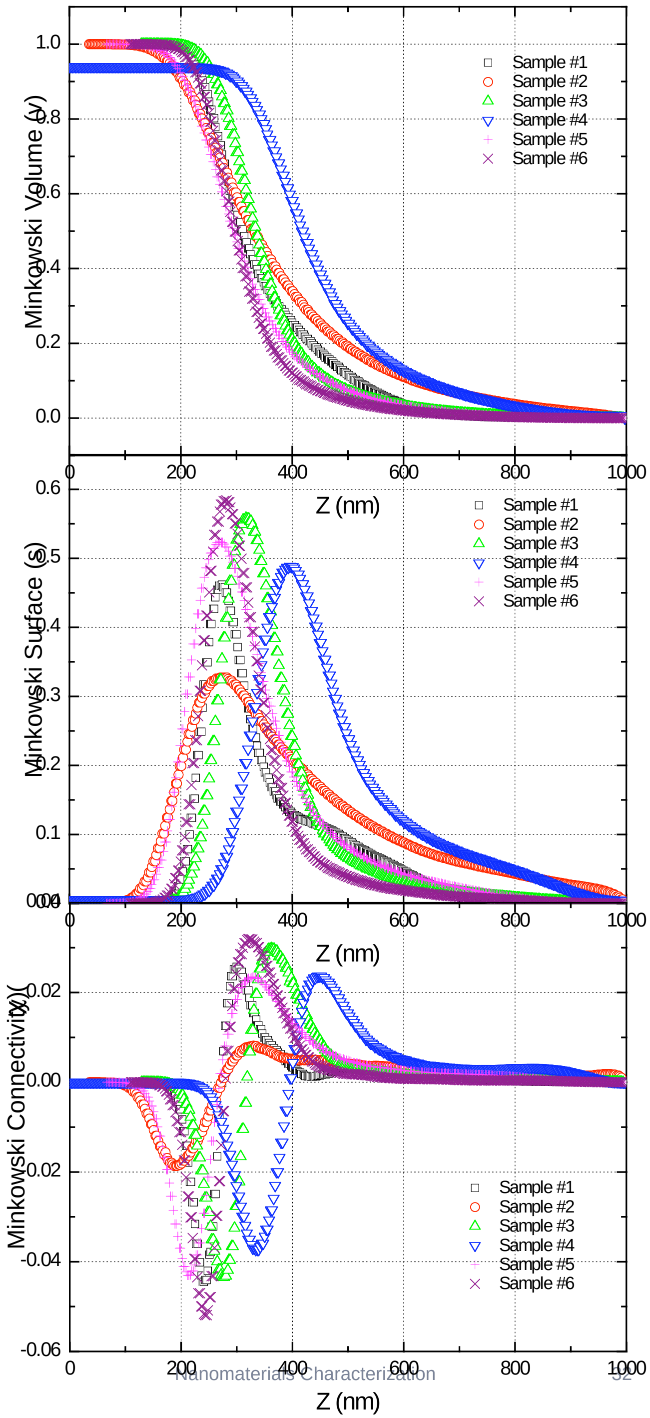
Radial Power Spectral Density
W [m^3 Aribtrary z]
k [m^-1]
4.5E-21
4E-21
3.5E-21
3E-21
2.5E-21
2E-21
1.5E-21
1E-21
5E-22
0
1.0E+05
2.1E+06
4.1E+06
6.1E+06
8.1E+06
1.0E+07
1.2E+07
1.4E+07
1.6E+07
1.8E+07
Sample 1
Sample 2
Sample 3
Sample 4
Sample 5
Sample 6



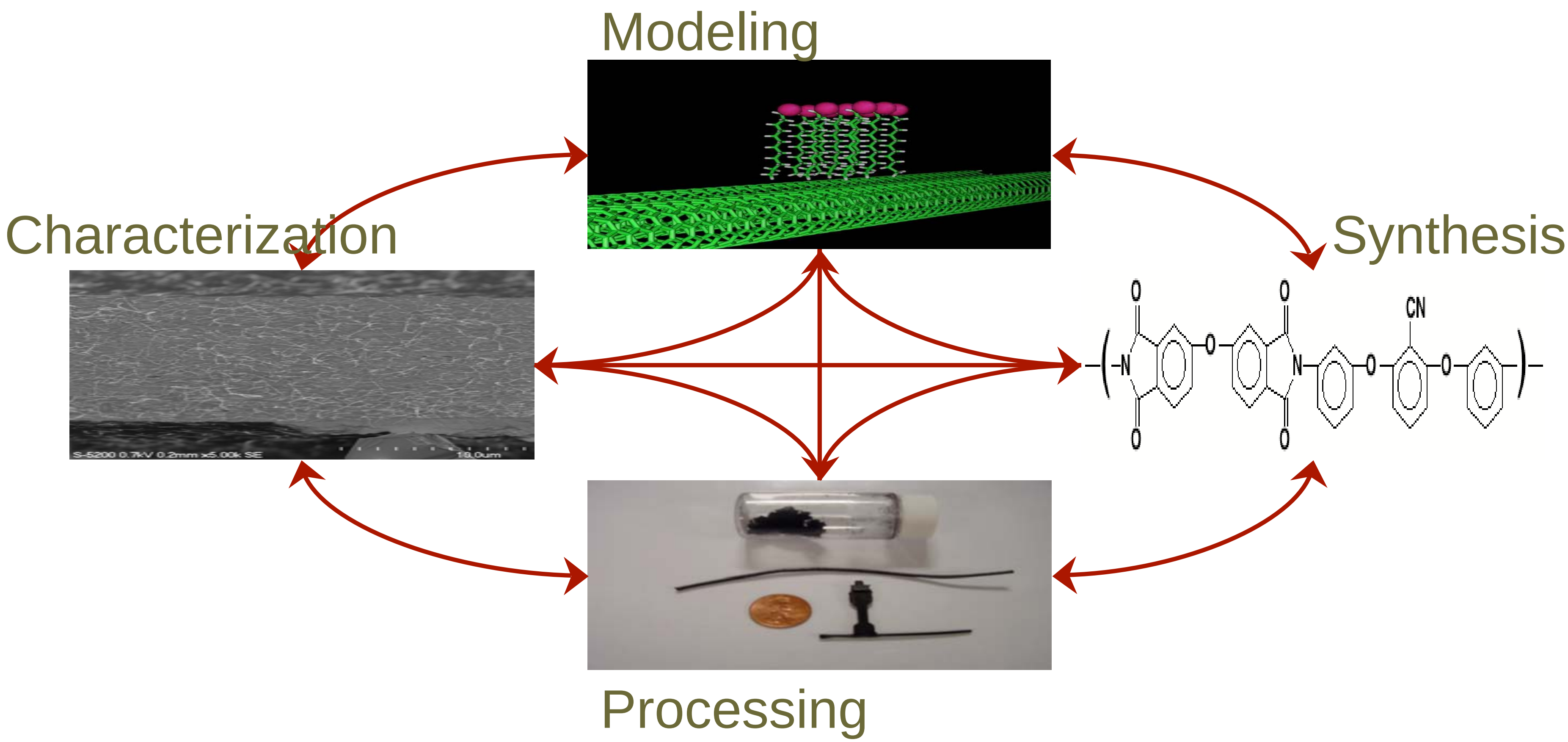
Dispersion Summary
bundle diameter
persistence length
bundle spacing
fractal dimension
Spacing [nm]
Fractal Dimension
1200.00
1000.00
800.00
600.00
400.00
200.00
0.00
3.00
2.95
2.90
2.85
2.80
2.75
2.70
2.65
2.60
2.55
2.50
181.0
746.1
721.9
83.0
719.3
184.0
63.1
821.5
151.7
67.1
932.2
268.9
44.1
715.0
227.9
122.2
767.1
332.1
Sample 1
Sample 2
Sample 3
Sample 4
Sample 5
Sample 6

Minkowski Functionals

- The Minkowski Functionals Volume (v), Surface (s) and Connectivity (χ) validate the results from the radial power spectral density measurements.
- The Minkowski functional connectivity (χ) is defined as the number of connected pixels minus the number of number of holes divided by the total number of pixels. Using this measure we were able to determine the local structure. Positive values of χ correspond to cylindrical structures. Negative values of χ correspond to connected structures with a lot of holes. The point at which χ = 0 is the length scale at which the image becomes periodic. Moving from low to higher values of the threshold parameter (z), we observed that sample 4 had a minima at the largest value of z. This indicated that sample 4 had the largest interconnected structure. Sample 4 also had the maxima at the largest value of z indicating the longest cylindrical structures, which also validates the RPSD results. The Minkowski functionals serve as another tool to help evaluate and quantify the local structure and are useful for 3-D computational modeling of practical nanocomposites.



Now we can consider field ready tools



Tools: consider your application

- Do you need a high enough electrical conductivity for lightning strike protection?
  - Then measure electrical conductivity
- The application will drive the QA/QC tool development
  - Other issues like “field ready”, user training, will be addressed later
- However, a fundamental understanding of the underlying physics is absolutely critical:
  - How is the bulk property affected by things like:
    - » Dispersion, aspect ratio, interfacial phenomena
    - » Primary, secondary, tertiary structure

Potential tools

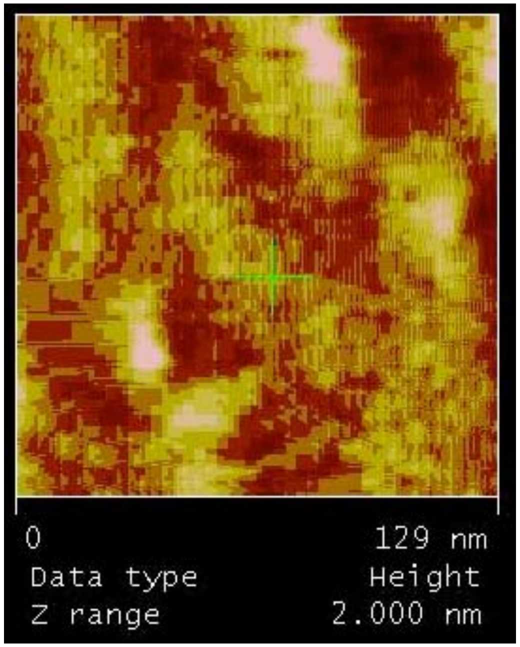
- The tools can be based on
  - Optical (absorbance, transmittance, scattering, spectroscopy, etc)
  - Electrical (conductivity, dielectric, etc.)
  - Ultrasound holography
- Critical length scale needs to be determined

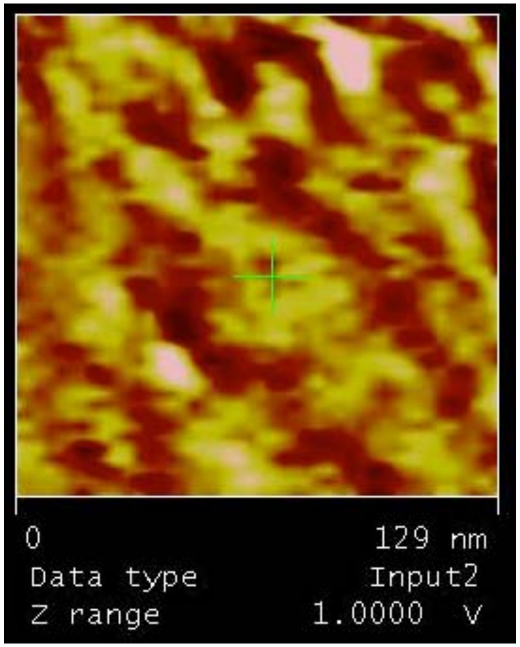
Highly Conductive

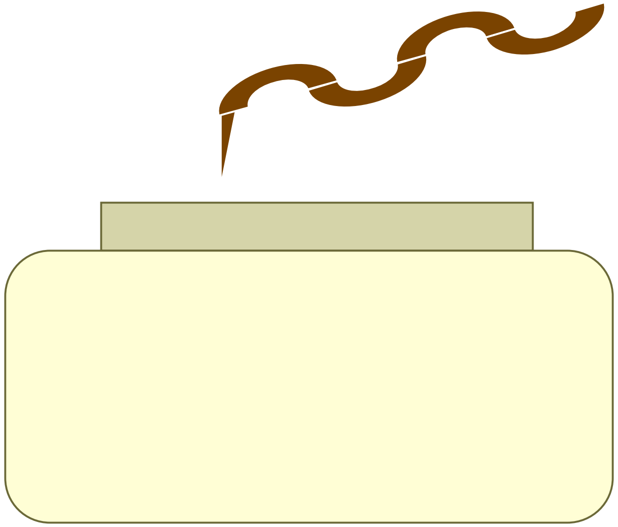
Not conductive

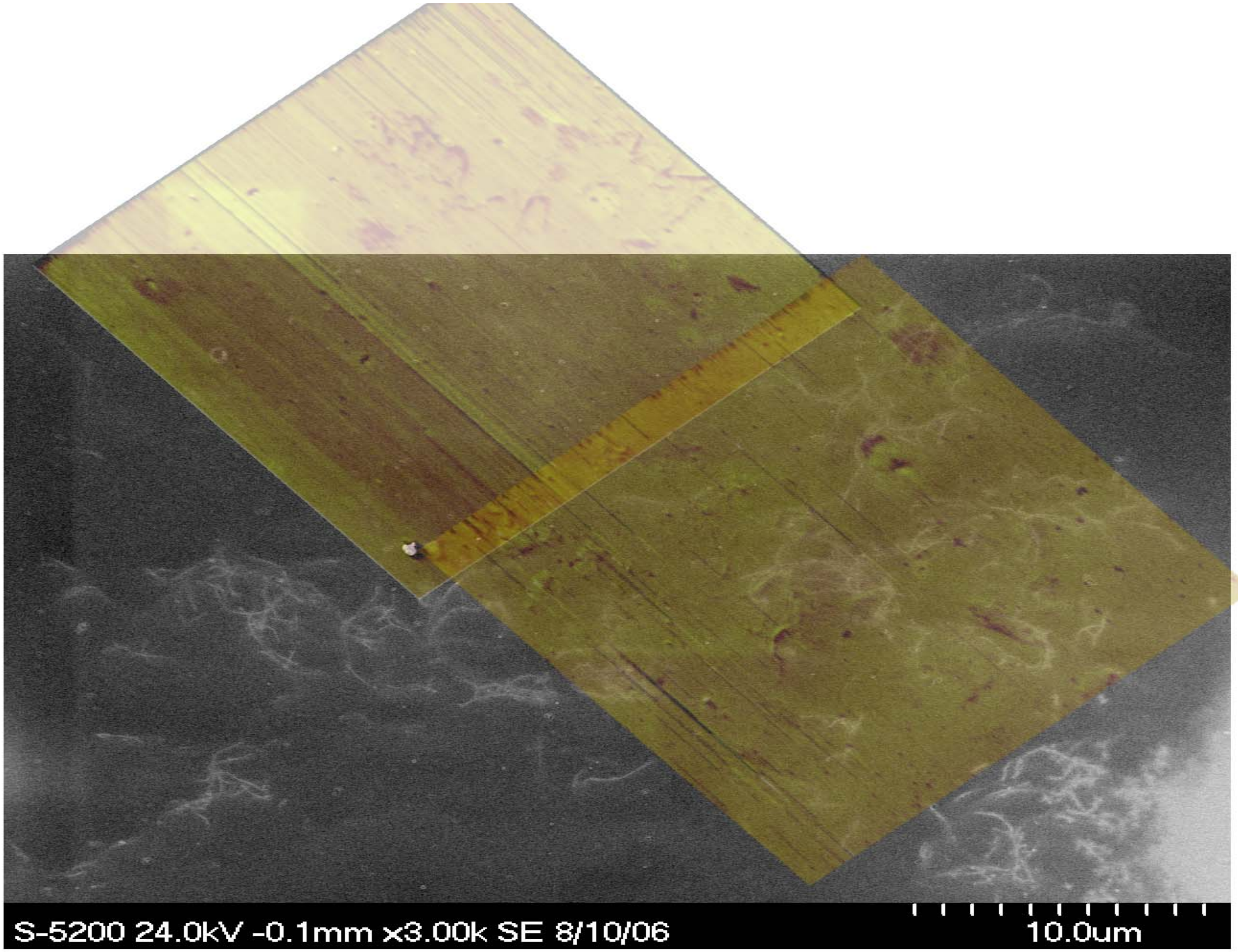
Ultrasound holography

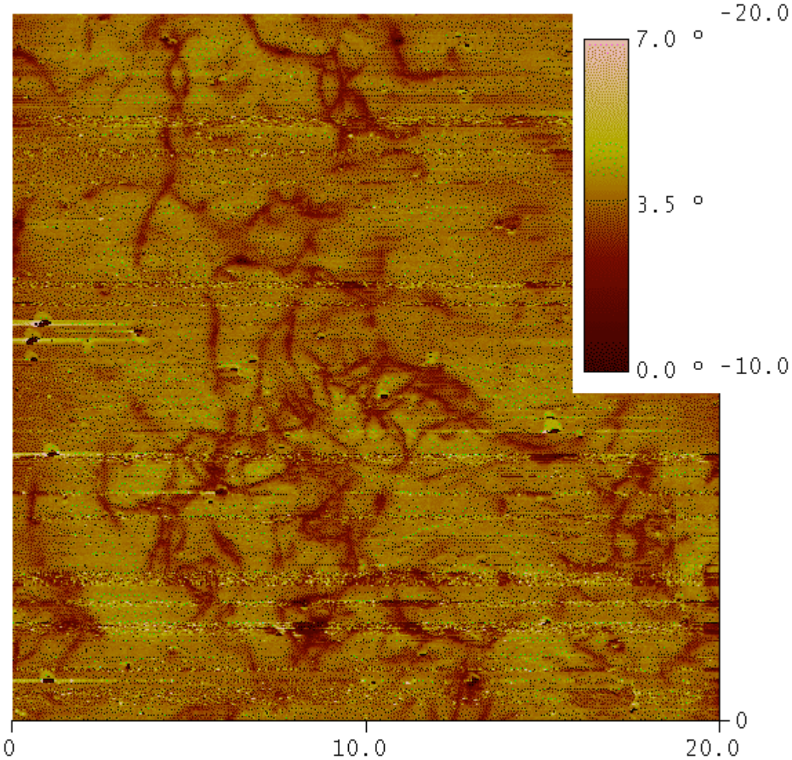
- A new tool for “seeing” the nanomaterials is being developed based on a combination of ultrasound and atomic force microscopy (AFM) techniques. The diffraction limit of the ultrasound is breached by using the nanometer sized probe of the AFM as an ultrasound transducer.



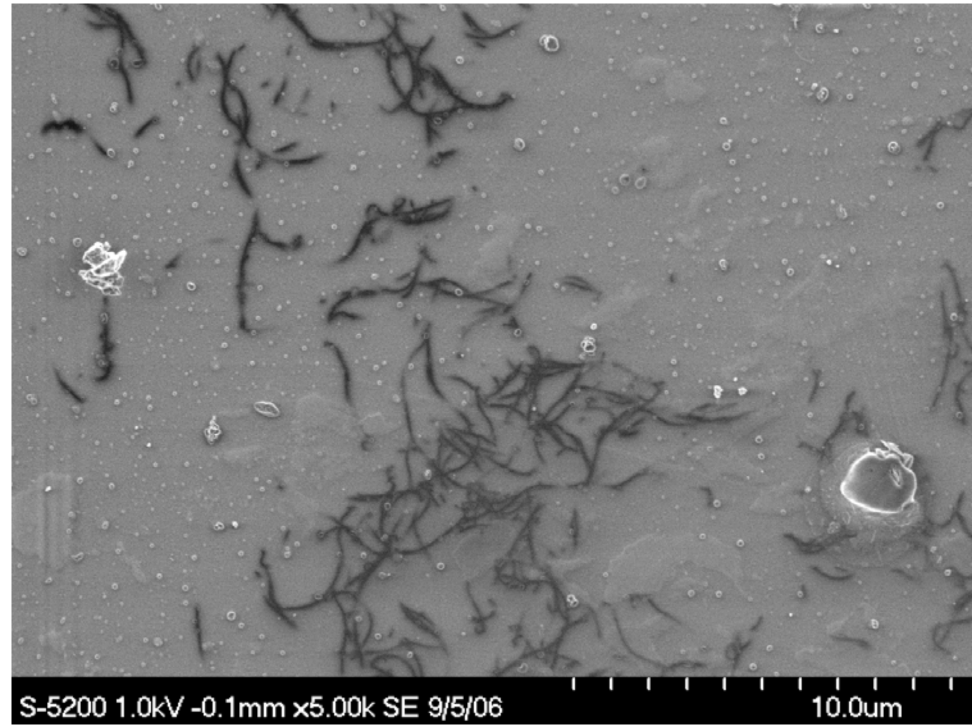




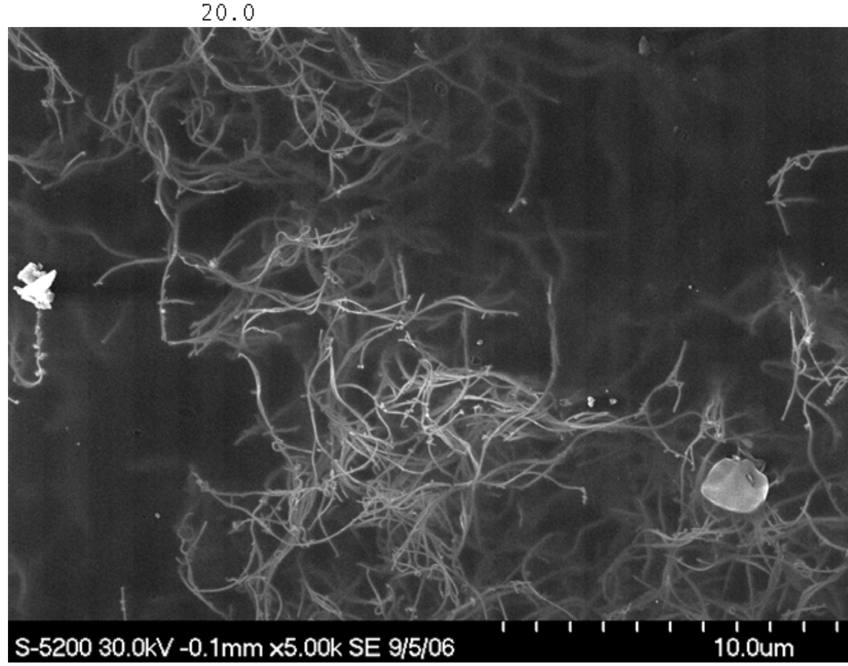

S-5200 24.0kV -0.1mm x3.00k SE 8/10/06
10.0um



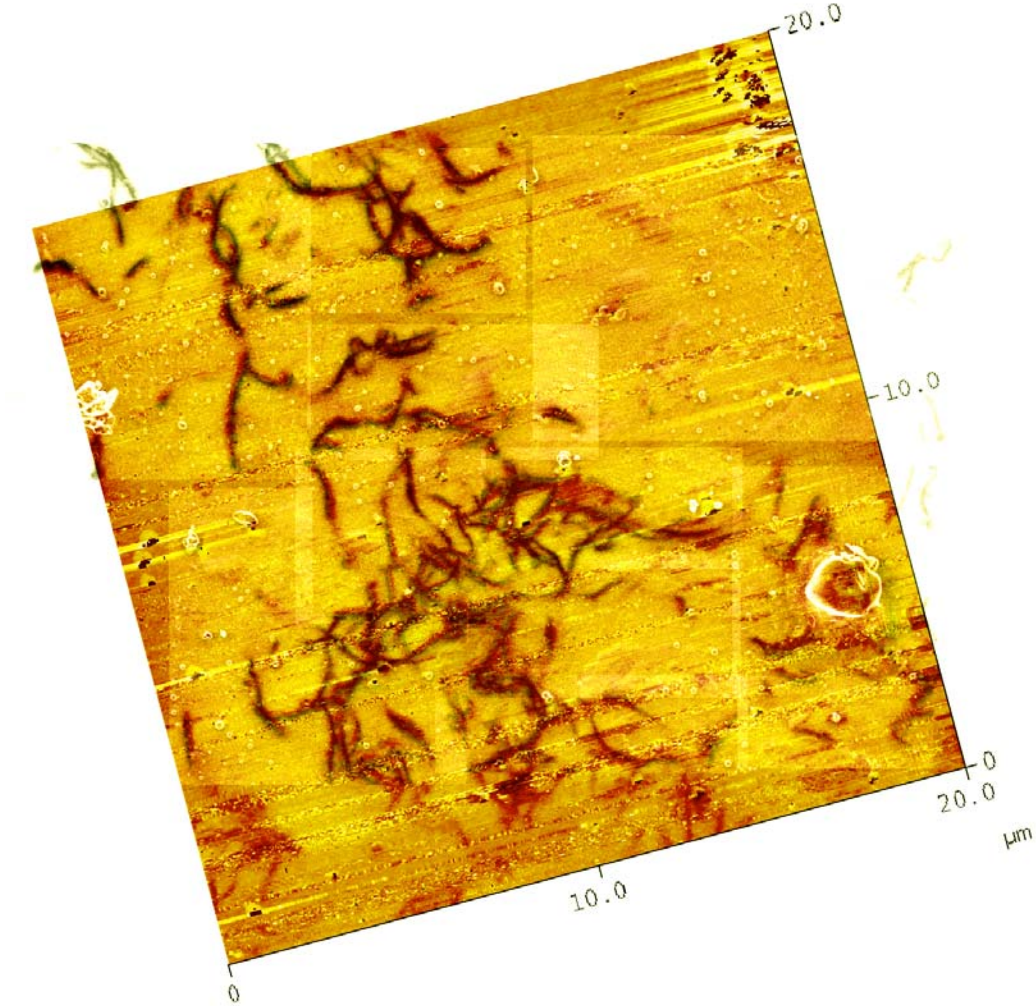
MFM



Low K image

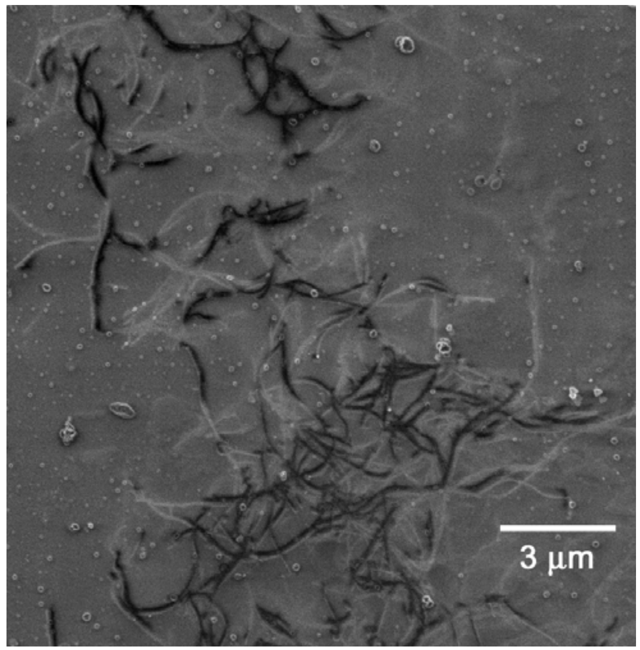


Poly-transparent image



Overlay between MFM and low K

Overlay between low K and high K

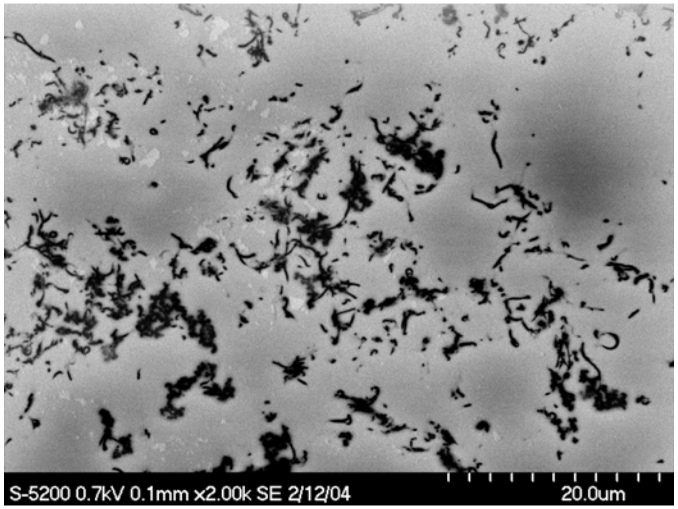


Final Summary

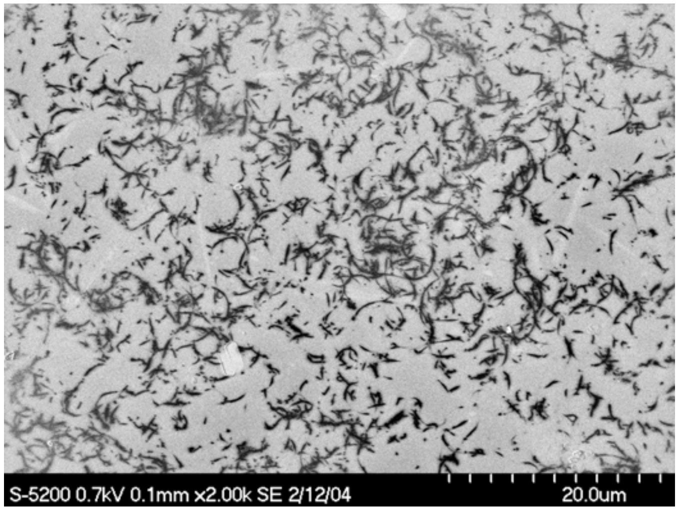
State of the work in 2006

- We had developed characterization protocols for **qualitatively** assessing the dispersion of carbon nanotubes in various resins.
- Developed a NIST practice guide to assess dispersion:
  http://www.msel.nist.gov/Nanotube2/Carbon_Nanotubes.htm

Bad dispersion



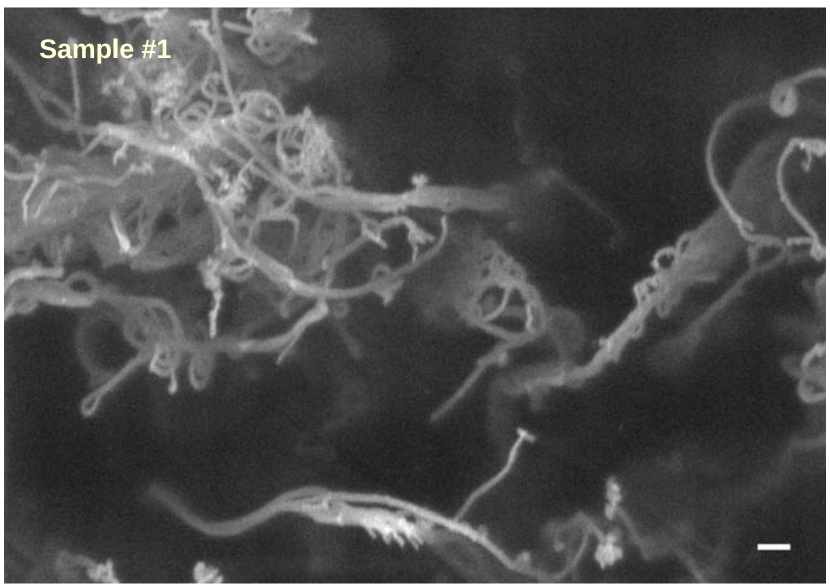
Good dispersion



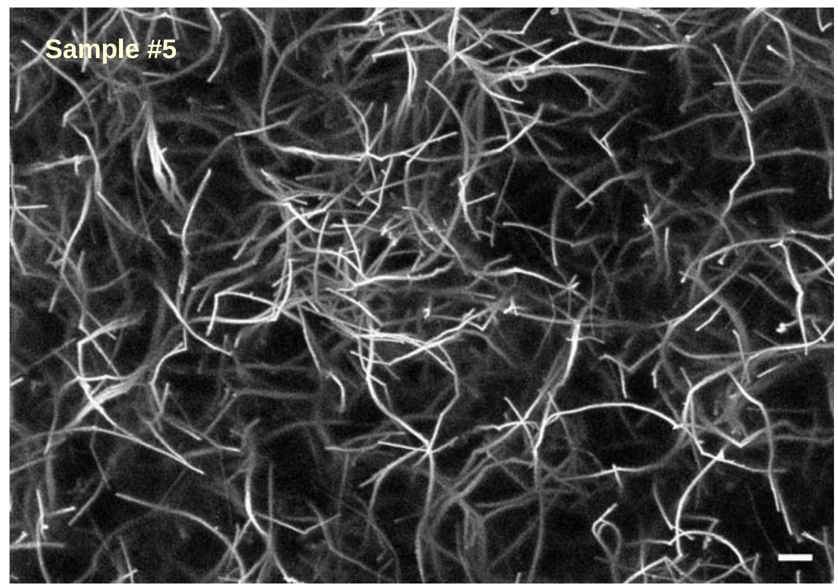
State of the work today

- It is now easy to see the difference between the well dispersed sample on the right and the poorly dispersed sample on the left
  - Now possible to **quantify** the dispersion
  - **Tertiary structure and orientation** can now be verified and quantified

Bad dispersion

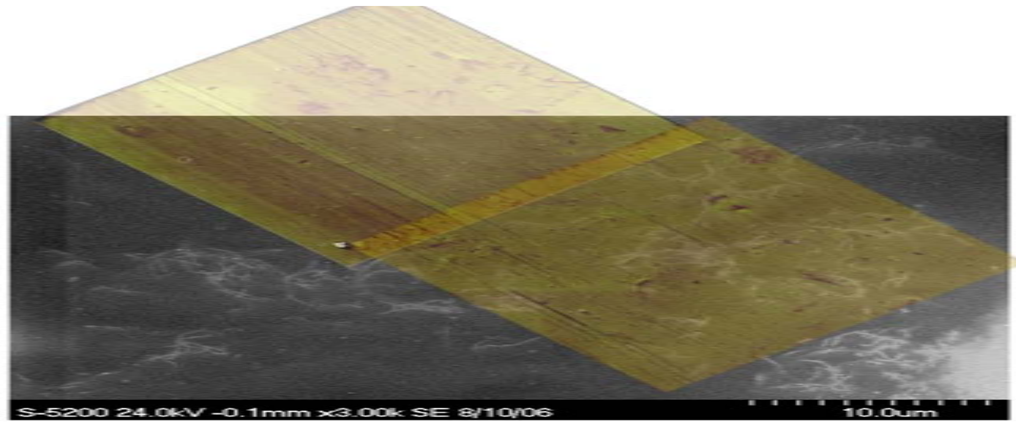


Good Dispersion

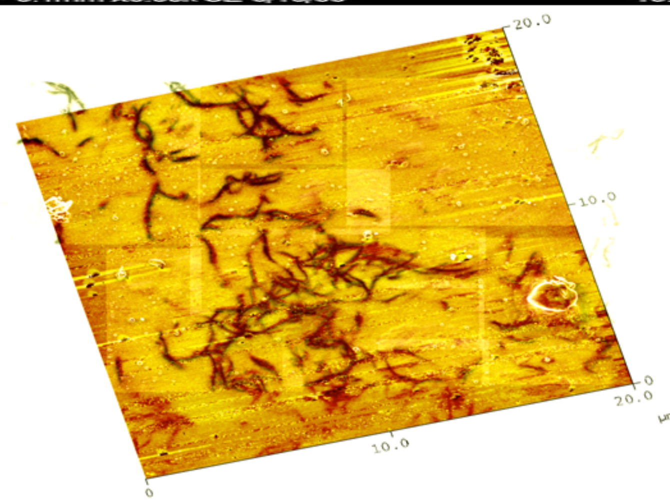


Moving forward

- Ultrasound Holography



- Magnetic Force Microscopy



Summary

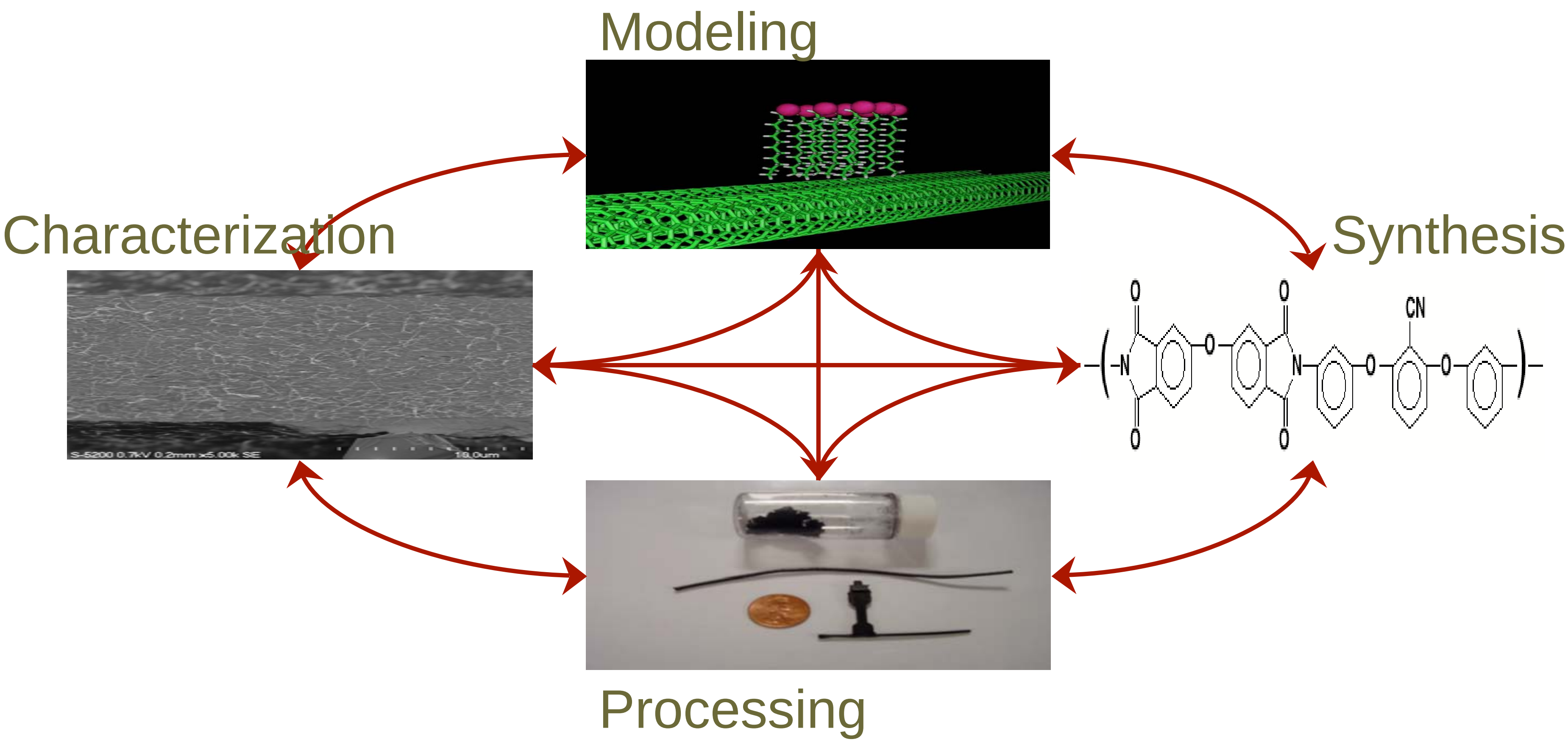
- NASA LaRC has established a new protocol for visualizing the nanomaterials in structural polymer matrix resins. Using this new technique and reconstructing the 3D distribution of the nanomaterials allows us to compare this distribution against a theoretically perfect distribution.

- Additional tertiary structural information can now be obtained and quantified with the electron tomography studies.

- These tools will be necessary to establish the structural-functional relationships between the nano and the bulk. This will also help define the critical length scales needed for functional properties.

- Field ready tool development and calibration can begin by using these same samples and comparing the response. i.e. gold standards of good and bad dispersion.

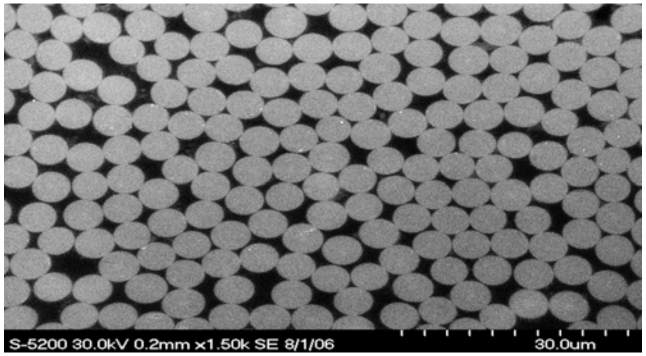
What's next? (Test, Predict, Validate)

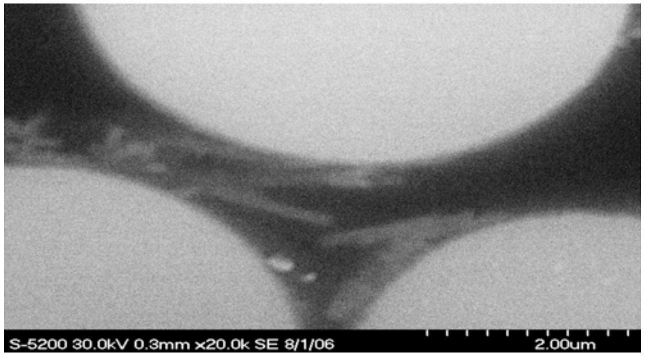


Thank you

NASA

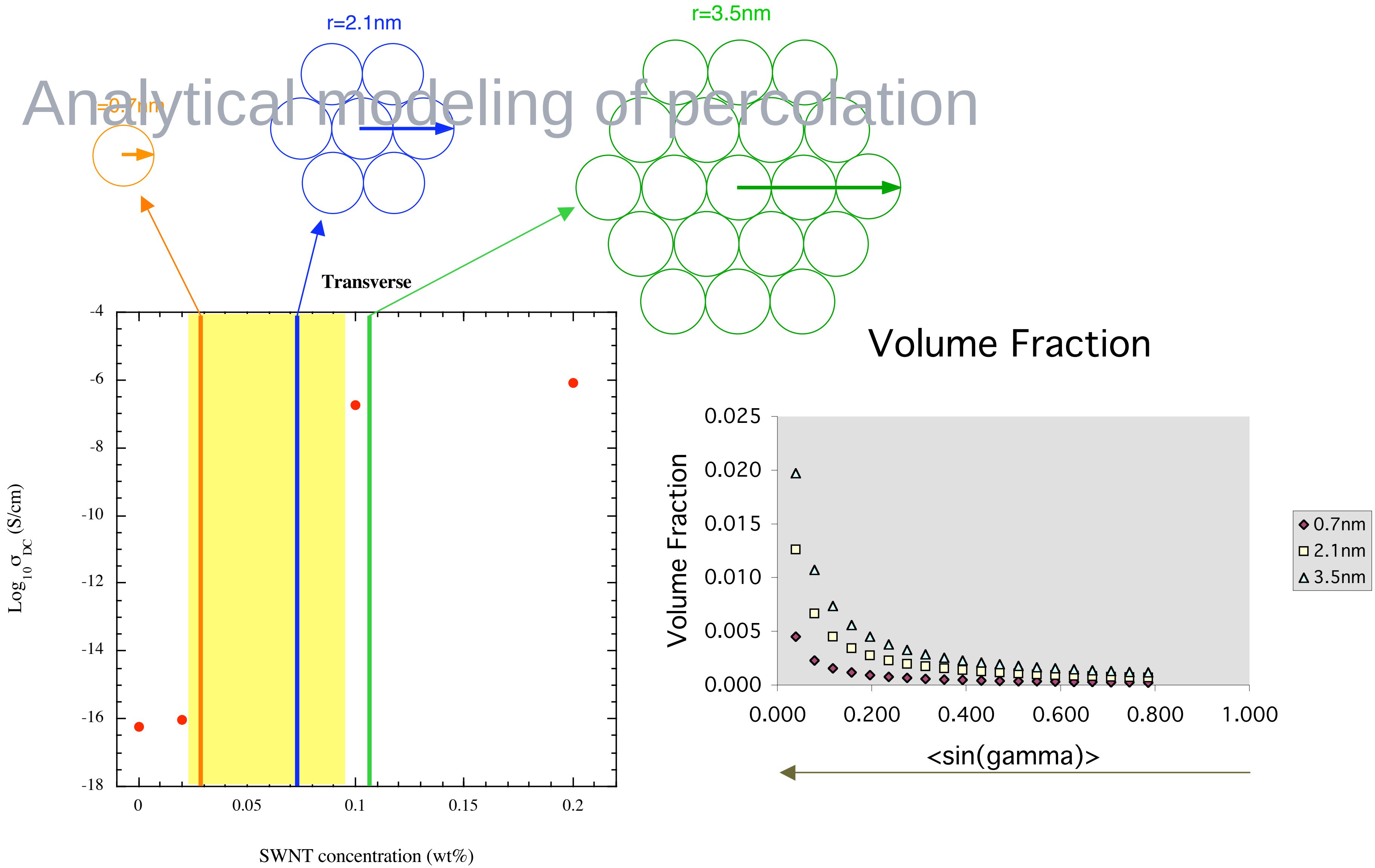
Lightning strike protection



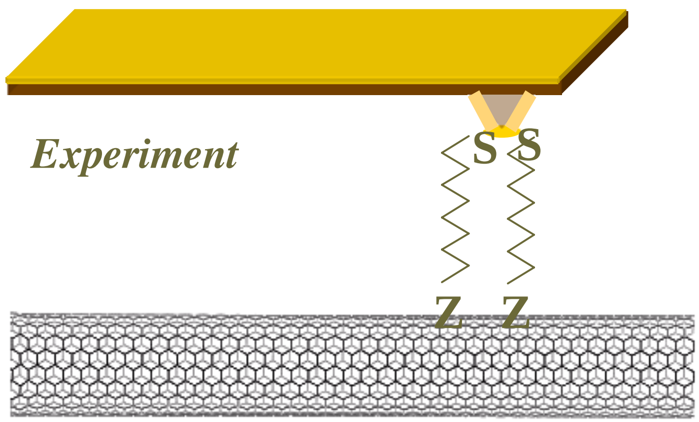


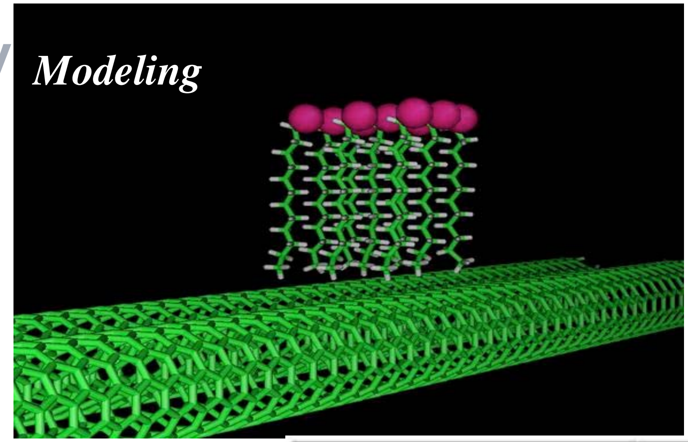
- Currently lightning strike protection in carbon fiber composites is provided by a copper wire (IWWF) that is used to create an electrical network between the conductive carbon fibers.
- Using nanomaterials to provide a percolation network would be ideal because it should be able to reduce weight, improve mechanical properties, and reduce lifecycle costs.

Analytical modeling of percolation



Probe microscopy





Thiol	Rupture Force per molecule (pN)	Standard Deviation
$-CH_3$	7.55	2.03
-S	8.24	2.55
$-CF_3$	8.74	2.64
-OH	9.62	2.49
-C=C	11.38	2.76
-COOH	12.2	2.65
$-NH_2$	23.42	4.11

Modeling
1.92 pN

2.98 pN

Thiol	Rupture Force per molecule (pN)	Standard Deviation
4-Methylbenzene	18.94	5.65
4-Nitrobenzene	21.79	5.29
4-Aminebenzene	22.64	4.66
4-Bromobenzene	26.92	3.55
4-Hydroxybenzene	32.00	8.39
4-Fluorobenzene	39.47	8.84
4-Methoxybenzene	41.51	10.9
H-Benzene	46.79	11.79
4-Nitrilebenzene	56.93	15.47

Probe microscopy

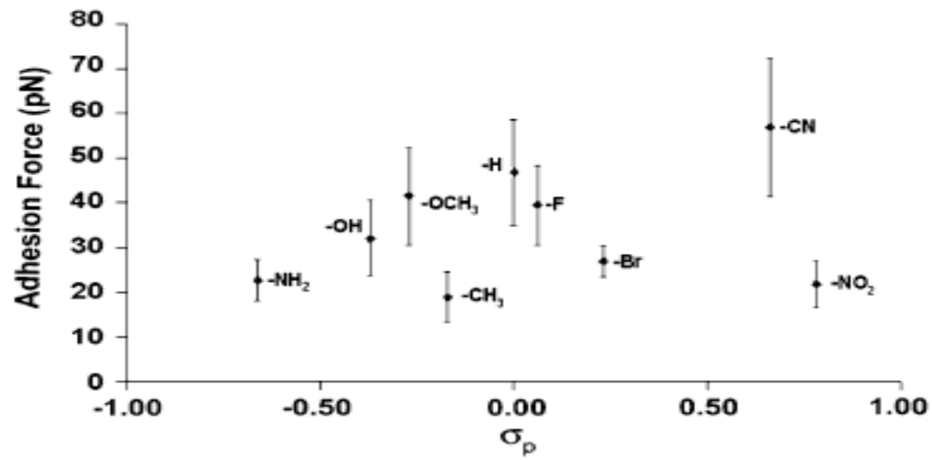
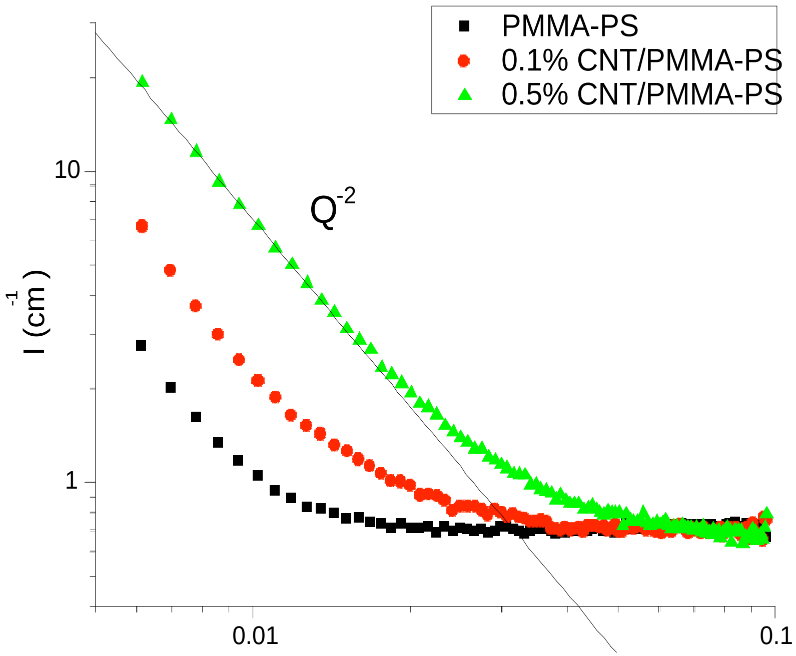
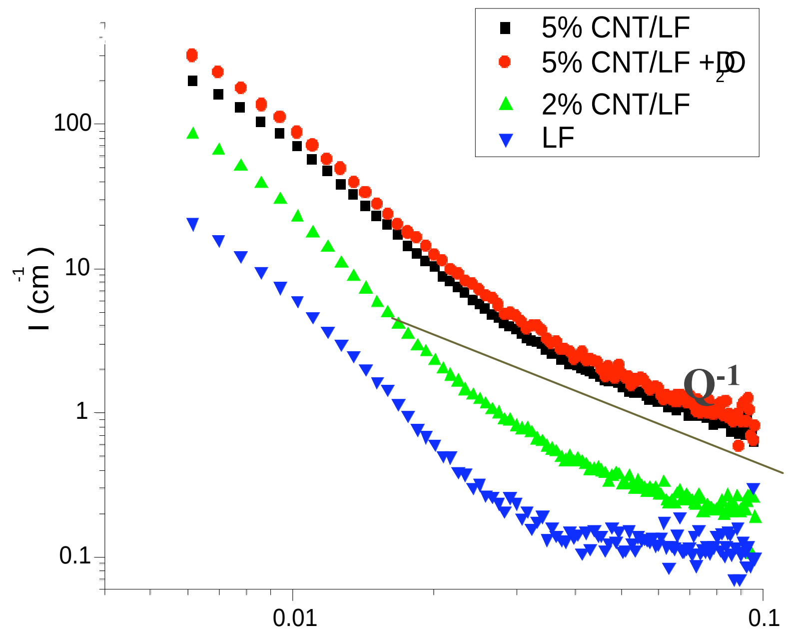


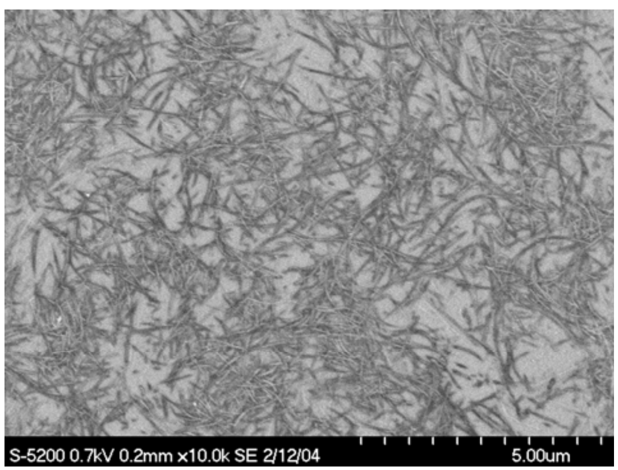
Figure 6. Plot of the adhesion force per molecule versus the corresponding Hammett parameter of a *para*-substituted benzenethiol molecule.

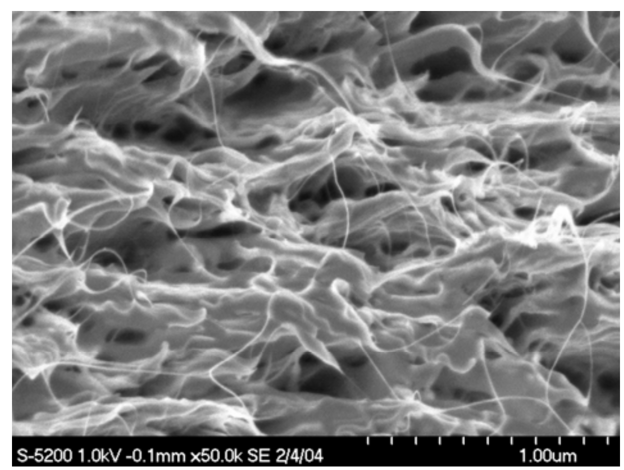
- http://dx.doi.org/10.1021/cm048346m

Small Angle Neutron Scattering: SWNT/Polymer

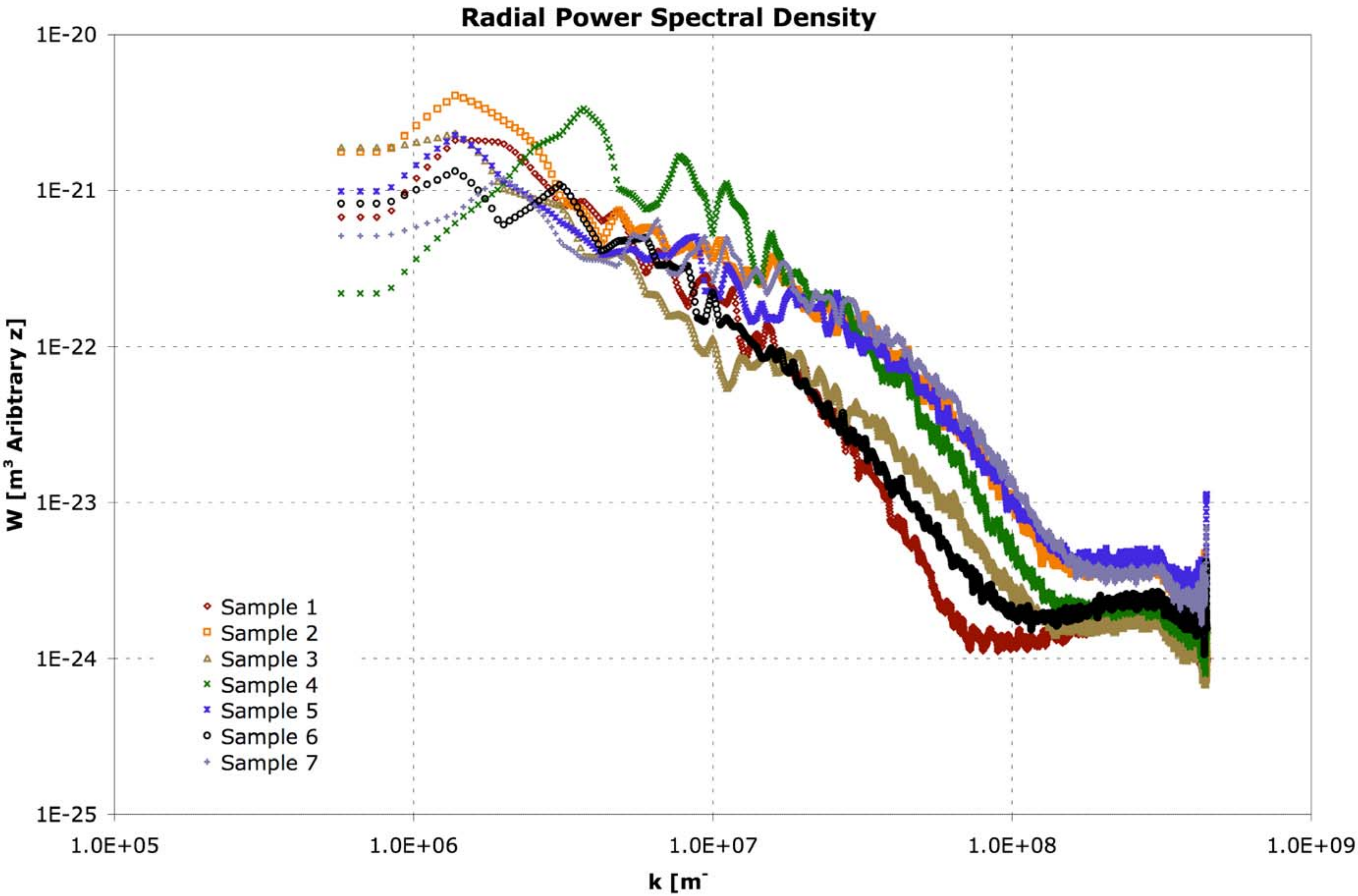








H. Wang (Michigan Tech, NIST)


Radial Power Spectral Density
1E-20
1E-21
1E-22
1E-23
1E-24
1E-25
W [m³ Aribtrary z]
1.0E+05
1.0E+06
1.0E+07
1.0E+08
1.0E+09
k [m⁻
Sample 1
Sample 2
Sample 3
Sample 4
Sample 5
Sample 6
Sample 7

Quality Assurance And Quality Control

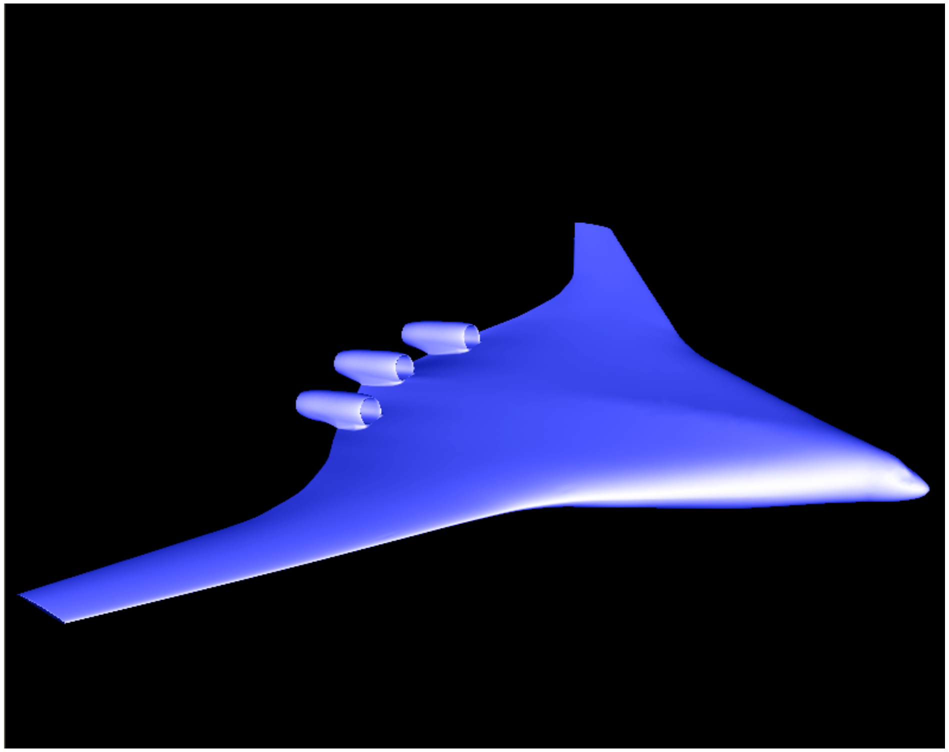
- For Quality Assurance and Quality Control (i.e. an electrical percolation network sufficient for lightning strike protection) the underlying property most responsible for the bulk scale function needs to be quantified.
- To quantify the property a means of measuring it must be available.
- To measure the property a means of “seeing” it must be available.

Moving Beyond Sporting Goods

- Requires us to understand:
  - What goes in (purity, defects, aspect ratio, …)
  - What it does
  - Where it is
  - How much is there
  - How it is dispersed
  - Degree of functionalization (if any) or modified surface chemistry
  - The sensitivity of all of the above on the physical properties of interest.

Requirements for nanomaterials

- Lightweight
- Radiation Protection
- Electrical Conductivity
- Actuation
- Thermal Conductivity
- Sensing, health monitoring
- Self healing
- Energy generation
- Energy storage



What materials will get us there?

- Carbon nanotubes towards multifunctional structures
- Boron nitride nanotubes for high temperature multifunctional structures
- Nanoporous materials for thermoelectric devices
- Solid electrolytes to enable self-repair, energy generation and storage