

10.524

Self-assembly and Nanotechnology



Instructor: Dr. Zhiyong Gu

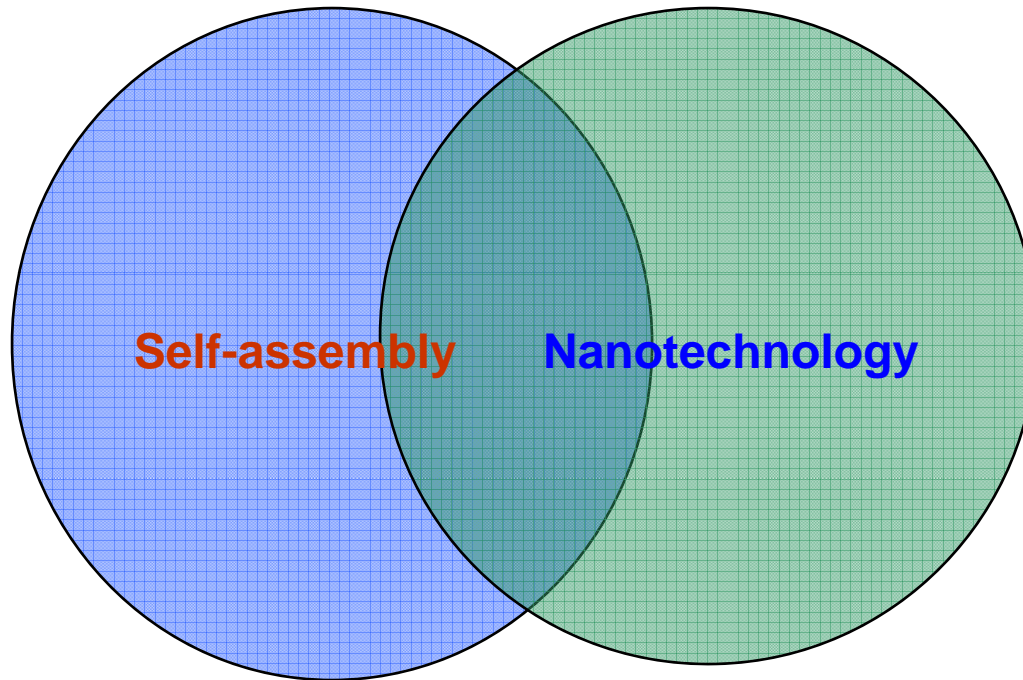
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Office hours: Mon 11:00am-12:30pm;
Wed 11:00am-12:30pm, and by appointment

Why Together?



Self-assembly and Nanotechnology

What's Nanotechnology??????

- Nanomaterials
- Nanoscience
- Nanoengineering
- Nanotechnology
- Nanomanufacturing
- Nano-xxxxxxx

- Your answers●●●●●

“Nanotechnology is the understanding and control of matter at dimensions of roughly 1 to 100 nanometers, where unique phenomena enable novel applications. Encompassing nanoscale science, engineering and technology, nanotechnology involves imaging, measuring, modeling, and manipulating matter at this length scale.”

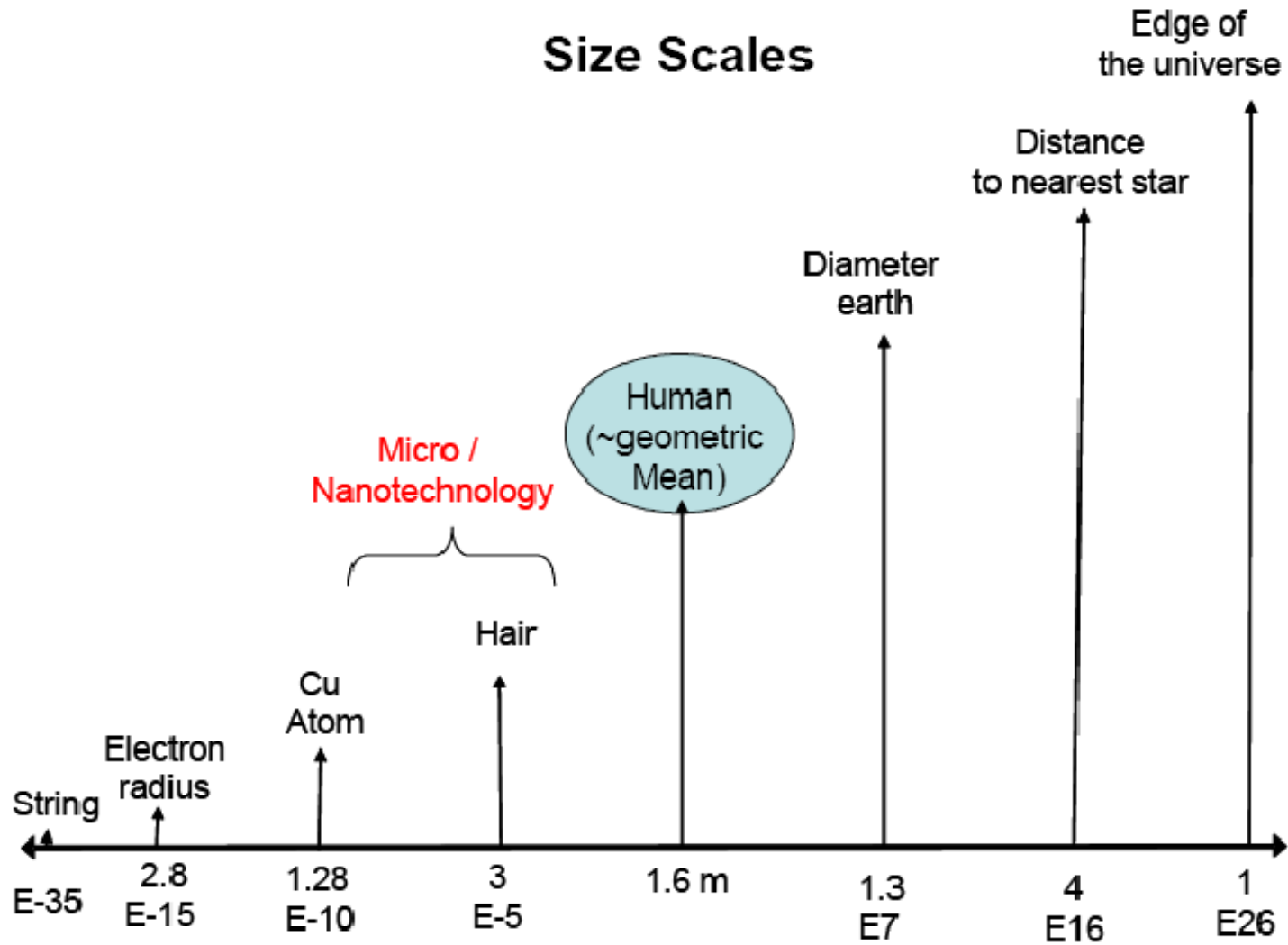
National Nanotechnology Initiative (NNI): <http://www.nano.gov/index.html>

(One nanometer (nm) is one billionth, or 10^{-9} of a meter)

Self-assembly and Nanotechnology



Size Scales



From Gracias, *Micro- and Nanotechnology*

The scale of things - nanometers and more

things natural



Dust mite
300 μm



Ant
- 5 mm



Fly ash
- 10-20 μm



Human hair
- 60-120 μm wide



Red blood cells
with white cell
- 5-8 μm



- 10 nm diameter



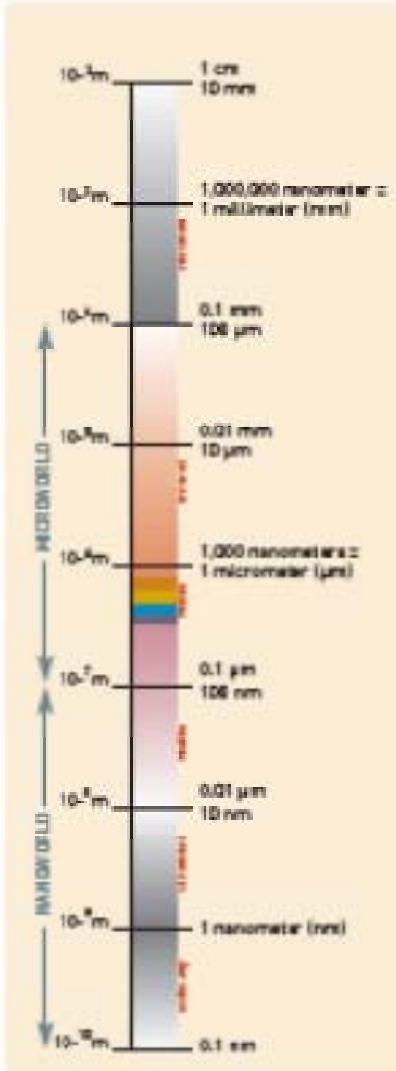
ATP synthase



DNA
- 2-12 nm diameter



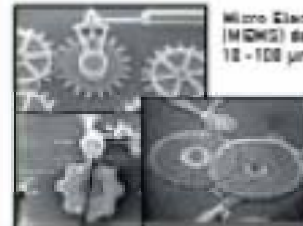
Atoms of silicon
spacing - tenths of nm



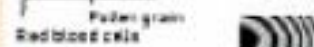
things manmade



Head of a pin
1-2 mm



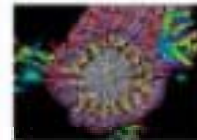
Micro Electro Mechanical
(MEMS) devices
10-100 μm wide



Pollen grain
Red blood cells



Zone plate x-ray Lens
outer ring spaces - 25 nm



Self-assembled,
nature-inspired structure
many 10s of nm



Nanoscale electrodes

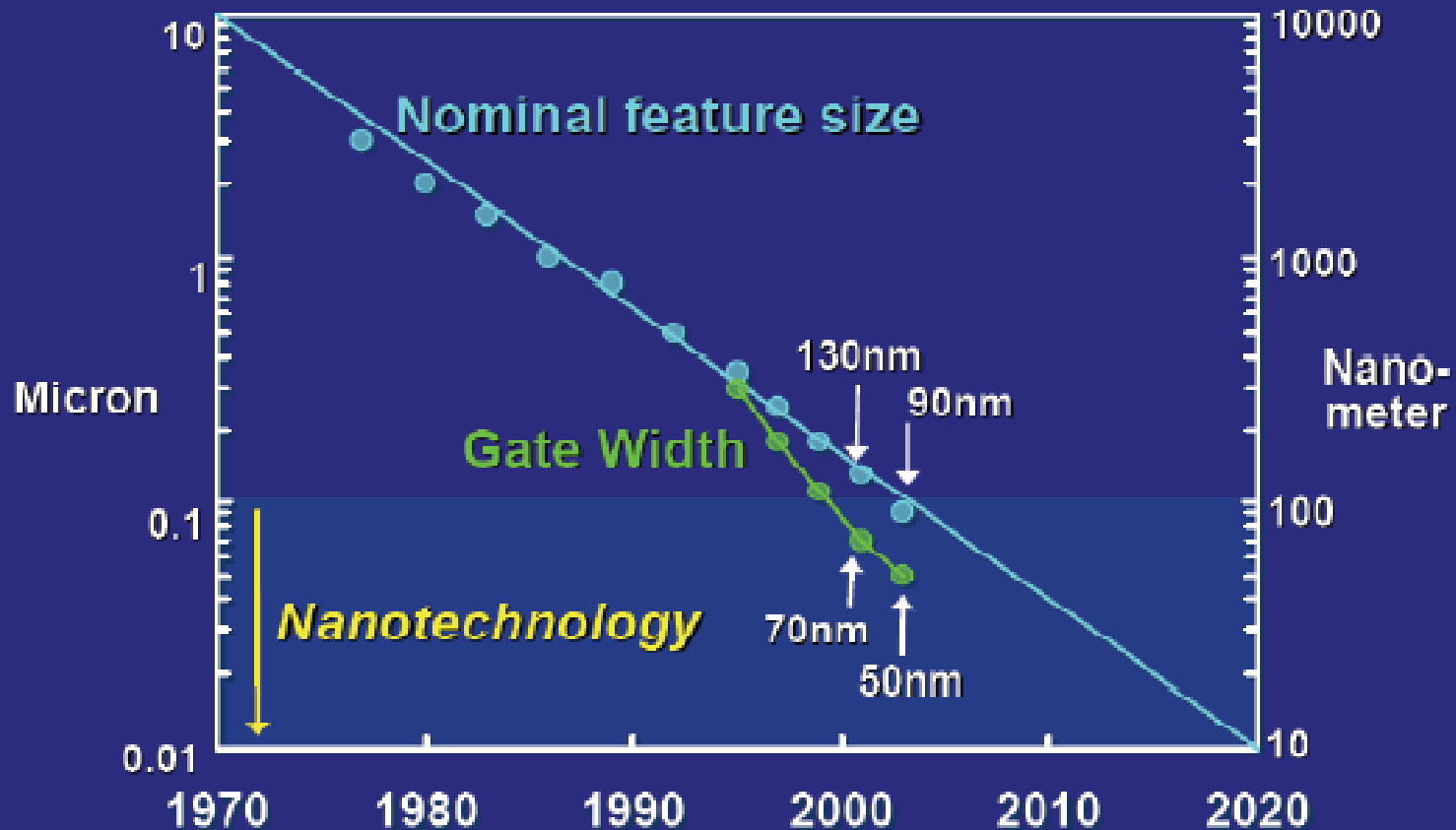


Quantum corral of 48 iron atoms on copper
surface positioned one at a time with an STM
tip Corral diameter 14 nm

THE CHALLENGE

Fabricate and control the molecular building blocks
to make useful devices,
e.g. a photoelectric
reaction center with an-
ginal controlled energy storage

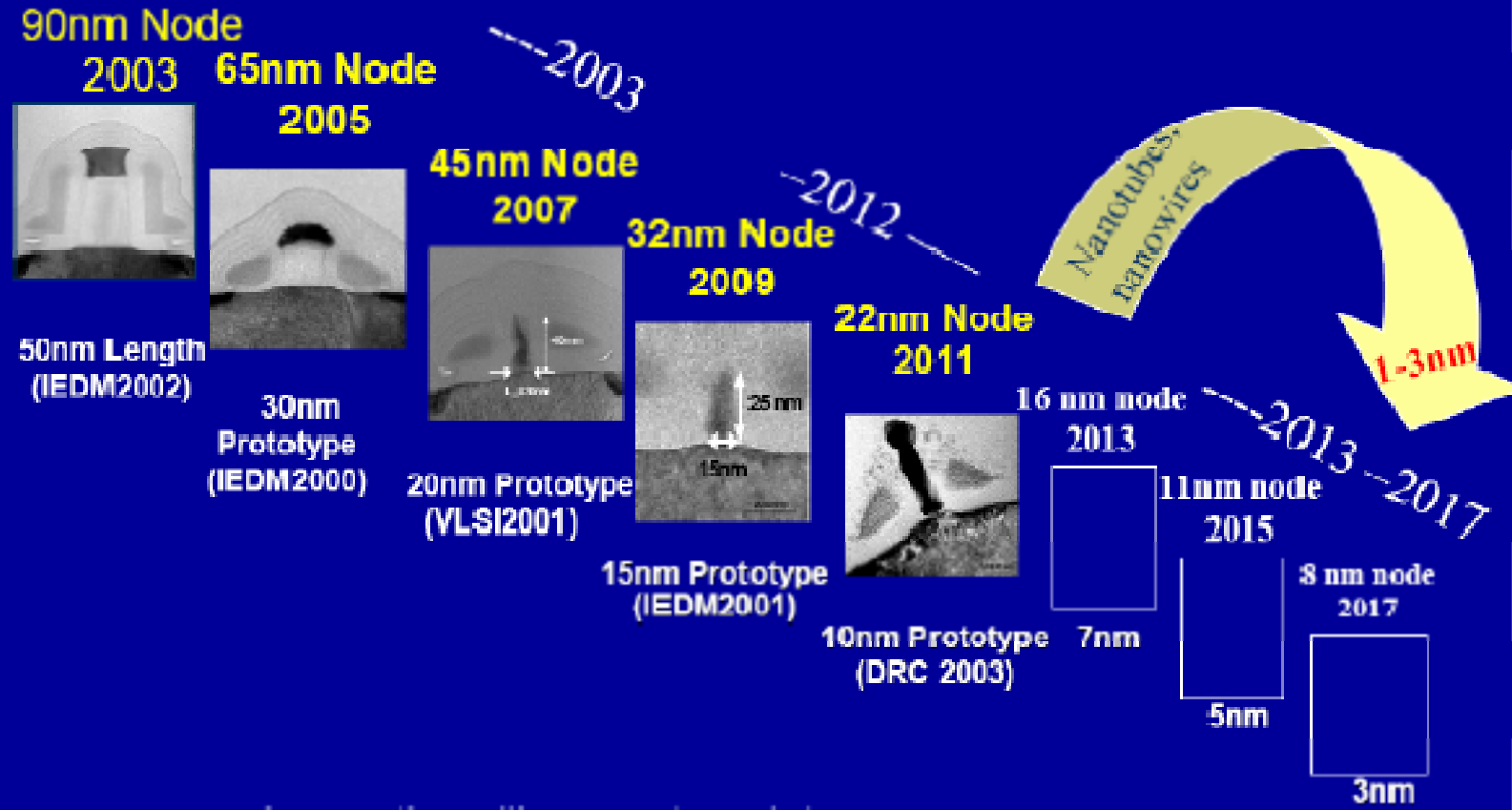
Silicon Nanotechnology is Here!



John Carruthers, Portland State University

Self-assembly and Nanotechnology

Nanotechnology will extend CMOS scaling



Innovations like quantum dots, Nanowires, Naotubes, etc.

6/11/2004

5

Feynman's Talk of "Nanotechnology" in 1959

I would like to describe a field, in which little has been done, but in which an enormous amount can be done in principle. This field is not quite the same as the others in that it will not tell us much of fundamental physics (in the sense of, "What are the strange particles?") but it is more like solid-state physics in the sense that it might tell us much of great interest about the strange phenomena that occur in complex situations. Furthermore, a point that is most important is that it would have an enormous number of technical applications.

What I want to talk about is the problem of manipulating and controlling things on a small scale.

.....

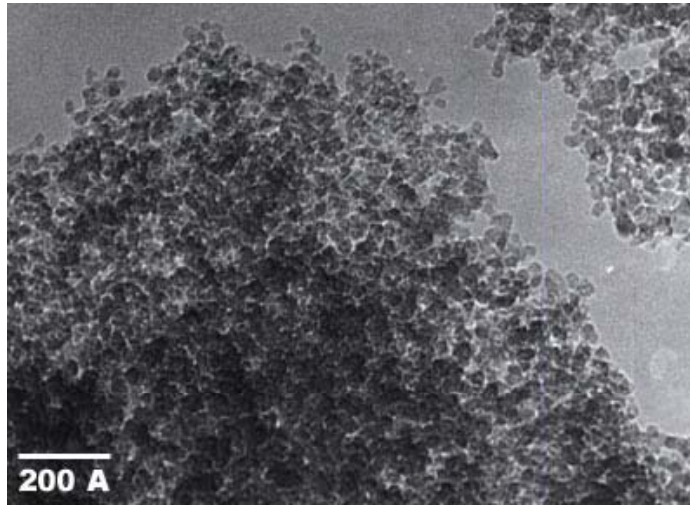
.....

There's plenty of room at the bottom; by Richard P. Feynman
1965 Nobel Prize in Physics, for quantum electrodynamics

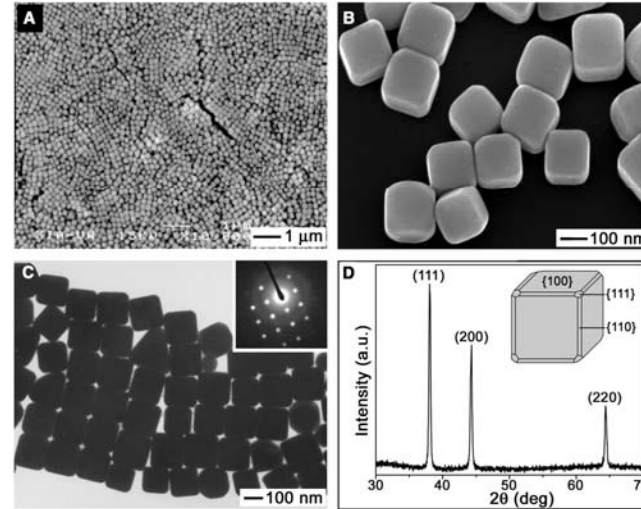
Self-assembly and Nanotechnology



Spherical and Shaped Nanoparticles

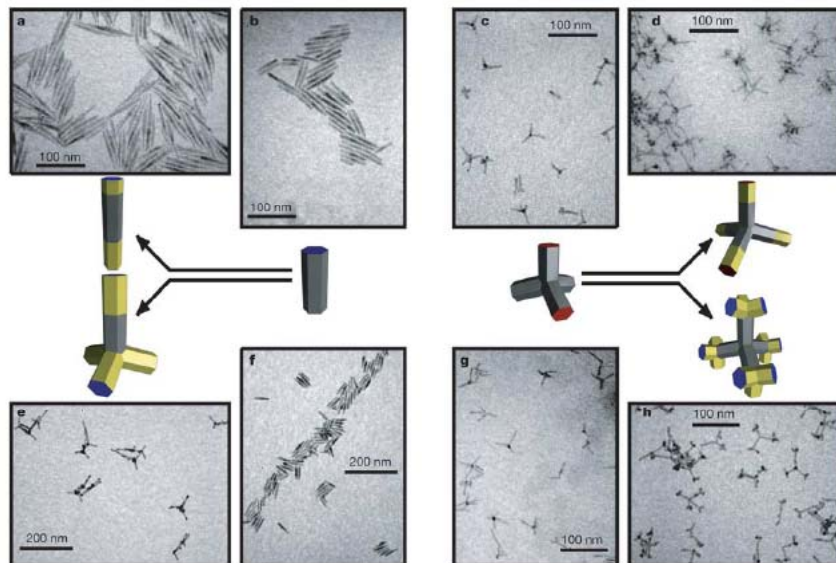


Nanodiamonds



Nanocubes

Sun & Xia, Science, 2002



Nature, 430, 2004, 190

Quantum Dots



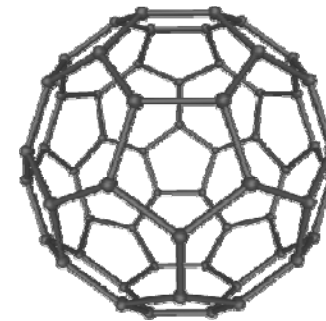
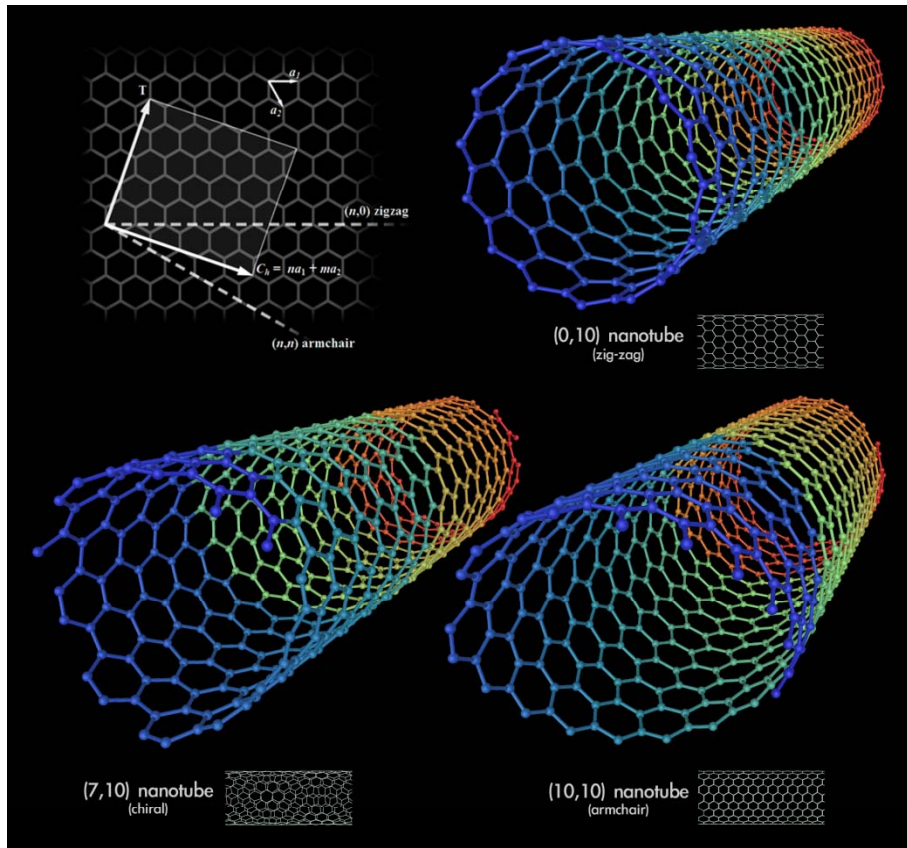
A **quantum dot** is a semiconductor nanostructure that confines the motion of conduction band electrons, valence band holes, or excitons (pairs of conduction band electrons and valence band holes) in all three spatial directions.

Fluorescence induced by exposure to ultraviolet light in vials containing various sized Cadmium selenide (CdSe) quantum dots

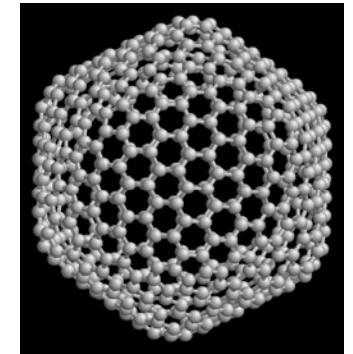
From: http://en.wikipedia.org/wiki/Quantum_dots

Self-assembly and Nanotechnology

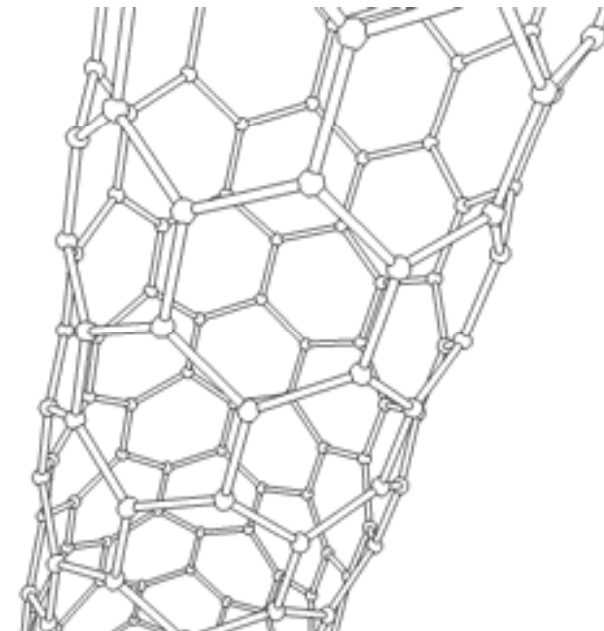
Carbon Nanotubes



Buckyballs: C₆₀



C₅₄₀

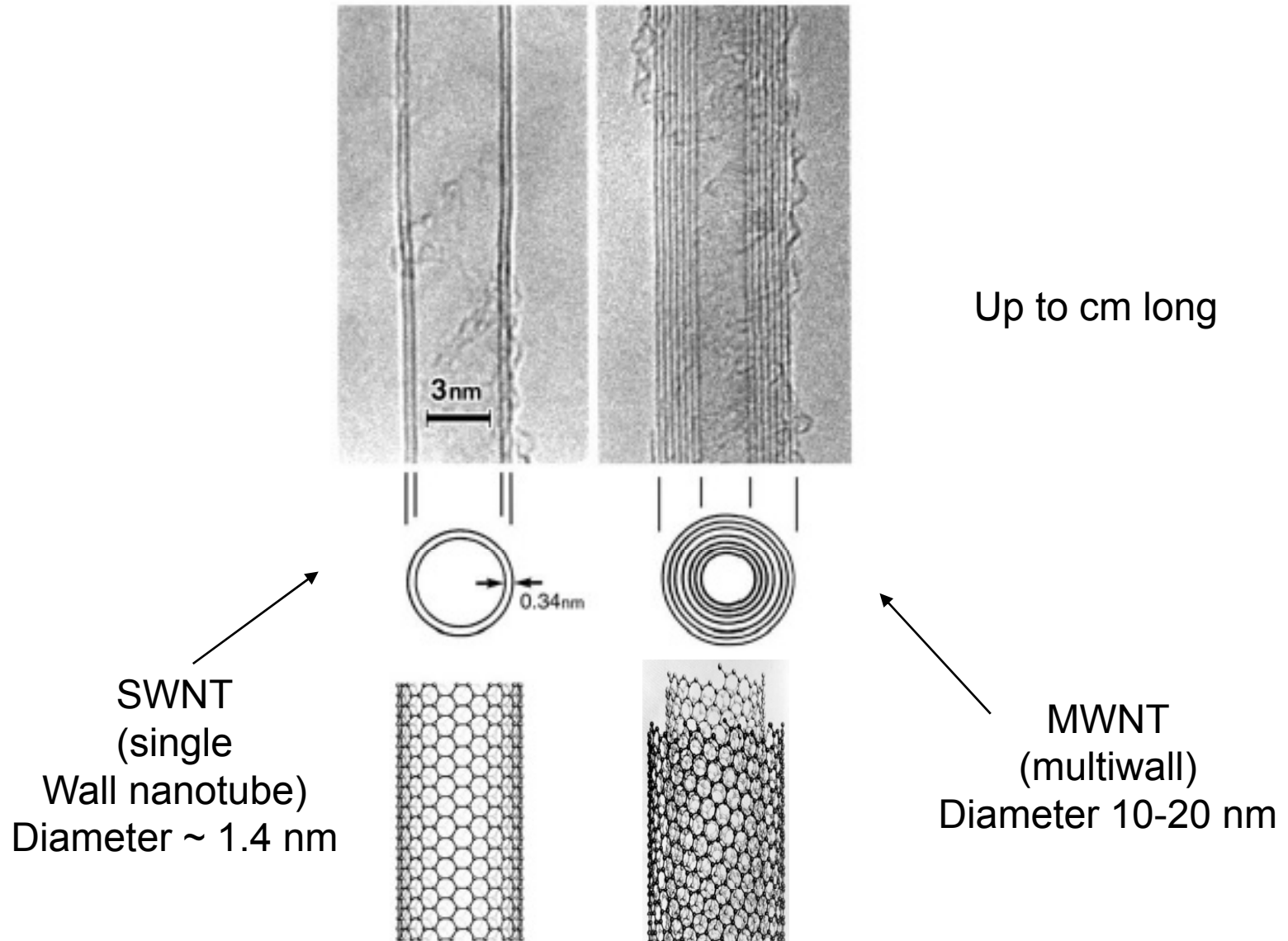


Carbon nanotubes (CNTs) are an allotrope of carbon

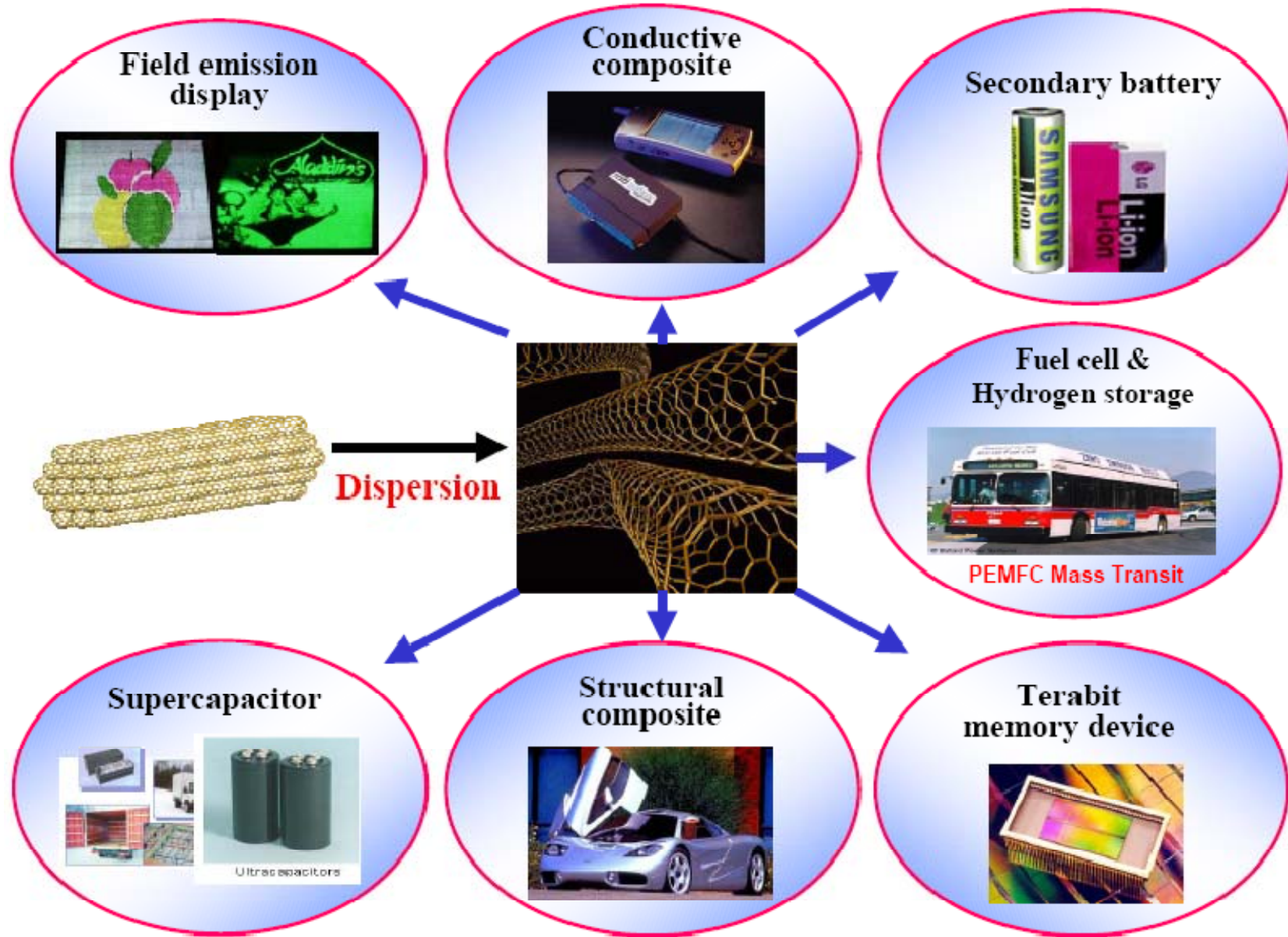
(Pictures from Wikipedia)

Self-assembly and Nanotechnology

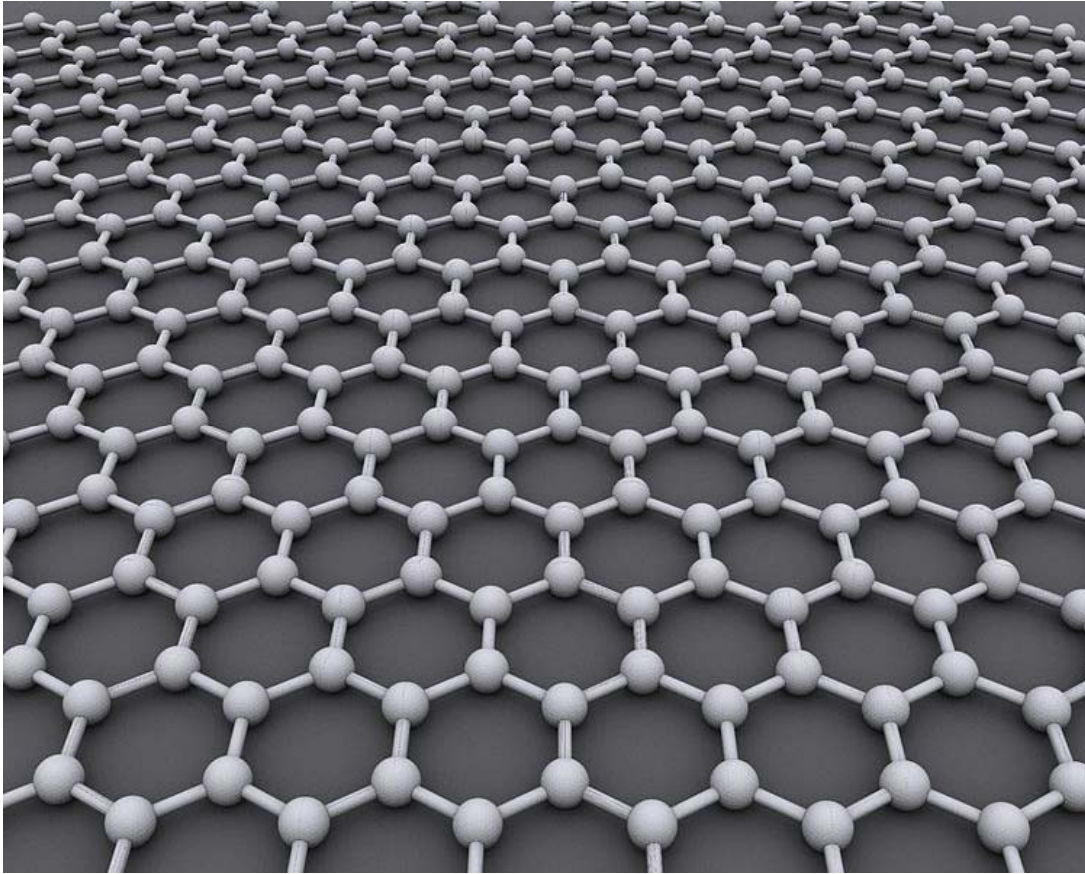
Single Wall and Multi Wall Carbon Nanotubes



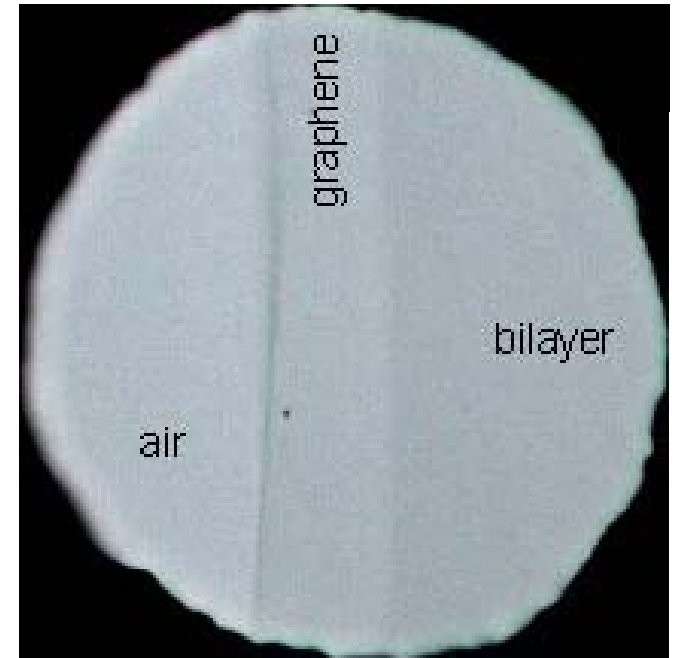
Potential applications of CNs



Graphenes



Graphene is an atomic-scale honeycomb lattice made of carbon atoms.



Optical property

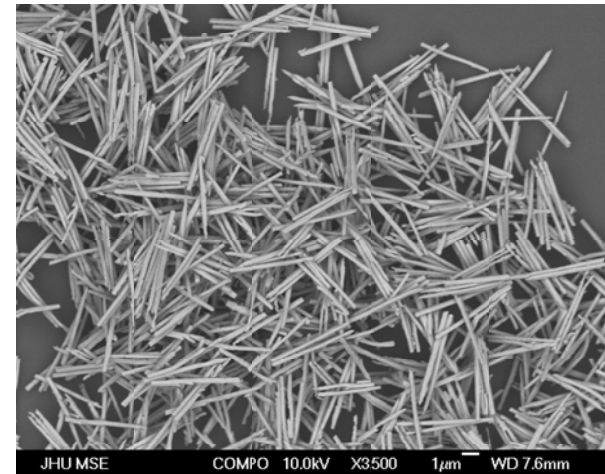
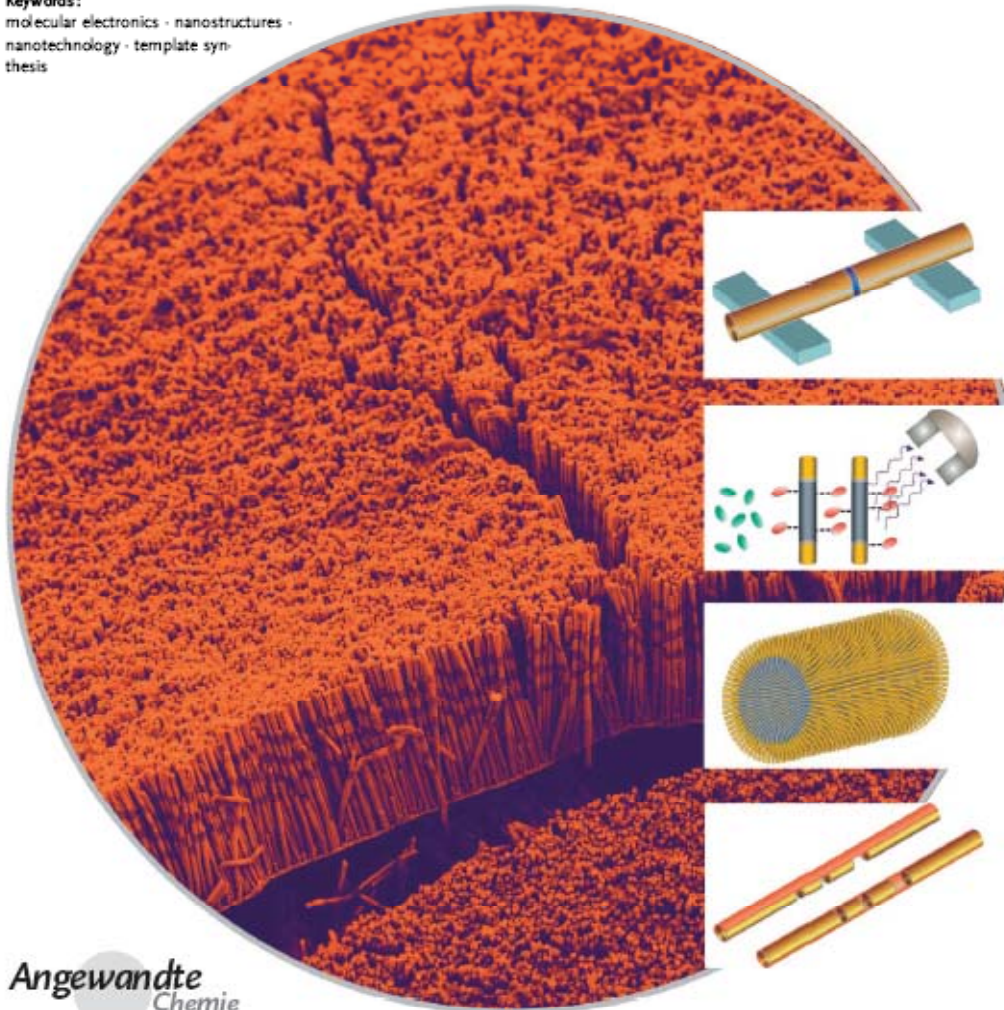
The Nobel Prize in Physics 2010

Andre Geim, Konstantin Novoselov

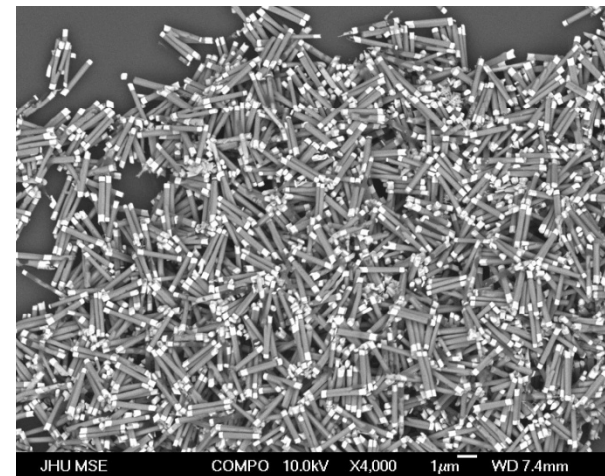
Nanowires/Nanorods

Keywords:

molecular electronics · nanostructures · nanotechnology · template synthesis



One component nanowires



Multicomponent nanowires

Angewandte
Chemie

2672 www.angewandte.org

© 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Angew. Chem. Int. Ed. 2006, 45, 2672–2692

Optical Properties of Nanoparticles and Nanowires

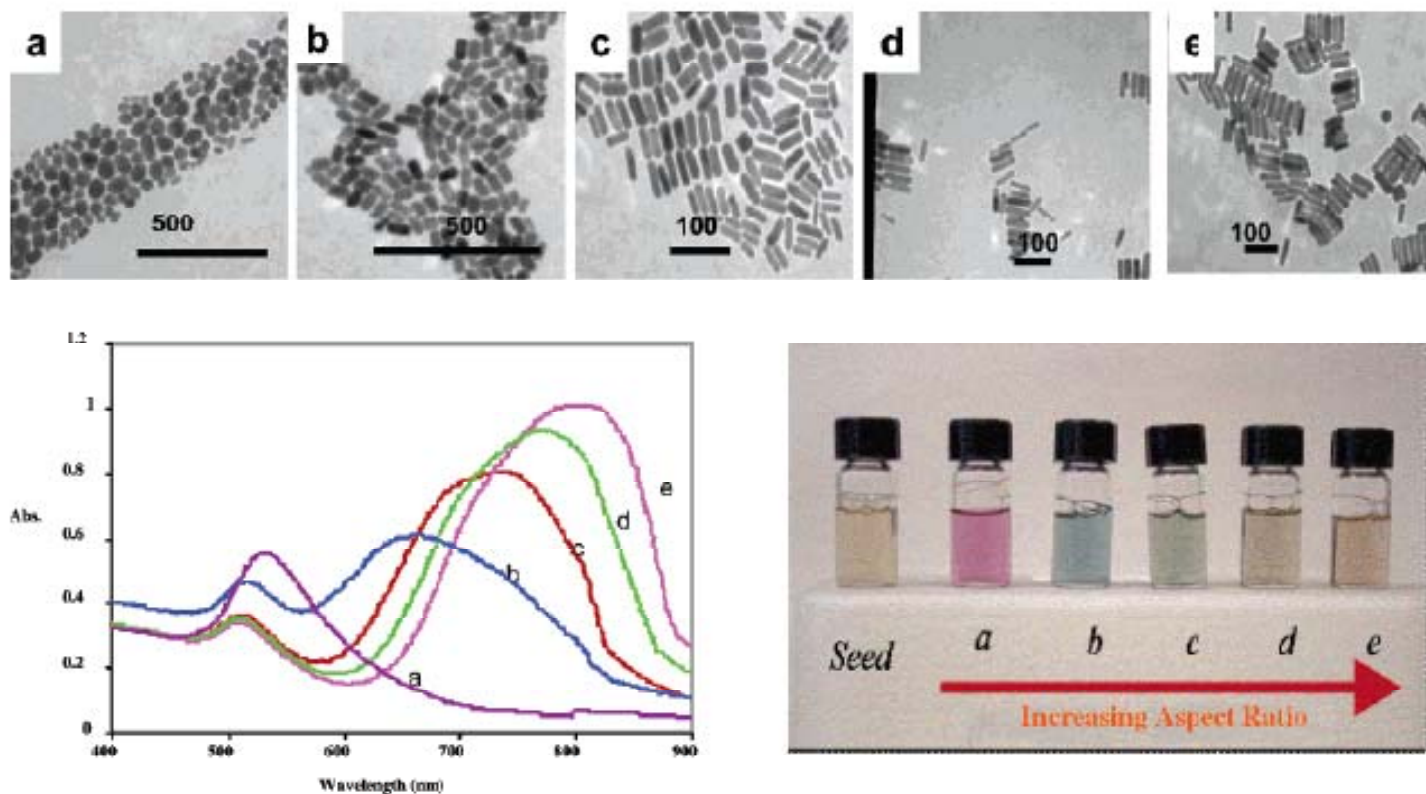
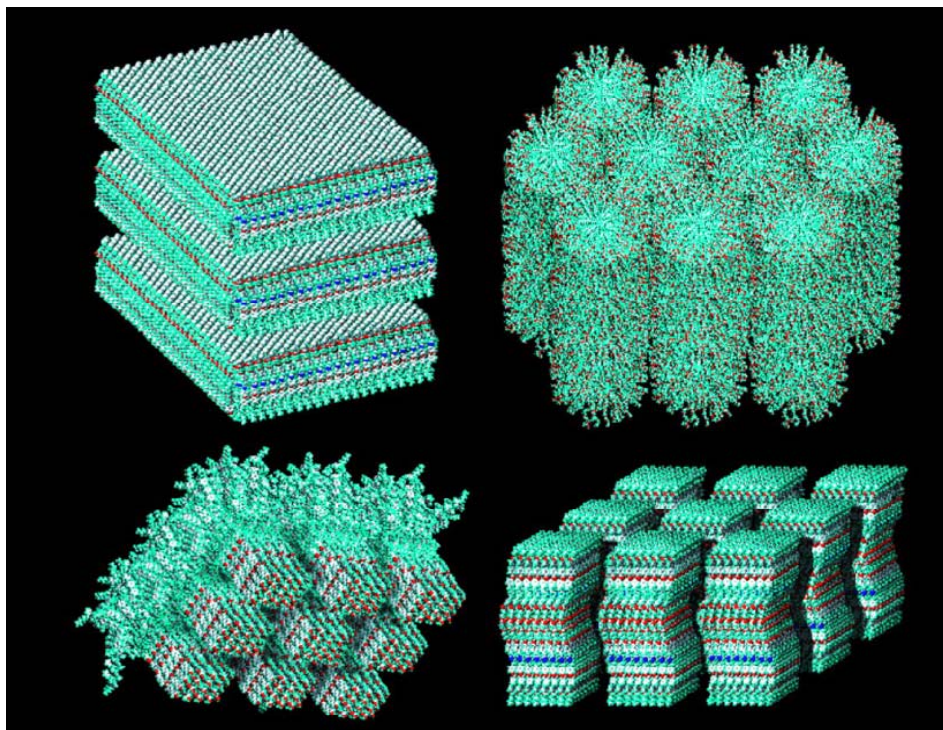


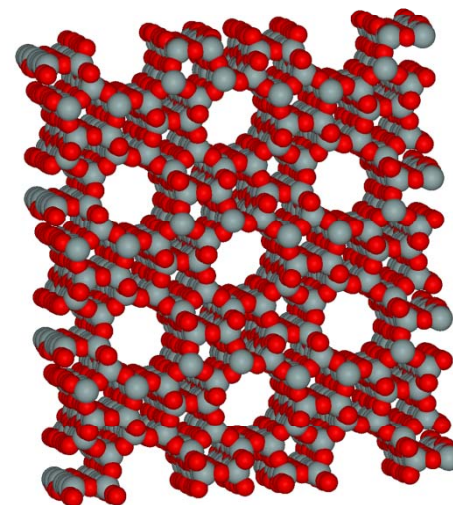
Figure 1. Transmission electron micrographs (top), optical spectra (left), and photographs of (right) aqueous solutions of gold nanorods of various aspect ratios. Seed sample: aspect ratio 1; sample a, aspect ratio 1.35 ± 0.32 ; sample b, aspect ratio 1.95 ± 0.34 ; sample c, aspect ratio 3.06 ± 0.28 ; sample d, aspect ratio 3.50 ± 0.29 ; sample e, aspect ratio 4.42 ± 0.23 . Scale bars: 500 nm for a and b, 100 nm for c, d, e.

J. Phys. Chem. B, Vol. 109, 2005, 13857

Molecular Nanostructures

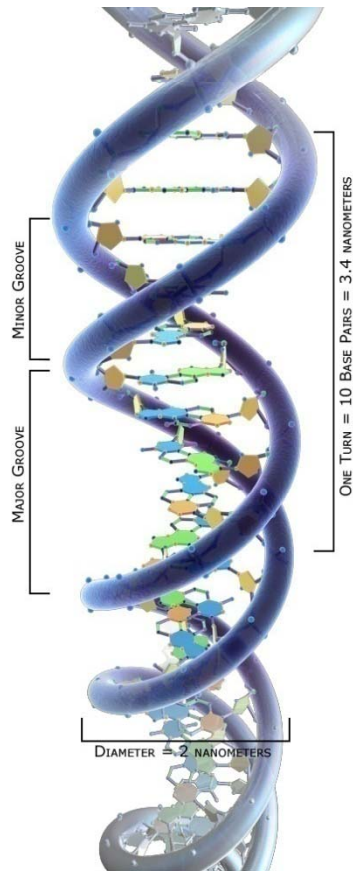


Supramolecular nanostructures

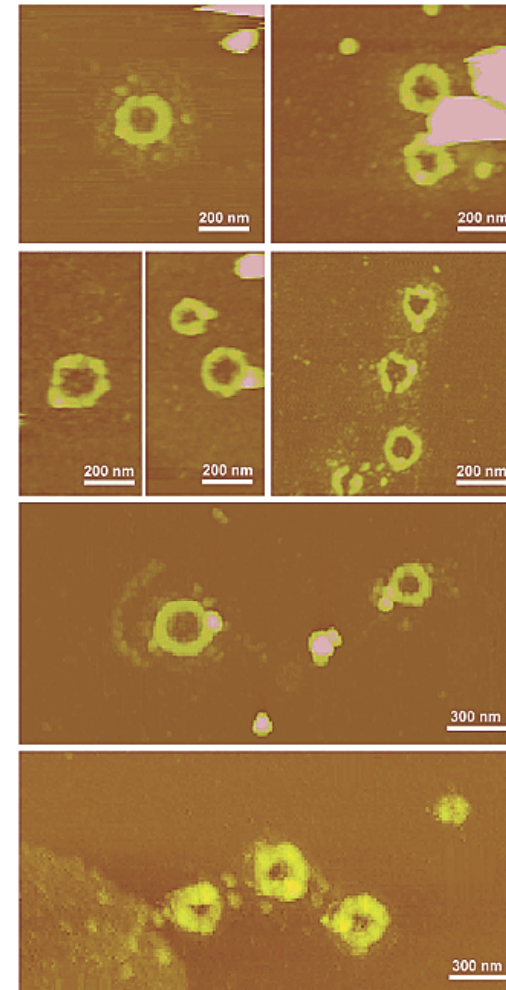
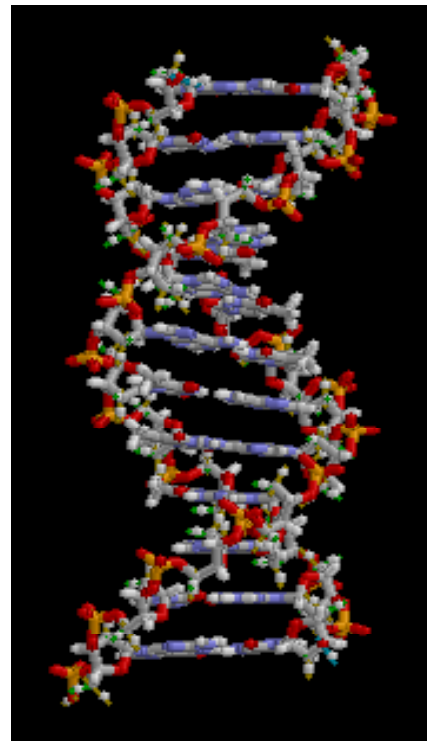


Zeolites

Biomolecules: Natural Nanostructures



DNA (22 to 24 angstroms wide)

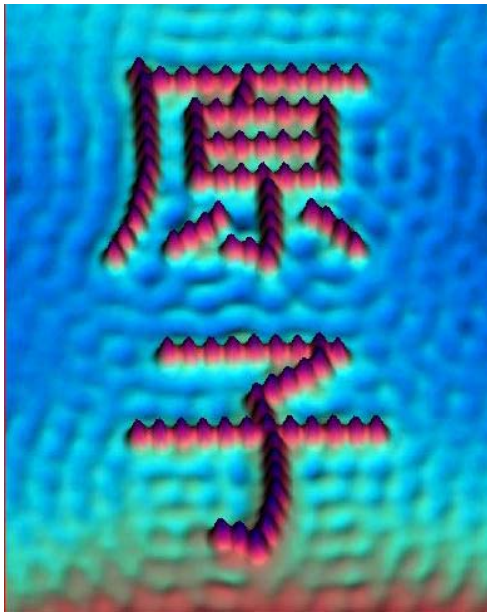


M13 virus-based ring structures observed by AFM on mica surface

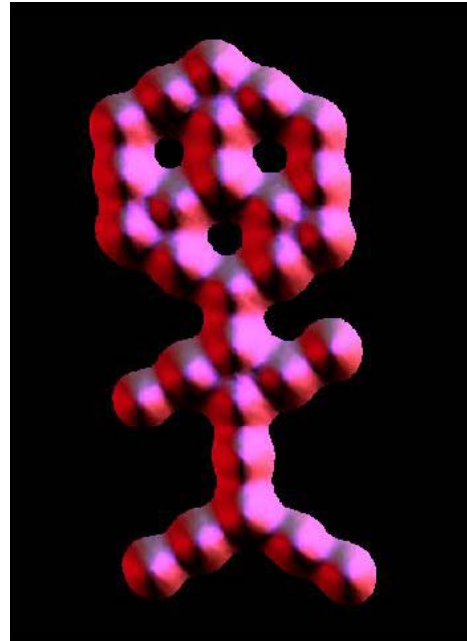
Nano Letters, 4 (1), 23 -27, 2004

Scanning Tunneling Microscopy (STM)

STM: a new method for confining electrons to artificial structures at the nanometer lengthscale

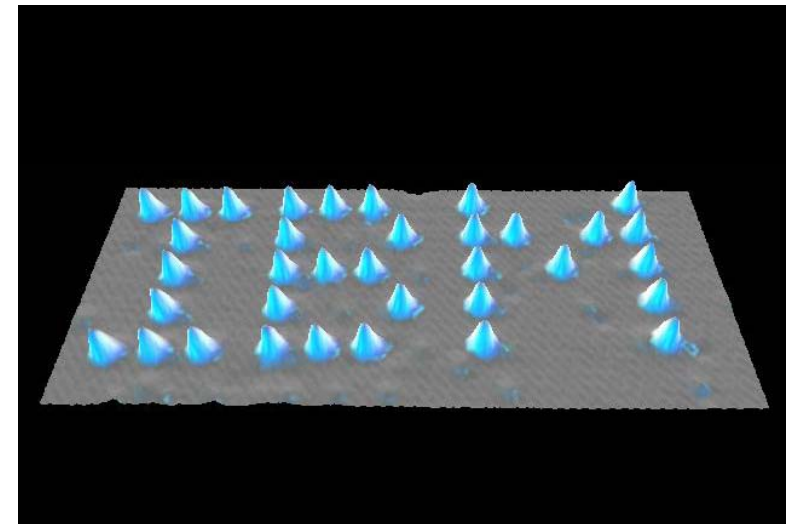


Atom (in Chinese)
Iron on Copper (111)

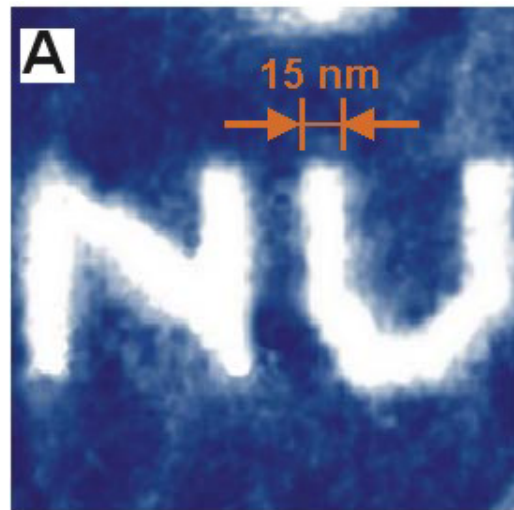
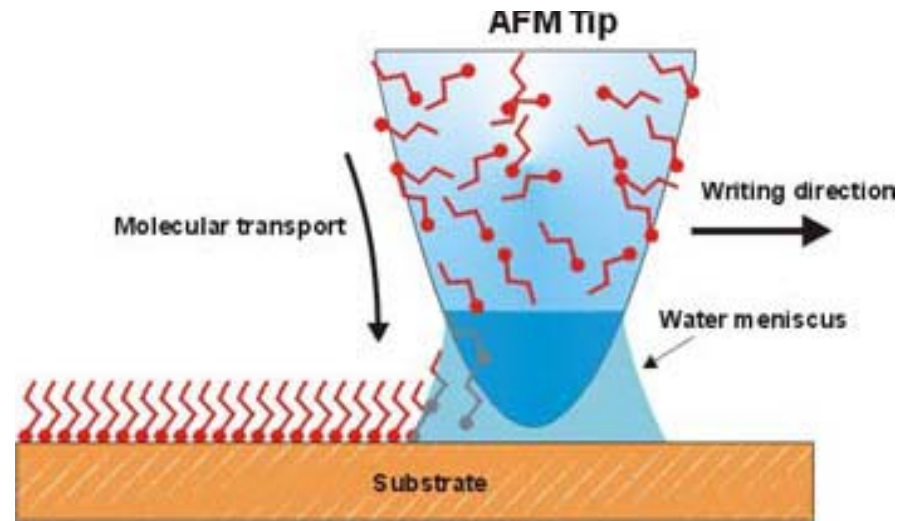


Carbon Monoxide Man
Carbon Monoxide on Platinum (111)

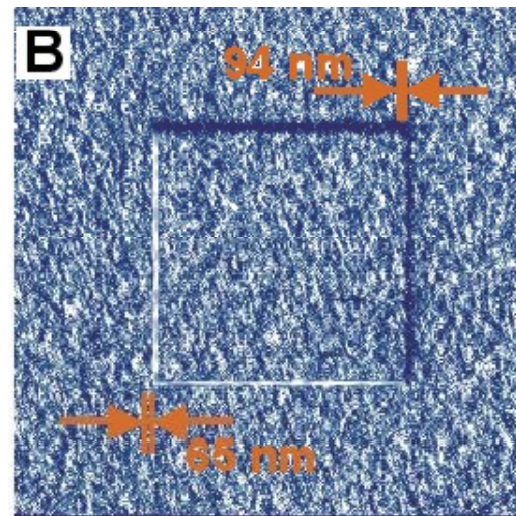
The beginning
Xenon on Nickel (110)



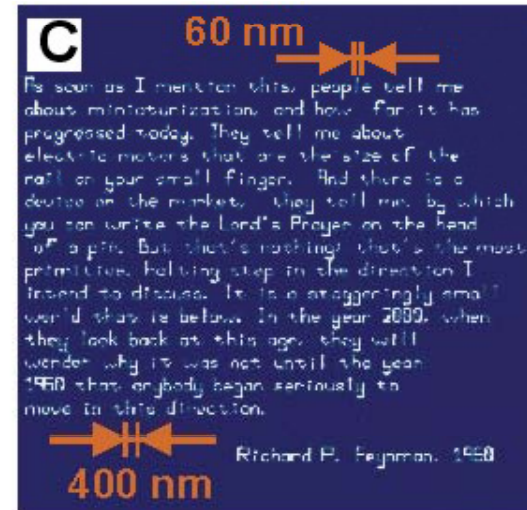
Dip Pen Nanolithography (DNP)



0 nm 180



0 μm 8

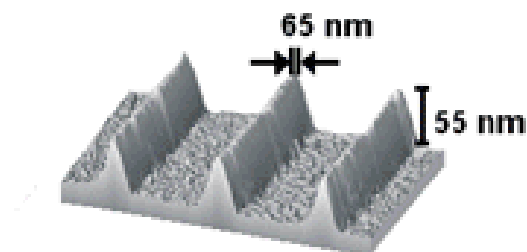


As soon as I mention this, people tell me about miniaturization and how far it has progressed today. They tell me about electronic motors that are the size of the nail on your small finger. And there is a device on the market, they tell me, by which you can write the Lord's Prayer on the head of a pin. But what's missing, that's the most pertinent, halting step in the direction I intend to discuss. It is an amazingly small world that is below. In the year 2000, when they look back at this age, they will wonder why it was not until the year 1960 that anybody began seriously to move in this direction.

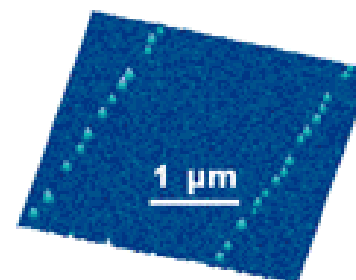
Applications of DPN



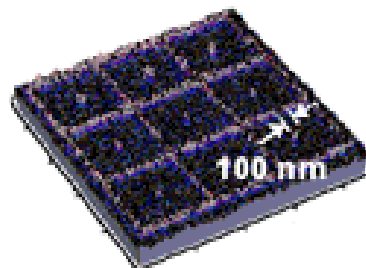
Conducting Polymers



Silicon Nanostructures

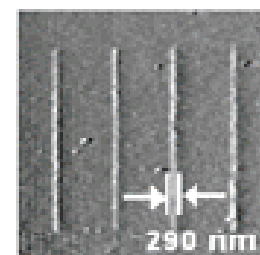
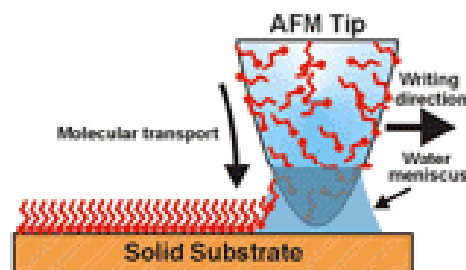


Single Nanoparticle Lines

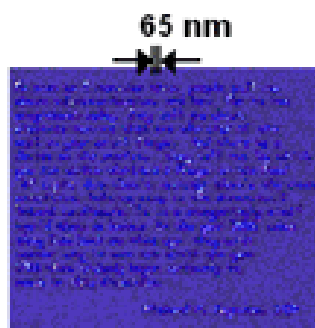


Protein Nanoarrays

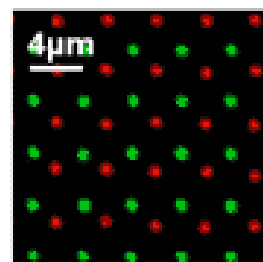
Dip-Pen Nanolithography



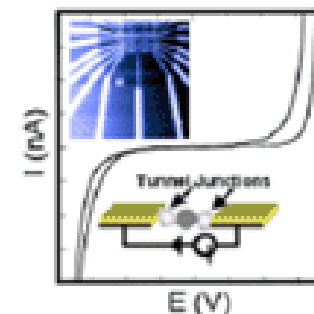
Sol Gel Templates



Small Organic Molecules

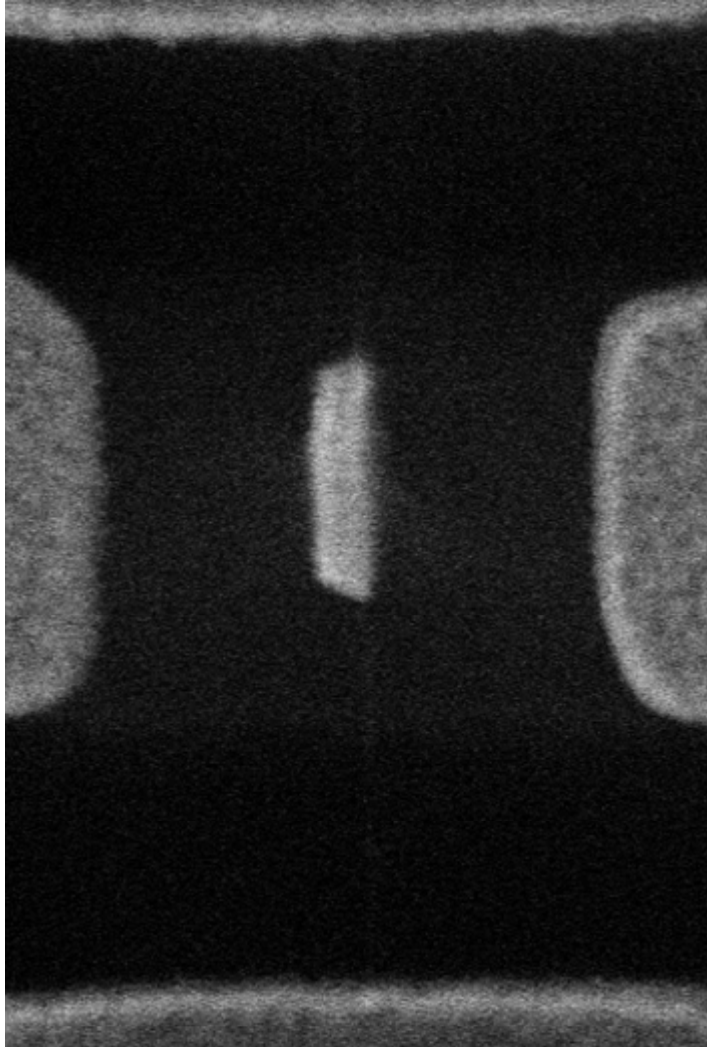


Ultrahigh Density DNA Arrays



Single Particle Devices

Nanomotors



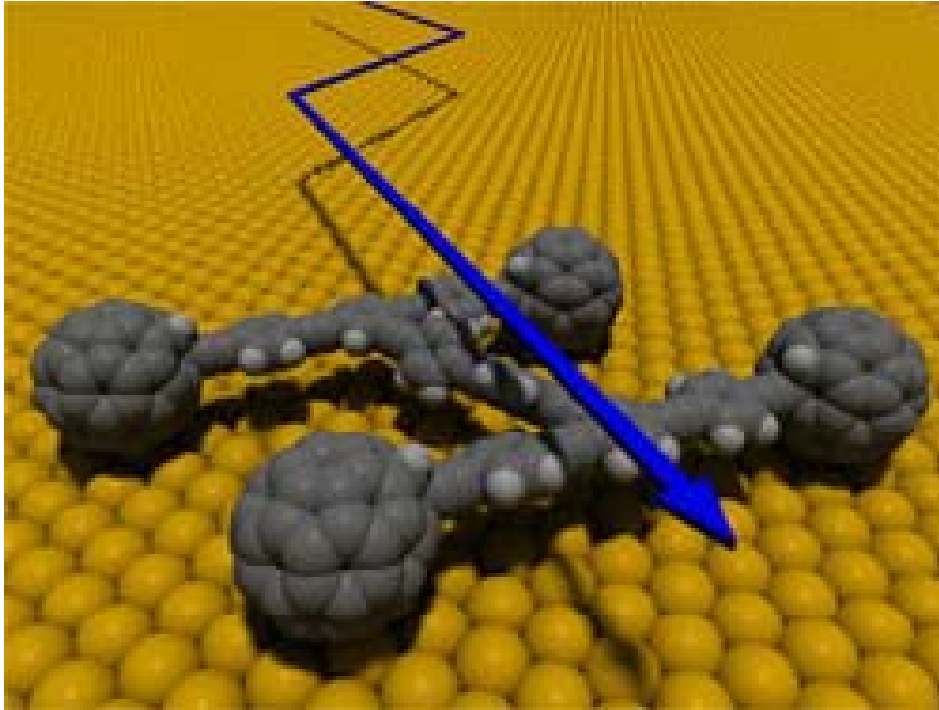
A **nanomotor** is a molecular device capable of converting energy into movement and forces on the order of the piconewtons.

By attaching a gold plate (with dimensions of order 100nm) to the outer shell of a suspended multiwall carbon nanotube (like nested carbon cylinders), they are able to electrostatically rotate the outer shell relative to the inner core. These bearings are very robust; Devices have been oscillated thousands of times with no indication of wear. The work was done in situ in an SEM.

<http://en.wikipedia.org/wiki/Nanomotor>

Nanomotor constructed at UC Berkeley. The motor is about 500nm across:
300 times smaller than the diameter of a human hair

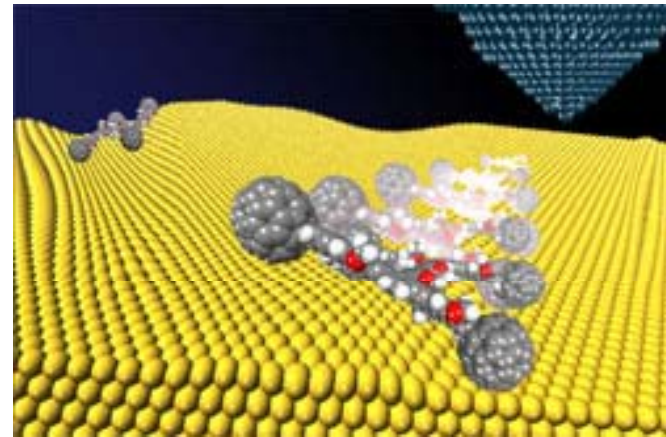
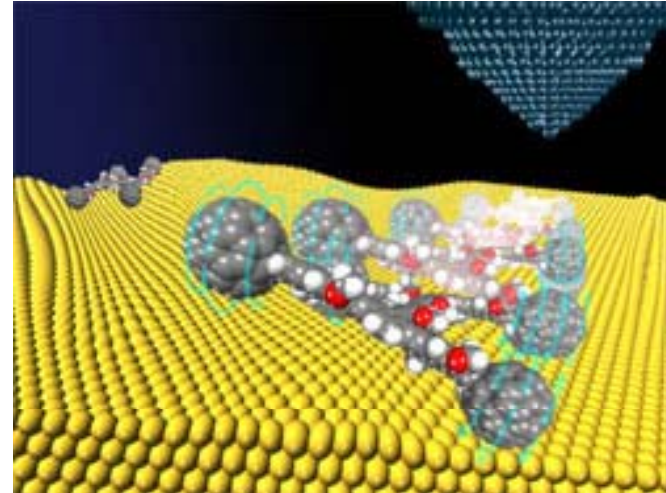
Nanocars



The nanocar consists of a chassis and axles made of well-defined organic groups with pivoting suspension and freely rotating axles. The wheels are buckyballs.

Rice's vehicle is the first that actually functions like a car, rolling on four wheels in a direction perpendicular to its axles.

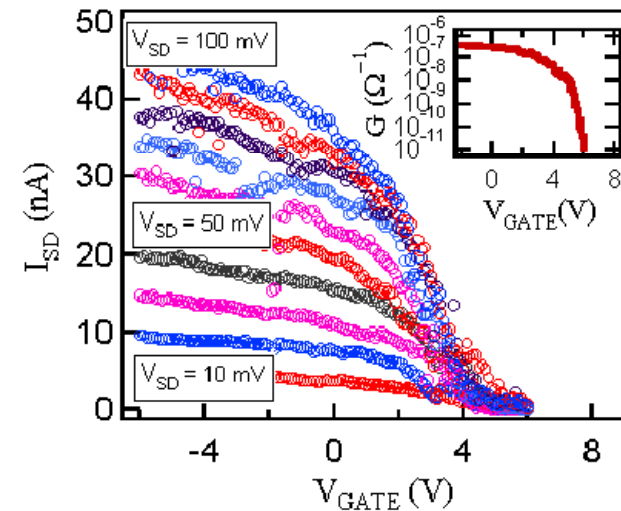
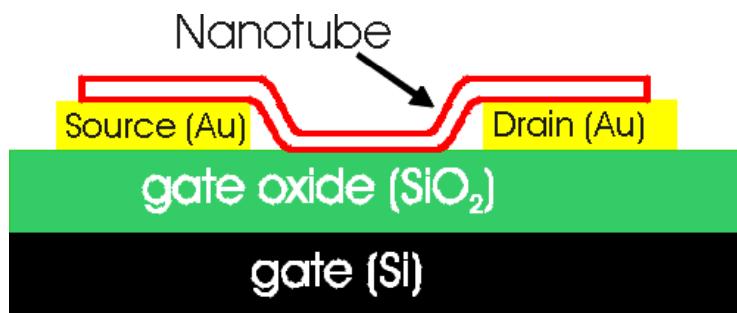
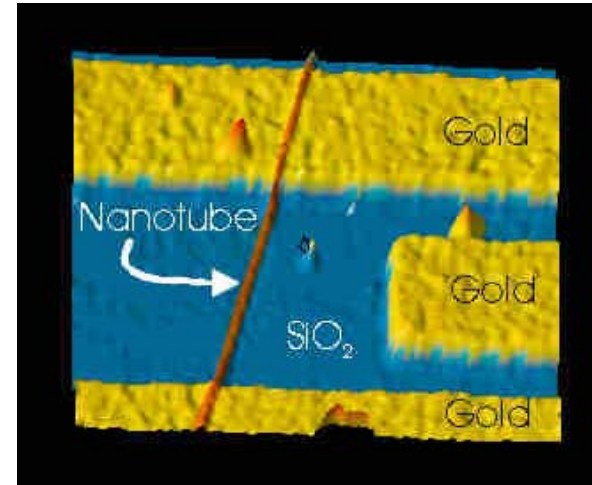
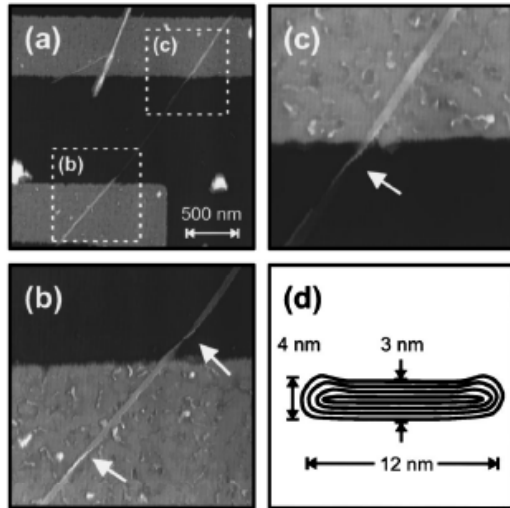
Scanning tunneling microscopy (STM), provided the measurements and experimental evidence that verified the rolling movement



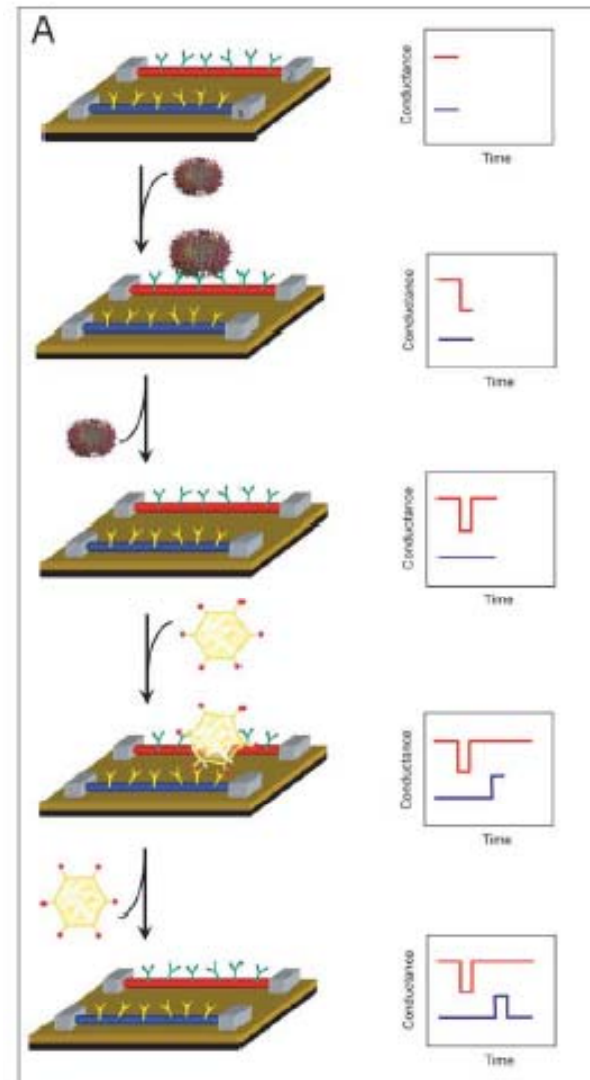
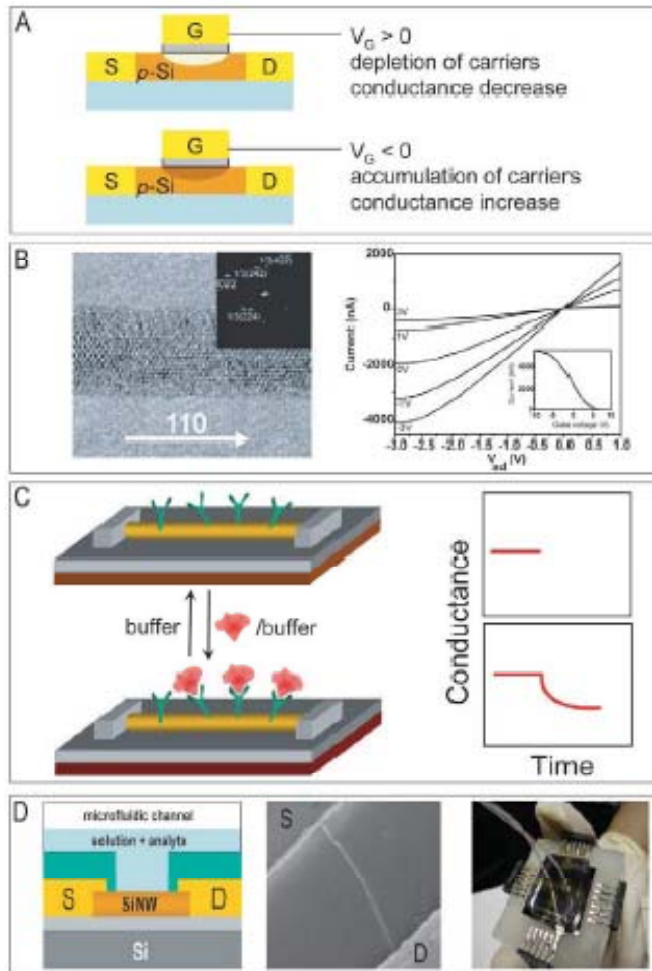
<http://en.wikipedia.org/wiki/Nanocar>

Nanotube Field-effect transistor (FET)

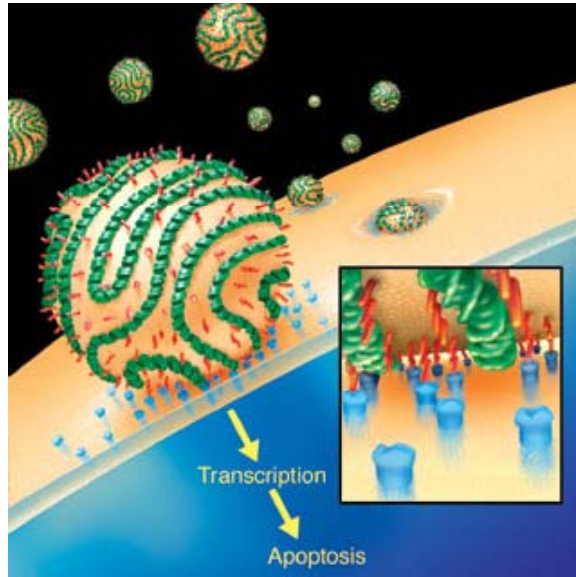
Transistors are the basic building blocks of integrated circuits (ICs)



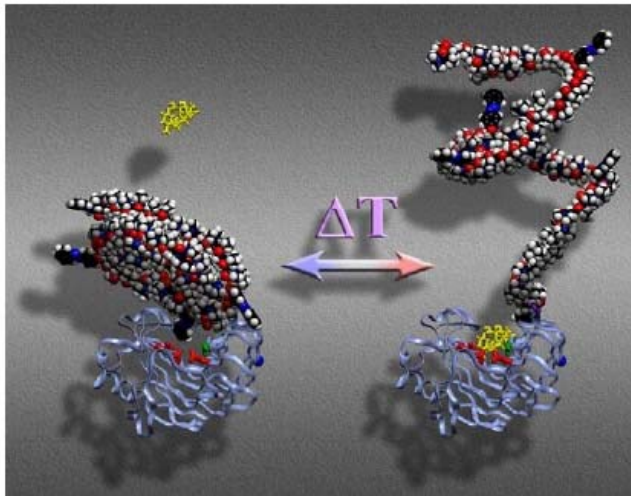
Nanowire-Based Biosensors



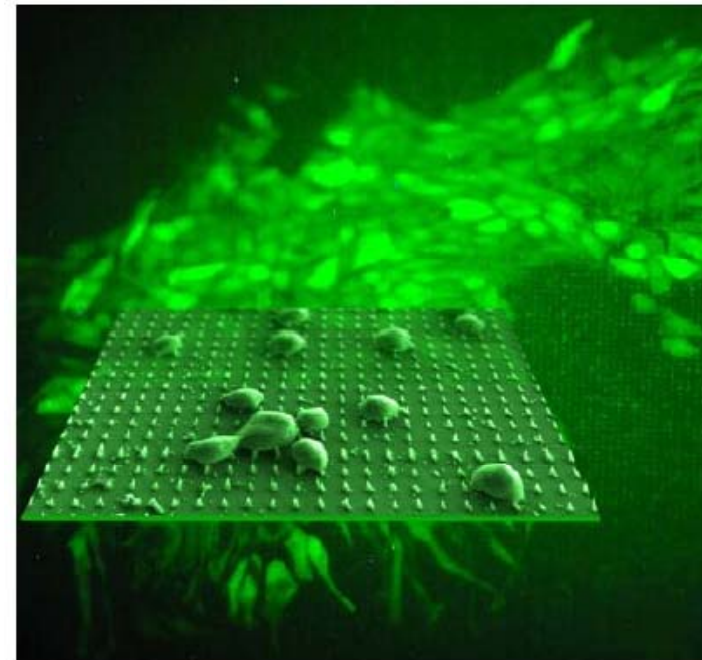
Nanobiotechnology and Nanomedicine



Nanoparticles packed with targeting molecules (red) anchor to integrins (blue) on the outside of a tumor blood vessel cell before shuttling mutant DNA (green) inside

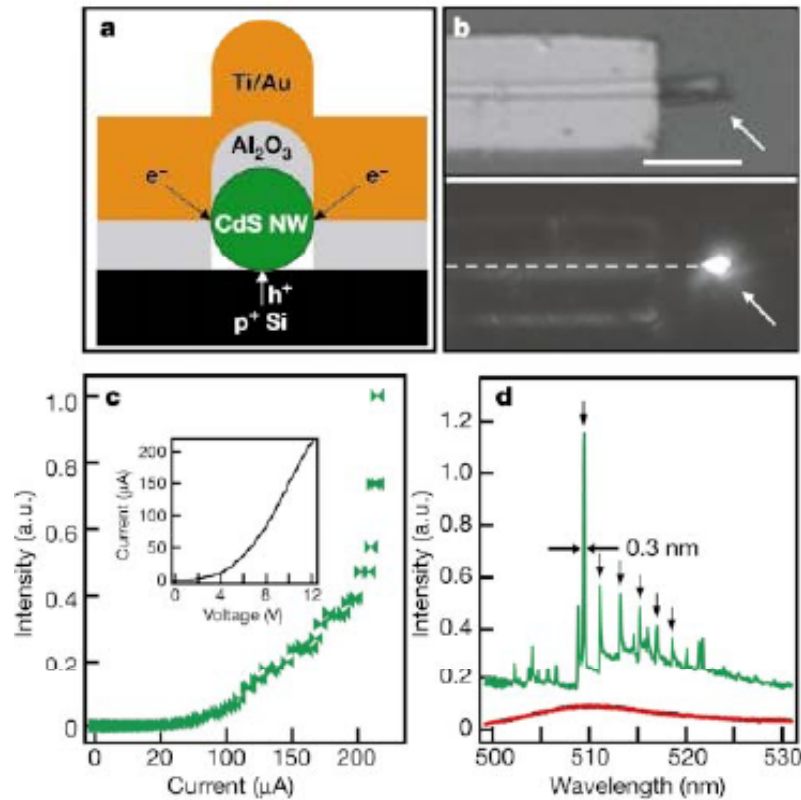


Molecular switches that can turn on and off enzyme



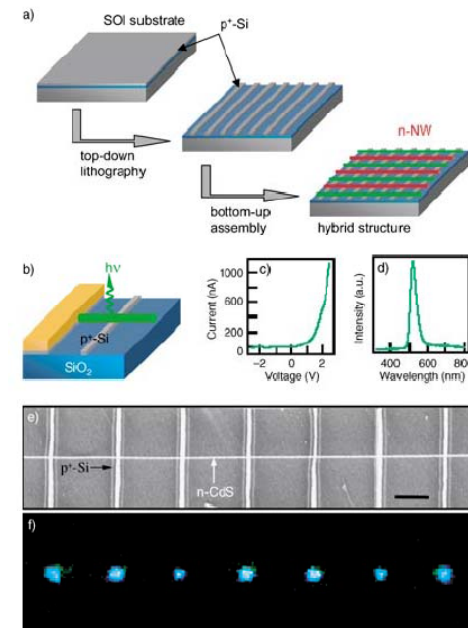
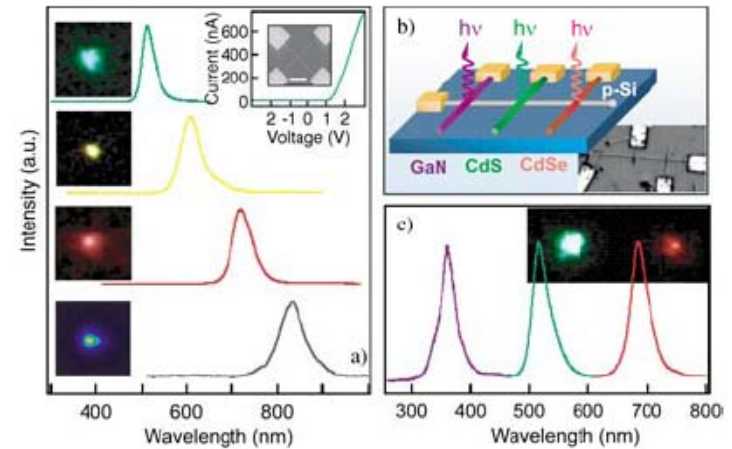
Patterned carbon nanofibers control chemical release to cells

Nanowire Lasers and Photonics



Nanowire lasers

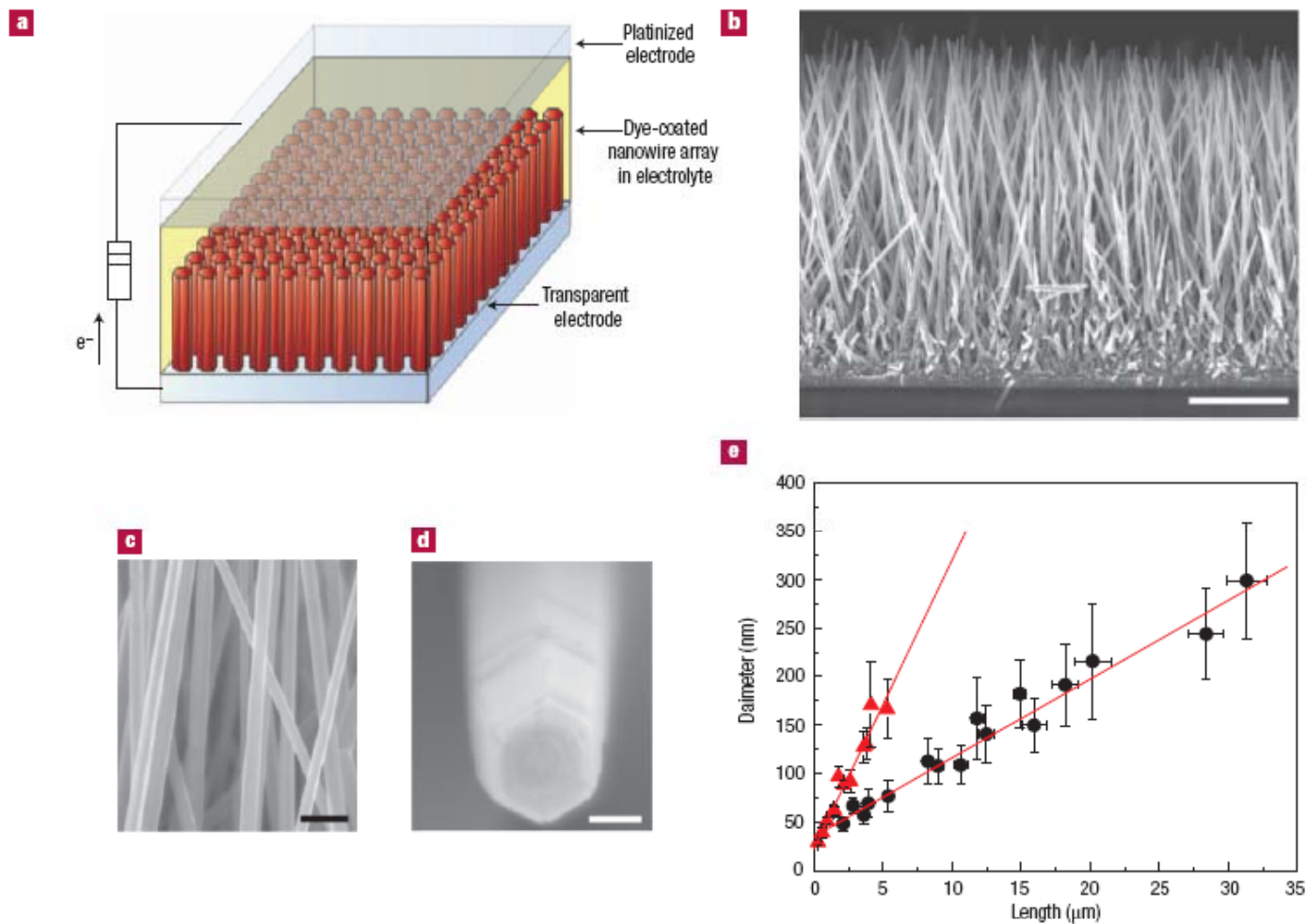
(Nature, Vol 421, 2003, 241)



Nanowires for Integrated Multicolor Nanophotonics

(Small, 2005, 1, 142)

Nanowire Dye-Sensitized Solar Cells



The nanowire dye-sensitized cell, based on a ZnO wire array

Nature Materials vol 4, 2005, 455

*More and more applications in
Nano-xxxxxx*



Break!

Nano-Break!!!



Section II: Self-assembly

What's self-assembly???

“**Self-assembly** is the fundamental principle which generates structural organization on all scales from molecules to galaxies.

It is defined as reversible processes in which pre-existing parts or disordered components of a preexisting system form structures of patterns.

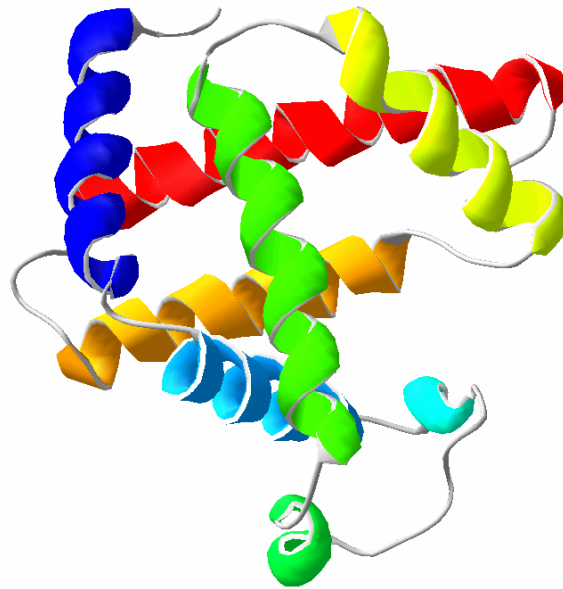
Examples of self-assembling system include weather patterns, solar systems, histogenesis (formation of different tissues from undifferentiated cells) and self-assembled monolayers. The most well-studied subfield of self-assembly is molecular self-assembly “

From Wikipedia: <http://en.wikipedia.org/wiki/Self-assembly>

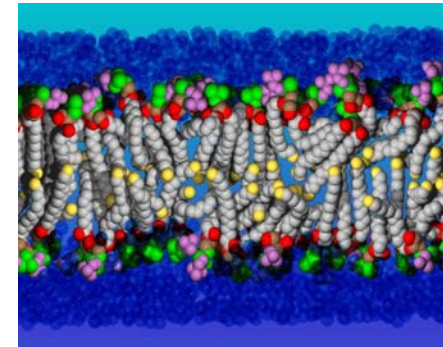
Self-Assembly in Living Systems



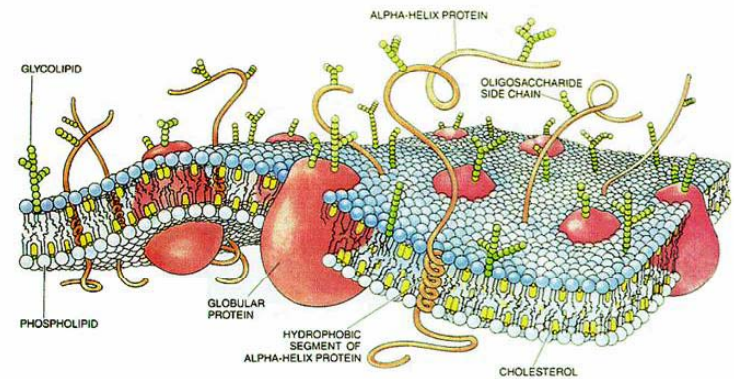
DNA double-helix



Protein: A representation of the 3D structure of myoglobin
"Protein folding"

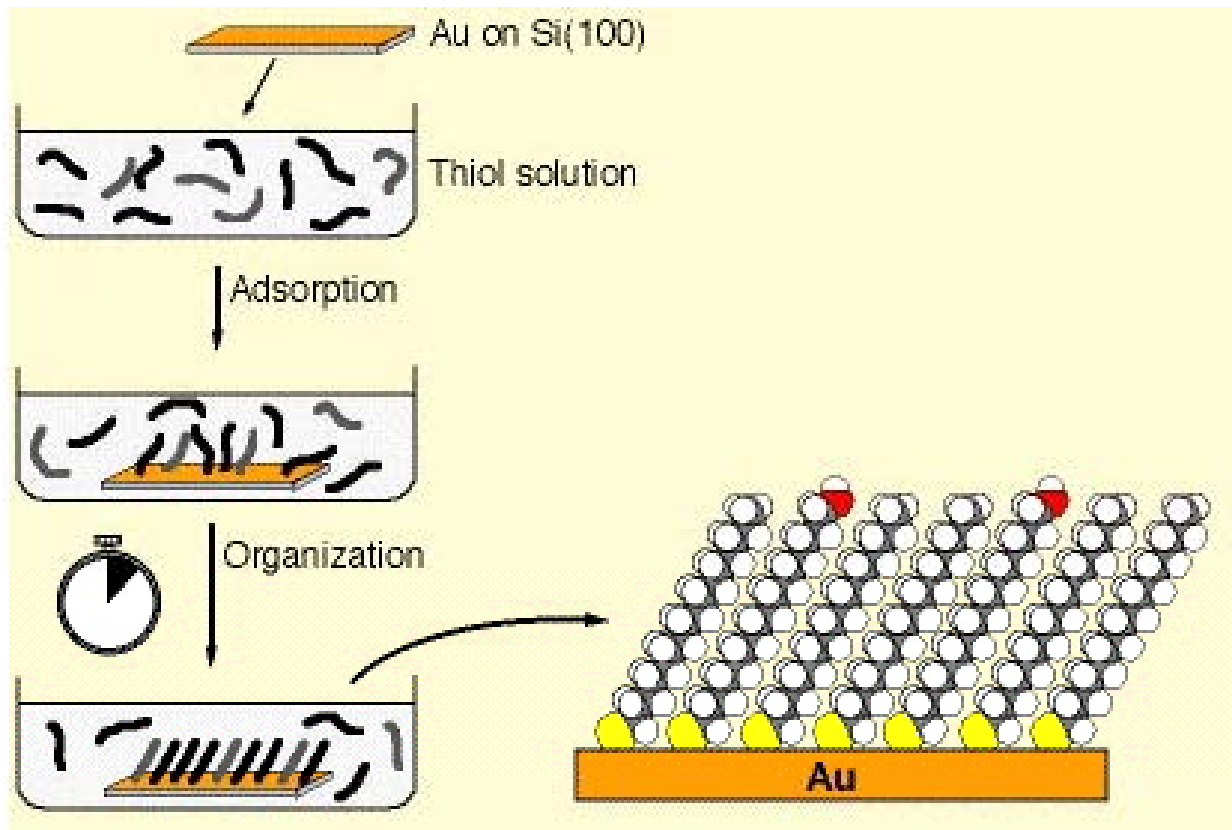


Lipid bilayer



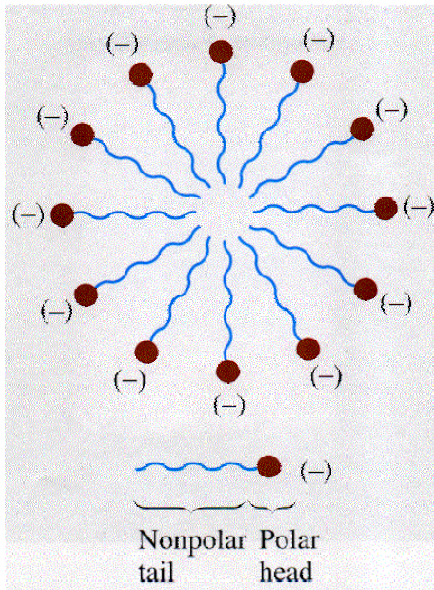
Cell Membrane

Self-assembled Monolayers (SAMs)

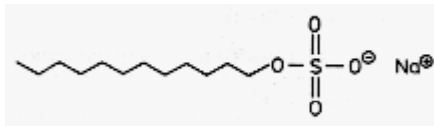


- Surface modification
- Corrosion inhibition
- Biocompatibility

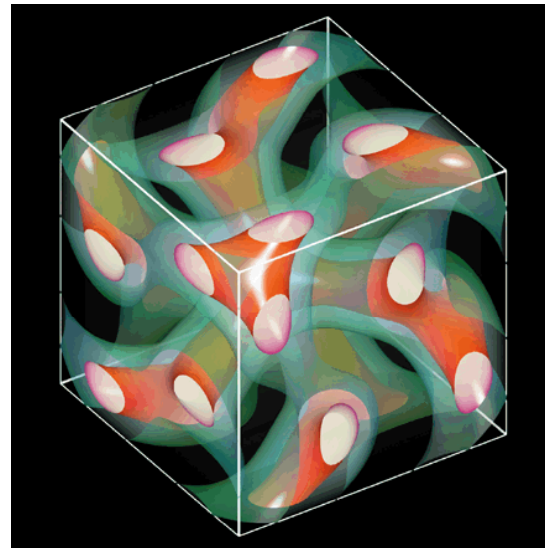
Self-Assembly of Molecules



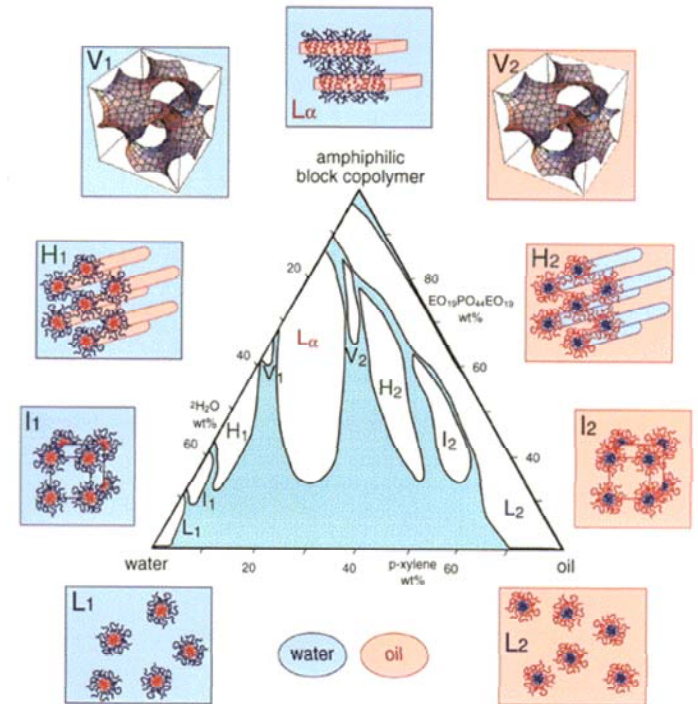
Surfactant micelles



Sodium dodecylsulfate (SDS)

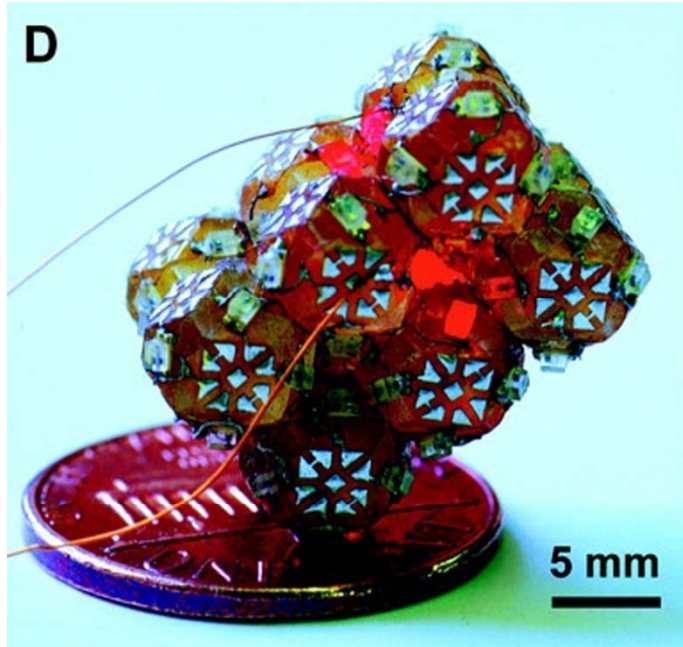


Complex block copolymer structures



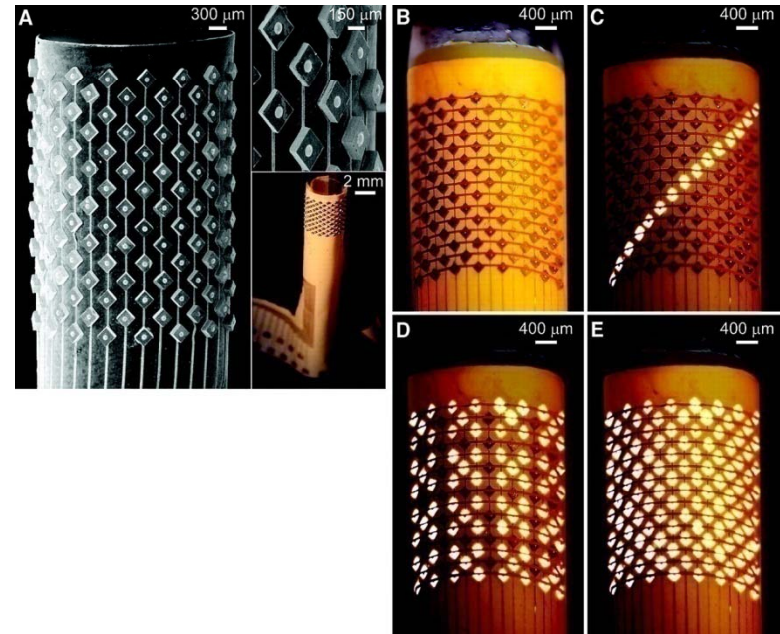
Amphiphilic block copolymers

Self-Assembly of Electronic Systems



Millimeter scale

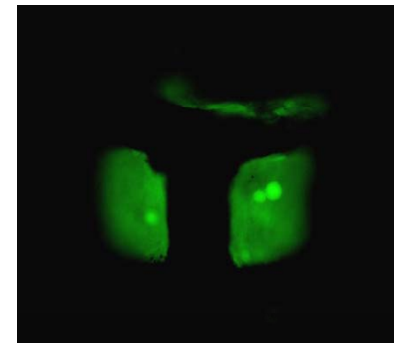
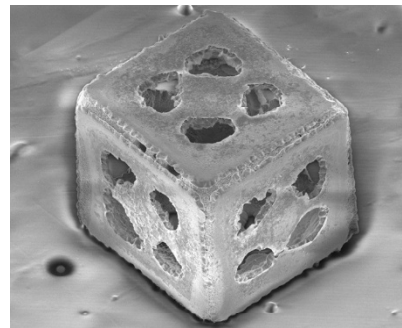
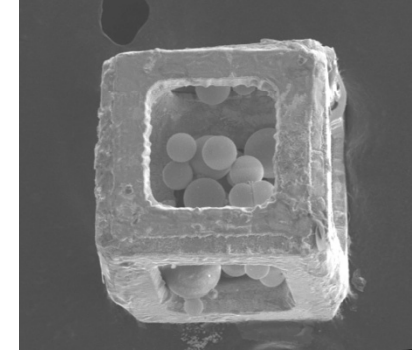
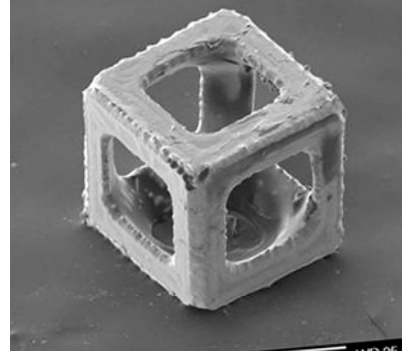
Gracias, Tien, Breen, Hsu, Whitesides.
Science **2000**, 289, 1170.



200 μm scale

Jacobs, Tao, Schwartz, Gracias, Whitesides.
Science **2002**, 296, 323.

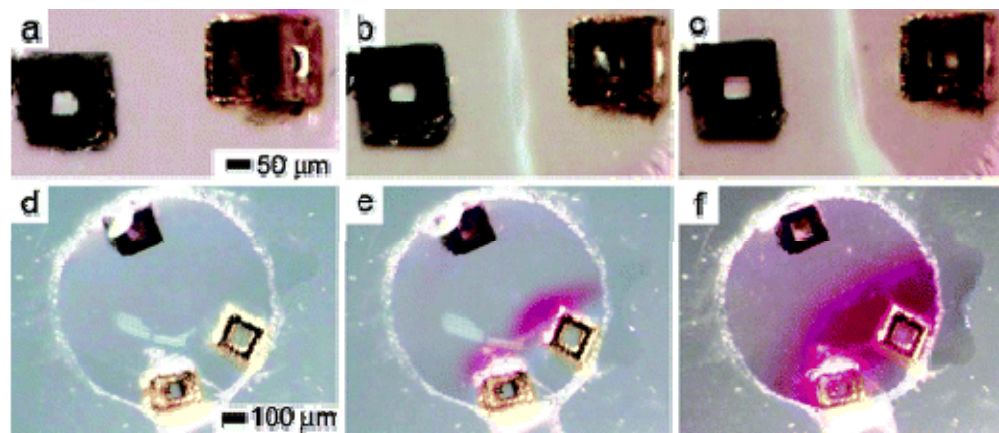
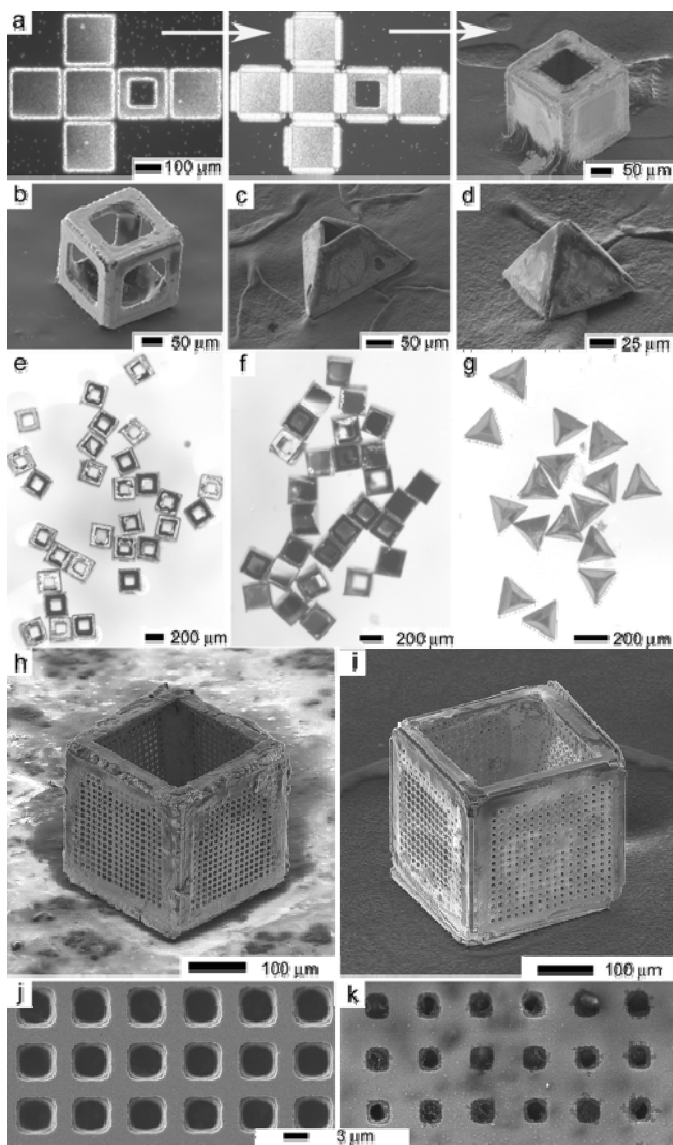
Self-Assembled Micro-Containers



100-200 μm

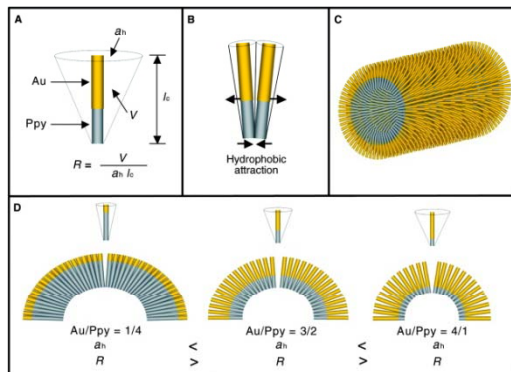
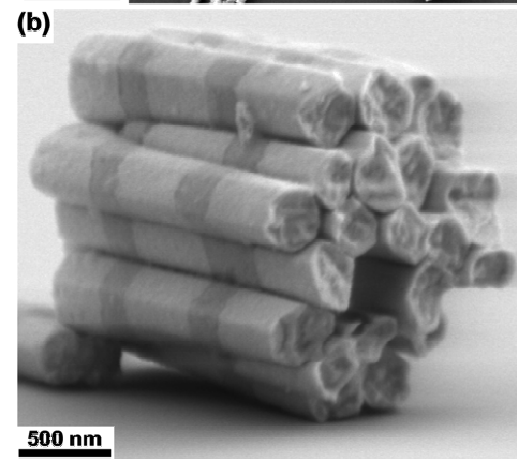
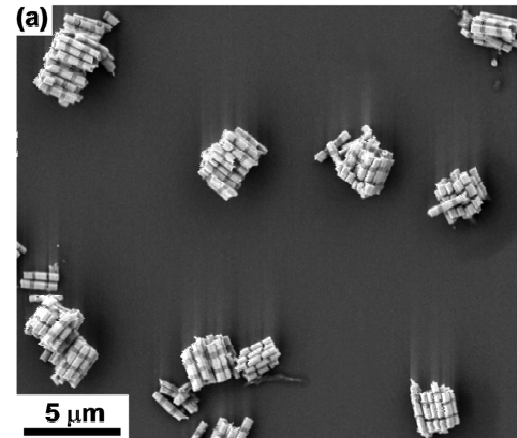
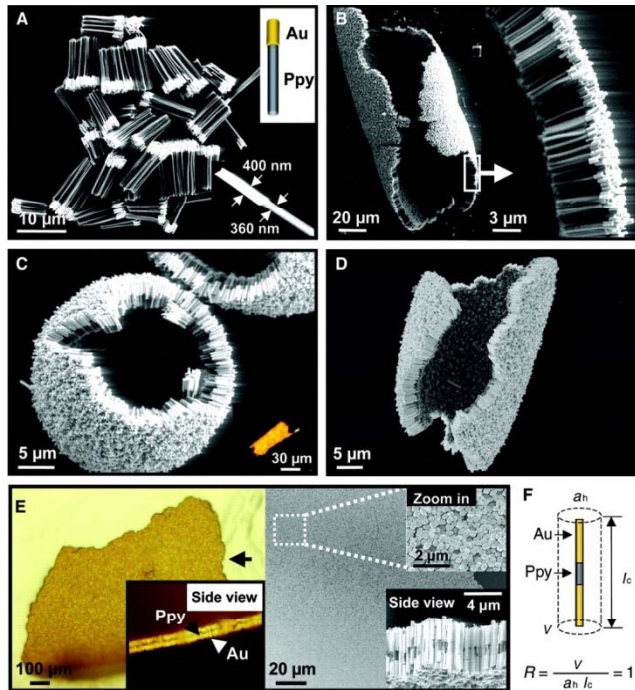
Gimi, Leong, Gu, Yang, Artemov, Bhujwala, Gracias. *Biomedical Microdevices* **2005**, 7, 341-345.

Self-Assembled Micro-Containers



Leong, Gu, Koh, Gracias. *JACS* **2006**, *128*, 11336-11337

Self-Assembly of Nanowires

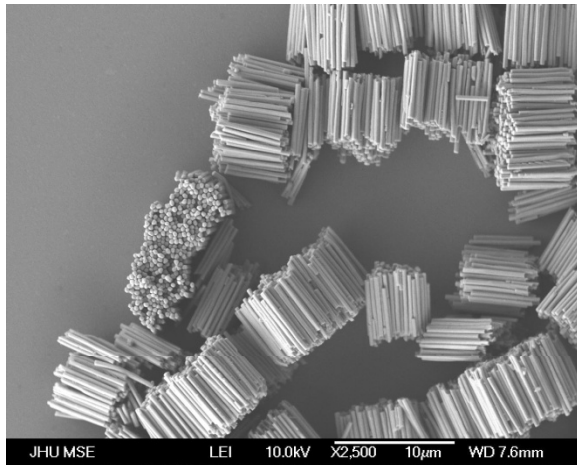


Magnetic assembly

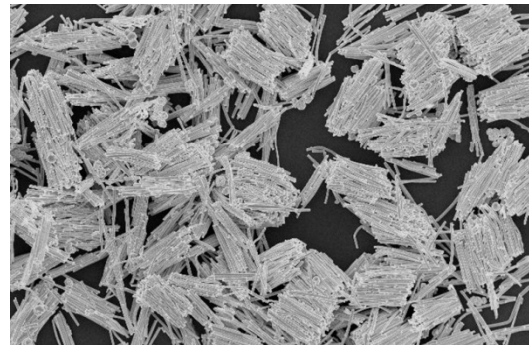
Love, Urbach, Prentiss, Whitesides. *JACS*, **2003**, 125, 12696.

Park, Lim, Chung, Mirkin. *Science* **2004**, 303, 348

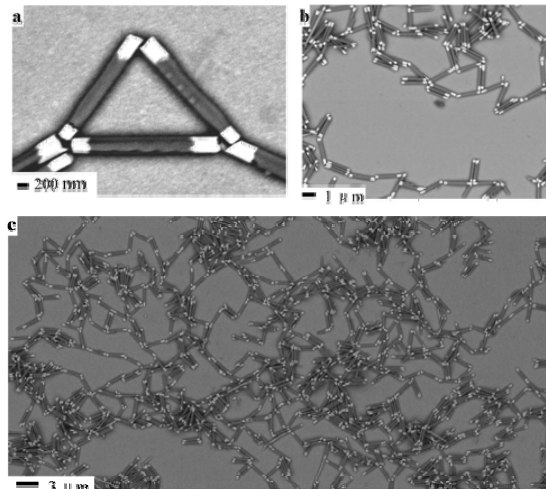
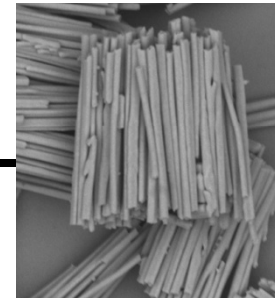
Self-Assembly of Nanowires



Large scale bundles during membrane dissolution

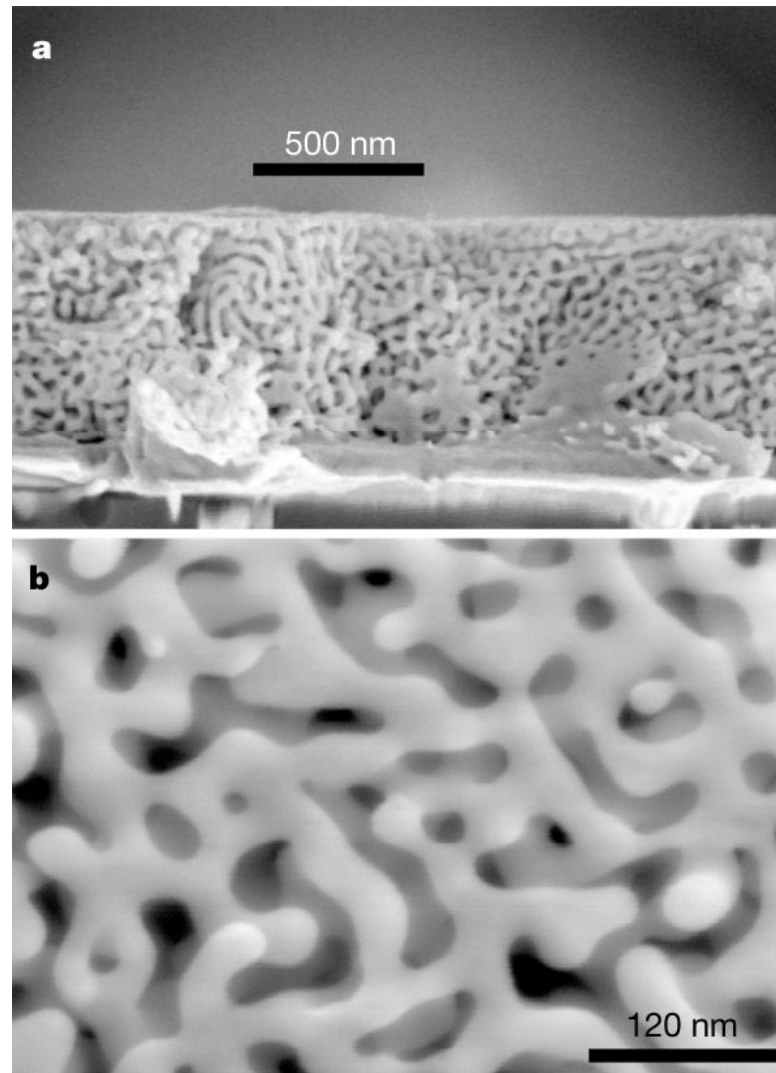


“Glued” 3D bundles



“Glued” 2D networks

Self-assembly: Nanoporous Gold



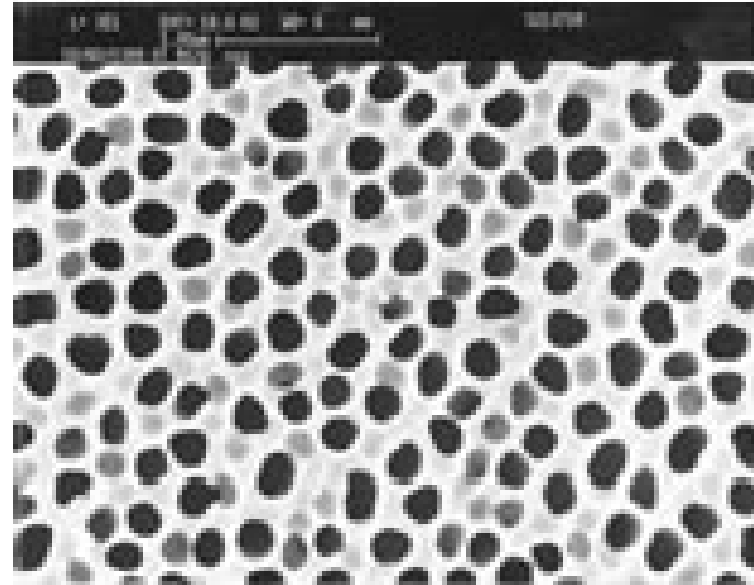
Erlebacher, Aziz, Karma, Dimitrov, Sieradzki. *Nature* **2001**, *410*, 450-453

Self-assembly and Nanotechnology

Self-assembly: Nanoporous AAO membranes



Whatman



20 -200 nm pore size

- Separation
- Nanowire, nanotube fabrication
- Biomedical engineering

Personal and Home Products



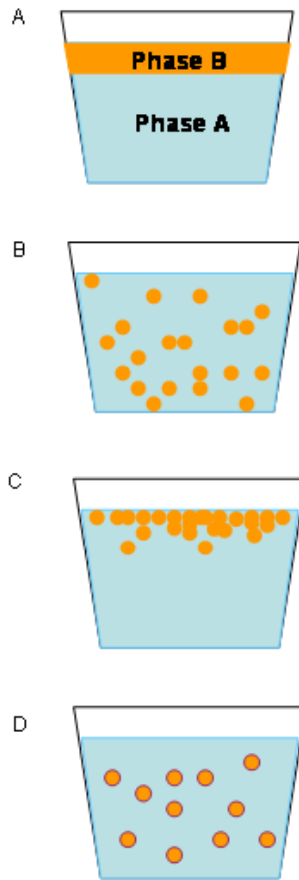
Soap



Detergent

Self-assembly and Nanotechnology

Pharmaceutical and Health Products



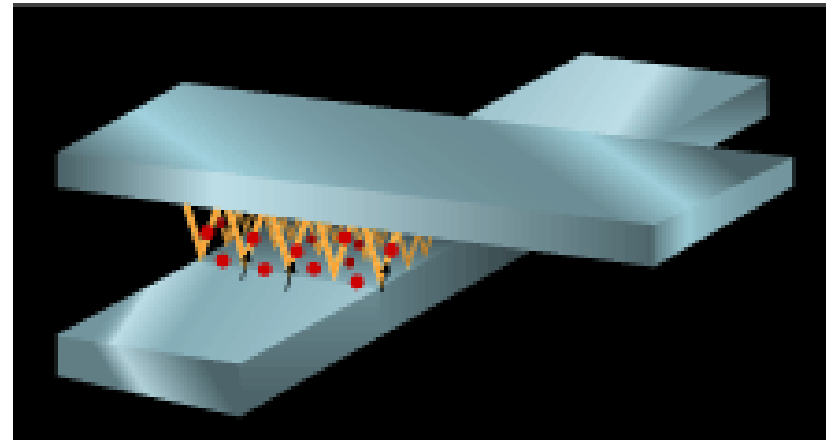
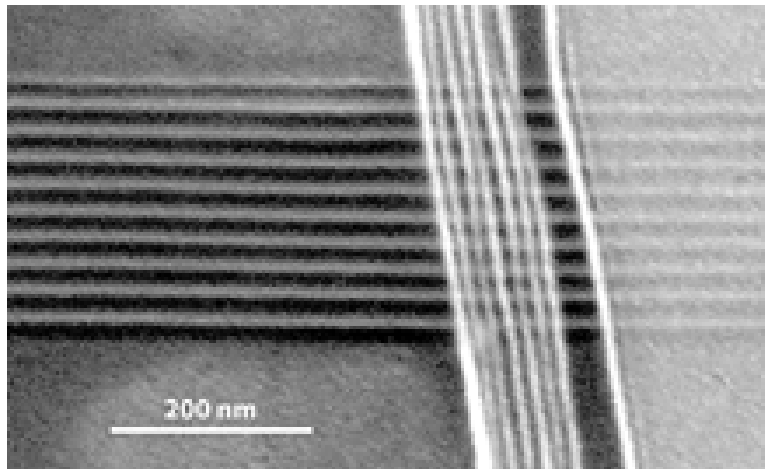
Emulsions

For creams and lotions



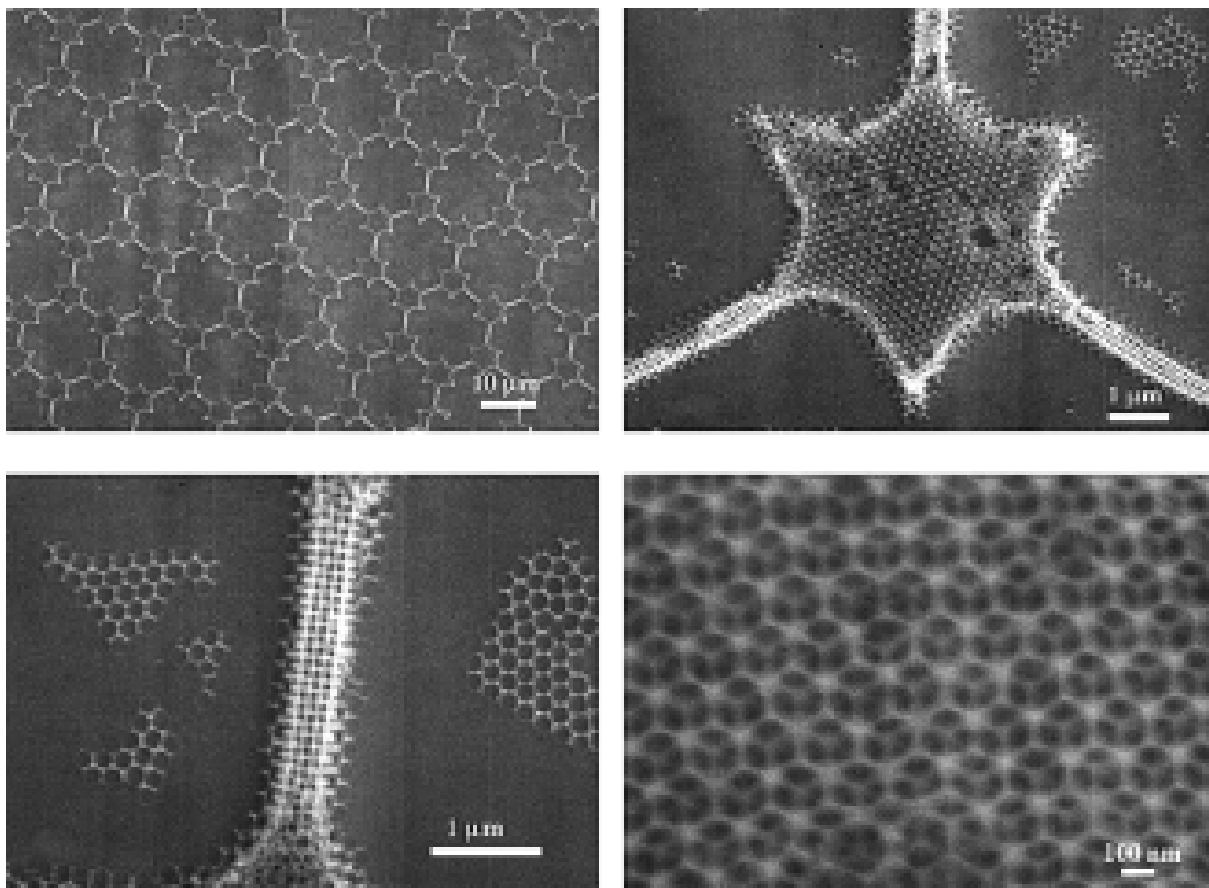
20 ml ampule of 1% propofol emulsion suitable for intravenous injection. The manufacturers emulsify the lipid soluble propofol in a mixture of water, soy oil and egg lecithin.

Self-assembly: Molecular Electronics



Nanowires are assembled into crossbars (*left*).
Organic molecules between crossing wires serve as transistors (*right*)

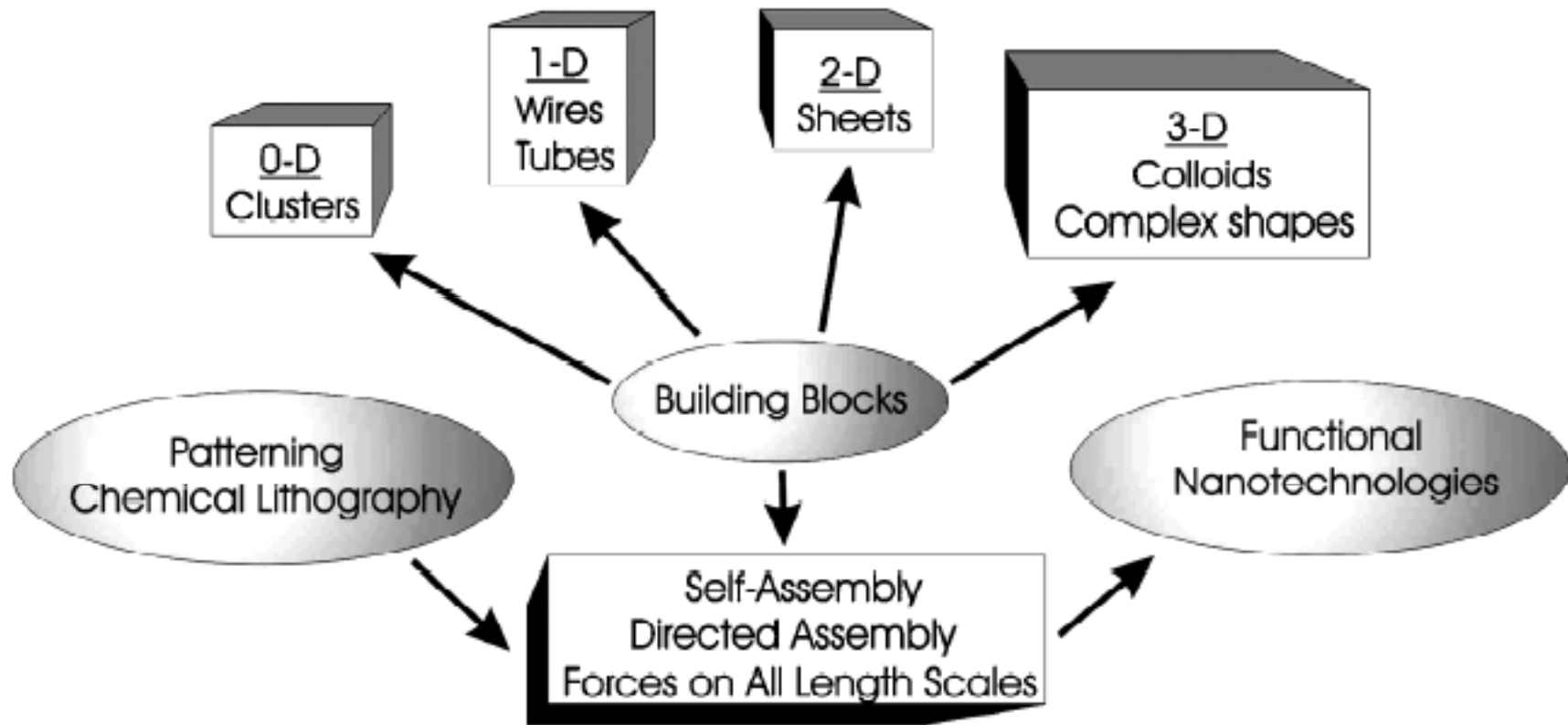
Self-assembly: New Structures and New Materials



Hierarchically ordered oxide through a combination of microchannel, microsphere, and block-copolymer templating

Ozin and Arsenault. *Nanochemistry: A Chemical Approach to Nanomaterials*. RSC Publishing, 2005

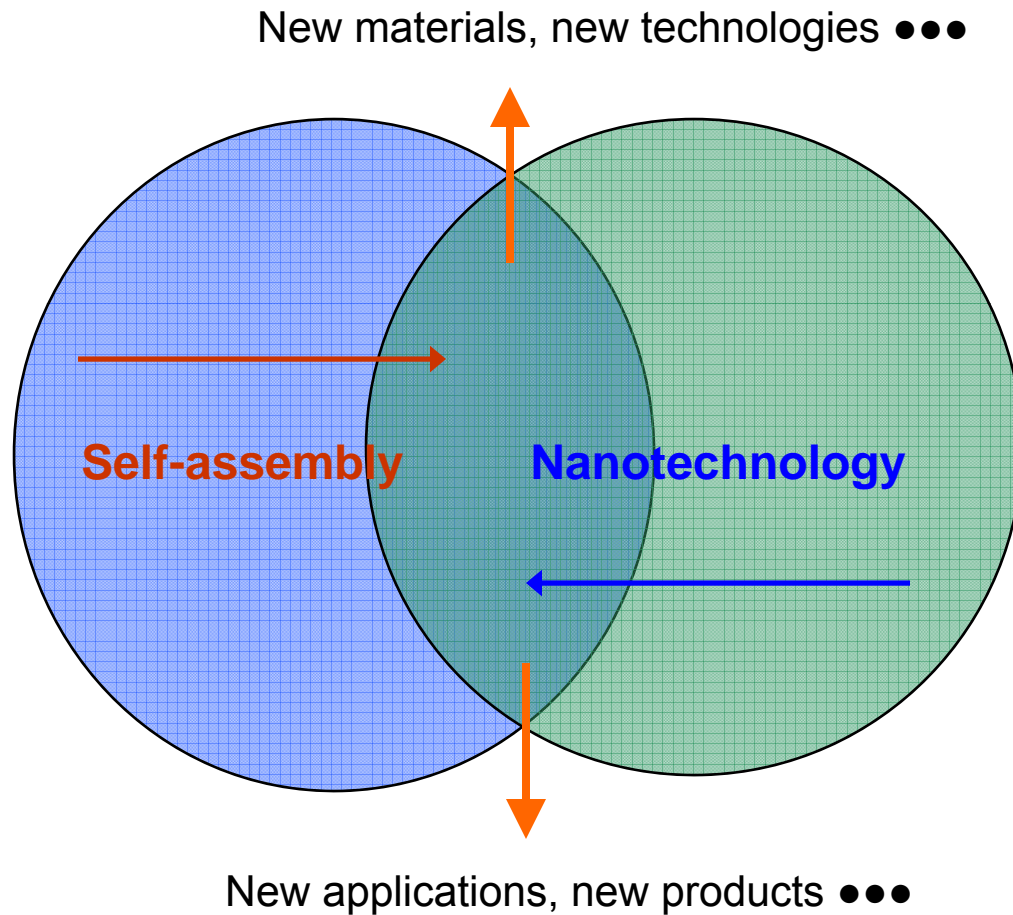
Self-assembling route to Nanotechnology



A flowchart delineating the factors that must be considered when approaching the self-assembly of a nanoscale system

Ozin and Arsenault. *Nanochemistry: A Chemical Approach to Nanomaterials*. RSC Publishing, 2005

Self-assembly and Nanotechnology



Self-assembly and Nanotechnology

Perspectives, Potentials and Challenges

- Trillions of dollars business in the next ten years or so
- Energy
- Information storage
- ●●●●●●●●
- Does everything have to be nano??
- Is nano good or not?
- Nanotoxicity
- Environment, health and safety



Course Project

- Literature search methods;
- 1-page Abstract/Outline, due on Feb. 6 (third week), preferred by email
- Literature review due, Feb. 27
- Project update presentation and discussion, Progress report (I) due, March 27.
- Final presentations, May 1
- Final Report Due on exam day, sent by email