Nanomaterials and Their Environmental Applications

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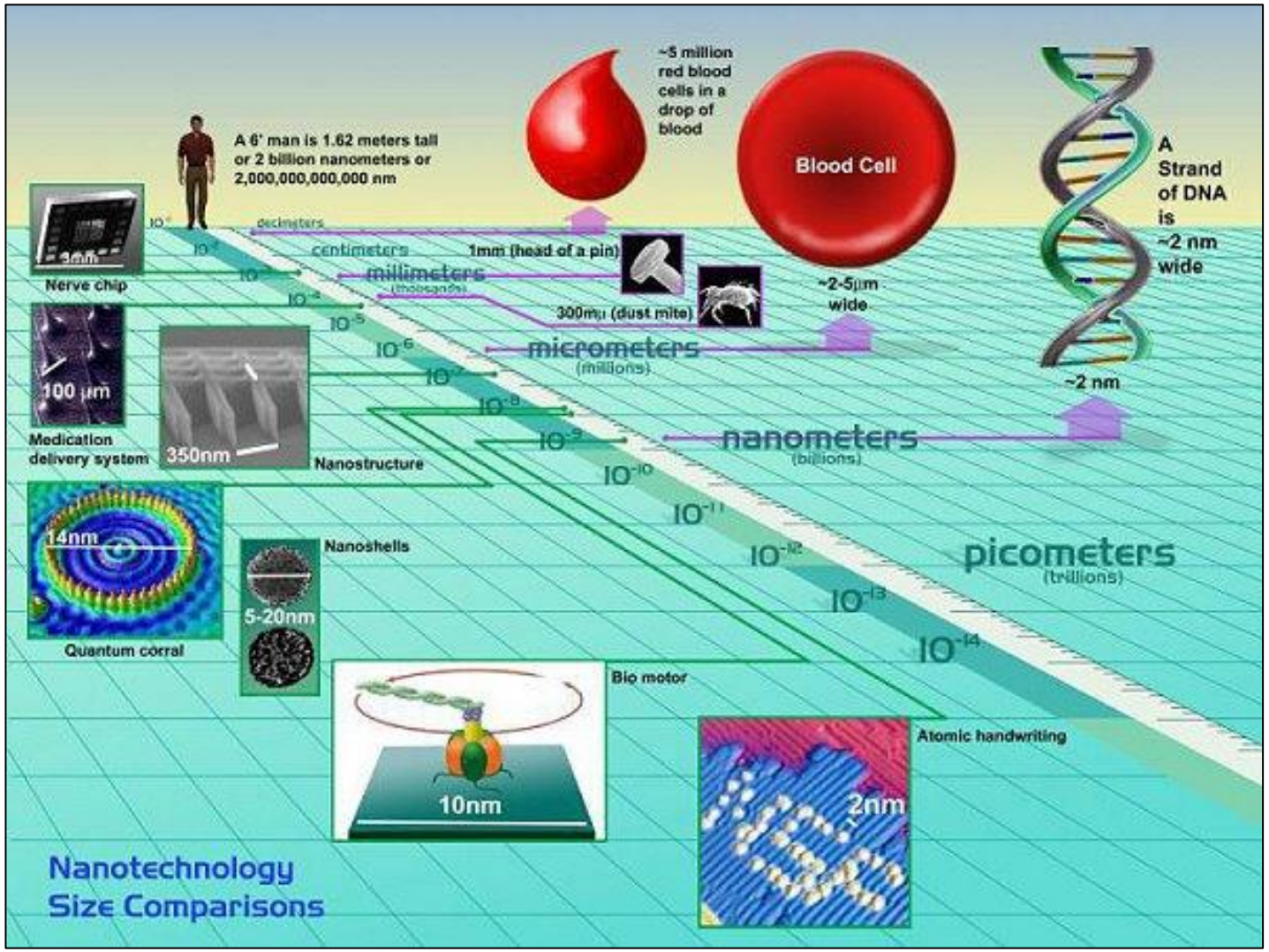
Nanomaterials - definitions

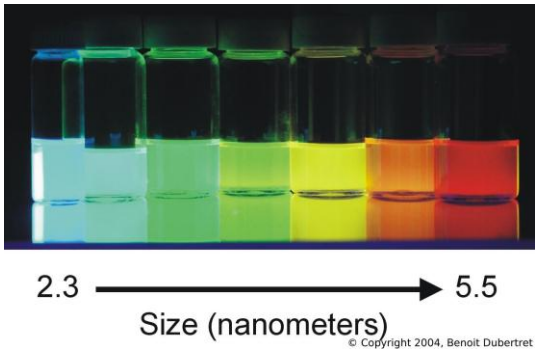


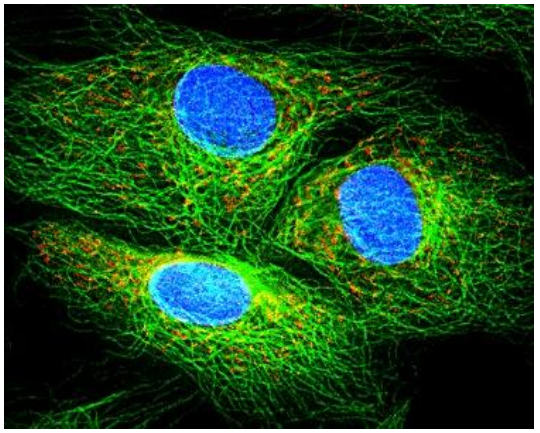
Source: US EPA www.epa.gov

What are nanomaterials useful for?

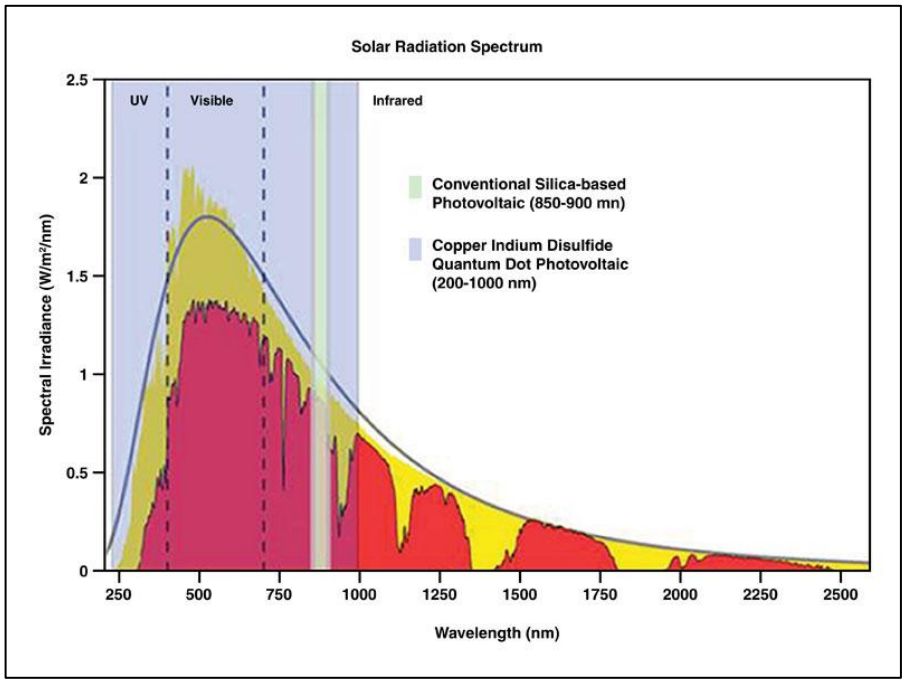
- **Cellular imaging (0D)**
  - Size-tunable emission wavelength
  - Greater brightness and photostability
- **Solar cells (0D)**
  - Improve matching to solar spectrum
  - Improved efficiency

e.g. CdSe, ZnS, 2-10nm diameter





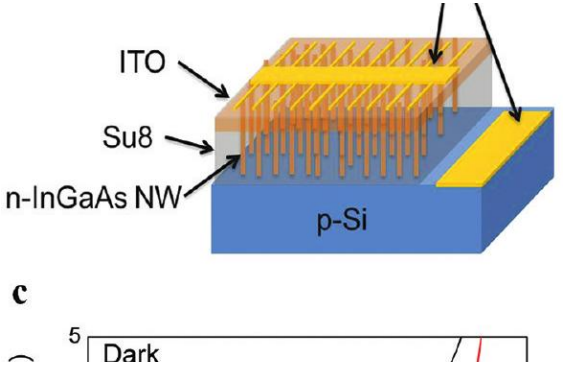
Source: Quantum Dot Corporation, Dec 2002



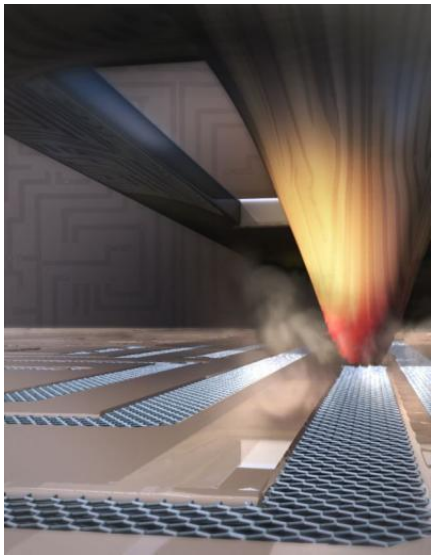
Source: Idaho National Lab, https://inlportal.inl.gov, 2009

What are nanomaterials useful for?

- **Solar cells (1D)**
  - Varying composition = varying bandgap
  - Accommodate lattice mismatch
  - Results in higher efficiency
- **Next-generation microprocessors (2D)**
  - Graphene offers higher intrinsic conductivity with atomic-level thinness (<1nm)
  - Faster (higher frequency) processors
- **Next-generation batteries (0D, 1D)**
  - Improved charge/discharge rates
  - Improved cycle lifetime



Shin et al., Nanoletters 2011 11, 4831

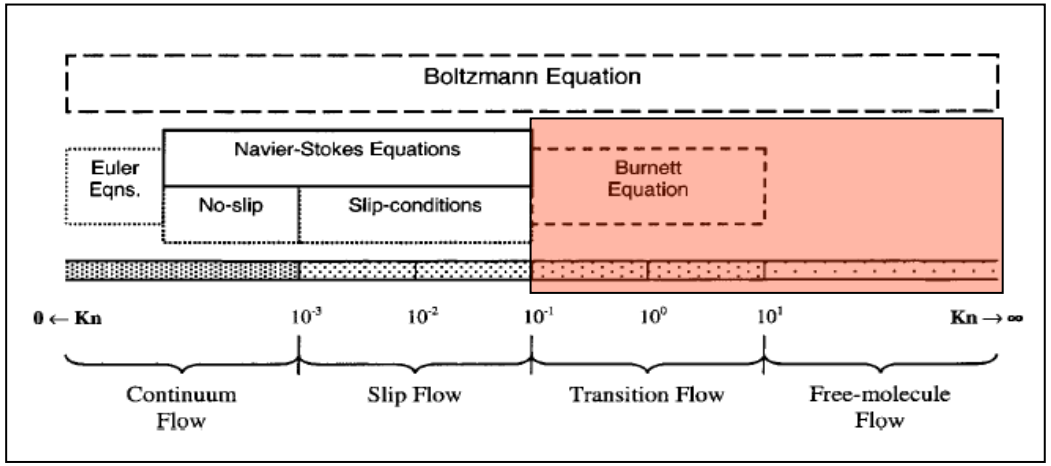


Graphene interconnects, Courtesy: Univ of Iillinois, Urbana-Champaign, 2010

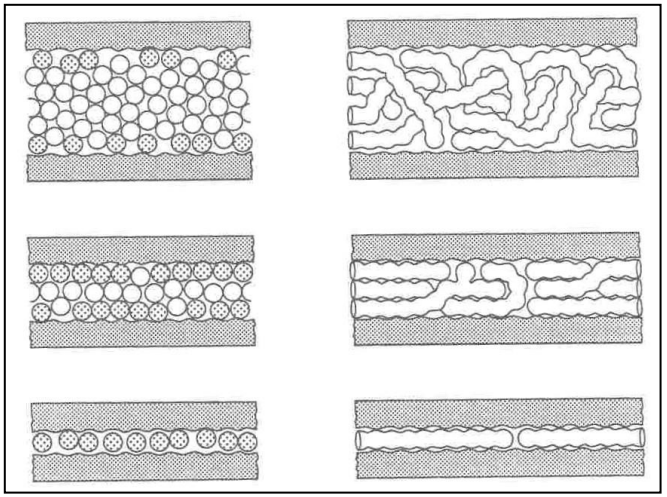
Nanofluidics

- Confined fluids behave differently than bulk fluids
- Must model discrete molecular interactions, **not a continuum**
- Field is not new, but the materials are

Flow regimes defined by Knudsen number



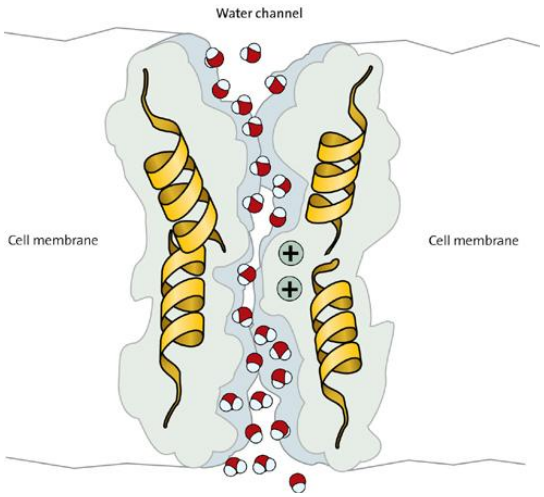
Surface-induced ordering of liquid molecules



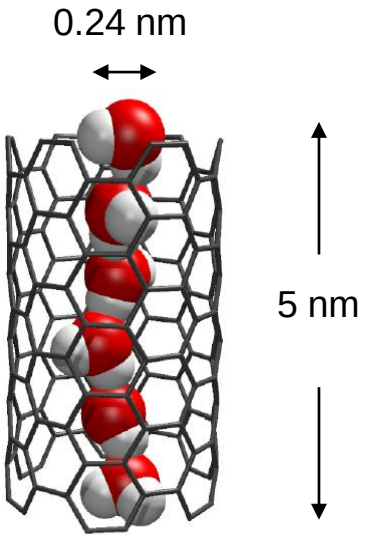
Courtesy: J.Israelachvili, Intermolecular & Surface forces, AP, 1991

Nanofluidic Applications

- **Separations** – the obvious choice
  - Biomimetic: aquaporins, ion channels
  - Synthetic: carbon nanotubes, silica nanopores

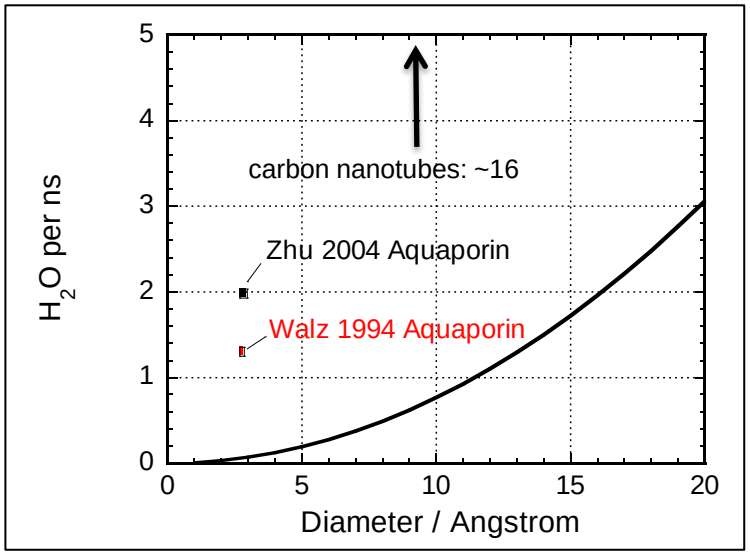


http://www.rsc.org/chemistryworld/Issues/2003/November/theflow.asp



(6,6) carbon nanotube

G. Hummer et al., Nature 414 (2001), 188.



- Conventional fluid theory does not work for these materials!

Nanofluidic separations and the environment

nanOasis

- Reduced energy and improved selectivity
  - Desalination
  - Solvent purification
  - Gas separations

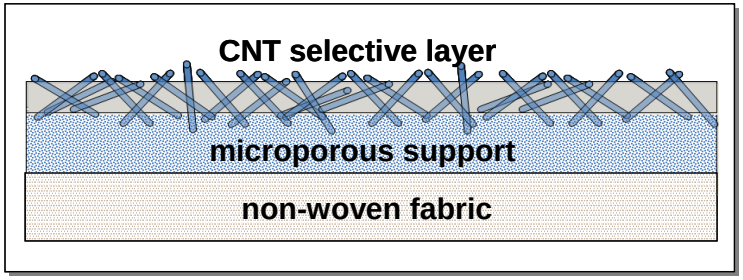
Reverse-osmosis plant, up to 1000psi operating pressures, courtesy water-technology.net

A typical petrochemical refinery and distillation facility, courtesy squibbdemolition.com

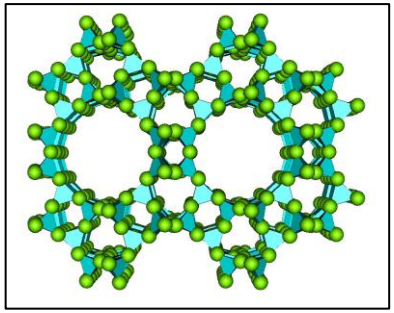
Polish Oil and Gas Co. cryogenic gas purification facility, courtesy icec-icmc.wroc.pl

Nanofluidics for desalination

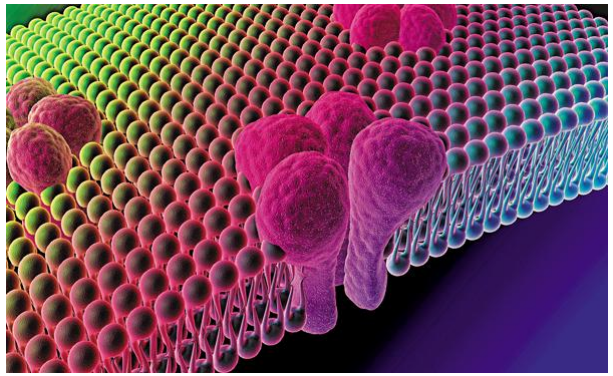
- **NanOasis**
  - carbon nanotubes = high water flux, selective pores
  - use existing membrane fab techniques
- **NanoH2O**
  - zeolite nanoparticles = higher water solubility polyamide
  - use industry-standard polyamide membranes
- **Danfoss AquaZ**
  - aquaporin proteins = high water flux + best selectivity in nature
  - how do you stabilize channels?



Cartoon of carbon nanotube thin film composite membrane, Courtesy NanOasis Inc.



Representative zeolite crystal structure, Prof. Price, U Tulsa

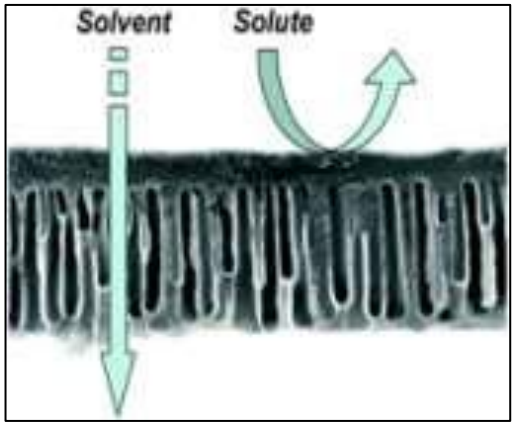


Cartoon of aquaporin protein channels inserted into lipid bilayer, Courtesy Danfoss AquaZ

Nanofluidics for solvent purification

- Possible >75% energy savings over distillation
- Few examples of large-scale implementation
- Challenges
  - polymer stability
  - CAPEX
- Nanopore-based solvent-resistant membrane
  - Choose any polymer
  - Nanpore determines transport properties

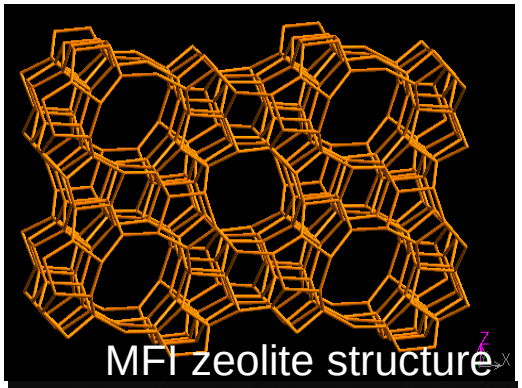
Exxon-Mobil's "Max-Dewax" Process 1999, www.ogj.com

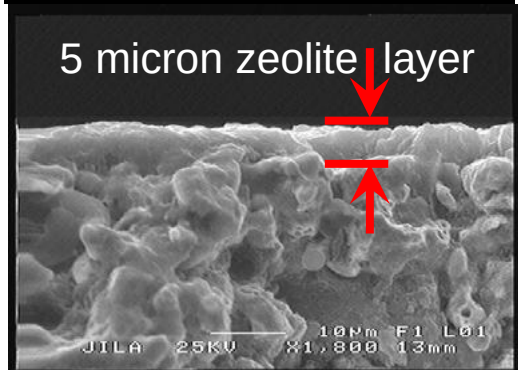


P. Vandezande et al., Chem. Soc. Rev. 2008

Nanofluidics for gas separations

- Similarly large energy savings versus cryo-separations
- Very early-stage
- Zeolites
  - highly selective, mixed-matrix membranes
  - transport resistance!
- Carbon nanotubes
  - highly selective, low transport resistance
  - hard to make small (<5Å ID)



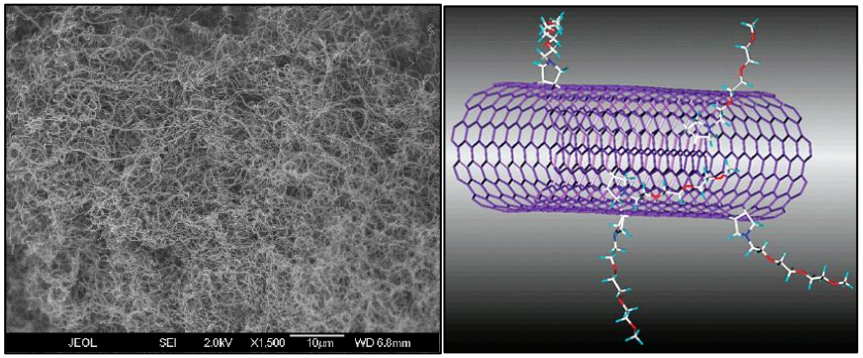


Profs. Noble and Falconer, UC Boulder

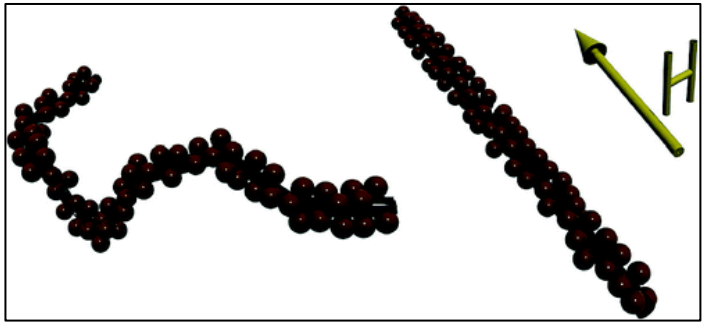
G. Arora et al., Nanolett. 2007, 7, 565.

Key Challenges in Nanofluidics

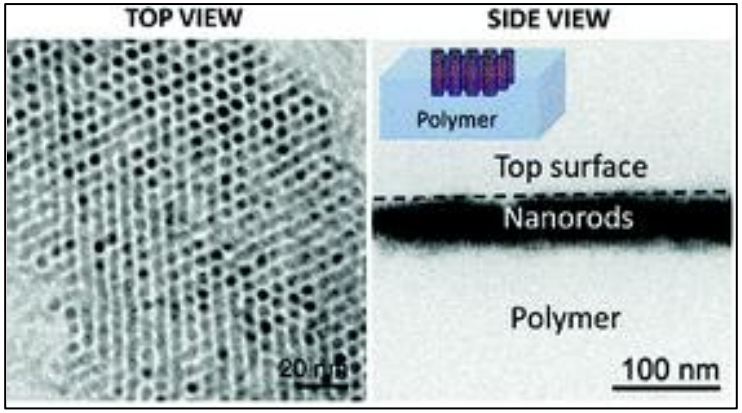
- Synthesis
- Deaggregation
- Assembly & Orientation



Left: CNT powder, courtesy NanoLab
Right: Cartoon of an ylide functionalized CNT, JACS 124, 760 (2002).



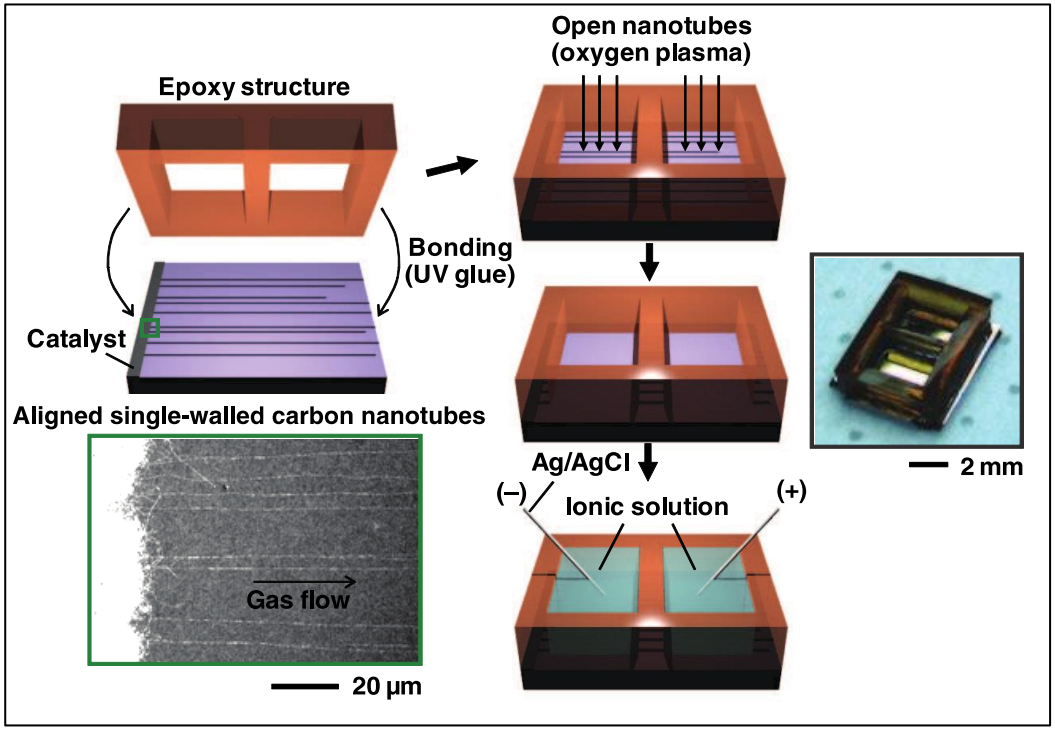
Alignment magnetite functionalized MWCNTs by an external magnetic field, J Phys Chem B 2005 109, 19060.

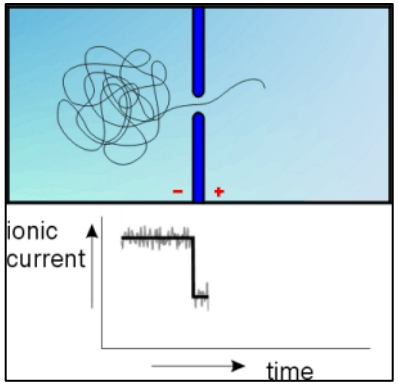


Alignment of nanorods through self-assembly onto polymeric supports, Macromolecules 2011, 44, 7364.

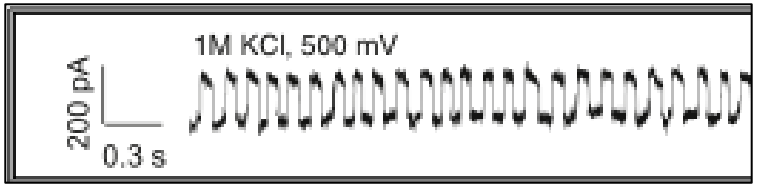
Key Challenges in Nanofluidics (cont'd)

- Diagnostics
  - materials properties ~ nanofluidic flow?
  - single molecule/ion(!) transport through CNTs





Courtesy Cees Dekker, U of Delft



Single CNT flow device; current trace showing Coulter-like blockade events from individual ions, Strano-group MIT, Science 329 1320 (2010).

Summary

- Nanomaterials long touted for optical/electronic properties
- Emerging interest in fluid properties for advanced separations
  - positive environmental effects through reduced energy
  - only desalination technologies are close to commercial realization
- Challenges remain to developing nanofluidic applications