17: **Purification, functionalization, and separation of nanostructures**

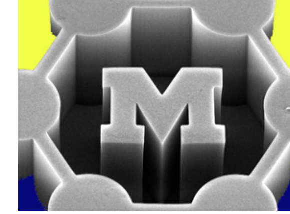
March 24, 2010

John Hart
ajohnh@umich.edu
http://www.umich.edu/~ajohnh

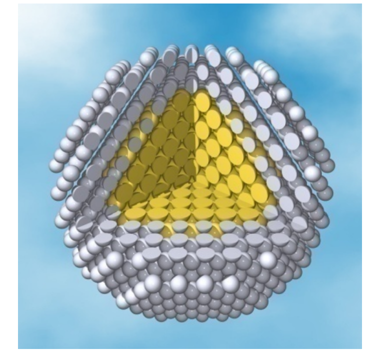
Announcements

- Project proposals due no later than Friday
  - Please give me printed copy, and register at http://bit.ly/9RWlEx
- Peer review on project proposals instead of video review
  - Due Fri Apr/2, but please do asap
  - Honor system, 5 reviews per person and per proposal
  - 2.5% grade (0.5% per review), no credit if late
  - Review sheet and updated project description to be posted later today
- PSET4 will be (relatively) brief, and will be a team assignment, due M Apr/12
- Project is 50% of course grade!
  - Start now and make a schedule
  - Don't get hung up on ideas
  - Divide and conquer
  - Meetings to be scheduled late next week

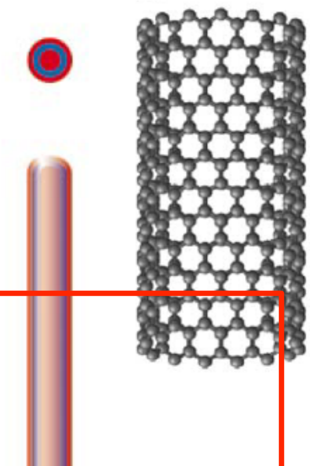
Nanomanufacturing: our mission



- Understand the fundamental properties of nanostructures, e.g., nanoparticles, nanotubes, and nanowires



- Understand how nanostructures interact with one another and their surroundings
- Understand how to make and assemble nanostructures; how to control their size, structure, and placement



- Understand how the properties of nanostructures scale based on their assembly and interactions
- Combine our knowledge to design new devices, materials, and manufacturing processes

7 lectures to go

IV: Assembly of nanostructures; property scaling		
18	Mar/24 (W)	Functionalization and separation
	Mar/26 (F)	-
19	Mar/29 (M)	Self-assembly of micelles and block copolymers
20	Mar/31 (W)	Monolayer and layer-by-layer assembly
21	Apr/5 (M)	Self-assembly using capillary forces
22	Apr/7 (W)	Self-assembly using applied fields and biomolecular interactions
23	Apr/12 (M)	Manipulation and joining methods
25	Apr/14 (W)	Percolation and network properties
	Apr/16 (F)	-
26	Apr/19 (M)	*No class*; project presentations in the evening
	Apr/20 (Tu)	Final report due by 5PM
	Apr/28 (W)	GCC examination, 10.30a-1.30p

What comes after bulk synthesis of nanostructures?

- **Purification**
  - Remove impurities such as undesired byproducts, unreacted catalyst
  - Anneal to improve crystallinity
  - Etch to control size

- **Stabilization and functionalization**
  - Attach/associate molecules with nanomaterial surfaces to facilitate interaction with other materials and phases

- **Separation/sorting**
  - Partition elements by size, shape, and/or electronic structure

- **Process order is generally interchangeable** based on application; however, it's useful to have structures isolated (dispersed) in solution before etching or sorting

- **Functionalization** is often a means of
  - dispersion (exfoliation/isolation), and
  - interfacing structures to one another, or to other materials

Today's readings

Nominal: (ctools)

- Athakul et al., "Size fractionation of metal nanoparticles by membrane filtration"
- Arnold et al., "Sorting carbon nanotubes by electronic structure using density differentiation"
- Ho et al., "Free flow electrophoresis for separation of CdTe nanoparticles"

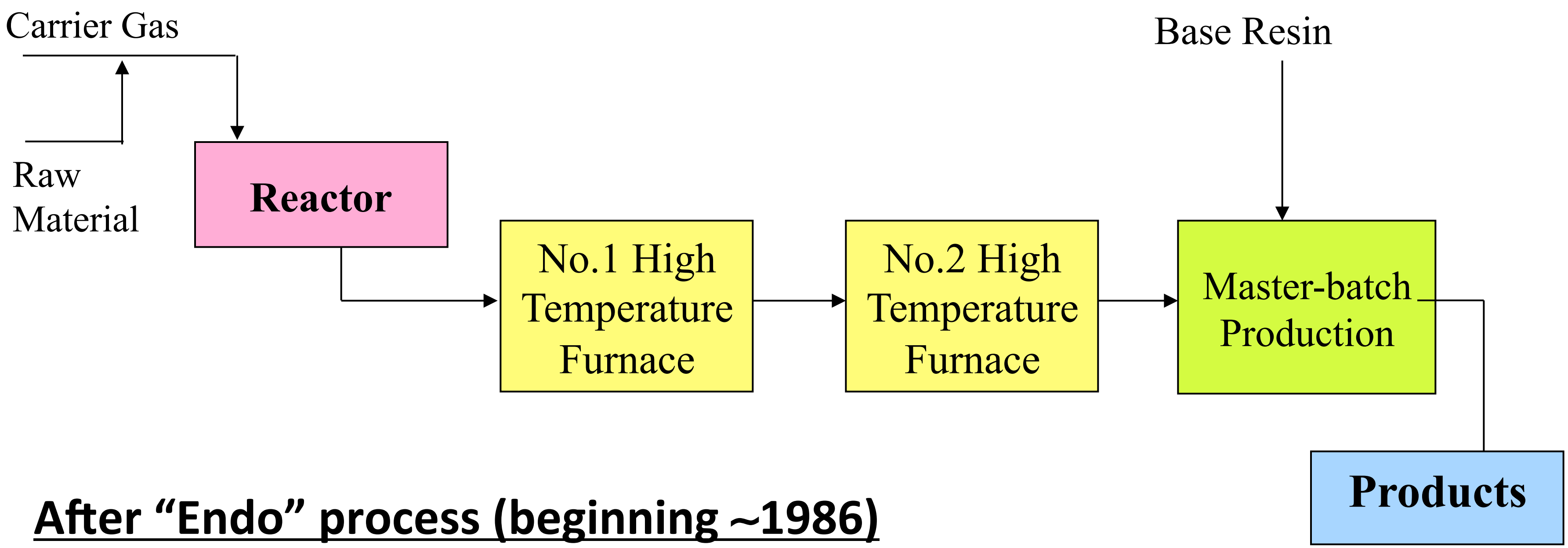
For reference: (ctools)

- Hirsch, "Functionalization of single-walled carbon nanotubes"
- Sharma et al., "Shape separation of gold nanorods using centrifugation"
- Williams, "Etch rates for micromachining processing"

Large-scale CNT manufacturing

only 100g!
(courtesy NCT Japan)

Large scale CNT manufacturing process: growth, annealing, mixing



<u>After "Endo" process (beginning ~1986)</u>

- Floating catalyst CVD
- Followed by two stages of high temperature treatment
- Now > 300 tons/yr
- High purity: 99.5 wt% as carbon
- CNT diameter 40-90 nm

Nano Carbon Technologies (NCT), Japan

High-temperature annealing of CNTs

- Heals defects by atomic rearrangement
- Also evaporates catalyst
- See also “welding” by ion/electron beams (later)

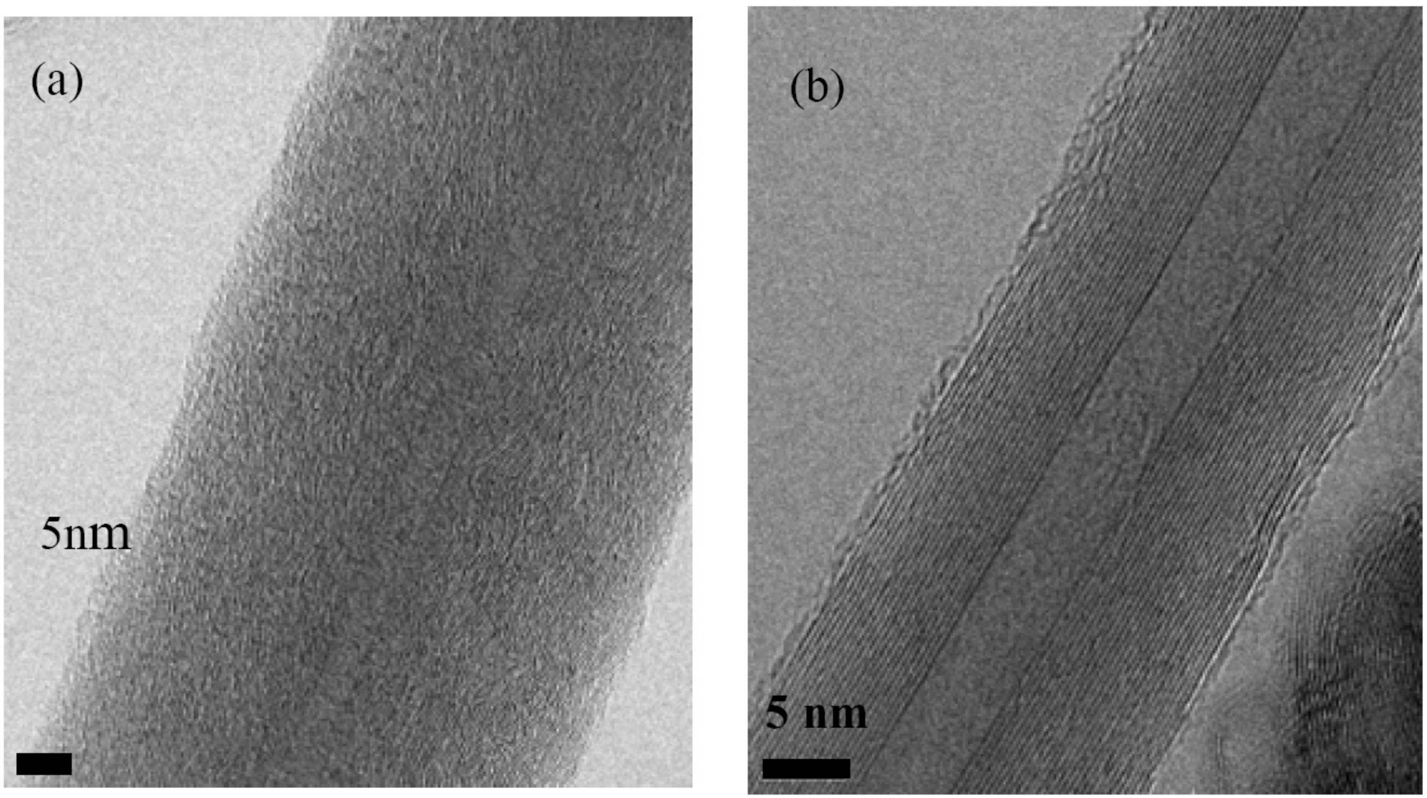


Figure 2.8. HRTEM images of (a) bulk grade and (b) high purity grade MWCNTs (Courtesy of NCT).

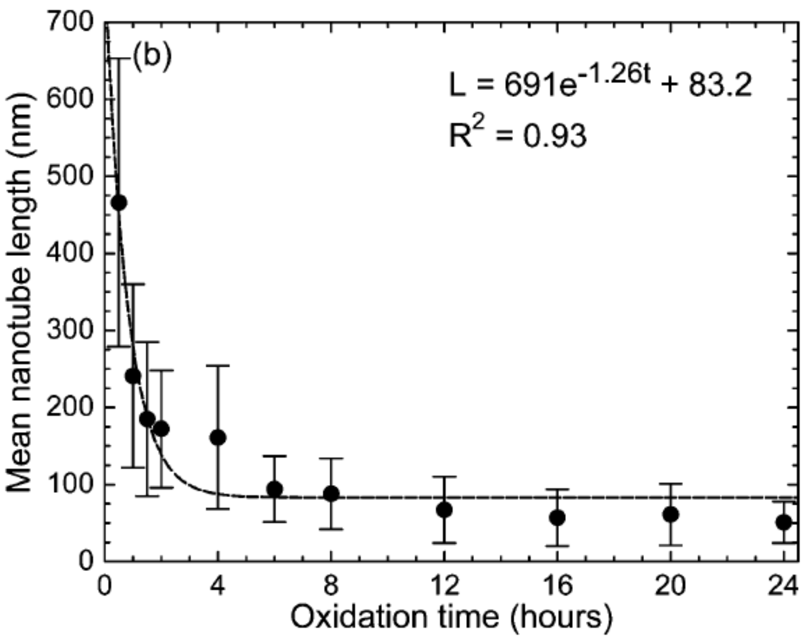
Nano Carbon Technologies (NCT), Japan

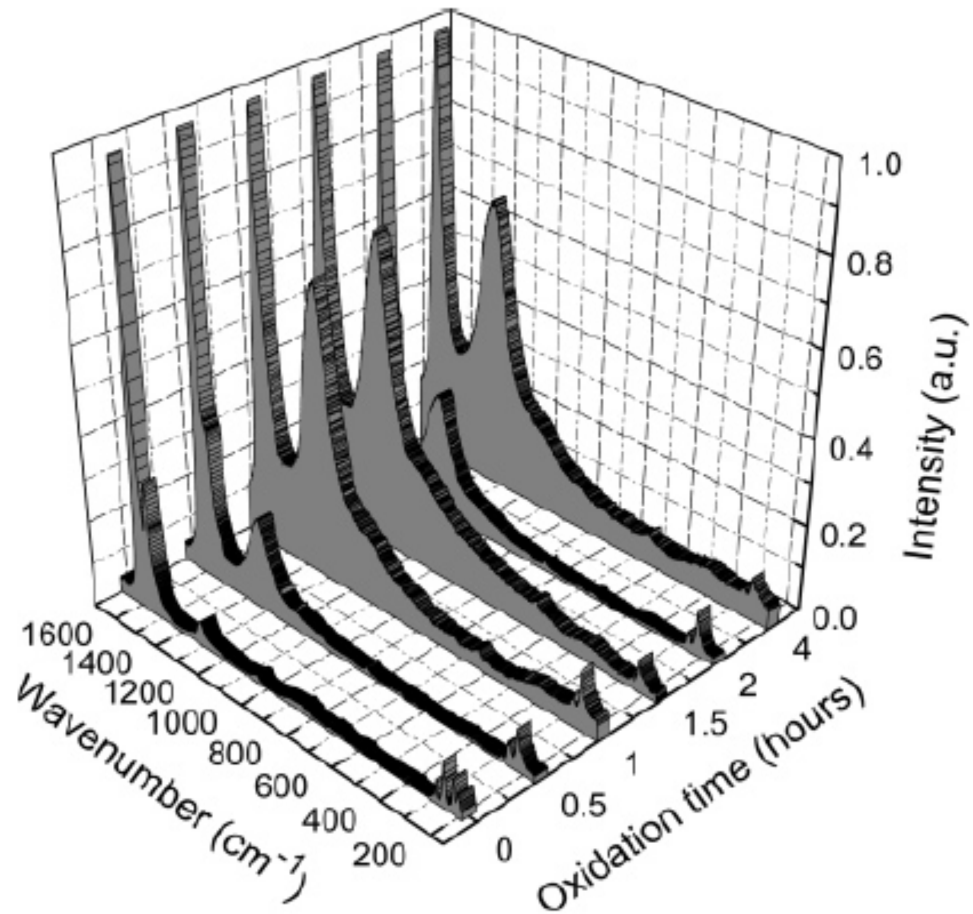
Purification: chemical etching

- Largely similar to "microfabrication etching", just be especially aware of geometry- and crystal-sensitive etch rates
- Some bulk-nano differences are driven by electronic structure
- Consider role of defects in propagating breakage or fast-etch directions → much more important for nanostructures than for thin films!

Example: acid purification (etching) of CNTs

- Mixture of HNO_3, H_2SO_4
- Cuts CNTs at defect sites → exponential length decay
- Acid can also remove catalyst





Forrest et al., *Journal of Physical Chemistry C* 111:10792, 2007.

Example: acid purification (etching) of CNTs

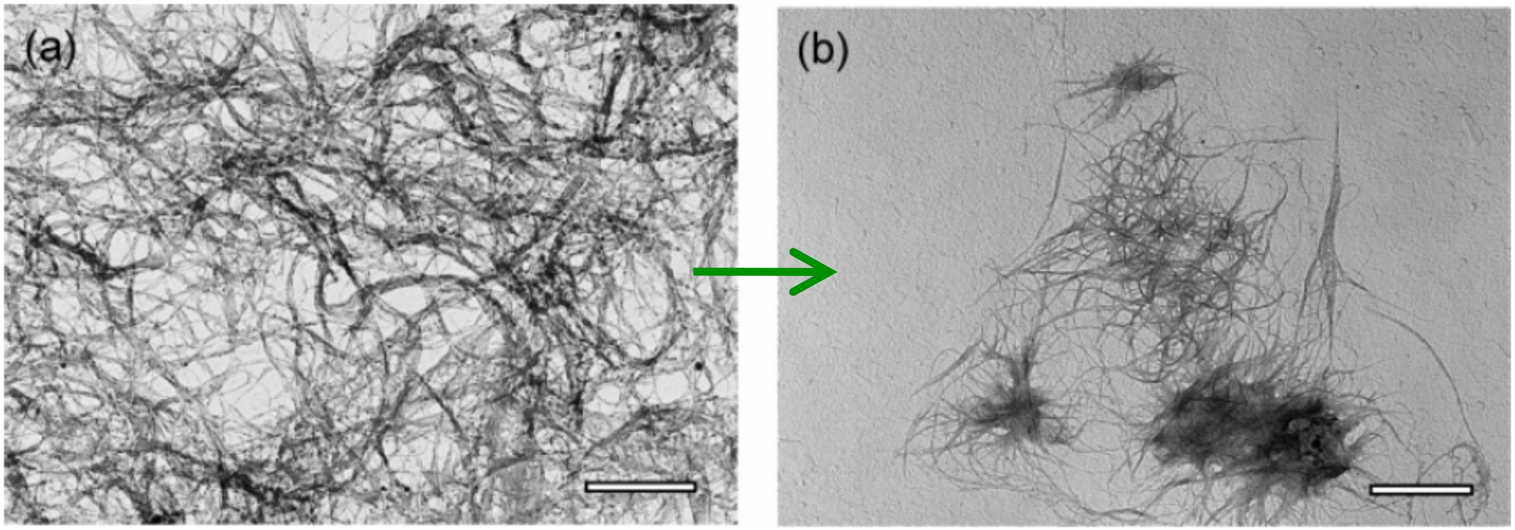
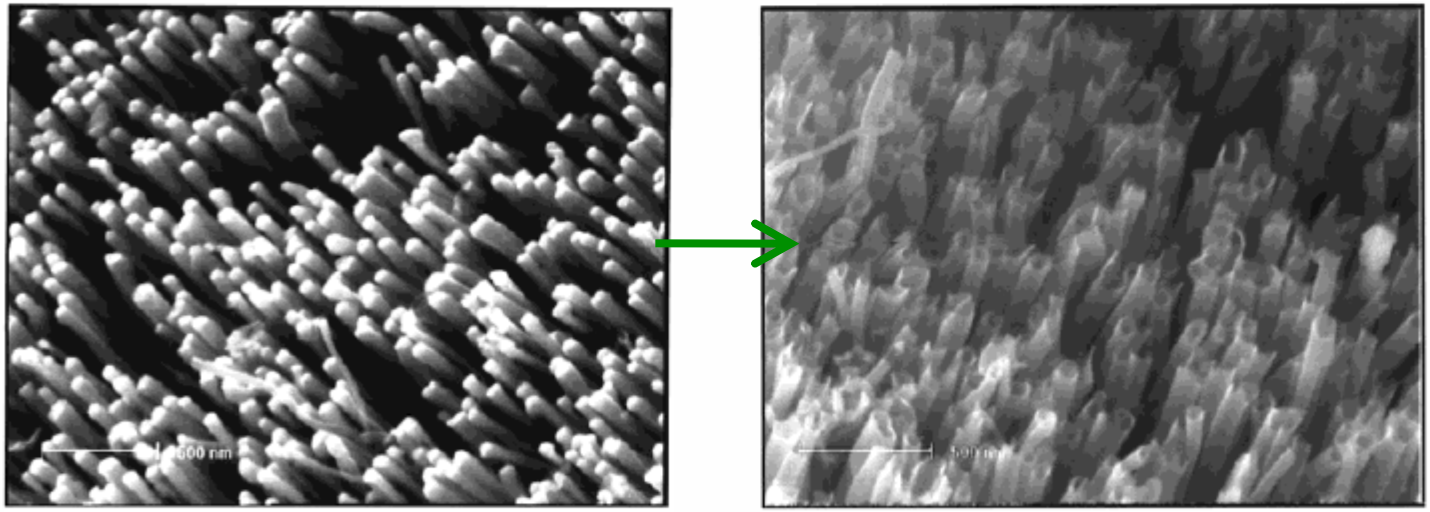


Figure 3. Pristine nanotubes (a) and tubes oxidized for 2 h and treated with Piranha solution to remove amorphous carbon (b). Scale bars = 500 nm.

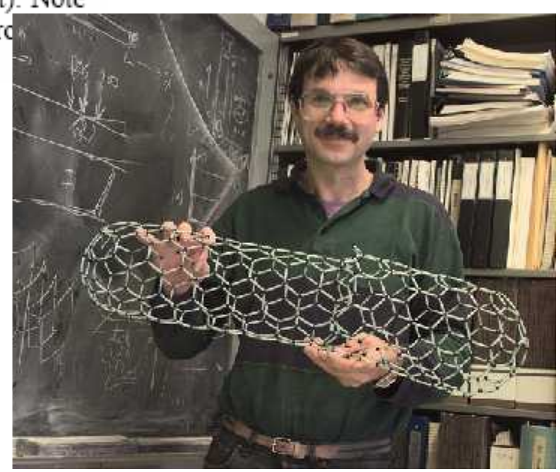
Forrest et al., *Journal of Physical Chemistry C* 111:10792, 2007.

Structural selectivity: opening CNT caps by plasma/oxygen etching

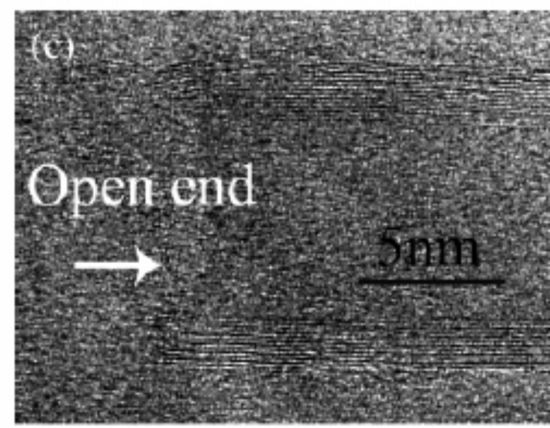


(a) (b)

Figure 3. SEM images of the aligned nanotubes (a) before and (b) after the plasma-treatment for 80 min, followed by a gentle wash with HCl (37%) to remove the Fe catalyst residues, if any (see text). Note that the micrographs shown in (a) and (b) were not taken fro
same spot due to technical difficulties.

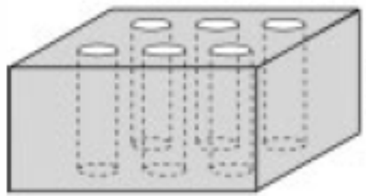


Prof. Alex Zettl, Berkeley



Huang et al., *J. Physical Chemistry B* 106:3543, 2002.

Plasma etching to expose NWs grown within a membrane template



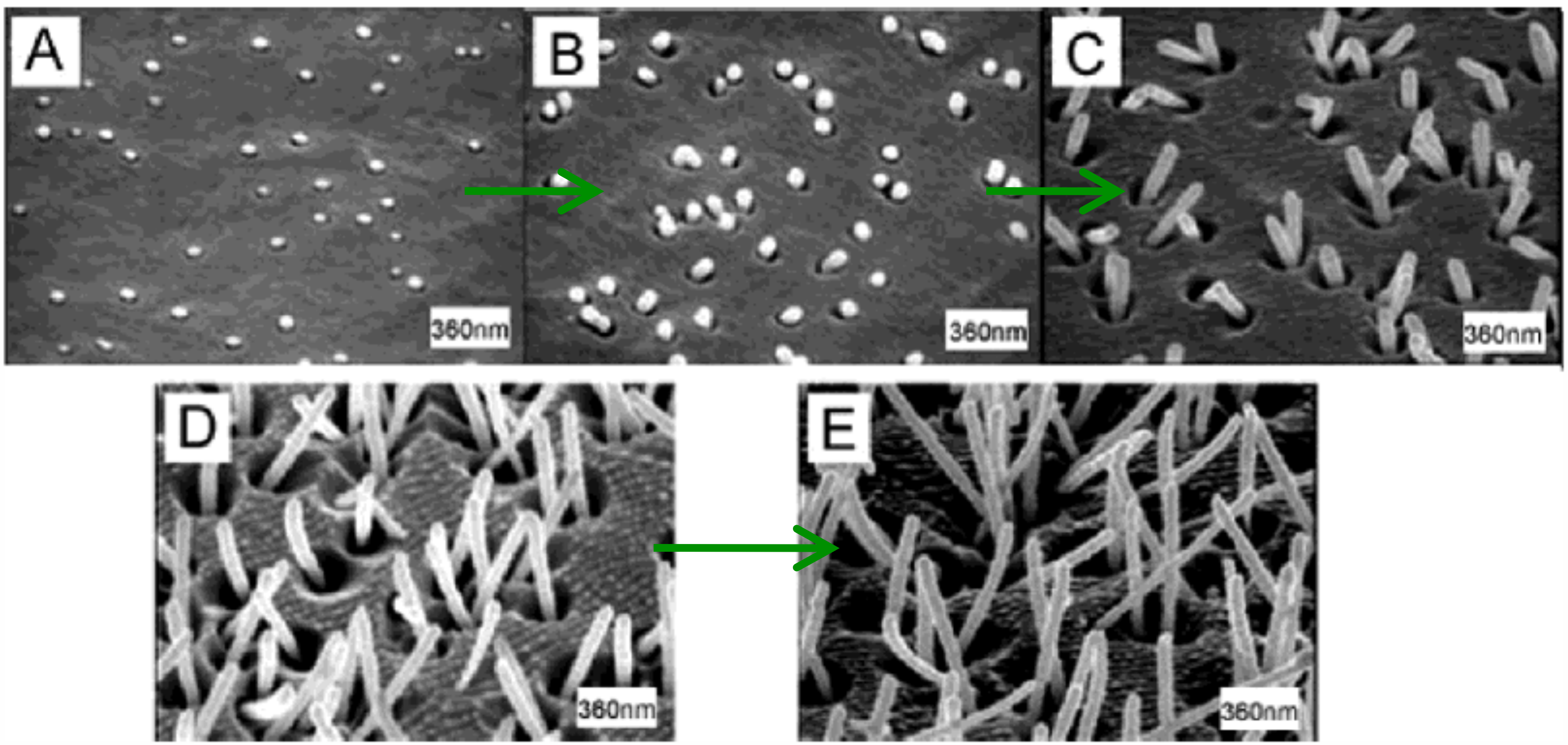


Figure 3. FESEMs of the surfaces of membranes that were O_2-plasma etched for 5 (A), 10 (B), 30 (C), 60 (D) and 120 (E) seconds.

Yu et al., *Nano Letters* 3(6):815, 2003

Etchants ("Williams chart")

Etchant	Etchant Abbrev.	Target Material
Isotropic Silicon Etchant "Trilogy Etch" (126 HNO_3 : 60 H_2O : 5 NH_4F), ~20ºC	Si Iso Etch	Silicon
KOH (30% by weight), 80ºC	KOH	Silicon ODE
10:1 HF (10 H_2O : 1 49% HF), ~20ºC	10:1 HF	Silicon Dioxide
5:1 BHF (5 40% NH_4F : 1 49% HF), ~20ºC	5:1 BHF	Silicon Dioxide
Pad Etch 4 from Ashland (13% NH_4F + 32% HAc + 49% H_2O + 6% propylene glycol + surfactant), ~20ºC	Pad Etch 4	SiO_2, not Al
Phosphoric Acid (85% by weight), 160ºC	Phosphoric	Silicon nitride
Al Etchant Type A from Transene (80% H_3PO_4 + 5% HNO_3 + 5% HAc +10%H_2O), 50ºC	Al Etch A	Aluminum
Titanium wet etchant (20 H_2O : 1 H_2O_2 : 1 HF), ~20ºC	Ti Etch	Titanium
Chromium etchant CR-7 from Cyantek (9% $(NH_4)_2Ce(NO_3)_6$) + 6% $HClO_4$ + H_2O), ~20ºC	CR-7	Chromium
Chromium etchant CR-14 from Cyantek (22% $(NH4)_2Ce(NO3)_6$) + 8% HAc+ H2O), ~20ºC	CR-14	Chromium
Molybdenum etchant (180 H_3PO_4 : 11 HAc : 11 HNO_3 : 150 H_2O), ~20ºC	Moly Etch	Molybdenum
Hydrogen peroxide (30wt% H_2O_2, 70wt% H_2O), 50ºC	H_2O_2 50ºC	Tungsten
Copper etchant type CE-200 from Transene (30% $FeCl_3$ + 3-4% HCl + H_2O), ~20ºC	Cu $FeCl_3$ 200	Copper
Copper etchant APS 100 from Transene (15-20% $(NH_4)_2S_2O_8$ + H_2O), 30ºC	Cu APS 100	Copper
Dilute aqua regia (3 HCl : 1 HNO_3 : 2 H_2O), ~30ºC	Dil. Aqua regia	Noble metals

Williams et al., *JMEMS* 12(6):3543, 2003.

Gold etchant AU-5 from Cyantek (5% I_2 +10% KI + 85% H_2O), ~20ºC	AU-5	Gold
Nichrome etchant TFN from Transene (10-20% $(NH_4)_2Ce(NO_3)_6$) + 5-6% HNO_3 + H_2O), ~20ºC	NiCr TFN	NiCr
1 H_2SO_4 : 1 H_3PO_4, 160ºC	Phos+Sulf	Sapphire
Piranha (~50 H_2SO4 : 1 H_2O_2), 120ºC	Piranha	Cleaning
Microstrip 2001 photoresist stripper, 85ºC	Microstrip	Photoresist
Acetone, ~20ºC	Acetone	Photoresist
Methanol, ~20ºC	Methanol	Cleaning
Isopropanol, ~20ºC	IPA	Cleaning
XeF_2, 2.6 mTorr, homemade chamber	XeF_2	Silicon
HF + H_2O vapor, 1 cm over dish with 49% HF	HF vapor	Silicon dioxide
Technics plasma, O_2, 400 W @ 30 kHz, 300 mTorr	Technics O_2	Photoresist
STS ASE DRIE, mechanical chuck, high frequency, typical recipe	DRIE HF mech.	Silicon
STS ASE DRIE, electrostatic chuck, high frequency, typical recipe	DRIE HF ES	Silicon
STS ASE DRIE, mechanical chuck, stop-on-oxide (low-frequency platen), typical recipe	DRIE LF mech.	Silicon
STS ASE DRIE, electrostatic chuck, stop-on-oxide (low-frequency platen), typical recipe	DRIE LF ES	Silicon
STS 320 RIE, SF_6, 100 W @13.56 MHz, 20 mTorr	STS 320 SF_6	Si, SiN, metals
STS 320 RIE, SF_6 + O_2, 100 W @13.56 MHz, 20 mTorr	STS SF_6+O_2	Si, SiN, metals
STS 320 RIE, CF_4, 100 W @13.56 MHz, 60 mTorr	STS 320 CF_4	Si, SiO, SiN
STS 320 RIE, CF_4 + O_2, 100 W @13.56 MHz, 60 mTorr	STS CF_4+O_2	Si, SiO, SiN
Ion milling with argon ions at 500 V, ~1 mA/cm^2, normal incidence (Commonwealth data)	Ion Mill	Everything

Notation:
BHF = buffered hydrofluoric acid
DRIE = deep reactive ion etch
RIE = reactive ion etch
STS ASE = Surface Technology Systems Advanced Silicon Etch

Williams et al., *JMEMS* 12(6):3543, 2003.

Catalytic etching of graphene

Purification: chemical etching

- Etch types
  - Wet
  - Dry
- What will etch?
  - Organics
  - Semiconductors
  - Oxides
  - Metals
- Considerations
  - Etch rate
  - Selectivity (e.g., rate_A/rate_B)
  - Compatibility with other materials in your process
  - Drying process (aggregation and capillary forces)

Dispersion vs. solution

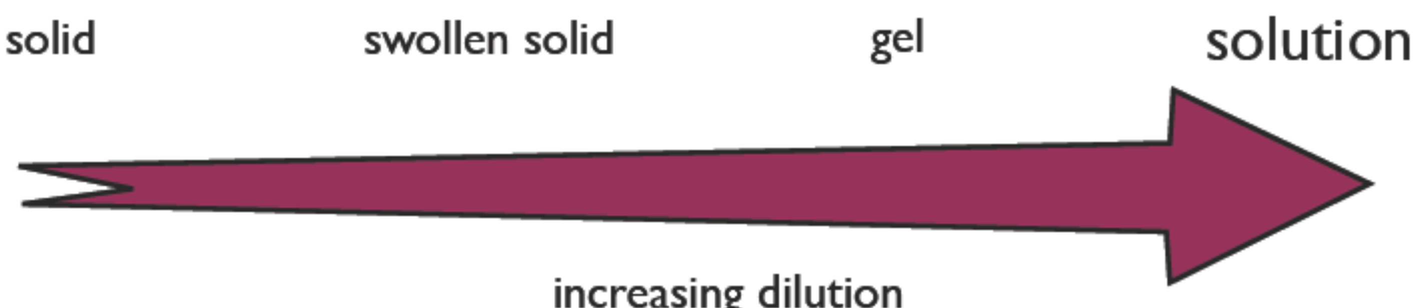
Dispersion

- Heterogeneous (mixture)
- Metastable
- does NOT form spontaneously
  (Think of a mayonnaise)

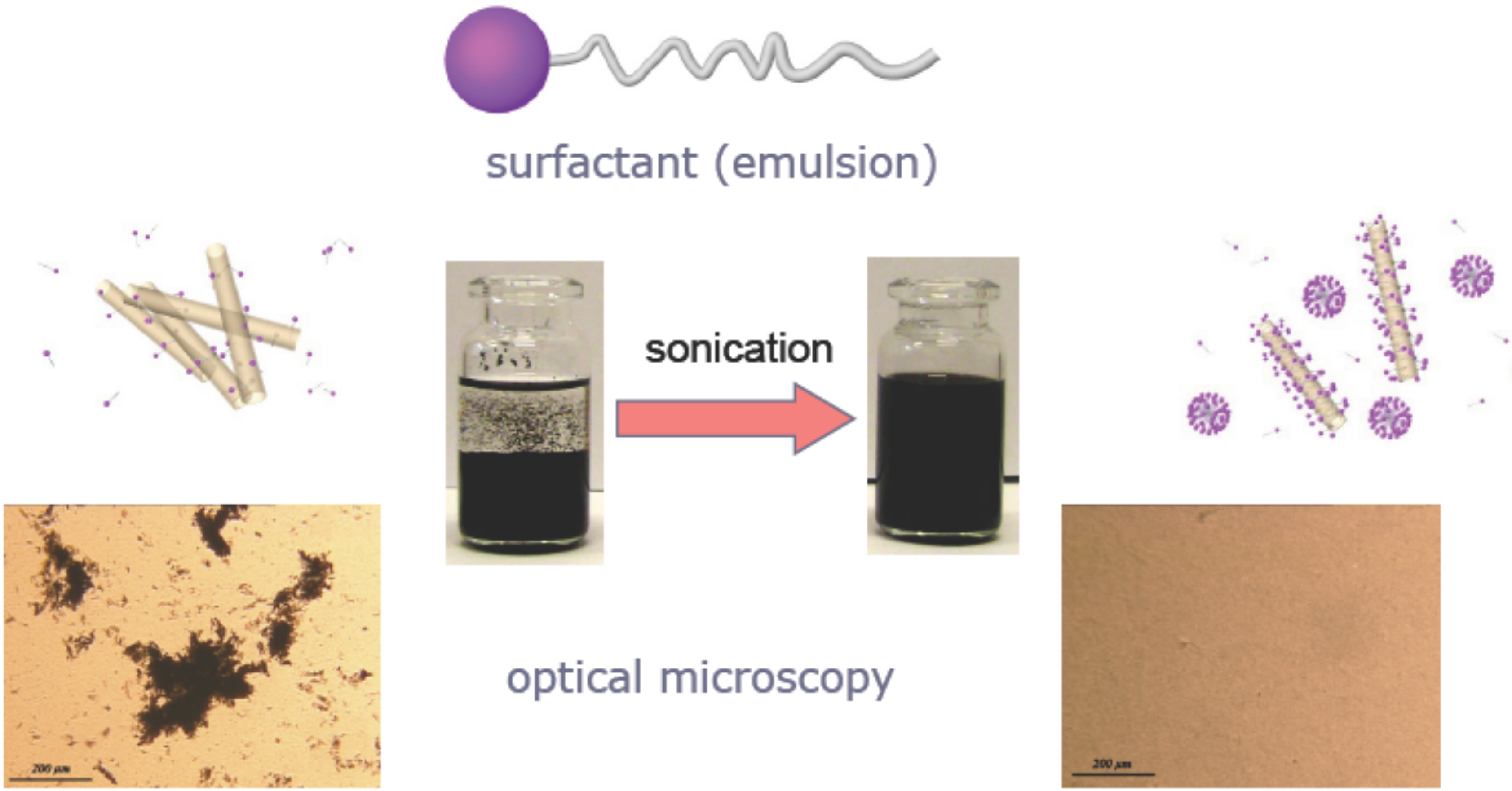
need for stirring, shearing,
sonicating....

Solution

- Homogeneous
- Stable
- Solution forms spontaneously
  (think of salt or sugar in water)

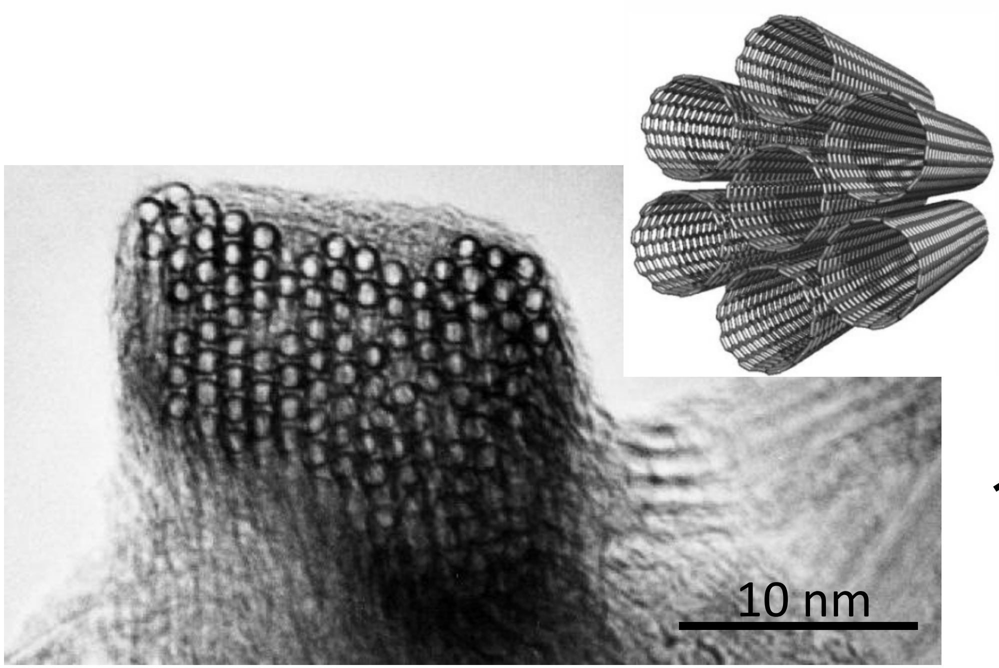


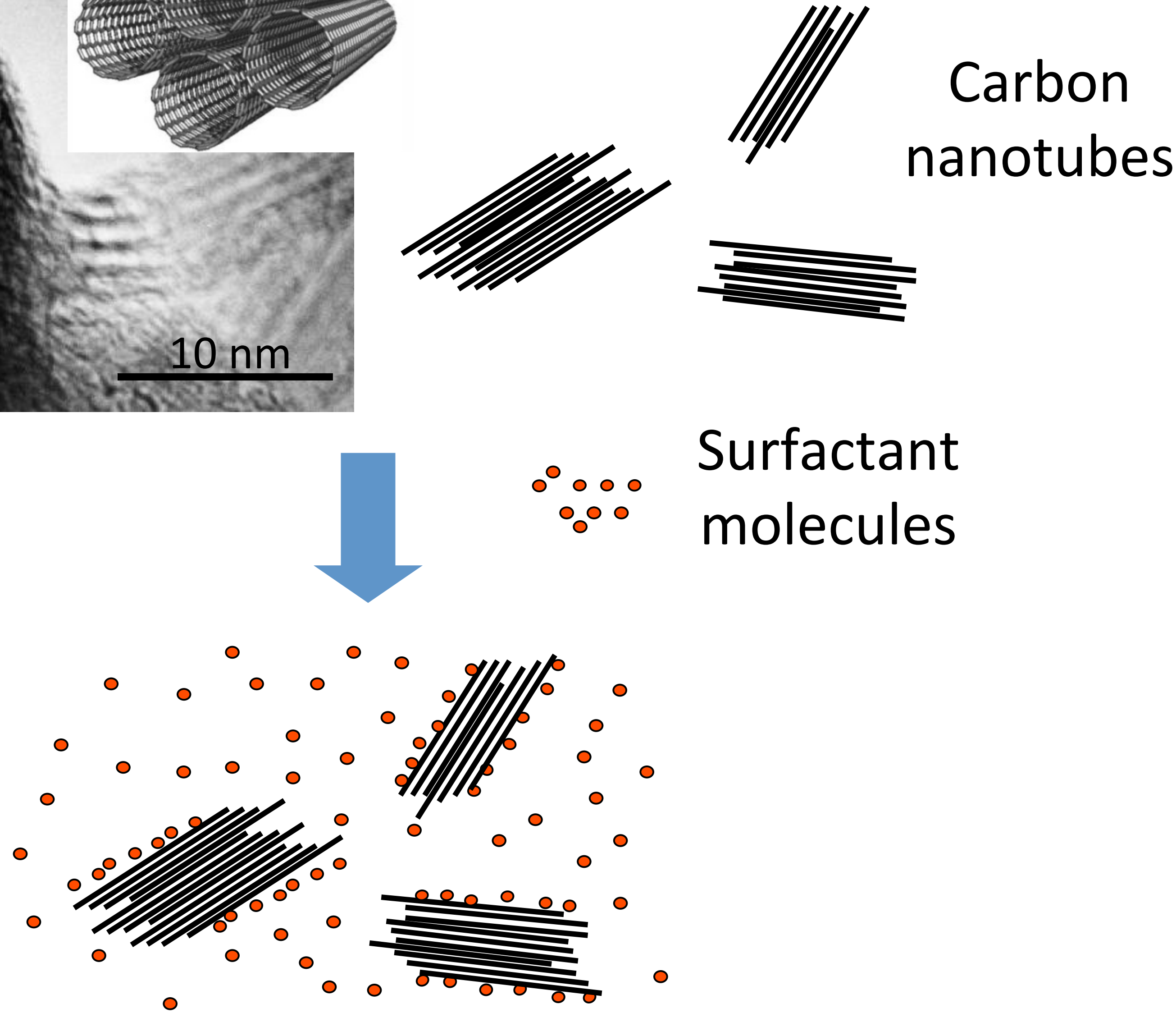
Basic dispersion of CNTs in H_2O

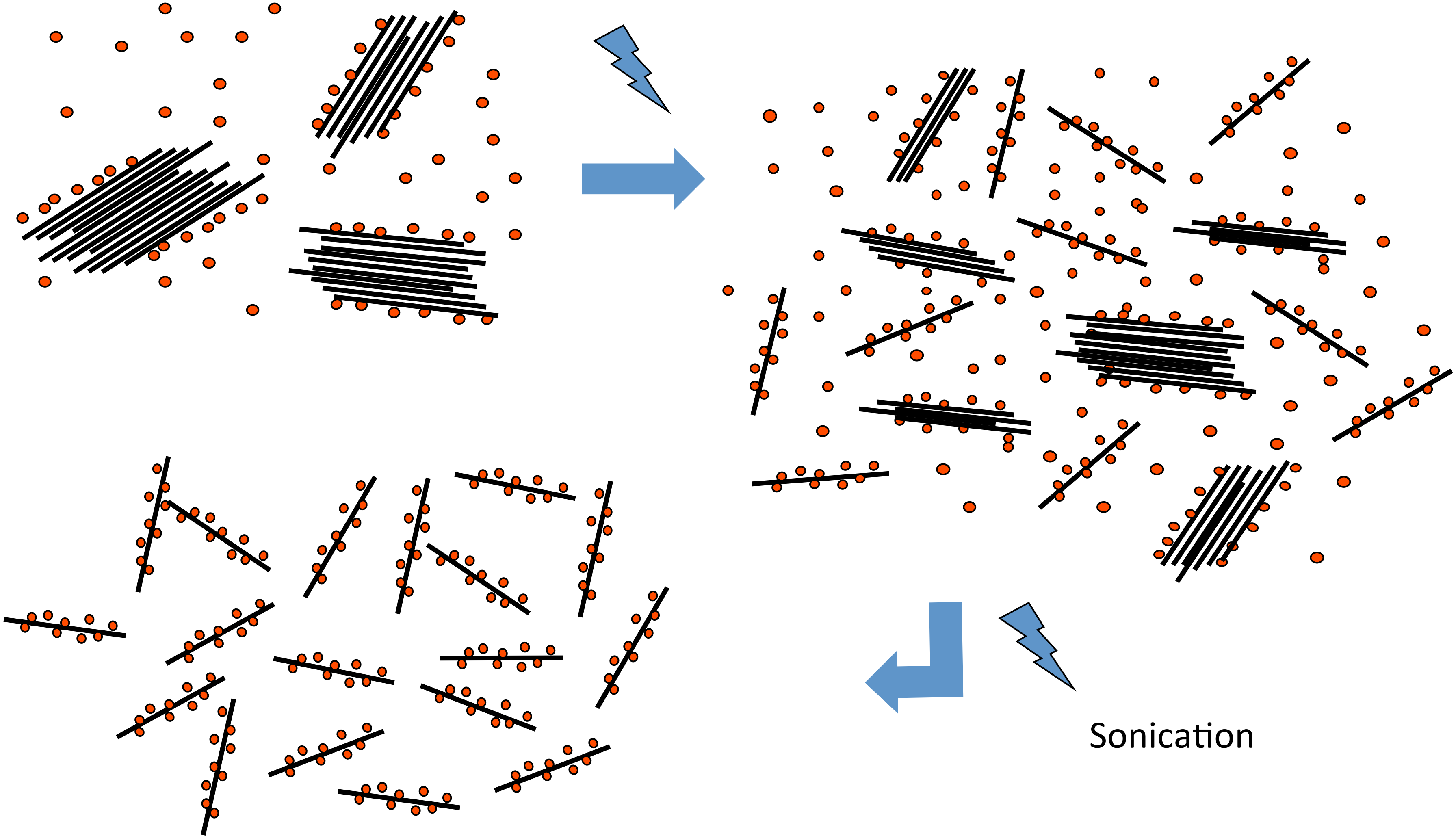


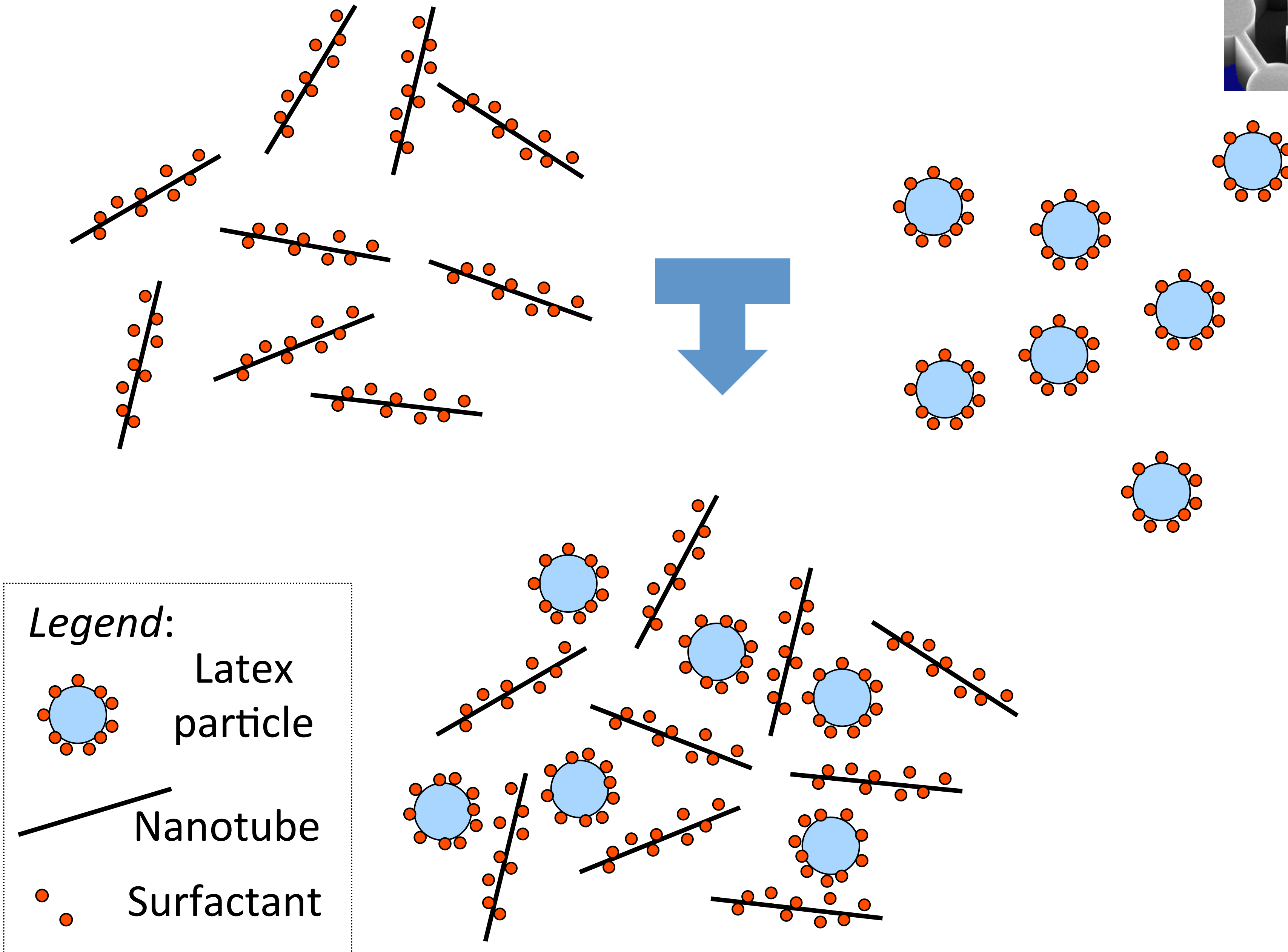
e.g., <0.1 wt% CNTs in 1% SDS (sodium dodecyl sulfate) in DI-H_2O

A. Penicaud


10 nm


Carbon nanotubes
Surfactant molecules


Sonication


Legend:
Latex particle
Nanotube
Surfactant

Horn sonicator

Monitoring exfoliation of CNTs

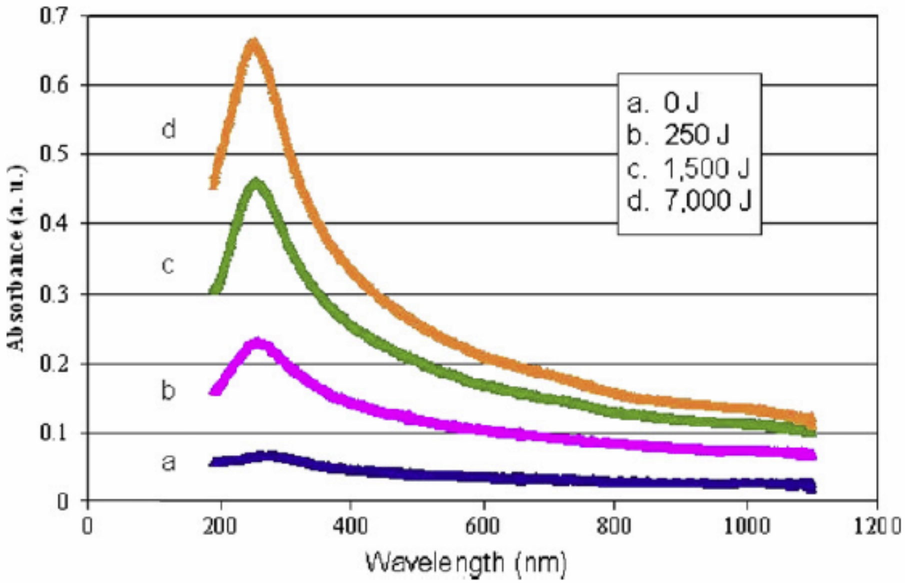


Fig. 1. Evolution of the UV spectra of Carbolex NT solution as function of the energy delivered. Carbolex solution 0.5 wt% (diluted 750 times; continuous power of sonication of 20 W). The absorbance increases continuously with increasing energy-input.

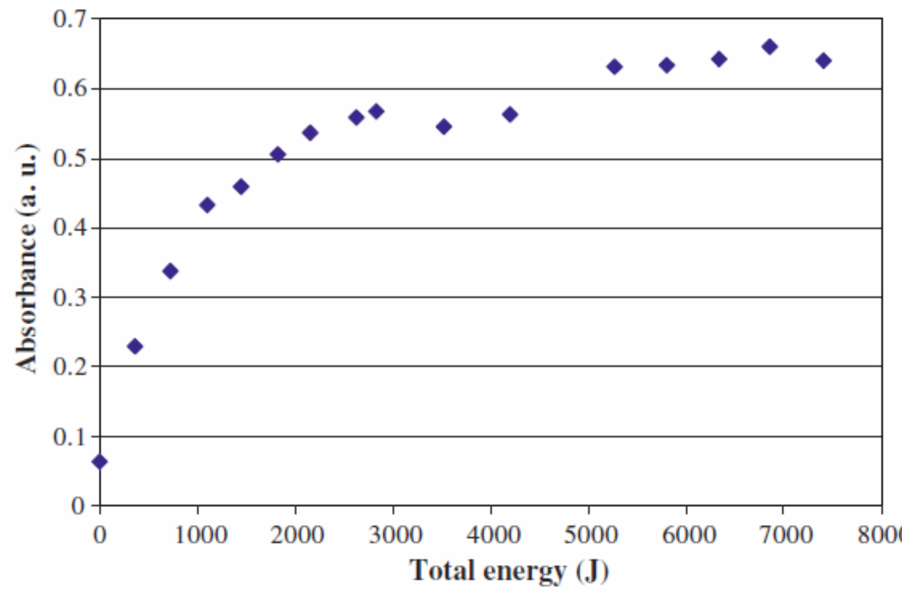
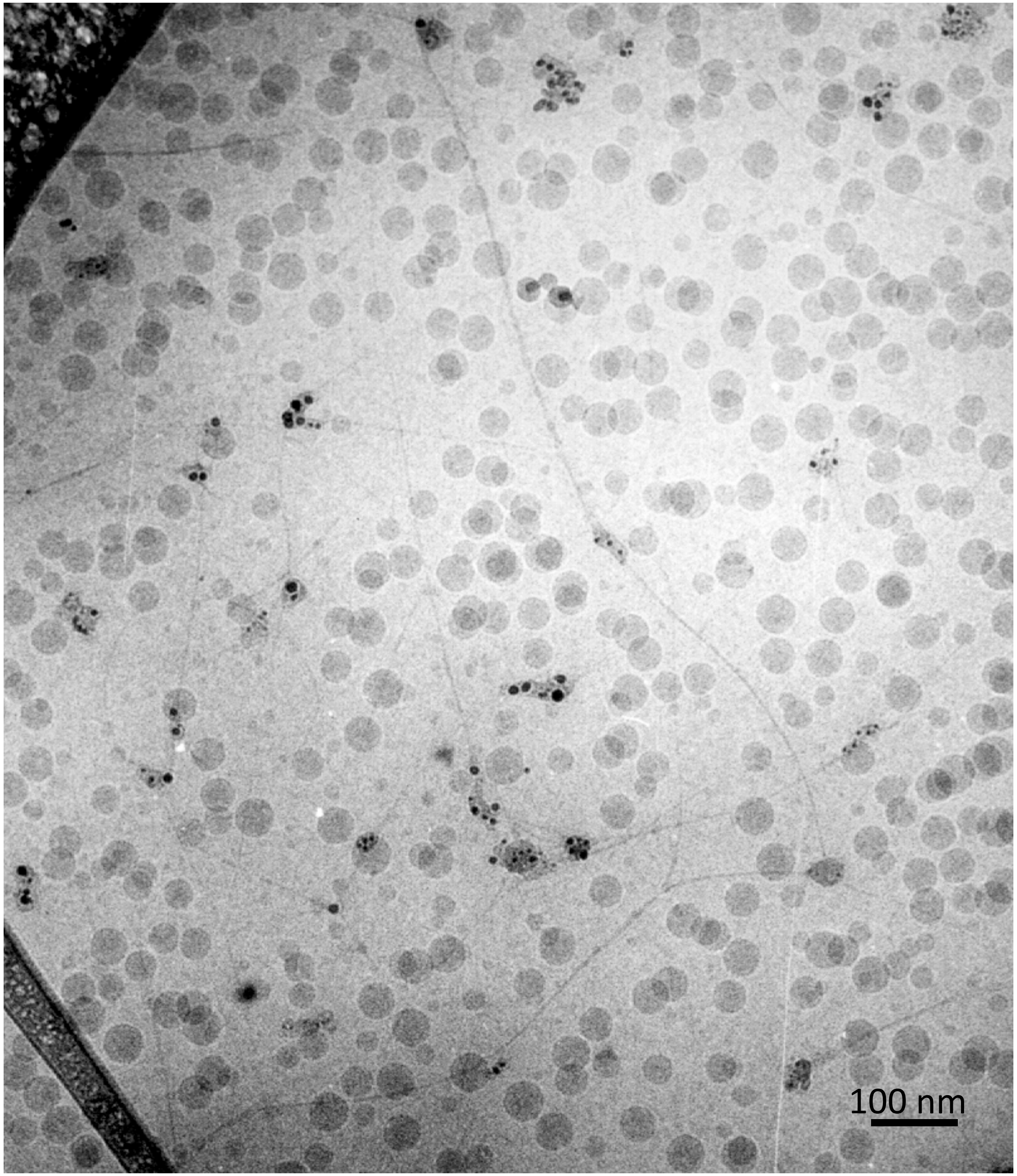


Fig. 2. Evolution of the height of the peak located around 250 nm for an aqueous 0.5 wt% Carbolex NT solution (diluted 750 times).

N. Grossiord et al., *Composites Science and Technology* 67:778-782, 2008.

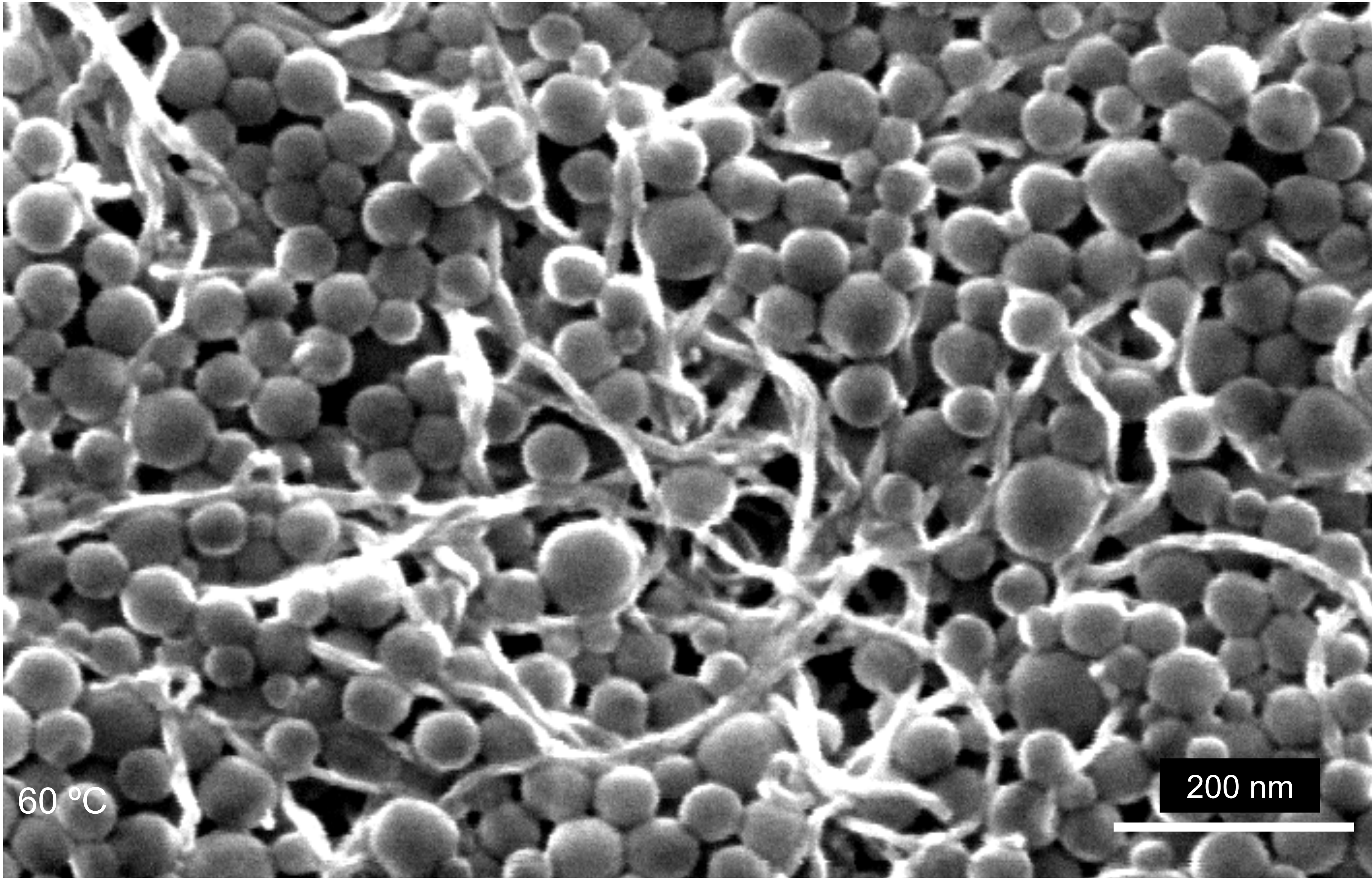
Step 2:

NTs mixed with a polymer latex



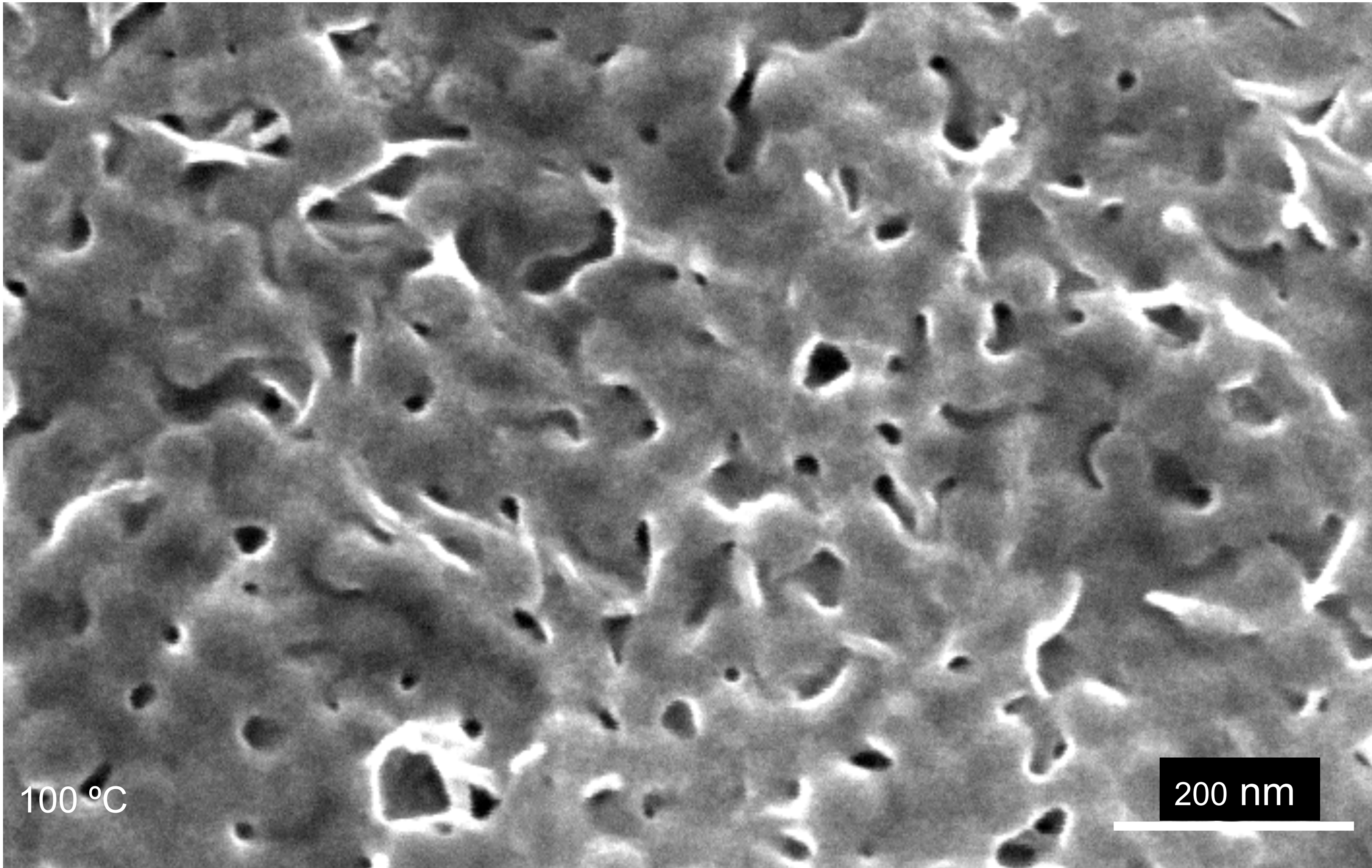
N. Grossiord et al.

Step 3: Freeze-drying of the mixture



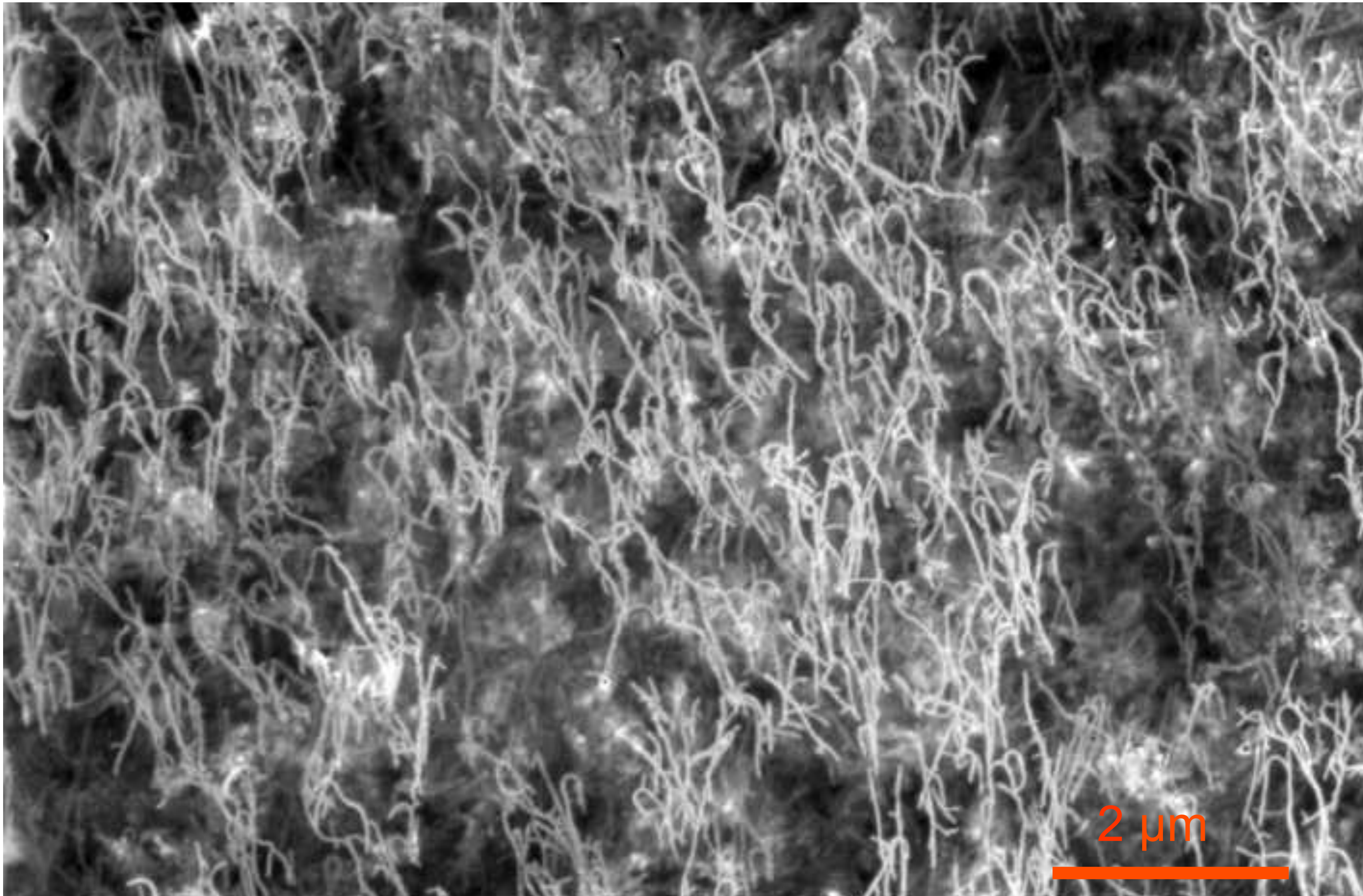
N. Grossiord et al.

Step 4: Compression Molding

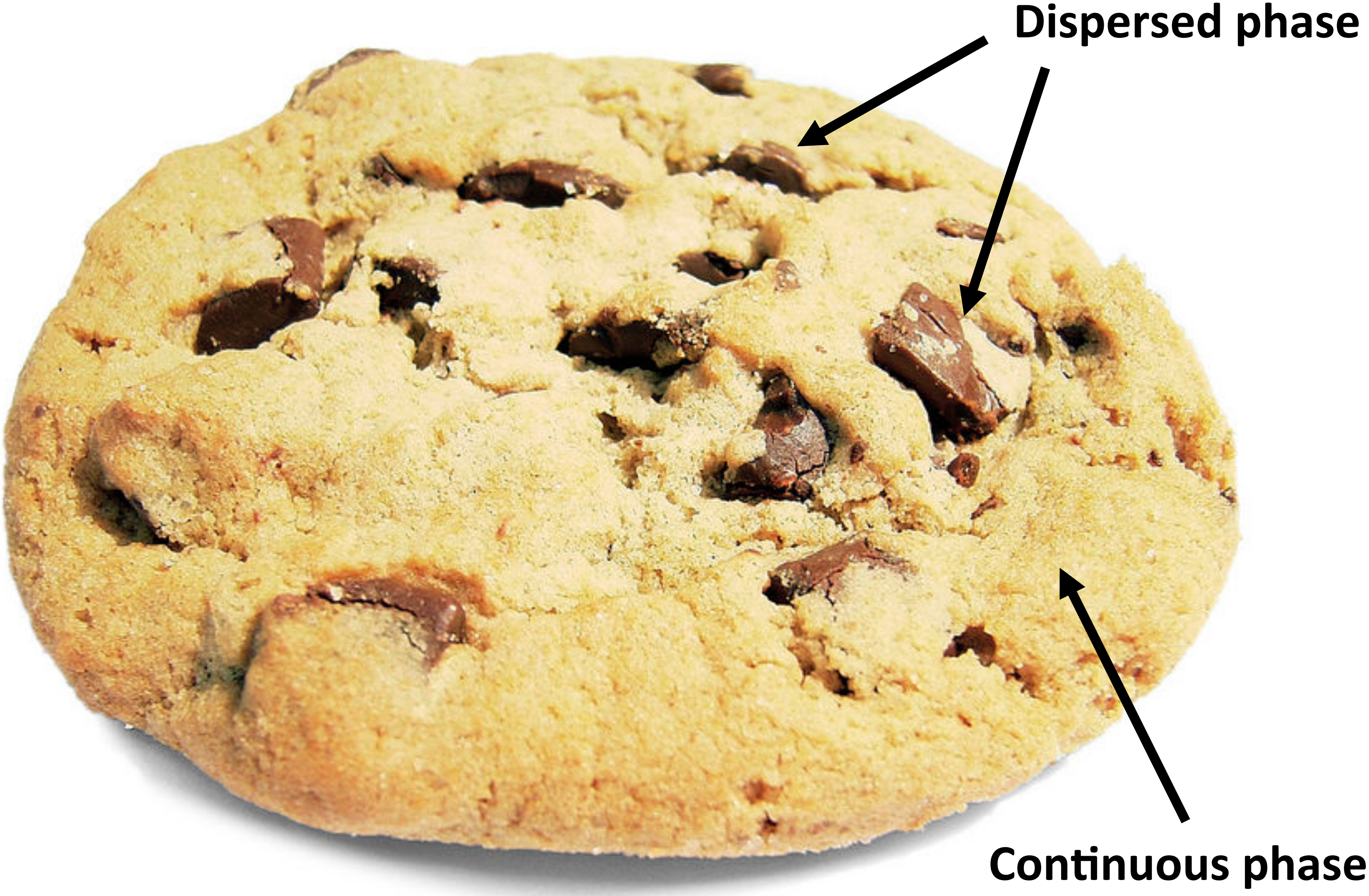


N. Grossiord et al.

Final product: Nanocomposite film



N. Grossiord et al.



N. Grossiord

Functionalization: approaches

- Covalent bonding
- Non-covalent association (e.g., polymer wrapping)
- Ionic (charge) stabilization

- Functional group: a specific group of atoms within a molecule that is responsible for chemical reactions involving the molecule

Initially associated molecules can be a template for secondary bonding to desired outer functional groups →functionalization "platforms"

Where do functional groups attach?

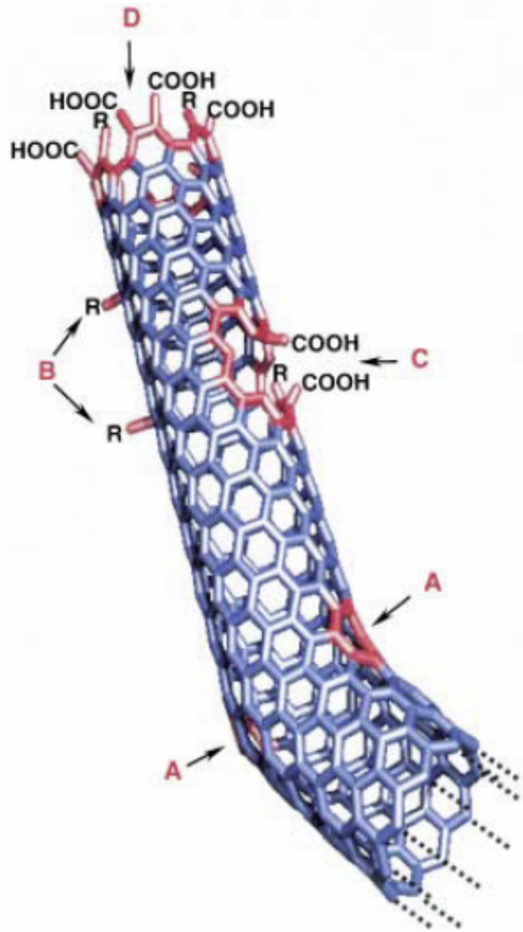


Figure 3. Typical defects in a SWNT: A) five- or seven-membered rings in the C framework, instead of the normal six-membered ring, leads to a bend in the tube, B) sp^3-hybridized defects (R = H and OH), C) C framework damaged by oxidative conditions, which leaves a hole lined with -COOH groups, and D) open end of the SWNT, terminated with -COOH groups. Besides carboxy termini, the existence of which has been unambigously demonstrated, other terminal groups such as $-NO_2$, OH, H, and =O are possible.

- Some functionalization typically native after growth, e.g., -COOH at ends

.

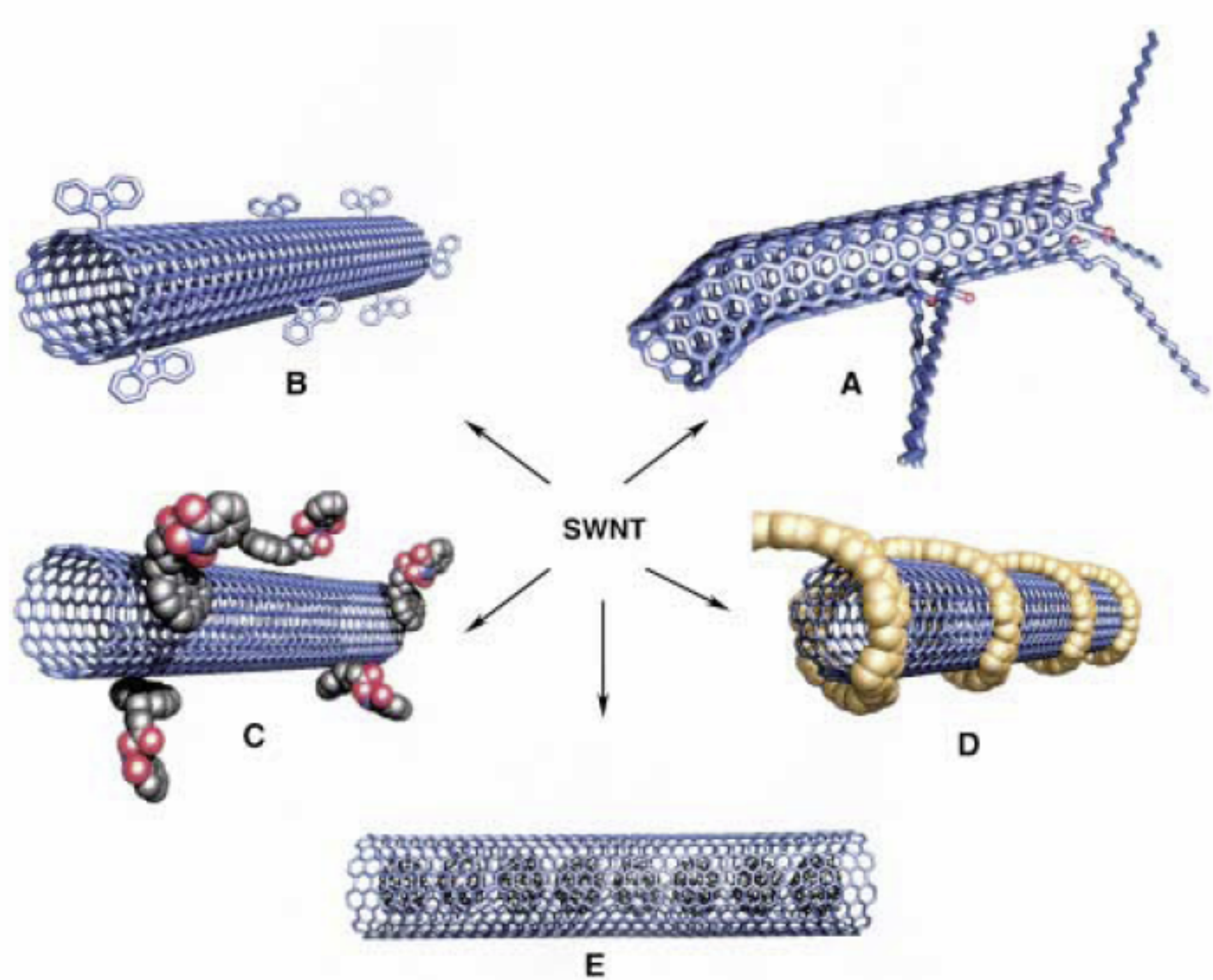


Figure 5. Functionalization possibilities for SWNTs: A) defect-group functionalization, B) covalent sidewall functionalization, C) noncovalent exohedral functionalization with surfactants, D) noncovalent exohedral functionalization with polymers, and E) endohedral functionalization with, for example, C_{60}. For methods B – E, the tubes are drawn in idealized fashion, but defects are found in real situations.

Example: CNT sidewall functionalization

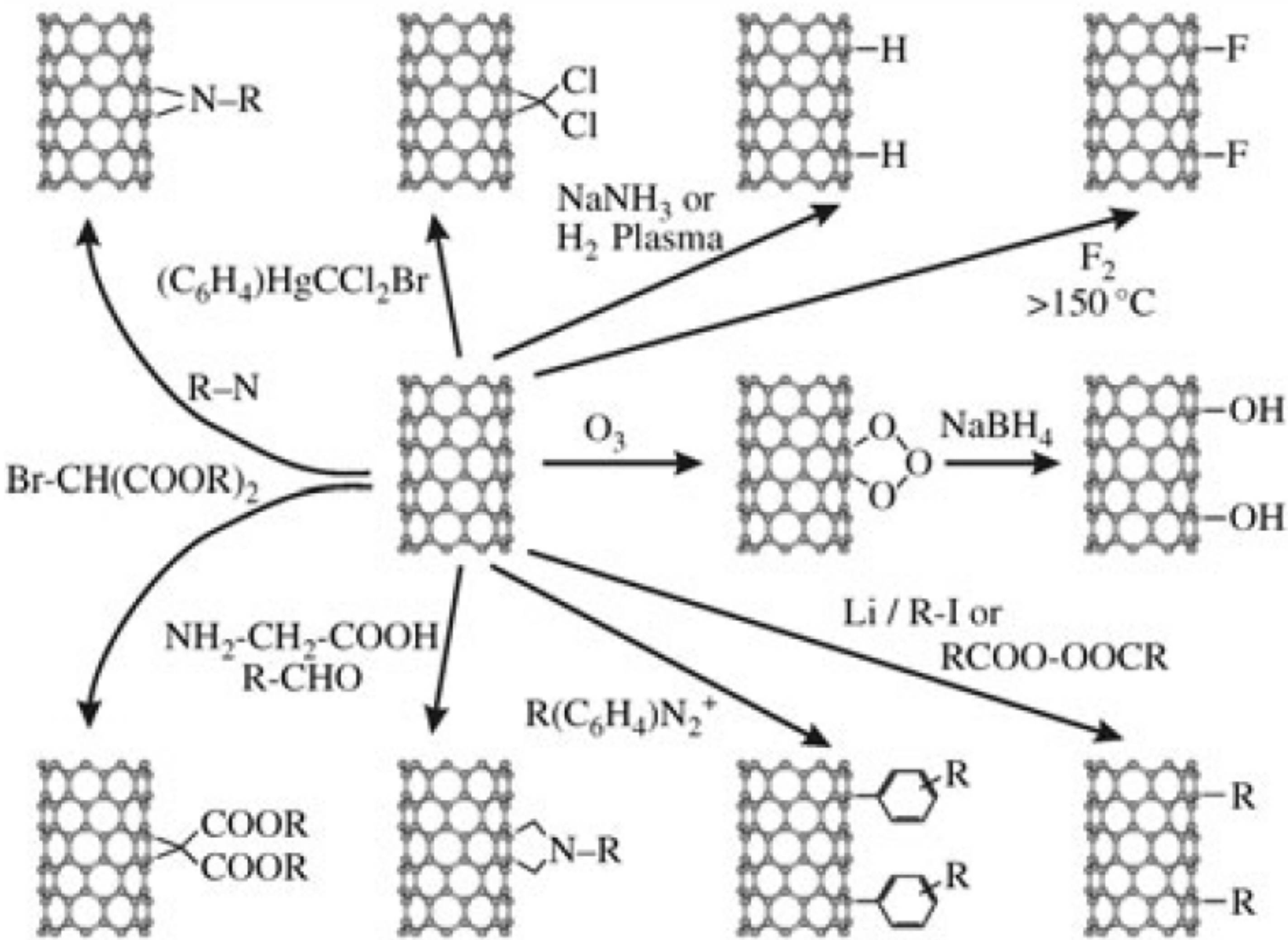
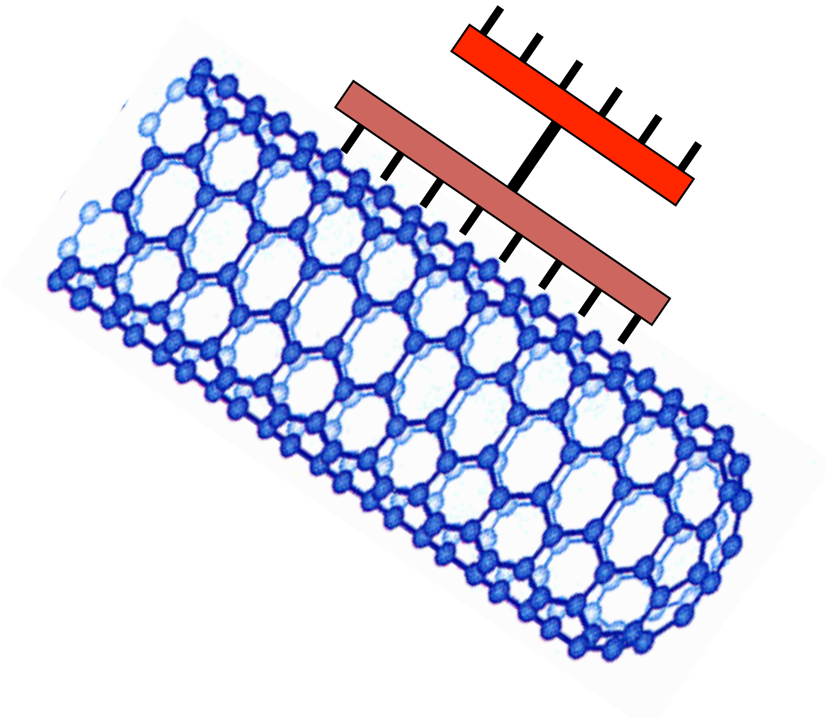


Figure 6. Overview of possible addition reactions for the functionalization of the nanotube sidewall.

- Smaller diameter = easier to substitute

Functionalization as a platform

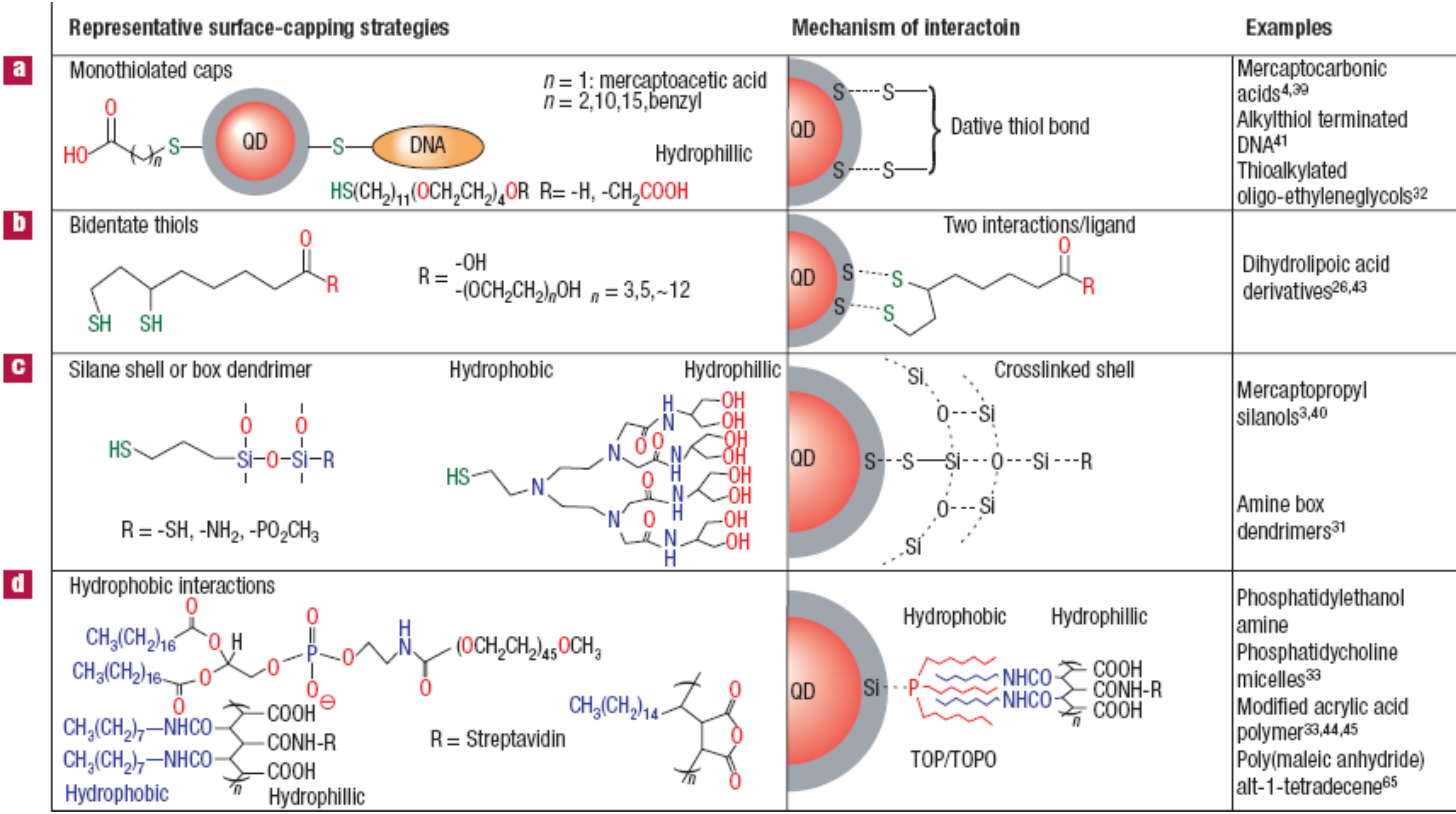
- **Two levels**
  - van der Waals (non-covalent)
  - covalent



Zyvex

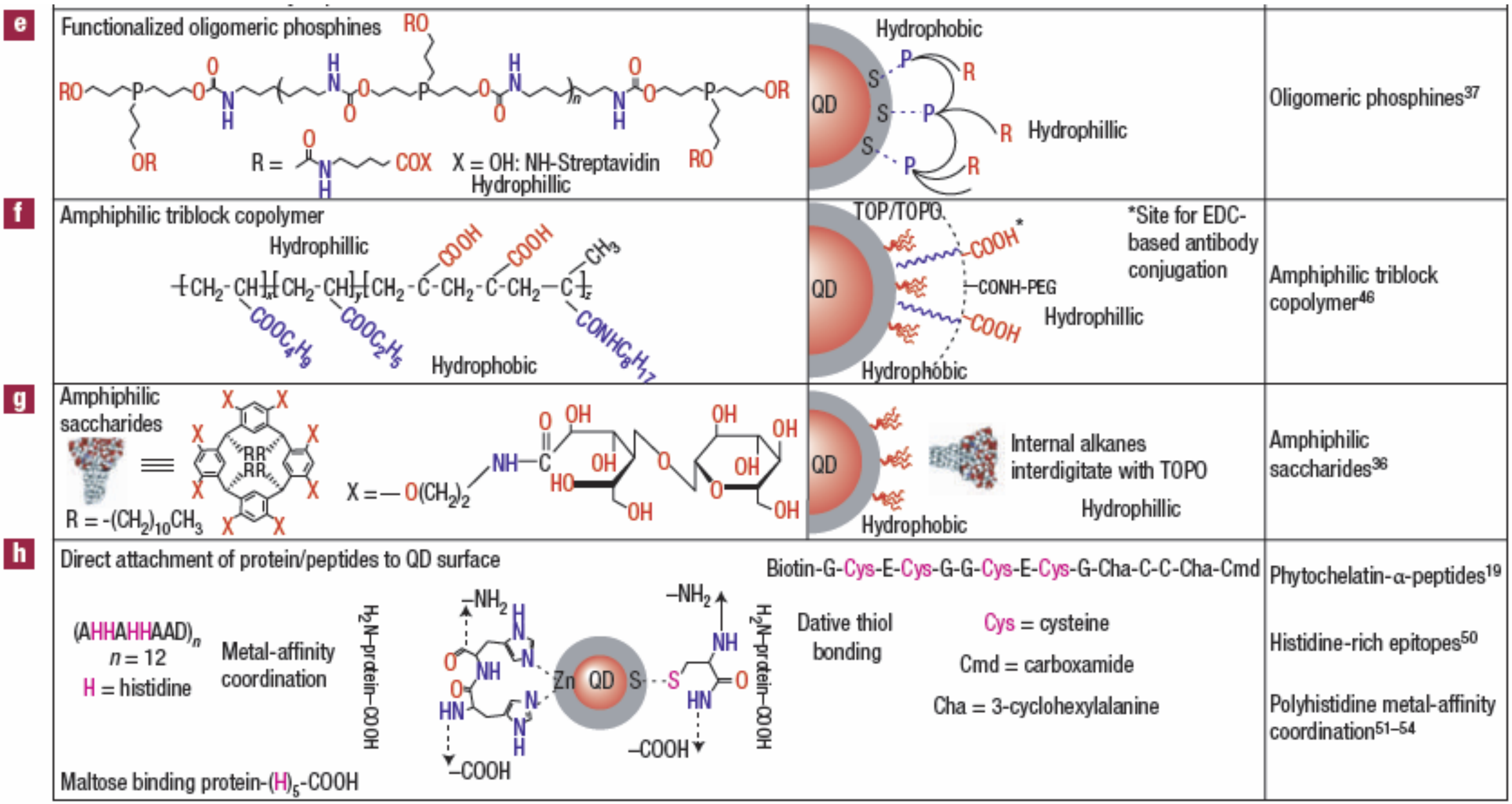
Application: composites for sporting goods

Functionalization of semiconductor NPs

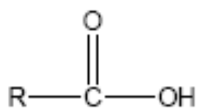
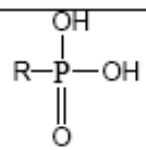
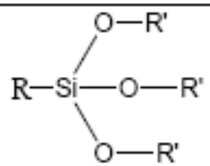
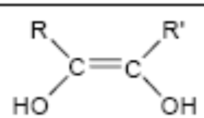
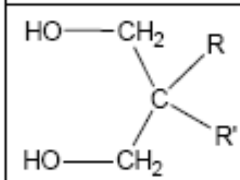


Medintz et al. *Nature Materials* 4:435, 2005.

Functionalization of semiconductor NPs



Functionalization of metal oxide NPs

Ligand	Name	Reacting surfaces	References
R-SH R-S-S-R'	thiols disulfides	Au, Ag, Cu, Hg, Fe	3-5, 112-115
	carboxylic acids	metal oxides	25, 26, 33, 35, 97, 98
	phosphonates phosphonic acids	metal oxides	6-8, 49, 99-102
	siloxanes	metal oxides	32, 43, 80-87, 89-96
	enediols	transition metal oxides (TiO_2, Fe_2O_3, ZrO)	3, 34, 103-109
	diols	Fe_2O_3	110, 111

-R = alkyl group

C_nH_{2n+1}

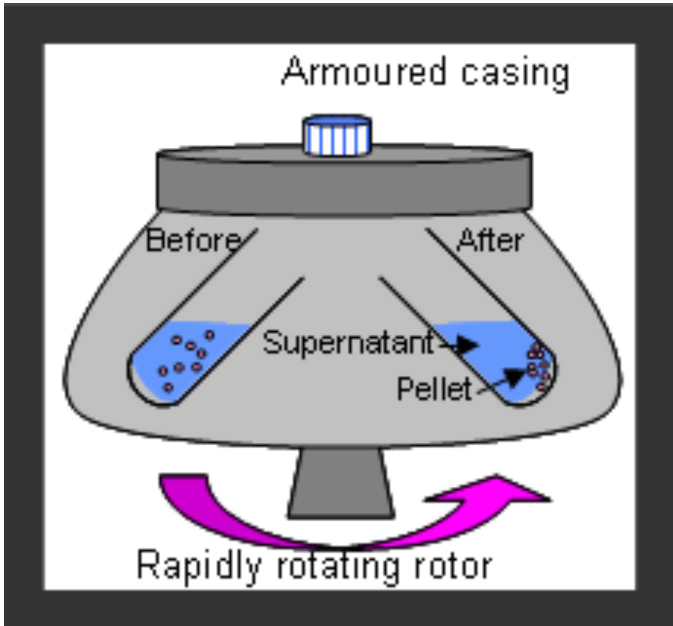
Koh, Ph.D. Thesis, U. Maryland, 2005.

Separation and sorting: methods

- Centrifugation
- Electrophoresis → when we discuss external fields later
- Filtering, size exclusion

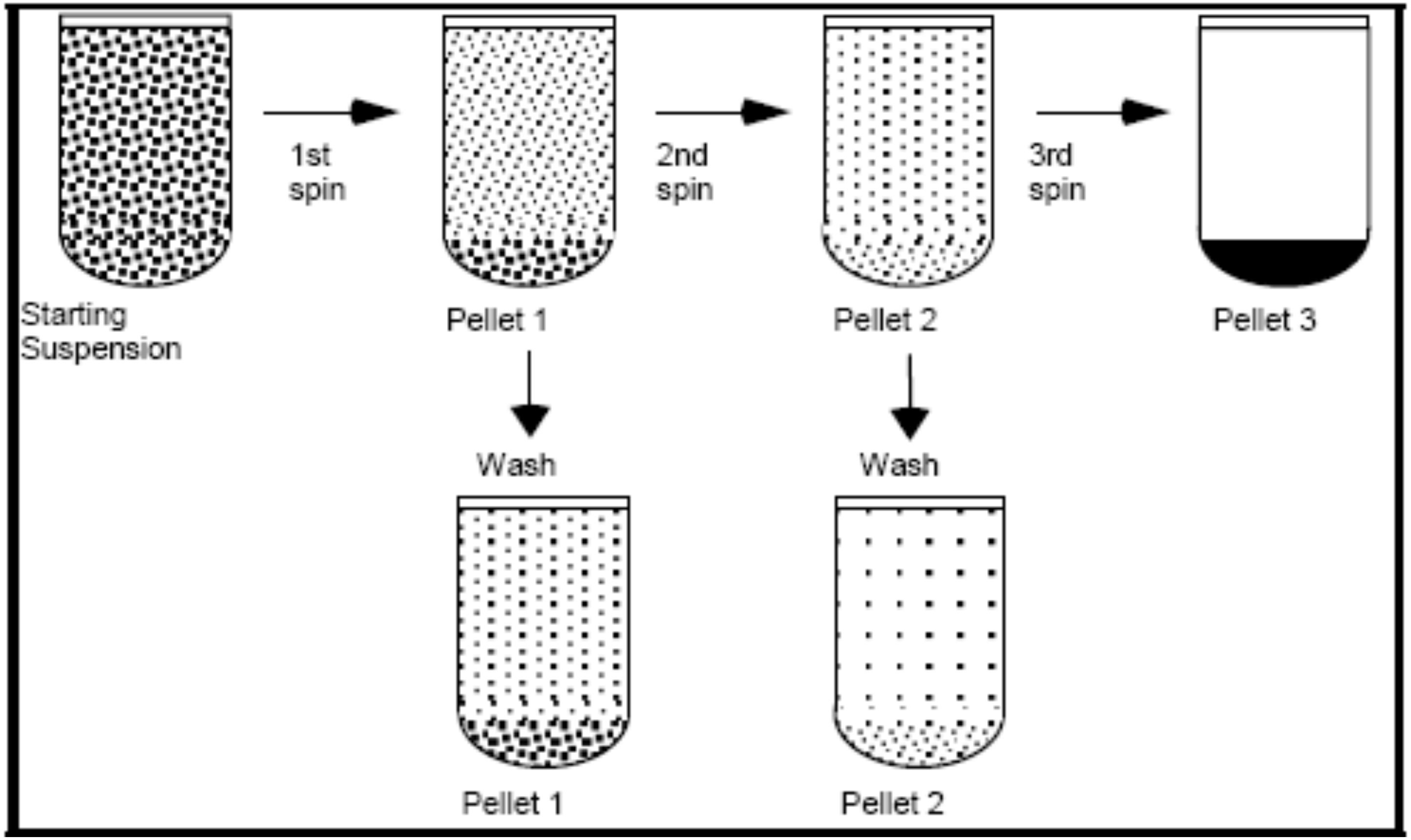
Overarching principle: create and amplify a difference in mobility of nanostructures in a fluid based on their size, shape, and/or surface charge

Centrifuge


Armoured casing
Before
After
Supernatant
Pellet
Rapidly rotating rotor

Differential centrifugation

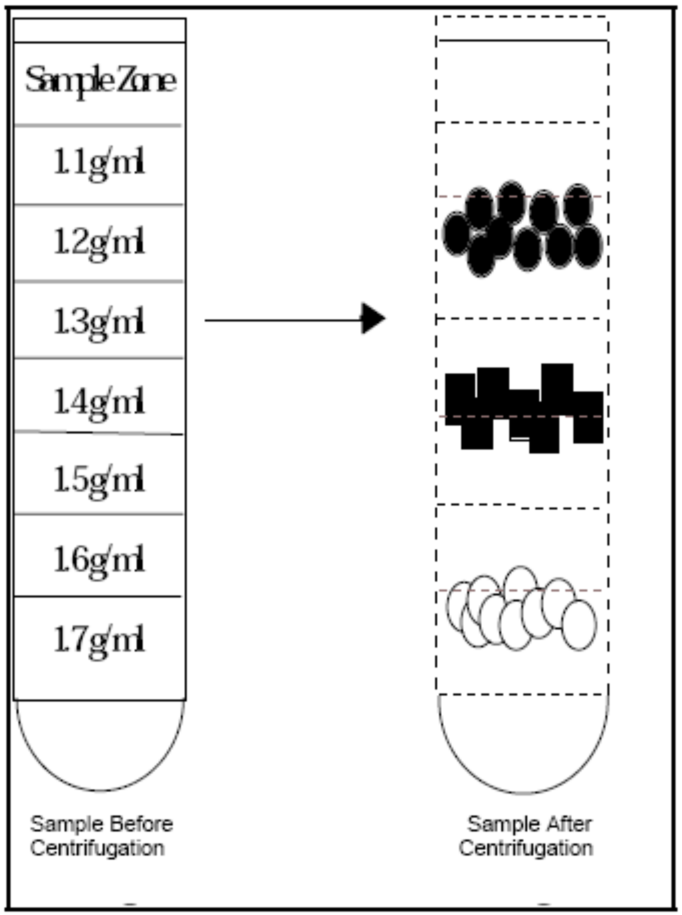
- Spin a solution (or suspension) in a uniform density solution
- Larger particles sediment faster (earlier steps shown below), and at lower speeds
- Wash sediment between steps to remove contaminants



http://www.coleparmer.com/techinfo/techinfo.asp?htmlfile=basic-centrifugation.htm&ID=30

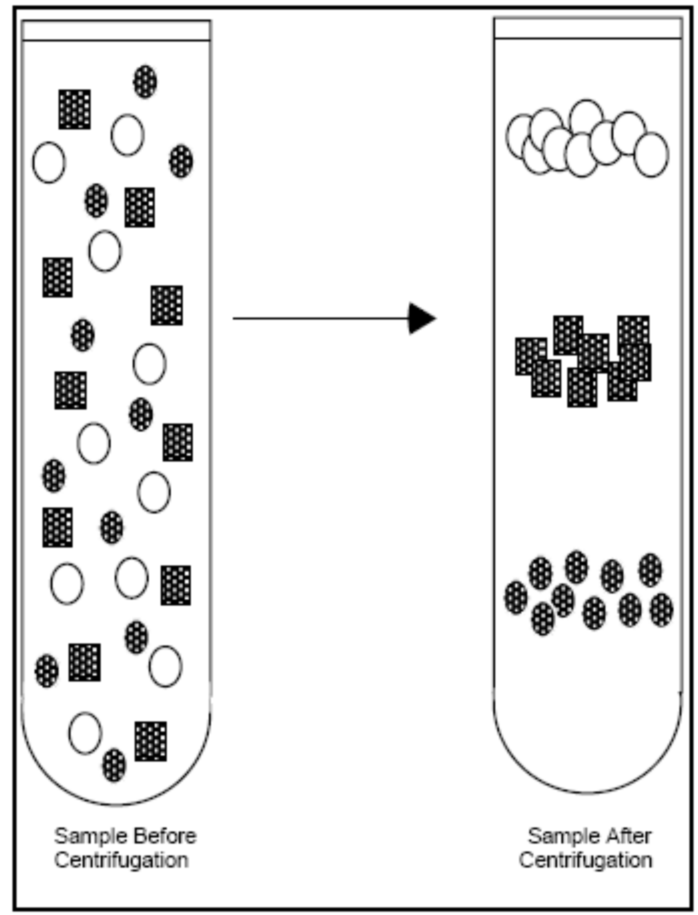
Density gradient centrifugation

rate-zonal (size, mass)



Useful if mass differs but density does not
If centrifuge too long, all particles settle

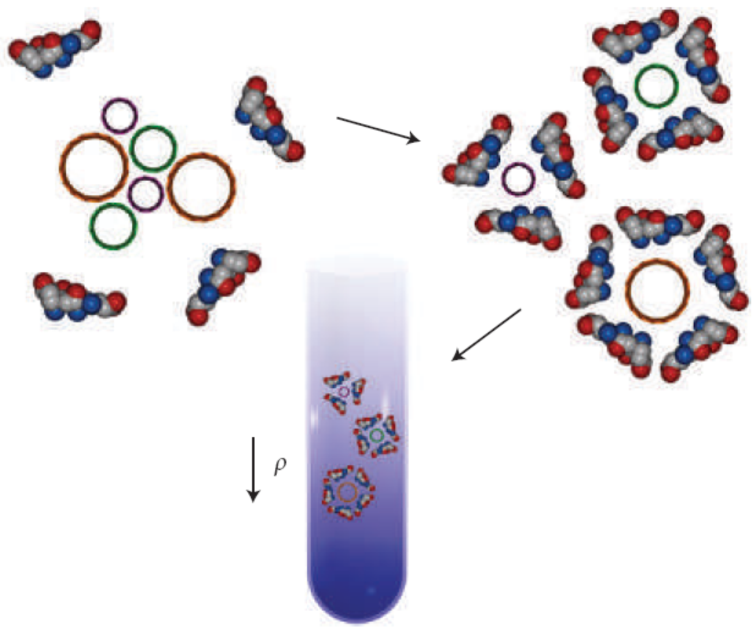
isopycnic (density)

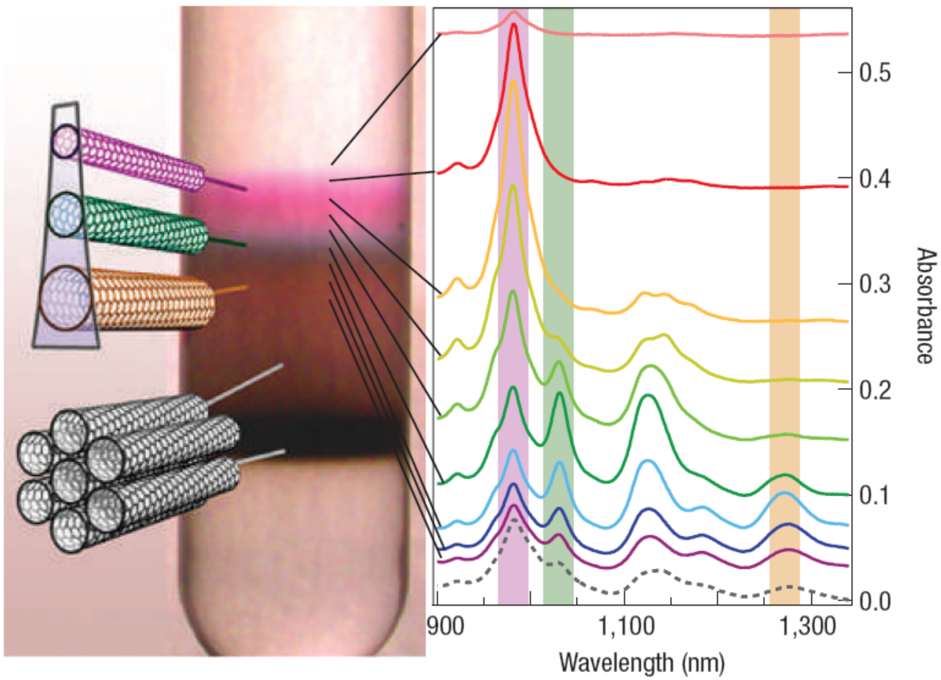


Reaches equilibrium

http://www.coleparmer.com/techinfo/techinfo.asp?htmlfile=basic-centrifugation.htm&ID=30

CNT separation using density gradients

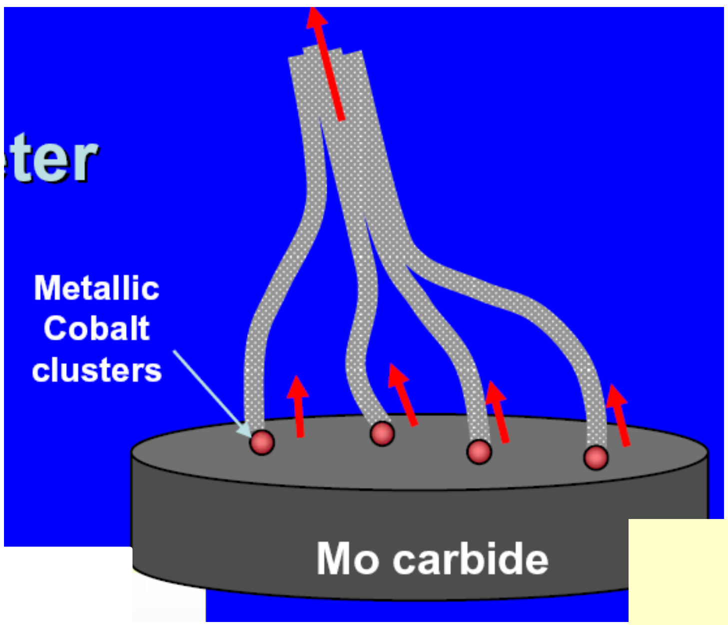


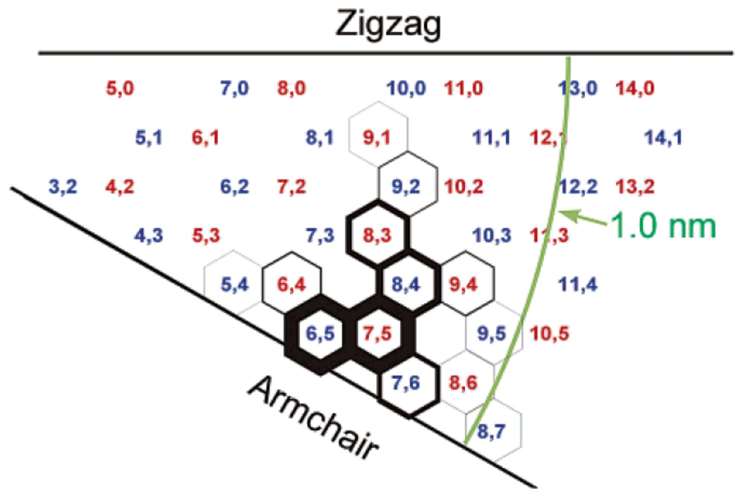


- Disperse CNTs in surfactant mix: competing surfactants adsorb based on CNT electronic structure
- Ultracentrifuge (≈50,000 rpm, ≈ 12h) in a density gradient and **repeat**
- Separation > 97% within 0.02nm diameter
- Differentiate metal/semiconducting as well

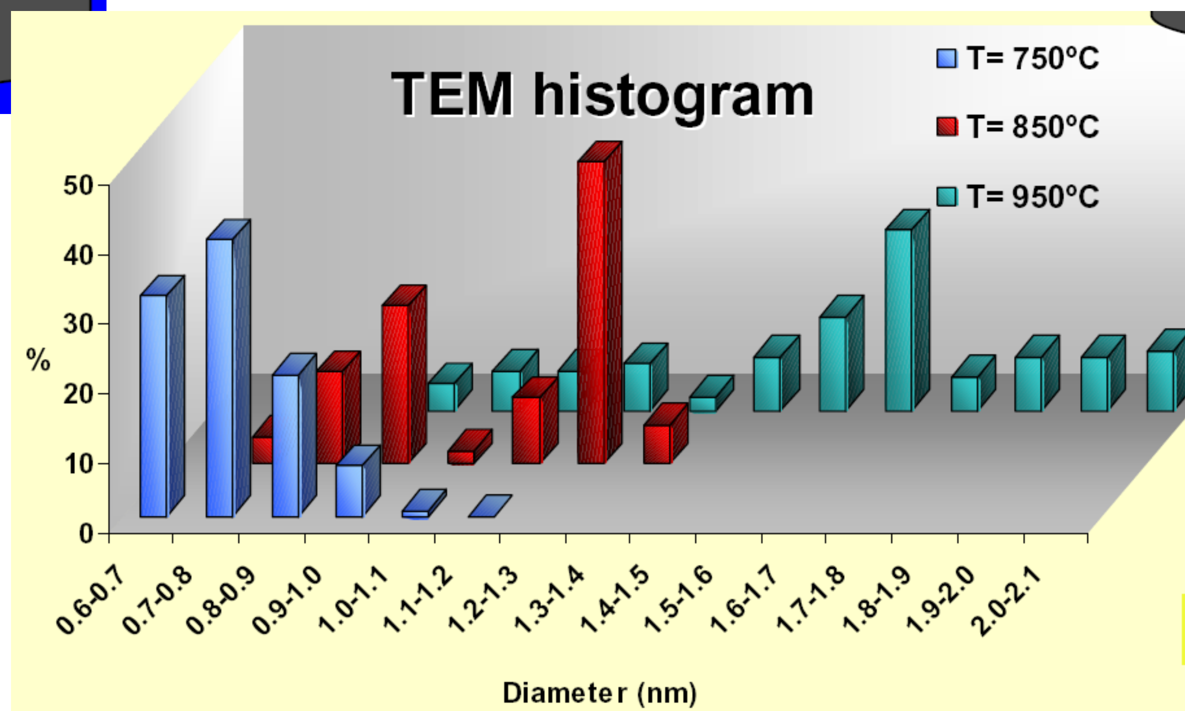
Arnold et al., *Nature Nanotechnology* 1:60-65, 2006

CoMoCat CNT growth process





CNT diameter increases with reaction temperature



Resasco et al., University of Oklahoma

Characterization: photoluminescence

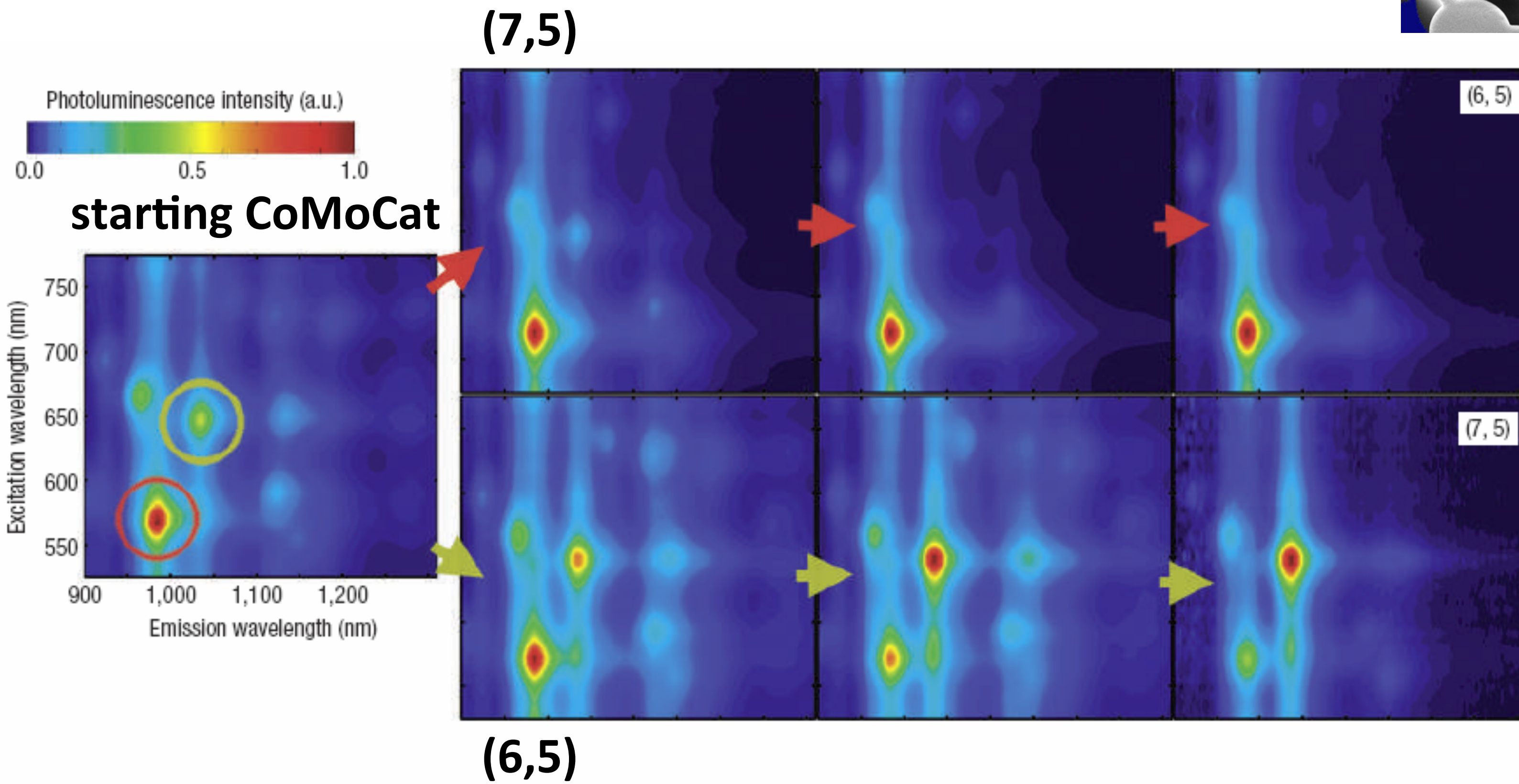
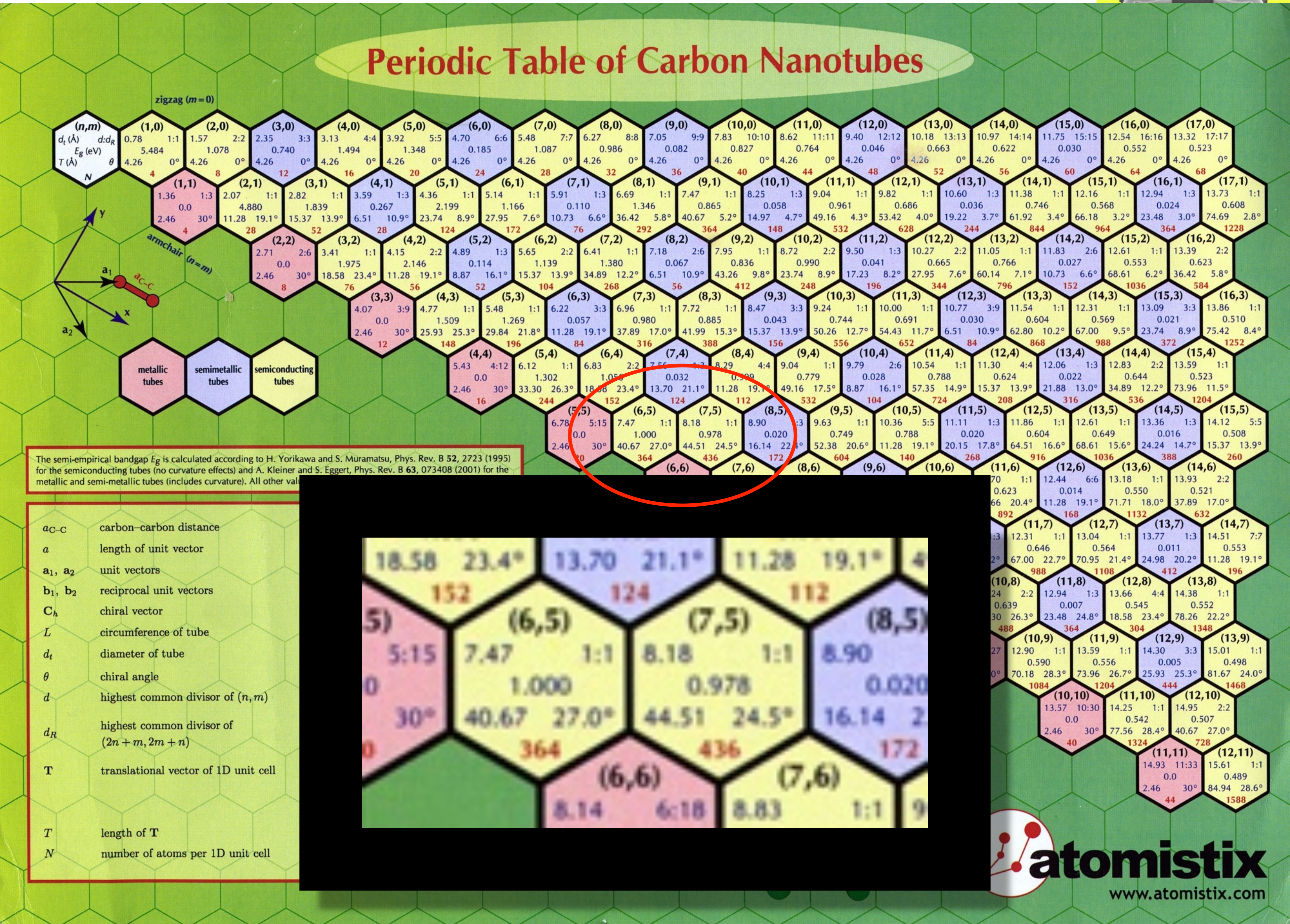


Figure 2 Refinement by repeated centrifugation in density gradients. By successively separating SC-encapsulated SWNTs, the isolation of specific, targeted chiralities improves. Plotted are photoluminescence intensities as a function of excitation and emission wavelengths. Here, the isolation of the (6,5) and (7,5) chiralities (circled red and green in the left-most plot) of SWNTs grown by the CoMoCAT-method before sorting, is improved (in the top and bottom panels, respectively) by successively repeating density gradient centrifugation for three iterations (from left to right). After three iterations of enriching the (6,5) chirality (7.6 Å), a narrow diameter distribution is achieved in which >97% of semiconducting SWNTs are within 0.2 Å of the mean diameter. Alternatively, refined isolation of the (7,5) chirality can be realized (bottom). In this case, after three iterations of sorting, the (7,5) chirality (8.3 Å), initially substantially less concentrated than the (6,5) chirality, becomes dominant. Further improvements may be possible with additional centrifugation cycles.

Arnold et al., *Nature Nanotechnology* 1:60-65, 2006

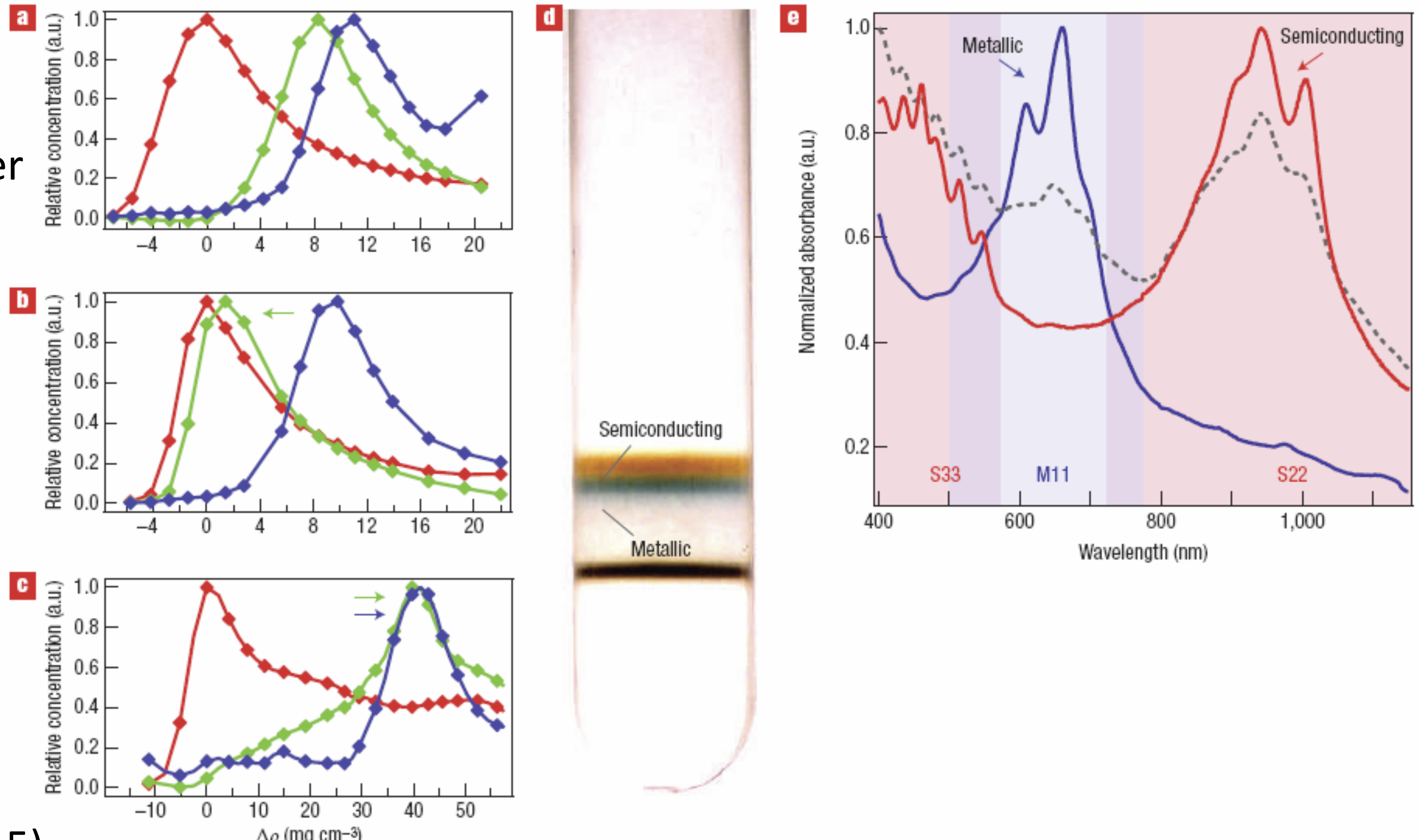

Periodic Table of Carbon Nanotubes
zigzag (m = 0)
armchair (n = m)
(n,m)
dt (Å) d:dR
Eg (eV)
T (Å) θ
N
a1
a2
aC–C
x
y
metallic tubes
semimetallic tubes
semiconducting tubes
The semi-empirical bandgap Eg is calculated according to H. Yorikawa and S. Muramatsu, Phys. Rev. B 52, 2723 (1995) for the semiconducting tubes (no curvature effects) and A. Kleiner and S. Eggert, Phys. Rev. B 63, 073408 (2001) for the metallic and semi-metallic tubes (includes curvature). All other val
aC–C carbon–carbon distance
a length of unit vector
a1, a2 unit vectors
b1, b2 reciprocal unit vectors
Ch chiral vector
L circumference of tube
dt diameter of tube
θ chiral angle
d highest common divisor of (n, m)
dR highest common divisor of (2n + m, 2m + n)
T translational vector of 1D unit cell
T length of T
N number of atoms per 1D unit cell
atomistix
www.atomistix.com

Tuning selectivity by surfactant mixture

Sodium cholate, no buffer pH 7.4

Sodium cholate, +buffer pH 8.5

SC+SDS



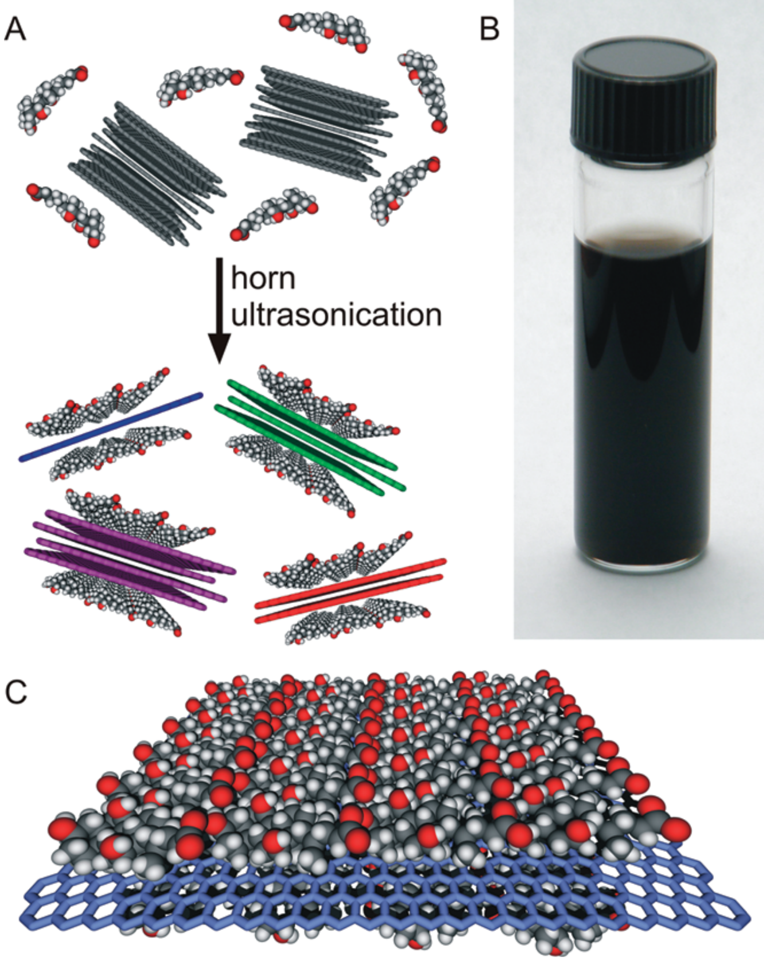
red = (6,5)
green = (7,5)
blue = (9,5) and (8,7)

Figure 3 Tuning the structure–density relationship for optimal separation by diameter and bandgap or electronic type (metal–semiconductor). a–c, Optimization of separation by diameter and bandgap. The concentration of the (6,5), (7,5) and (9,5)/(8,7) chiralities of CoMoCAT-grown SWNTs (coloured red, green and blue; diameters (ref. 5) of 7.6, 8.3 and 9.8/10.3 Å, respectively) are plotted against $\Delta\rho$. Concentrations were determined from absorbance spectra (Fig. 1c and Supplementary Fig. S1). The encapsulation agents and conditions were SC, no buffer, pH 7.4 (**a**), SC, 20 mM Tris buffer, pH 8.5, enhanced isolation of the larger diameter SWNTs, (9,5)/(8,7) (**b**), SC with the addition of SDS as a co-surfactant (1:4 ratio by weight, SDS/SC), enhanced isolation of the smaller diameter SWNTs, (6,5), pH 7.4 (**c**). ρ for the fractions with the highest (6,5) chirality relative concentration in **a–c** are all 1.08 ± 0.02 g cm^{-3}. Arrows mark shifts with respect to **a**. **d**,**e**, Optimization of separation by electronic type. **d**, Photograph of laser-ablation-grown SWNTs separated in a co-surfactant solution (1:4 SDS/SC). The top band (orange) corresponds to predominantly semiconducting SWNTs (absorbance spectra plotted in red in **e**) and the band just below it (green) is highly enriched in metallic SWNTs, although some semiconducting SWNTs remain (absorbance spectra plotted in Supplementary Fig. S6). $\Delta\rho$ between the two bands and ρ for the top band are 0.006 g cm^{-3} and 1.12 ± 0.02 g cm^{-3}, respectively. Further tuning of the structure–density relationship (3:2 ratio by weight SDS/SC) results in the isolation of predominantly metallic SWNTs (absorbance spectra plotted in blue in **e**; heterogeneous mixture before sorting plotted with a dashed grey line). (S33, M11, S22 highlighted as in Fig. 1g.)

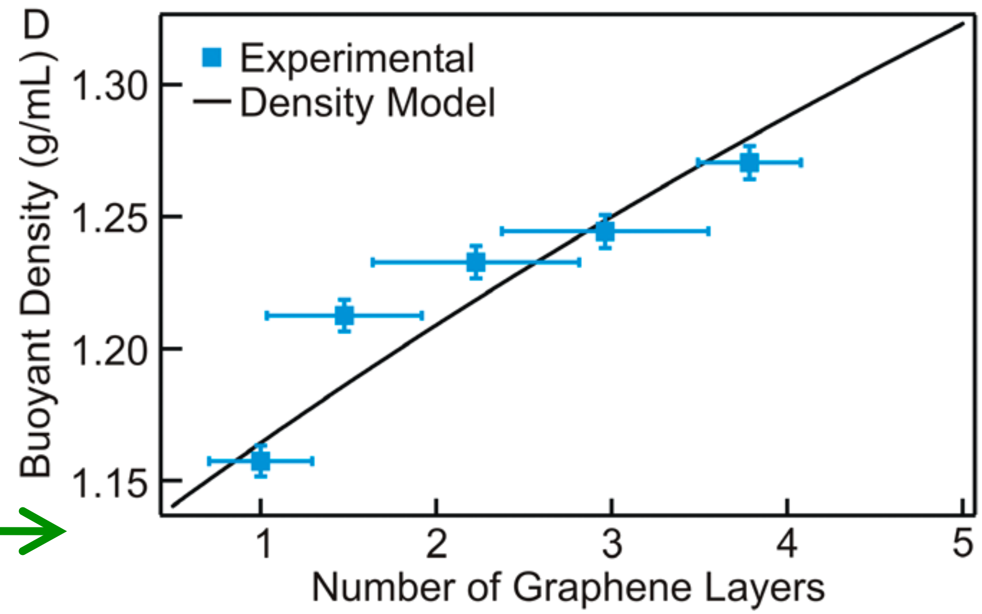
Arnold et al., *Nature Nanotechnology* 1:60-65, 2006

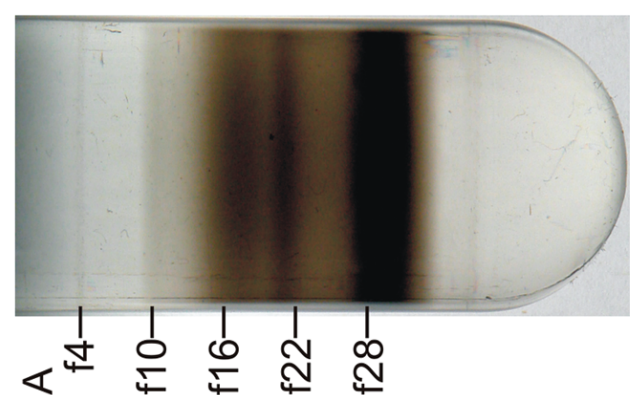
Separation of graphene by N_{layers}

Disperse



Centrifuge





Green and Hersam, *Nano Letters* 9(12):4031-4036, 2009.

Shape separation of Au nanostructures

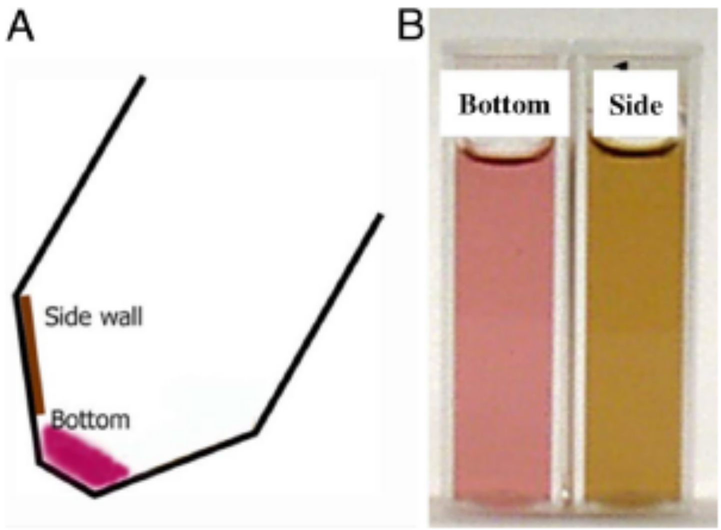
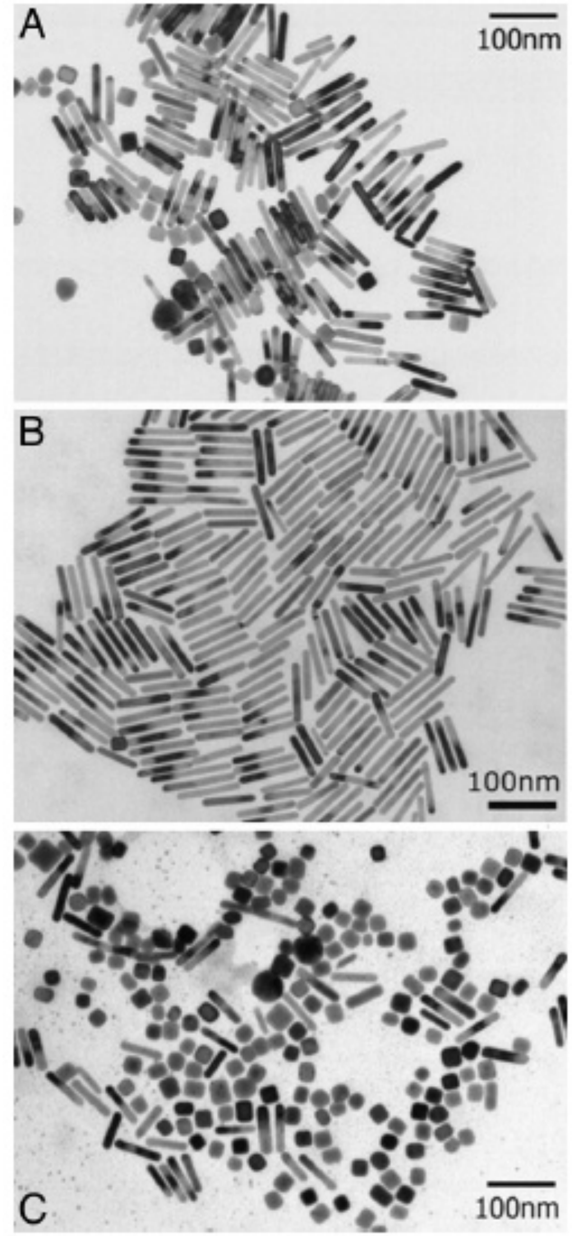


Fig. 3. Separated Au nanoparticles. (*A*) Schematic drawing of a centrifuge tube after the centrifugation and the color of resulting solutions. (*B*) The color of the solution taken from 2 different locations shown in *A*.

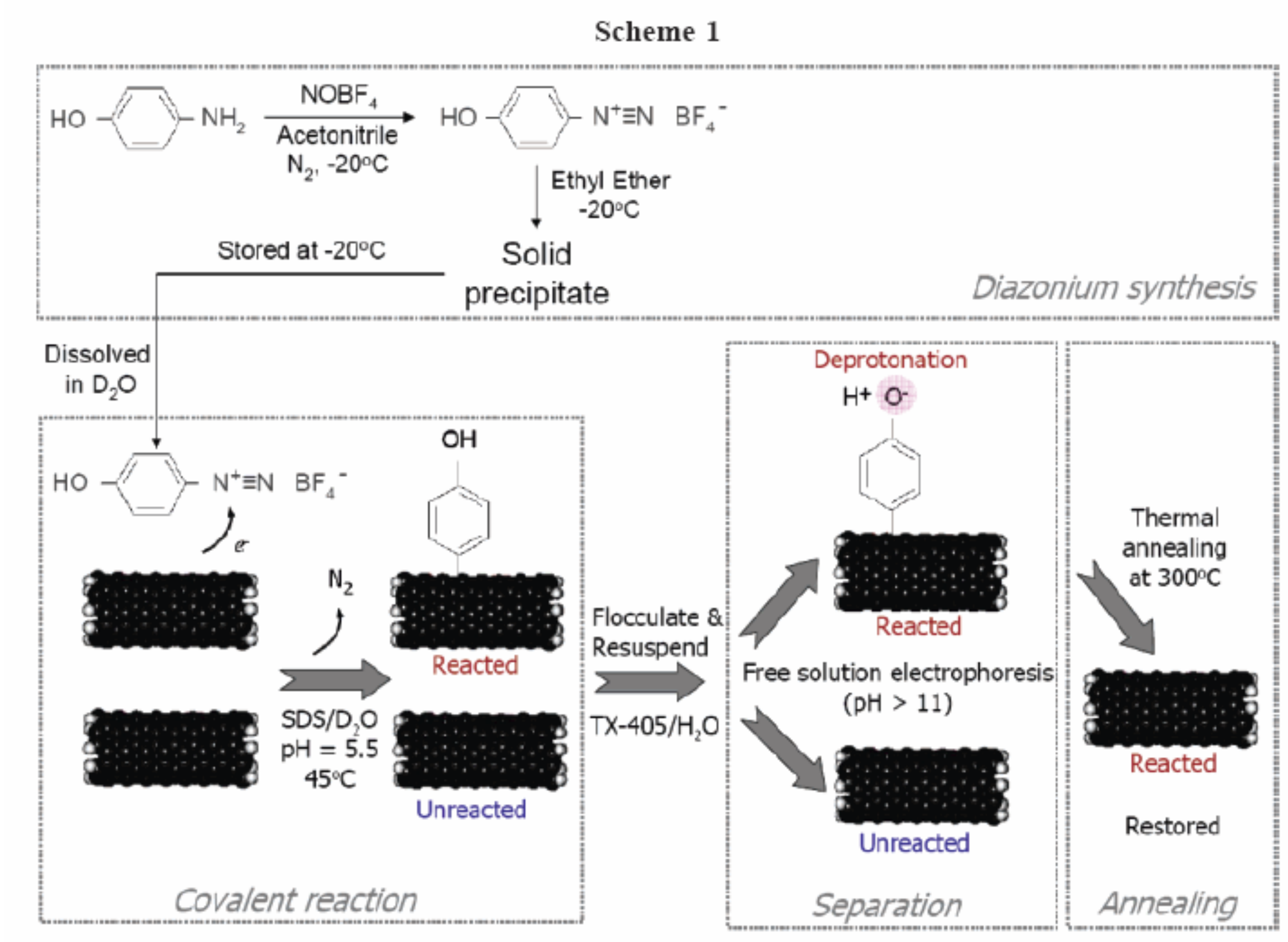


Start

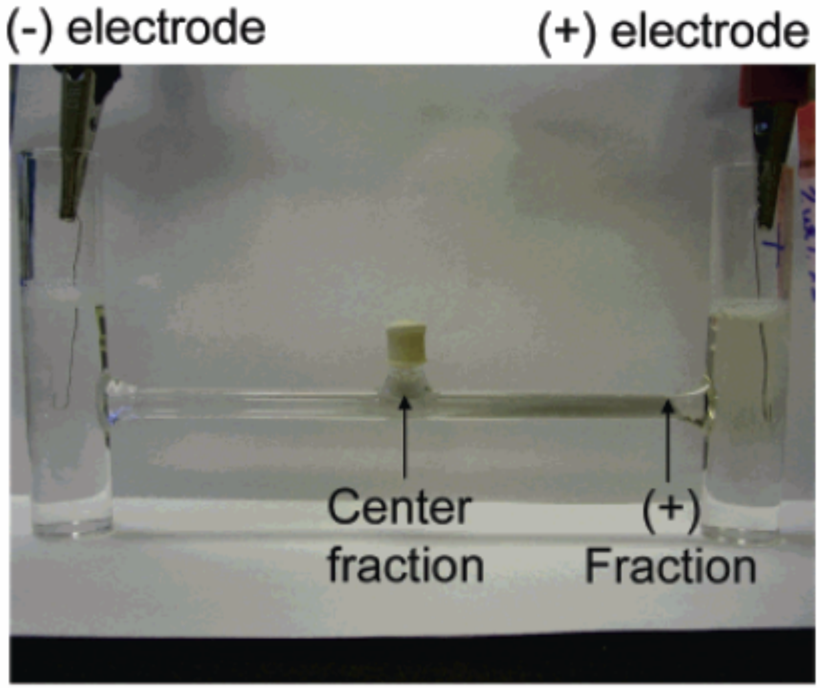
Sidewall

Bottom

CNT separation by functionalization then electrophoresis



Kim et al., *Chem. Mater.* 19:1571, 2007.



(b)

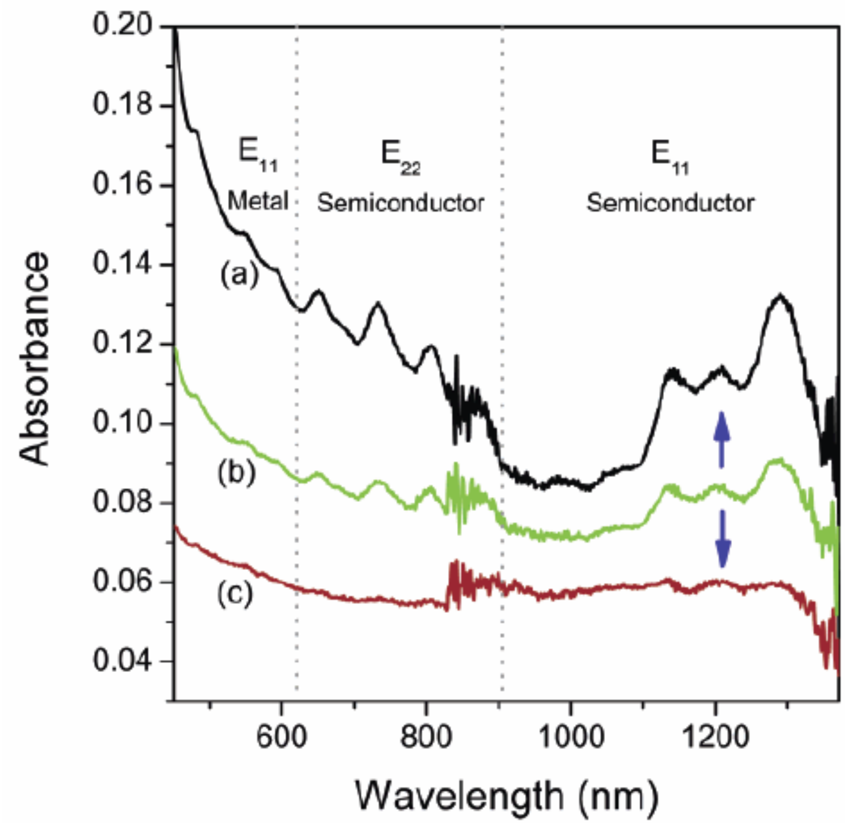


Figure 4. UV−vis−nIR absorption spectra of separated fractions in reaction 1: (a) center fraction, (b) original sample, and (c) (+) fraction.

Kim et al., *Chem. Mater.* 19:1571, 2007.

Membrane filtration

Membrane

From Wikipedia, the free encyclopedia

Look up *membrane* in Wiktionary, the free dictionary.

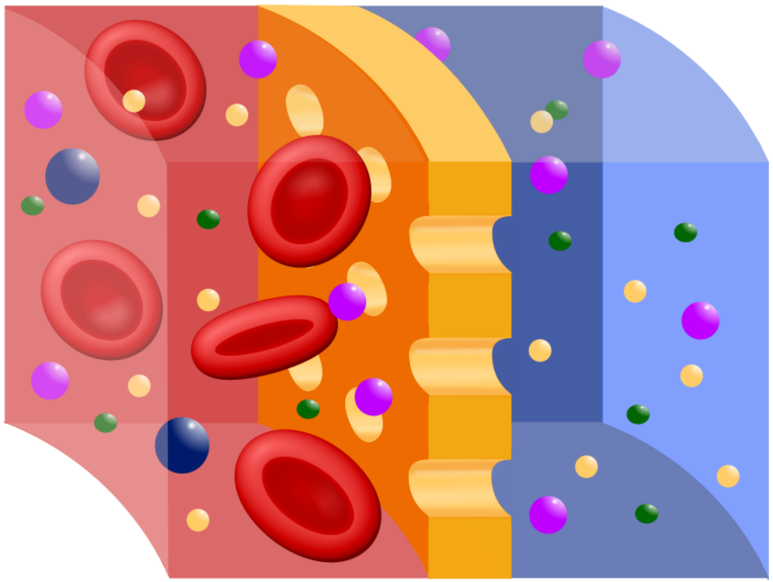
In medicine, microbiology, cellular physiology and biochemistry a **membrane** is a thin layer that separates various cellular structures or organs. It usually includes lipid bilayer reinforced by proteins and other macromolecules, and can refer to:

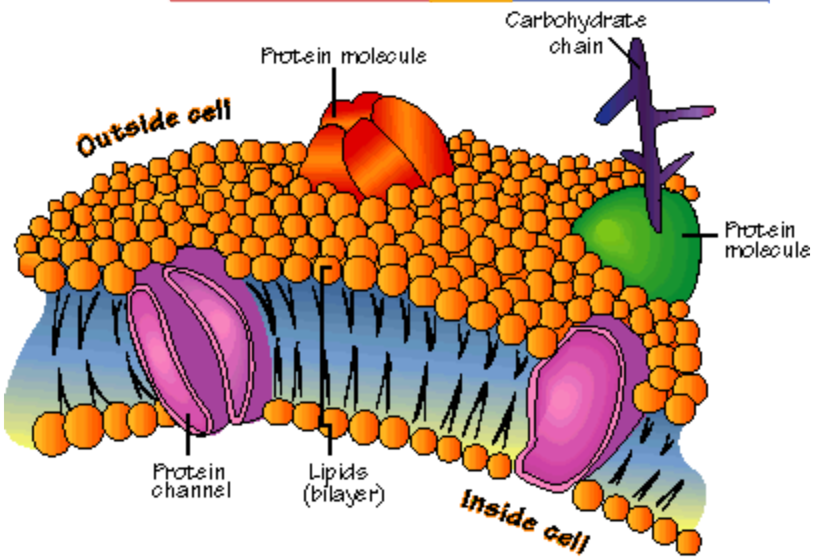
- Basement membrane, the combination of the basal lamina and lamina reticularis or of two basal laminae
- Biological membrane
  - Cell membrane
  - Endomembrane system that divides the cell into organelles
  - Outer membrane or inner membrane of an organelle
  - S-layer, a cell membrane of bacteria
- Mucous membrane
- Serous membrane and mesothelium that surround organs, including:
  - Peritoneum that lines the abdominal cavity
  - Pericardium that surrounds the heart
  - Pleura that surround the lungs
  - Periosteum, membrane that surrounds bone
  - The meninges that surround the brain: the dura mater, arachnoid mater, and the pia mater
- Skin, part of the integumentary system

Membrane may also refer to:

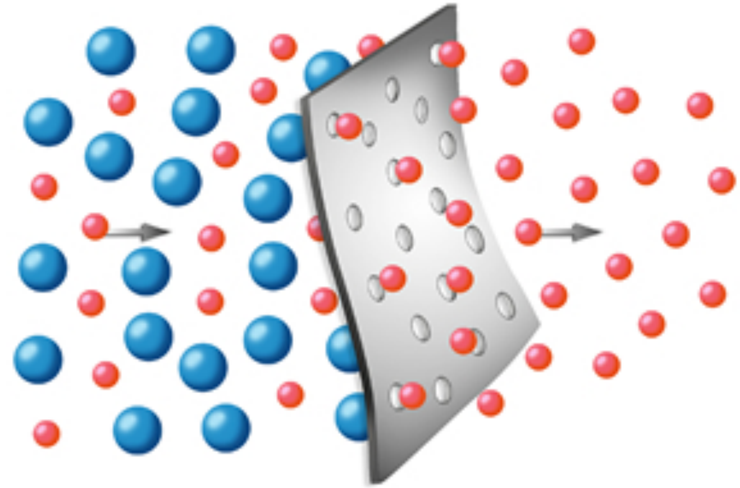
- A mechanical membrane, a thin, flat flexible part that can deform or vibrate when excited by an external force.
- Membrane keyboard
- Artificial, semipermeable membranes which are used to separate species in a fluid on the basis of size, charge or other characteristics. Such membranes are employed in a range of applications from water and wastewater treatment (see reverse osmosis, diffuser (sewage), landfill liners, nanofiltration, ultrafiltration and microfiltration) to hydrogen fuel cells (see proton exchange membrane).
- The Membranes - an English post-punk band
- Membranes also refered to as branes in string theory

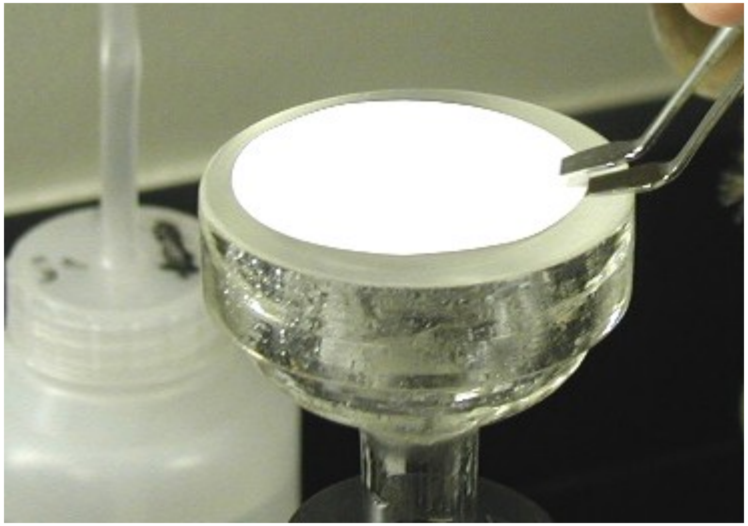
Dialysis/cell membrane





Fuel cell



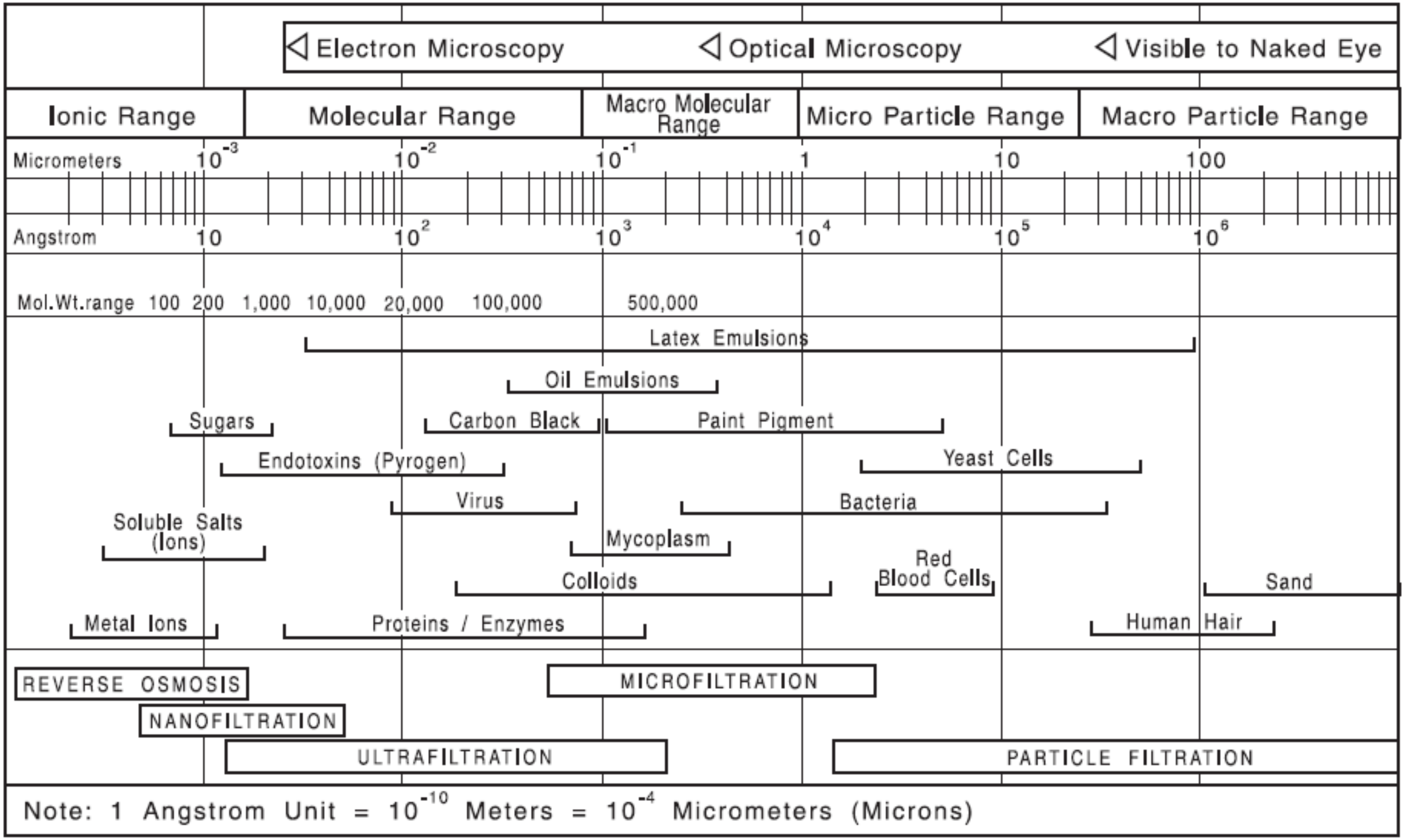


Disc filter

pore size uniformity is important

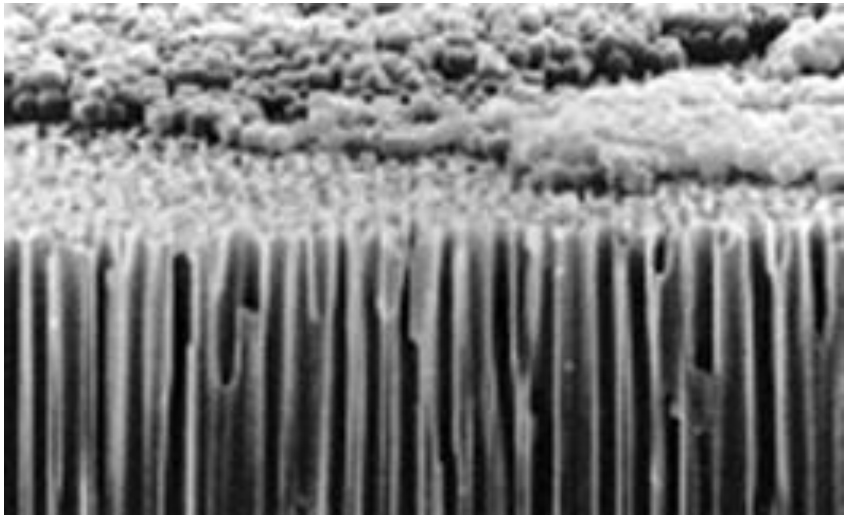
http://en.wikipedia.org/wiki/Semipermeable_membrane

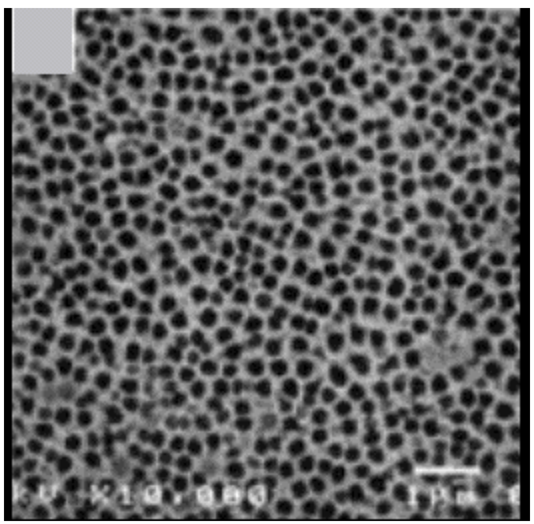
Regimes of membrane filtration



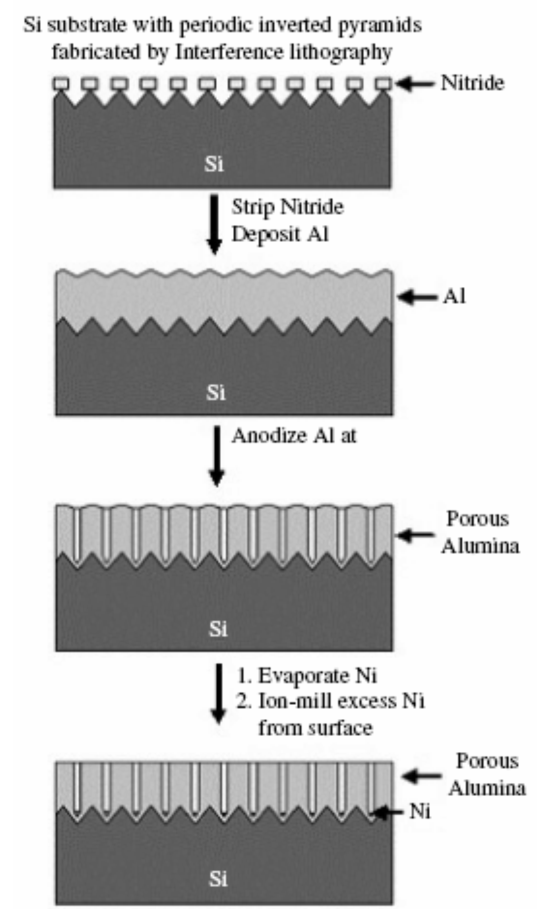
http://www.dow.com → membrane separations

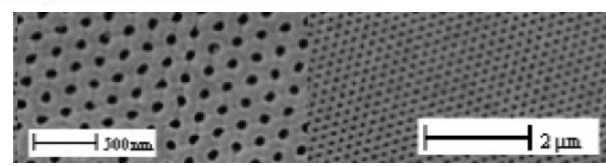
Nanoporous anodic alumina membranes





Whatman anopore membranes (not templated)





Template method: control size and spacing→ regular arrays

Krishnan et al., *Nanotechnology* 16:841, 2005.

Membrane filtration of nanoparticles by size exclusion (polymer membranes)

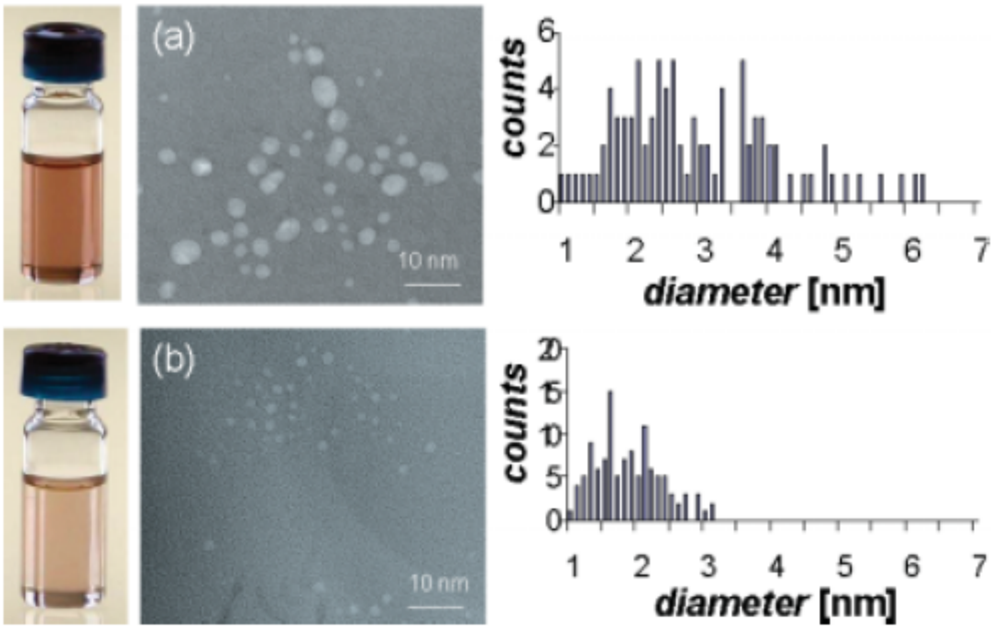
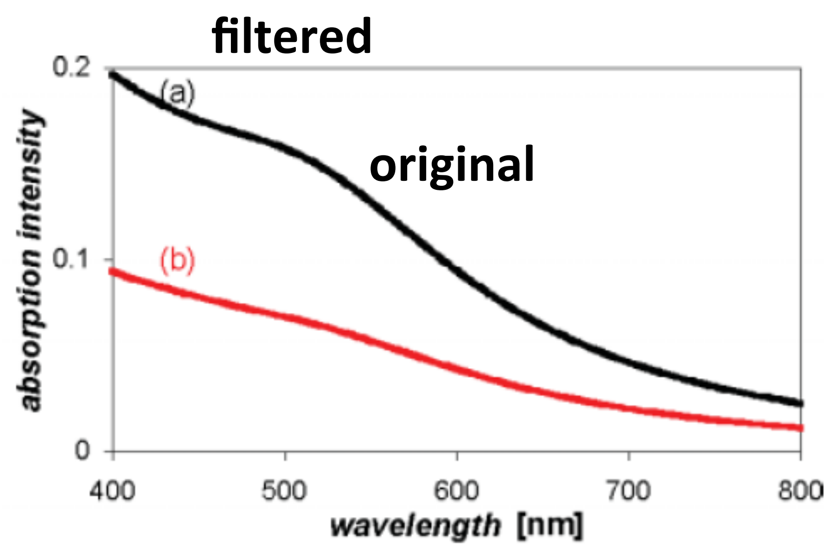
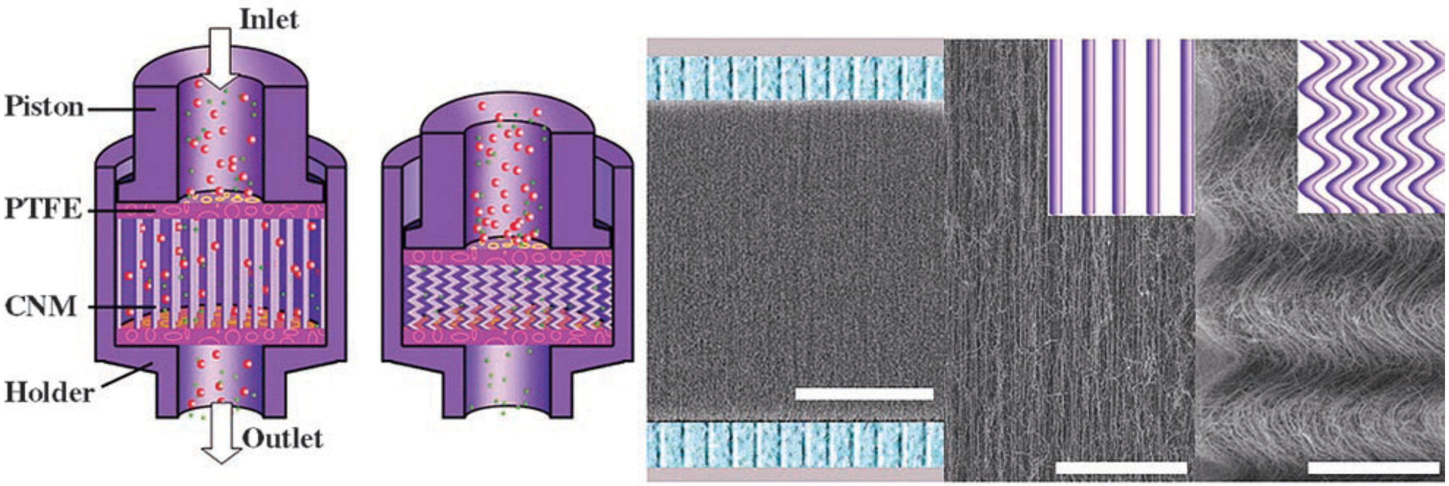


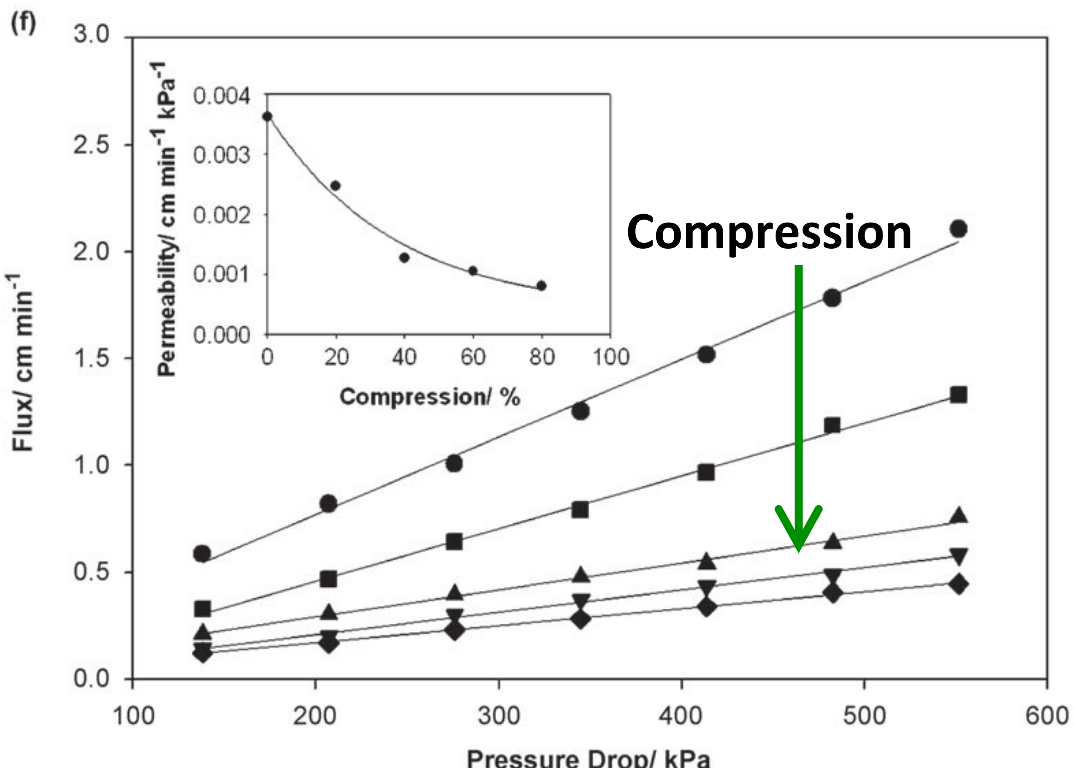
Figure 2. Optical absorption spectra and TEM images with metal core size statistics of nanoparticles prepared with 1:1 molar ratio of HS–C_{18}/Au in toluene. a) Feed solution (average size ~3.0±1.2 nm); b) solution permeated through PVDF-*g*-POEM-coated membrane with cutoff ~3.2 nm (average size ~1.9±0.5 nm).



Athakul et al., *Adv. Mater.* 17(5):532, 2005.

CNT forests as mechanically tunable filters





Li et al., *Small* 3(4):595-599, 2007.

A combination of methods usually seeks the desired final result (e.g., seed amplification)

Scheme 1. A Depiction of the Amplification Growth Process of a Carbon Nanotube