CNTs as components in bulk materials: synthesis and properties

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Oct. 25, 2011

Overall outline

<u>**Martedi 25 Ottobre**</u>
Lecture 1) Synthesis and properties of CNTs
Lecture 2) Applications

<u>**Mercoledi 26 Ottobre 2011**</u>
Lecture 3) CNT arrays
Lecture 4) Modifying CNT arrays and creation of multilayer materials

<u>**Venerdi 4 Novembre 2011**</u>
Lecture 5) Multiscale modeling I
Lecture 6) Multiscale modeling II

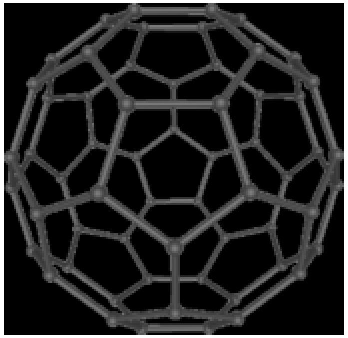
Outline for part 1: synthesis and properties of CNTs

CNT properties and their physical basis

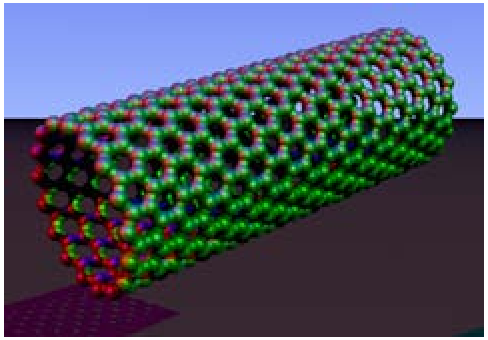
Synthesis methods

Measurement of CNT mechanical properties

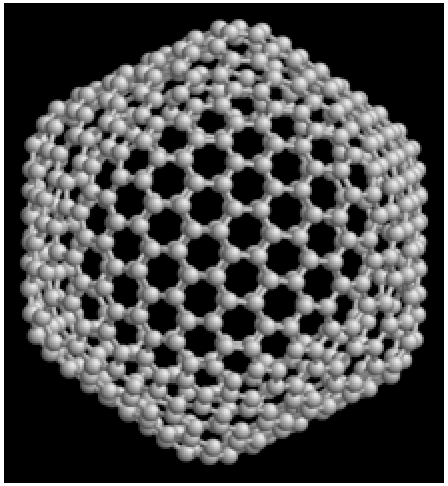
Fullerenes



“Buckyball” – C_{60}
Discovered 1985



Carbon nanotube
“re”discovered 1991



Other structures possible
C_{540}

-Structure is entirely made out of carbon
-Mostly graphitic structure
-Hollow

Images from Wikipedia

Why CNTs? Phenomenological motivation

- Highest strength-to-weight ratio of any known material
- 1 TPa Young's modulus
- 60 GPa tensile strength
- Stable in temperatures up to more than 3000 K in vacuum
- 1000 times greater electrical conductivity than Cu
- Can be either conducting or semiconducting depending on chirality

5x stiffer and > 100x stronger than steel, but 6x lighter

If you could obtain properties like these at the macroscopic scale you would fundamentally alter the way in which buildings, automobiles, aircraft, etc. are built.

Problem: CNTs are very, very small (1-100 nm diameter).

How do you get benefits in macroscopic materials from the extraordinary properties of individual CNTs?

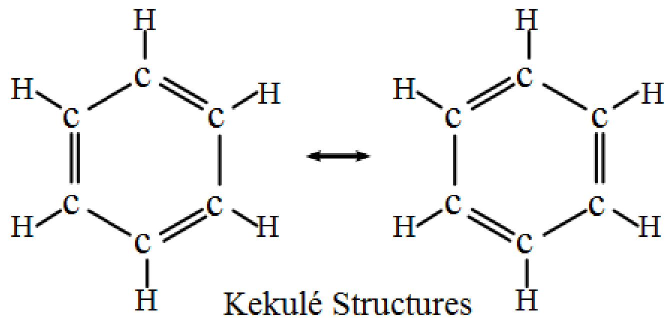
Y. Sáez de Ibarra, Phys. Stat. Sol. a 2006;203:1076. C.M. Wang et al., Appl. Mech. Rev. 2010;63:030804.

The physical/chemical basis for CNT properties I: sp^2 bonds

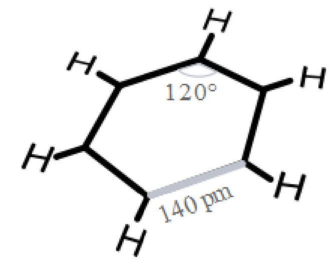
The stable, strong structure of aromatic (conjugated) hydrocarbons

C_6H_6

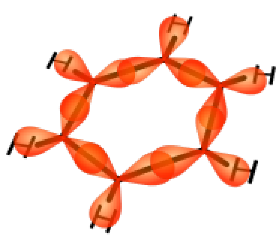
Benzene
Molecular formula



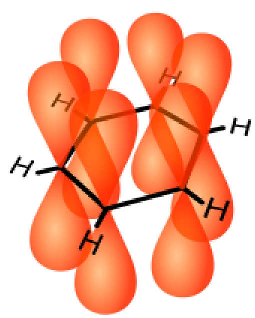
Kekulé Structures
(Isomers)



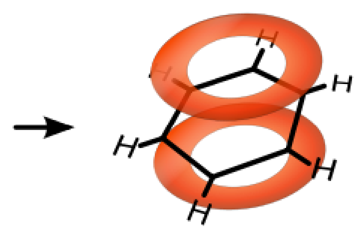
Planar Hexagon
Bond Length 140 pm



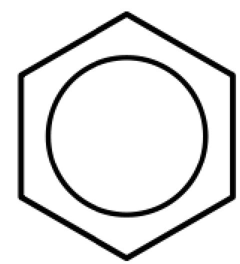
Sigma Bonds
sp^2 Hybridized orbitals



6 p_z orbitals



delocalized pi system

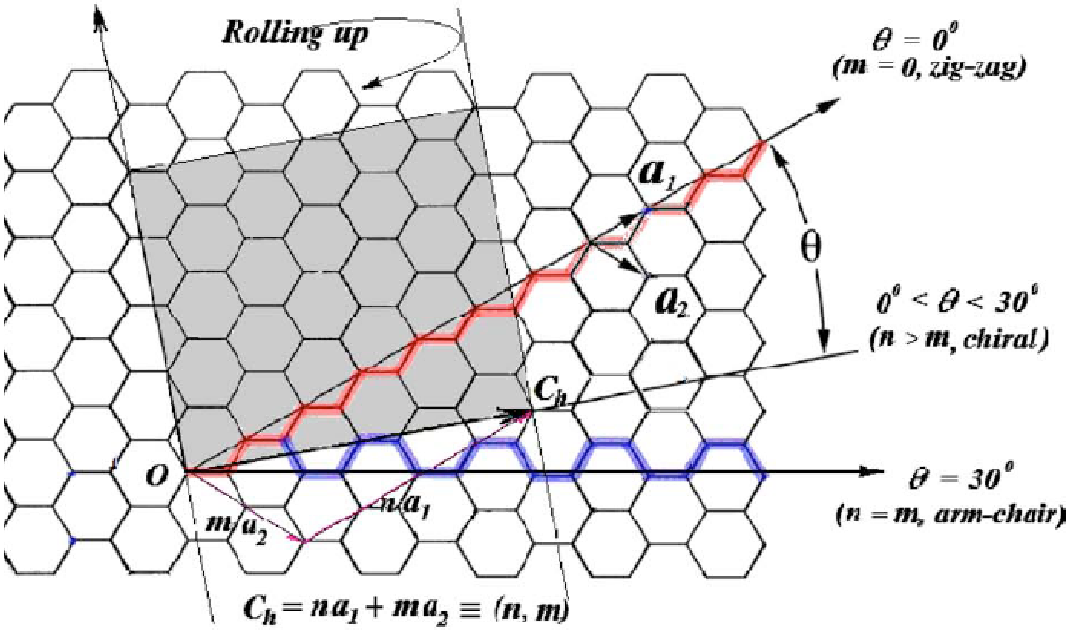


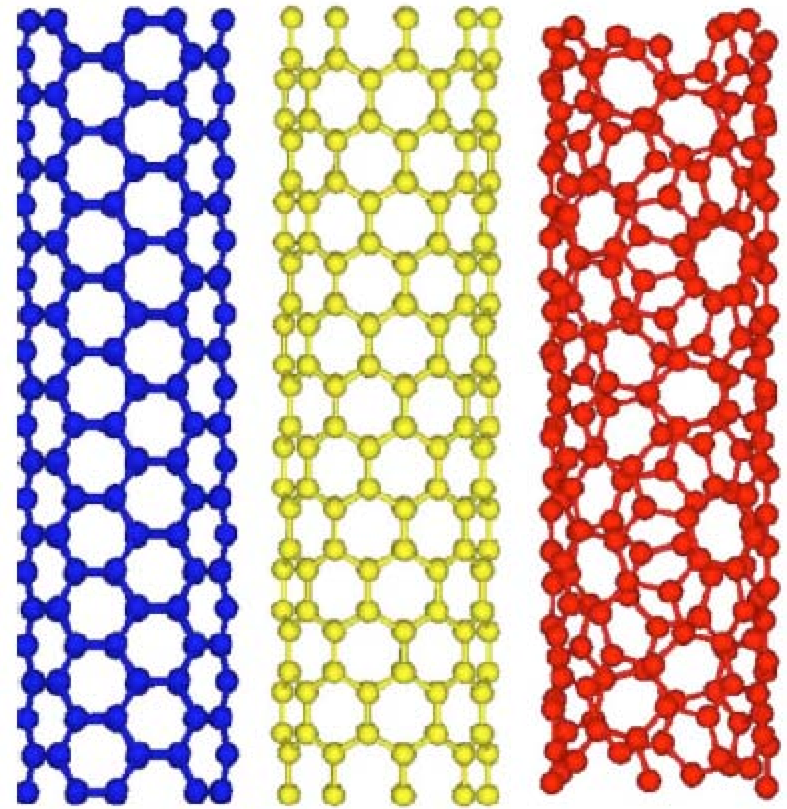
Benzene ring
Simplified depiction

The delocalized pi system plays an important role in van der Waals interactions and non-covalent functionalization

Images from Wikipedia

The physical/chemical basis for CNT properties II: chirality





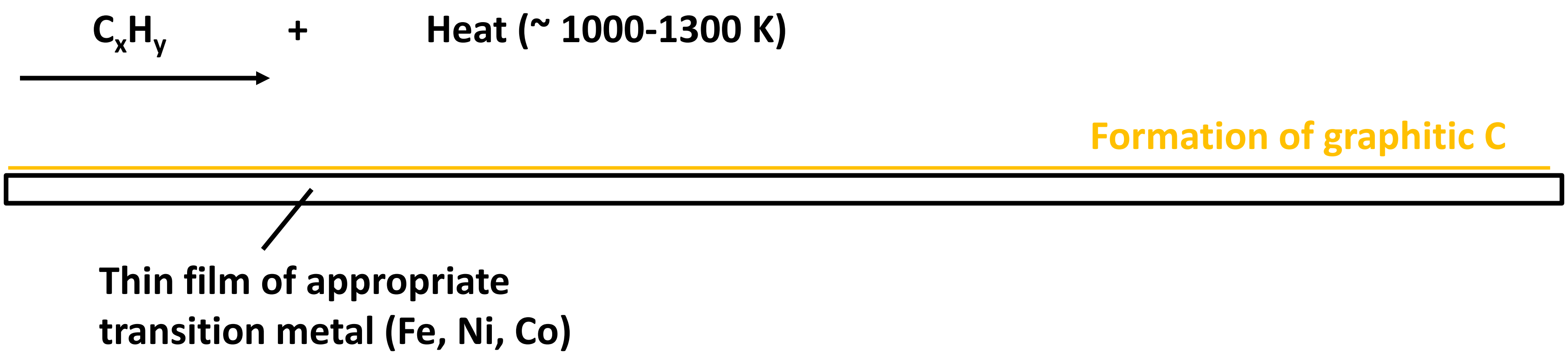
If (m-n) = multiple of 3 then the CNT is metallic, otherwise semiconducting

C.M. Wang et al., Appl. Mech. Rev. 2010;63:030804.

Synthesis of graphitic carbon

Steps for formation of graphitic carbon

1. Catalytic decomposition of hydrocarbon precursor
2. Diffusion of carbon into the metal catalyst
3. Excretion of graphitic carbon



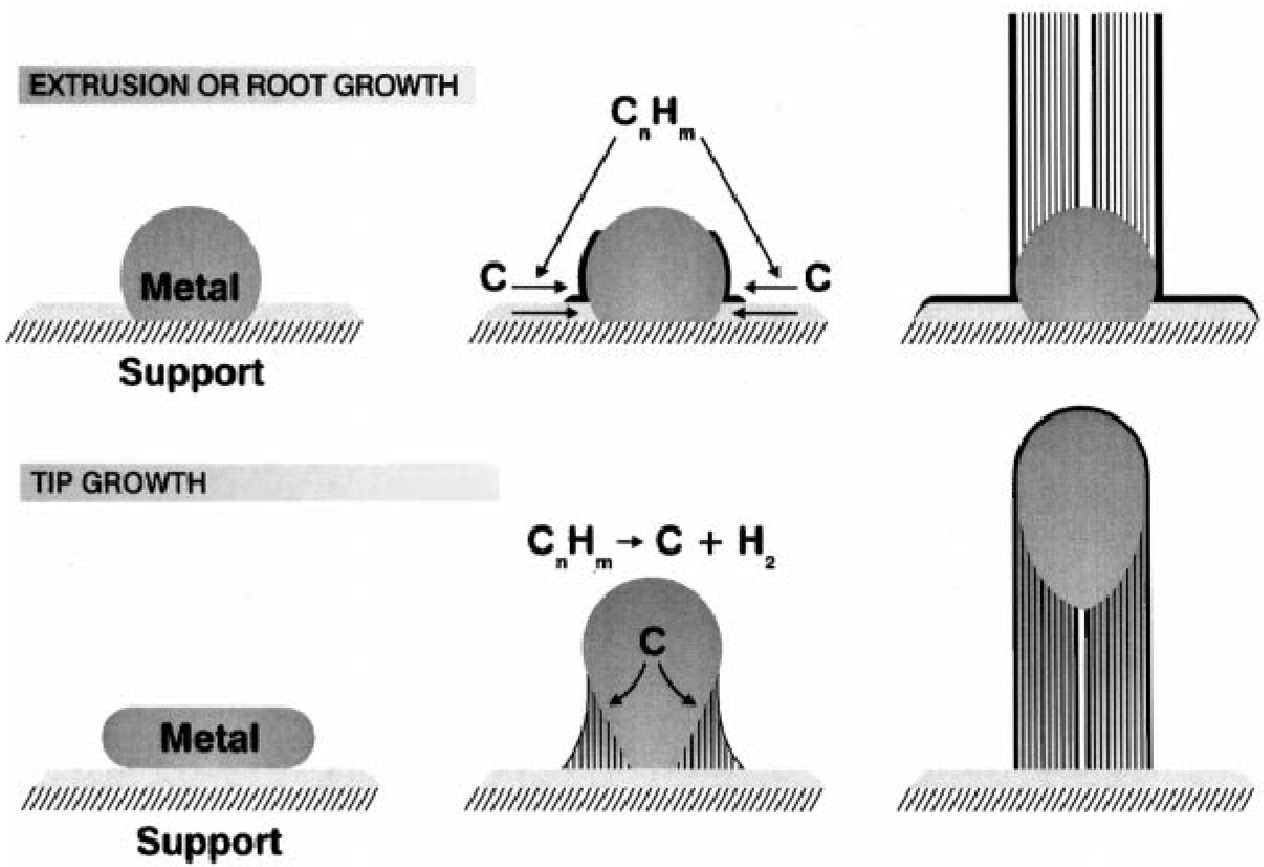
Criteria for selecting an appropriate metal:

1. Catalytic activity for decomposition of the carbon source
2. Ability to form metastable carbides
3. Structure that allows rapid diffusion of C

S.B. Sinnott et al., Chem. Phys. Lett. 1999;315:25.

Importance of particle shape/size

Particle shape determines the form of excreted graphitic carbon

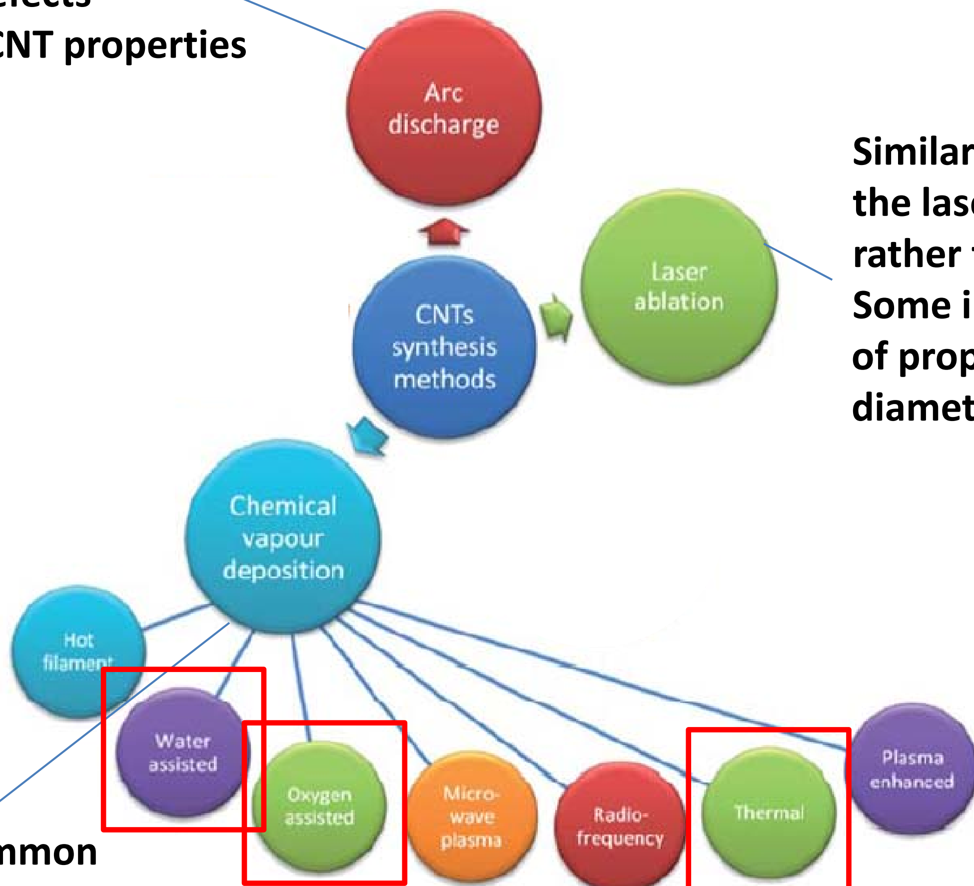


CNT diameter correlates with catalyst particle size

S.B. Sinnott et al., Chem. Phys. Lett. 1999;315:25.

Common methods of synthesis

-Used by Iijima in 1991
-High T (~2000 K)
-CNTs with few defects
-Hard to control CNT properties

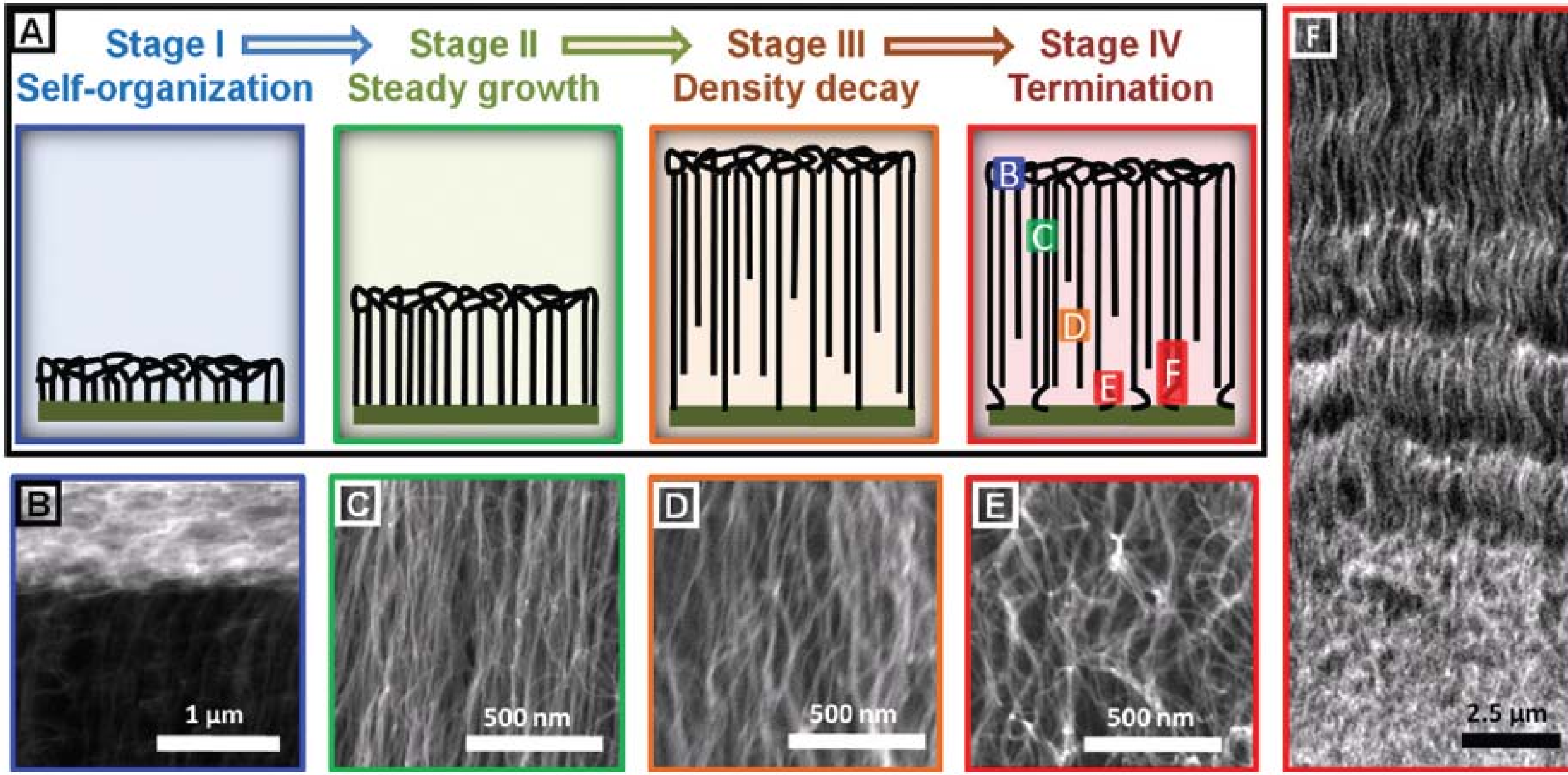


Similar to arc discharge but with the laser as the source of energy rather than DC
Some improvements for control of properties (laser power ~ CNT diameter)

-By far the most common
-Excellent control of CNT properties
-Good candidate for mass production

J. Prasek et al., J. Mater. Chem. 2011;21:15872.

Synthesis of CNTs via thermal chemical vapor deposition



Pre-deposited or "fixed" catalyst

-First deposit thin film of catalyst (often ~2 nm Fe with ~10 nm Al_2O_3)

-Requires careful tuning of flow gas to keep growth going

Vapor phase or "floating" catalyst

-Inject catalyst during synthesis, along with the carbon source

-Easier to get long CNT growth, but gives more catalyst contaminant

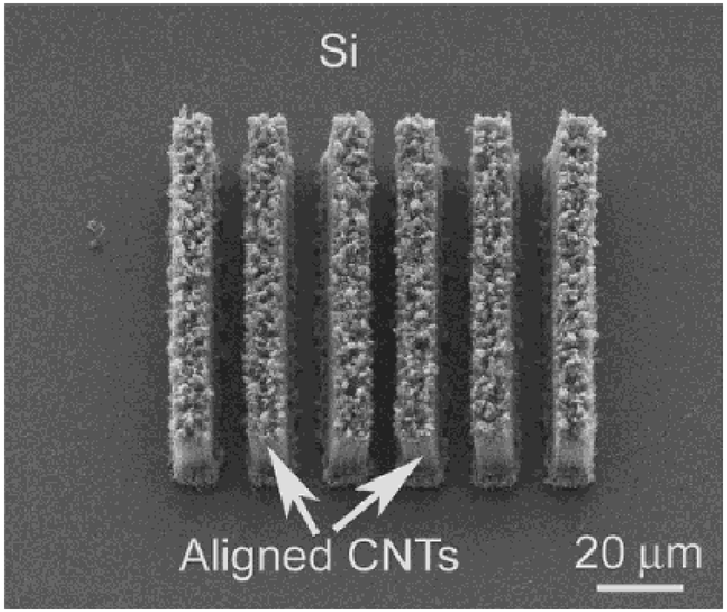
M. Bedewy et al., J. Phys. Chem. C 2009;113:20576.

Challenges during the synthesis of CNTs: formation of silicides

Silicon wafers are inexpensive and can utilize the same processing infrastructure as the electronics industry

Problem: Si reacts with catalyst particles to form silicides, halting CNT growth

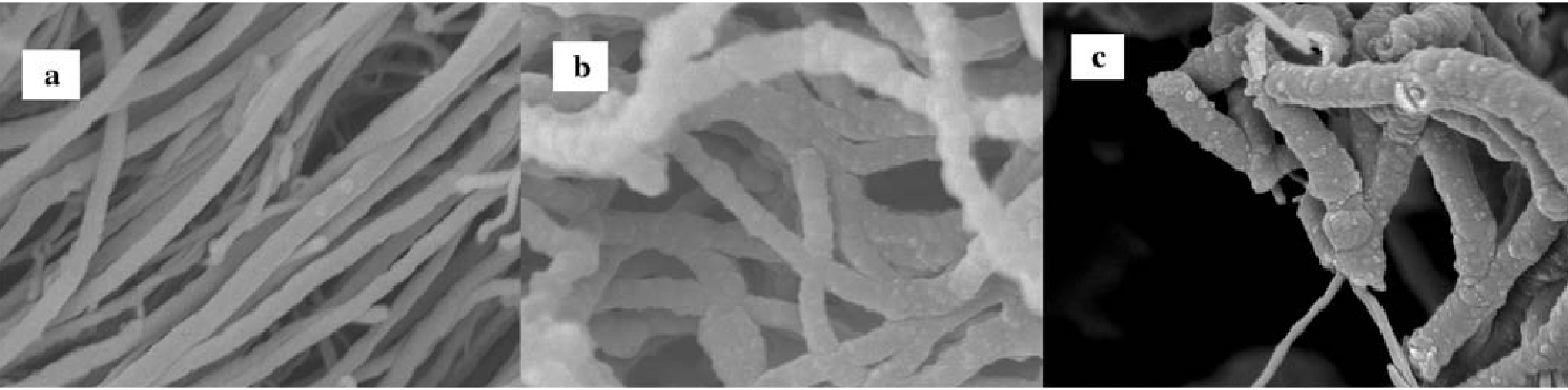
Solution: First oxidize the surface of the wafer to form SiO_2, which prevents this. This allows silicide formation to be controlled in designated regions for desirable patterns:



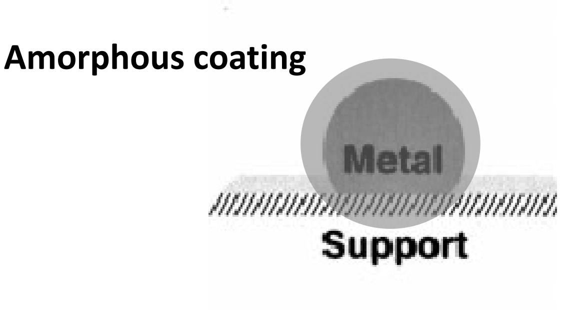
Y.J. Jung et al., Nano Lett. 2003;3:561.

Challenges during the synthesis of CNTs: formation of amorphous carbon on catalyst particles

Increasing distance from the furnace entrance (increasing T)



Pyrolytic and catalytic processes exist in competition with one another
High T can favor pyrolytic processes, which can block the catalyst from C absorption

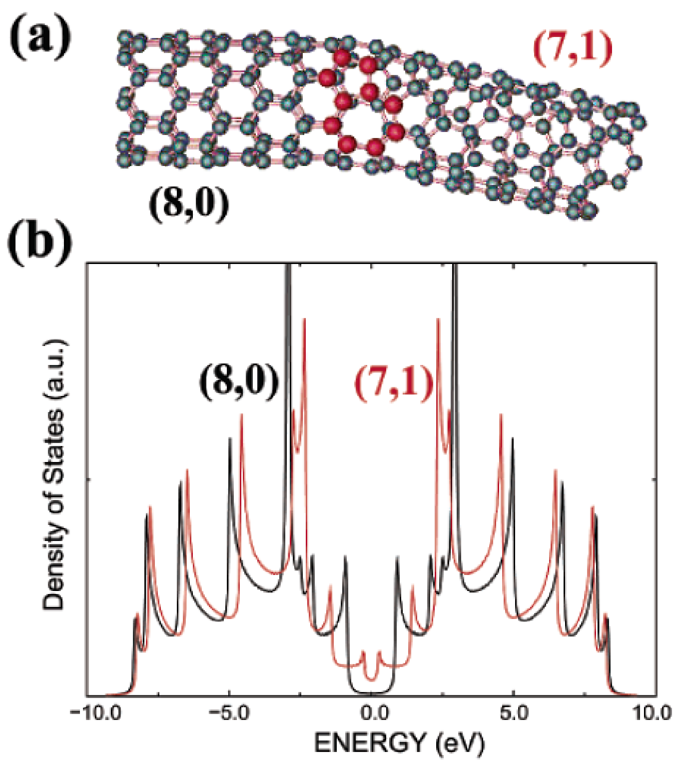


Partial solution: include hydrogen or a mild oxidizing agent in the feed gas

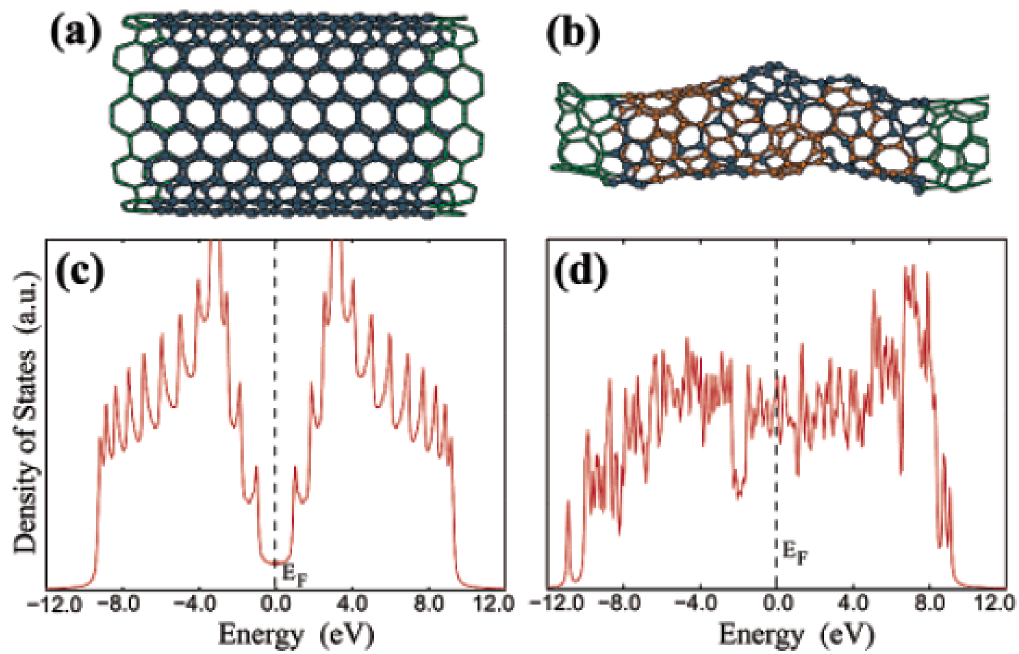
M. Maghrebi et al., Appl. Phys. A 2009;97:417.

Defects

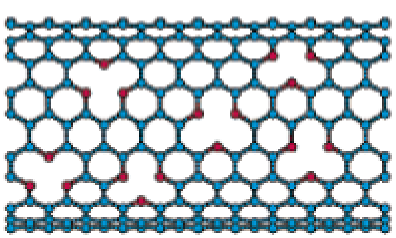
Pentagon-heptagon (5/7) defects



Irradiated CNT (C atoms removed randomly)



Nitrogen doped CNT



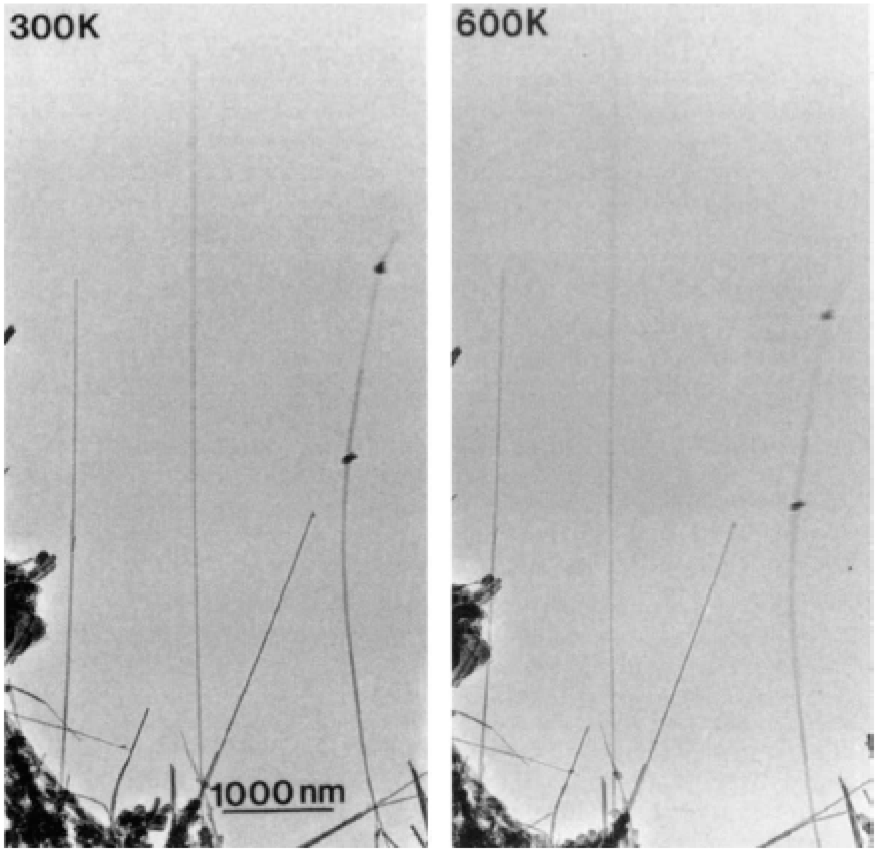
-Defects can result from statistical fluctuations during growth or from other effects such as irradiation, acid exposure, etc.

-Negative effects: disrupts the conjugated structure responsible for excellent mech/elec/thermal properties

-Positive effects: creates locations for potential surface modification, also for doping to change the electronic properties

J.C. Charlier, Acc. Chem. Res. 2002;35:1063.

Mechanical properties of CNTs: Indirect measurements



Transmission electron microscope images at different temperatures

Indirect calculation of Young's modulus (assumptions: classical clamped cantilever)

$$W_n = \frac{1}{2} c_n u_n^2$$

$$c_n = \frac{\pi \beta_n^4 Y (a^4 - b^4)}{16 L^3}$$

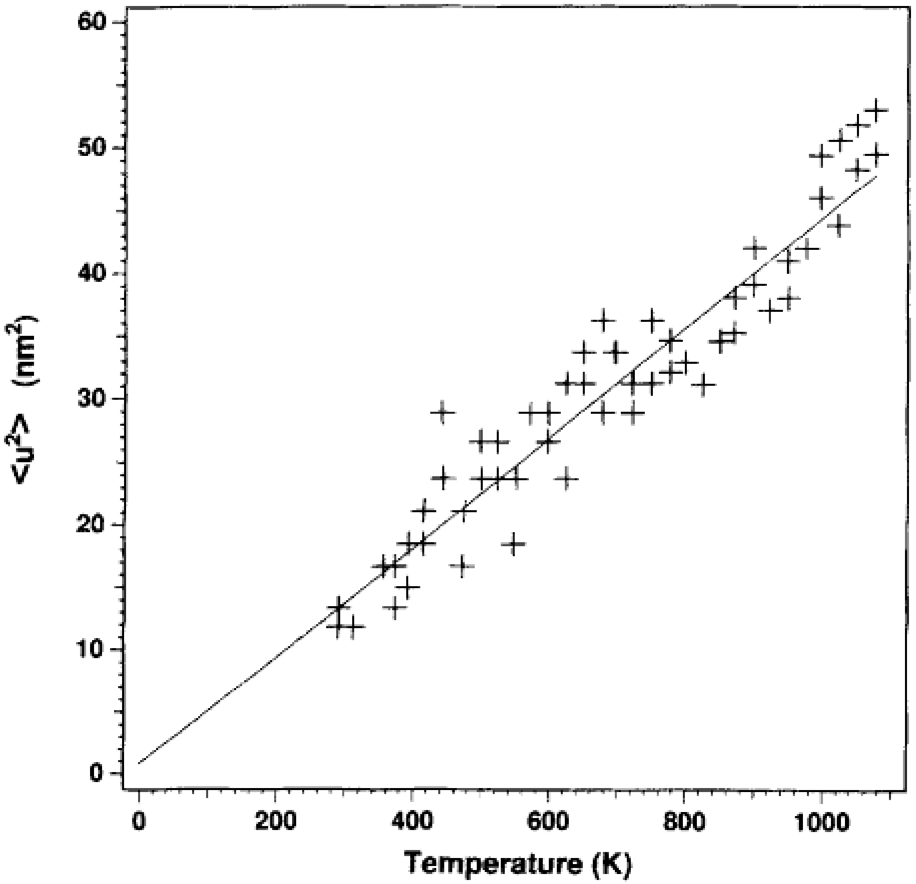
$$\cos\beta \cosh\beta + 1 = 0$$

$$\omega_n = 2\pi f_n = \frac{\beta_n^2}{2L^2} \sqrt{\frac{Y(a^2 + b^2)}{\rho}}$$

$$\boxed{\sigma^2 = \frac{16 L^3 kT}{\pi Y (a^4 - b^4)} \sum_n \beta_n^{-4} \approx 0.4243 \frac{L^3 kT}{Y (a^4 - b^4)}}$$

M.M.J. Treacy et al., Nature 1996;381:678.

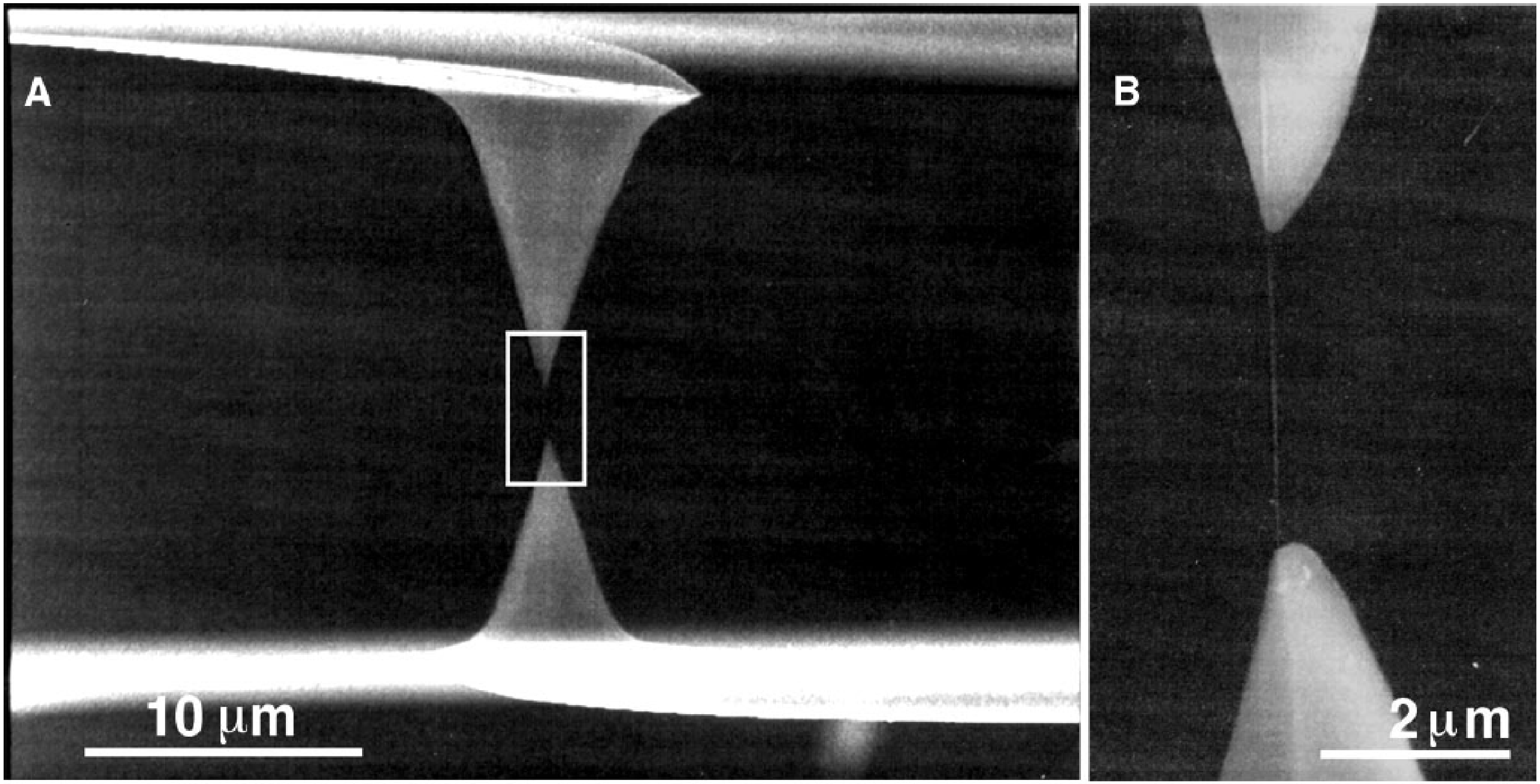
Mechanical properties of CNTs: Indirect measurements



Estimate from many different CNTs: Y = 1.8 TPa

M.M.J. Treacy et al., Nature 1996;381:678.

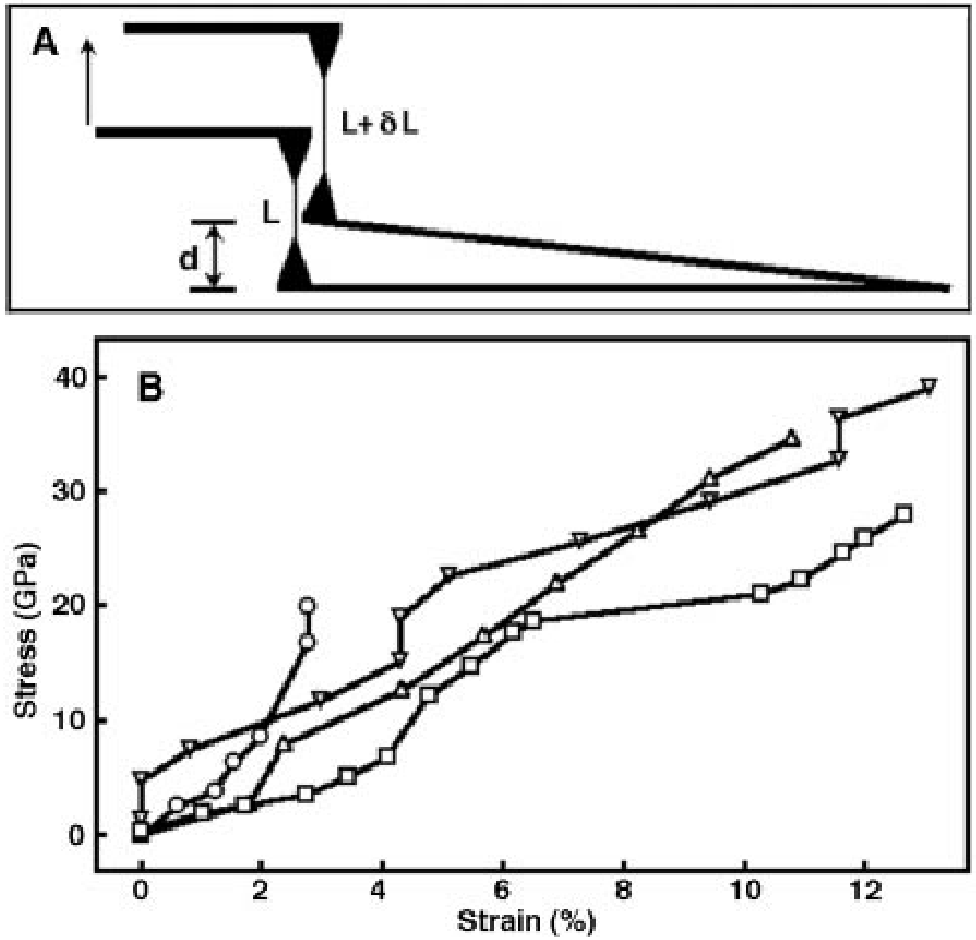
Mechanical properties of CNTs: Direct measurements



CNT attached to two different atomic force microscope tips using the electron beam

M.-F. Yu et al., Science 2000;287:637.

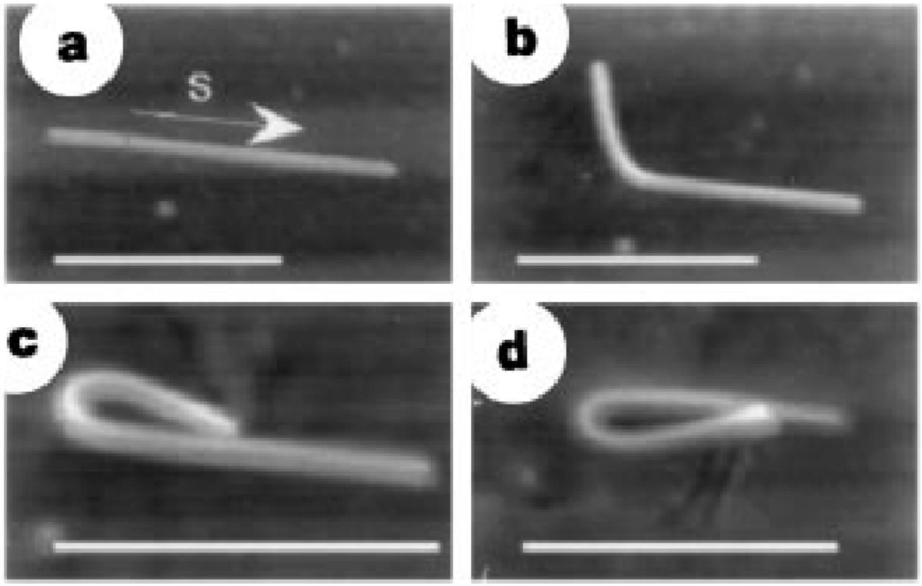
Mechanical properties of CNTs: Direct measurements



-Stiffness varied between 270 and 950 GPa for different CNTs
-Failure occurred in outermost layer of the multiwalled CNTs
-The strength of this layer ranged from 11 to 63 GPa

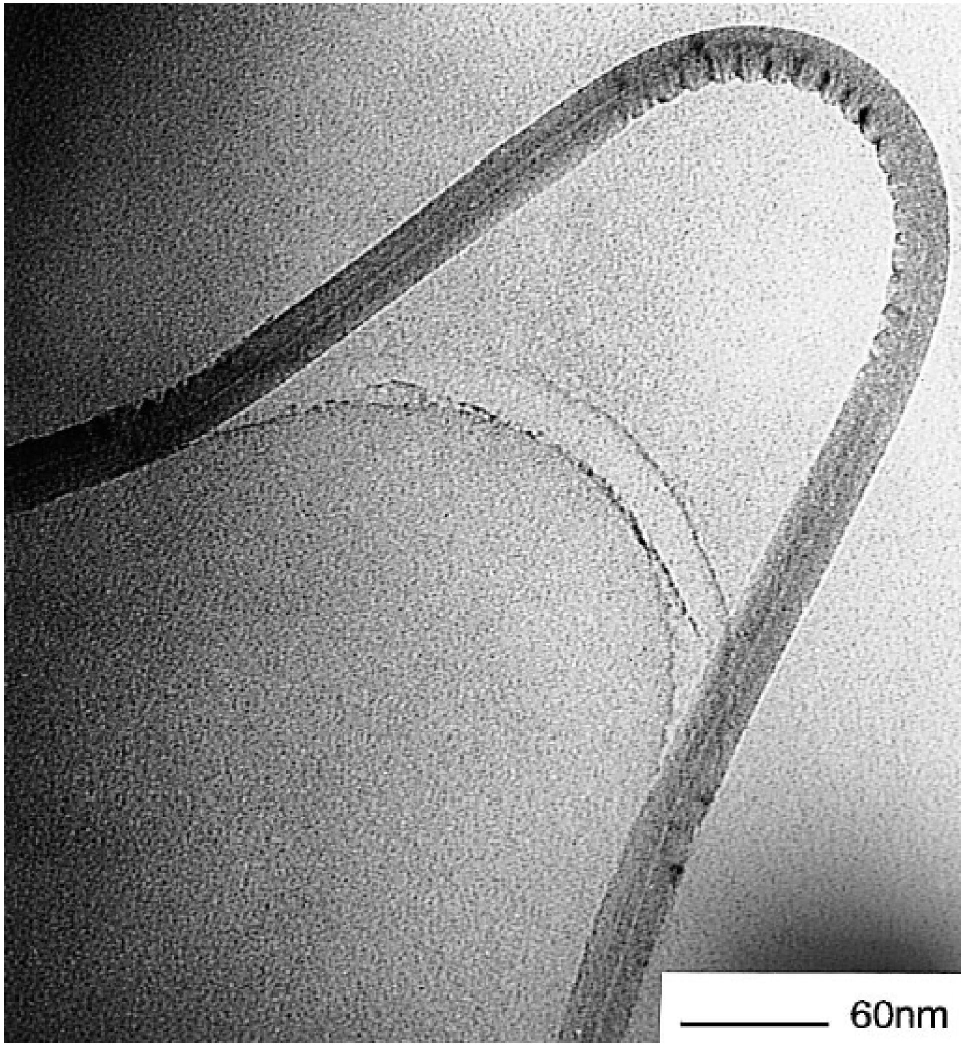
M.-F. Yu et al., Science 2000;287:637.

Mechanical behavior: Flexibility and elastic bending



Manipulation of individual CNTs with an atomic force microscope

$$\lambda = \frac{2\pi}{(12(1-\nu^2))^{1/4}}(r_0 t)^{1/2} \approx 3.5(r_0 t)^{1/2}$$

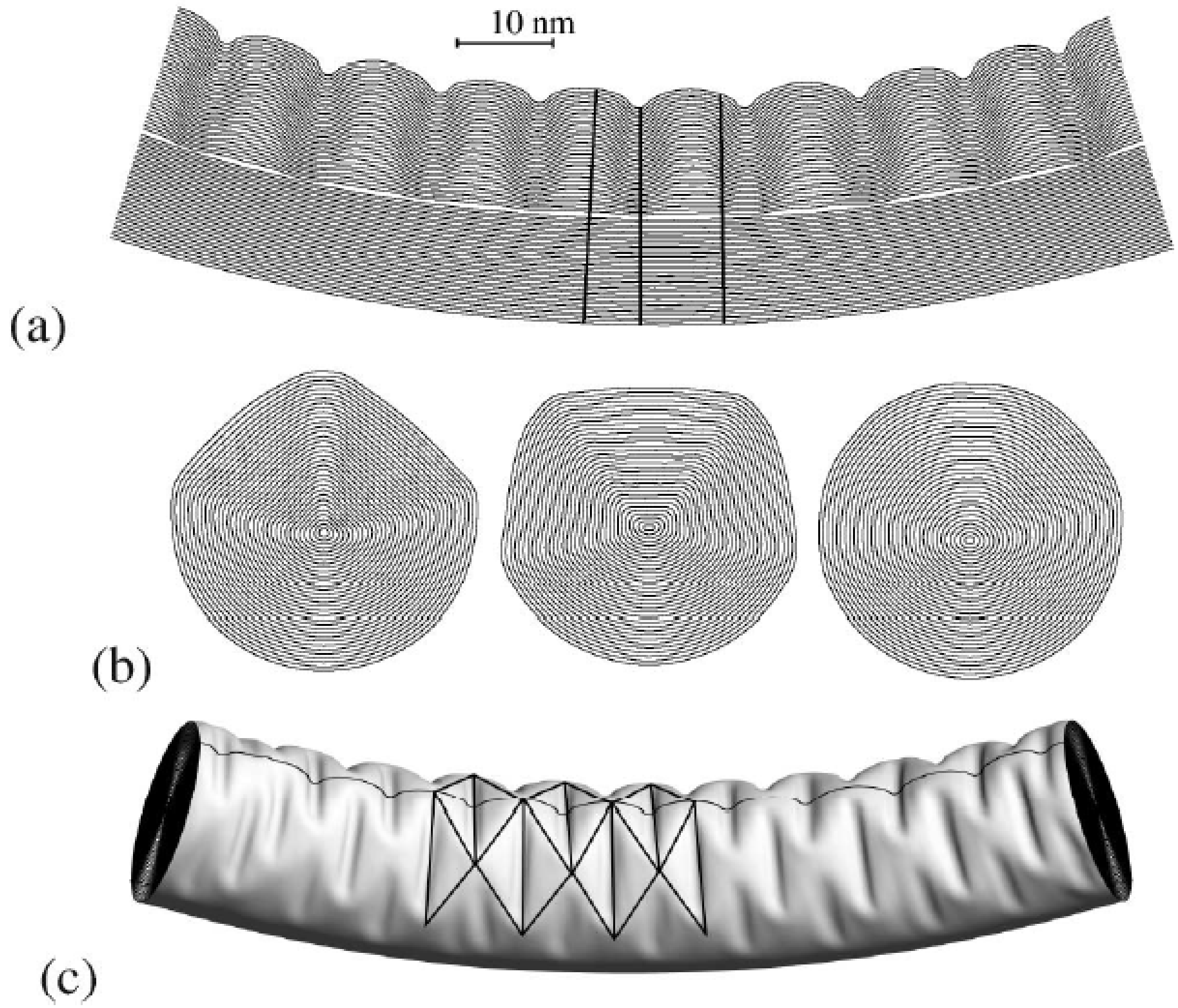


CNTs embedded in epoxy, which underwent polymerization shrinkage

M.R. Falvo et al., Nature 1997;389:582.

O. Lourie et al., PRL 1998;81:1638.

Mechanical behavior: Flexibility and elastic bending

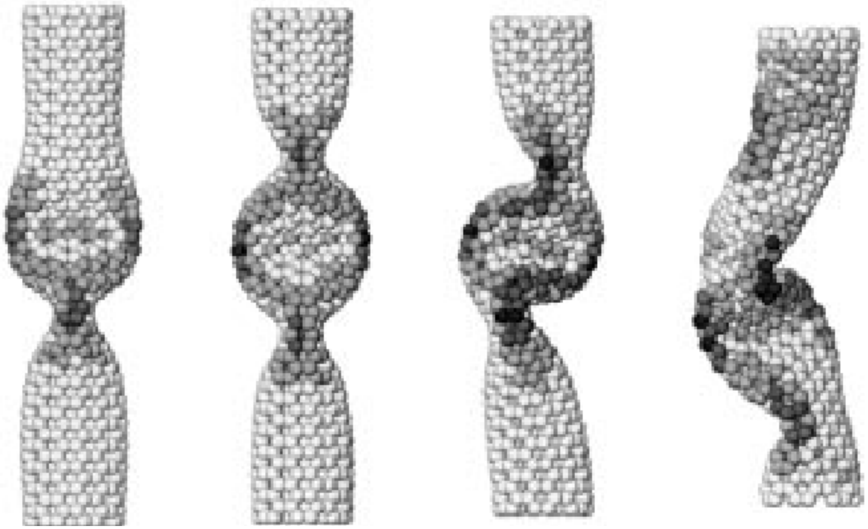


Formation of ripples lowers the effective bending stiffness

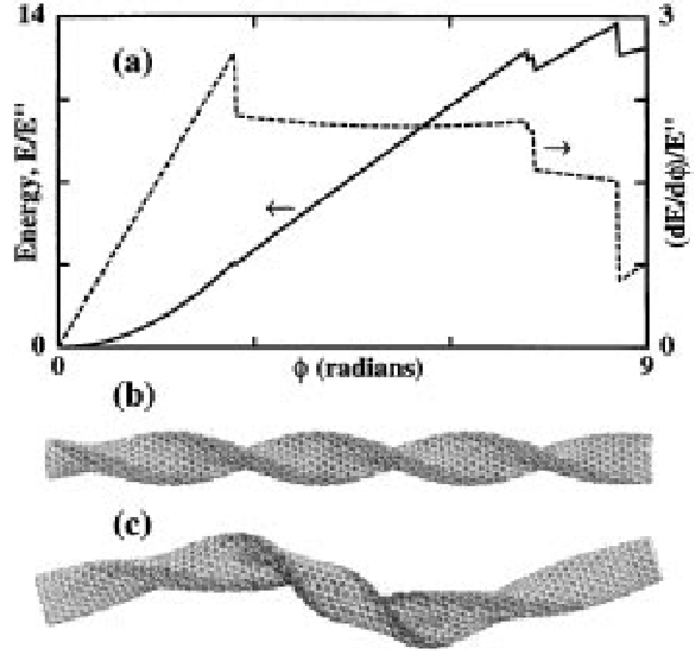
M. Arroyo and T. Belytschko, PRL 2003;91:215505.

Mechanical behavior: instabilities beyond linear response

Molecular dynamics simulation of uniaxially compressed CNT

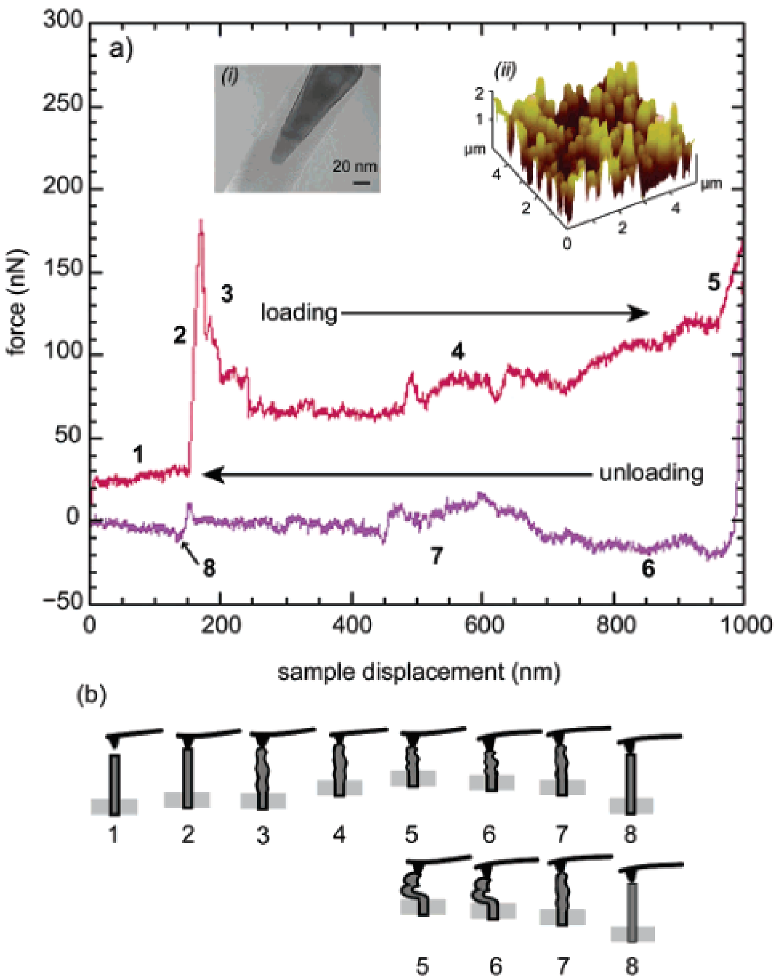


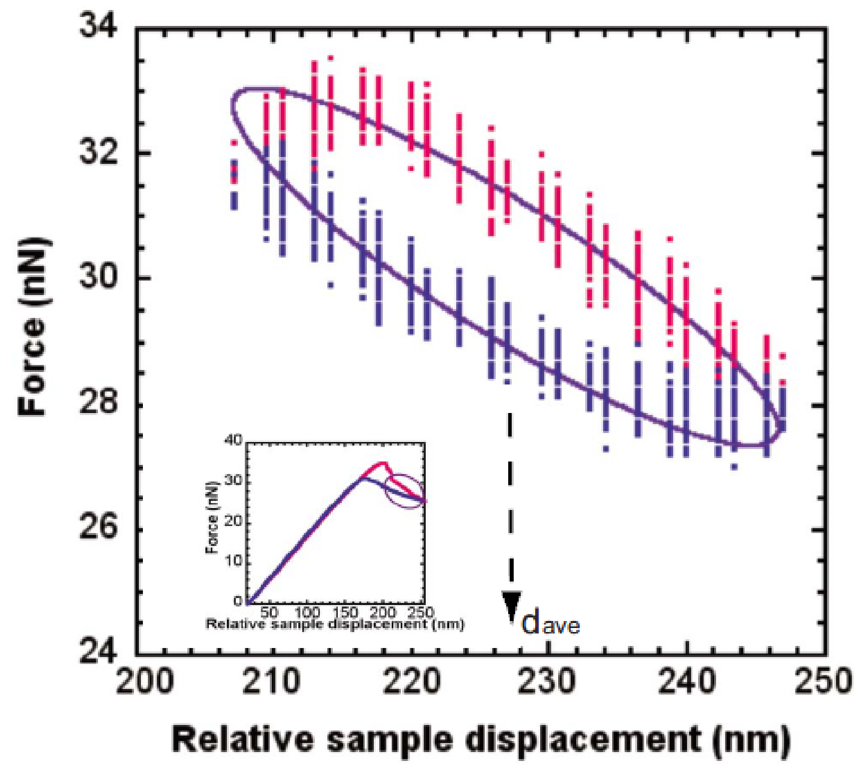
Molecular dynamics simulation of CNT under torsion



B.I. Yakobson et al., PRL 1996;76:2511.

Mechanical behavior: instabilities beyond linear response



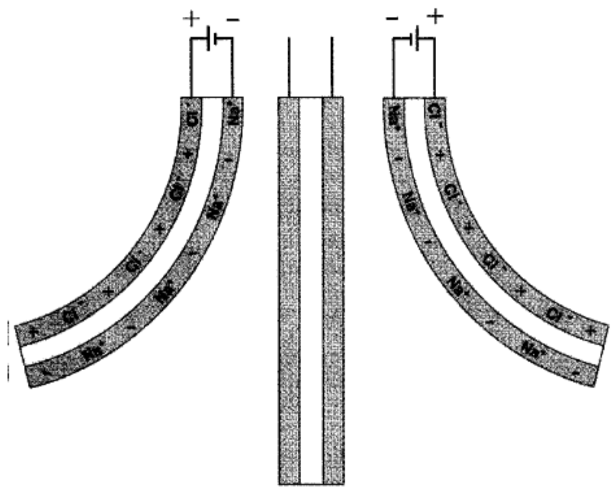


H.W. Yap et al., Phys. Rev. B 2008;77:045423.

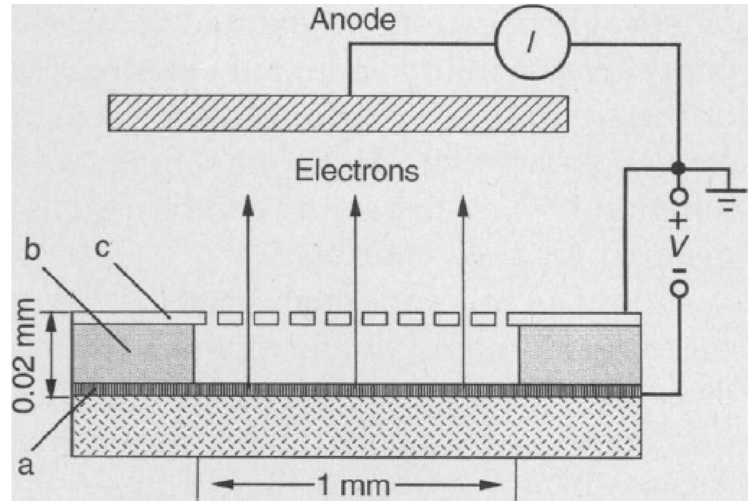
H.W. Yap et al., Nano Lett. 2007;7:1149.

Other important properties of CNTs

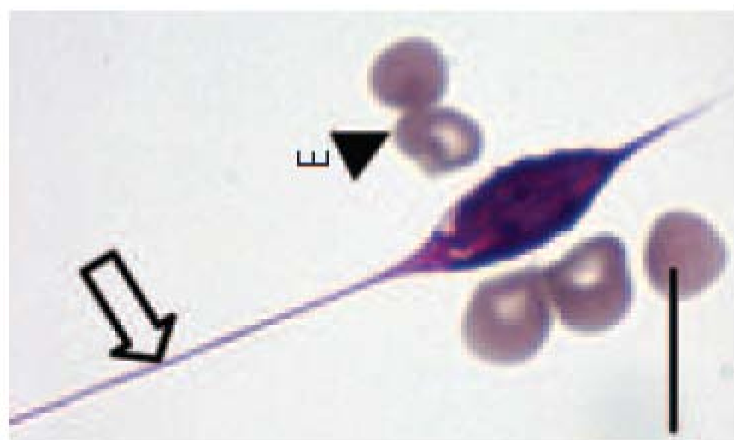
Actuation



Field emission electron source



Toxicity?



R.H. Baughman et al., Science 1999;284:1340.

W.A. de Heer et al., Science 1995;270:1179.

C.A. Poland et al., Nature Nanotechnol. 2008;3:423.

CNTs as components in bulk materials: applications

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Oct. 25, 2011

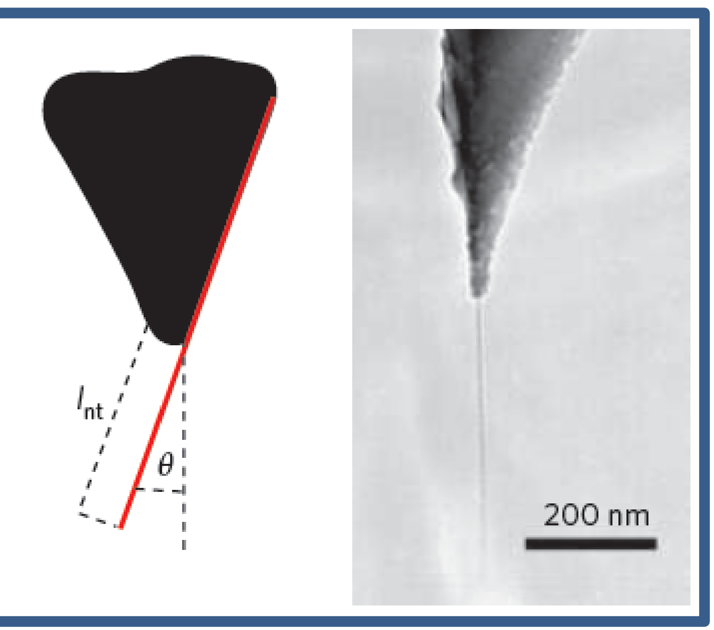
CNTs as *useful* materals?

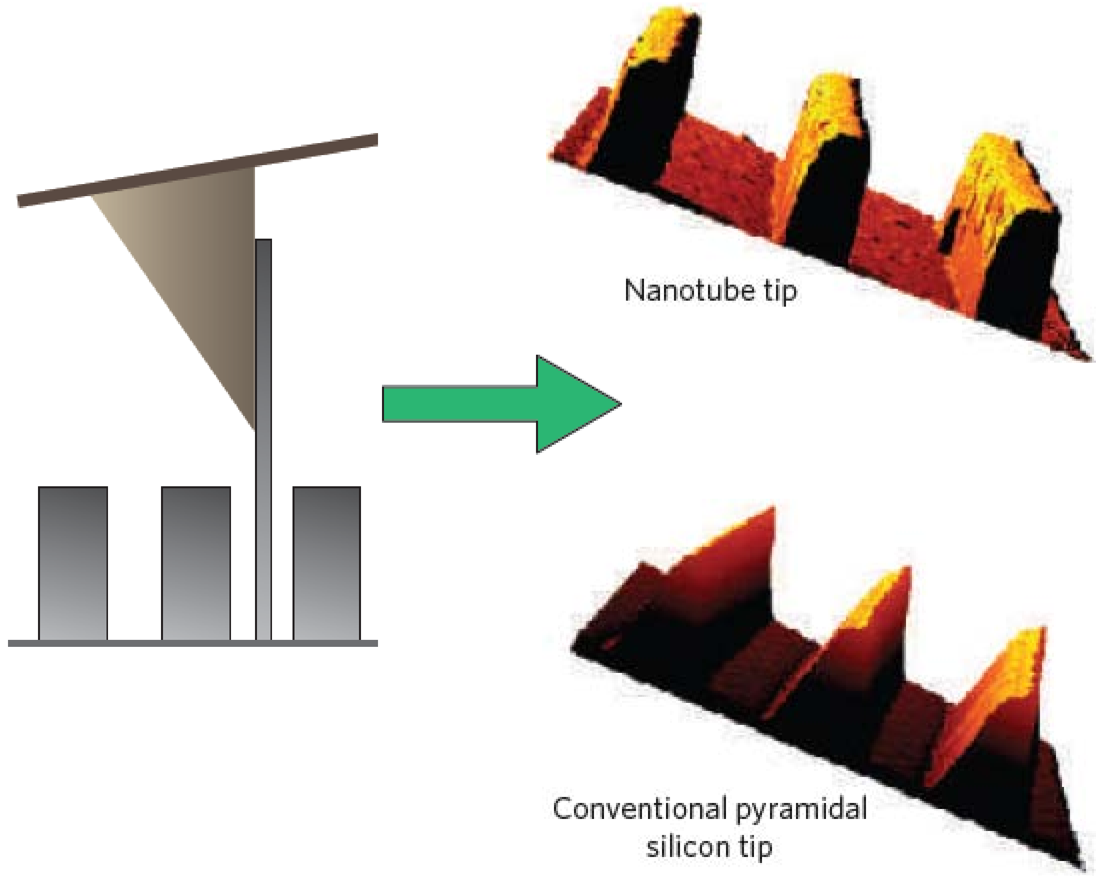
Approaches:

- Use an individual CNT for a specialty nanotechnology application
  - E.g., the tip of an atomic force microscope
- Use CNTs to improve the properties of another material
  - E.g., fibrous reinforcement in polymer
- Combine CNTs into stand-alone (e.g., structural) materials
  - E.g., CNT yarns/fibers

Applications for individual CNTs: AFM tips

CNTs as tips in atomic force microscopy (AFM)
- Good for imaging high aspect ratio features
- Good elastic recovery from bending
- Resilient against wear

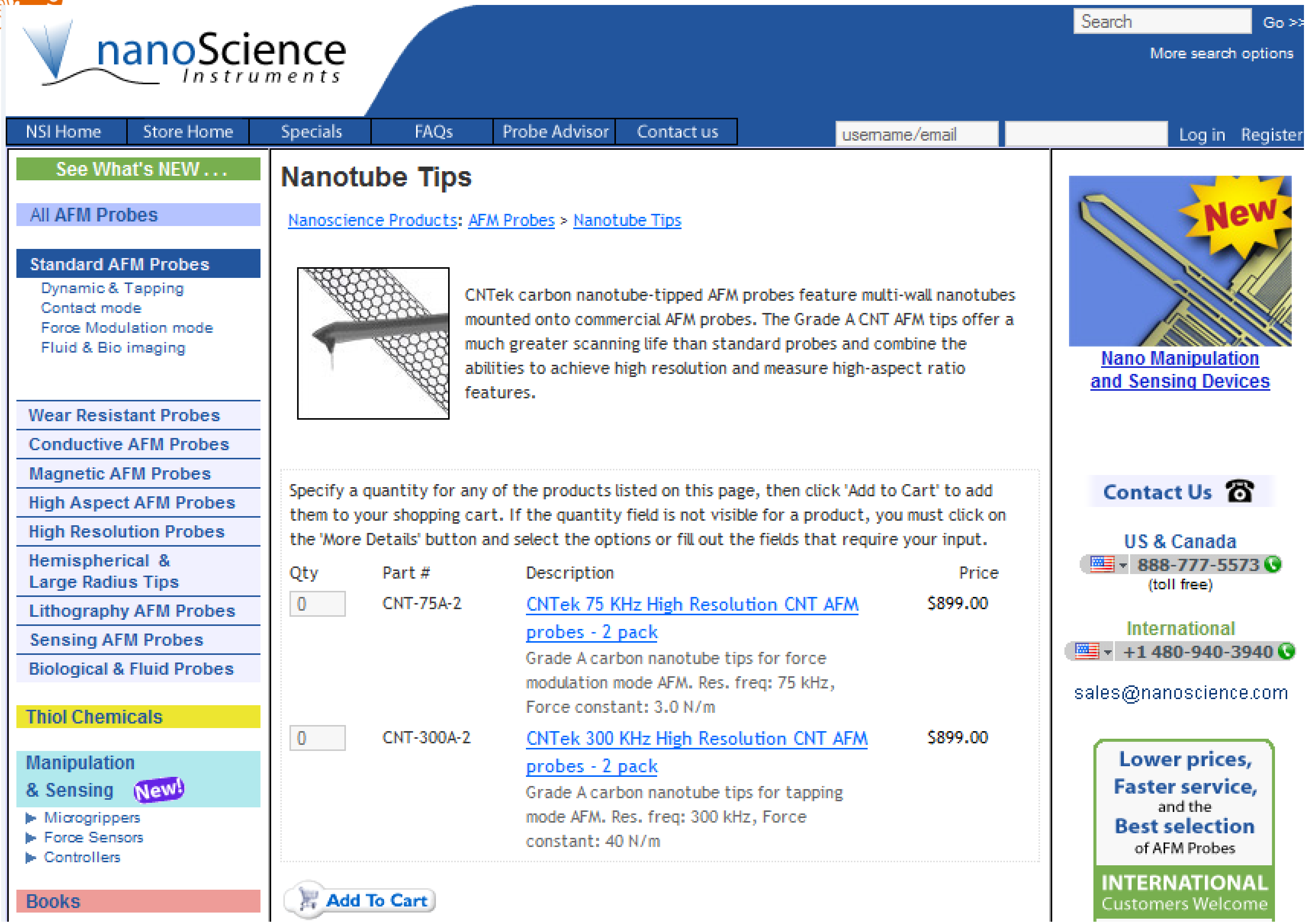




Resistance against wear during friction is vital for accurate deconvolution calculation!

N.R. Wilson & J.V. Macpherson, Nat. Nanotech. 2009;4:483

Applications for individual CNTs: AFM tips



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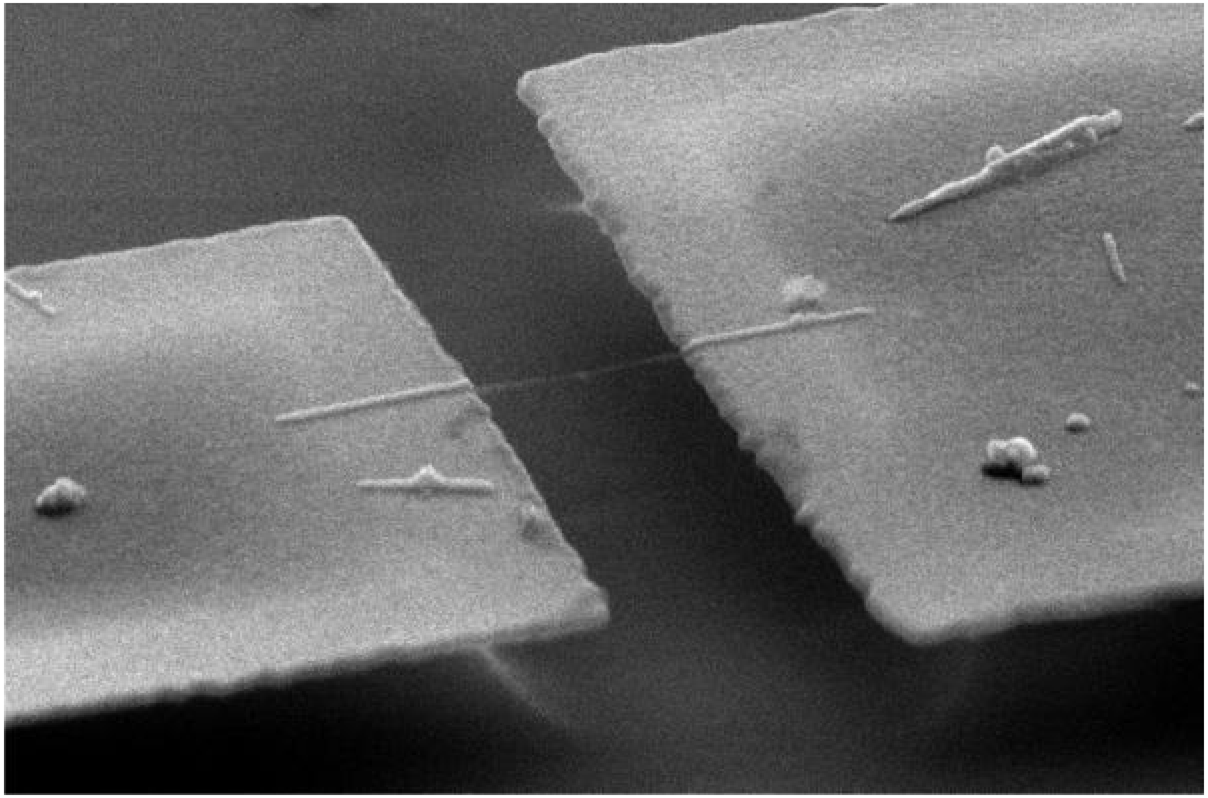
Applications for individual CNTs: mass detection

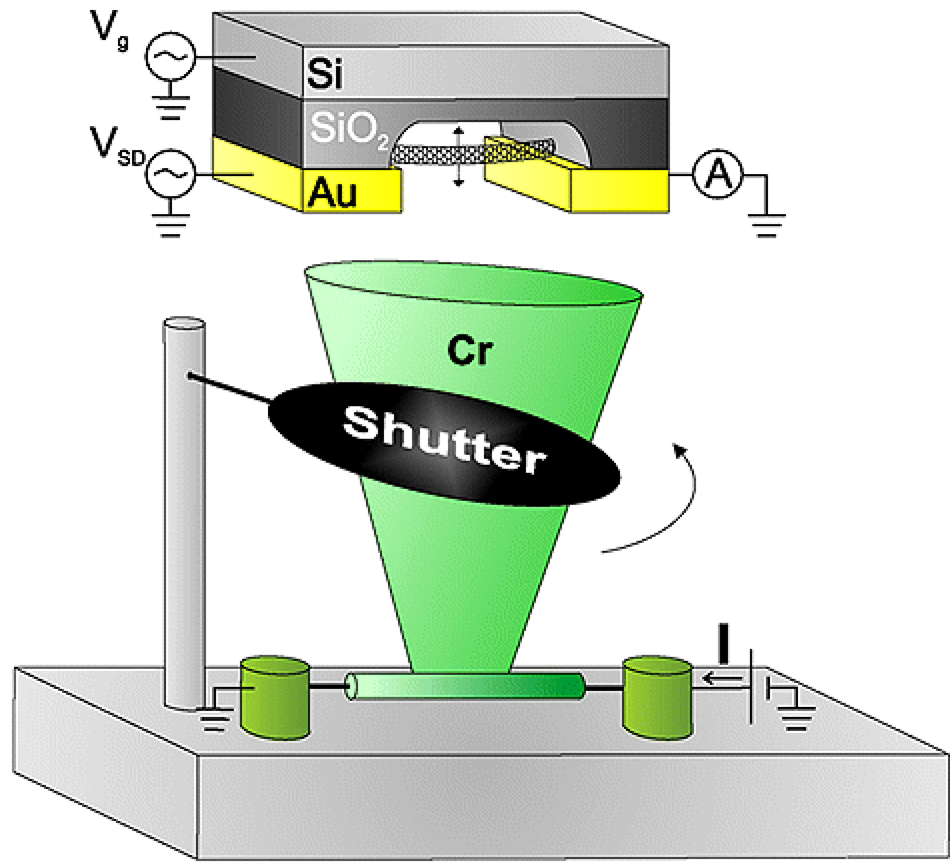


Lassagne et al., Nano Lett. 2008;8:3735.

Applications for individual CNTs: mass detection

$$f_0 = \frac{1}{2\pi}\left(\frac{k}{m_{\text{eff}}}\right)^{1/2}$$

$$\delta m = \frac{2m_{\text{eff}}}{f_0}\delta f_0$$



Low mass and high rigidity of the CNT allows mass resolution down to ~ 10^{-21} g

Lassagne et al., Nano Lett. 2008;8:3735.

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- Use CNTs to improve the properties of another material
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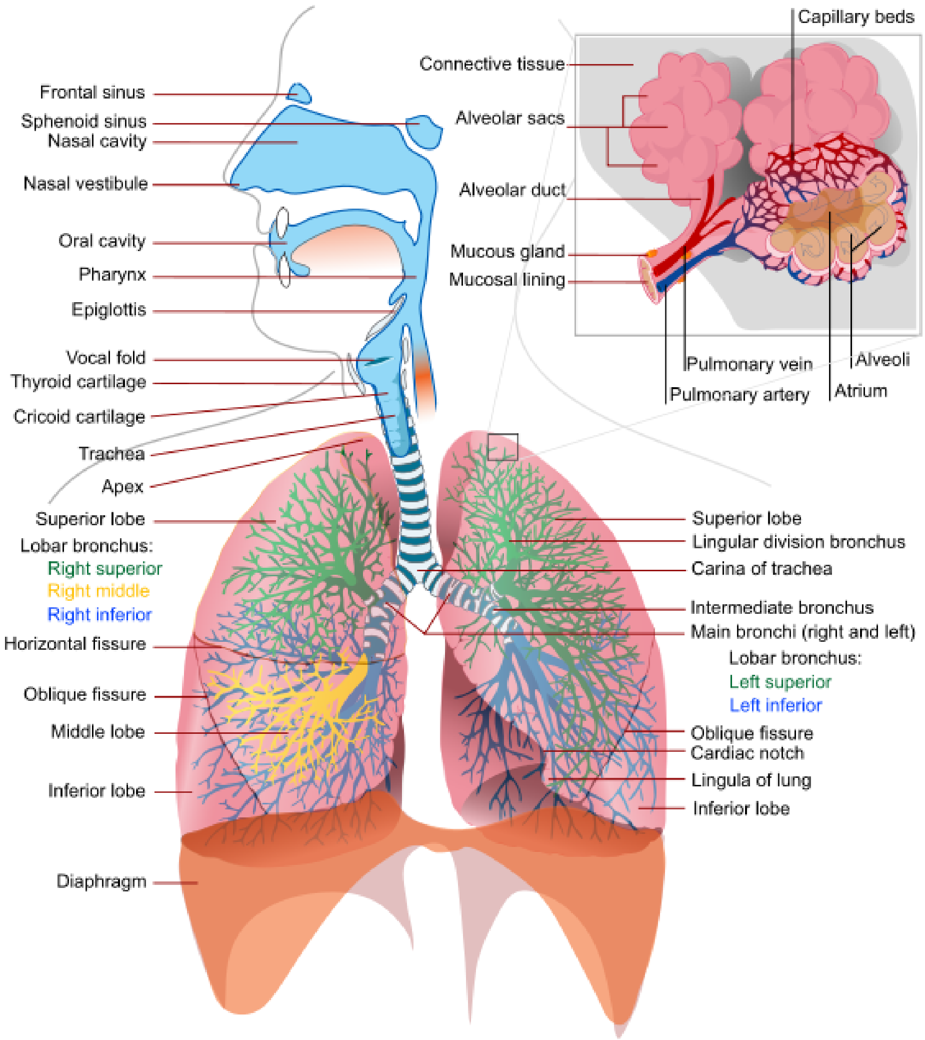
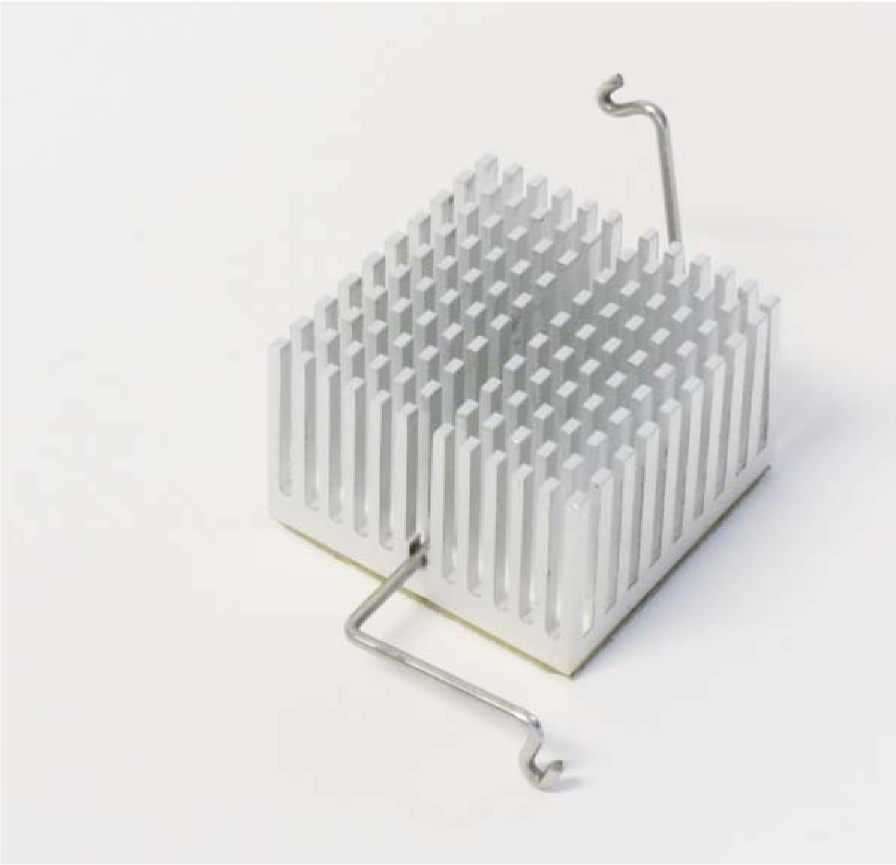
Examples where increased surface area is vital





Images from Wikipedia

Scaling behavior

$V \sim r^3$ and $S \sim r^2$.

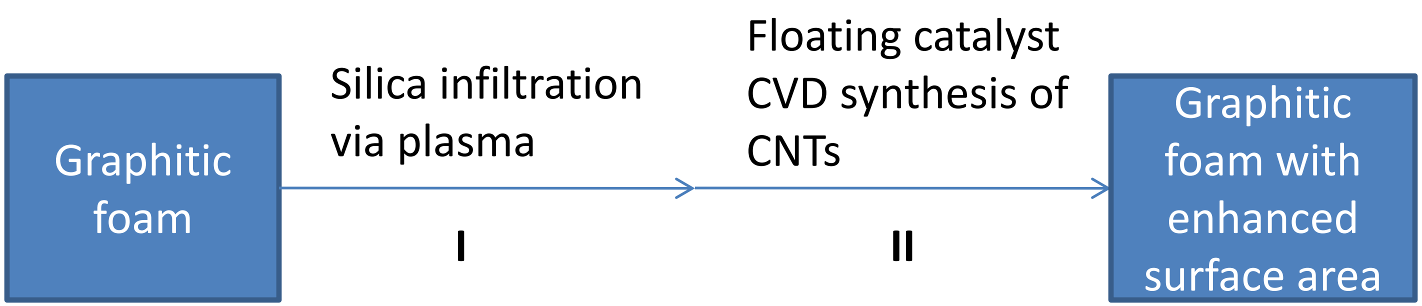
For many power applications, heat generation ~ V and heat dissipation ~ S.

For many biological systems, metabolic waste generation ~ V and metabolic waste/nutrient interface ~ S.

$S/V \sim r^{-1}$. Need large surface area to meet biological/technological needs.

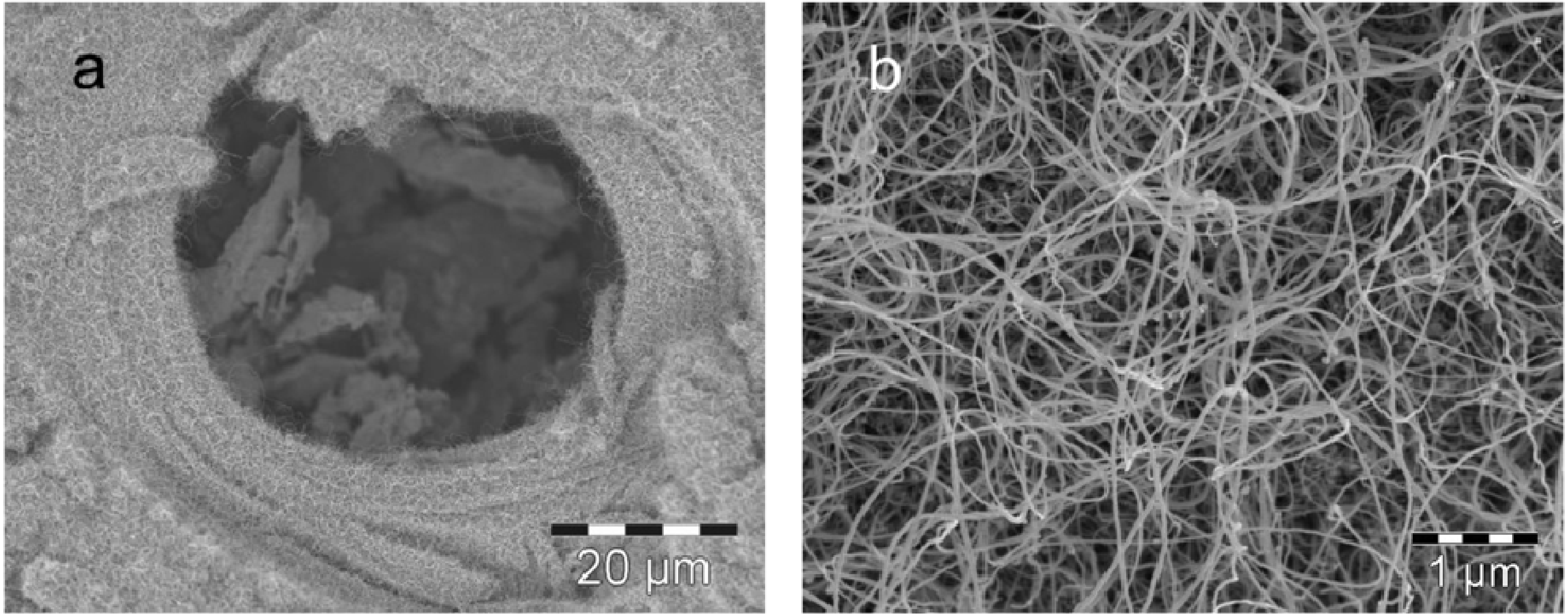
Improving geometrical properties of a material by utilizing CNTs as elements with high surface-to-volume ratio

- Mukhopadhyay et al. increased the surface area of a graphitic foam by 2-3 orders of magnitude by synthesizing CNTs on its surface
- Note: only the geometry of the CNTs is exploited



Mukhopadhyay et al. J. Phys. D: Appl. Phys. 2009;42:195503

Improving geometrical properties of a material by utilizing CNTs as elements with high surface-to-volume ratio



Mukhopadhyay et al. J. Phys. D: Appl. Phys. 2009;42:195503

Improving geometrical properties of a material by utilizing CNTs as elements with high surface-to-volume ratio

Can use synthesis parameters to change the morphology of the CNTs, and affect properties:

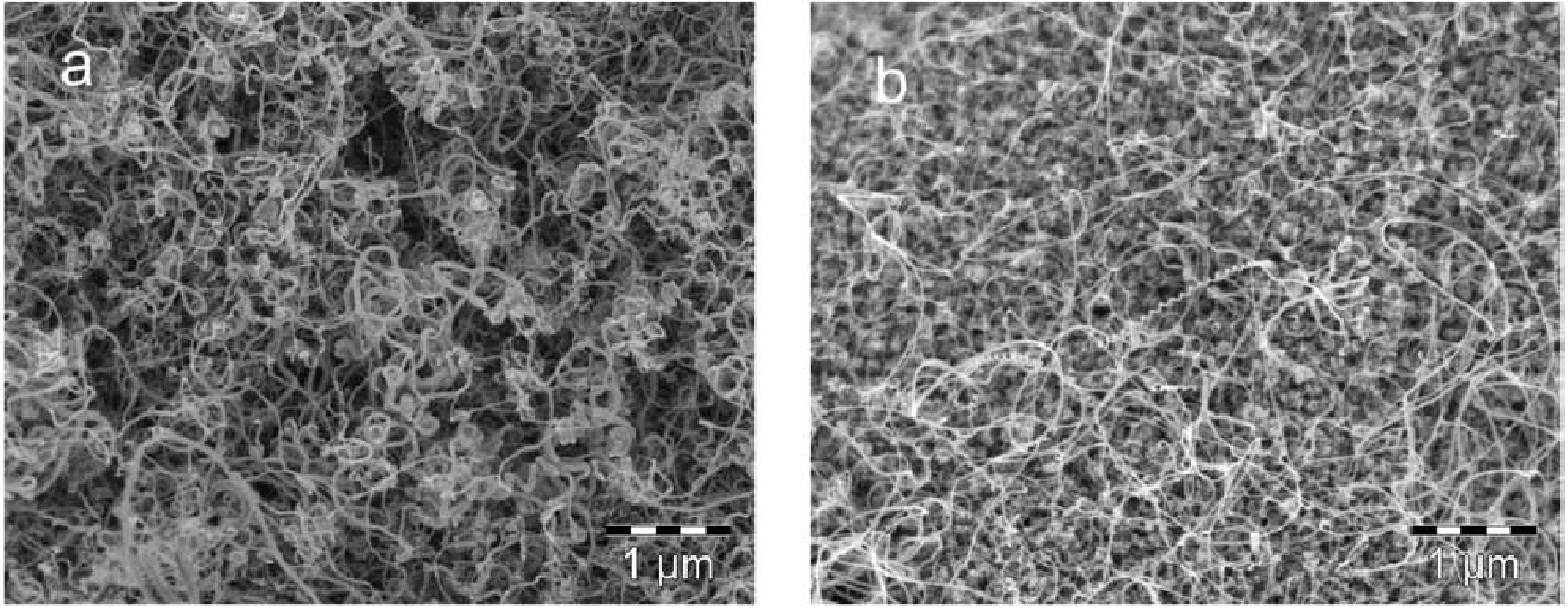


Figure 5. CNT grown with (*a*) high ferrocene content and (*b*) low hydrogen content.

Mukhopadhyay et al. J. Phys. D: Appl. Phys. 2009;42:195503

Improving properties of other materials with a small amount of CNTs

Material matrix
(polymer, concrete, etc.)

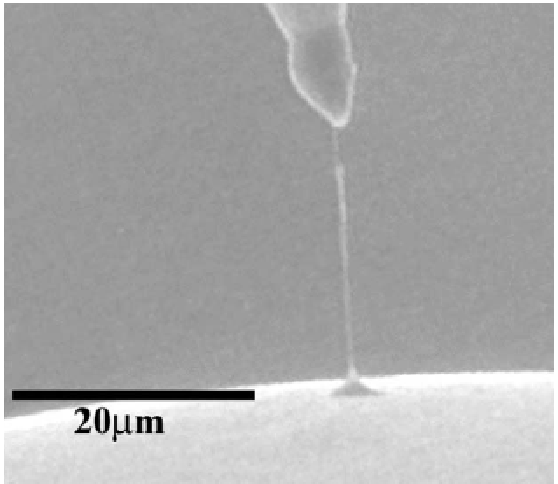
+ CNTs → **Improved material**
(mechanical/electrical/thermal properties)

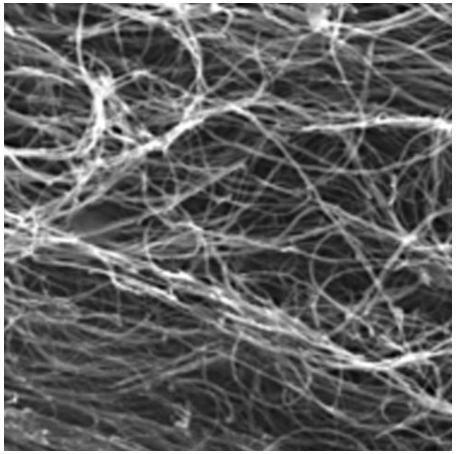
Stirring
Ultrasound
Shearing
Sonication
Surfactants
Compatibilizer
***In situ* polymerization**
Polymer-assisted melt blending
Chemical functionalization (covalent)
Non-covalent “functionalization”

Xie, X. L., et al. Materials Science and Engineering: R: Reports 2005;49:89-112.

Roadblocks to getting benefits from CNTs in other matrices

- Interfacial adhesion[a]
  - Suboptimal stress transfer
  - Functionalize walls of CNTs with chemical groups (e.g., carboxyl) that interact better with the polymer[b]
- Dispersion
- Uniform manufacture
- Cost
- Toxicity
  - Analogies with asbestos[c]





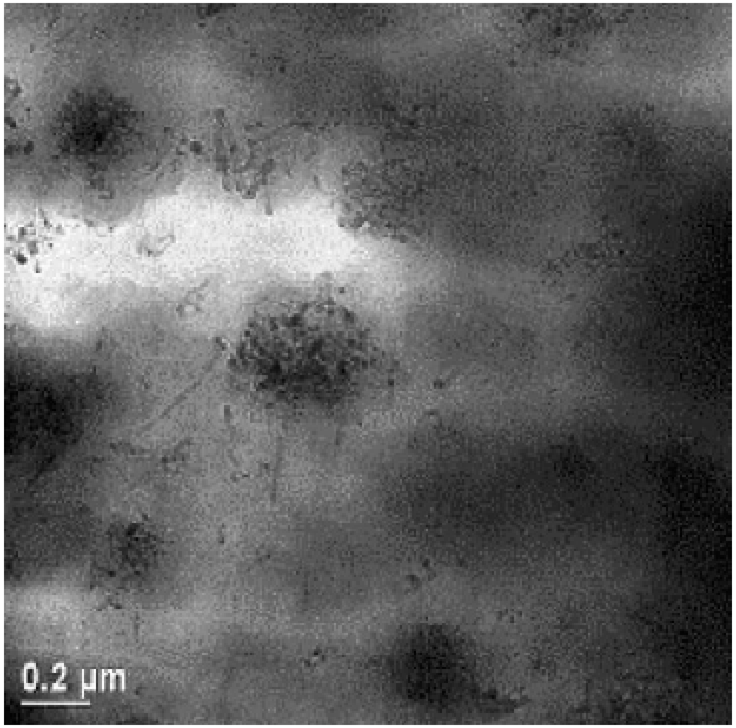
a. Wagner, H.D. and R.A. Vaia. Materials Today 2004;7:38-42.
b. Kim, J.Y., et al. Polymer 2008;49:3335-3345.
c. Poland, C.A., et al. Nat Nano 2008;3:423-428.
d. Shih, Y.F., et al. Polymer 2008;49:4602-4611.

The dispersion problem

High aspect ratio and strong van der Waals interaction among CNTs means **clumping.**[a]

Approach

- Shortening the CNTs with acids, ultrasonication, or fluorination[b]
  - Creates holes in walls, degrades properties
  - Can create widely varying tube lengths—may require sorting[c]
  - Clever improvement: form buckypaper, cut with microtome[d]
  - Shorter CNTs can improve some properties

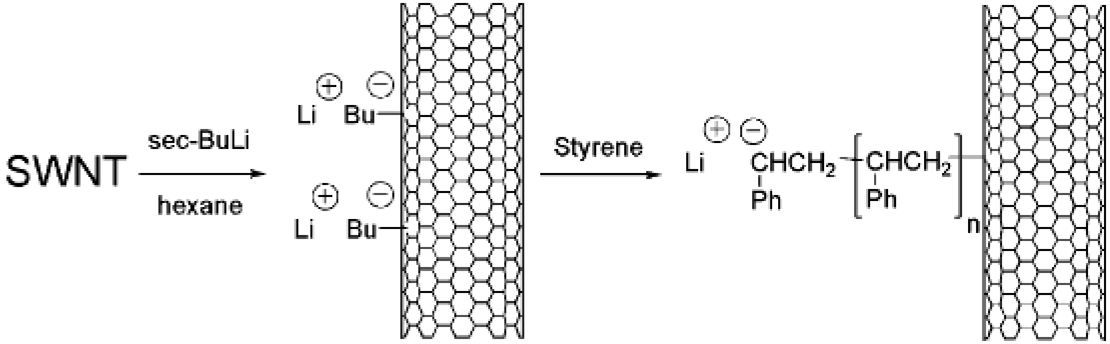


TEM image of 5% multiwall-CNT/HDPE composite[e]

a. Tang, W., et al. Carbon 2003;41:2779-2785.
b. Gu, Z., et al. Nano Letters 2002;2:1009-1013.
c. Farkas, E., et al. Chemical Physics Letters 2002;363:111-116.
d. Wang, S., et al. Carbon 2009;47:53-57.
e. Shih, Y.F., et al. Polymer 2008;49:4602-4611.

Another approach: covalent modification[a,b]

- Functionalization can be an effective method of dispersion
- Improves interfacial adhesion
- Techniques are well-cataloged (e.g., see below)
- Can severely degrade CNTs, and therefore composite properties, especially with single-wall CNTs



Grafting of polystyrene chains by anionic polymerization[c]

a. Liang, F., et al. *Nano Letters*, 2004. **4**(7): p. 1257-1260.
b. X. Lou, et al. *Advanced Materials*, 2004. **16**(23-24): p. 2123-2127.
c. Tasis, D., et al. *Chemical Reviews*, 2006. 106(3): p. 1105-1136.

Covalent modification

Tasis, D., et al. *Chemical Reviews*, 2006. 106(3): p. 1105-1136.

An excellent review of the various chemical techniques to covalently modify CNTs with just about any functional group

Contents

Covalent modification

Tasis, D., et al. *Chemical Reviews*, 2006. 106(3): p. 1105-1136.

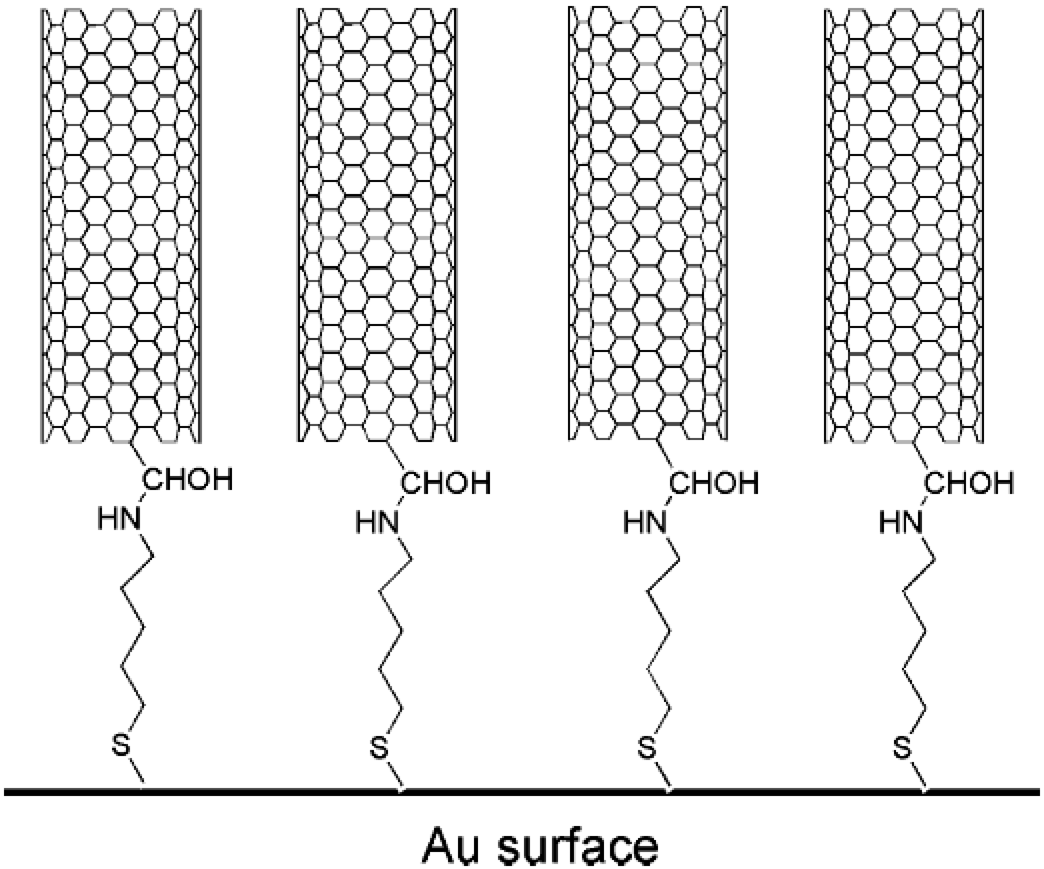
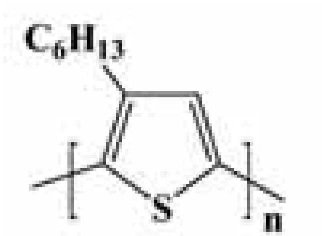


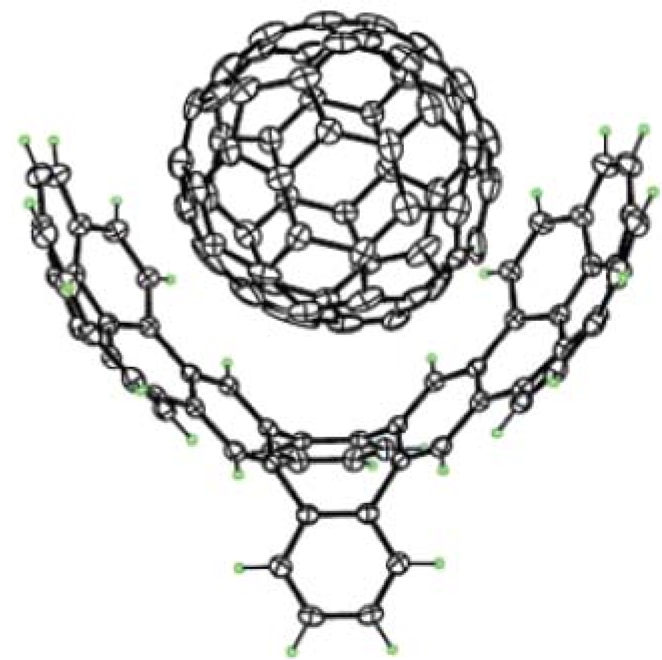
Figure 18. Controlled deposition of oxidized nanotubes onto gold surfaces by using aminothiols as chemical tethers.

Another approach: non-covalent techniques

- Effective dispersion with only minor loss of desired properties
- Utilize π-π interactions
- These can be exploited by conjugated block copolymers to "functionalize" the exteriors of CNTs and give excellent dispersion[a]
- Because of its conjugated nature, P3HT interacts well with the CNT surface— **and it can carry important functionality with it in the form of another block**[b]



poly(3-hexylthiophene), or P3HT



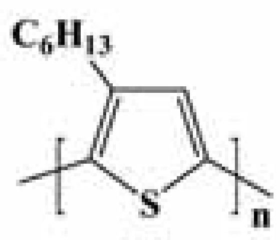
Example of π-π interaction: a "buckyball catcher".[c]

a. Lee, J.U., et al. Carbon 2007;45:1051-1057.
b. Zou, J.H., et al. Advanced Functional Materials 2009;19:479-483.
c. Sygula, A., et al. Journal of the American Chemical Society 2007;129:3842-3843.

Non-covalent techniques

Zou, J.H., et al. *Advanced Functional Materials*, 2009. 19(3): p. 479-483.

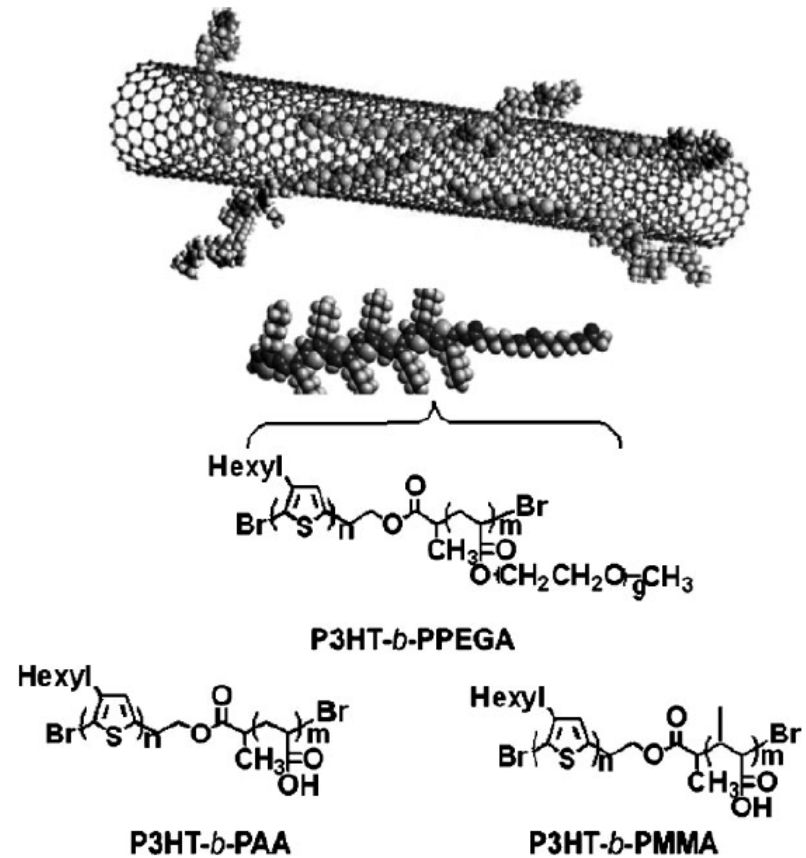
CNTs +(



P3HT

$+ [\text{-B-}]_m$)

= **Solubility in anything B-like?**



CNT reinforcement of cement

General scheme: disperse CNTs in water prior to beginning cement mix

Problems: (1) CNTs are highly hydrophobic; (2) CNTs have high aspect ratios

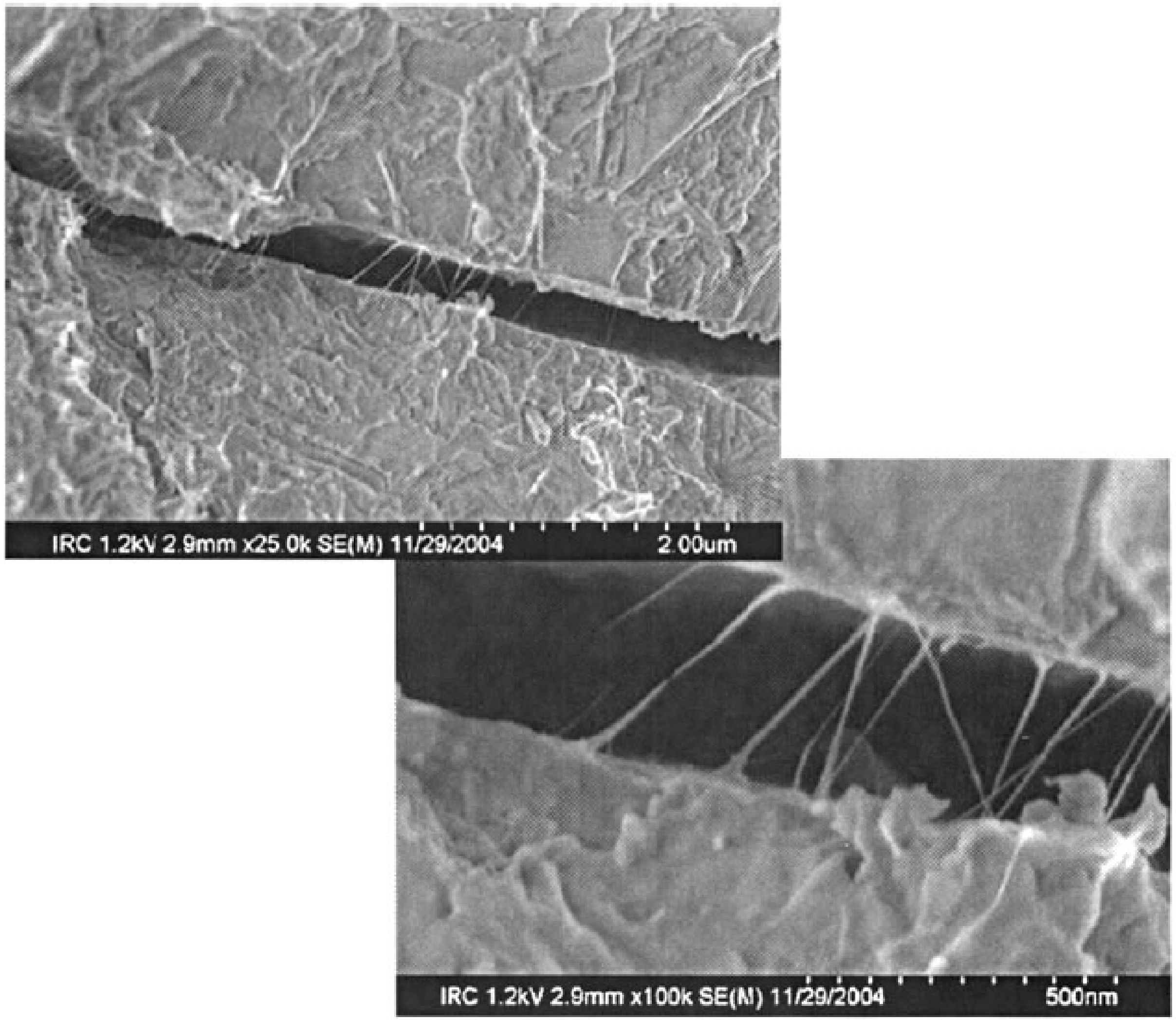
The result is a tendency for the CNTs to form clumps via van der Waals interactions.

POCKETS OF CLUMPED CNTS DECREASE THE PERFORMANCE OF THE CEMENT

Partial solution: include gum arabic or another agent in the water to improve dispersion

Y. Sáez de Ibarra, Phys. Stat. Sol. a 2006;203:1076.

CNT reinforcement of cement

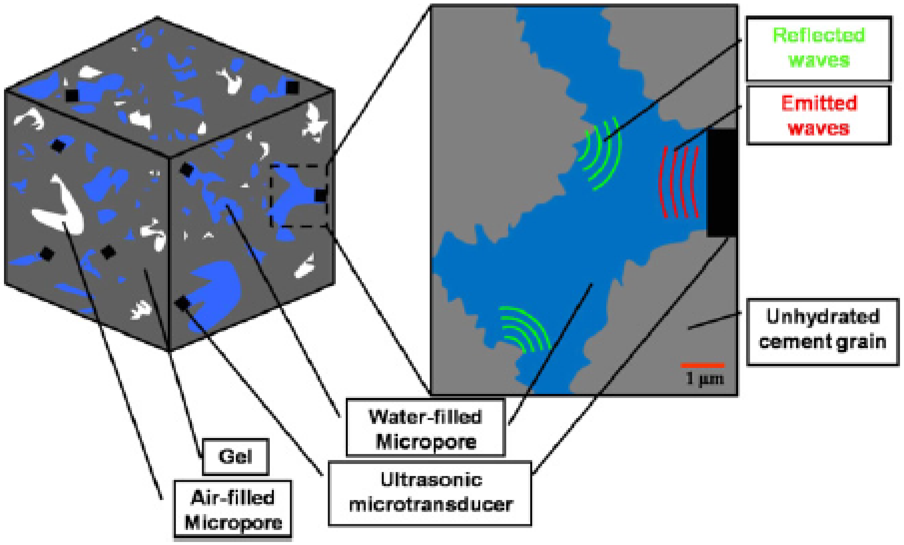


Crack bridging of CNTs in cement is associated with increased toughness and stiffness

F. Sanchez & K. Sobolev, Construction and Building Materials 2010;24:2060.

CNT-based sensors for structural health monitoring of concrete

Concrete exhibits a porous structure that could in theory allow the implantation of sensors

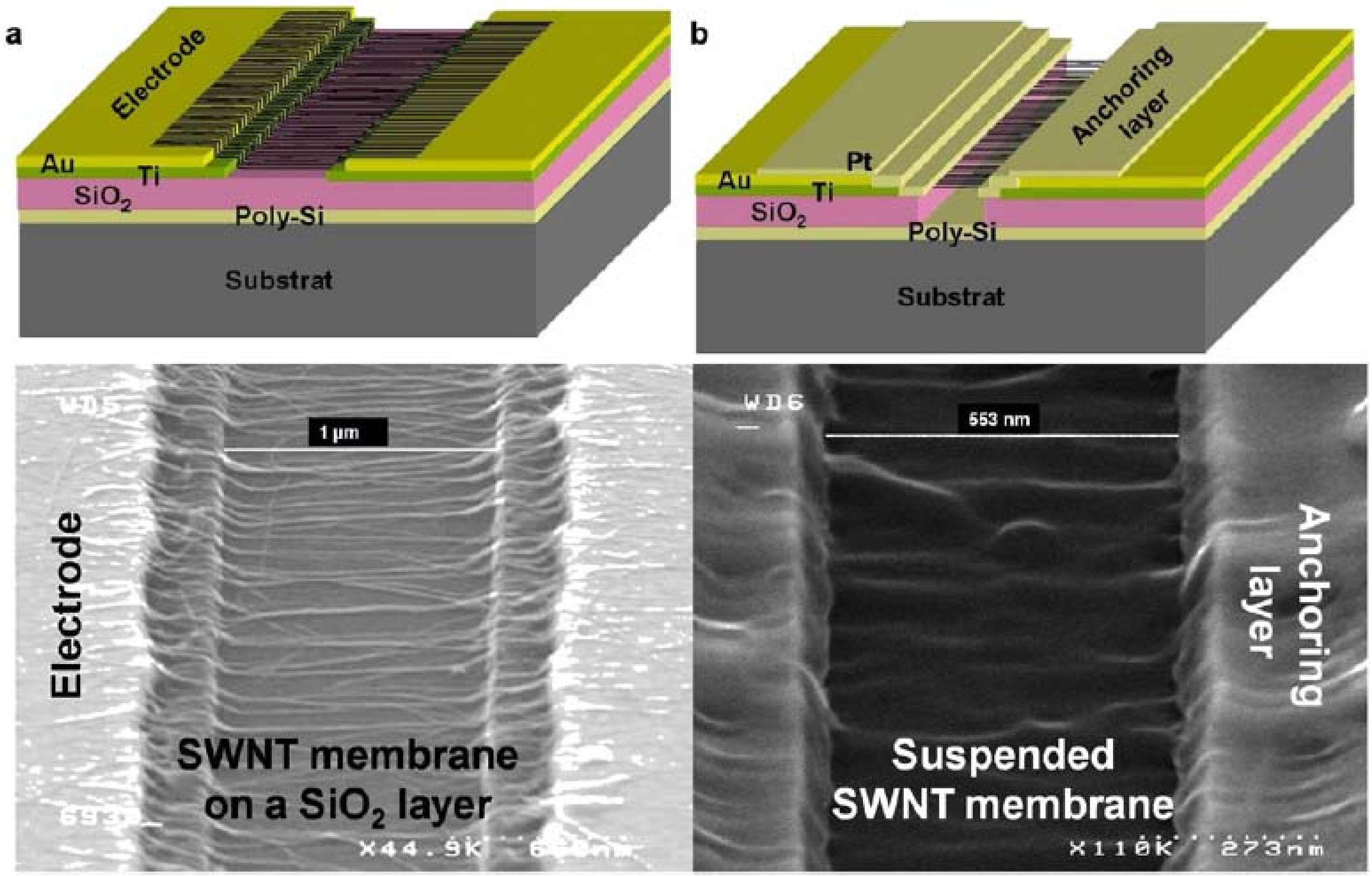


Ultrasonic transducers fabricated from CNT membranes:

(1) CNT dispersion
(2) alignment between electrodes in AC field
(3) spin coat PMMA, ebeam lithography, deposit Pt clamps
(4) HF or RIE to remove SiO_2 layer, giving free membrane

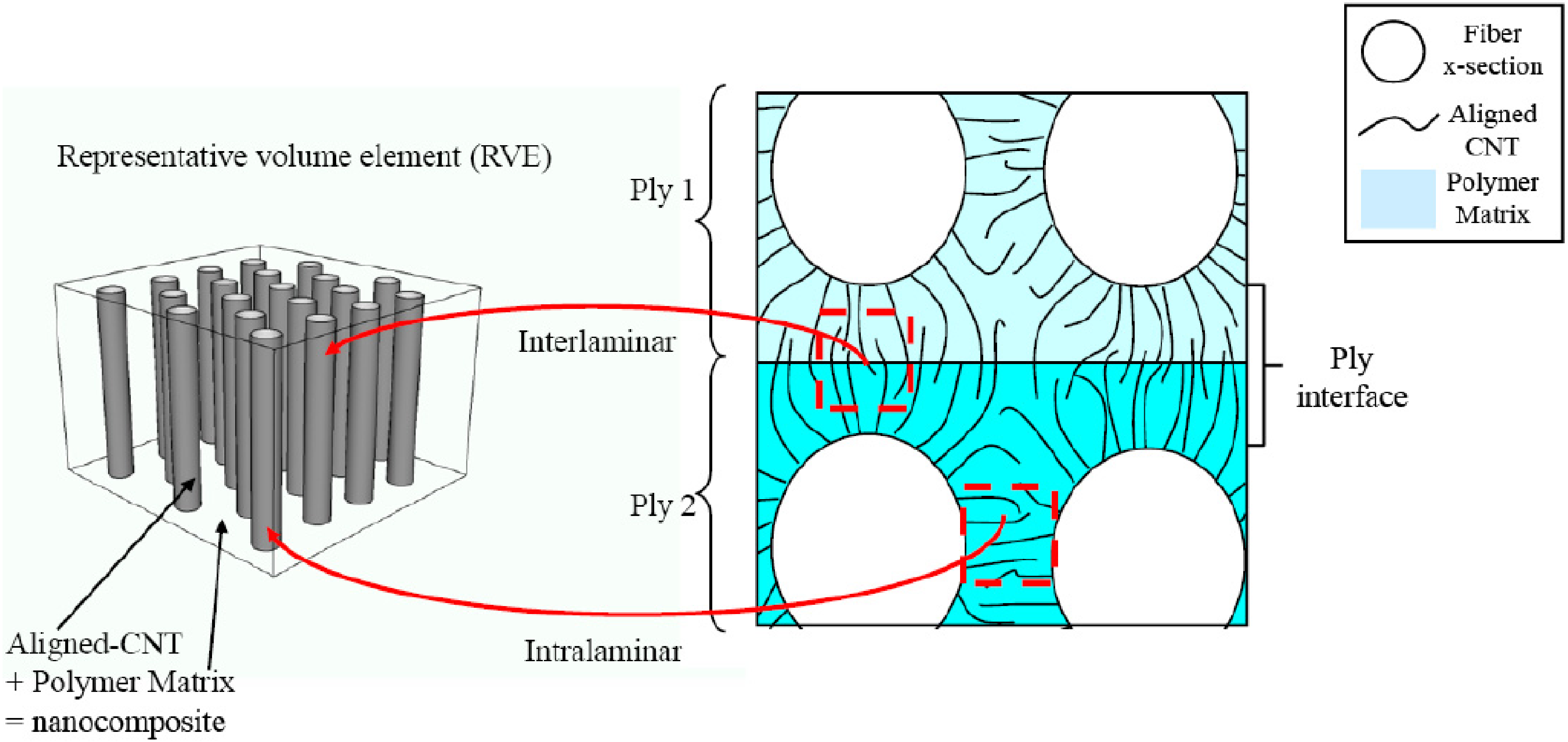
B. Lebental et al., Nanotechnology 2011;22:395501.

CNT-based sensors for structural health monitoring of concrete



B. Lebental et al., Nanotechnology 2011;22:395501.

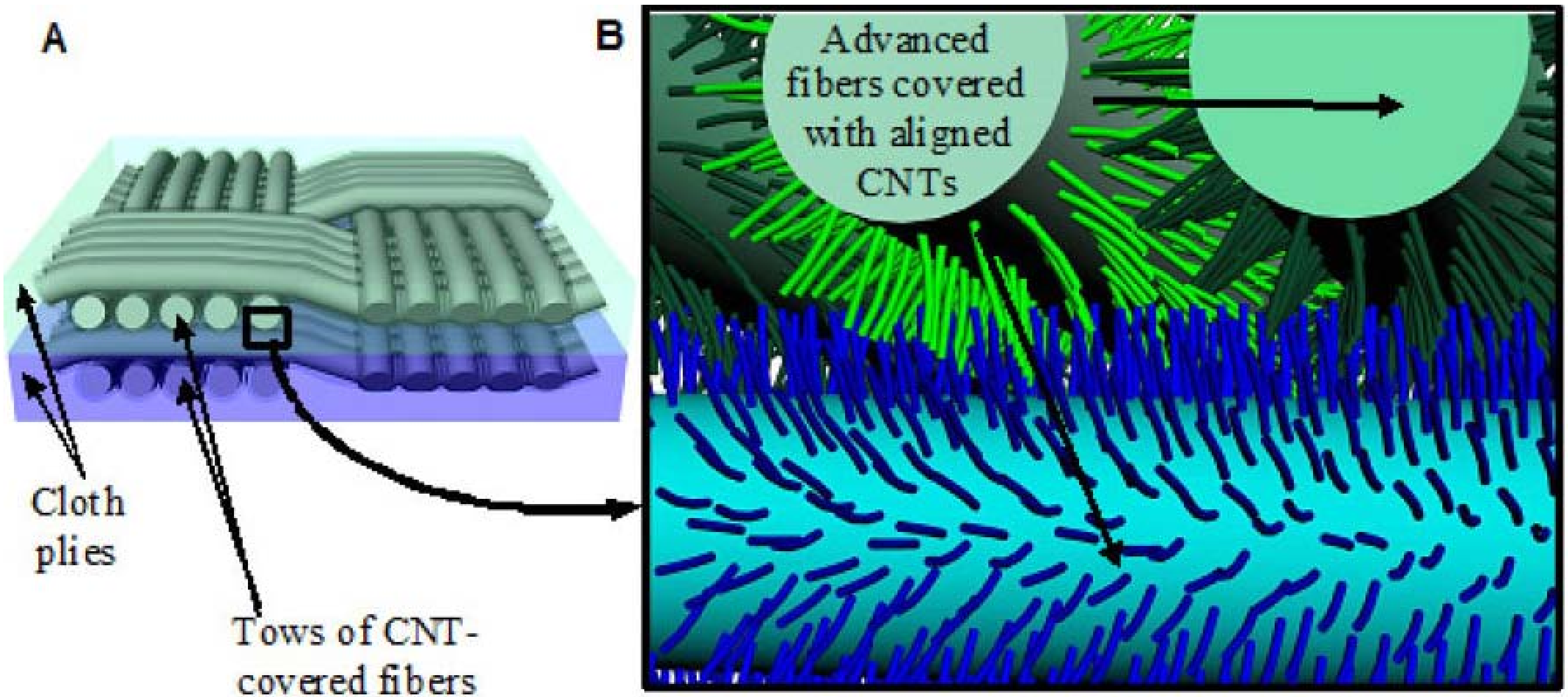
"Fuzzy fibers": CNTs as components in hierarchical materials



MIT - Wardle Group (e.g., Nanotechnology **20 (2009) 155702**)

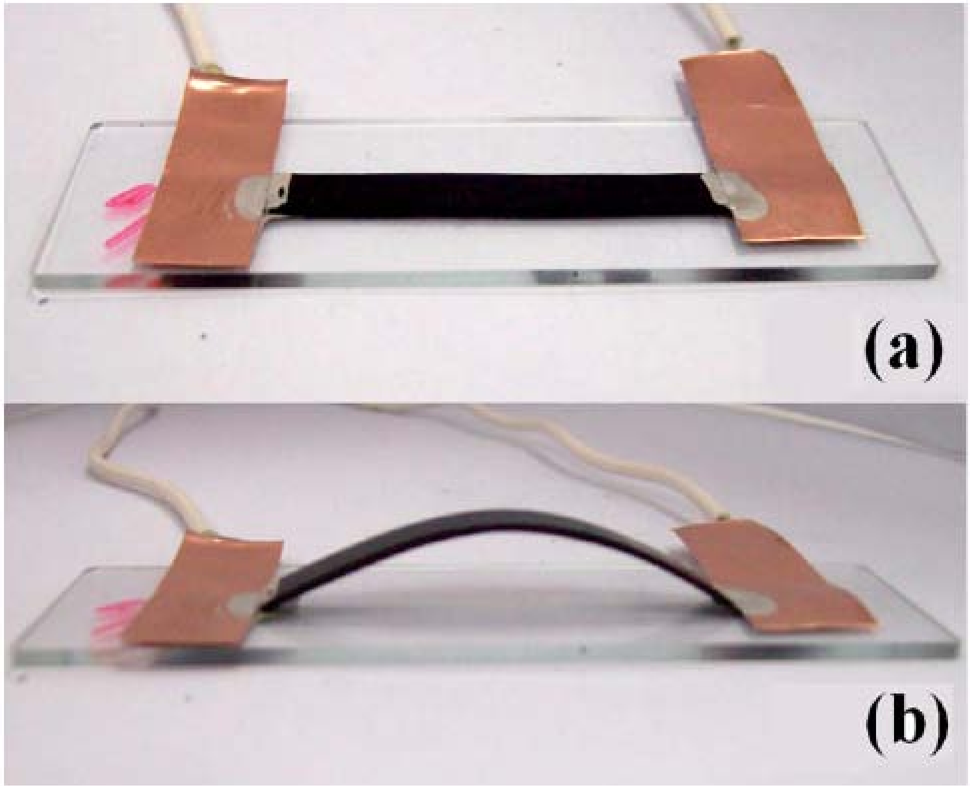
“Fuzzy fibers”: CNTs as components in hierarchical materials

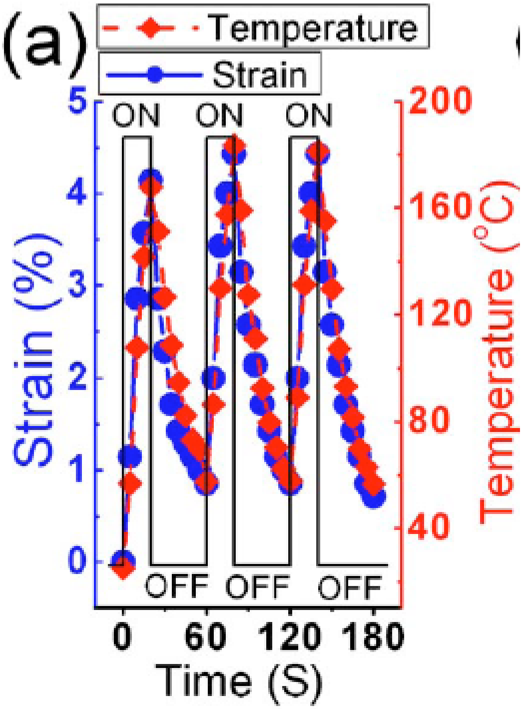
Increased interlaminar shear stiffness (+69 %)
Increased toughness
Increased electrical conductivity (possibility for structure health monitoring)



MIT - Wardle Group (e.g., Nanotechnology **20 (2009) 155702**)

Active materials





CNTs have been dispersed in polymeric matrices not only to improve mechanical/electrical/thermal properties, but also to create an active material such as artificial muscle.

L.Z. Chen et al. Appl. Phys. Lett. 2008;92:263104.

CNTs as *useful* materals?

Approaches:

- Use an individual CNT for a specialty nanotechnology application
  - E.g., the tip of an atomic force microscope
- Use CNTs to improve the properties of another material
  - E.g., fibrous reinforcement in polymer
- Combine CNTs into stand-alone (e.g., structural) materials
  - E.g., CNT yarns/fibers

CNT Yarns

Cotton, wool, … CNTs?

- **Yarns of strength up to 460 MPa from MWCNTs** (lower than it could be because CNT strength is not the limiting factor)
- **No loss in strength/flexibility over wide ranges of T (~ 100 – 700 K)**
- **Resistant to abrasion and sharp bending**
- **Excellent toughness (20 J/g versus 33 J/g for Kevlar, though using SWCNTs and polymer can beat this by an order of magnitude)**

Zhang, et al. *Science* **306**, 1358 (2004);

CNT Yarns

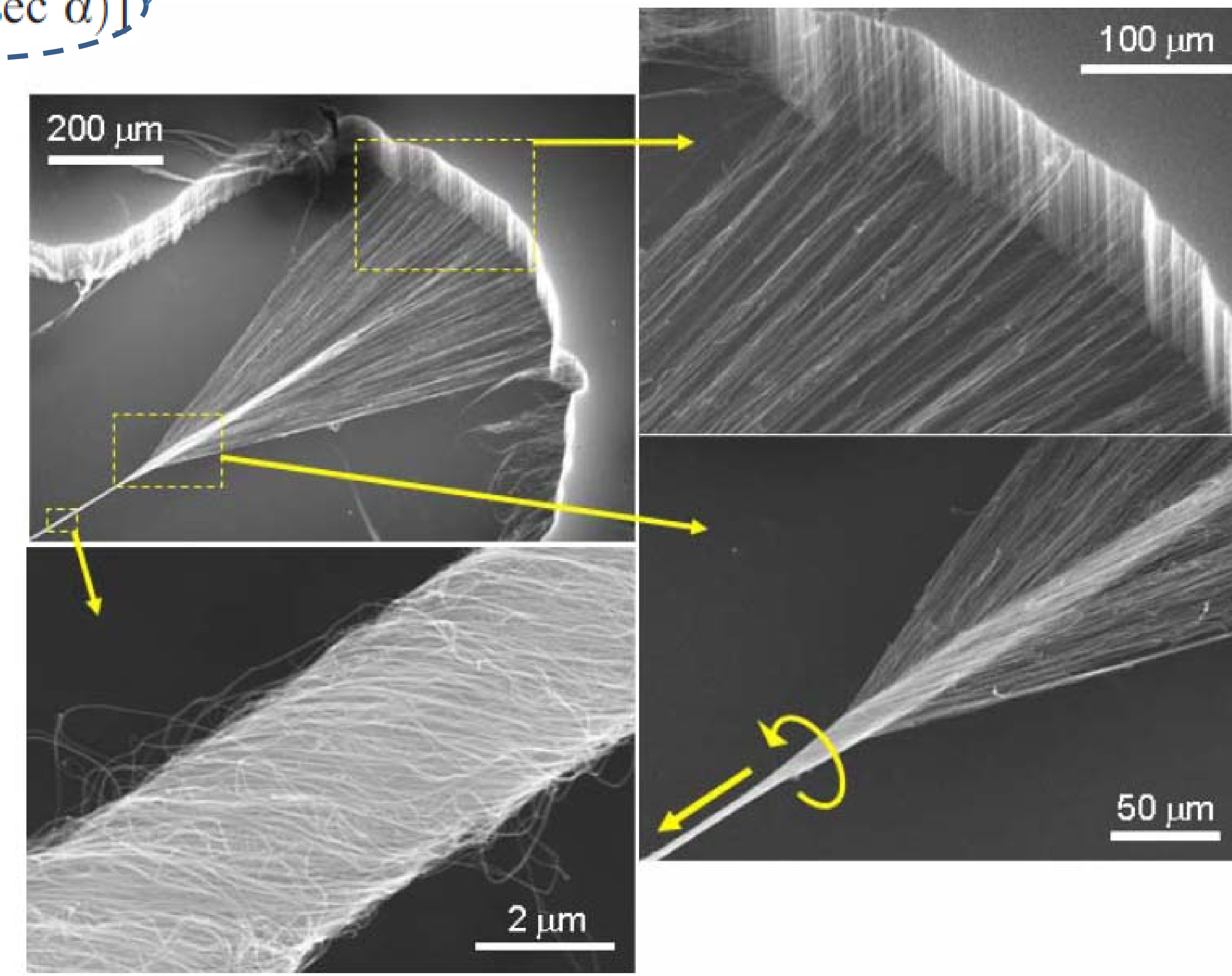
Strength decrease due to twisting

Transfer from tensile to transverse force, holding yarn together

$$\sigma_y/\sigma_f \approx (\cos^2 \alpha)[1 - (k \operatorname{cosec} \alpha)]$$

$$k = (dQ/\mu)^{1/2}/3L$$

α = helix angle
d = fiber diameter
L = fiber length
Q = migration length
σ_y = yarn tensile strength
σ_f = fiber tensile strength



Zhang, et al. *Science* **306**, 1358 (2004);

CNT Yarns

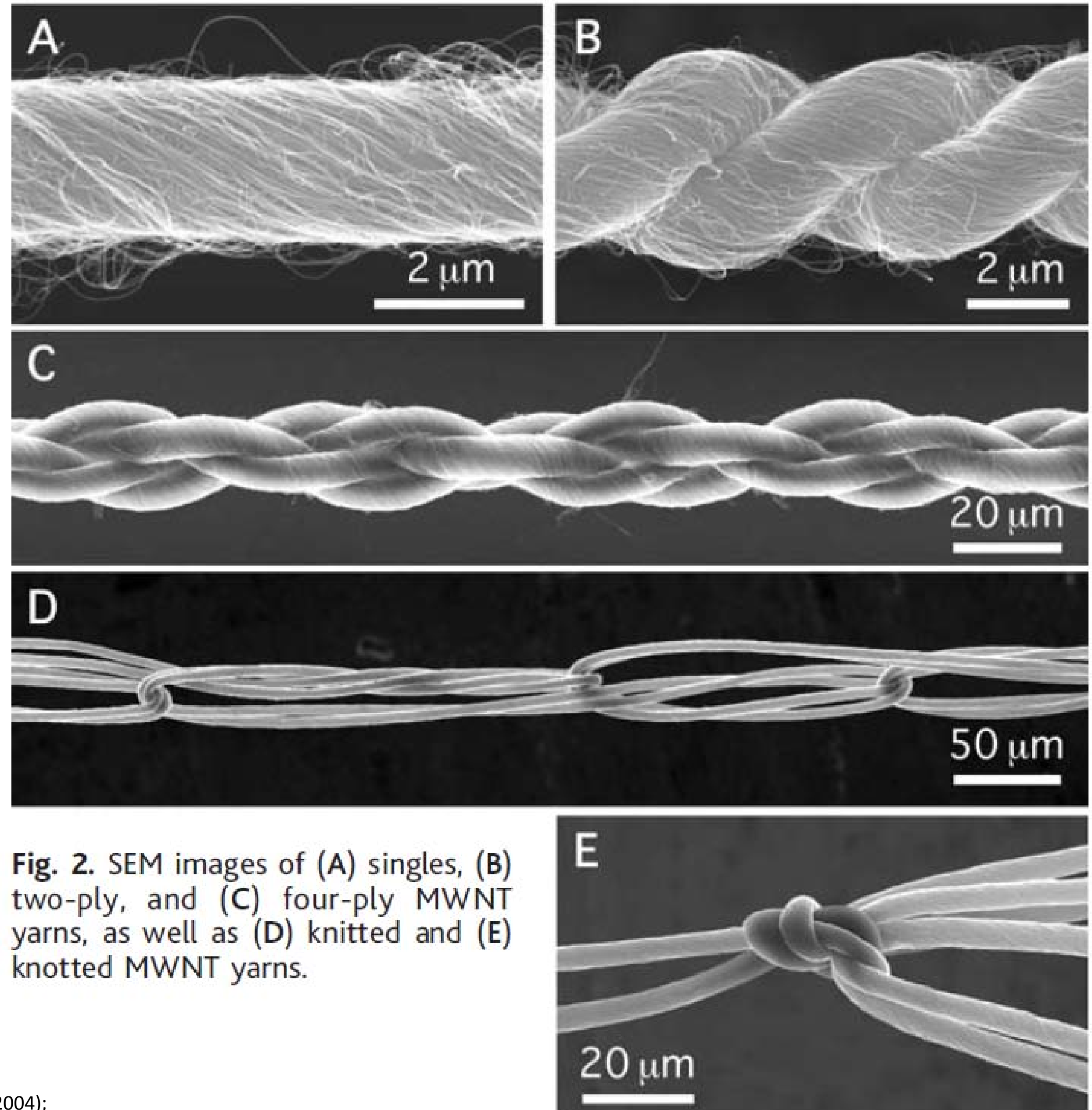
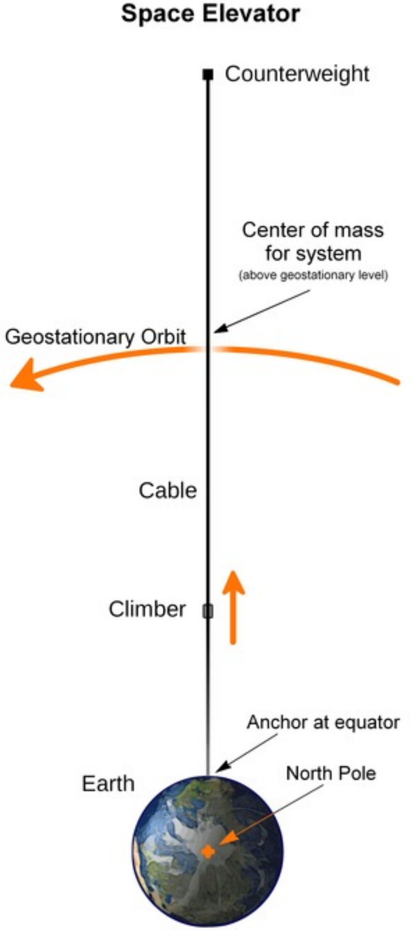
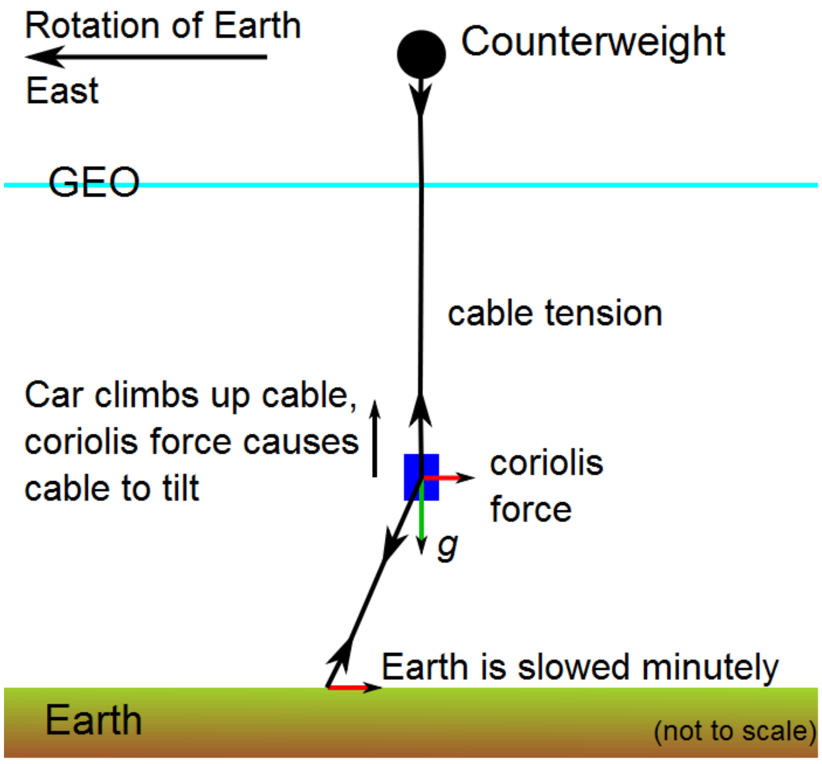


Fig. 2. SEM images of (**A**) singles, (**B**) two-ply, and (**C**) four-ply MWNT yarns, as well as (**D**) knitted and (**E**) knotted MWNT yarns.

Zhang, et al. *Science* **306**, 1358 (2004);

Space elevators





- **Maximum stress will be at geosynchronous orbit**

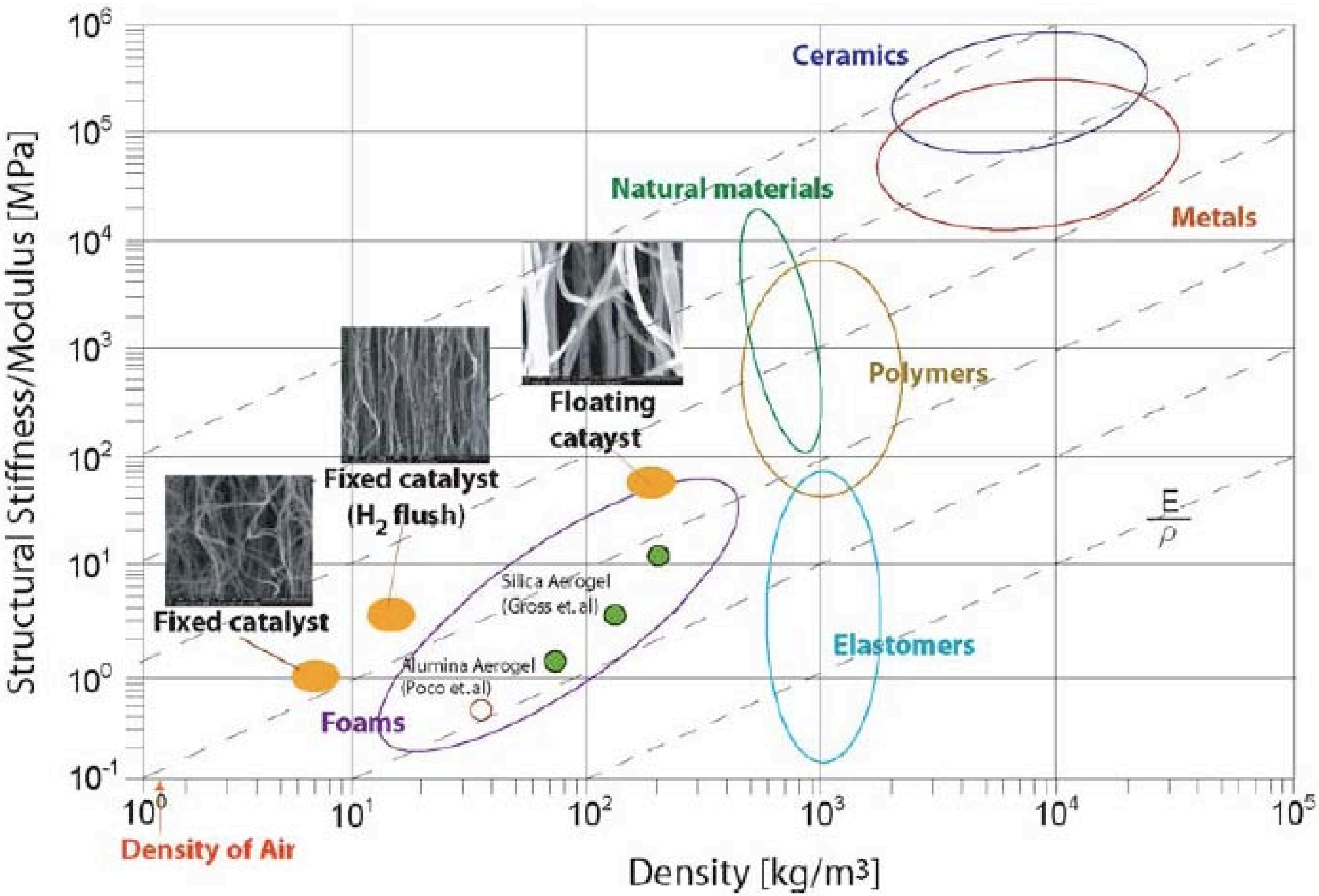
- **Need high strength-to-weight ratio (only graphitic materials are known to meet the requirements)**

Images from Wikipedia

CNTs as components in bulk materials: arrays/forests of CNTs

Jordan R. Raney
Engineering and Applied Science
California Institute of Technology
Oct. 26, 2011

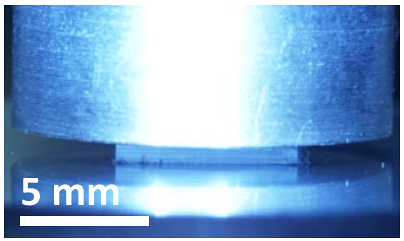
Aligned CNTs as energy dissipative materials

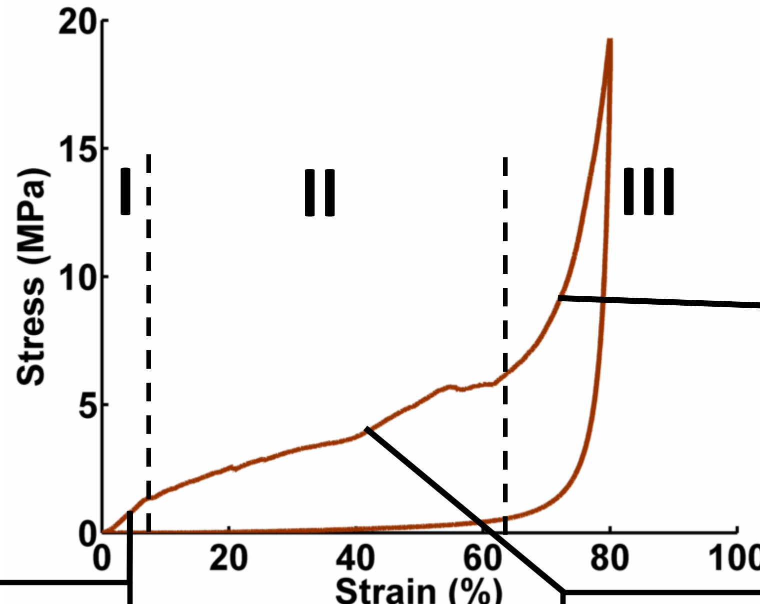


O. Yaglioglu, MIT PhD Thesis 2007.

Quasistatic mechanical response

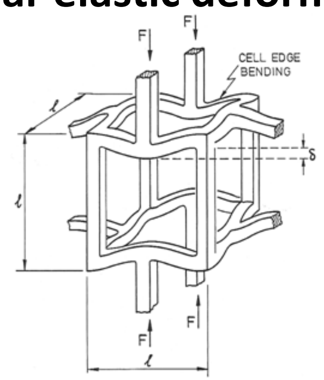
Aligned CNTs ≈ open cell foams



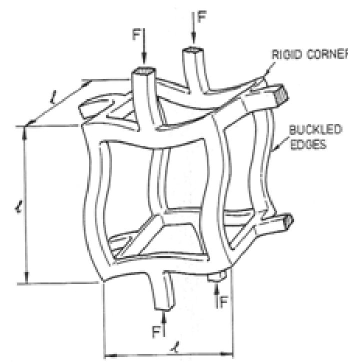


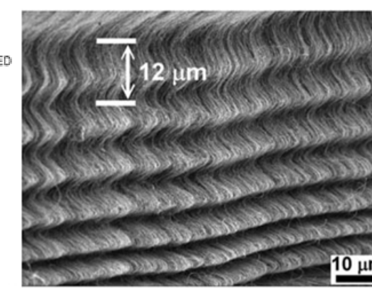
III. Densification

I. Linear elastic deformation



II. Plateau (buckling)





A.Cao et al., Science 2005;310:1307. Gibson & Ashby, Cellular Solids 1988. A. Misra et al., Adv. Mater. 2009;21:334.

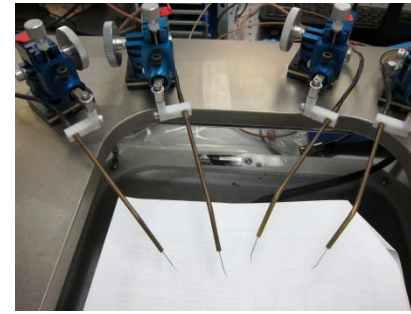
Experimental setup for *in situ* optical and electrical measurements

Optics up to 100X

↓

Strain localization

- 1 μm displacement resolution
- Up to 3000 N
- Tension or compression



4 point electric probe station

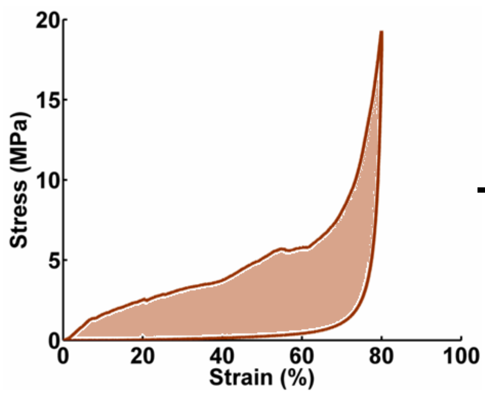
↓

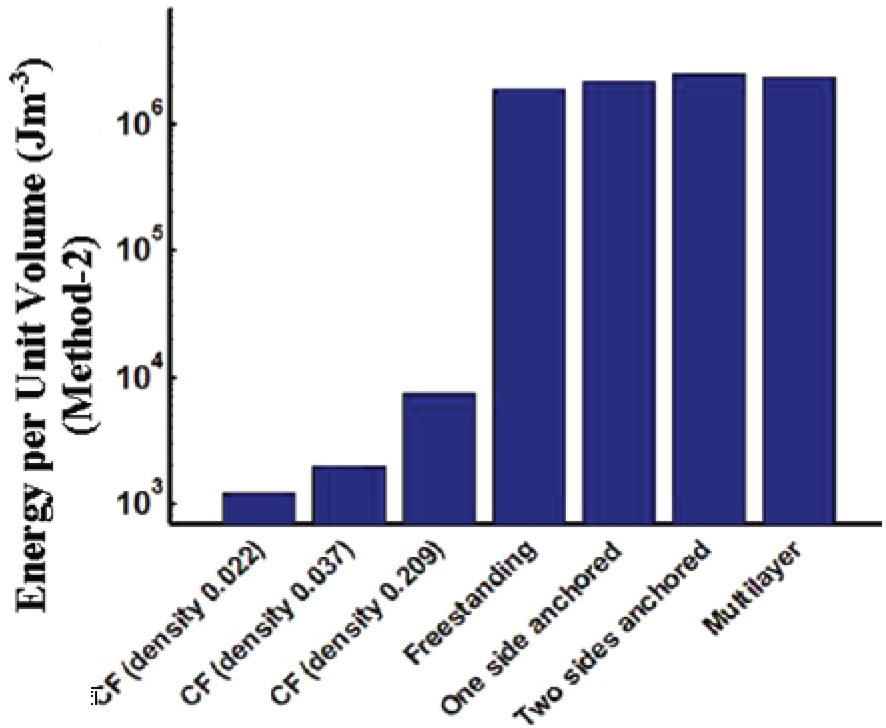
Electromechanical properties

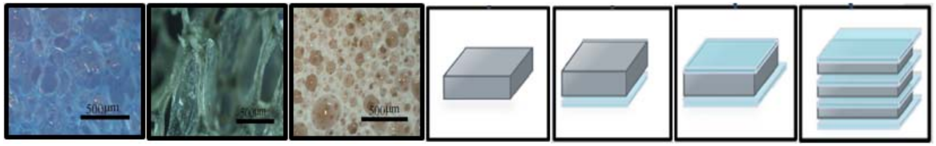
Capable of testing samples in vacuum as well as in liquid

Quasistatic energy dissipation: comparison with commercial foams

$\rho_{CNTs} = 0.15 – 0.3\ g/cm^3$



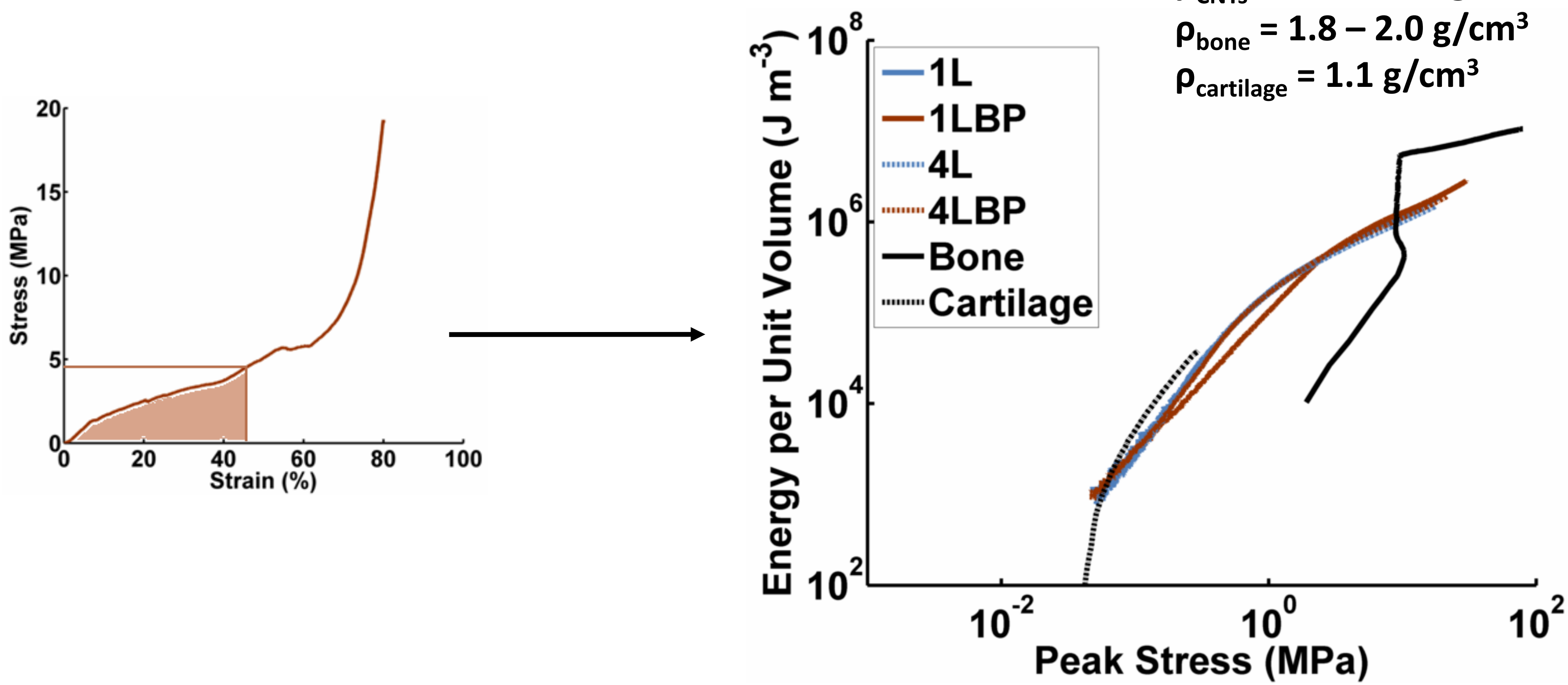




CNT-based architectures absorb approximately 200 times the energy of commercial foams of the same density

A. Misra et al., ACS Nano 2011; in press.

Quasistatic energy absorption: comparison with biomaterials



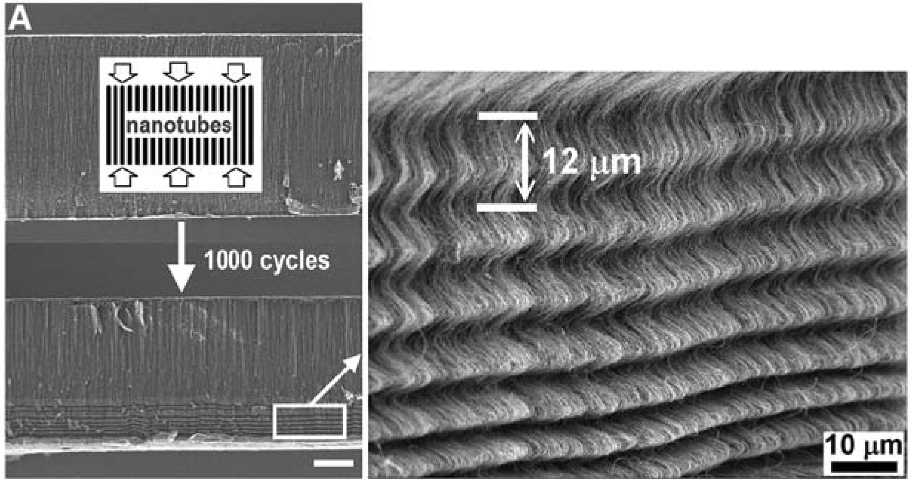
ρ_{CNTs} = 0.15 – 0.3 g/cm^3
ρ_{bone} = 1.8 – 2.0 g/cm^3
$\rho_{cartilage}$ = 1.1 g/cm^3

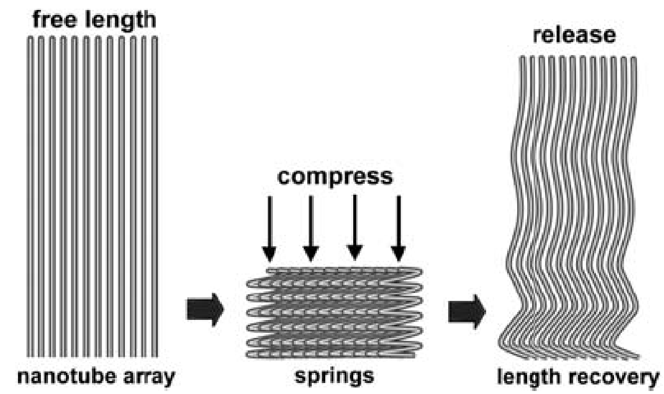
- CNT-based architectures absorb similar amounts of energy as bone and cartilage during compressive loading
- CNT-based architectures have much lower density

A. Misra et al., ACS Nano 2011; in press.

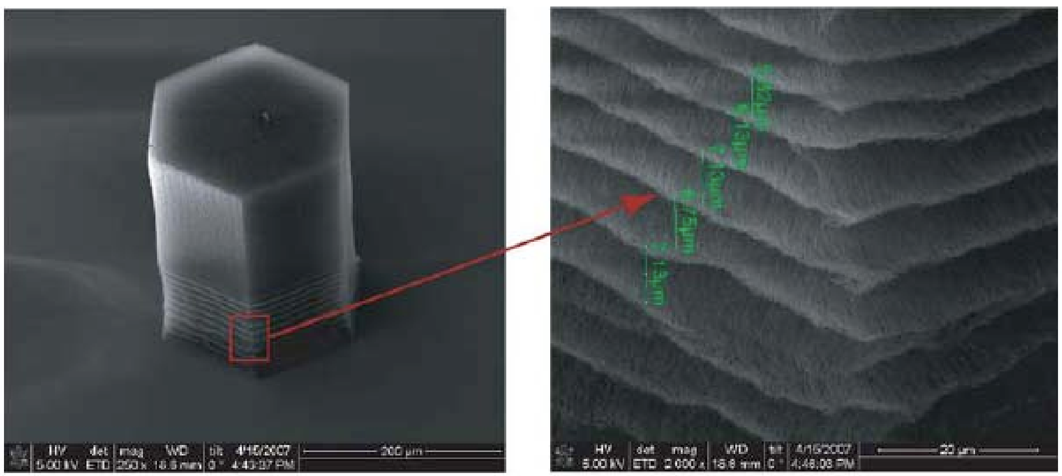
Quasistatic mechanical response: localization

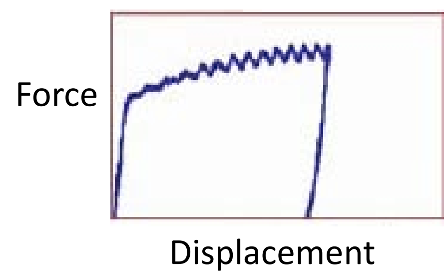
MACROSCALE





MICROSCALE

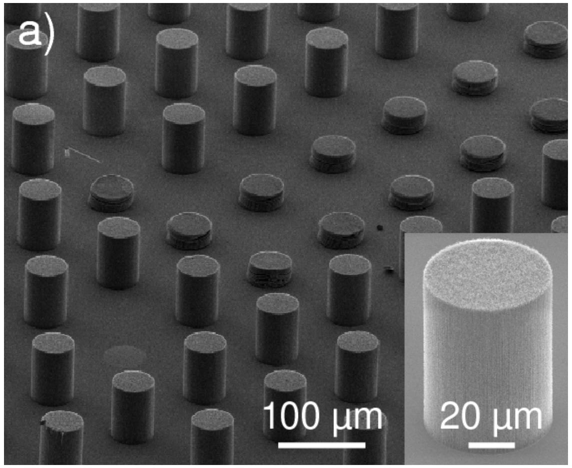


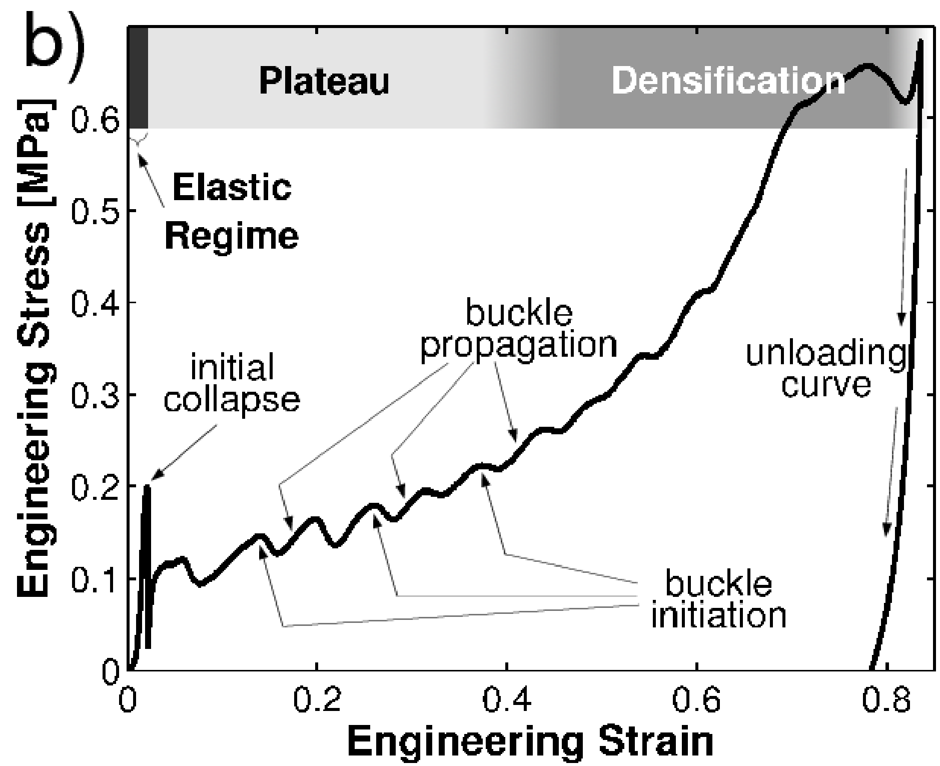


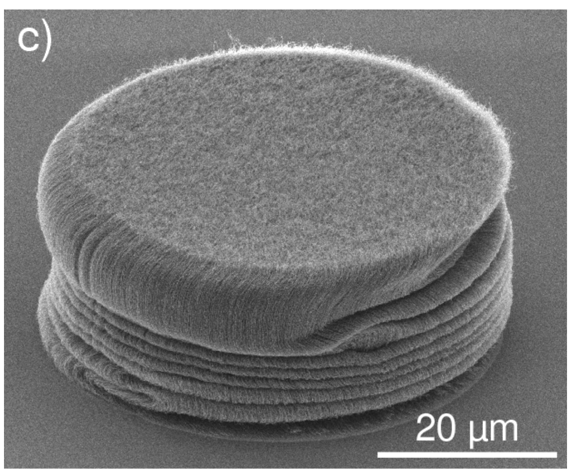
Strain localization is a result of a gradient in structural properties, including CNT diameter, density, and tortuosity

A.Cao et al., Science 2005;310:1307. O. Yaglioglu, MIT PhD Thesis 2007.

Characterization of buckling

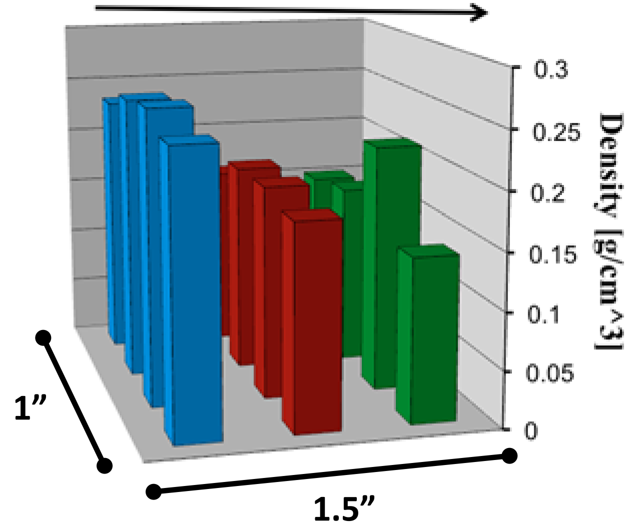


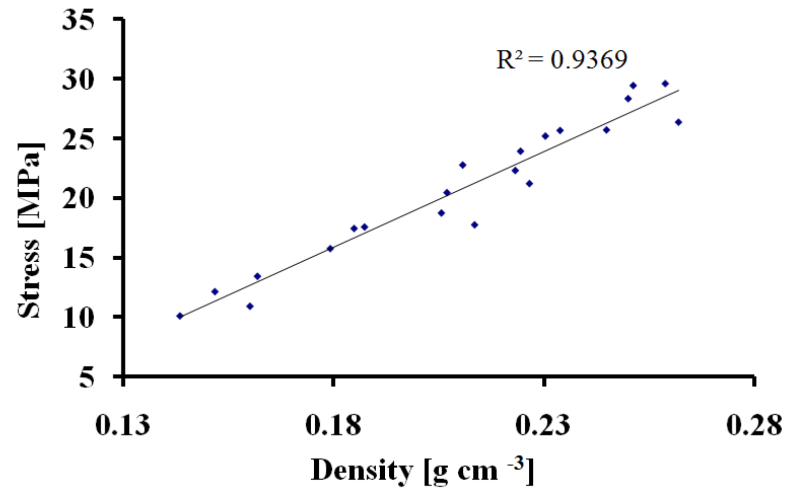


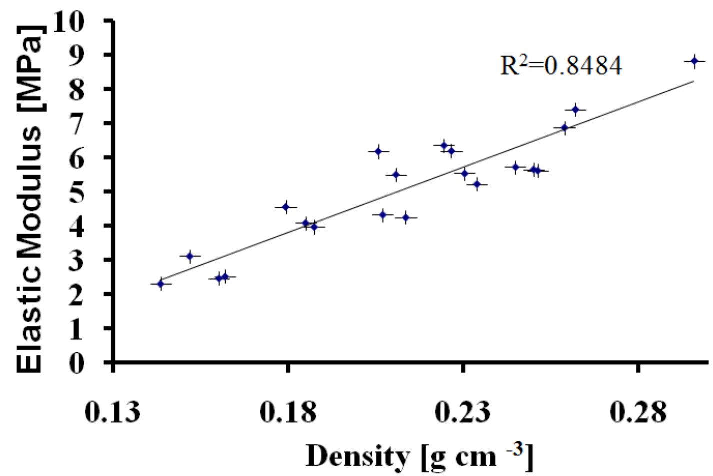


S.B. Hutchens et al., Adv. Mater. 2010;20:2338.

Variation of density and its effect on mechanics







A. Misra et al., Nanotechnology 2011;22:425705.

CNTs as components in bulk materials: modification of CNT arrays and creation of multilayer materials

Jordan R. Raney

Engineering and Applied Science

California Institute of Technology

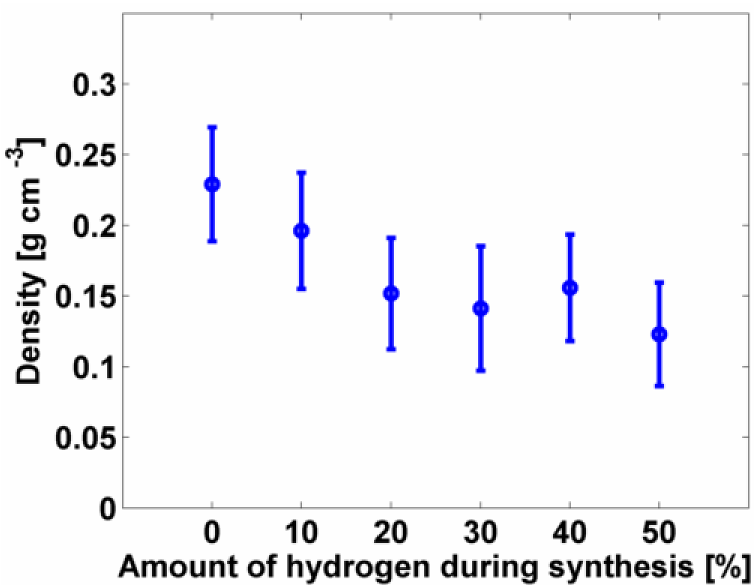
Oct. 26, 2011

Control of density and mechanical properties

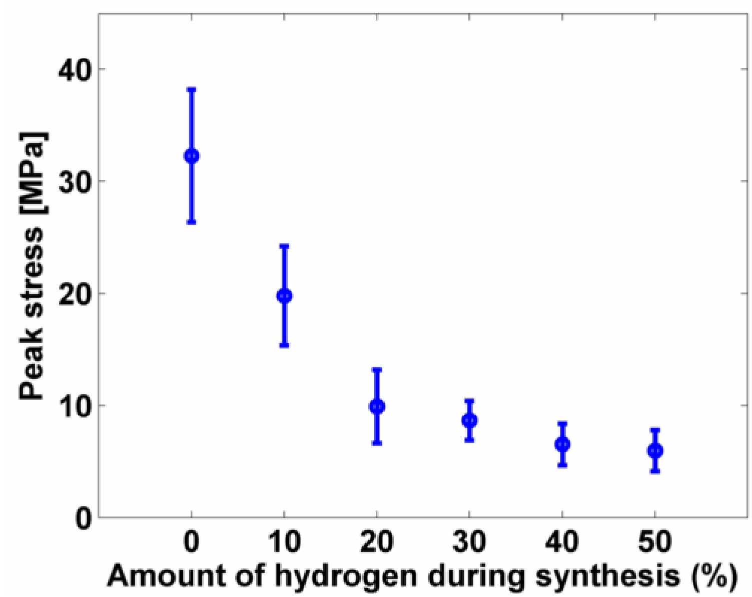
Density can be varied with:

1) **Substrate position during growth**
2) **Control of reactor conditions**

Effect of hydrogen on density

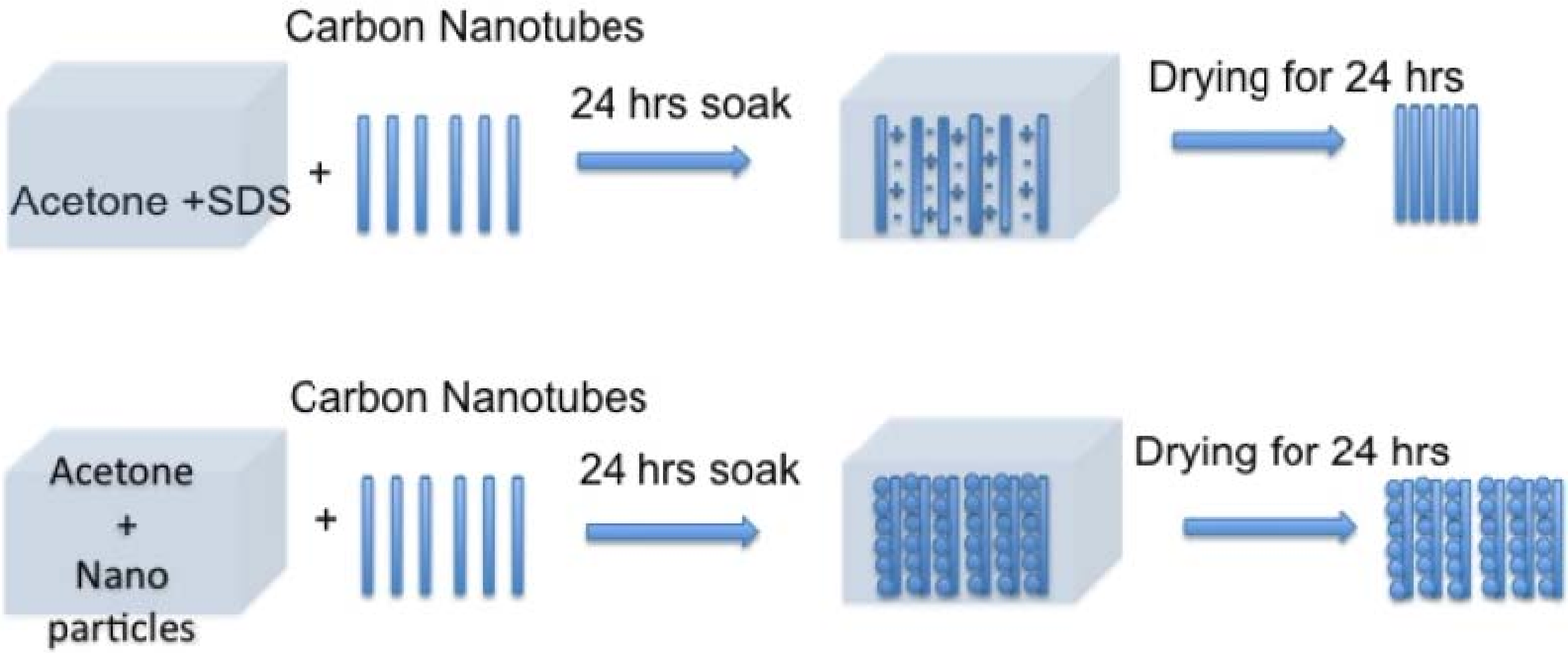


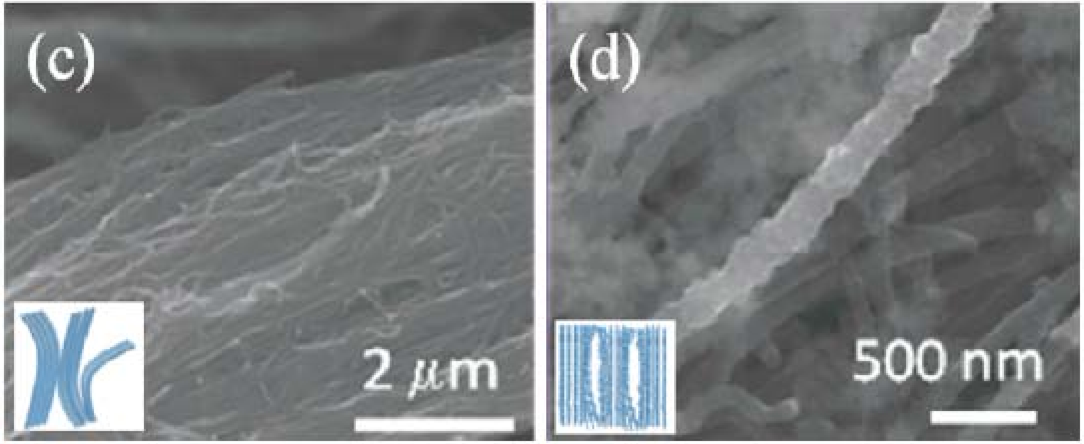
Stress at compressive strain of 0.8



J.R. Raney et al., Carbon 2011;49:3631.

Modification of CNTs using fluid-based techniques





A. Misra et al., Nanotechnology 2011;22:425705.

Deposition of SnO_2 particles in graphitic materials

Graphitic matrix

Sonicate in Aqueous $SnCl_2$ (~ 2 days) →

Suspension

↓ Ammonia vapor | Stirring, hydrolysis of $SnCl_2$

Precipitation of Sn(OH)Cl

← 1.Drying 2.Heat

SnO_2 particles in a graphitic matrix

Note: all steps proceed regardless of presence of CNTs

H.-L. Zhang & D.E. Morse, J. Mater. Chem. 2009;19:9006.

Deposition of MnO_2 particles in graphitic materials

Graphitic matrix

Sonicate in Aqueous $KMnO_4$ (~2-4 days)

MnO_4^- precipitates to MnO_2 with CNTs acting as reducing agents

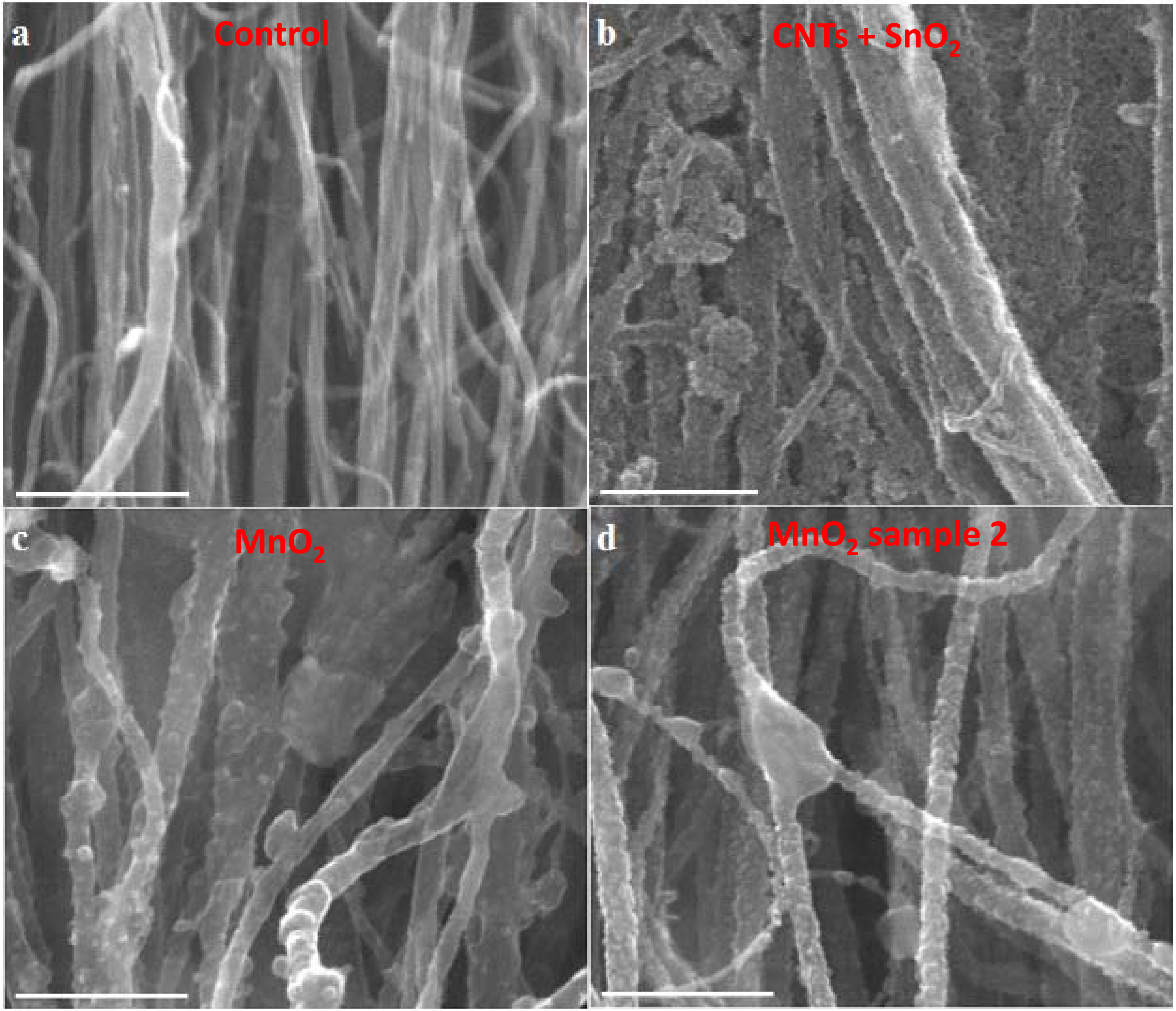
At CNT surface+:

$$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$$

MnO$_2$ synthesis at a decent rate can only take place at the CNT surfaces whereas SnO$_2$ synthesis takes place wherever the SnCl$_2$ precursor is found (i.e., everywhere in the CNT array interstices)

+ S.B. Ma et al., Carbon 2007;45:375.

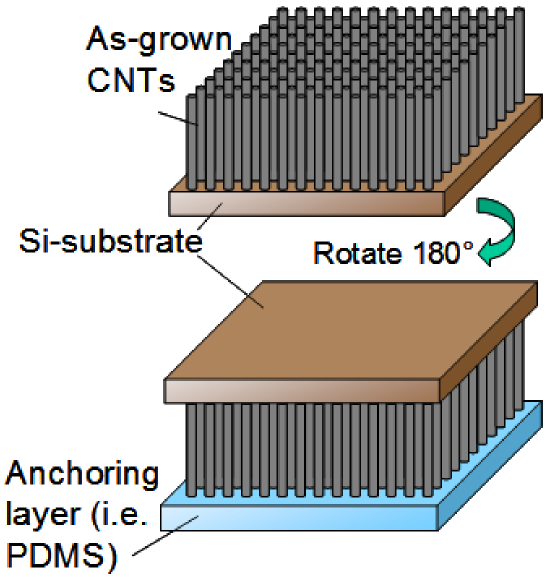
SEM images of CNTs with deposited particles



J.R. Raney et al., Adv. Func. Mater. 2011; In review.

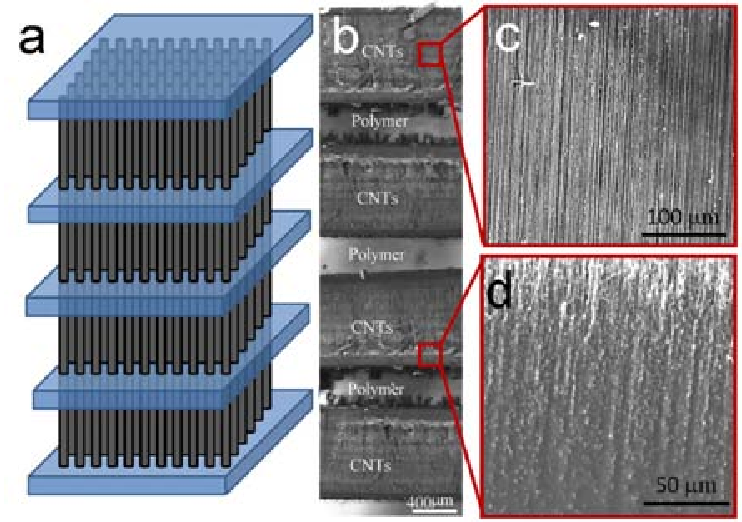
Construction of multilayer structures

Anchoring CNT arrays in polymer

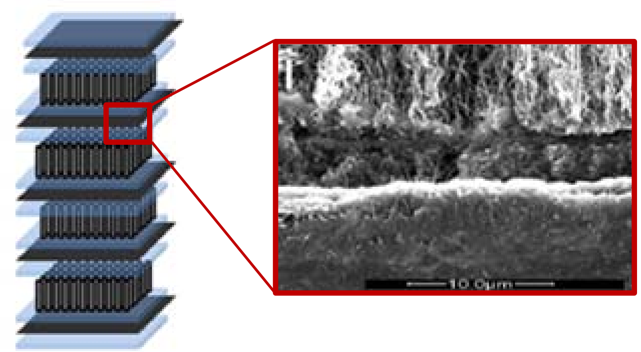


The PDMS layer improves structural stability

Connect multiple VACNT arrays with interlayers



Optionally, insert buckypaper to provide electrical conductivity across layers



E.B. Sansom et al., Nanotechnology 2008;19:035302.
A. Misra et al., Adv. Mater. 2009;21:334.
A. Misra et al., ACS Nano 2011; In press.