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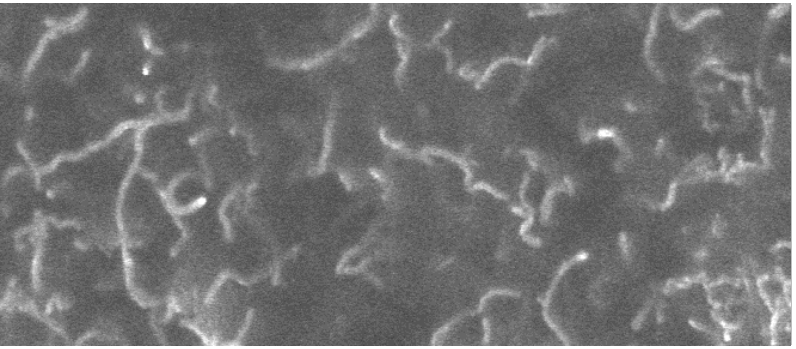

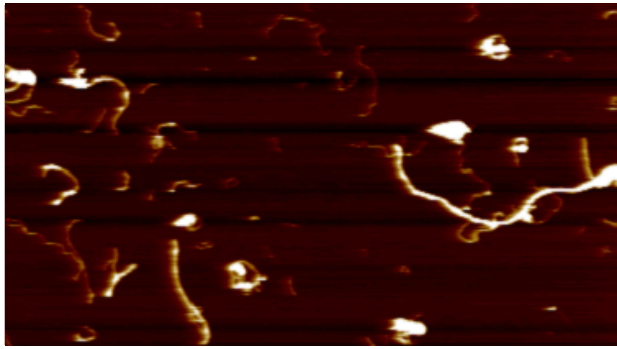

Nanoscale Optimization of Ultrasonic Dispersion of Multi-Walled Carbon Nanotubes in Polyelectrolyte Aqueous Solution

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U.S. DEPARTMENT OF ENERGY

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NNSA National Nuclear Security Administration

Usage of Fiber-Reinforced Composites

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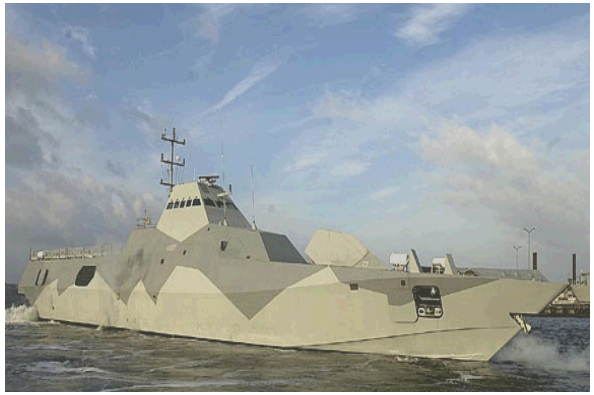
- Over the past 50 years, increased usage of composite materials

Commercial aircraft systems

Future and legacy spacecraft

Military aircraft



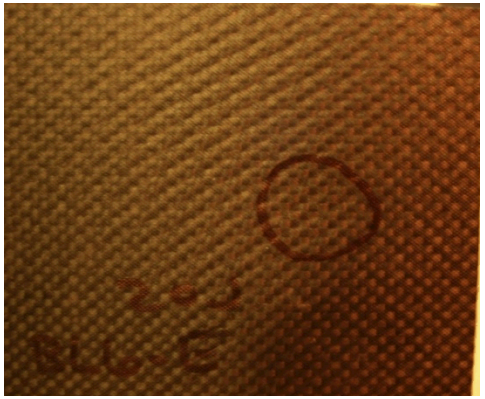
Naval structures

Wind turbine blades

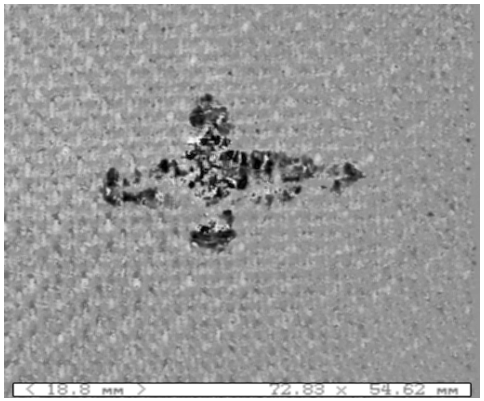
CFRP cable stay bridge

Composite Damage Modes

- Susceptible to damage due to:
  - Strain, impact, chemical penetrants, multi-axial fatigue
- Damage modes:
  - Matrix cracking
  - Fiber-breakage
  - Delamination
  - Transverse cracking
  - Fiber-matrix debonding
  - Matrix degradation
  - Blistering
- Difficult to detect
  - Internal to laminate structure
  - Nearly invisible to naked eye
  - Current methods are laborious



Visual inspection



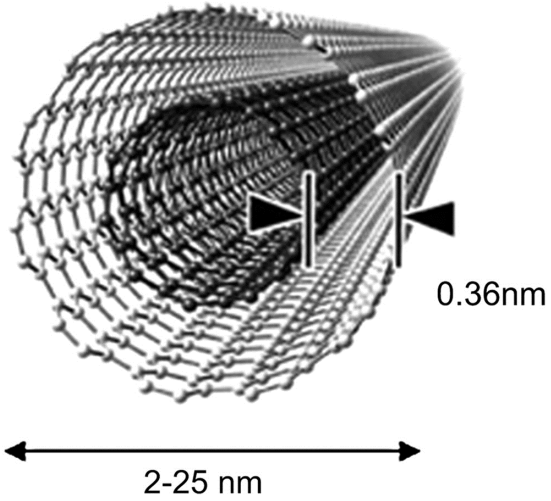
C-SCAN ultrasound image

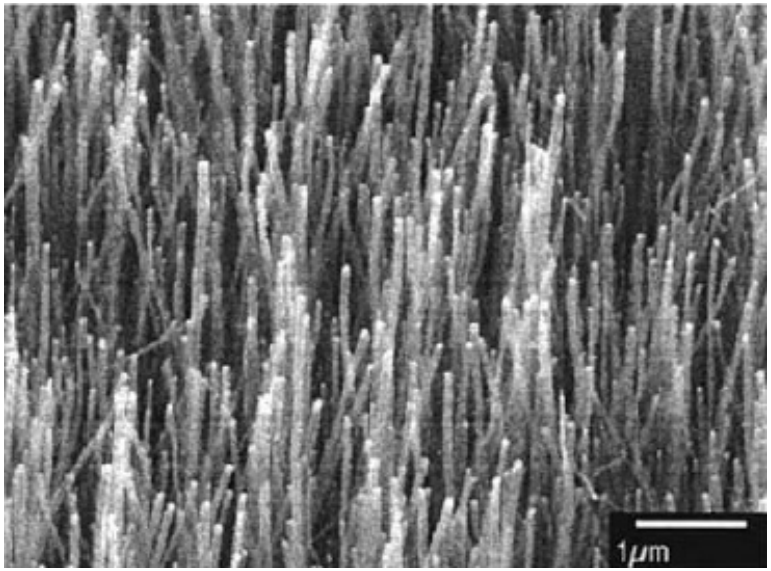
CFRP panel after 20 Joule impact

Aircraft ultrasonic inspection (Composites World)

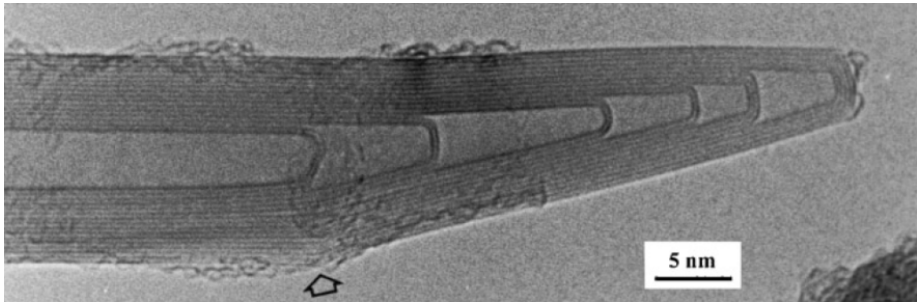
Carbon Nanotubes

- Multi-walled carbon nanotubes (MWNT):
  - Rolled concentric cylindrical structures constructed of graphene sheets
  - Diameter: 6 ~ 100 nm
  - High-aspect ratios: ~10^3 to 10^7
  - Metallic conductivity
  - Five times stiffer and ten times stronger than steel





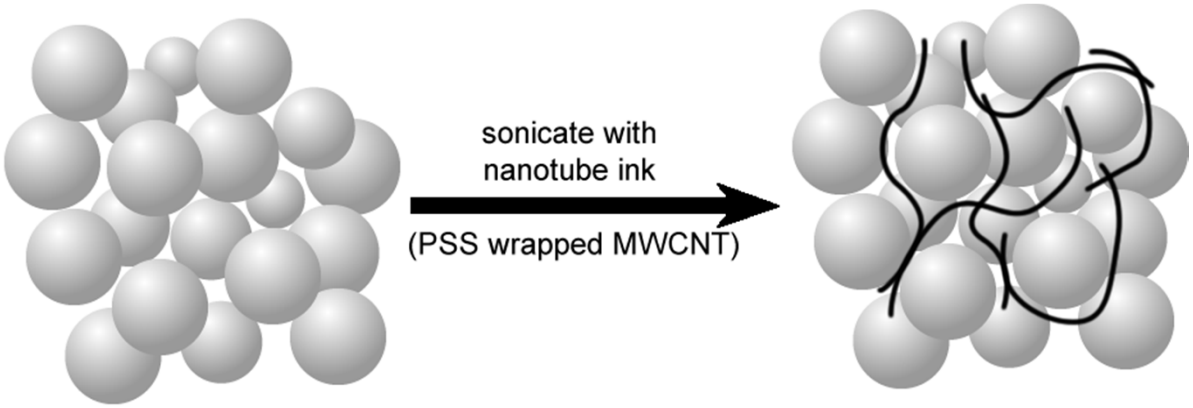
Aligned carbon nanotube forest
Thostenson, et al. (2001)



TEM imagery of an end cap of a MWNT
Harris (2004)

Sprayable MWNT-Latex Thin Film

- Rapid large-scale deposition
  - Required for mass deployment of methodology
- MWNT-PSS/Latex paint formulation
  - Collaborated to improve initial Sandia formulation
  - Sub-micron PVDF creates mold for MWNT organization
  - Off-the-shelf deposition method

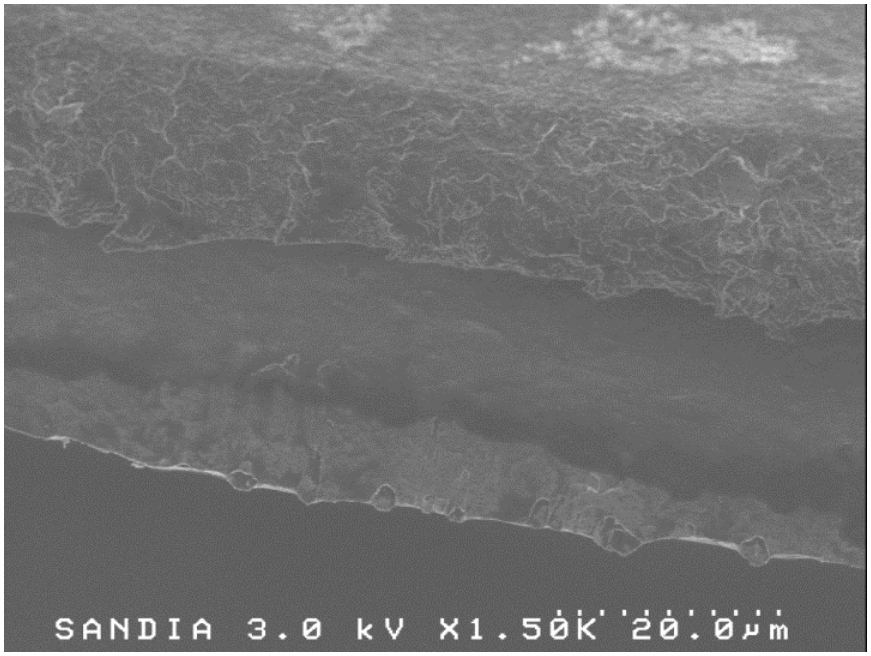


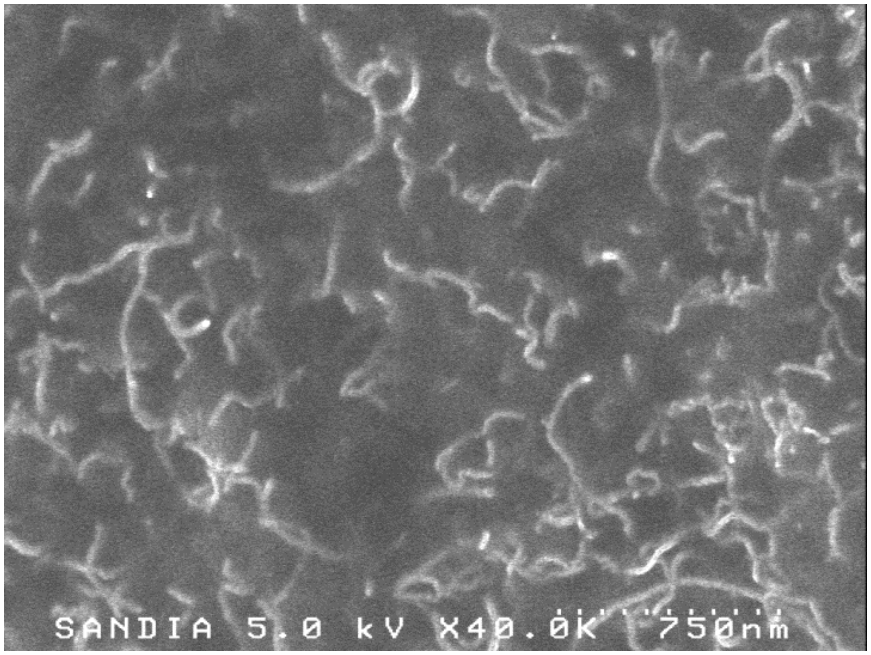
Kynar Aquatec™ latex solution
(avg. particle size 150nm)

Forms segregated
MWCNT network

MWNT-Latex Morphology

- Creation of MWNT networks:
  - Electrical percolation above 1 wt% MWNTs
- Fiber-reinforced polymer deployment:
  - Surface applied to post-cured composites
  - Applied to fiber weaves for embedded sensing

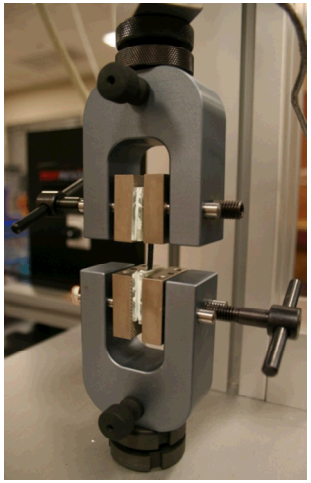


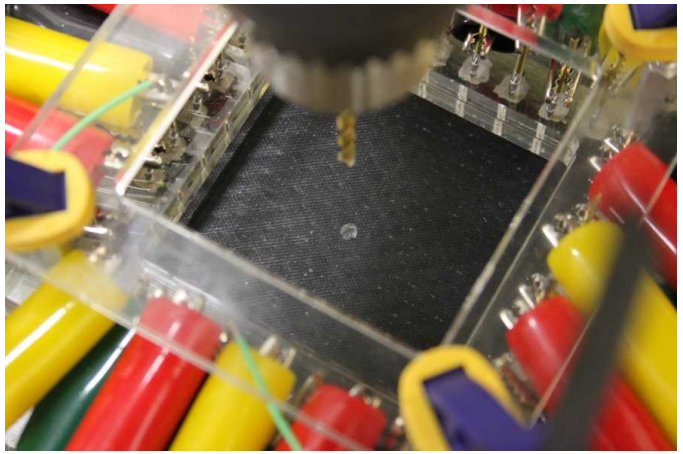


Cross-section and MWNT network SEM images of 3wt% MWNT-Latex film

Optomizing Electronic Properties

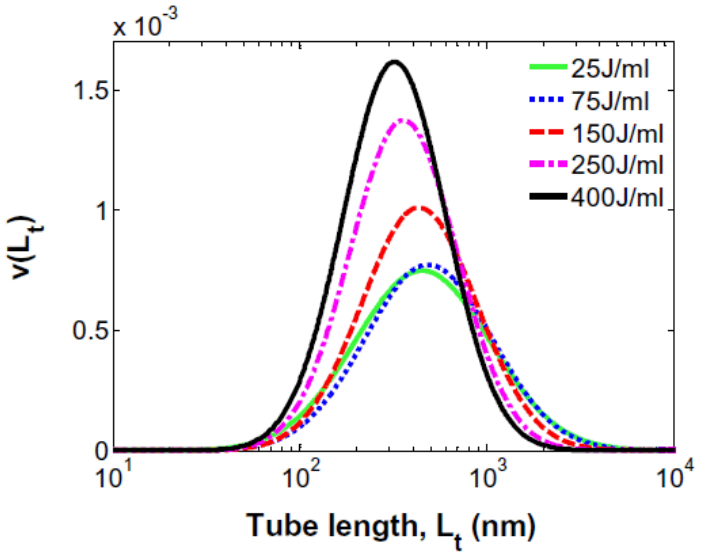
- Tailored Sensitivities
  - Strain sensitivity
    - Near percolation threshold
  - Damage detection
    - Mid-range conductivity
    - ~ 1,000 Ω / □
  - Fatigue
    - ???
- CNT nanocomposite parameters
  - Weight percentage
  - SWCNT vs. MWCNT
  - Length
  - Doping (iodine, etc.)
  - Agglomerates



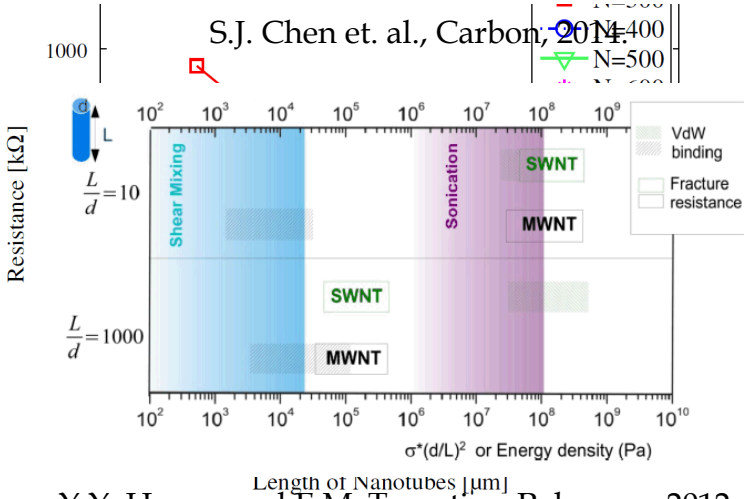


Ultrasonication Effects

- Nanocomposite conductivity
  - Percolation threshold
    - Length and geometry dominated
  - Conductivity
    - Junction dominated
    - Length/wt.% limit junctions
- Ultrasonication
  - Method for deagglomeration
  - Energy can cleave CNTs
  - Optimization is necessary



S.J. Chen et. al., Carbon, 2014.



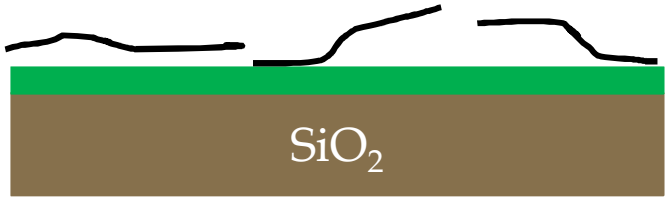
Y.Y. Huang and E.M. Terentjev, Polymers, 2012.
B.M. Lee and K.J. Loh, Journal of Mat. Sci., 2015

Experimental Approach

- We want to quantitatively understand the dependence of CNT length to ultrasonication parameters
- Ultrasonication parameters
  - Sonics Vibra-Cell VCX 750
    - 750 W
    - ¼" tip
    - 159.5 mm^2
  - Power: 0 – 100% (750 W)
  - Ultrasonication time
    - Total time sonic power on
  - Pulse
    - Time on, time off
- CNT "ink"solution
  - SWeNT 100 MWCNTs
    - ~ 8nm diameter
    - 10-30 µm length
  - 2 wt.% solution PSS
  - NMP
- CNT Processing
  - 1:20 dilution of CNT ink
  - Spin coated onto ¼ wafer at 2,000 RPMs
- Parameters tested
  - Power/ultrasonication time:
    - 150 W / 10 min
    - 188 W / 10 min
    - 225 W / 7, 10, 15, 20 min
      - 225 W / 10 min (original)
    - 263 W / 10, 12.5, 15 min
    - 300 W / 10 min
  - Pulse: 10 sec on, 5 sec off

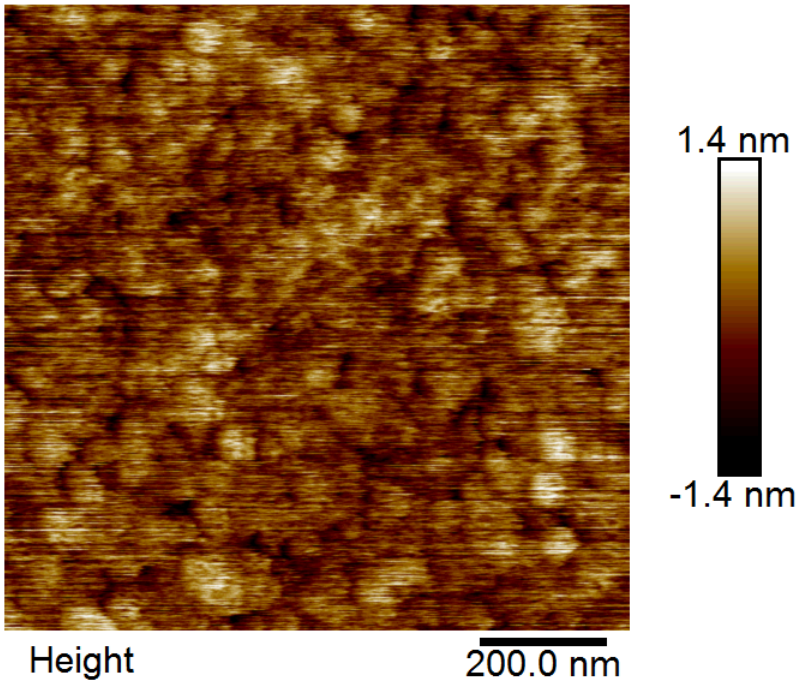
Wafer Preparation

- SiO_2 wafer cleaned
  - O_2 plasma clean
- Adhesion promoter
  - APTES
    - 1:10 ratio APTES: Ethanol
    - Vapor deposition
    - Rinse with ethanol
  - PEI
    - 1:50 ratio PEI/DI water
    - Adjust ph to 9 with 1M HCl
    - Submerge wafer in PEI solution
    - Submerge in 0.1M HCl for 1 min
    - Dry with N_2



MWCNTs
APTES/PEI

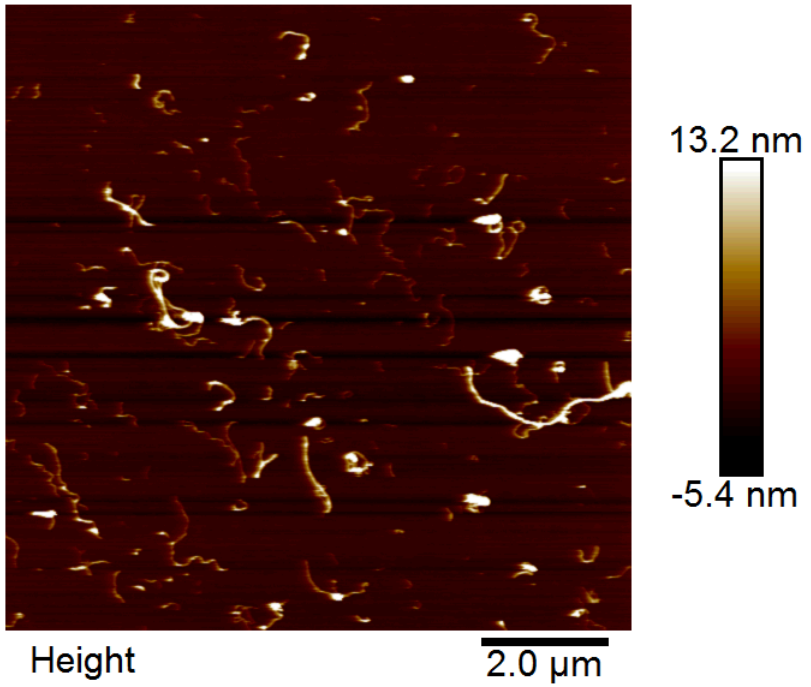
Deposition cross-section



PEI on SiO_2

CNT Length Characterization

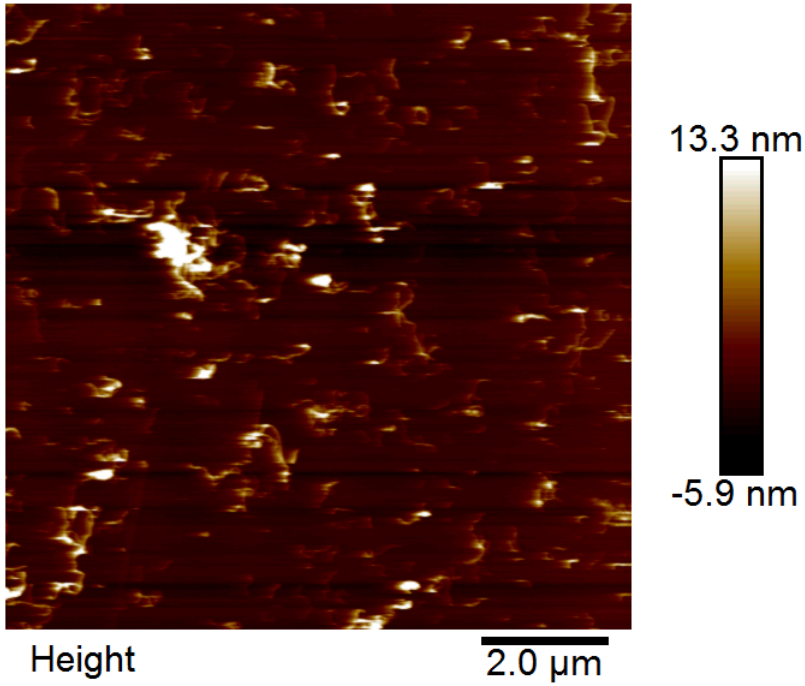
- Bruker AFM
  - 10 x 10 µm scan size
  - Tip:___
- Length measurements
  - Segmented line tool in ImageJ
  - Measured in quadrants of the APF image
  - Included CNTs fully in image
  - At least 30 CNT lengths measured per image



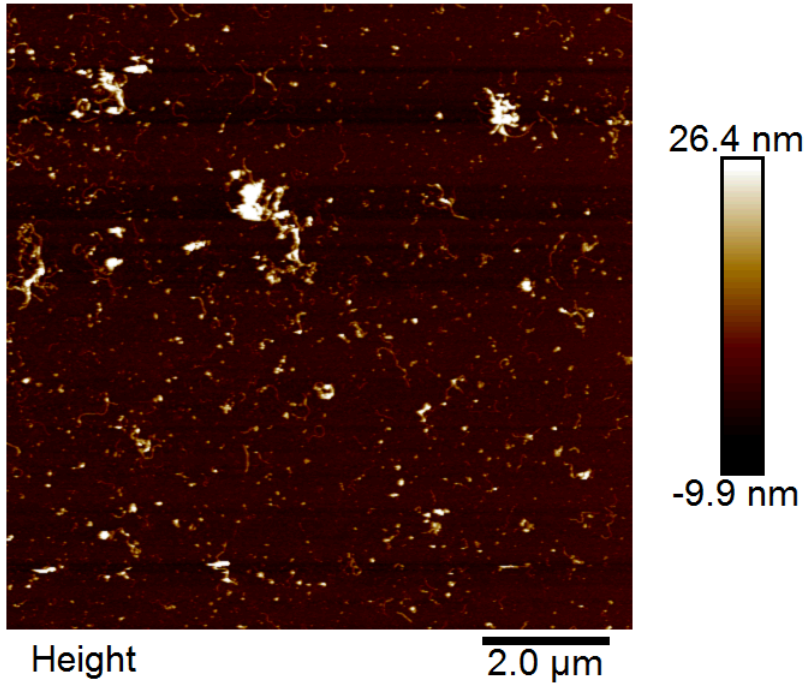
120W / 7 min on APTES

APTES /PEI Comparison

- APTES
  - Due to hydrophobicity, localized areas of CNTs
- PEI
  - Better CNT coverage on wafer
  - Found more agglomerates captured on PEI



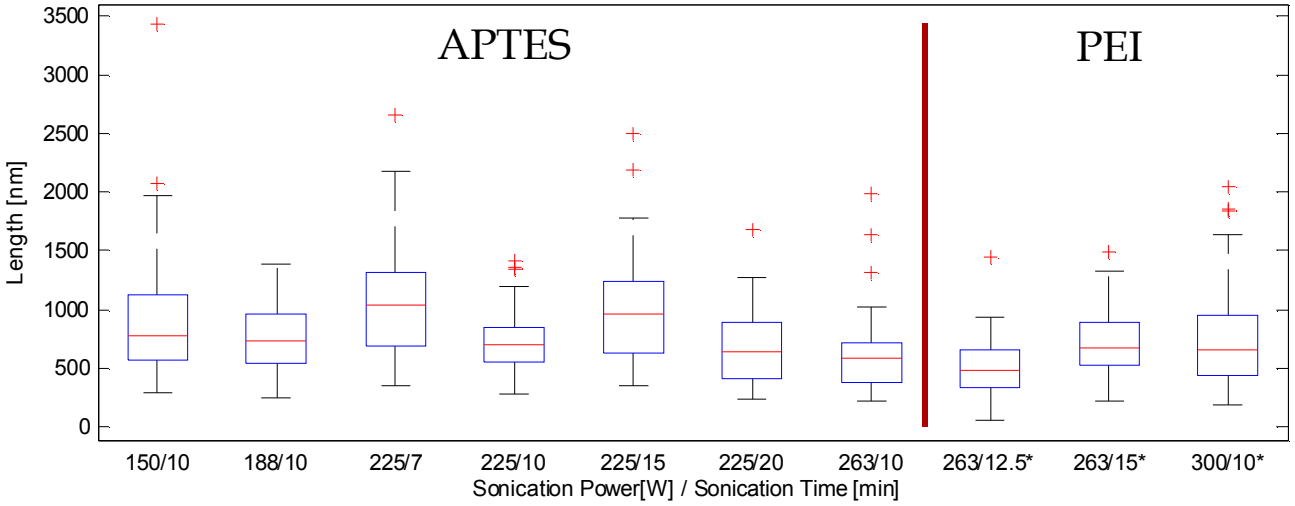
160W/10 min on APTES



160W/10 min on PEI

Characterization Results

- Adhesion promoter effects
  - APTES coated specimens captured agglomerates ≤ [1 µm]^2
  - PEI coated wafers captured agglomerates up to ~[3 µm]^2
- Highest length distributions
  - 225 W / 7 and 15 min
    - Median: ~ 1 µm
    - 75 Percentile: ~1.2 µm
- Agglomerates
  - Lowest: 225 W / 20 min
    - Several at ~ [50 nm]^2
  - Second lowest: 225 W / 7 min
    - A few at ~ [200 nm]^2
  - Largest: 263 W / 12.5 min
    - Several at ~[3 µm]^2



Conclusions

- PEI is an superior adhesion agent for CNT-containing aqueous solutions
  - Hydrophbicity
  - Agglomerate capture
- Ultrasonication radically cleaves the length of MWCNTs
- 225 W / 7 and 15 min sonication parameters offer the longest MWCNT lengths
- Next Steps
  - Will be investigating deagglomeration using high shear mixing

Thank You!

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Questions?

Acknowledgements:

Center for Critical Application Sensing

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