Nanomaterials: An Overview of Concepts, Developments and Promises

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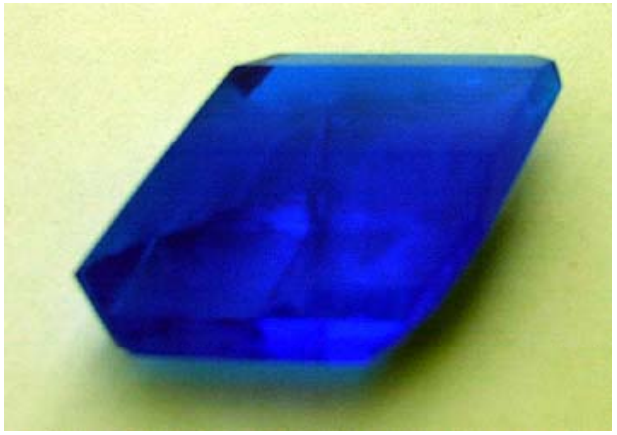
Different chemical compositions

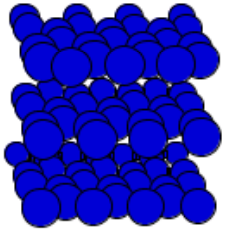


$CuSO_4.5H_2O$

$K_2Cr_2O_7$

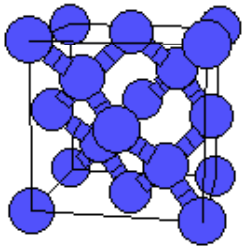
$(NH_4)H_2PO_4$

Different structures

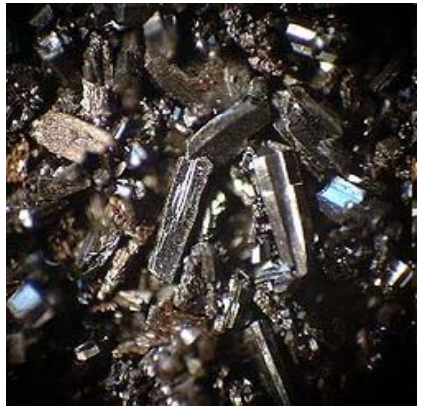


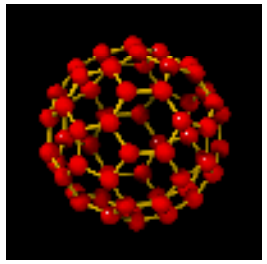
Graphite

Carbon



Diamond





Fullerene (C_{60})

Properties of materials depend upon :

Chemical composition

Structure

Size changes

Silicon

centimeter

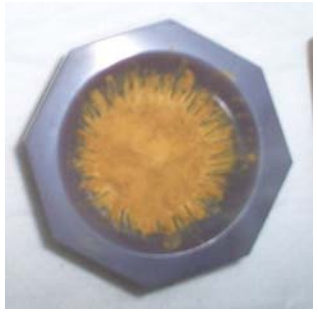
Chemical composition
Structure

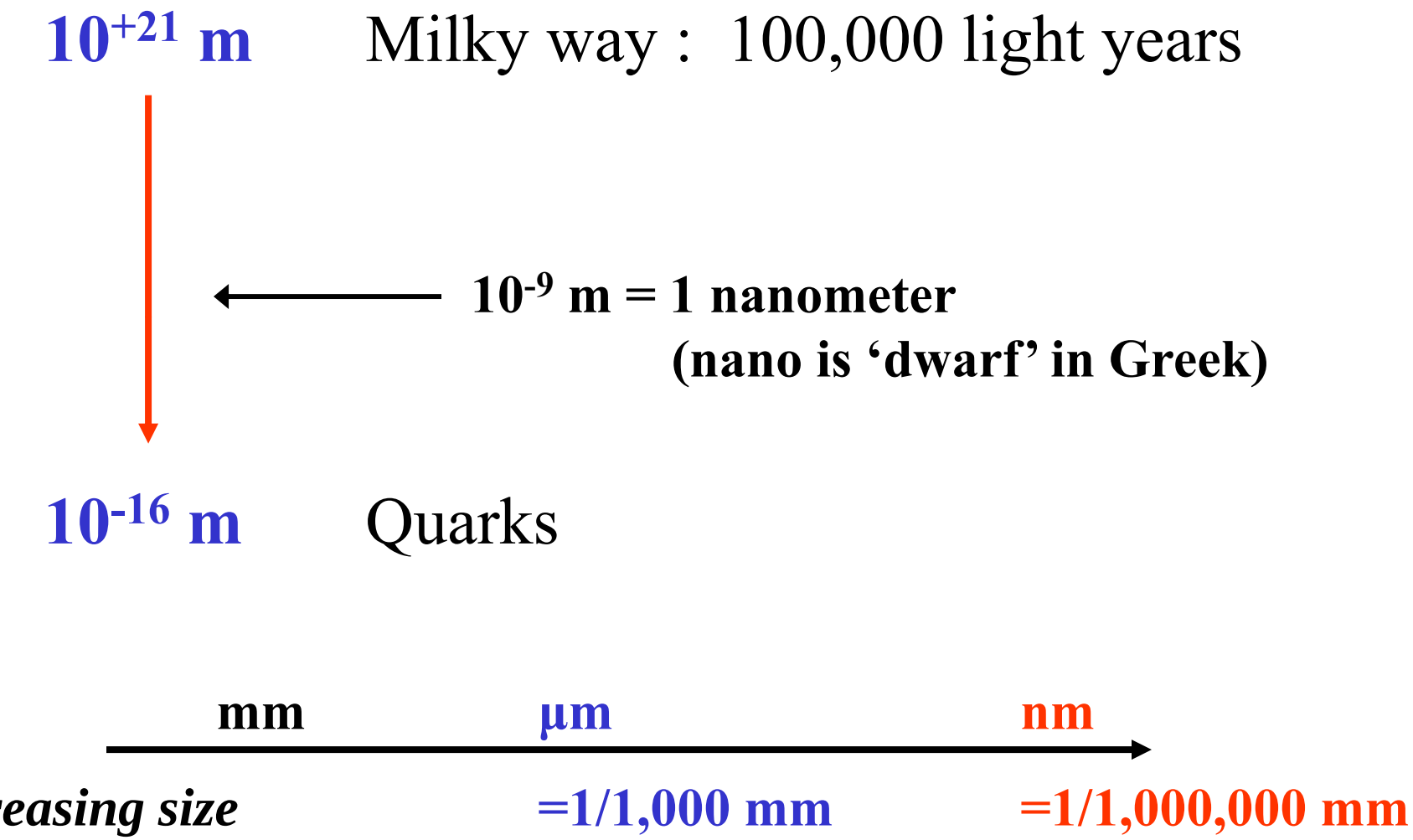
Identical

micrometer

Silicon

nanometer



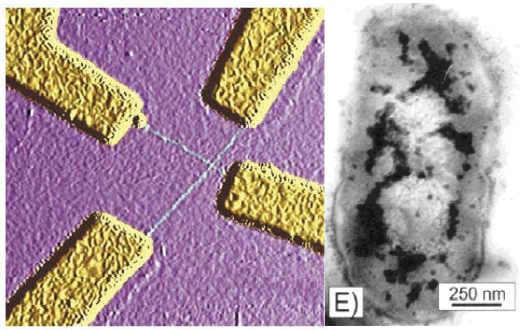

10^{+21} m
Milky way : 100,000 light years
10^{-9} m = 1 nanometer
(nano is 'dwarf' in Greek)
10^{-16} m
Quarks
mm
µm
nm
Decreasing size
=1/1,000 mm
=1/1,000,000 mm

The next big thing is small…

Nanoscopy

Chemistry connection

Physics connection



Electronics /
biology connection

Richard Feynmann

December 29, 1959 - Annual Meeting of
The American Physical Society at Caltech

There's Plenty of Room at the Bottom

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

"As soon as I mention this, people tell me about miniaturization, and how far it has progressed today.

They tell me about electric 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.

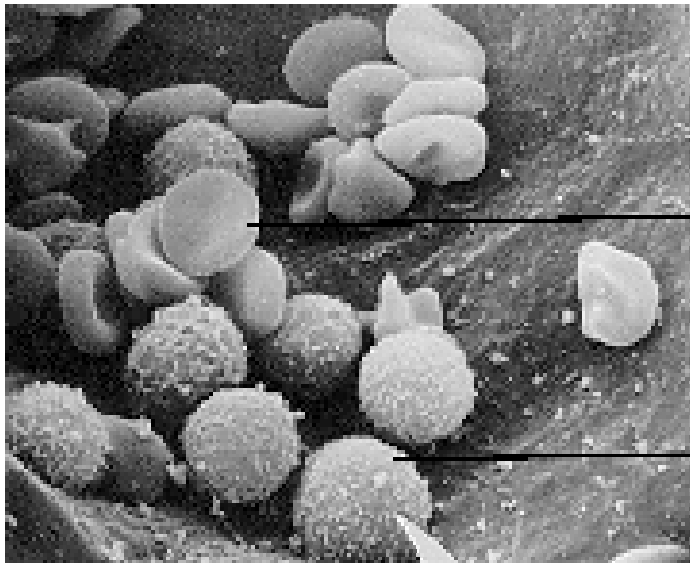
But that's nothing; that's the most primitive, halting step in the direction I intend to discuss.

It is a staggeringly small world that is below."

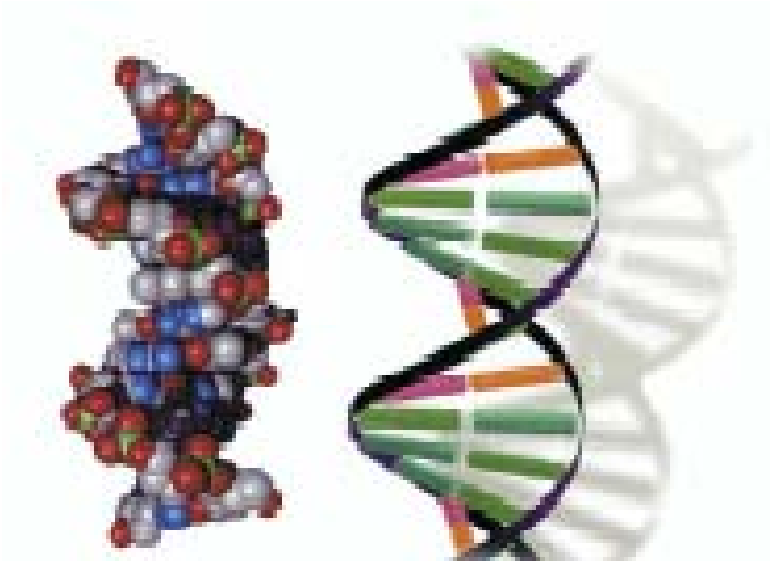
Feynmann received the Nobel Prize for Physics in 1965

Natural micro and nano objects

Human hair
~ 50 – 150 µm wide



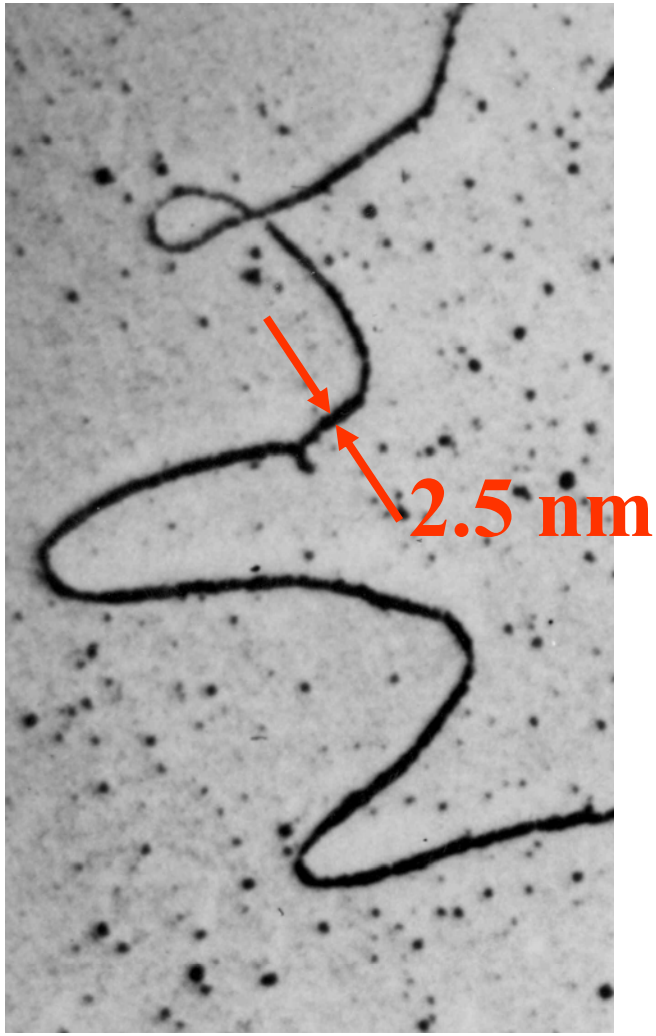
Red & white blood cells ~ 2 - 5 µm



DNA ~ 2.5 nm diameter

(Courtsey : Nanoscale Science, Engineering, and Technology in the Office of Basic Energy Sciences (BES) of the U.S. Department of Energy (DOE))

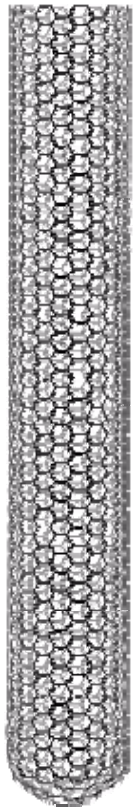
Electron microscope image of DNA



Man-made micro and nano objects

Head of a pin
~ 1 – 2 mm

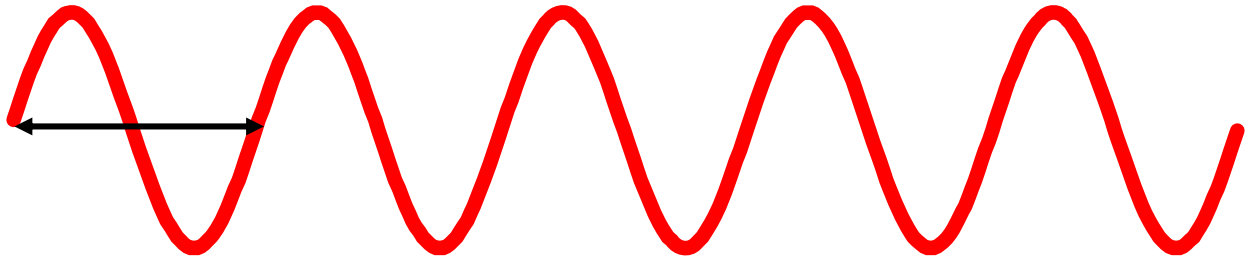
Microelectromechanical (MEM) devices
~ 10 – 100 µm wide



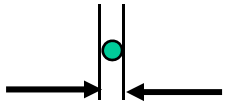
Carbon nanotube
~ 2 nm wide

(Courtsey : Nanoscale Science, Engineering, and Technology in the Office of Basic Energy Sciences (BES) of the U.S. Department of Energy (DOE))

Seeing is believing



Wavelength, λ = 650 nm



10 nm

Focal spot of a light beam

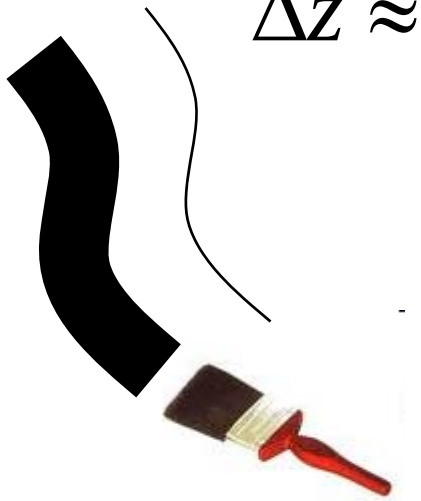
Resolution in focal plane

$$\Delta r \approx \frac{\lambda}{2n\sin\alpha} \sim \frac{\lambda}{4}$$

Resolution normal to plane

$$\Delta z \approx \frac{\lambda}{n\sin^2\alpha} \sim \frac{\lambda}{2}$$

λ = wavelength of light
α = aperture angle of lens
n = refractive index



Diffraction limit

How do we get to ‘see’ these nano objects ?

A variety of very powerful microscopies are available these days :

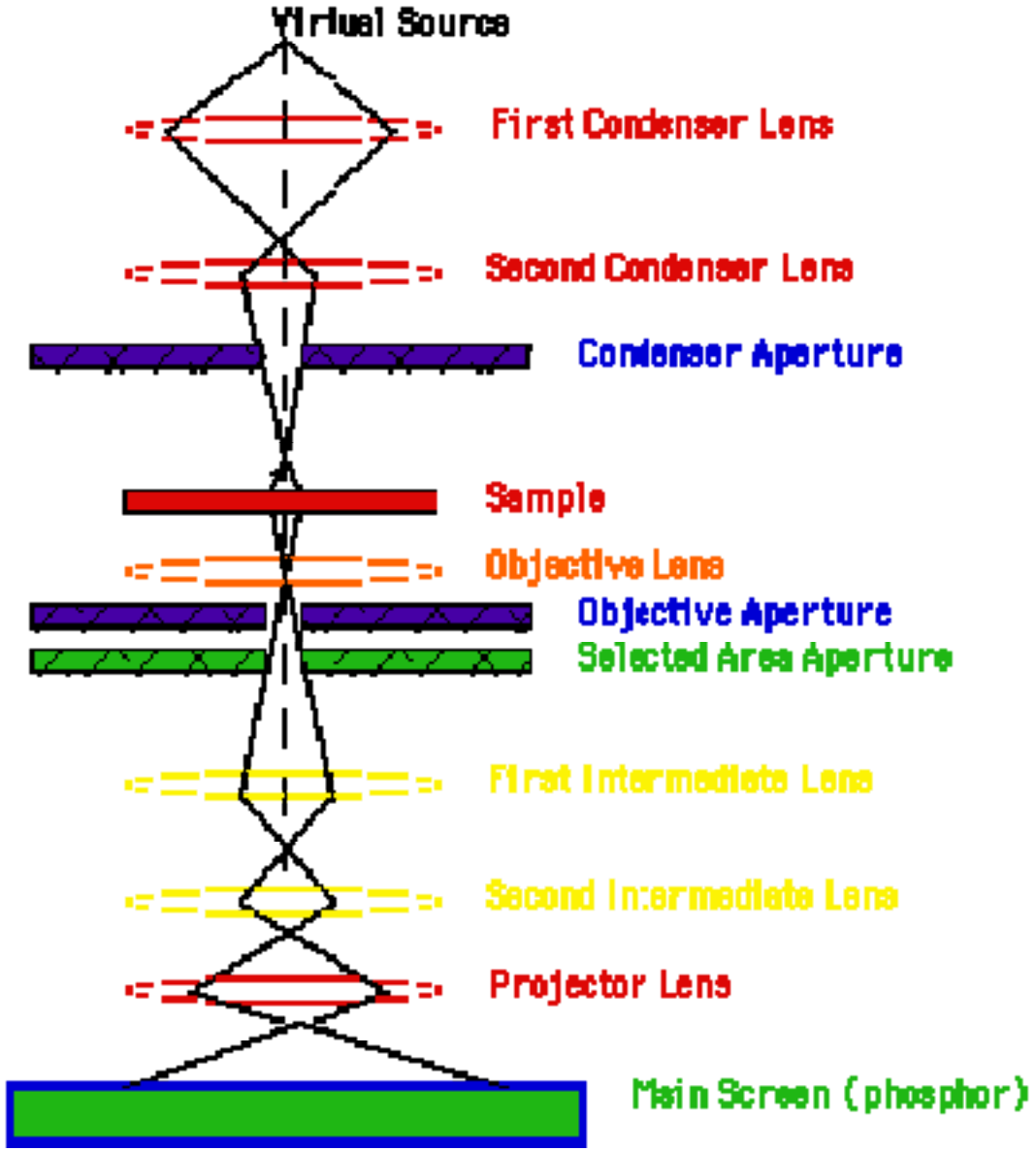
Electron microscopy

- **Scanning electron microscopy (SEM)**
- **Transmission electron microscopy (TEM)**

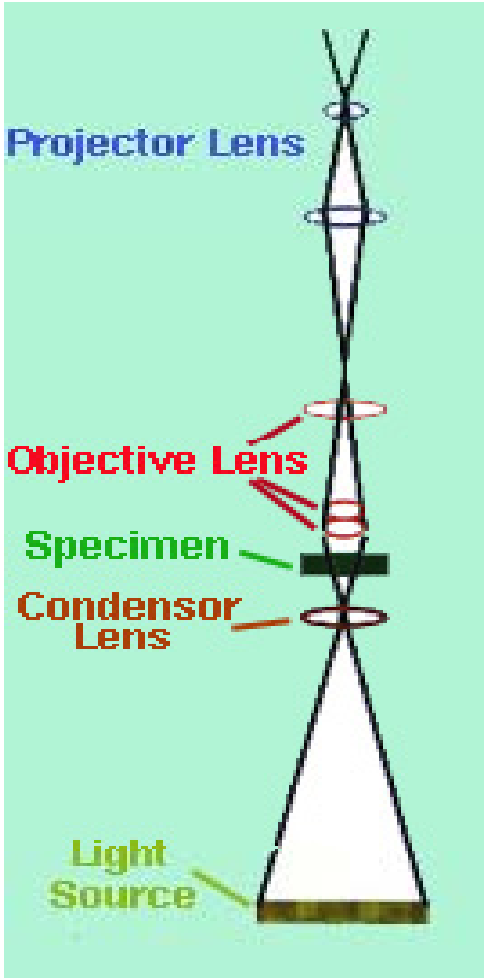
Scanning probe microscopy

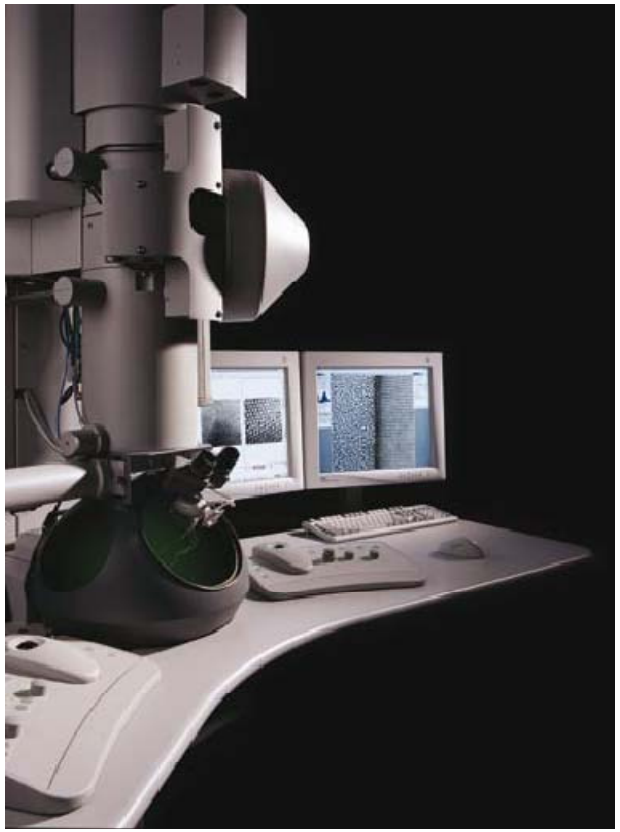
- **Atomic force microscopy (AFM)**
- **Scanning tunneling microscopy (STM)**

Transmission Electron Microscope

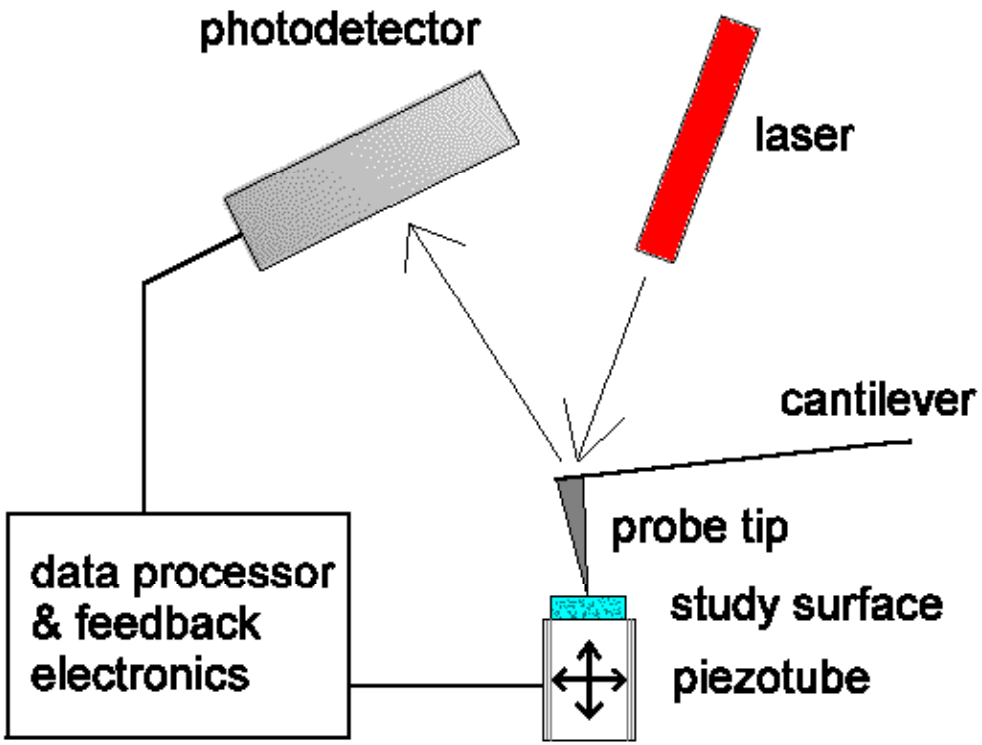


Optical Microscope





Atomic Force Microscope



In an AFM, nano features are detected by monitoring the movement of a very fine cantilever probe using a laser system. In an STM, a current tunneling between the probe tip and the surface is monitored.

The big question :

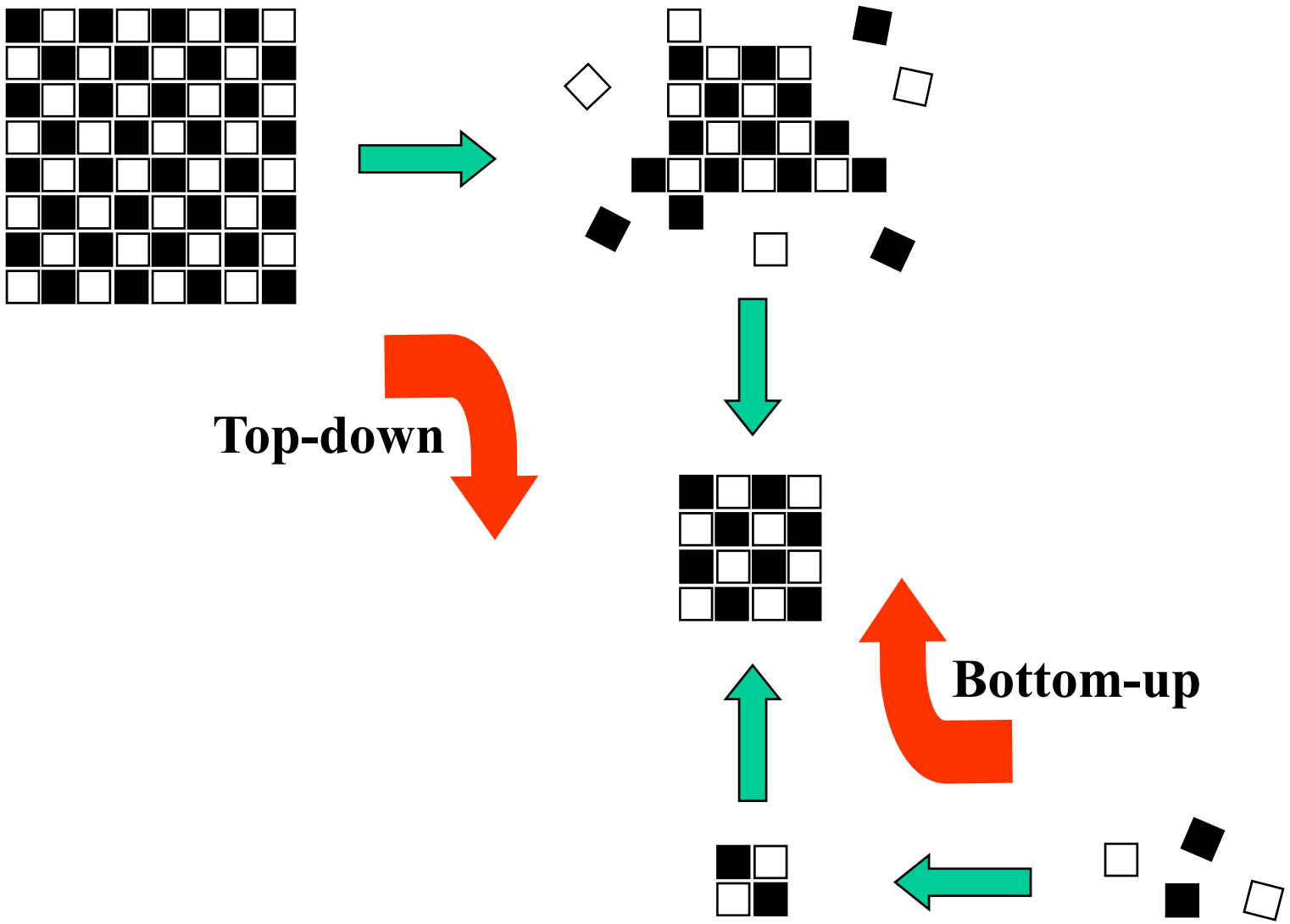
How does one make these tiny tiny objects ?

Fabrication of nanomaterials

Two general approaches

Top-down (Break down)

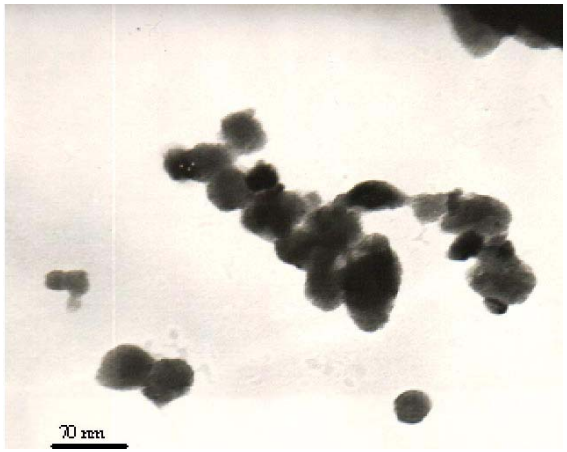
Bottom-up (Build up)


Top-down
Bottom-up

Swarna Bhasma in Ayurvedic medicine

1. Cut purified gold foil into pieces (~ 10 g).
2. Add to 20 g of mercury in a stone mortar & grind.
3. Place the amalgam in an earthen crucible
4. Add sulphur in a 1:1 proportion.
5. Cover with an inverted earthen crucible.
6. Seal by 3 layers of cotton cloth and wet clay.
7. Cover with cow dung cakes (4, 250 g each) in a pit.
8. Heat for 8 h; maximum temperature was ~ 900^{o}C.
9. After cooling, grind the incinerated matter.
10. Repeat the heating with sulphur 42 times.
11. Swarna Bhasma is obtained as a brown red powder.

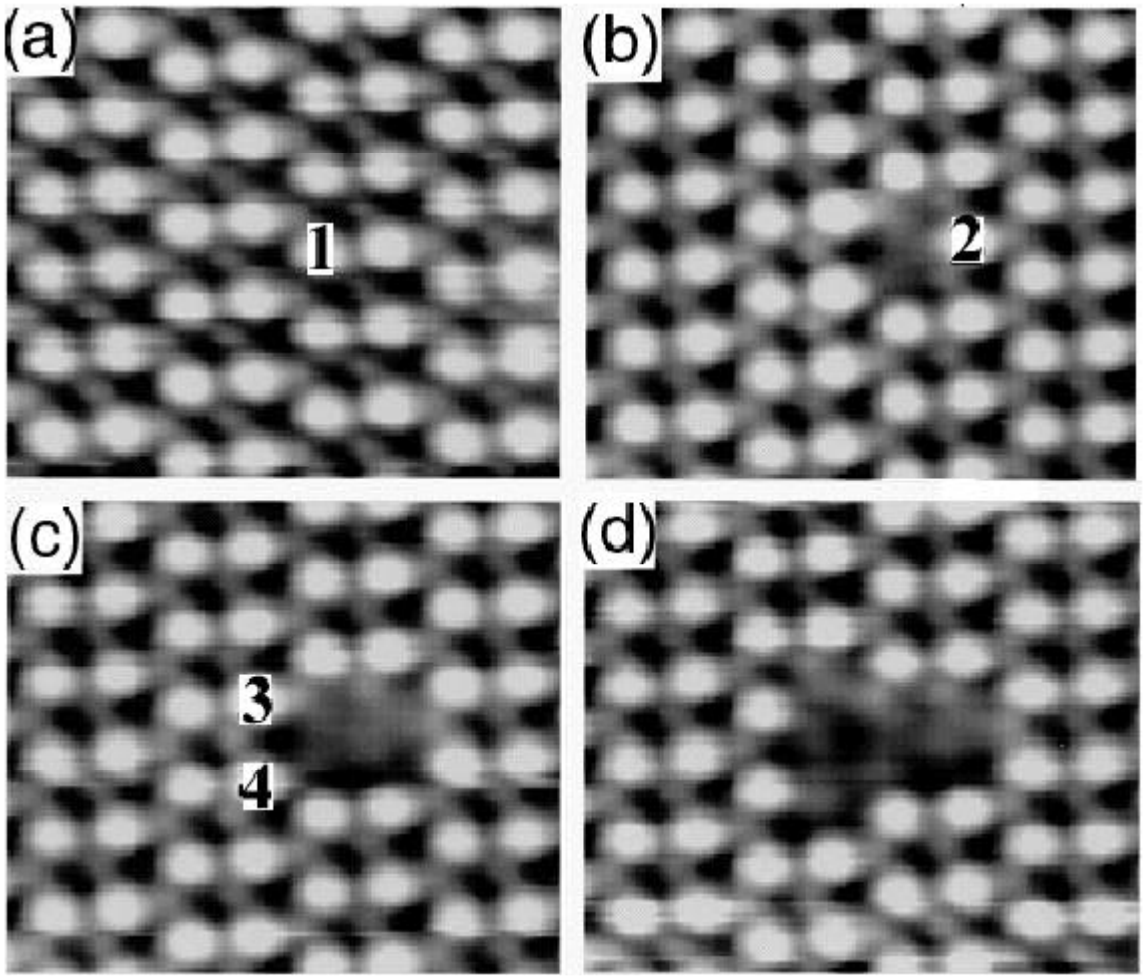
.....Sarangadhara-Samhita



Gold nanoparticles with
size ~ 50 nm

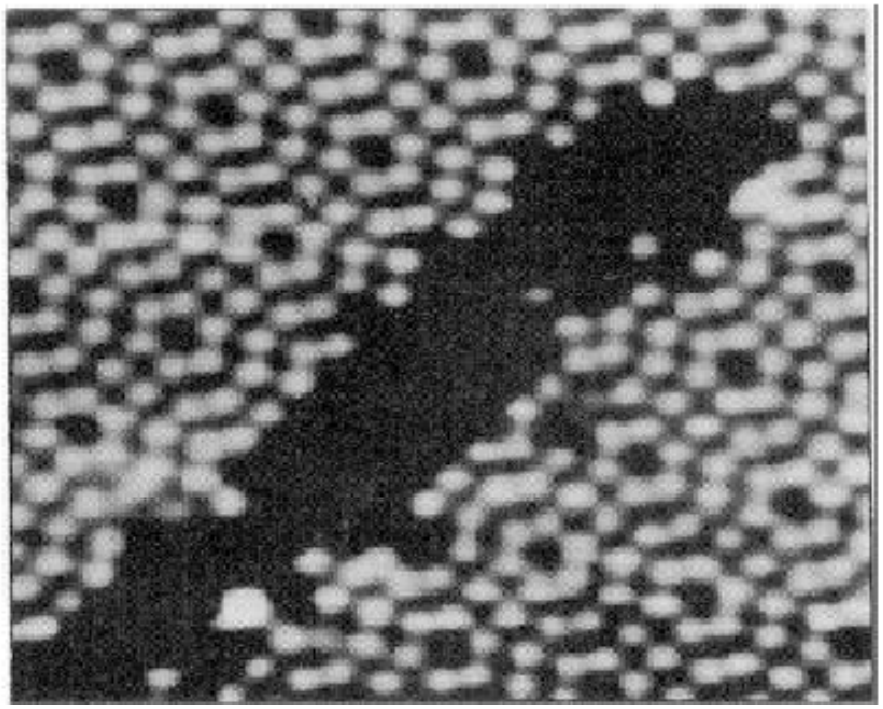
Brown et al, *Gold Bulletin* **2007**, *40*, 245

Sequential extraction of adsorbed atoms - one by one - from Germanium surface



Dujardin, G., Mayne, A., Robert, O., Rose, F., Joachim, C., and Tang, H. Science **1998**, *251*, 1206.

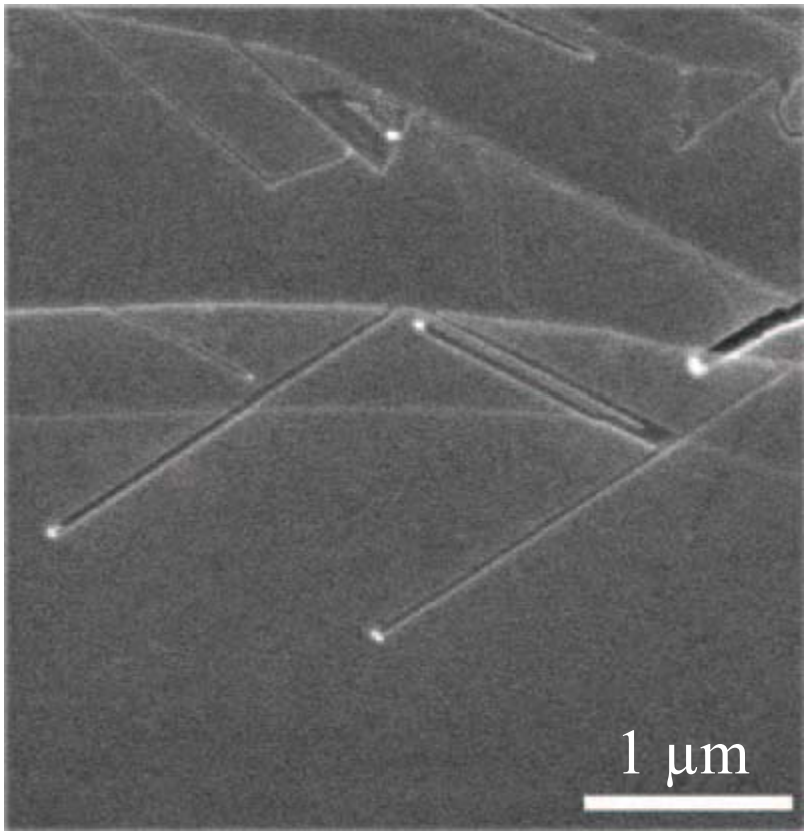
Straight groove formed on Silicon surface by repeated scanning at high current

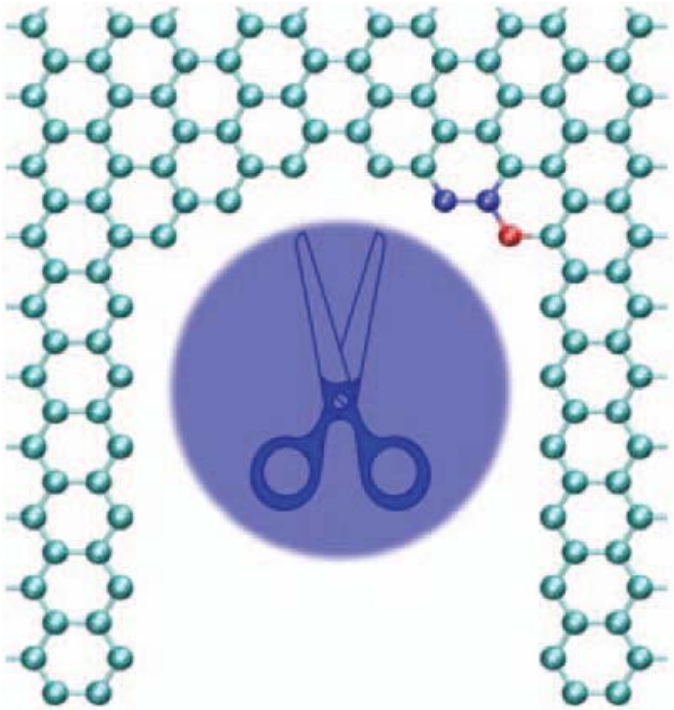


(15 nm ×12 nm)

Ma, Z.L., Liu, N., Zhao, W.B., Gu, Q.J., Ge, X., Xue, Z.Q., and Pang, S.J. *J. Vac. Sci. Technol. B* **1995**, *13*, 1212.

Nanocutting with a Nickel nanoparticle knife





Ni nanoparticles deposited on HOPG and kept at high temperature under Ar/H_2 atmosphere – catalytic hydrogenation of carbon

(Ci et al, *Nano Res.* **2008**, *1*, 116)

Chemical route to prepare metal nanoparticles

$HAuCl_4$ + Reducing agent → Au + biproducts

$AgNO_3$ + Reducing agent → Ag + biproducts

Reducing agents : $NaBH_4$
Citrate
Alcohol etc..

Stabilising agents : Surfactants
Polymers etc..

Faraday's 'diffused, divided gold'

'finely divided metallic state' of gold (M. Faraday, Philos. Trans. R. Soc.London, **1857**, 147, 145)

Source: Whipple Library, Department of History and Philosophy of Science, University of Cambridge [http://www.hps.cam.ac.uk/library/].

Synthesis of gold colloid

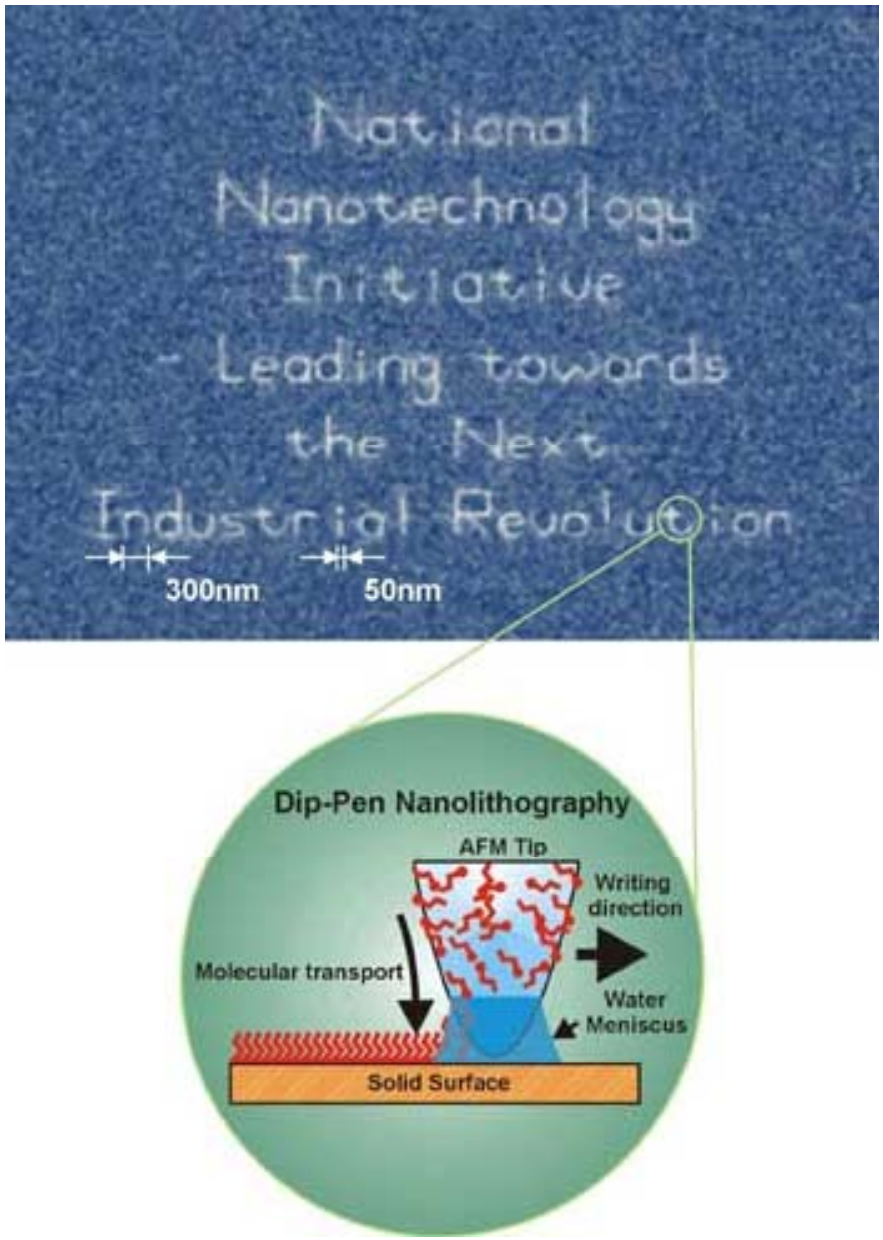
10 mg $HAuCl_4$ is weighed out using a spatula wrapped in teflon tape.

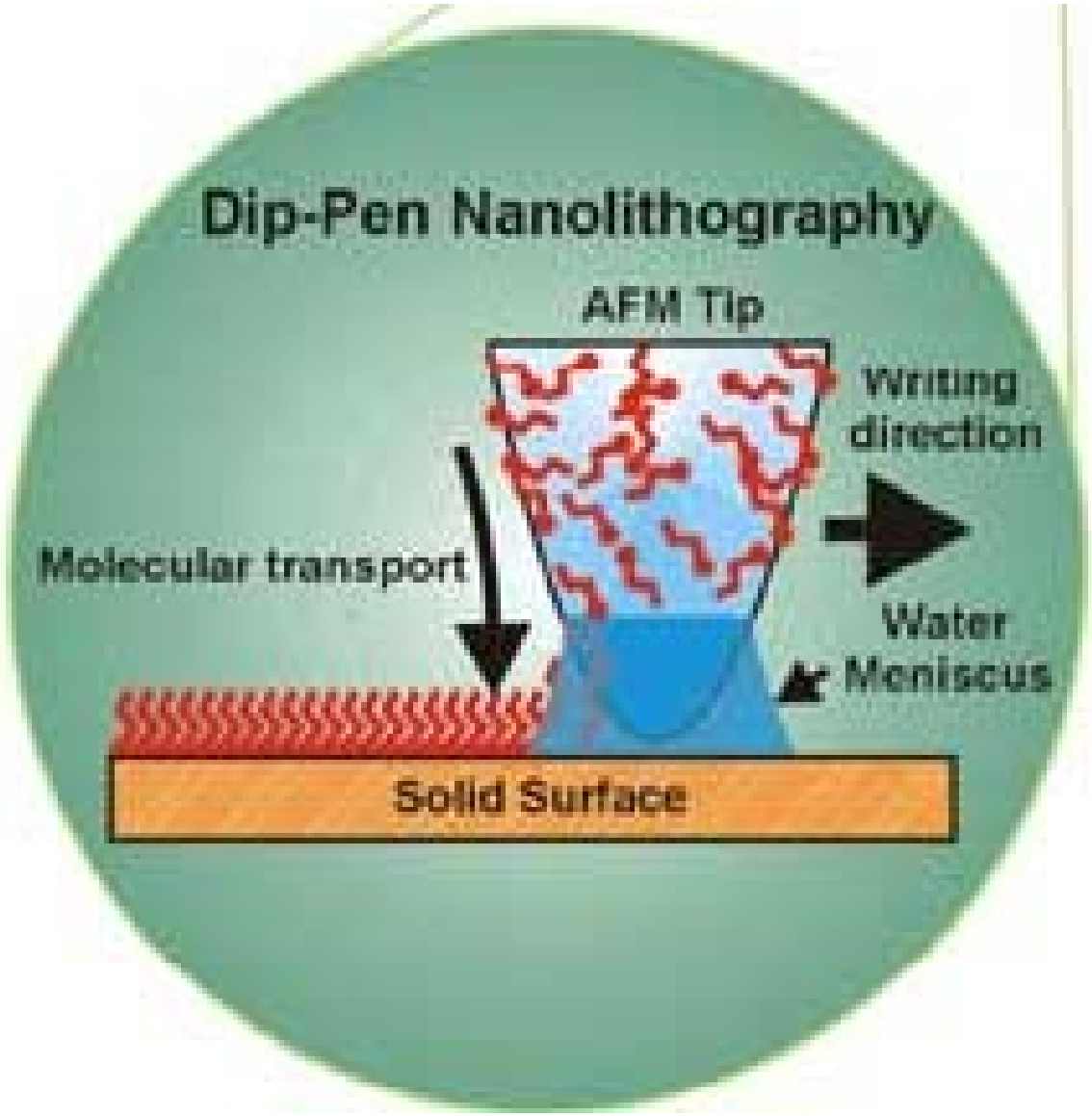
The $HAuCl_4$ is dissolved in 95 mL water on a hotplate stirrer. Heat the solution to boiling.
Citrate reduces the gold(III).

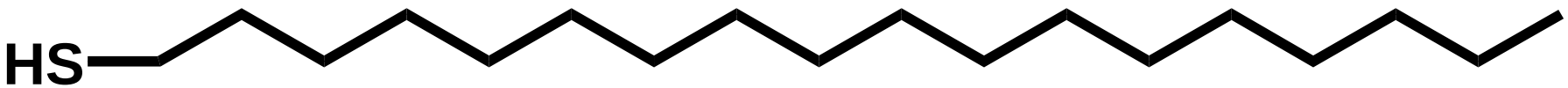
Turkevich method
(Courtsey : University of Wisconsin - Madison Materials Research Science and Engineering Center – Interdisciplinary Education Group)

And now you can write nano letters !

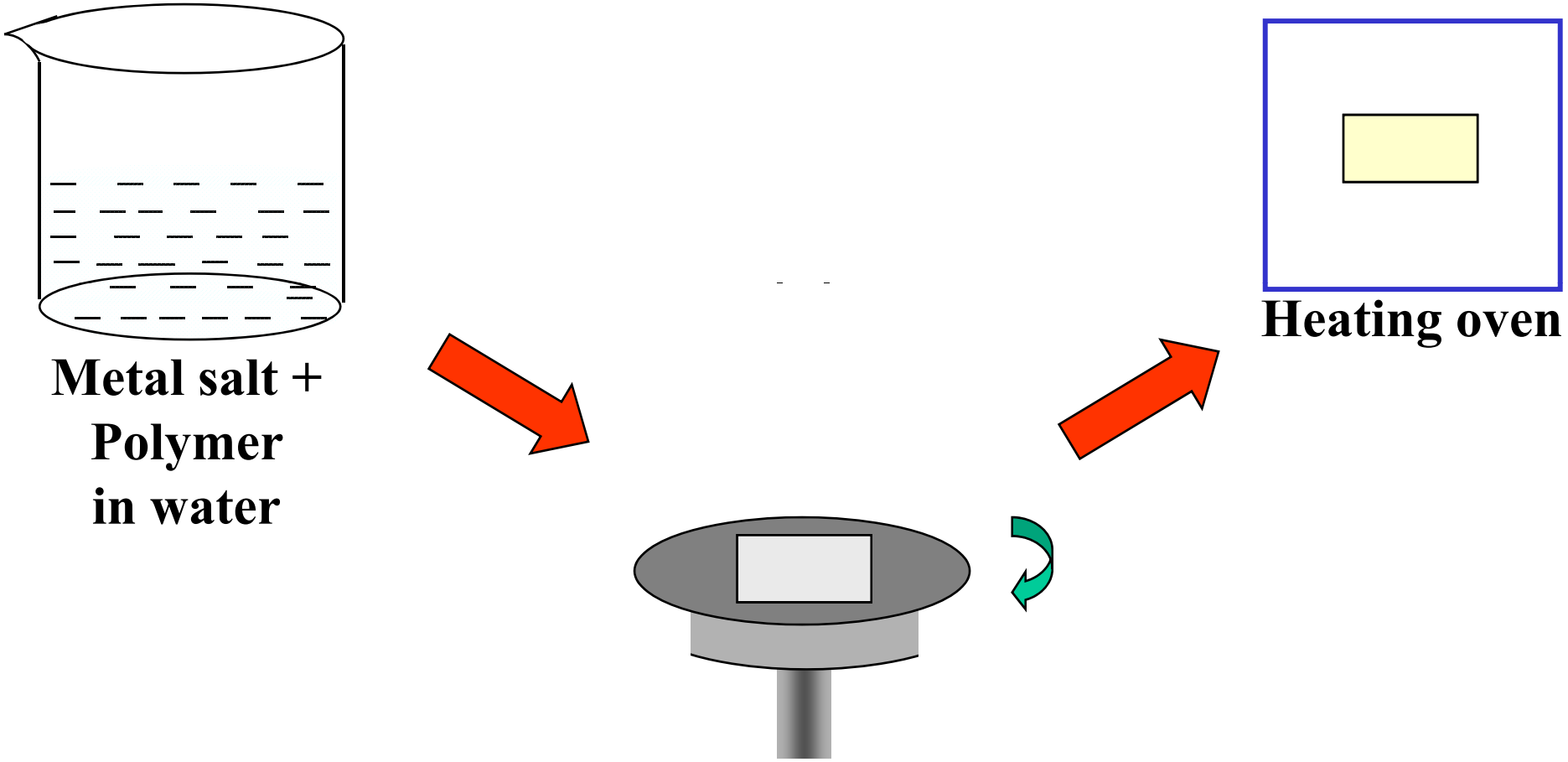
The technique is called dip pen nanolithography. One molecule thick letters are written on the surface of a piece of gold using a molecule called octadecanethiol as the ink. It is then visualized using an atomic force microscope



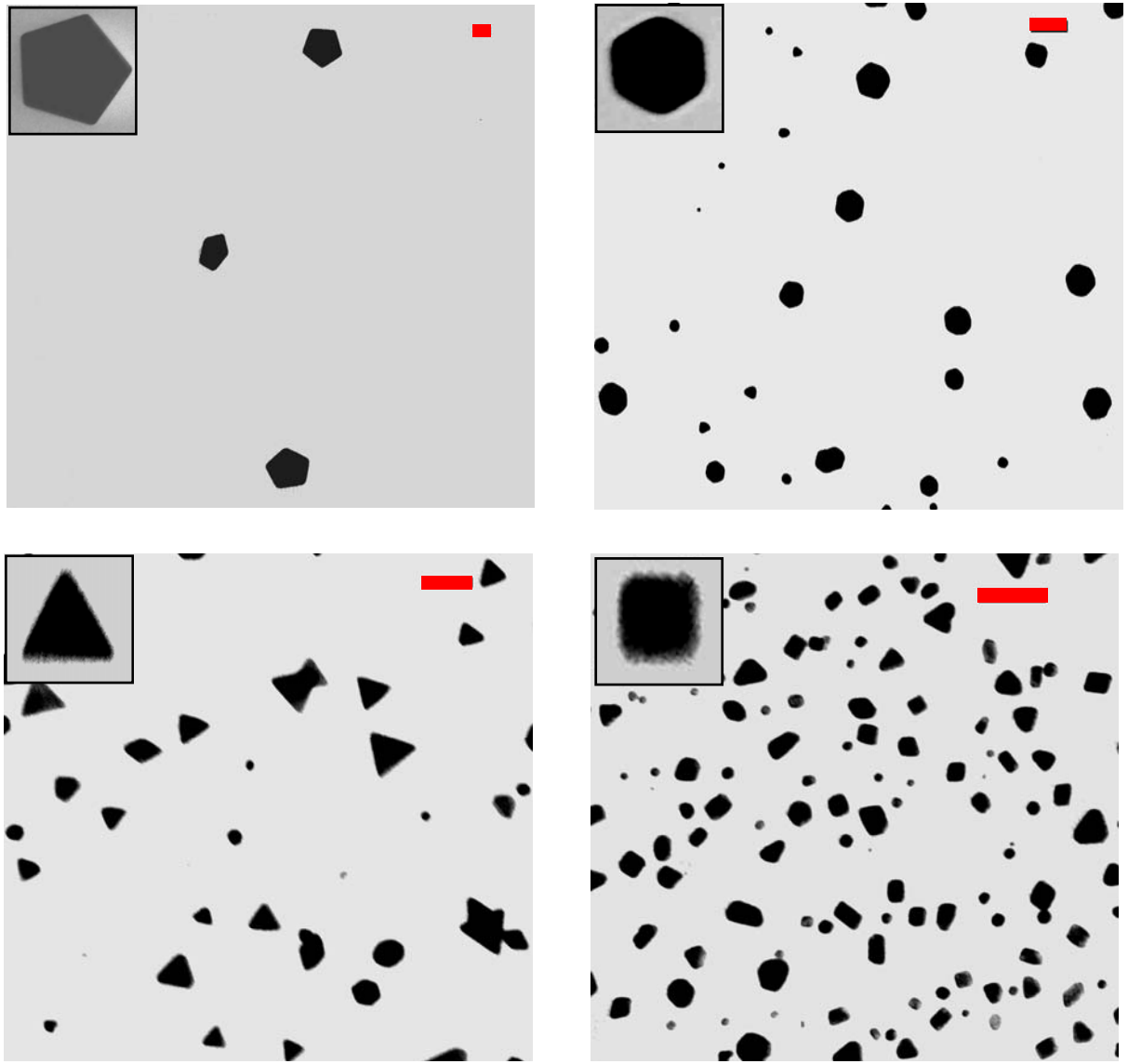

Dip-Pen Nanolithography
AFM Tip
Writing direction
Molecular transport
Water Meniscus
Solid Surface


HS

Growing nanoparticles inside polymer film



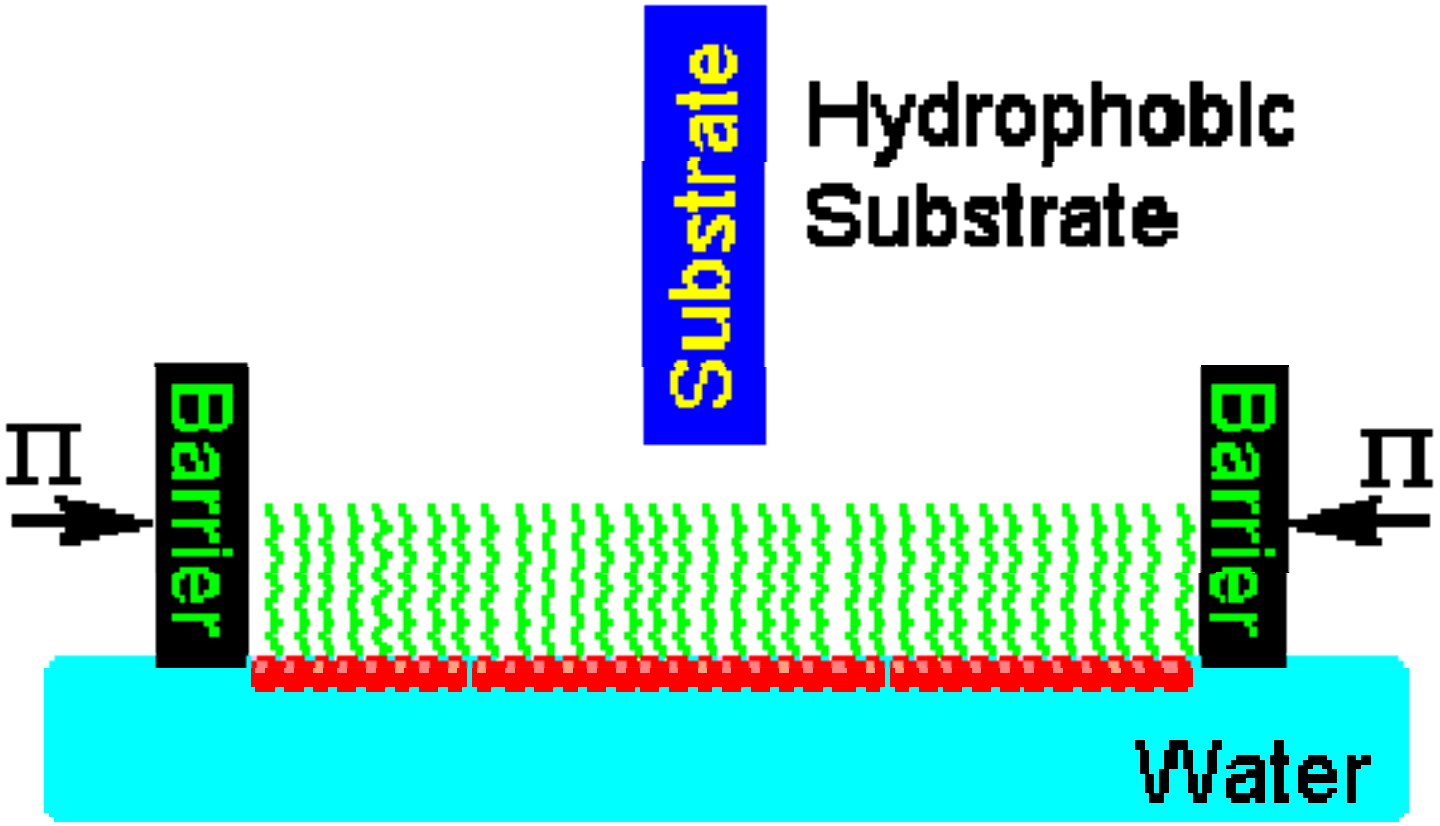
Au nanoplates in PVA matrix

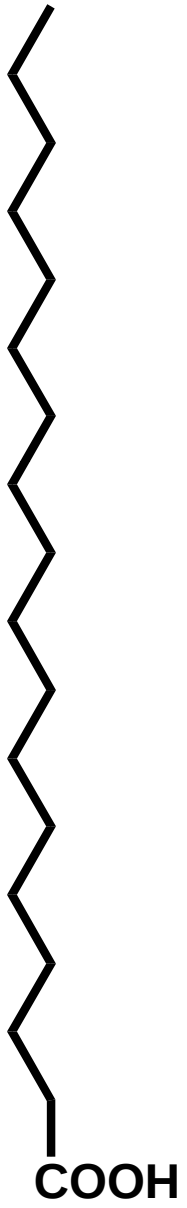


Scale bar = 50 nm

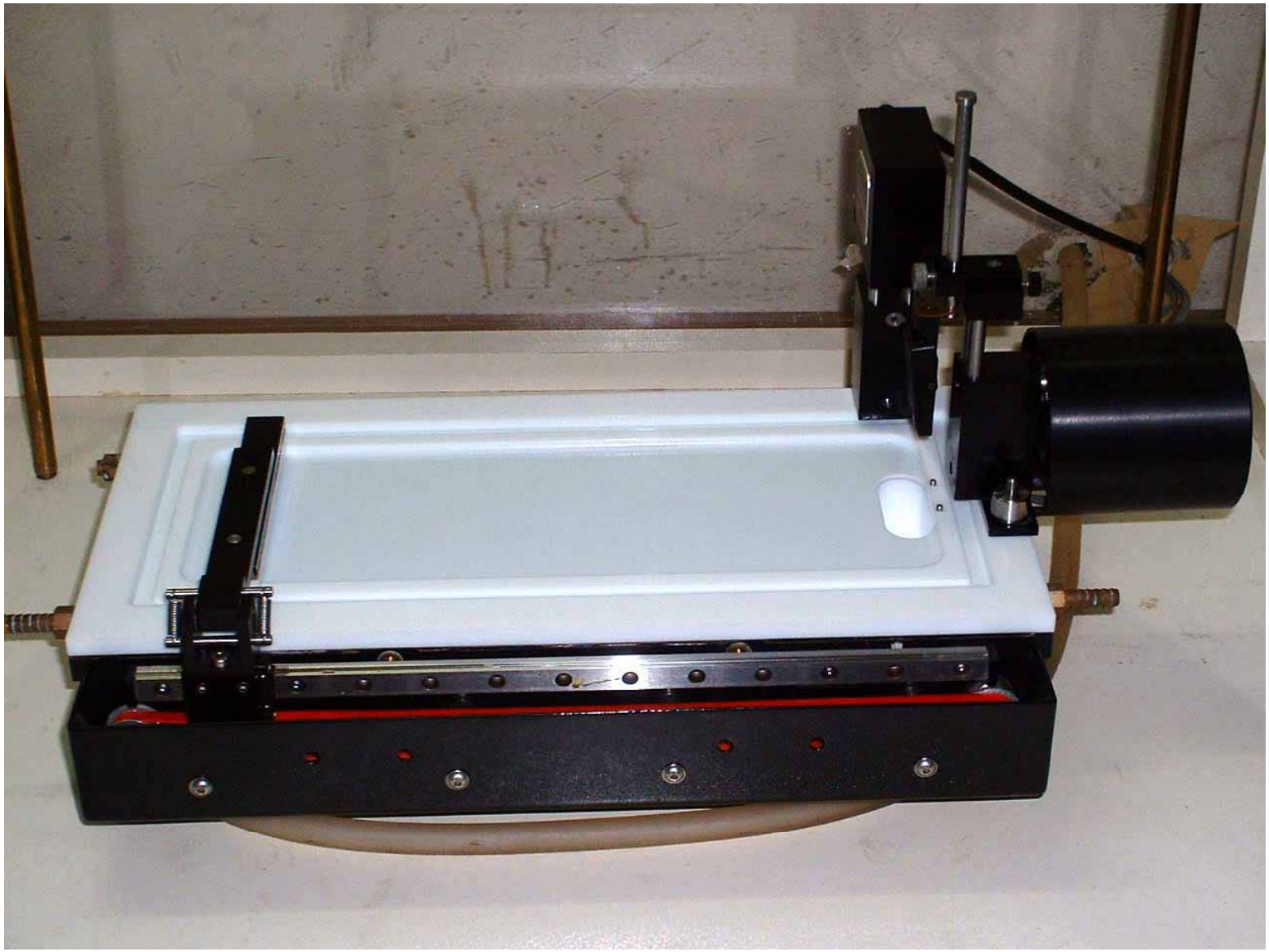
Thickness ~ 8 - 10 nm

Langmuir-Blodgett Method - formation of ultrathin films (1932)

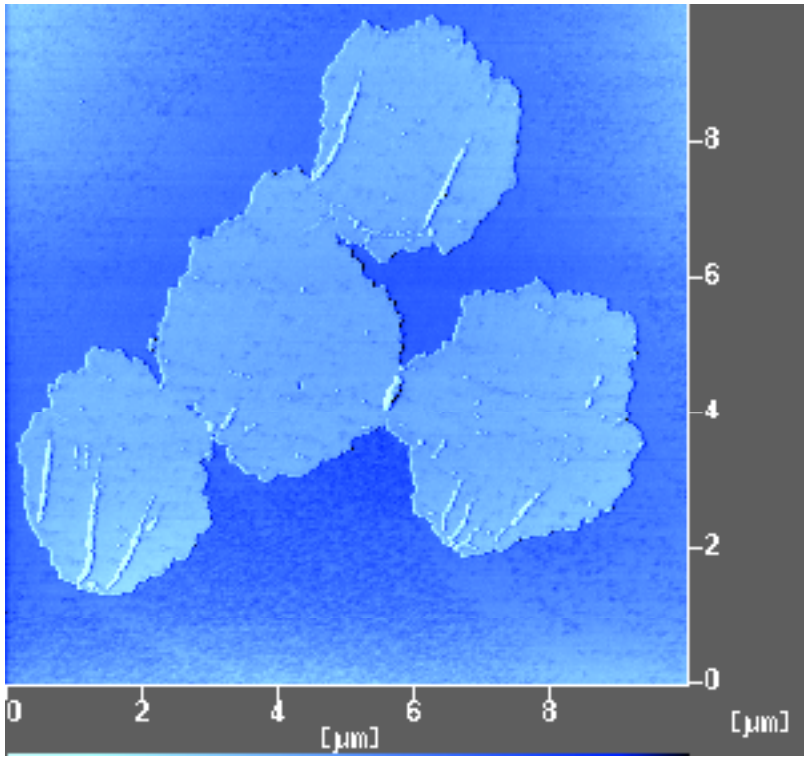


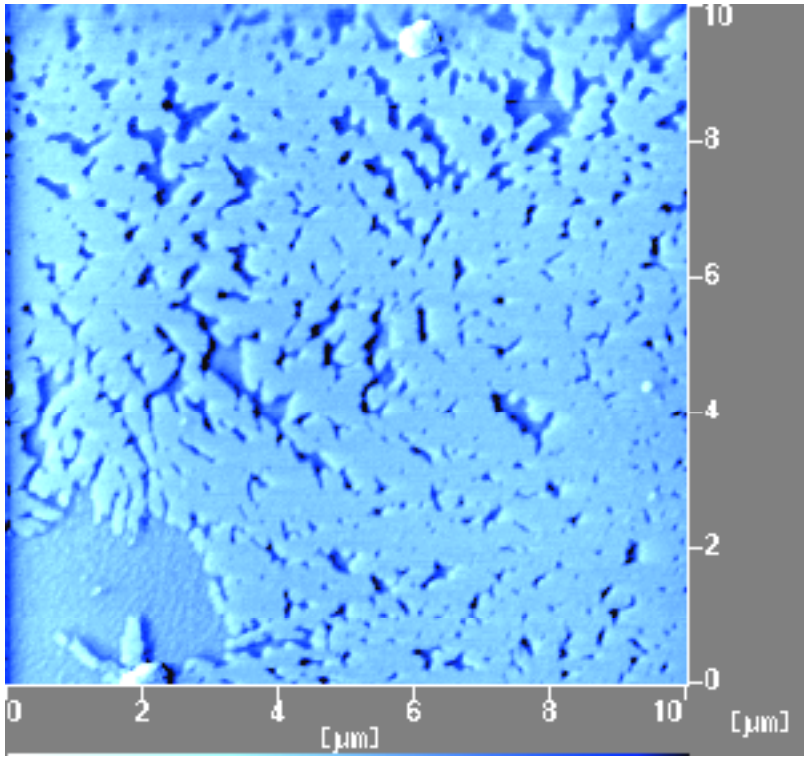


Langmuir-Blodgett trough

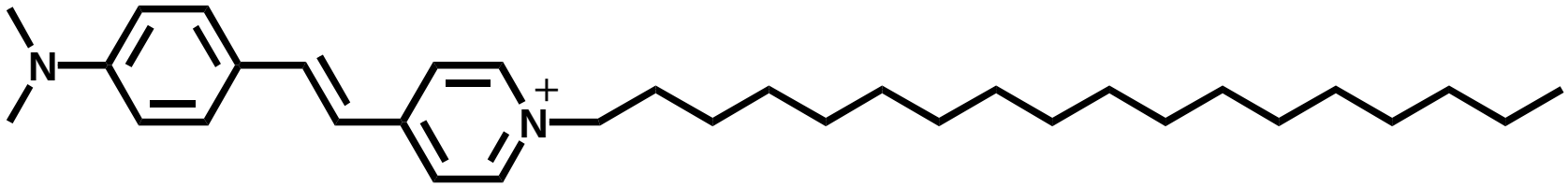


AFM images of LB films

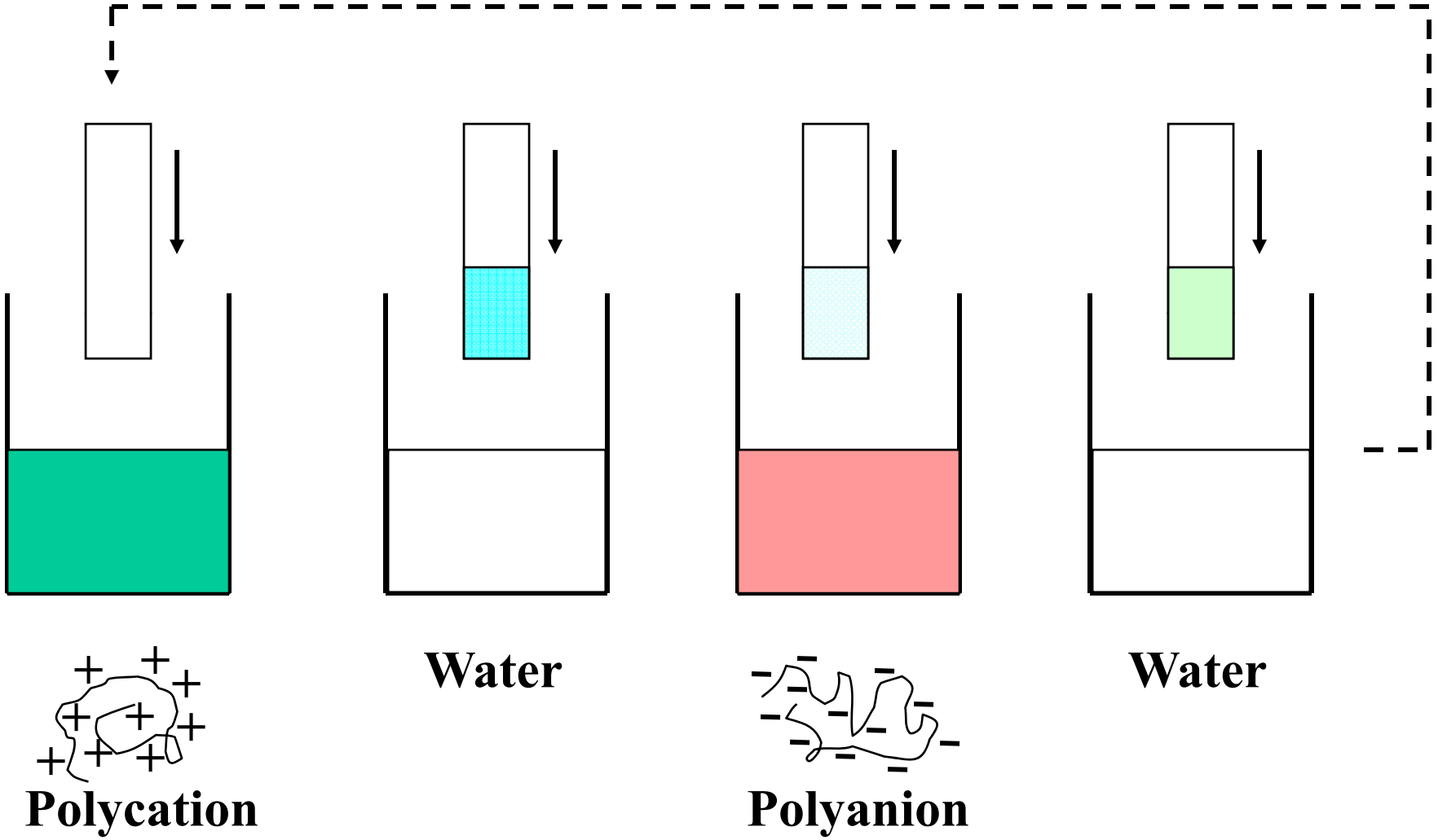




Thickness ~ 2 – 4 nm



Layer-by-layer Assembly



Is it only the size that is important ?

Or are there any special physical and chemical properties associated with the size ?

And where on earth (or heavens for that matter) would you use them ?

Nanoparticles exhibit very different properties as compared to their bulk counterparts

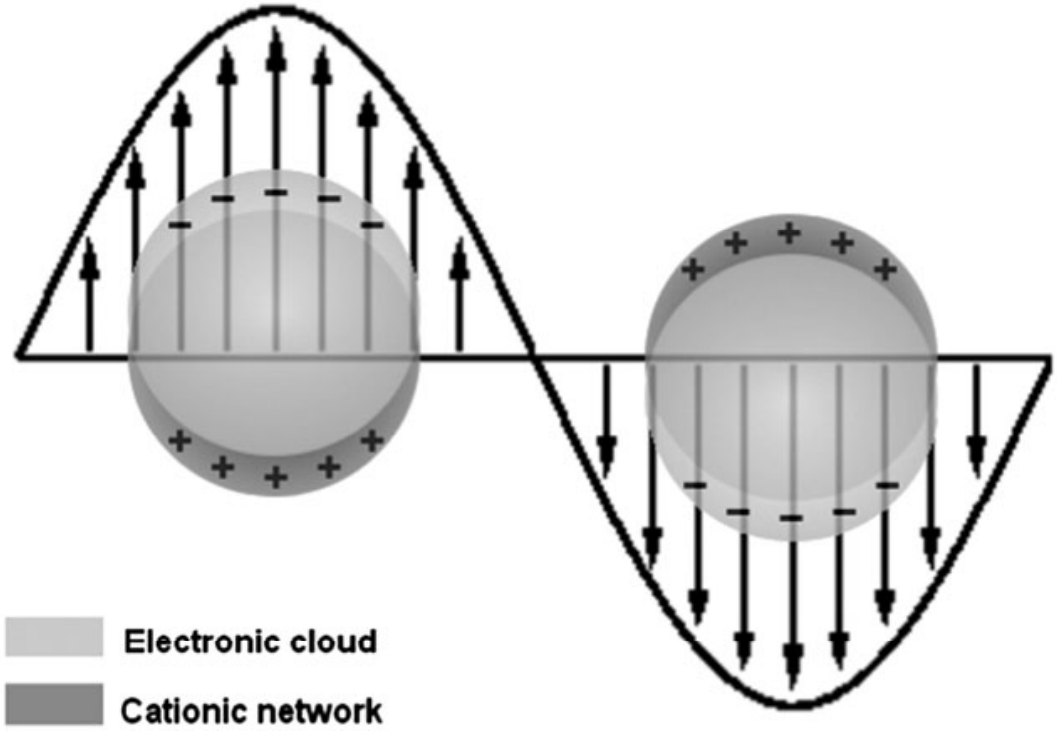
Example :

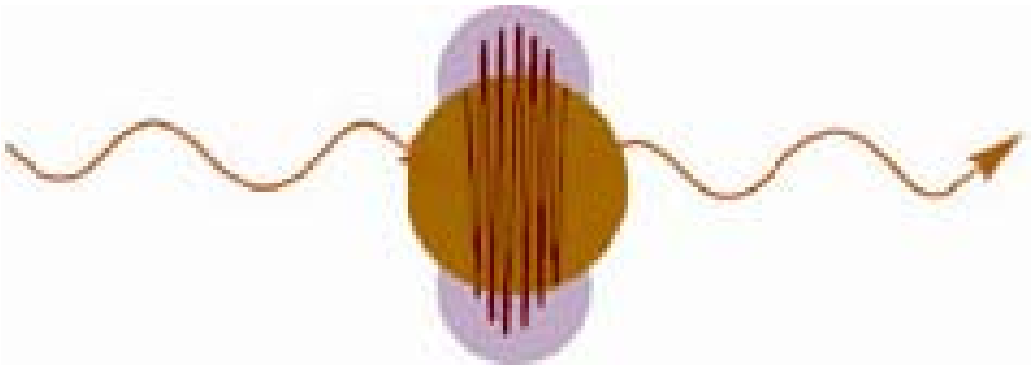
colour
solubility
surface area / volume ratio
mechanical, electronic, magnetic properties

Colour and Solubility

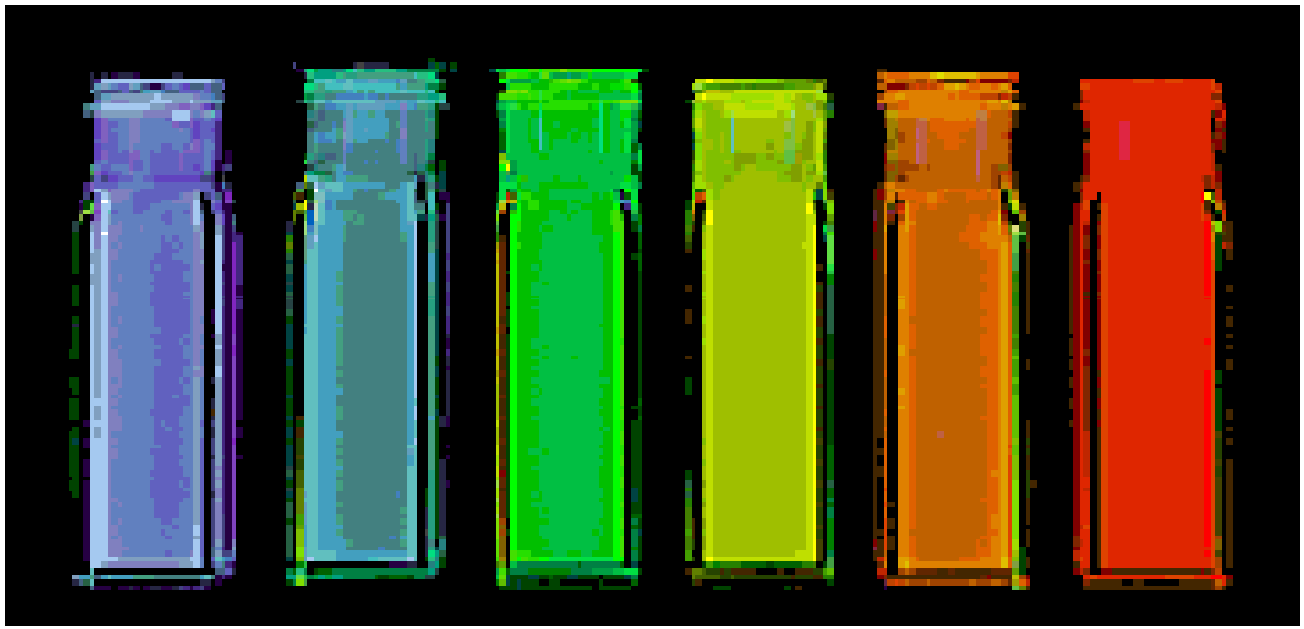
Faraday's gold (1857)

Plasmon Resonance Absorption





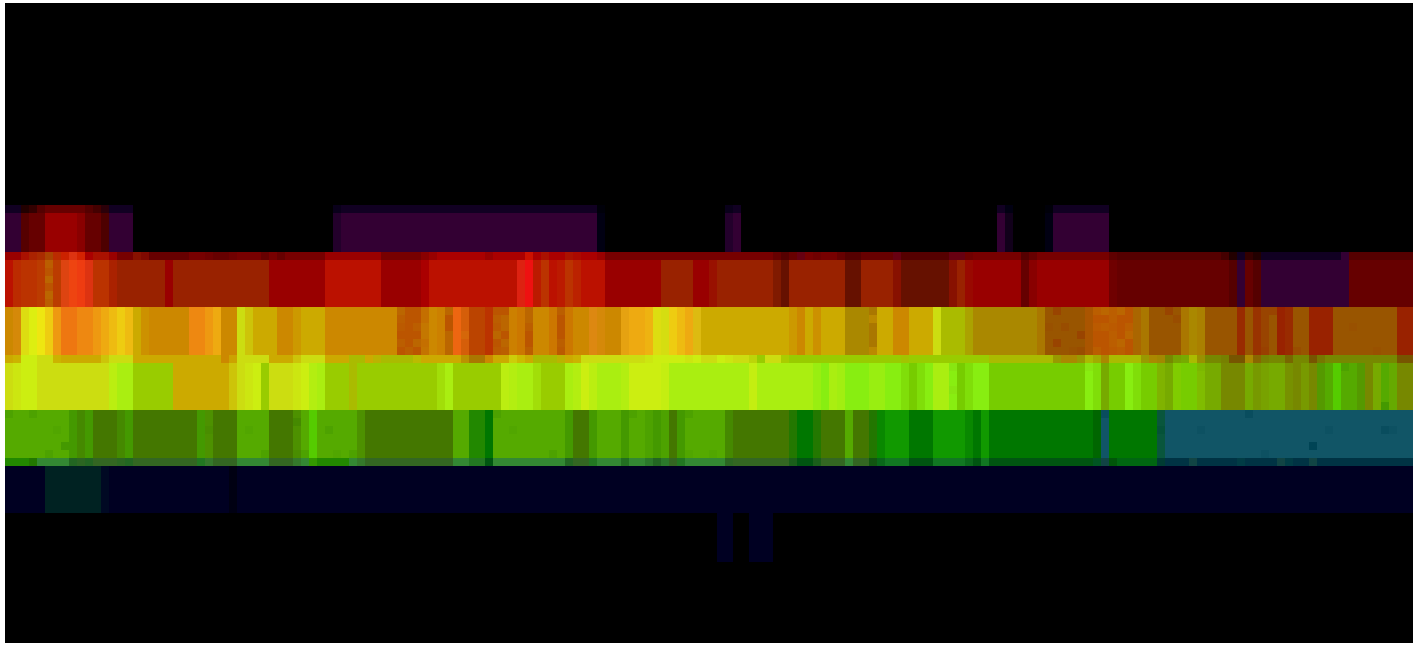
Same chemical composition but colour changes with size !



Increasing particle size

Quantum dots, nanoparticles of semiconductors, of different sizes, illuminated by a single light source, emit intense fluorescence of different colours
(Felice Frankel, MIT)

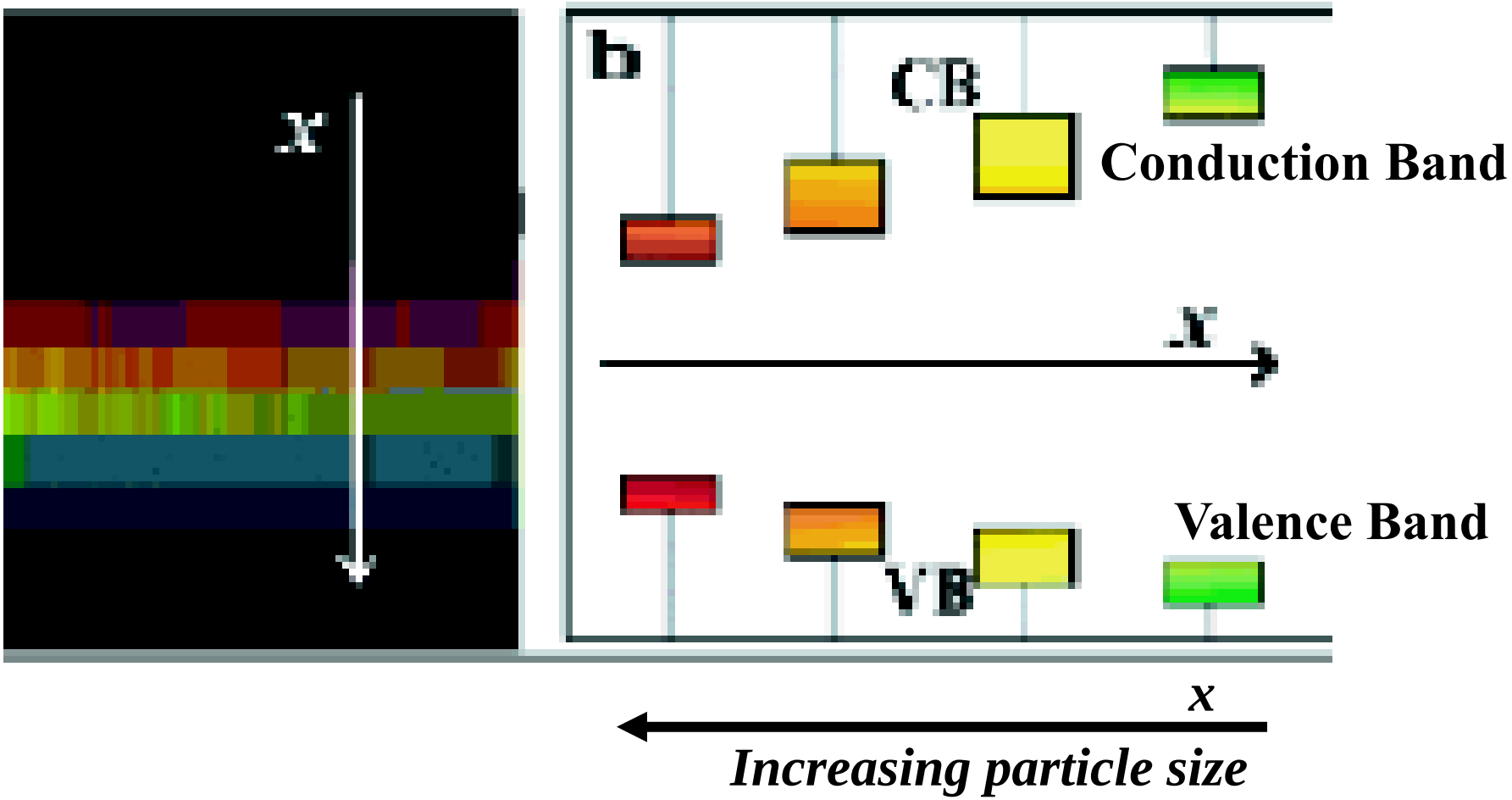
One can even make ‘nano rainbows’ by assembling layers of nanoparticles with different sizes



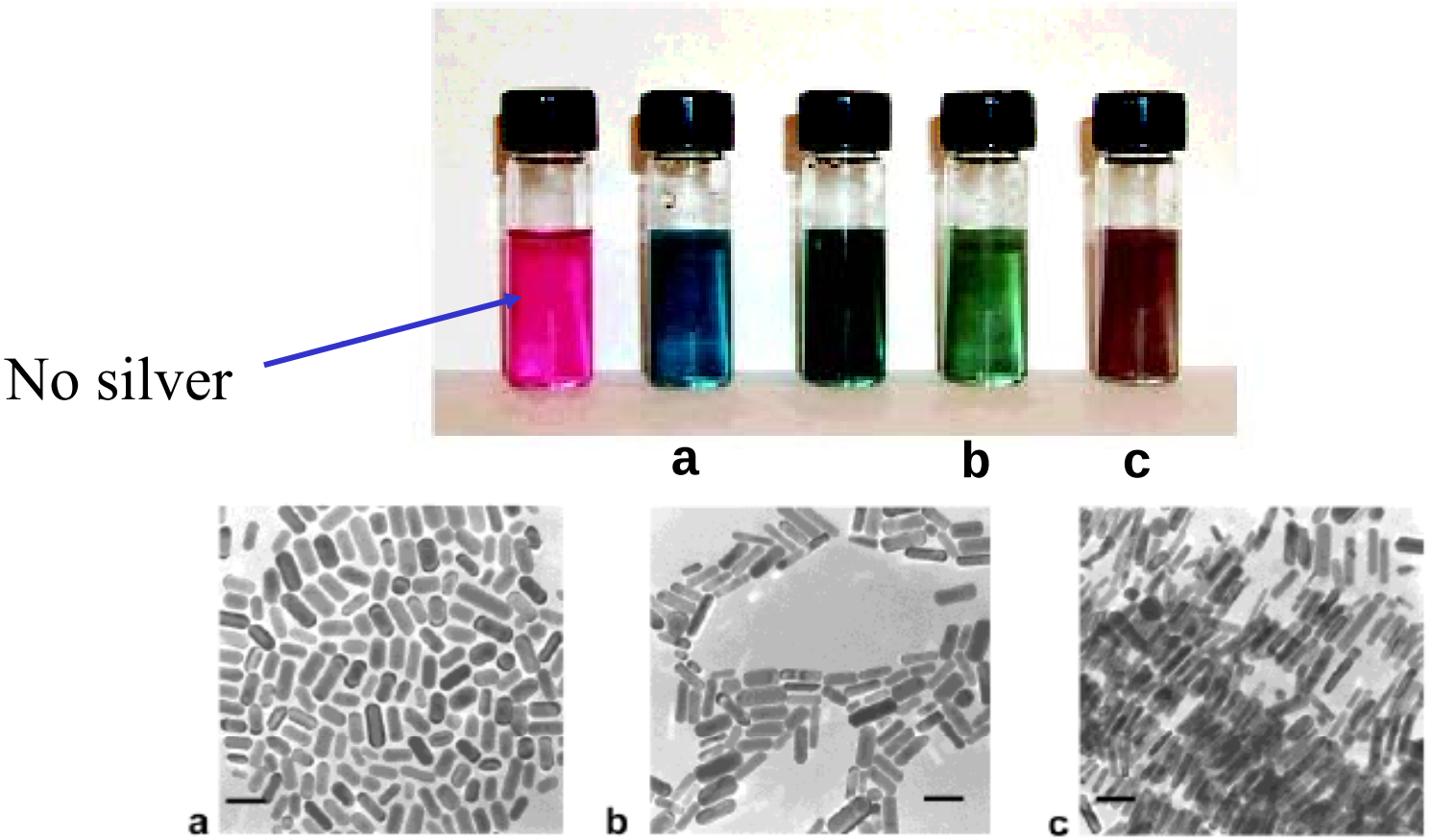
CdTe nanoparticles of different sizes assembled on polymer [PDDA - poly(diallyldimethylammonium chloride)] layers deposited in layer-by-layer fashion

(A. A. Mamedov, A. Belov, M. Giersig, N. N. Mamedova, N. A. Kotov *J. Am. Chem. Soc.* **2001,** *123,* 7738-7739)

The physics behind these colour changes



Gold nanorods :
Growth controlled by addition of silver



(F. Kim, J. H. Song, P. Yang, *J. Am. Chem. Soc.* **2002**, *124*, 14316)

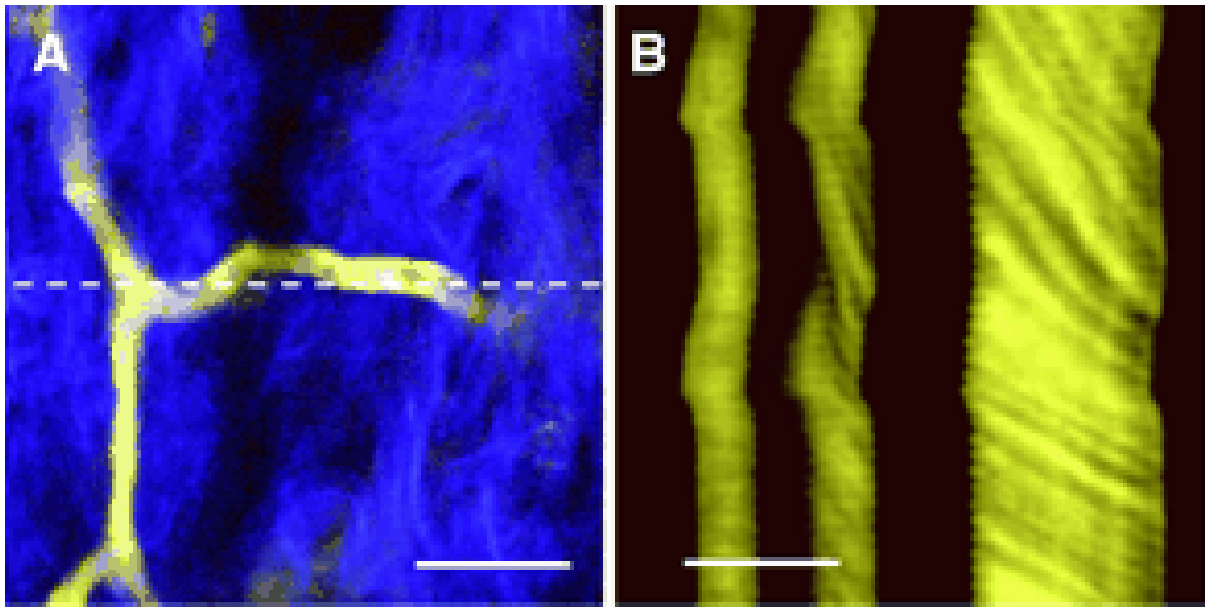
Two-photon induced fluorescence imaging using CdSe-ZnS quantum dots

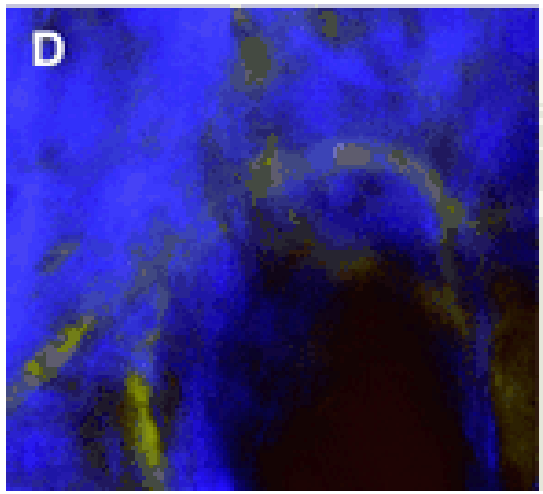
Rat vasculature injected with water solution of Quantum Dots

Excitation at 780 nm

TPF 550 nm

Larson et al, *Science* **2003**, *300*, 1434

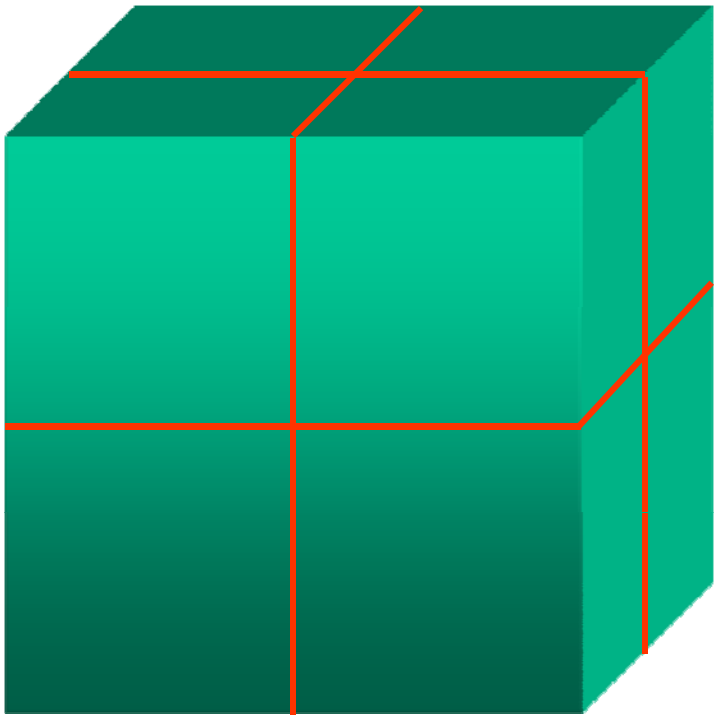




Using conventional fluorescent dyes

Surface Area

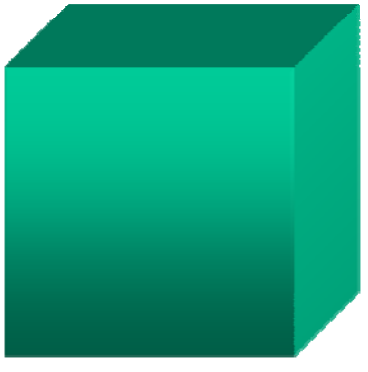
Surface area of 10 g of nanoparticles is equivalent to that of a cricket stadium



2 cm

Surface area = $6 \times 2^2 = 24$ cm^2

8



1 cm

Surface area of 1 cube = 6 cm^2

Surface area of 8 cubes = 48 cm^2

10^{21}

1 nm

Total surface area = 6×10^{21} nm^2

= 6×10^7 cm^2

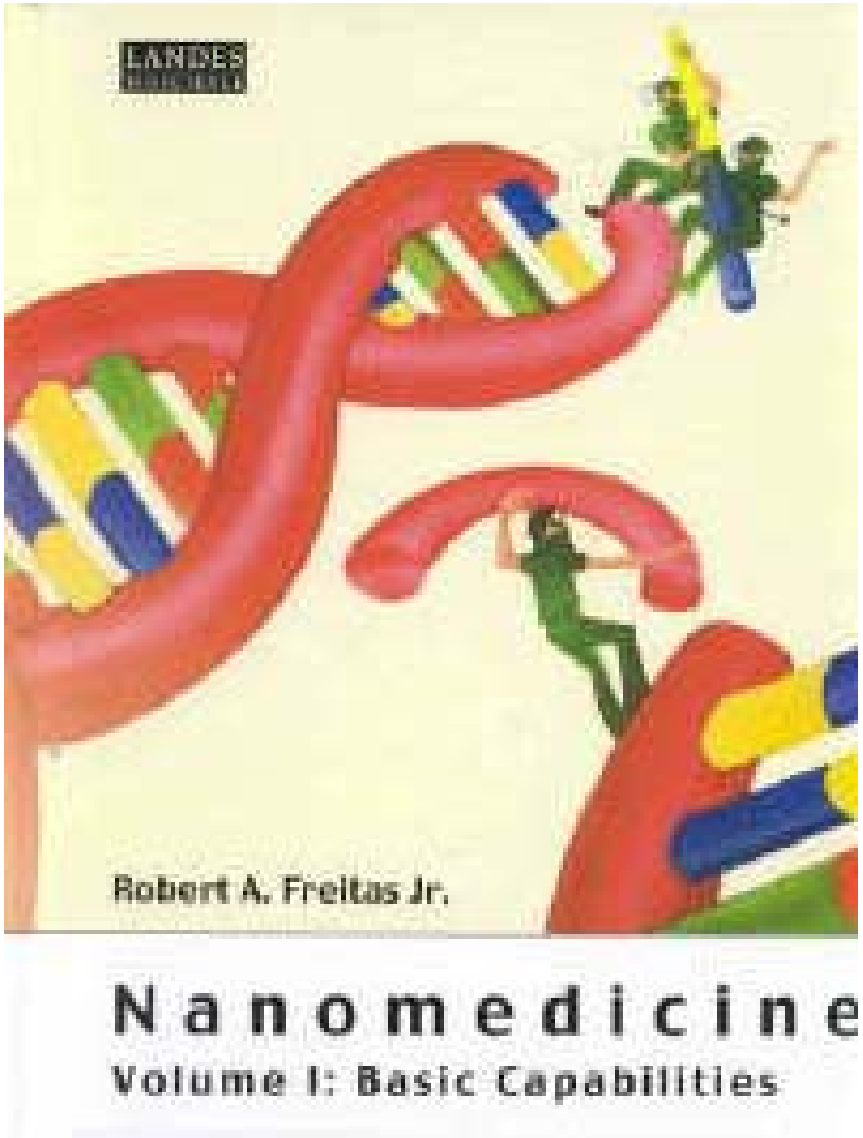
= 6000 m^2 = 1.5 acre

Increased surface area means more efficient chemical reactions when used as a catalyst

Micro-carnation ?

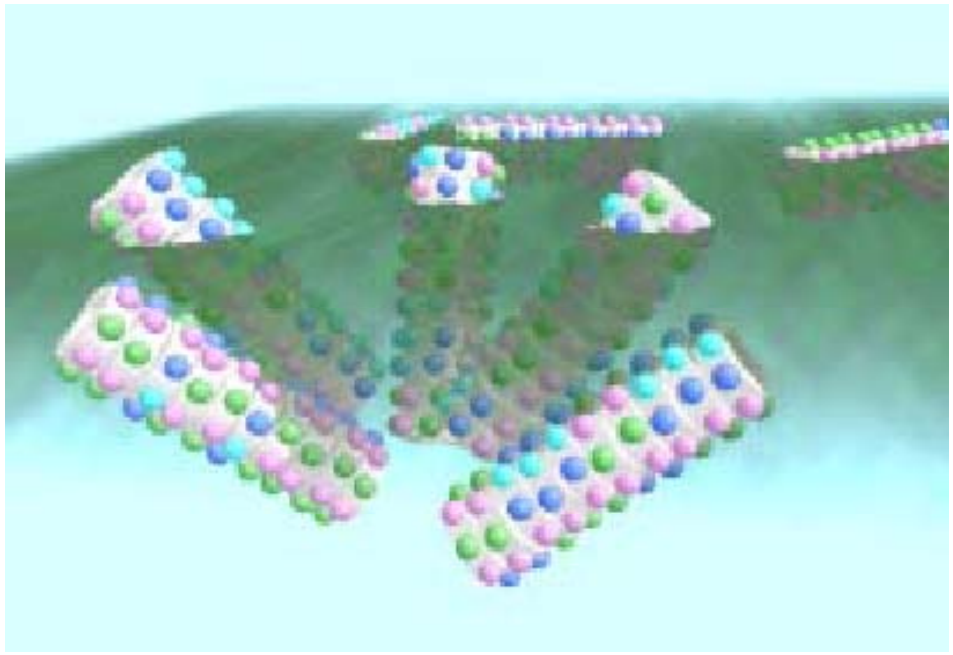
This 'micro-carnation' is actually a catalyst containing phosphorus and vanadium ($V(OH)PO_4.½H_2O$). It is a selective catalyst used in a natural gas purifying process (changing normal butane into maleic acid anhydride). The petal structure of the flower increases surface area and improves performance of the catalyst.

Cover picture of a book on nanomedicine



What is already possible ?

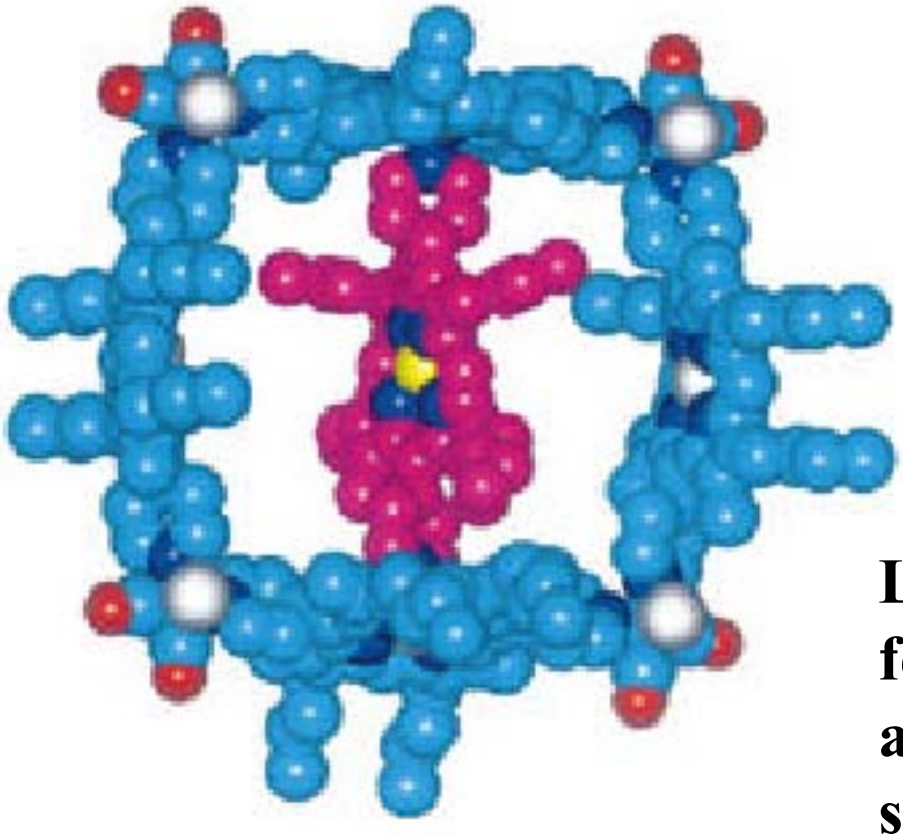
These for instance …



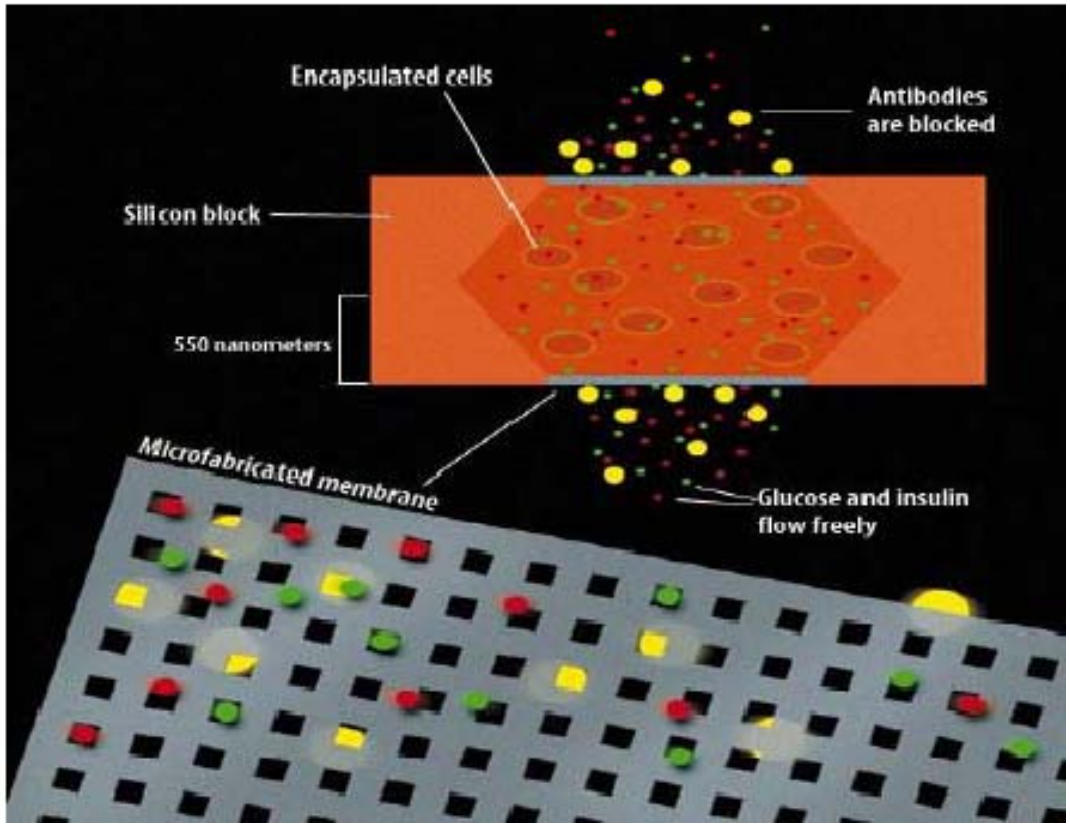
These polypeptide nanotubes are anti-bacterial ! They seem to assemble within the membrane of bacterial cells, forming a channel from inside to outside the cells. The bacteria become leaky and die within minutes.

(Art Olson, The Scripps Research Institute)

Molecular filters



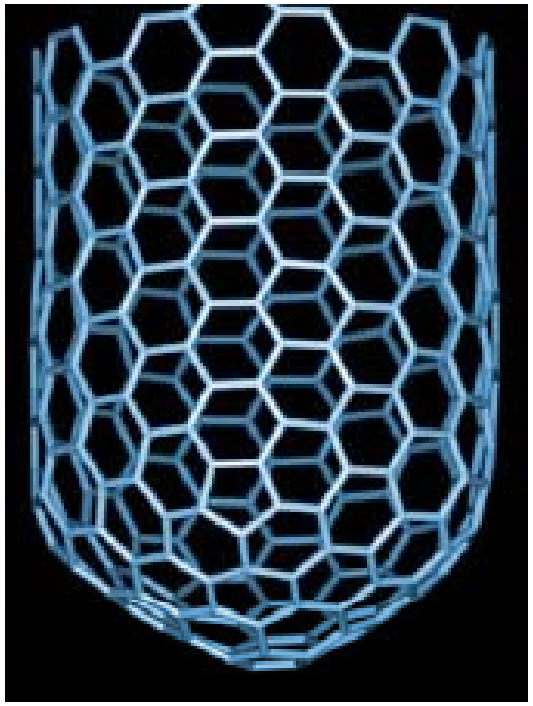
Large molecules are generally a few nanometers in size. They can act as very efficient filters selectively allowing the passage of some substances while blocking others. A network of these can act as a molecular filter and catalyst.

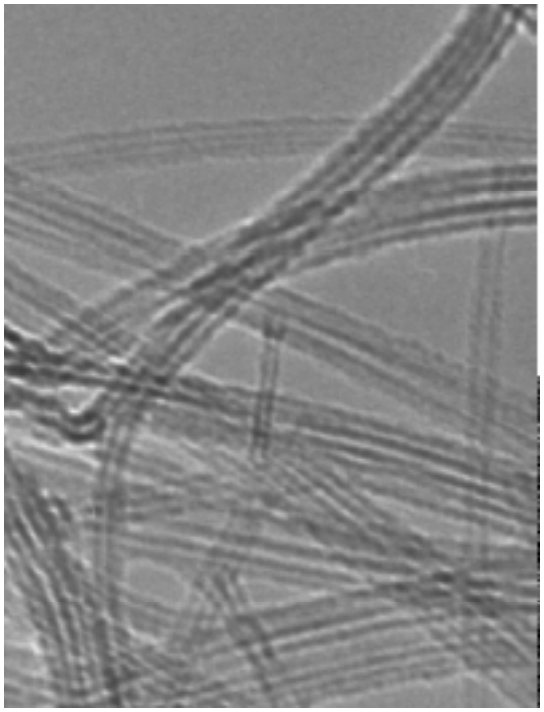


Even nano-sized pores are useful !

Transplanted pancreatic cells are shielded in a silicon block having pores so small that they allow glucose and insulin to flow through freely allowing normal metabolism, but are too small to allow antibodies to enter and attack the cells.

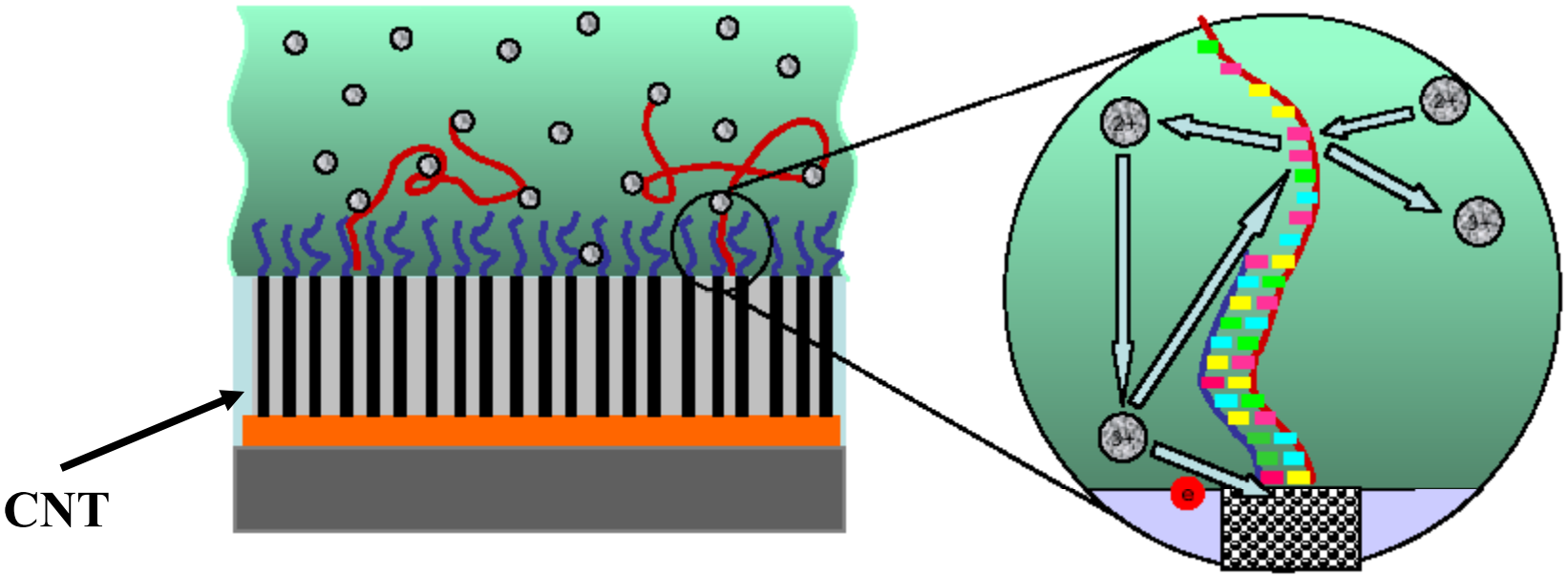
Carbon nanotubes - highly versatile nanomaterials





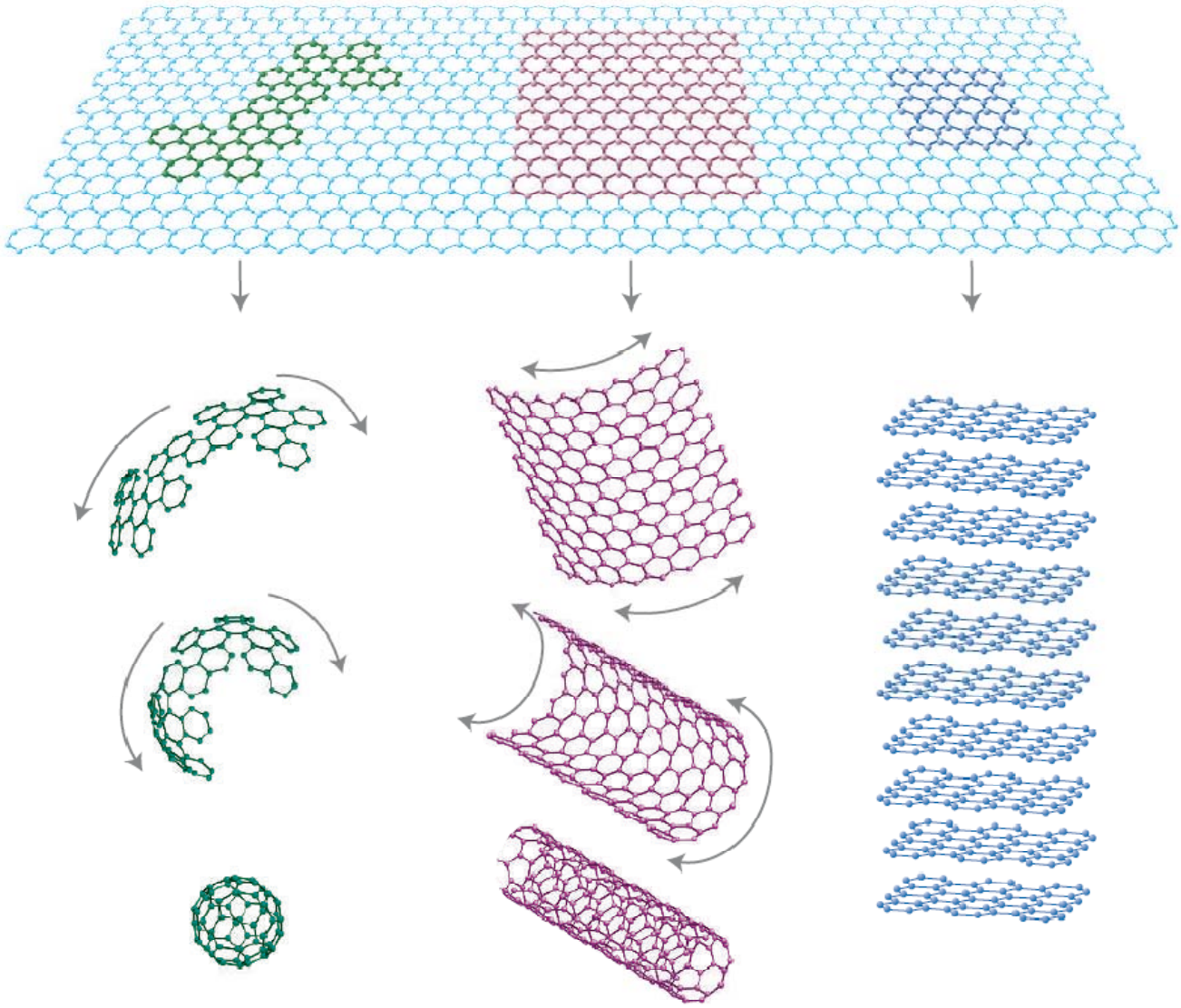
- The strongest and most flexible molecular material
- High thermal conductivity
- Very good electrical conductivity
- Can be metallic or semiconducting depending on structure
- Can be chemically modified

Carbon nanotube based DNA sensor

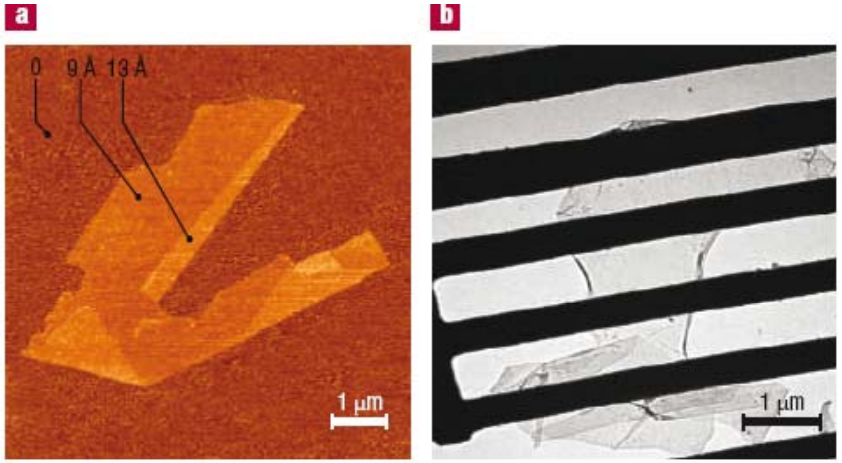


Carbon nanotube (CNT) array with attached DNA probe acts as an ultrasensitive sensor for detecting the hybridisation of target DNA from the sample using signals from the redox bases in the excess DNA single strands. The signal is amplified using metal ion mediators– oxidation of $[Ru(bpy)_3]^{2+}$ by guanine.

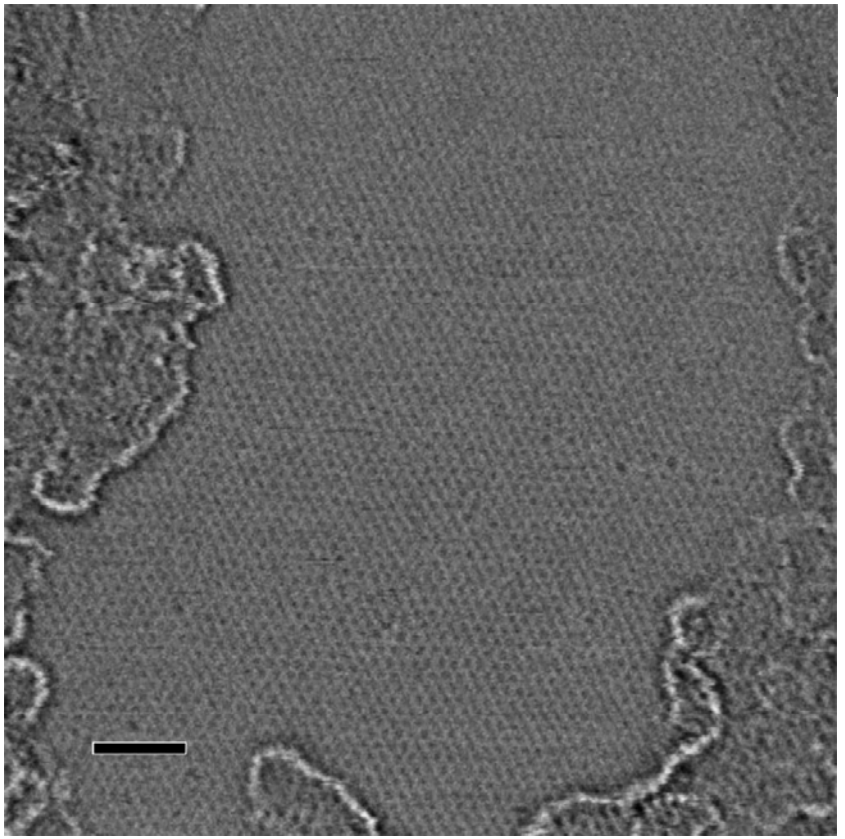
Graphene – the thinnest material you will ever see



(A. K. Geim, K. S. Novoselov, *Nature Mater.* **2007**, *6*, 183)



(**a: AFM, b: TEM:** Geim, Novoselov, *Nature Mater.* **2007**, *6*, 183)



(**STEM image of graphene**: Booth et al, *Nano Lett.* **2008**, *8*, 2442)

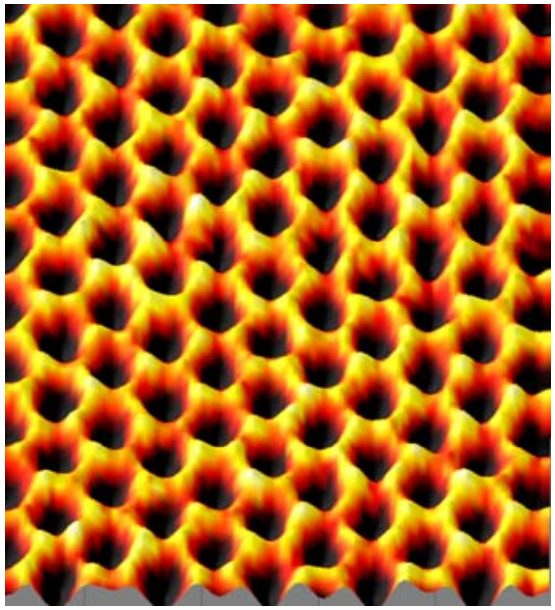
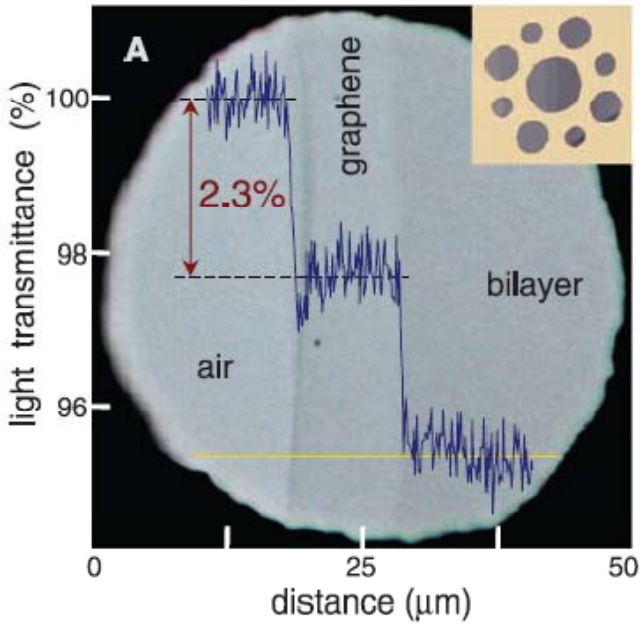


Image from TEAM 0.5 (Very high resolution TEM) http://newscenter.lbl.gov/wp-content/uploads/team-05-graphene.jpg



Optical absorption = $\pi\alpha$

$\alpha = e^2/\hbar c$

(Nair et al, *Science* **2008**, *320*, 1308)

Very large electron mobility

Very high mechanical strength

Potential applications in:

Efficient gas sensor

Transparent electrode

FET & Integrated circuits

Nanotechnology and Industry

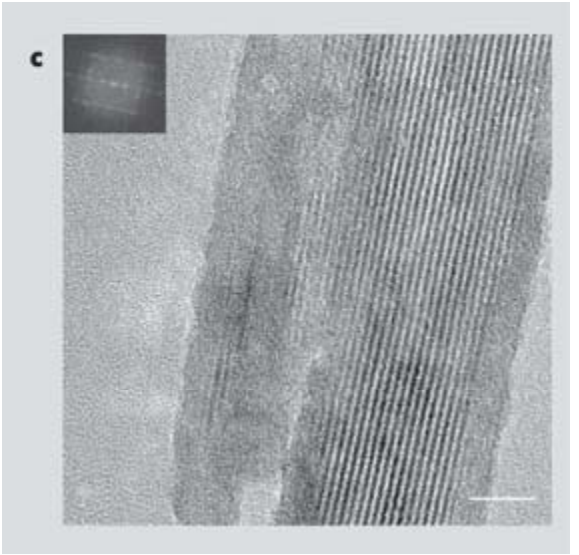
- Computing, data storage and communication
- Materials
- Manufacturing industry
- Health & medicine
- Energy & environment
- Transportation & space exploration

From the Ancient …..

Gothic cathedral windows:
gold nanoparticles

Tipu's sword

Wootz steel containing Carbon nanotubes



Scale bar = 10 nm

Reibold et al, *Nature* **2006**, *444*, 286

Lycurgus chalice – 5th century AD

Illuminated from outside

Illuminated from inside

Contains silver and gold nanoparticles (~ 70 nm) in 14:1 ratio

Colour due to polarization dependence of reflected/transmitted light

To the modern …..

Spill and dirt-resistant fabrics

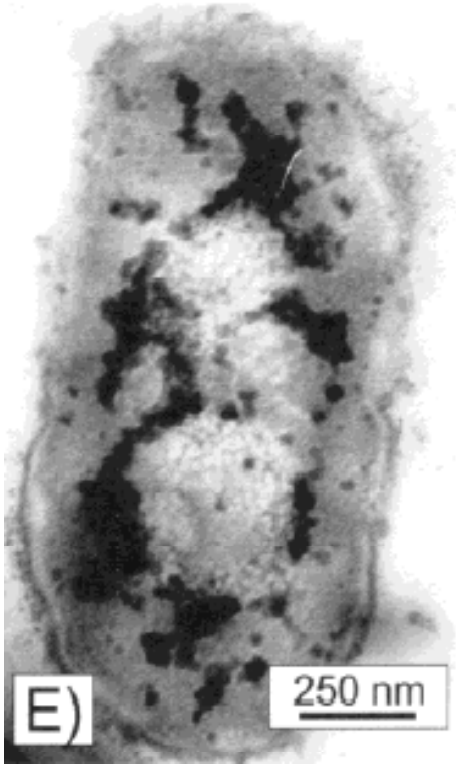
Grape juice on a polo shirt !

Tiny “whiskers” aligned by proprietary “spines,” are designed to repel liquids and are attached to the fibers utilizing molecular “hooks”. These “whiskers” and “hooks” are no more than 1/1000th the size of a cotton fiber.

(Courtsey : www.nano-tex.com)

Antibacterial Magnesium Oxide Nanoparticles

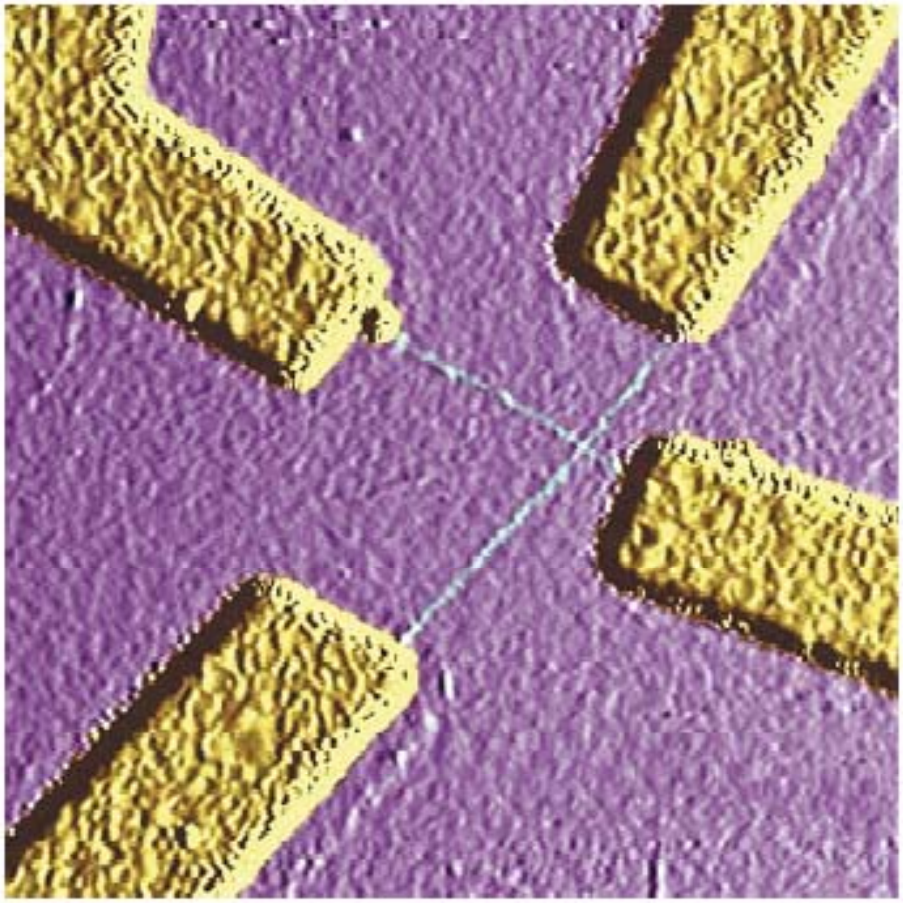
***E. coli* bacteria not treated**



***E. coli* treated with MgO nanoparticles (aerogel MgO with adsorbed Cl_2)**

Klabunde *et al*, *Langmuir* **2002,** *18*, 6679

Nanoscale electronics



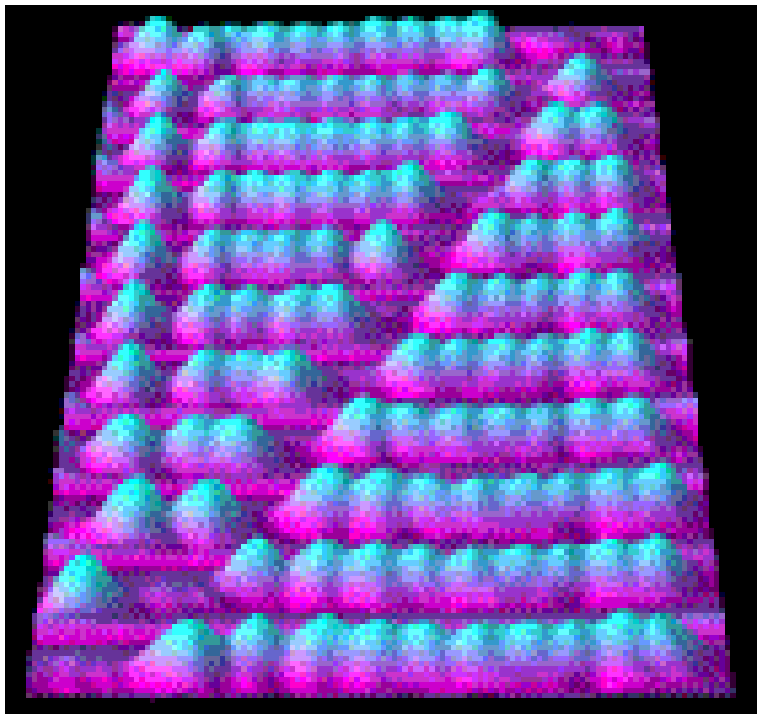
Carbon nanotubes (the thin blue lines) connected to gold contacts forming molecular wires !

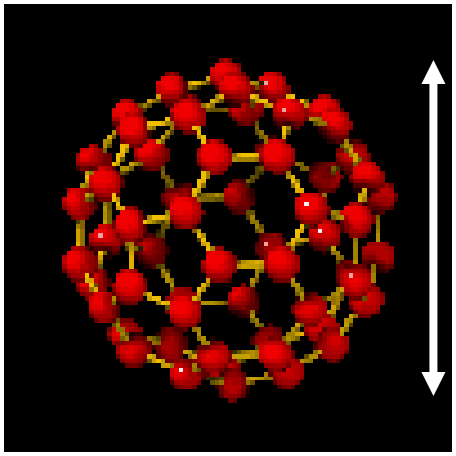
(Courtsey : Nanoscale Science, Engineering, and Technology in the Office of Basic Energy Sciences (BES) of the U.S. Department of Energy (DOE))

Space Elevator

The Amazing Nanoworld

World's Smallest Abacus

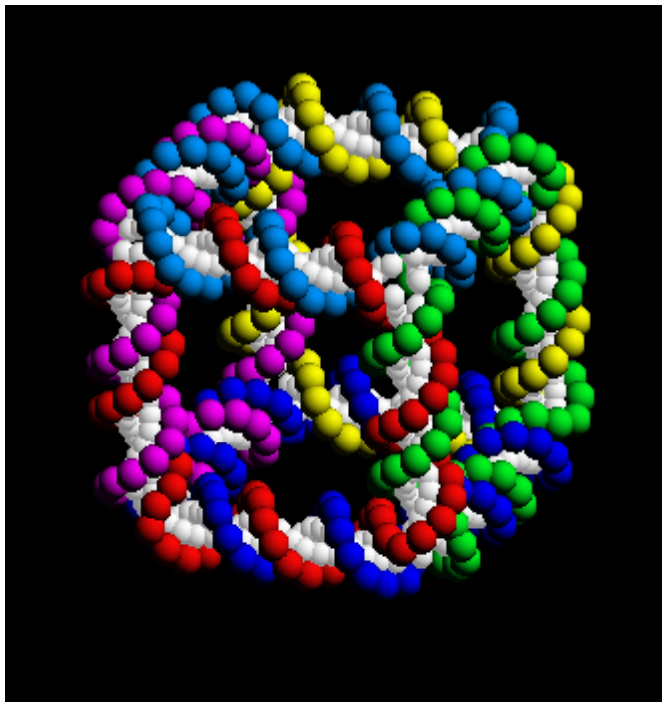




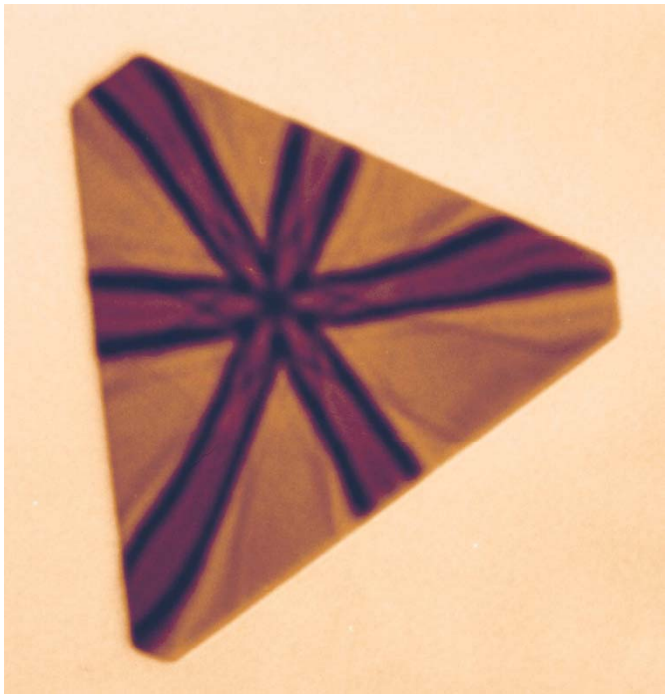
Built with individual molecules of C_{60} as beads with a diameter of less than 1 nm, arranged on steps patterned on copper surface. They are arranged and moved around using a scanning tunnelling microscope tip.

(*Applied Physics Letters*, **1996**, *69*, 3016)

Small has always been beautiful !



DNA Cube
(chemical synthesis)



Gold nano-triangle
with stress patterns

Thank you