Nanoscience and Nanotechnology: Introduction, Synthesis and Applications

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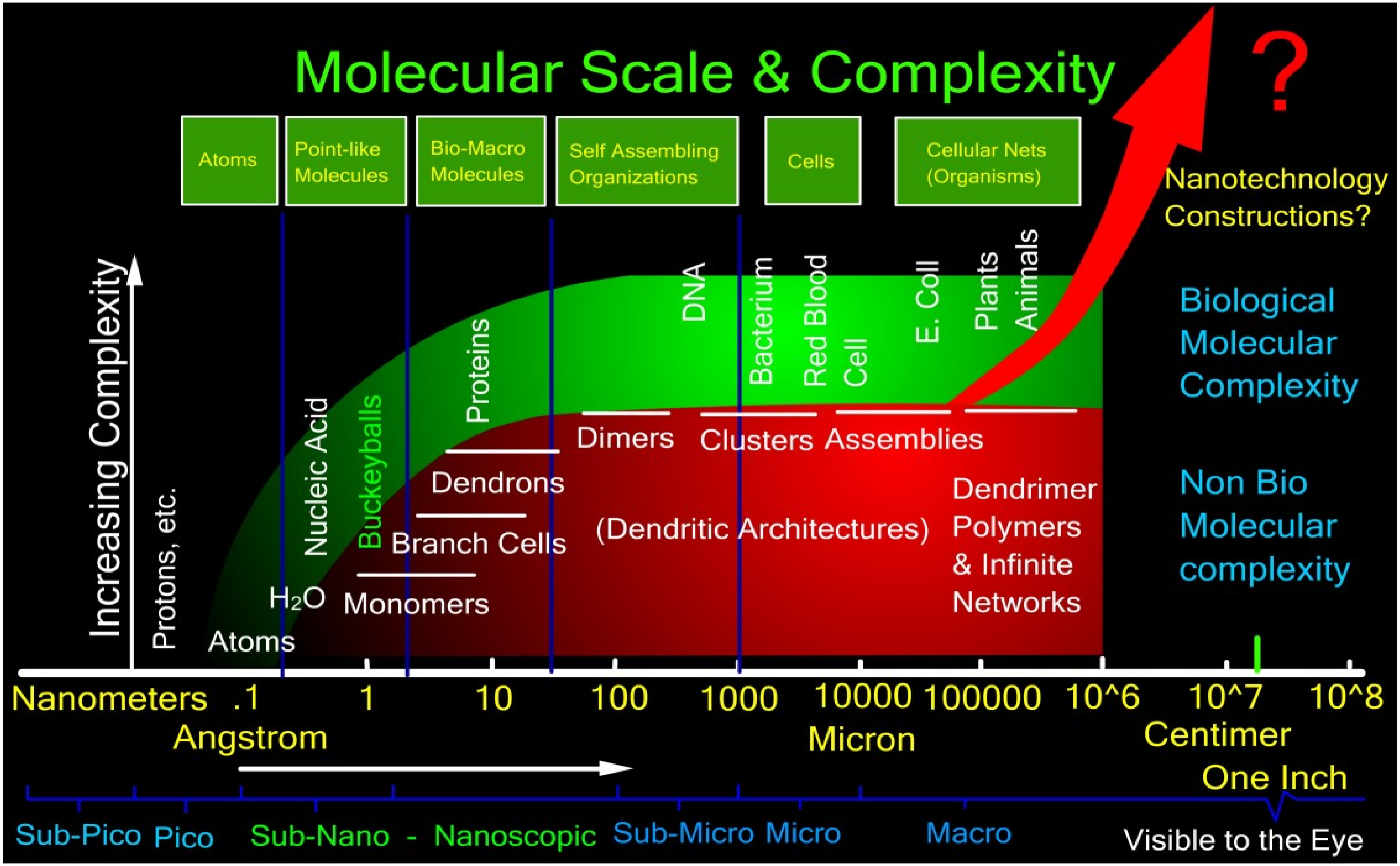
Department of Chemistry



"Bottom-up"

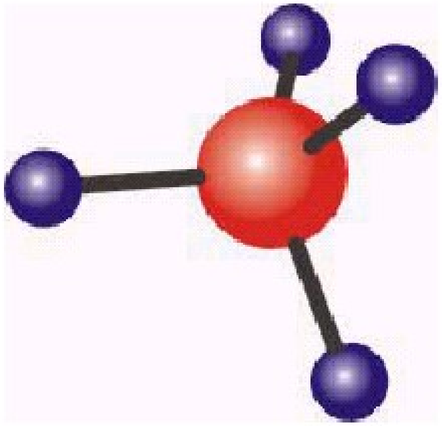
"Top-down"

0 . 000 000 001 metre

- One **nanometer** is thus one billionth of metre (or one millionth of millimetre, etc.). It can be expressed as 10^{-9} metres and shortened to ***nm***.

  The radius of one atom of **gold** is 0.14 nm.

-



- Half a nanometre is the linear dimension of a small molecule like **methane** (CH_4). One human ***hair*** is around 100 thousand times bigger.

HISTORY

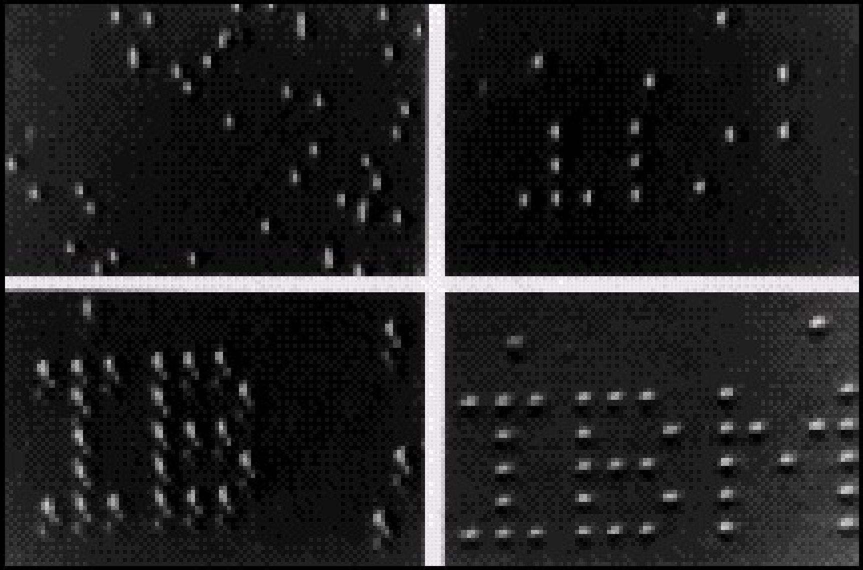
- 1959 -FEYNMAN – APS MEETING
- 1974 -NORIO TANIGUCHI (Tokyo Sci. Univ)
- 1980- ERIC DREXLER – Mechano-synthesis
- 1981 – BINNIG & ROHRER – STM
- 1985 – C60
- 1986 – AFM; 1989-WRITING WITH ATOMS
- 1991 – CNT; 1998 – ALIGNED CNT
- 1999 – MOLECULAR LOGIC GATE
- 2002 – CNT TRANSISTOR; DPN
- 2004 – SINGLE ELECTRON DEVICES; GRAPHENE

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

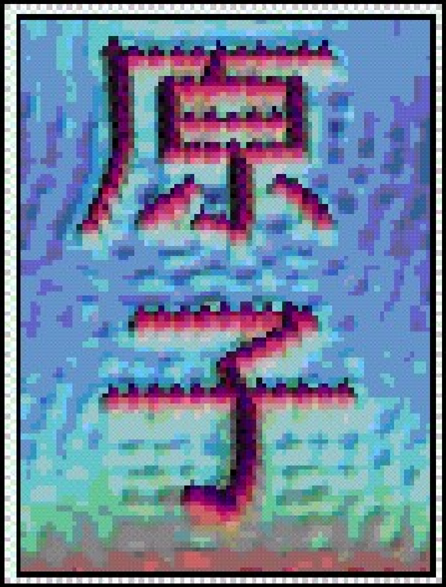
As soon as I mention this, people tell me about miniaturization, and how far it has progressed today. They tell me about electric motors that are the size of the nail on your small finger. And there is a device on the market, they tell me, by which you can write the Lord's Prayer on the head of a pin. But that's nothing; that's the most primitive, halting step in the direction I intend to discuss. It's a staggeringly 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……

Prof. Richard Feynman in "There's plenty of room at the bottom", lecture delivered at the annual meeting of the APS, Caltech, 29 December, 1959.

Nanostructures, atom-by-atom



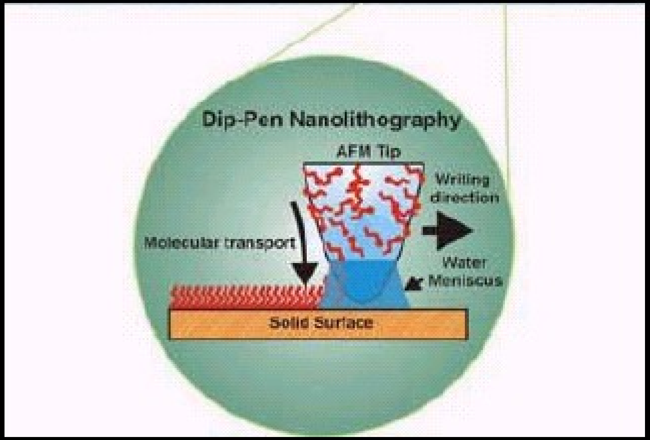
STM writing of “IBM” with Xe atoms on Ni (110) surface [Eigler and Schweizer, Nature **344**, 524 (1990)].



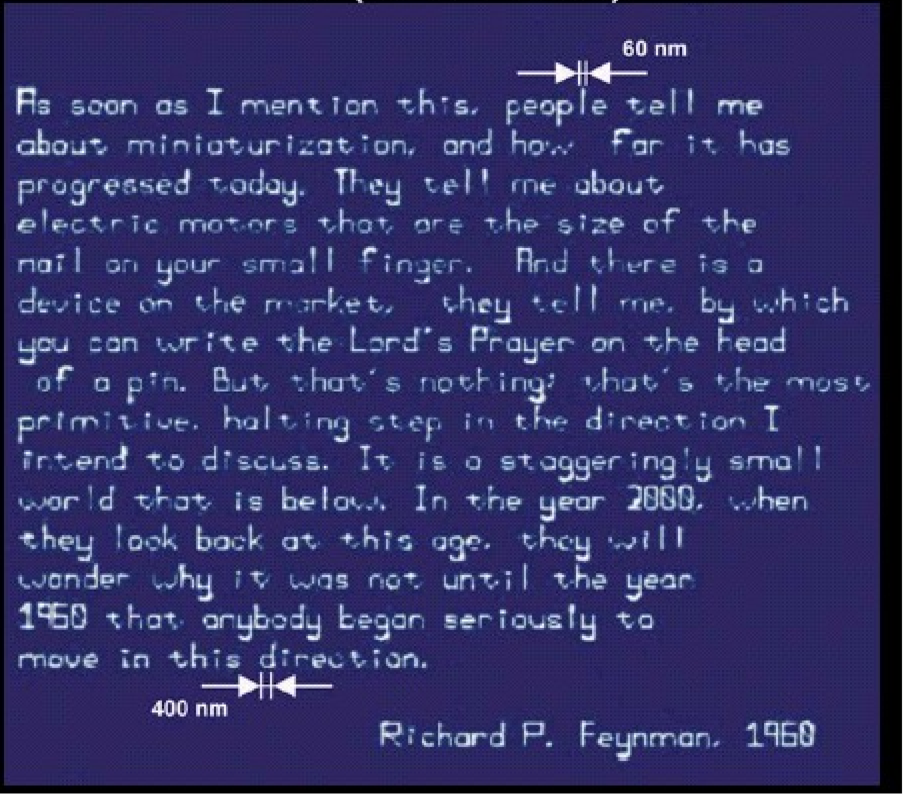
Writing with atoms : “atom” in Japanese

Nanoscale writing

Nanoscale writing with an STM



Nanoscale writing with an AFM (Mirkin et al.)



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Richard P. Feynman, 1960

NANOTECHNOLOGY AND OUR ENVIRONMENT

- **Ultrasmall sensors and sensor arrays for environmental monitoring , with very low mass, volume and power consumption**

- **Revolutionary Energy generation capability with out environmental contamination that allow reconfigurable, autonomous, "thinking" batteries and fuel cells**

- **Nanotechnology presents a whole new spectrum of opportunities to alleviate environmental problems**
- **Branson’s offer**

SYNTHETIC TREES: 1000 times more

CO_2 absorbing capability

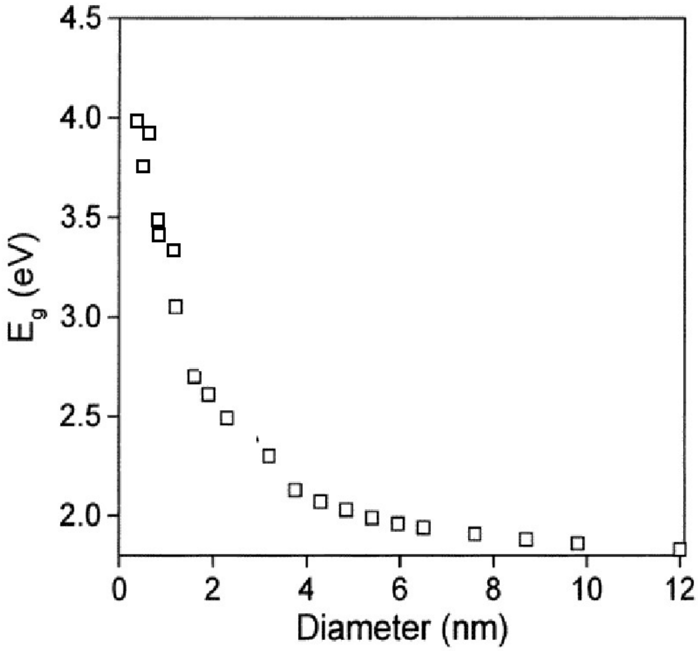
A prototype hydrogen powered vehicle from BMW refuels

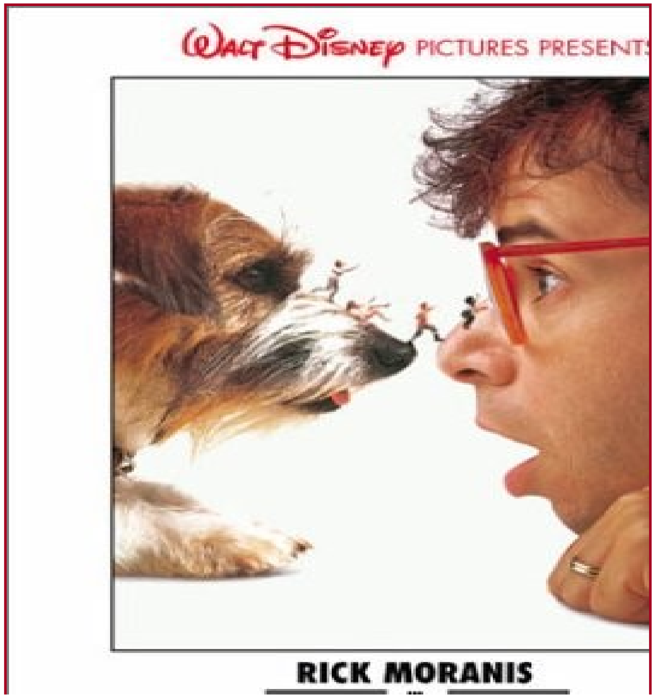
Global temperature rise

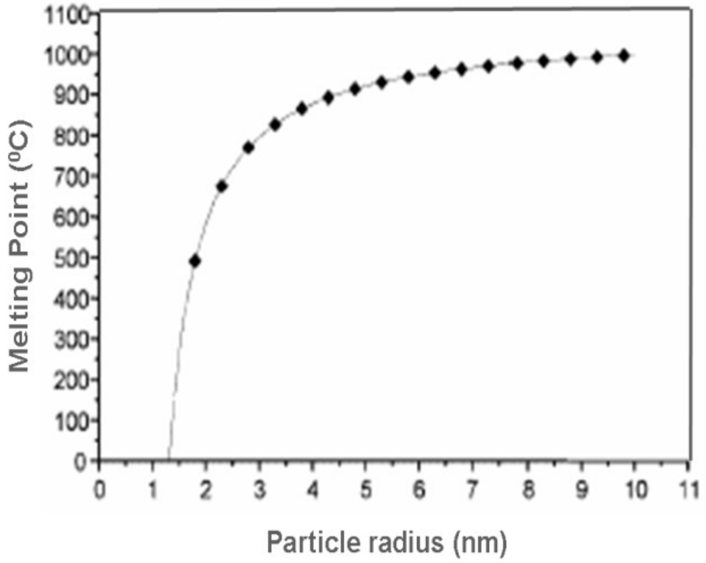
SIZE MATTERS A LOT!

- PROPERTIES DIFFERENT FROM THAT OF BULK
- SCALING UP OR DOWN WITH SIZE - CONVERGENCE
- ILLUSTRATIVE EXAMPLES FOR SIZE AND SHAPE DEPENDANT PROPERTIES

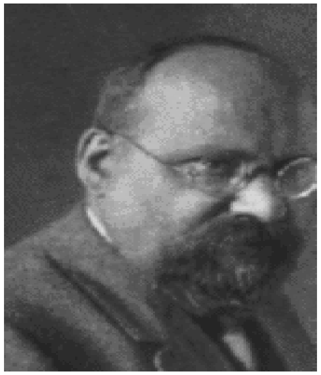
(e.g., melting point of Au/Ag, band gap of semiconductor-band gap engineering)



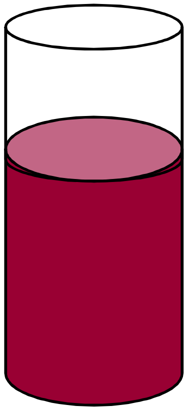




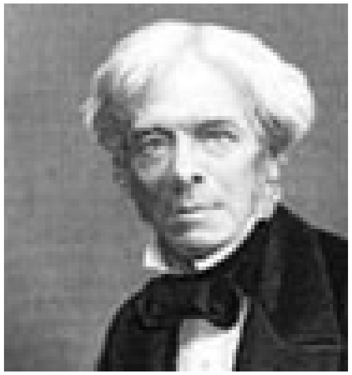
Optical Properties of Metal Clusters:
The Mie Theory


Gustav Mie

1908

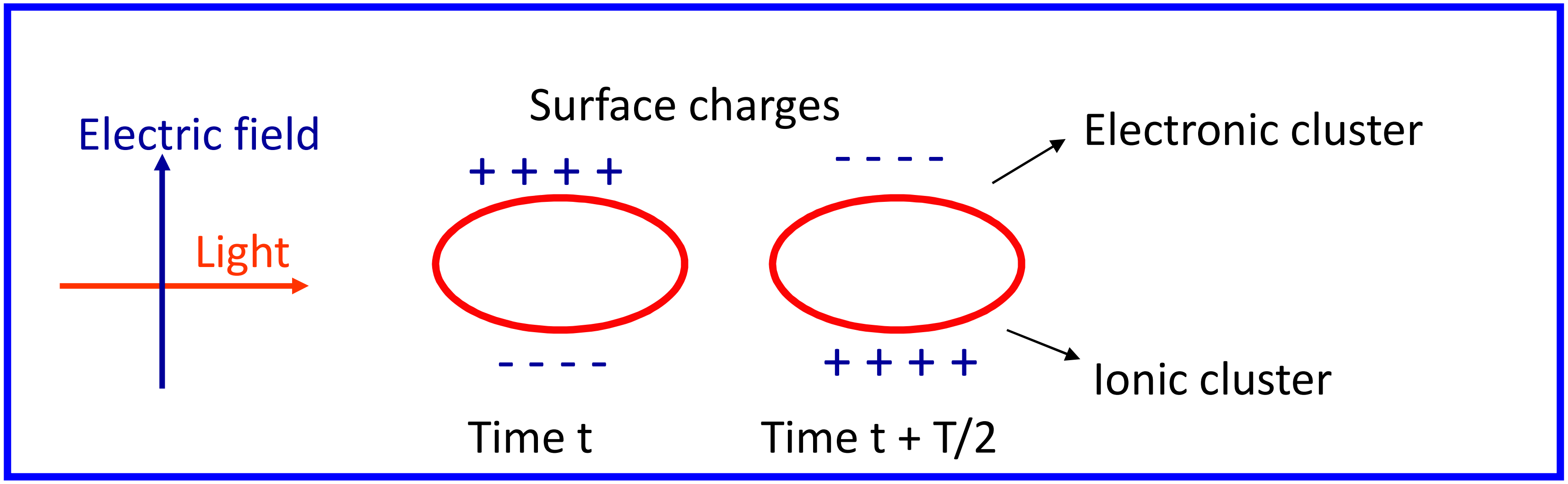

Royal Society of Chemistry, London

1857


Michael Faraday

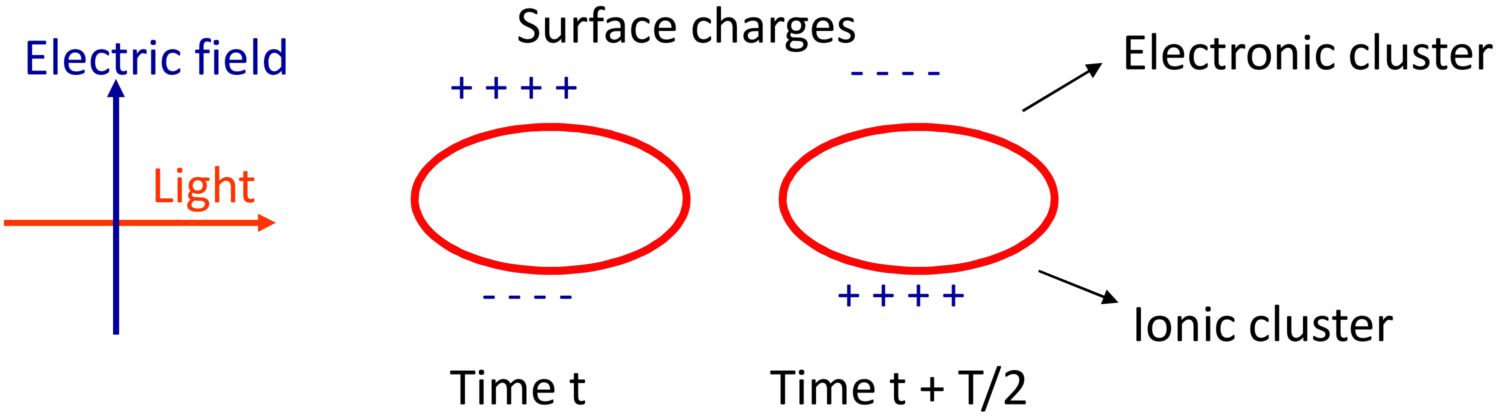
Creation of Surface Plasmon

Size Effect



M. A. El-Sayed et al. *Int. Reviews in Physical Chemistry* **2000**, *19*, 409.

Surface plasmon resonance



Electric field

Light

Surface charges

\+ + + +

\- - - -

\- - - -

\+ + + +

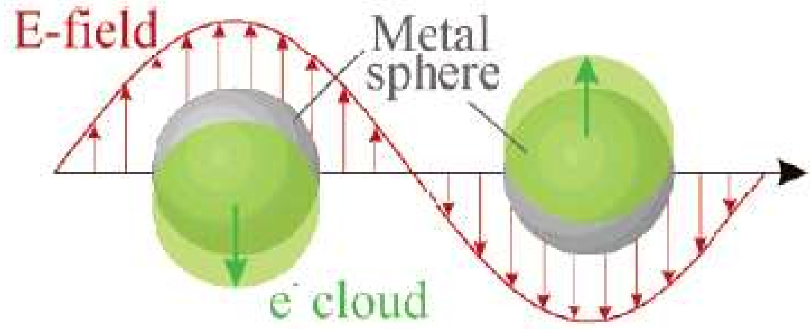
Electronic cluster

Ionic cluster

Time t

Time t + T/2

- A surface Plasmon is generated when the size of the metal is smaller than the wavelength of incident radiation.
- An electric field of an incoming light induces a polarization of the free electrons relative to the cationic lattice.
- The net charge difference occurs at the nanoparticle surface which in turn acts as a restoring force.
- This creates a dipolar oscillation of electrons with a certain frequency.
- The surface Plasmon resonance is therefore a dipolar oscillation of electrons.

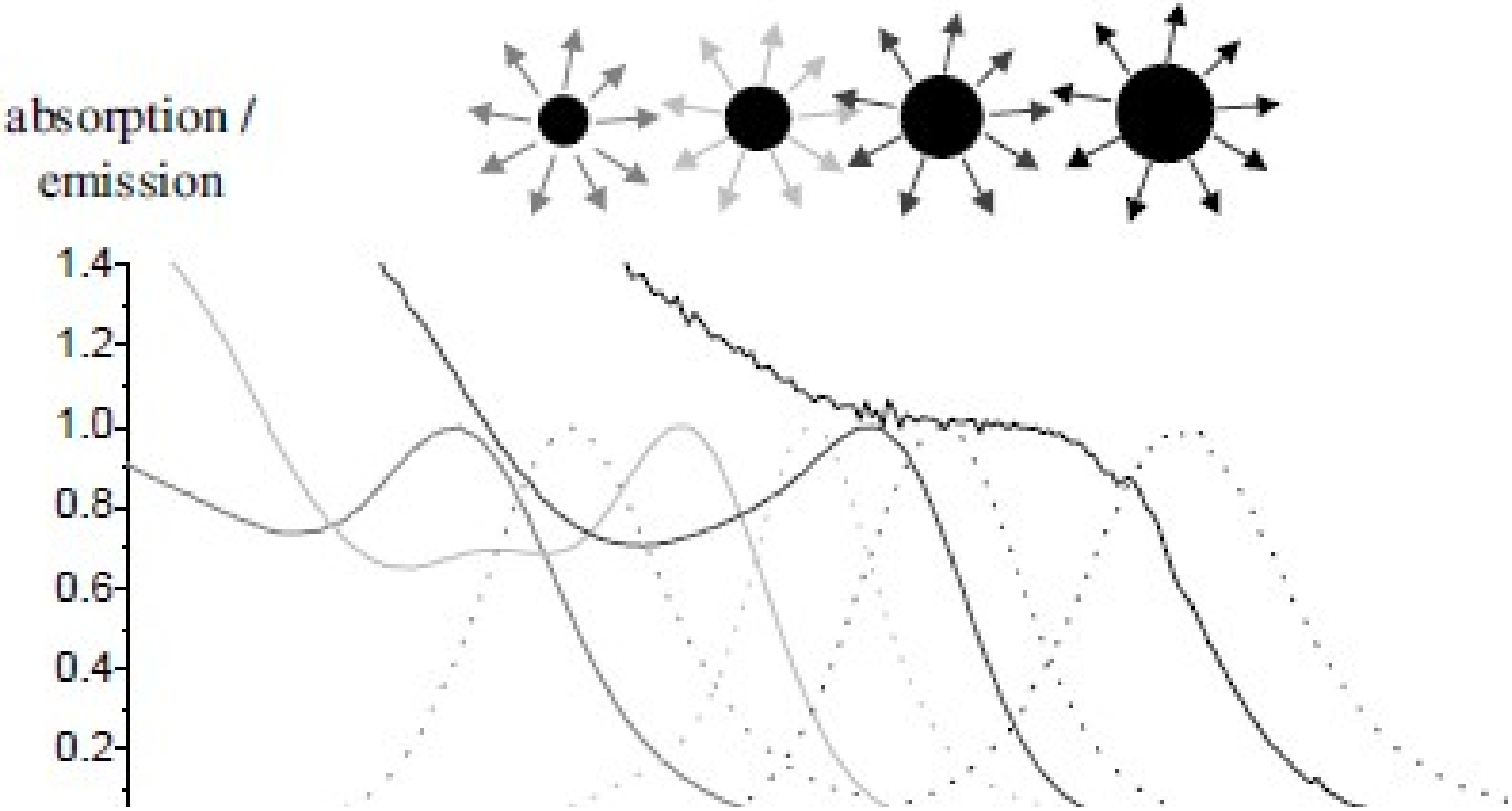


Kelly et al. *J. Phys. Chem. B* **2003**, *107*, 668.

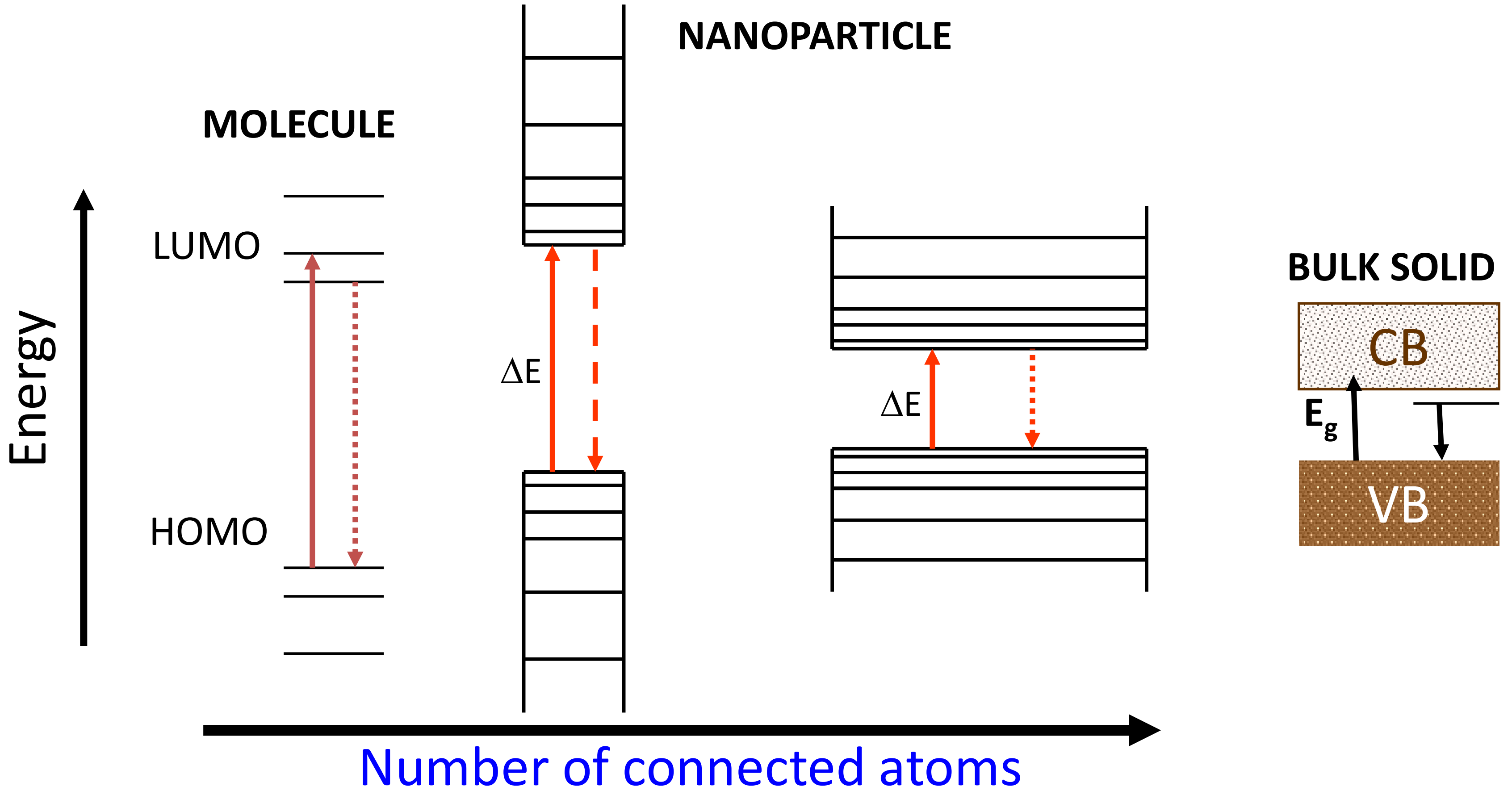
- Interaction of incoming light with nanoparticles results into collective oscillation of surface free electrons with respect to the nanoparticle lattice

- Frequency changes with size, shape, local and surrounding dielectric medium, inter-particle coupling interaction

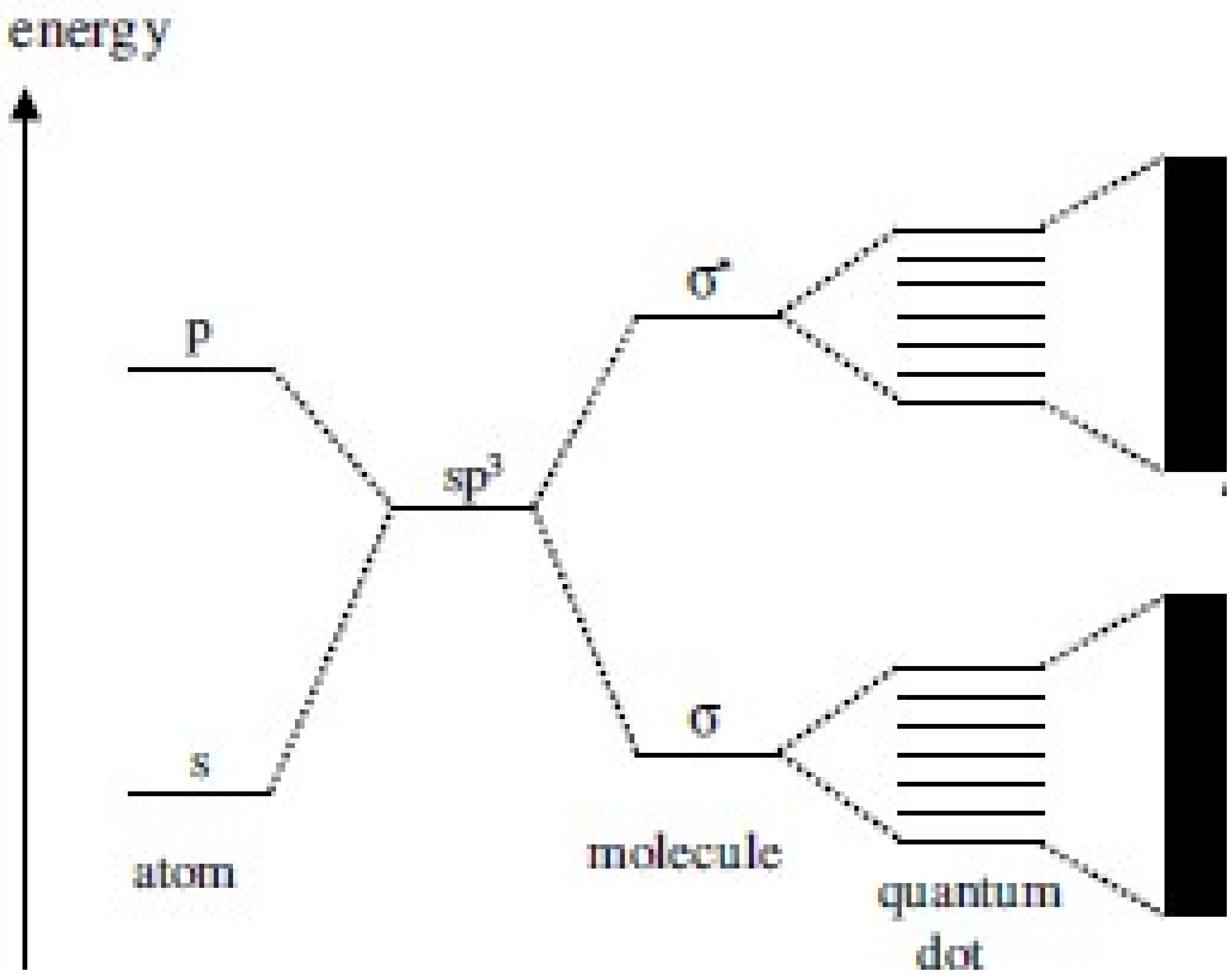
Wavelength (nm)	Absorbed Color	Complementar
650-780	red	blue-gre
595-650	orange	greenish
560-595	yellow-green	purpl
500-560	green	red-pur
490-500	bluish green	red
480-490	greenish blue	orang
435-480	blue	yello
380-435	violet	yellow-g


absorption / emission
1.4
1.2
1.0
0.8
0.6
0.4
0.2

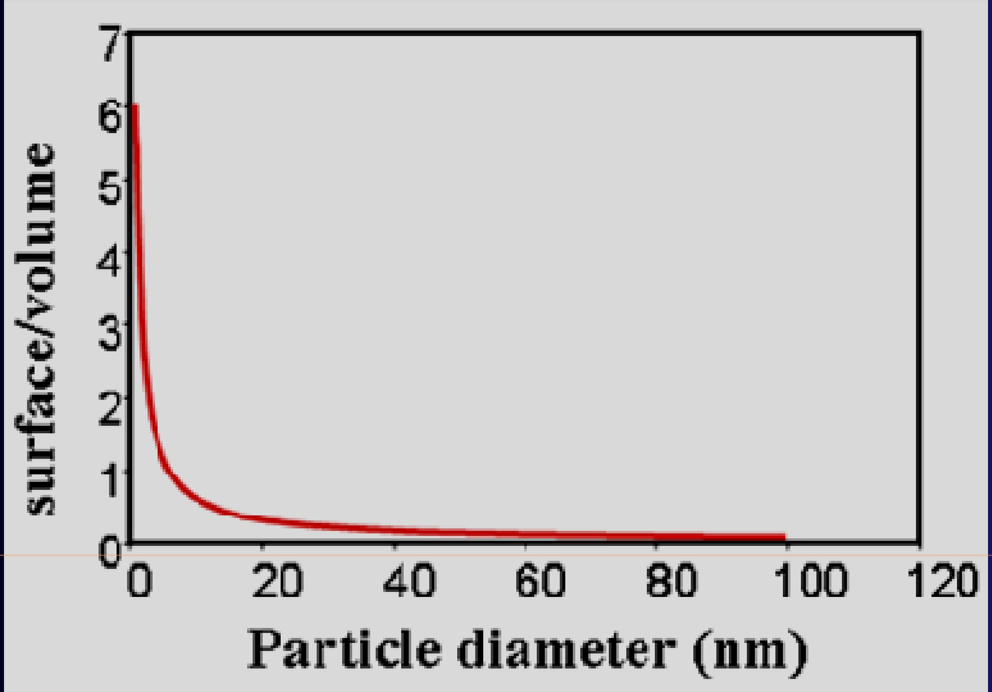
Energy Diagrams: Nanoparticle Intermediate of Molecules and Bulk Solids



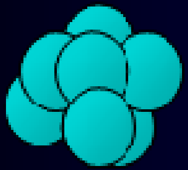
Self Assembly of number atoms or molecules together, the discrete energy levels of atomic orbitals merge into energy bands


energy
p
s
sp^3
σ^*
σ
atom
molecule
quantum
dot

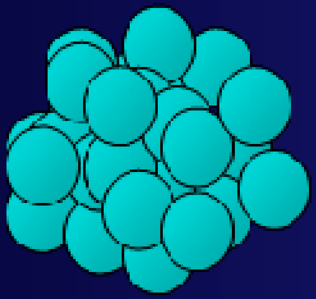
Surface/volume ratio increases upon decreasing gold nanosize



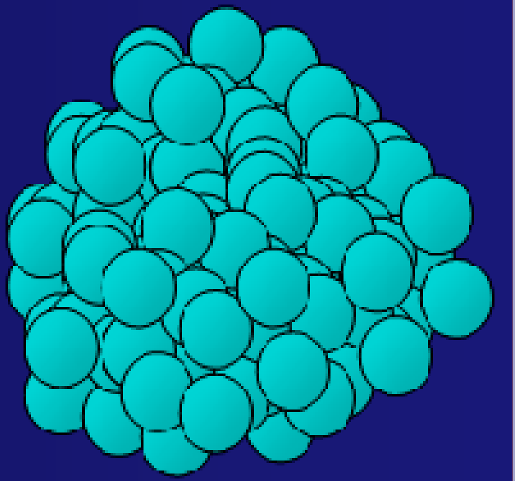
Proportion of surface atoms increases



3 nm
50 % atoms
on the surface



10 nm
30 %



30 nm
5 %

Influence of Particle size and Nucleophile on Electrode Potential

Variation of Nucleophiles

Ag^+(1 ion) + e = Ag (atom) E^0 = -1.80 V

Ag_2S + 2e = Ag + S^{2-} E^0 = -0.69 V

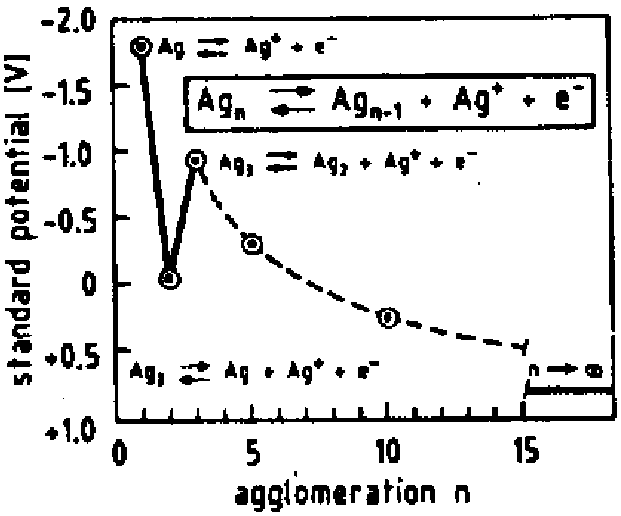
AgCN + e = Ag + CN^- E^0 = -0.31 V

AgI + e = Ag + I^- E^0 = -0.15V

AgBr + e = Ag + Br^- E^0 = +0.09 V

AgCl + e = Ag + Cl^- E^0 = +0.22 V

Ag^+_{aq} + e = Ag E^0 = +0.79 V



Particle size

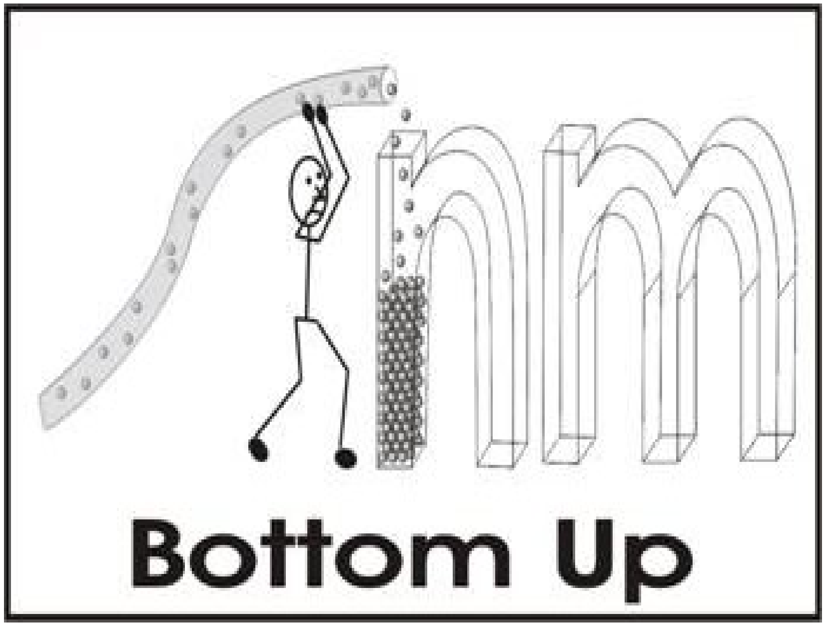
$E^0\,[Ag^+ / Ag_1] = -1.8$ V

$E^0\,[Ag^+_5 / Ag_5] = -0.4$ V

$E^0\,[Ag^+_{11} / Ag_{11}] = -0.17$ V

J. Phys. Chem. **1993**, *97*, 5457.

TWO APPROACHES



How to Fabricate Nanostructures

Top-down method

Bottom-up method

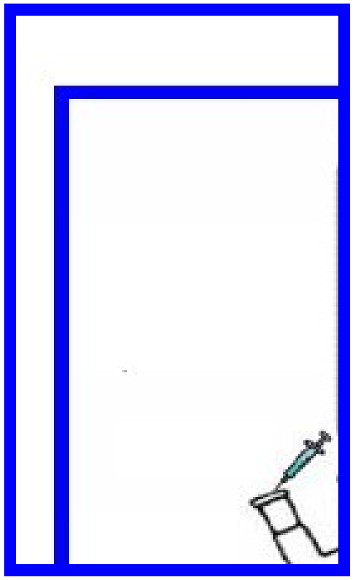
Nanostructures from macrostructures

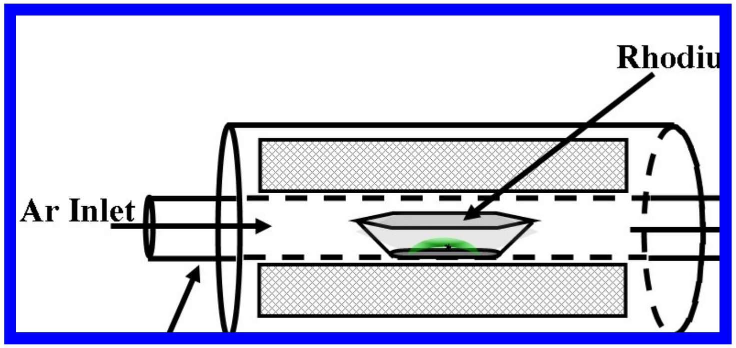
Self assembly of atoms or molecules-nanostructures

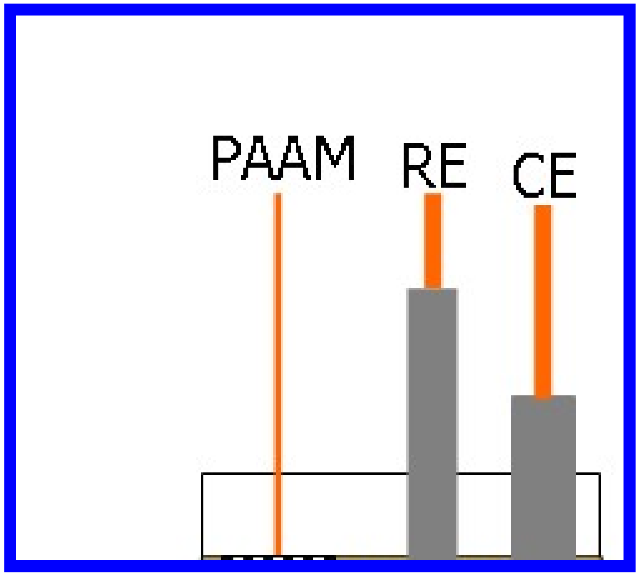
Chemical

Chemical Vapour Deposition

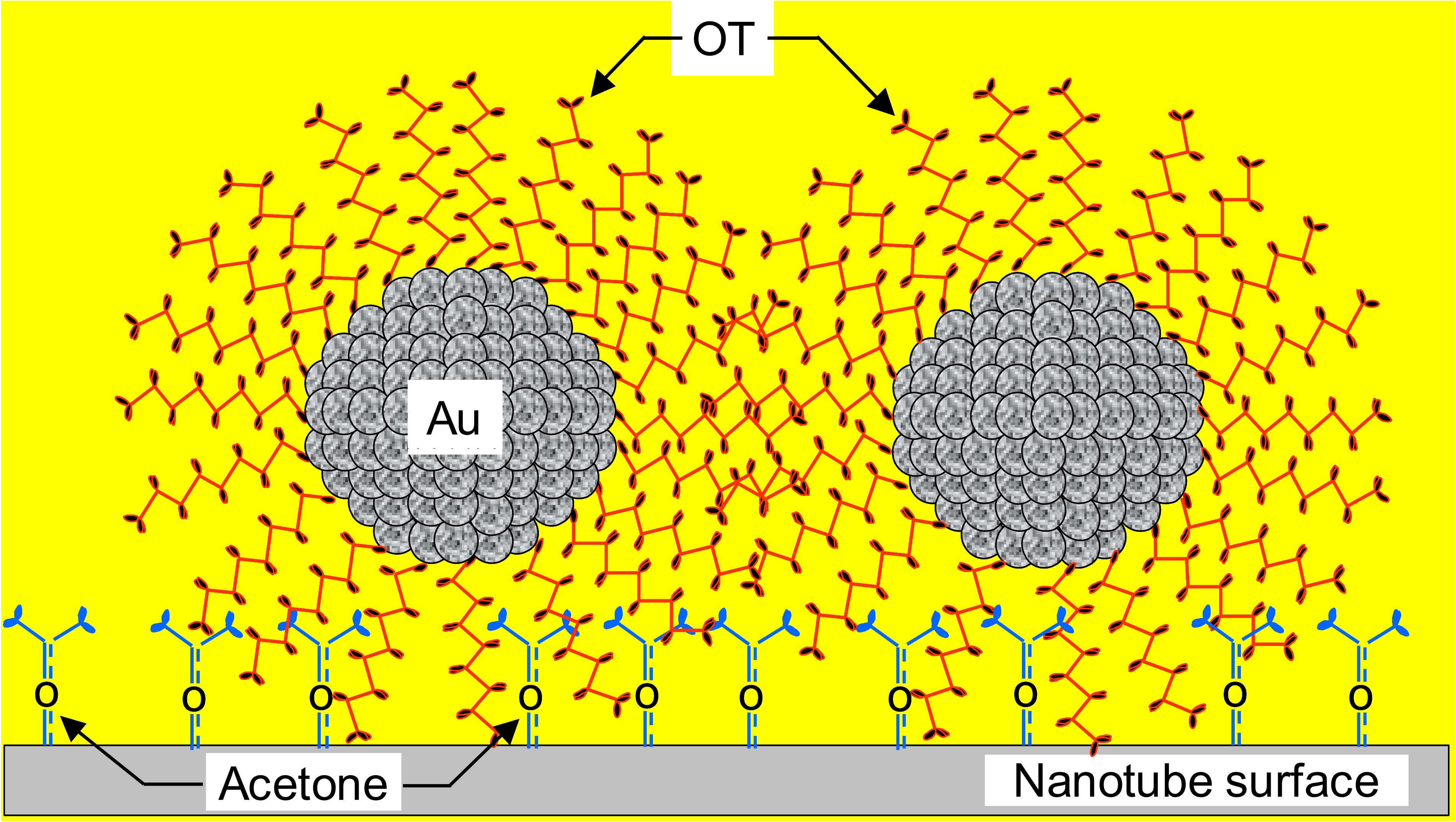
Electrochemical



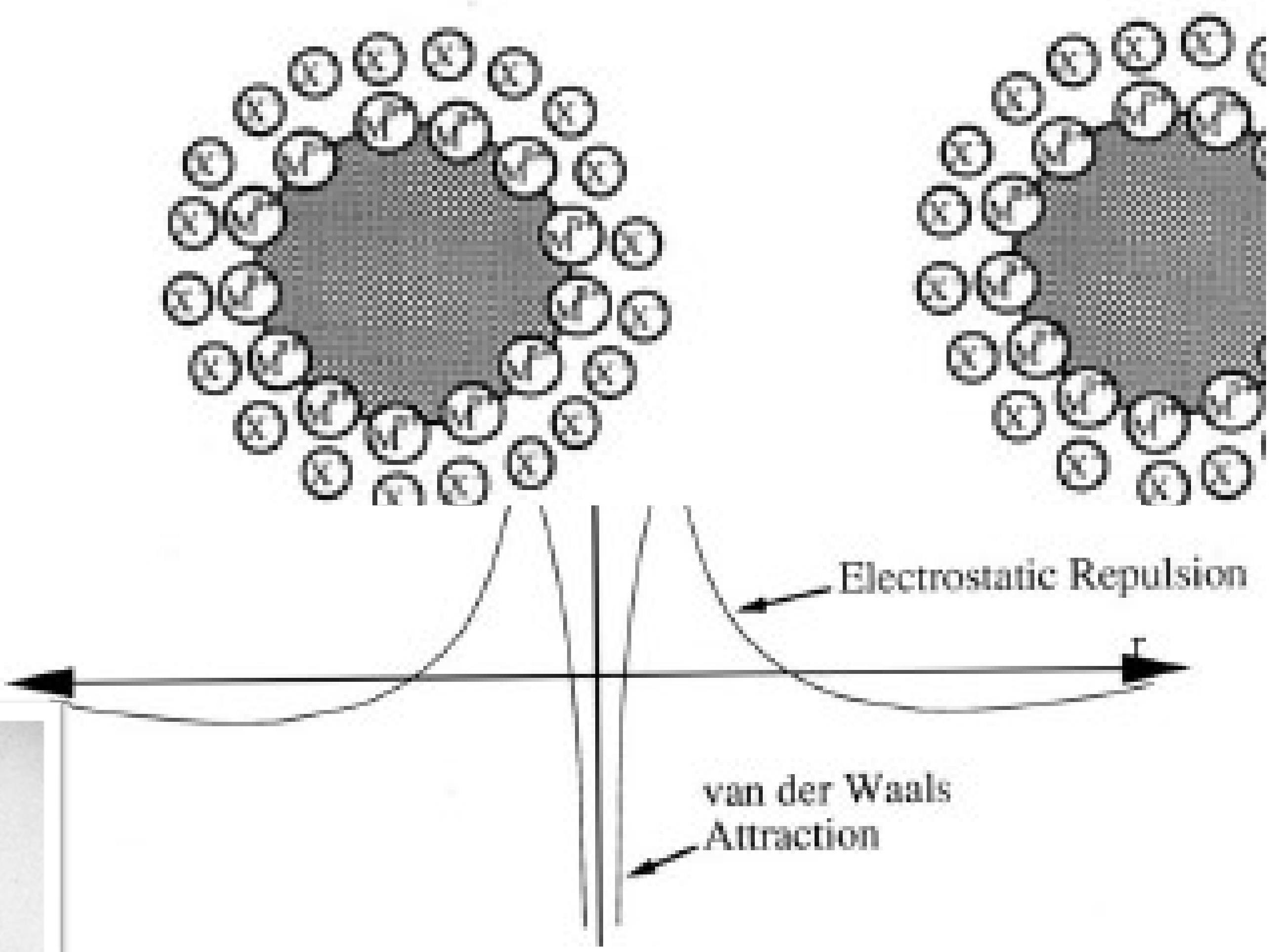


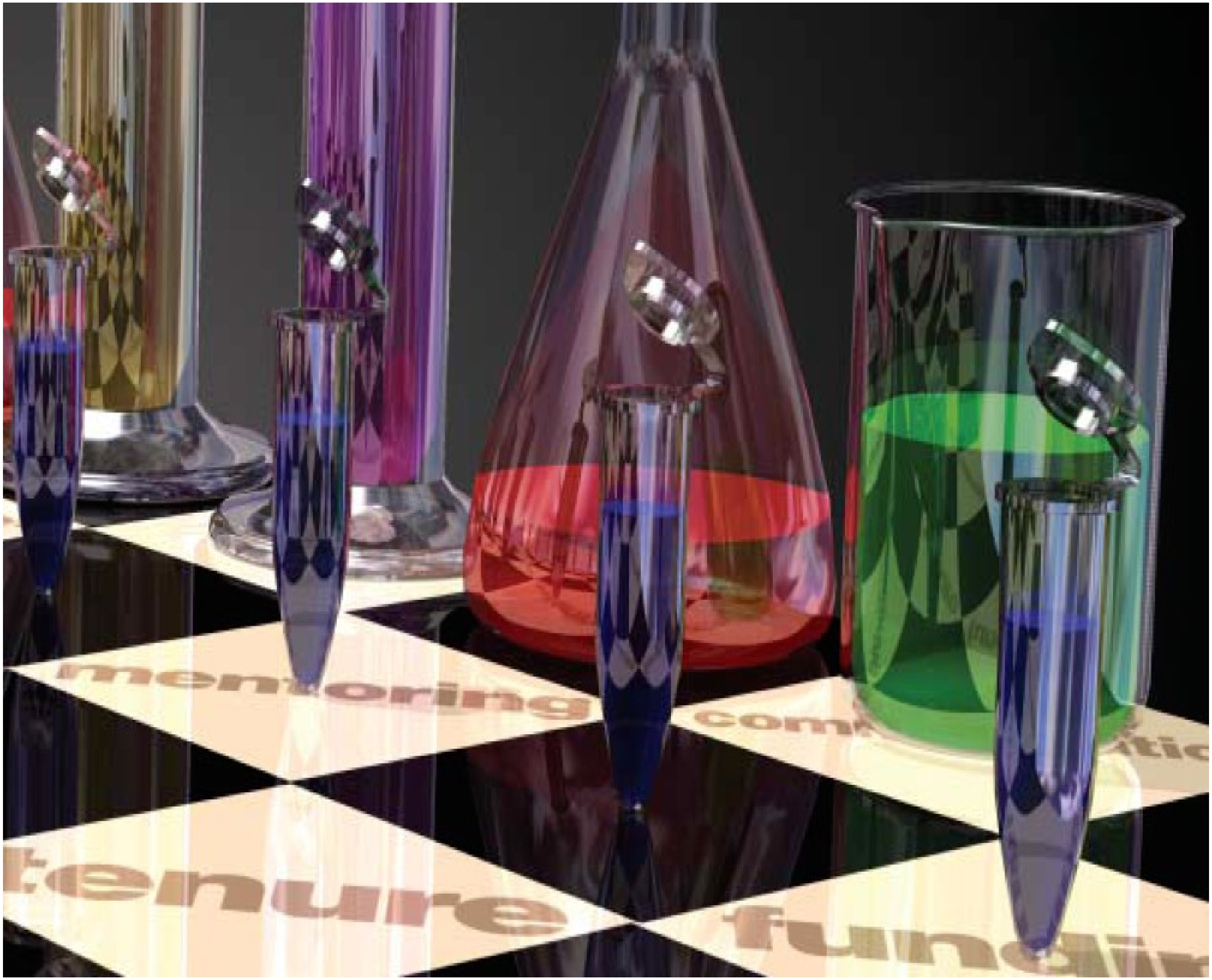


Colloidal Synthesis Approach
(Solution Chemistry)

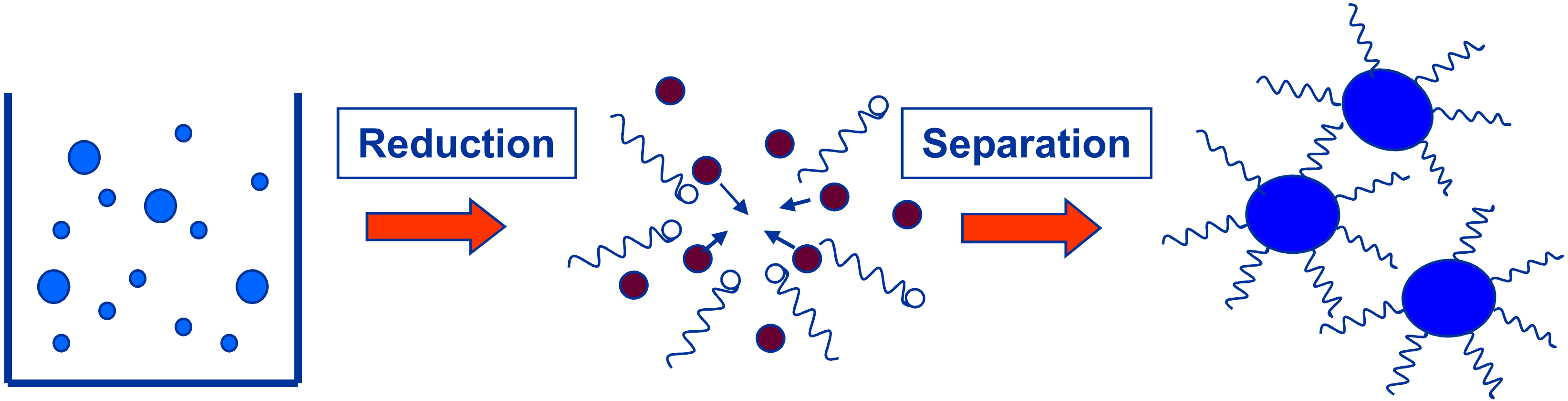

OT
Au
O
Acetone
Nanotube surface

Interactions of Colloids (Inter and intera)




mentoring
com
tic
tenure
fundi

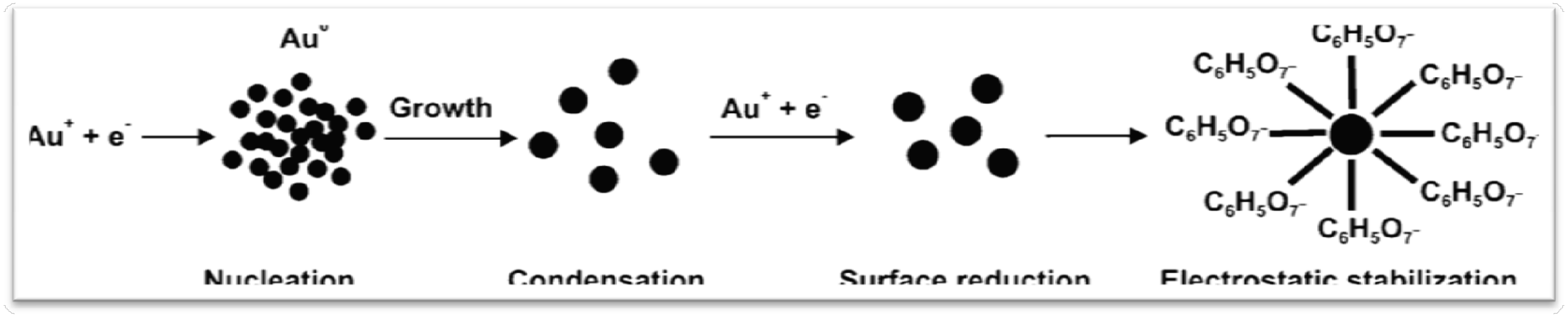
Synthesis of Colloidal nanoclusters

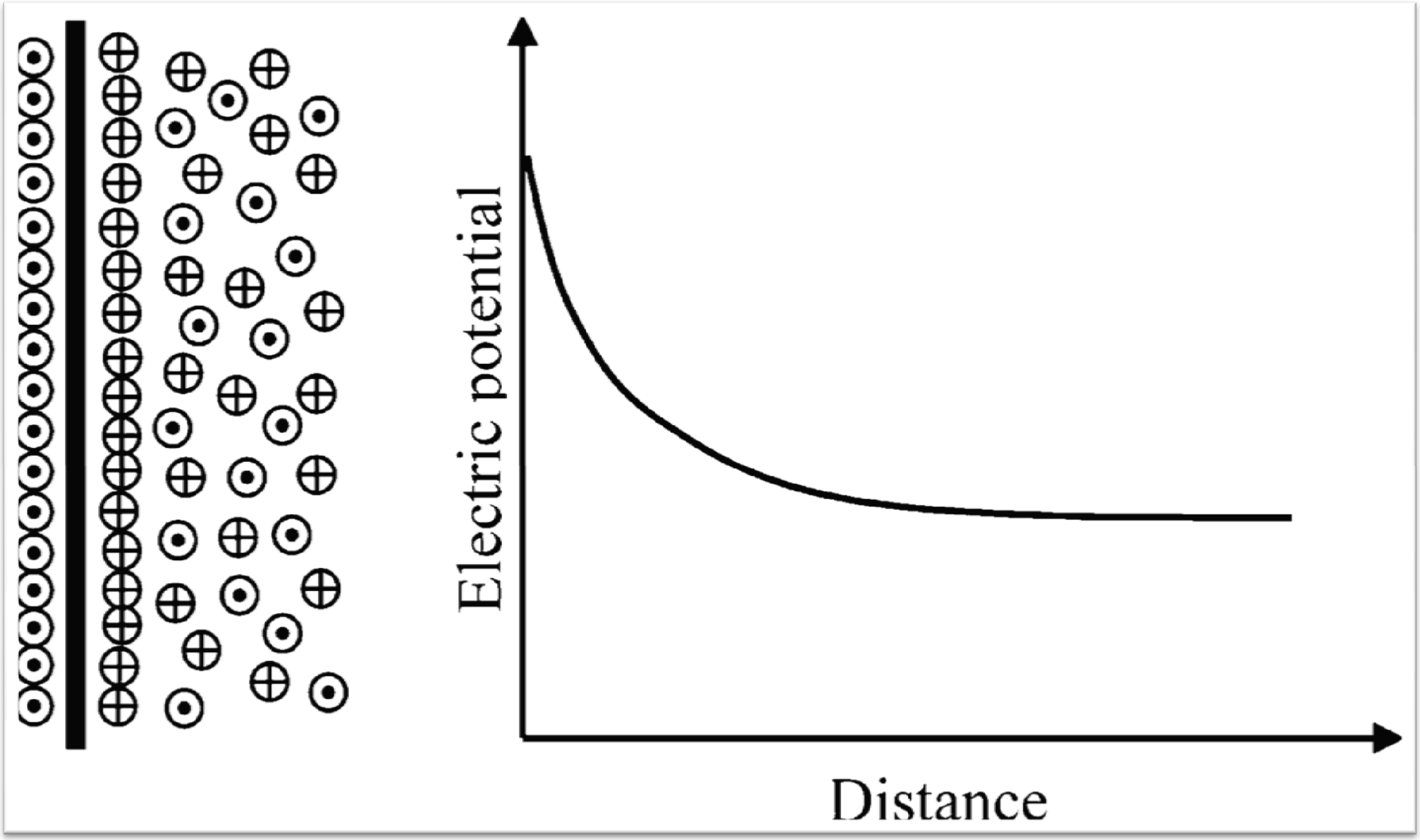


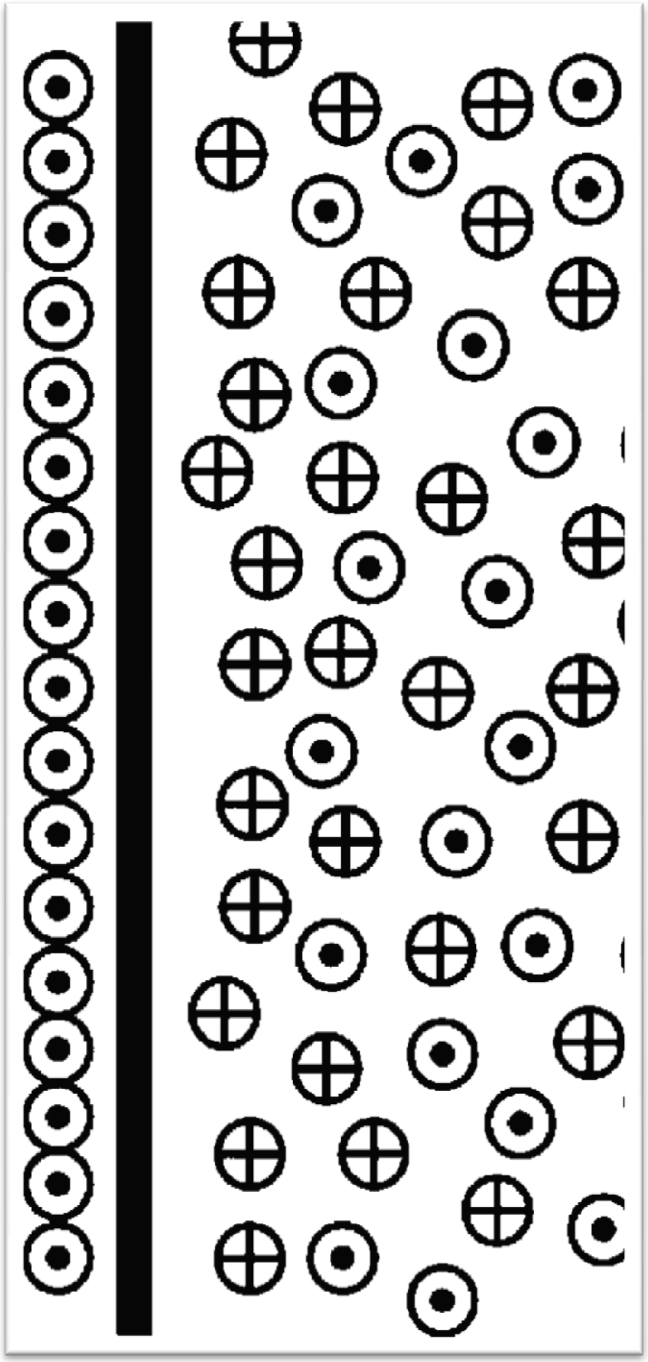
- Control of Cluster-Cluster spacing
- Size and shape

Methods

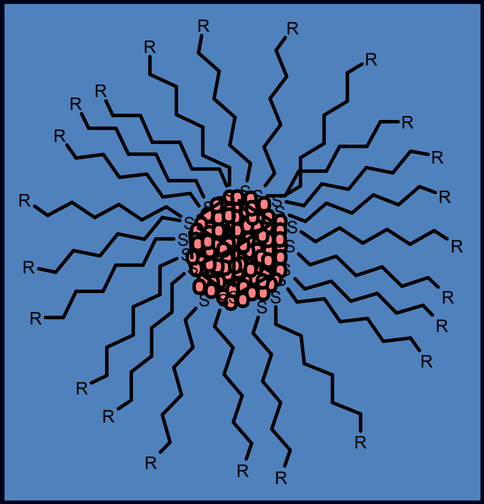
- *Solubility Fractionation*
- *Chromatography*
- *Capillary Electrophoresis*
- *Digestive Ripening*


Au⁺ + e⁻
Au⁰
Growth
Au⁺ + e⁻
C6H5O7⁻
Nucleation
Condensation
Surface reduction
Electrostatic stabilization


Electric potential
Distance



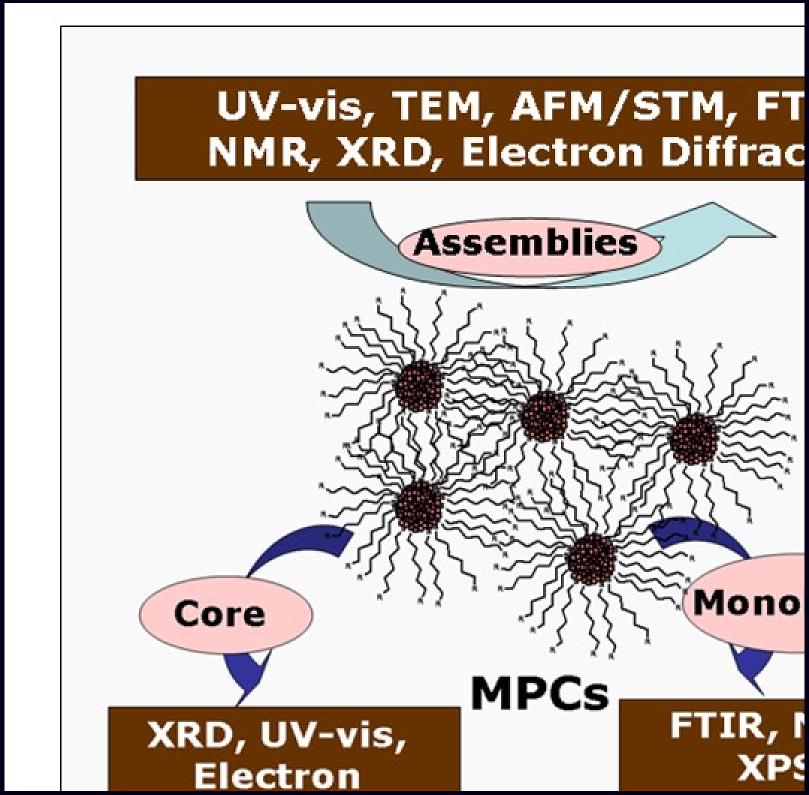
Monolayer Protected Clusters (MPCs)



Inorganic Core
(Metallic, semiconducting or insulating)
+

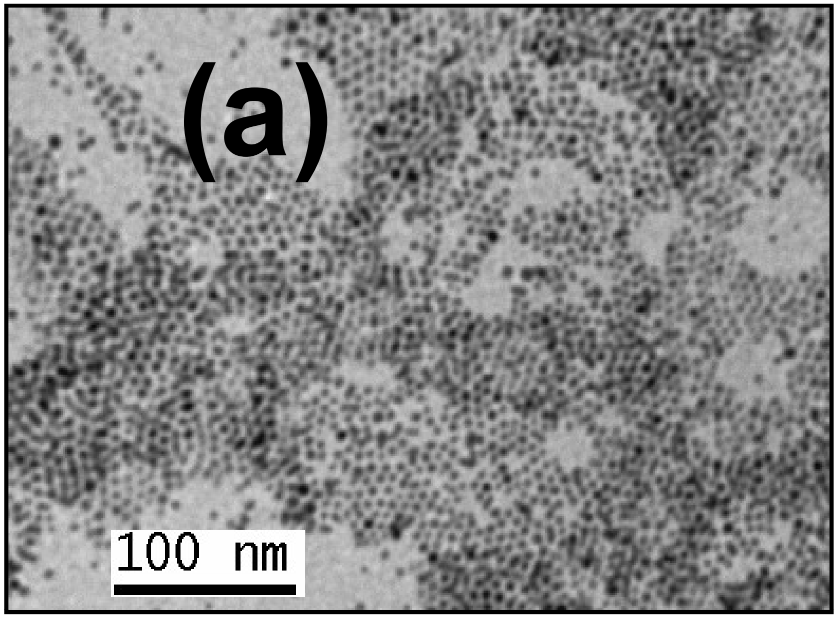
Organic Monolayer
(Organic thiols, amines, acids etc.)

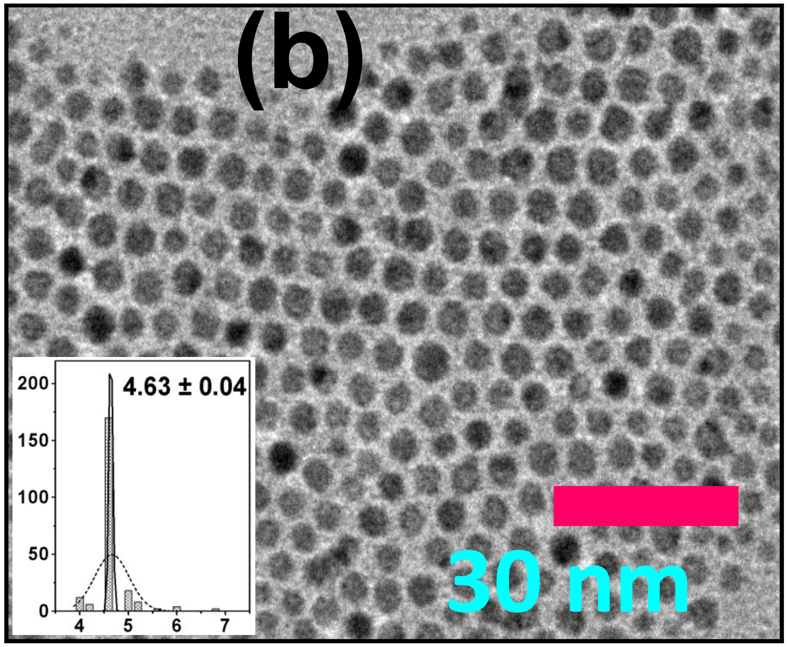
- A unique class of Inorgano-organo Hybrid Materials
- Attraction:
  - Enhanced Stability
  - Size, Shape and Capping Molecule: Flexibility
- Size dependent Catalytic, Optical, Electronic, Magnetic Property
- Nanoarchitecture/Superlattice:
  - Novel Properties Due to Collective Interactions

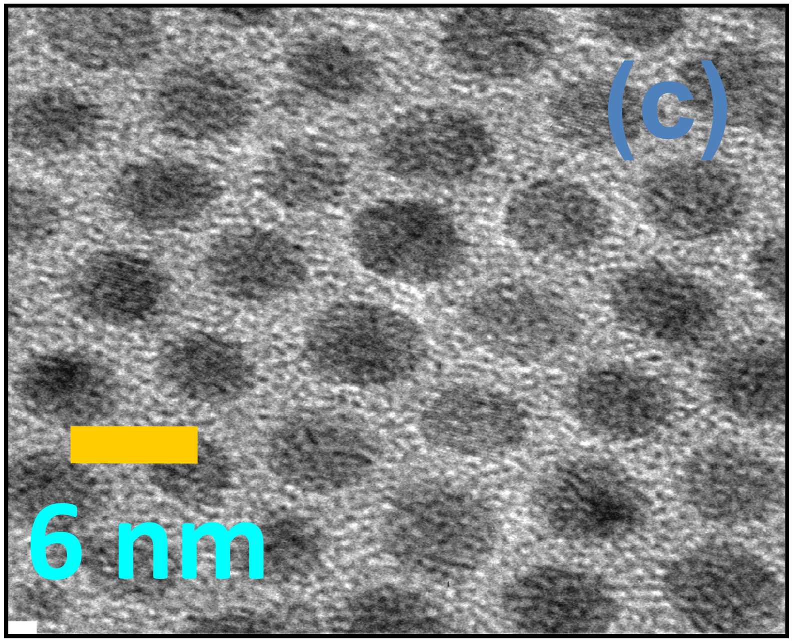


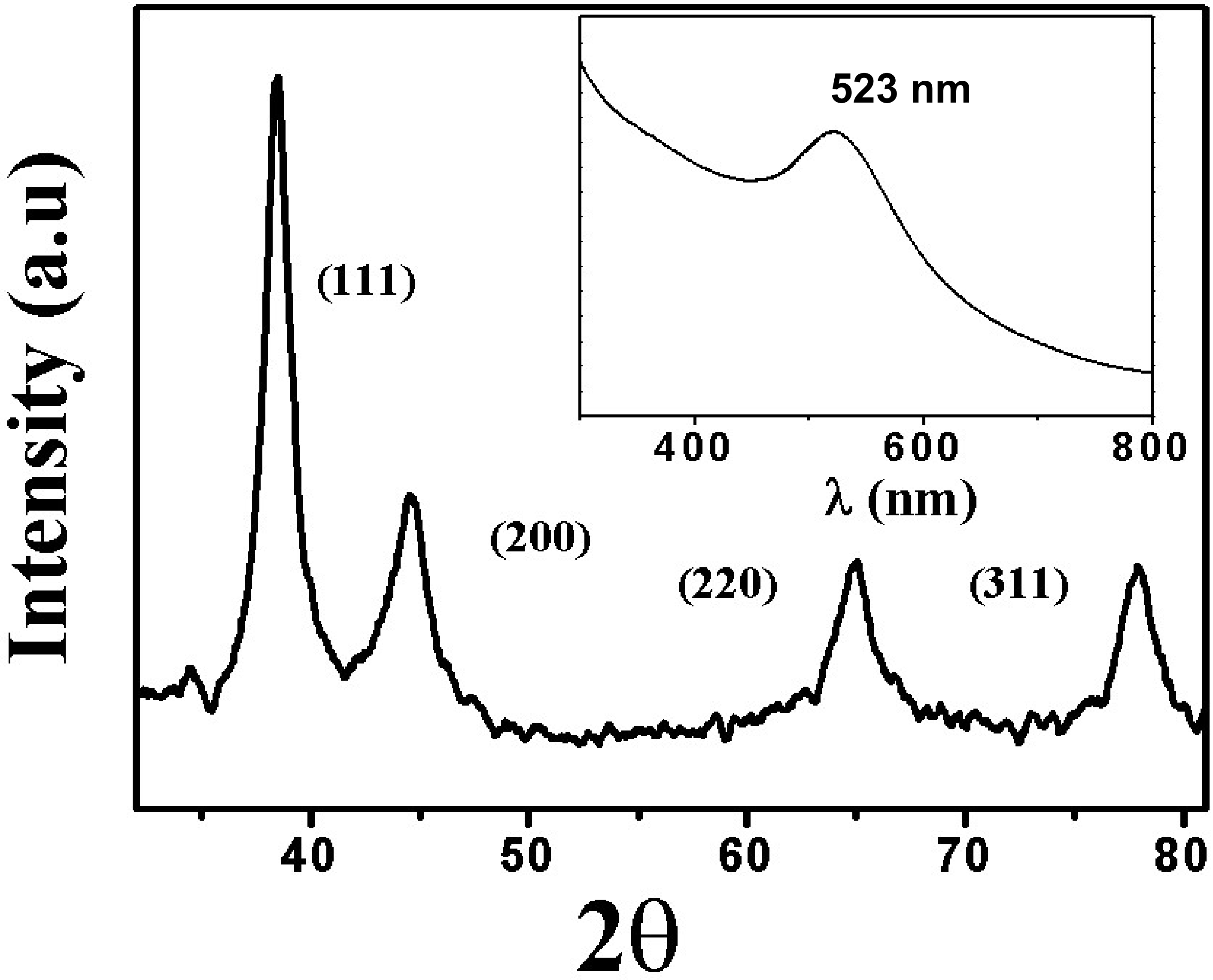
Various Characterization Tools

TEM





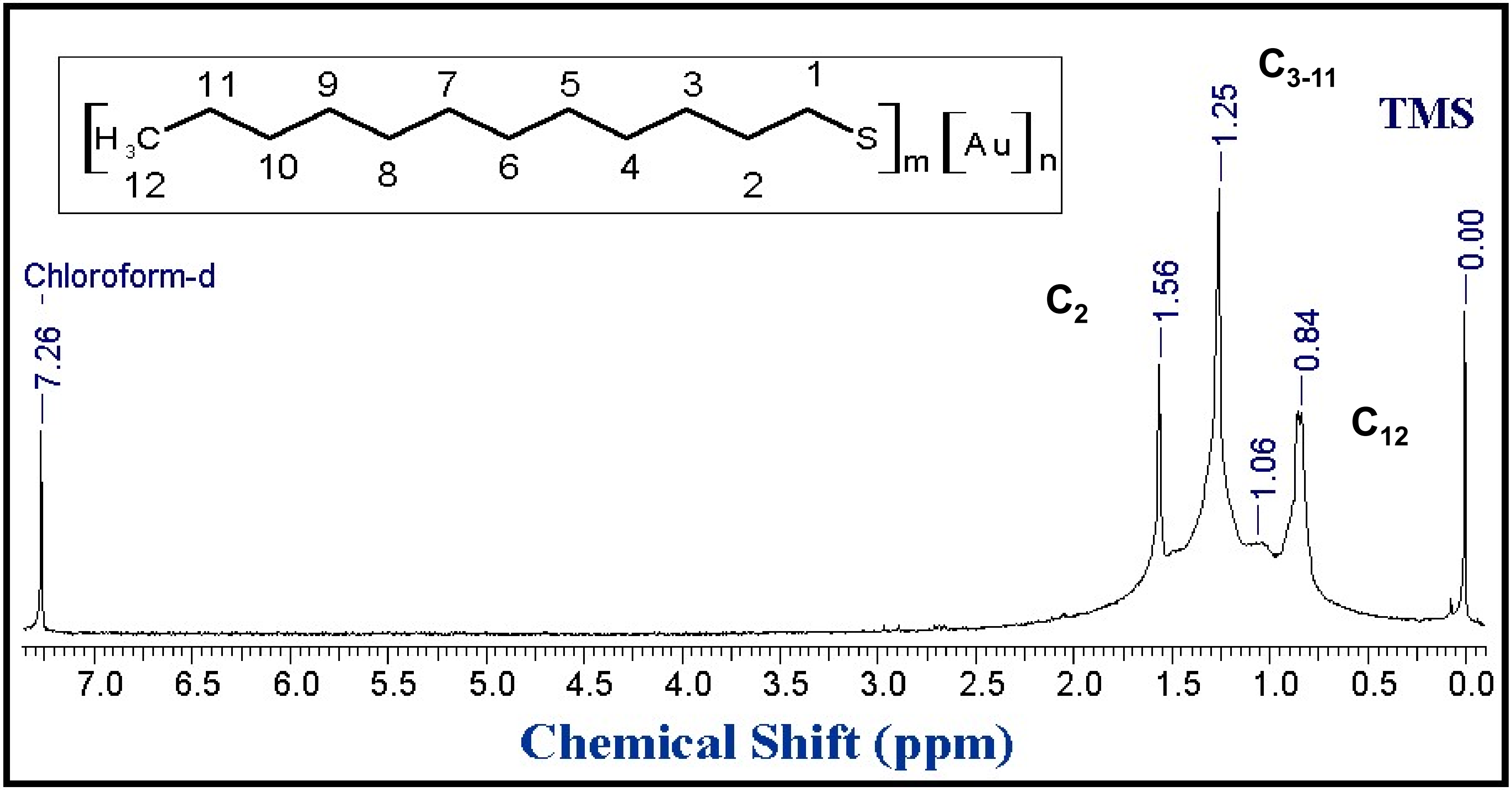


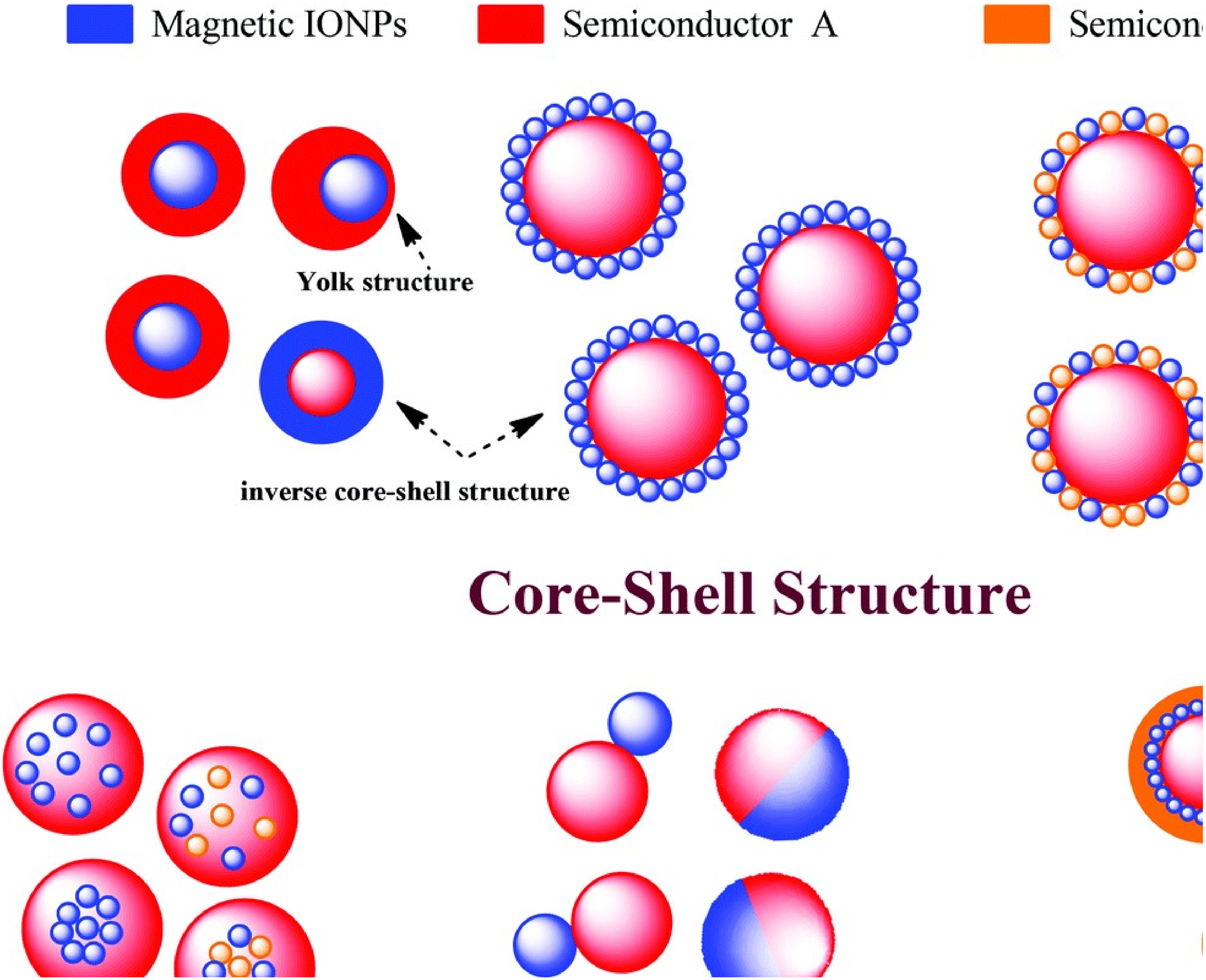


fcc structure

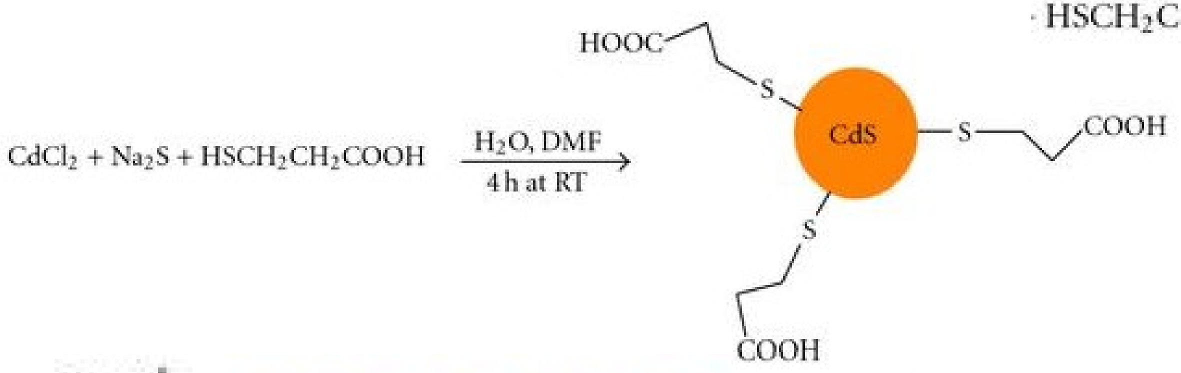
NMR analysis

- Passivation of DDT
- Absence of unbound thiol

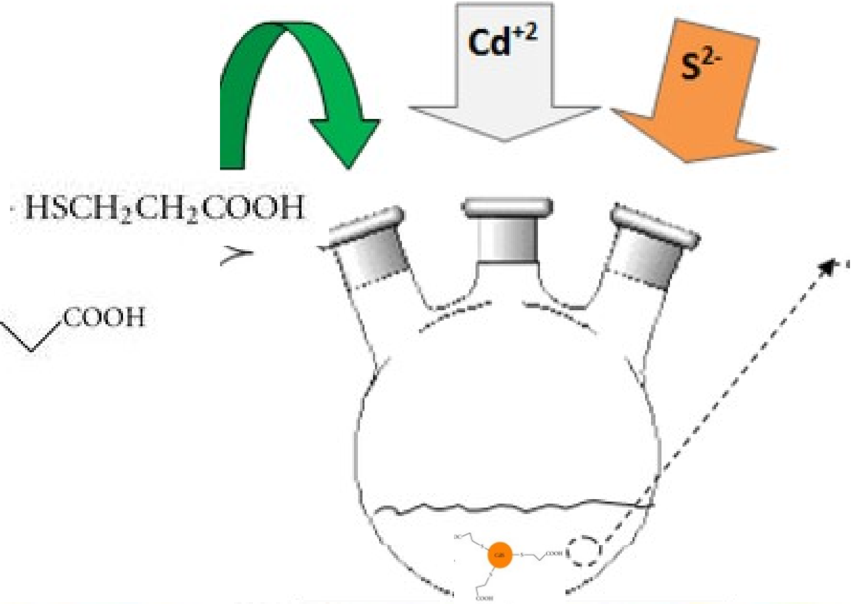


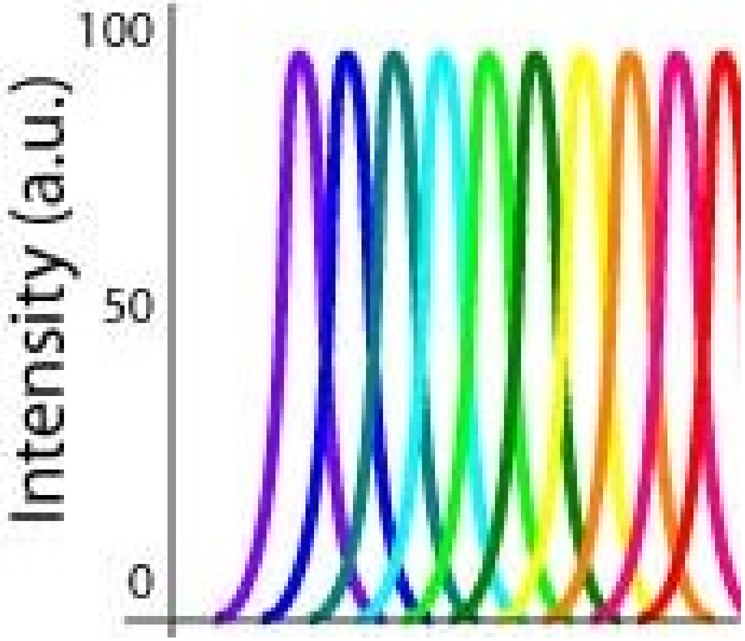

Magnetic IONPs
Semiconductor A
Semicon
Yolk structure
inverse core-shell structure
Core-Shell Structure

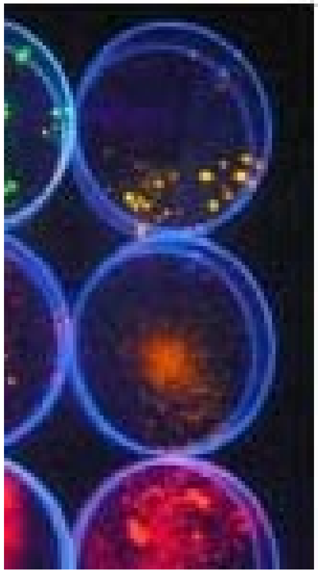
Semiconductor(Compound) Nanoparticle: Synthesis

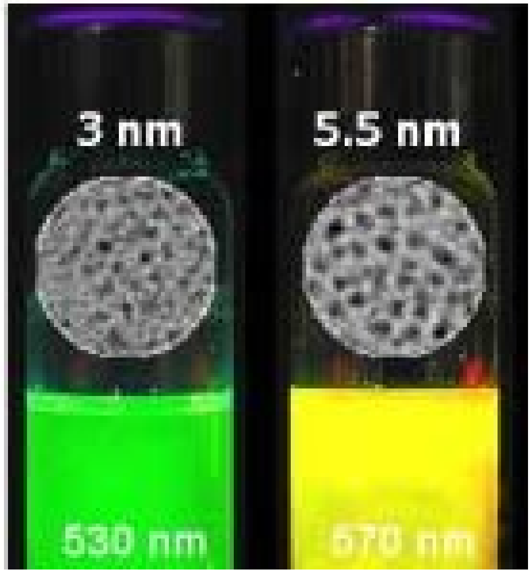


$$CdCl_2 + Na_2S + HSCH_2CH_2COOH \xrightarrow[4\text{ h at RT}]{H_2O,\ DMF}$$









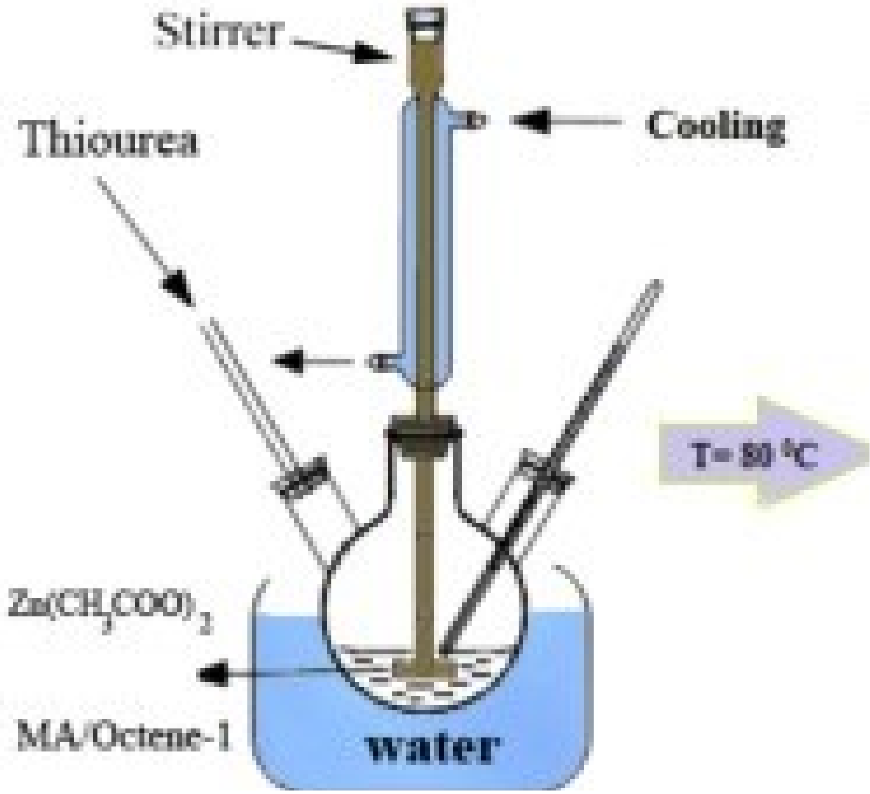
Photoluminescence Spectra of ZnS NPs

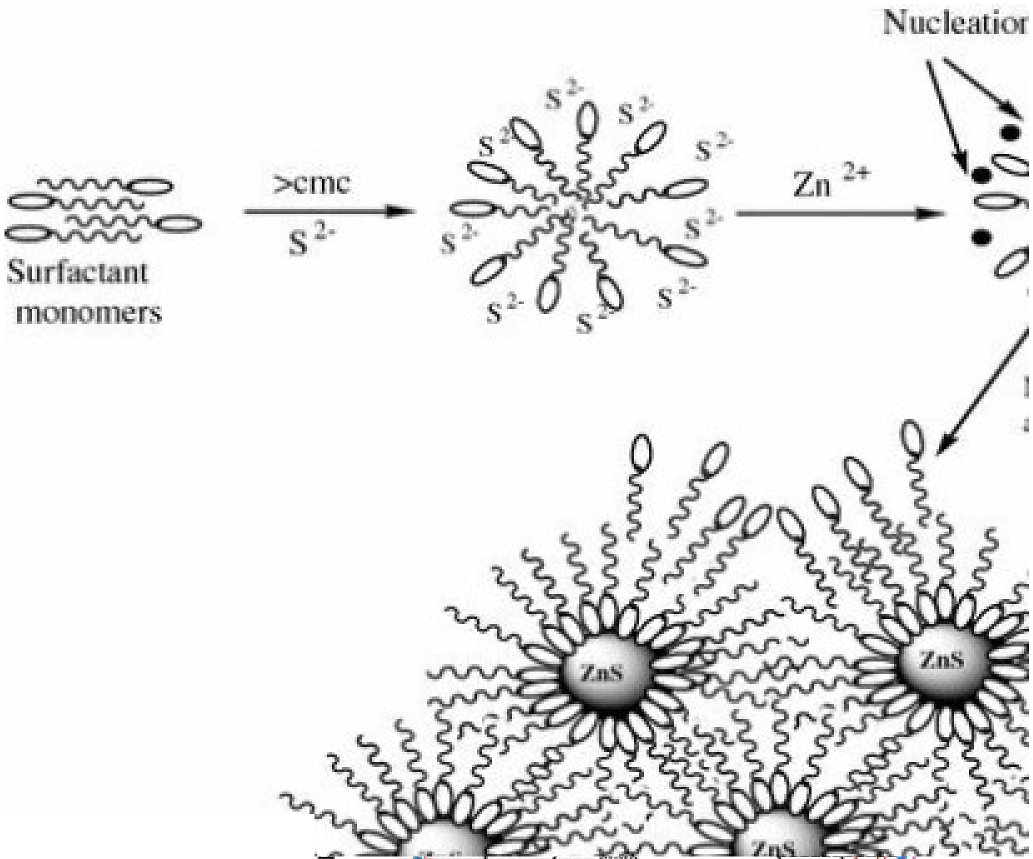
Synthesis of Zinc oxide nanopart

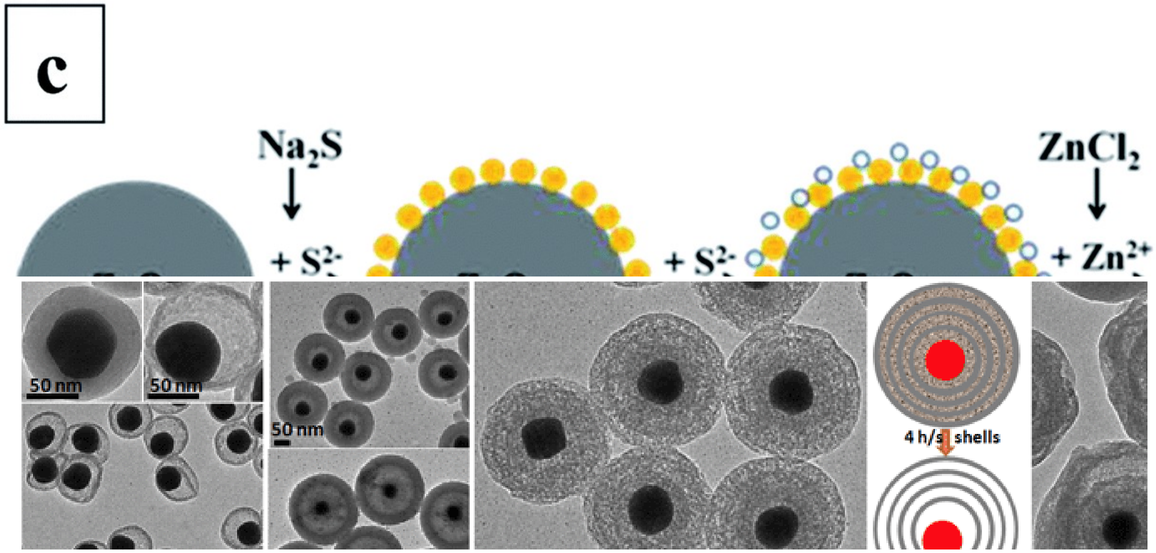
- Chemical wet method

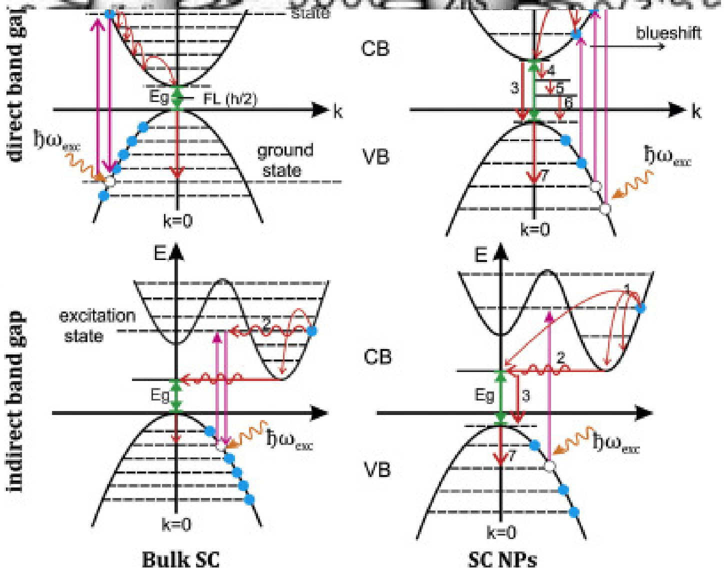
$$ZnCl_2 + 2NaOH \longrightarrow Zn(OH)_2 + 2N$$

$$Zn(OH)_2 \longrightarrow ZnO + H_2O$$


Stirrer
Cooling
Thiourea
T= 80 °C
Zn(CH$_3$COO)$_2$
MA/Octene-1
water


Nucleatio
Surfactant monomers
>cmc
S^{2-}
Zn $^{2+}$
ZnS
ZnS
ZnS


c
Na$_2$S
+ S^{2-}
+ S^{2-}
ZnCl$_2$
+ Zn^{2+}
50 nm
50 nm
50 nm
4 h/s shells


direct band gap
state
Eg
FL (h/2)
k
ground state
ħω$_{exc}$
k=0
CB
VB
blueshift
3
4
5
6
7
k
ħω$_{exc}$
k=0
indirect band gap
E
excitation state
2
Eg
ħω$_{exc}$
k=0
CB
VB
E
1
2
Eg
3
7
ħω$_{exc}$
k=0
Bulk SC
SC NPs

Langmuir-Blodgett Films (

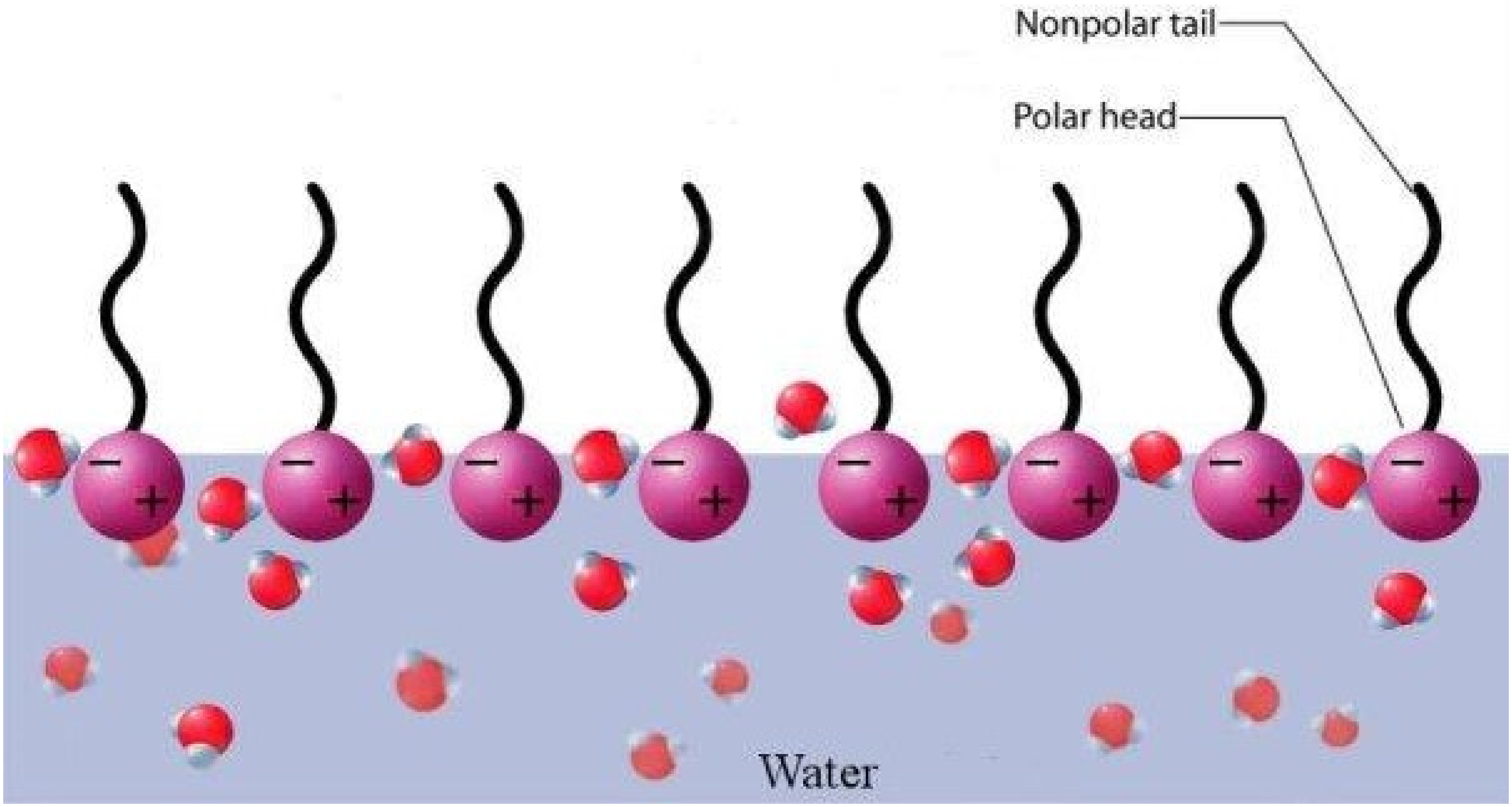
- Definition of LB films
  - History and development
- Construction with LB films
- Building simple LB SAMs
- Nano applications of LB films
  - Surface derivatized nanoparticles
  - Functionalized coatings in LB films

Langmuir-Blodgett Films

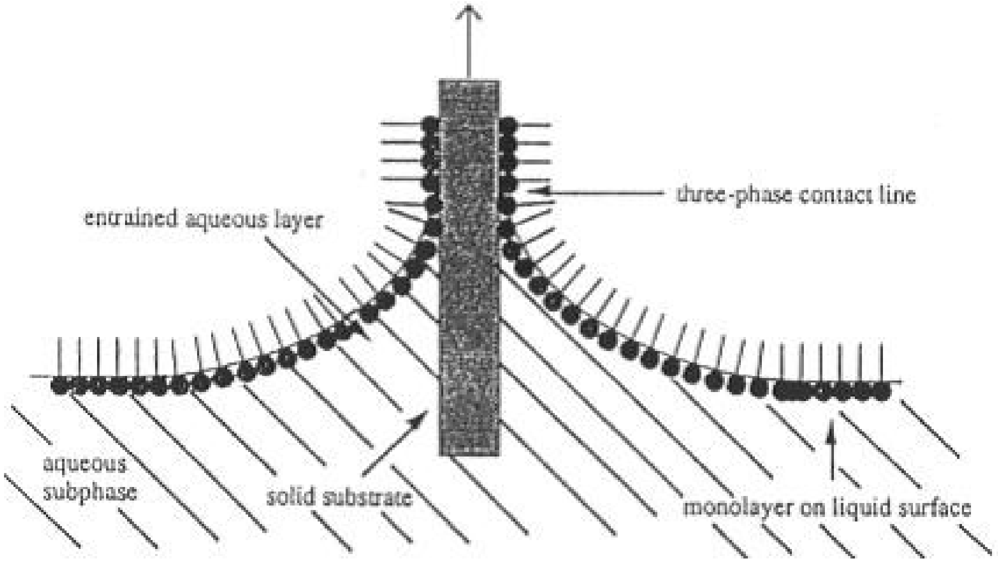
- A **Langmuir-Blodgett film** contains of one or more monolayers of an organic material, deposited from the surface of a liquid onto a solid by immersing (or emersing) the solid substrate into (or from) the liquid. A monolayer is added with each immersion or emersion step, thus films with very accurate thickness can be formed. Langmuir Blodgett films are named after Irving Langmuir and Katherine Blodgett, who invented this technique. An alternative technique of creating single monolayers on surfaces is that of self-assembled monolayers. Retrieved from "http://en.wikipedia.org/wiki/Langmuir-Blodgett_film"

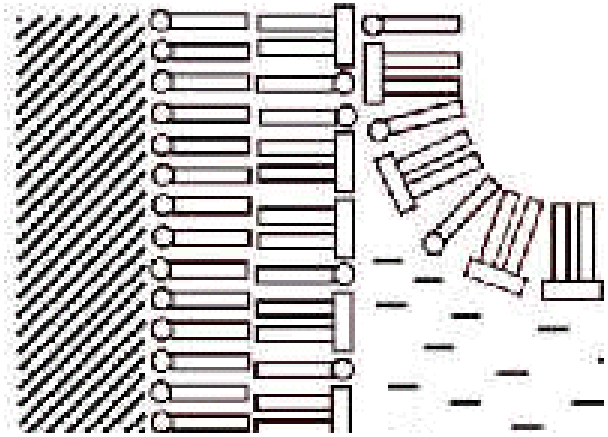
Benjamin Franklin in 1773

1926 Irving Langmuir and Katherine Blodgett : transfer of Langmuir monolayers onto substrates



Langmuir-Blodgett Films

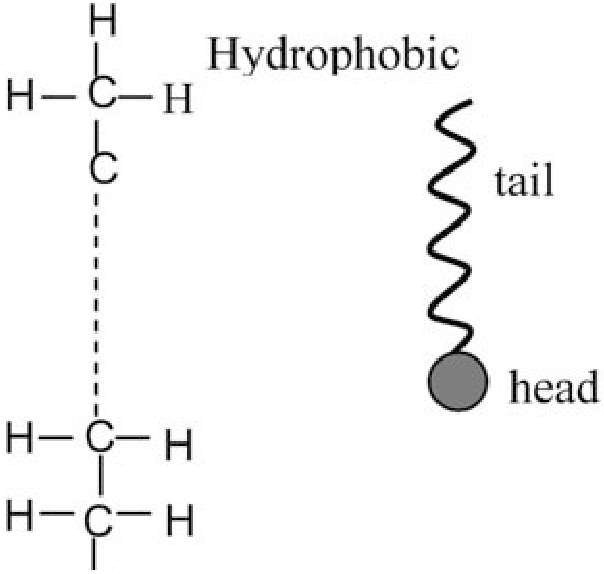


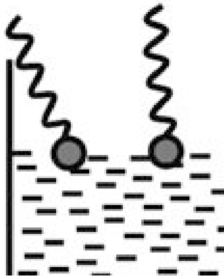


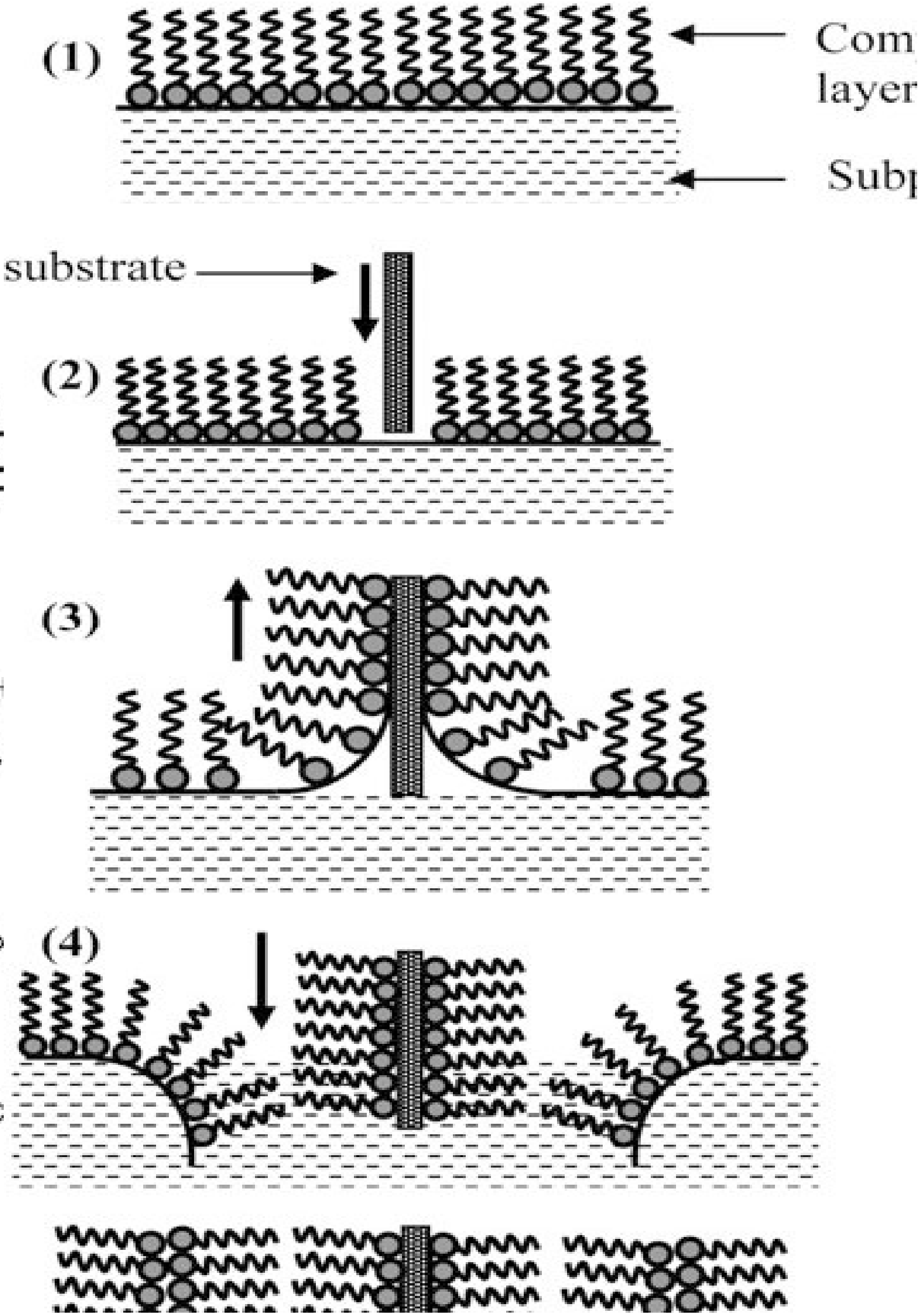
http://www.bio21.bas.bg/ibf/PhysChem_dept.html

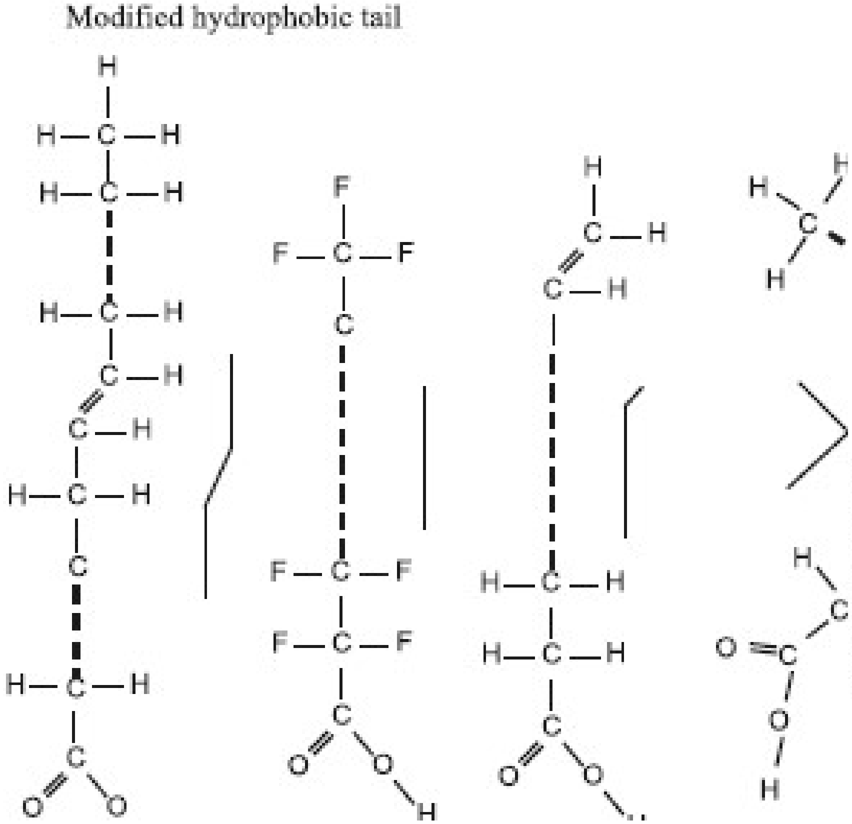
http://www.ksvltd.com/pix/keywords_html_m4b17b42d.jpg

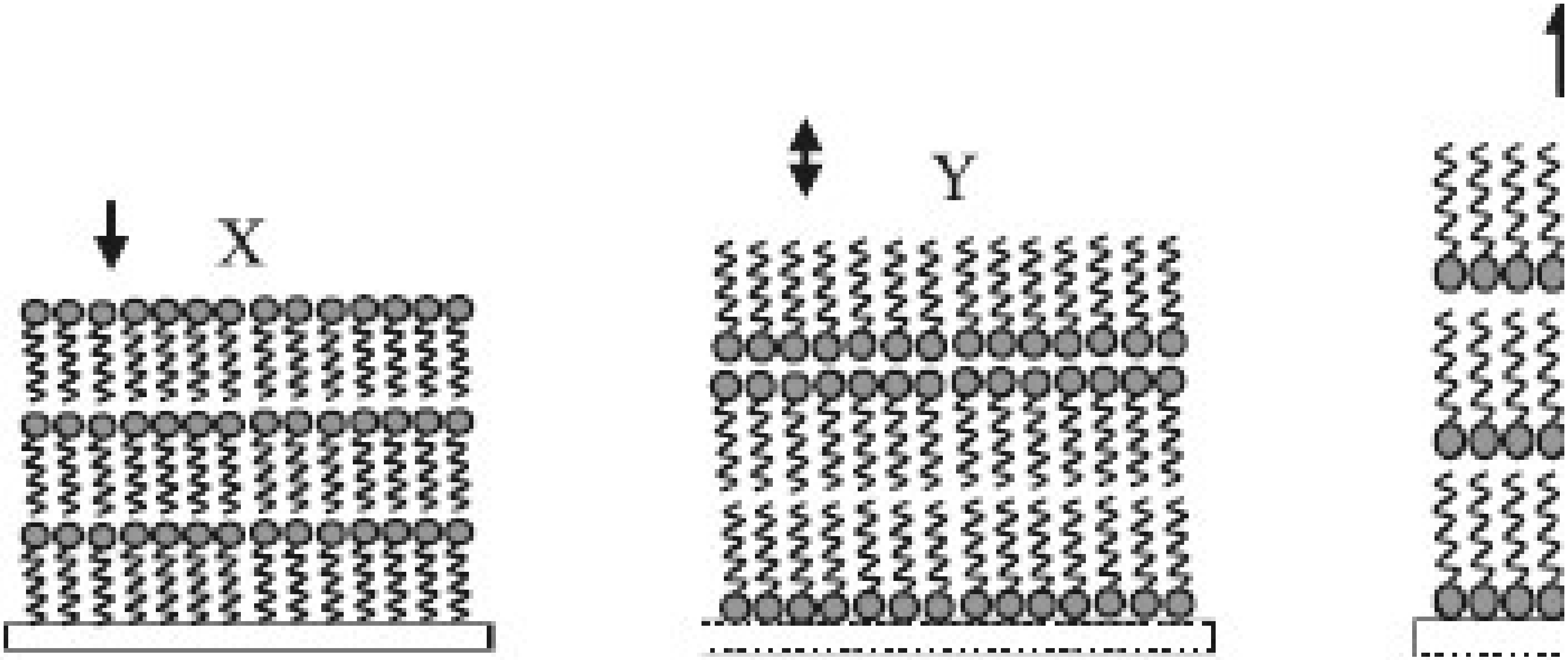
***Deposition of Langmuir-Blodgett molecular assemblies of lipids on solid substrates*.**


Hydrophobic
tail
head




(1)
Com
layer
Subp
substrate
(2)
(3)
(4)


Modified hydrophobic tail

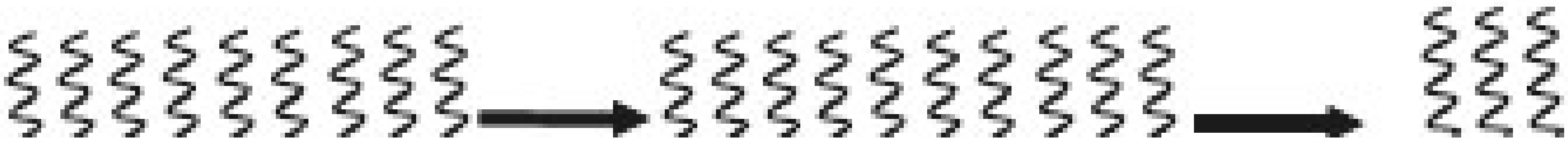


Deposition only during insertion of substrate.

Deposition both the times except no deposition during first immersion.

Deposi
remova

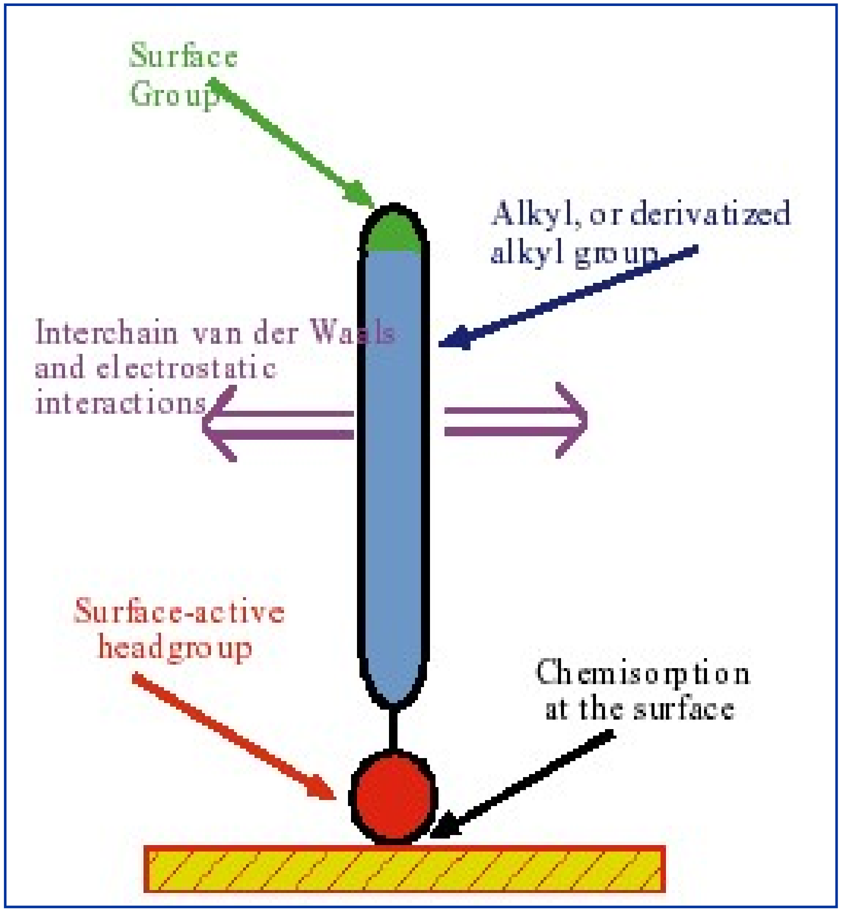
Fig. 4.22 X, Y and Z type L-B films



Thermodynamics of Langmuir-Blodgett Films

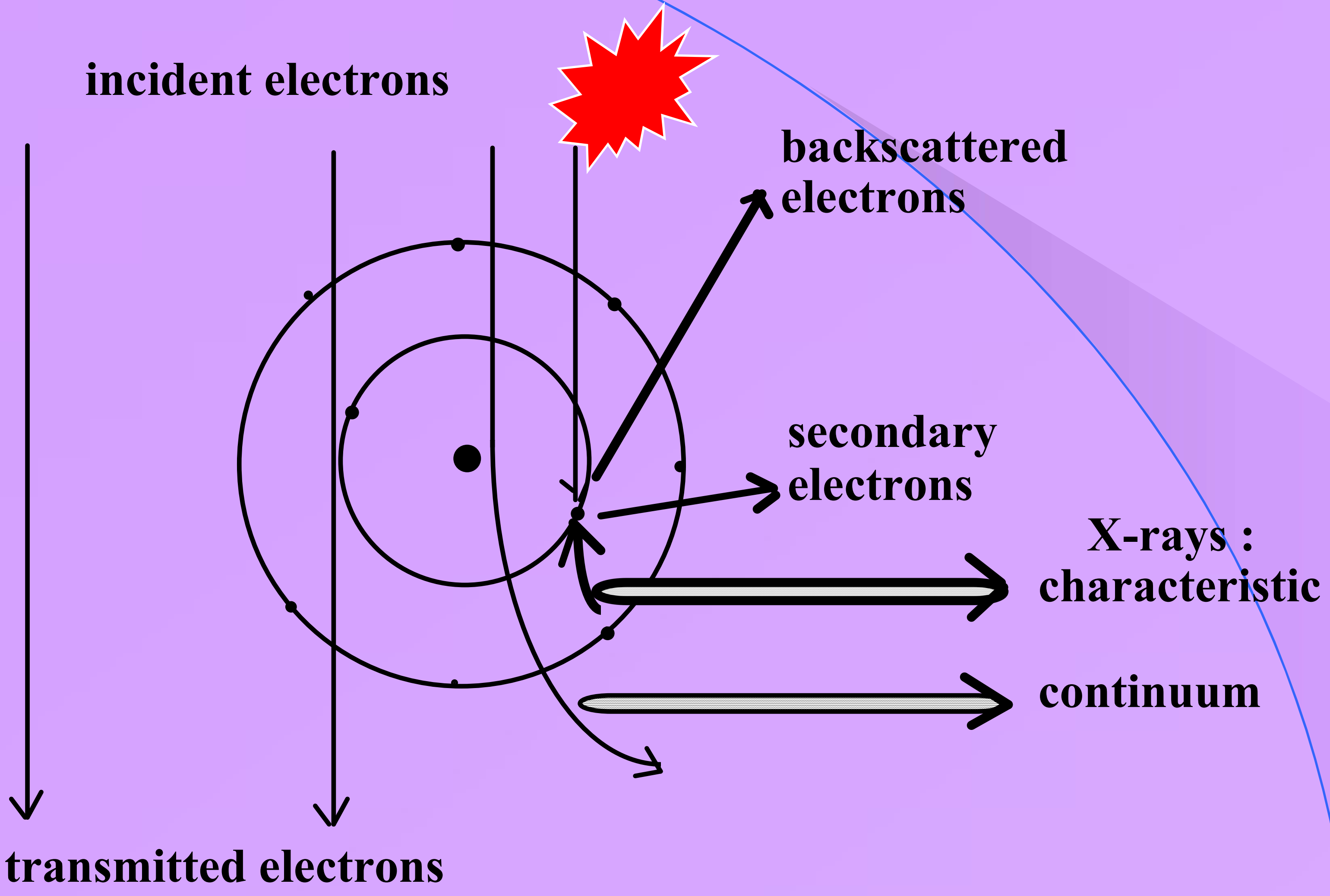
The free energy of a self-assembled monolayer is minimized because of three main processes:

- Chemisorption of the surfactant onto the surface, ~40-45 kcal /mole
- Interchain van der Waals interaction,<10 kcal/mole
- Terminal Functionality, ~0.7-1.0 kcal/mole for CH_3 termination



Characterization of Nanomaterials

when electrons hit matter ..



incident electrons

backscattered electrons

secondary electrons

X-rays : characteristic

continuum

transmitted electrons

when electrons hit matter ..

(1) they may collide with an inner shell electron, ejecting same

> the ejected electron is a low-energy, *secondary* electron detected & used to from SEM images

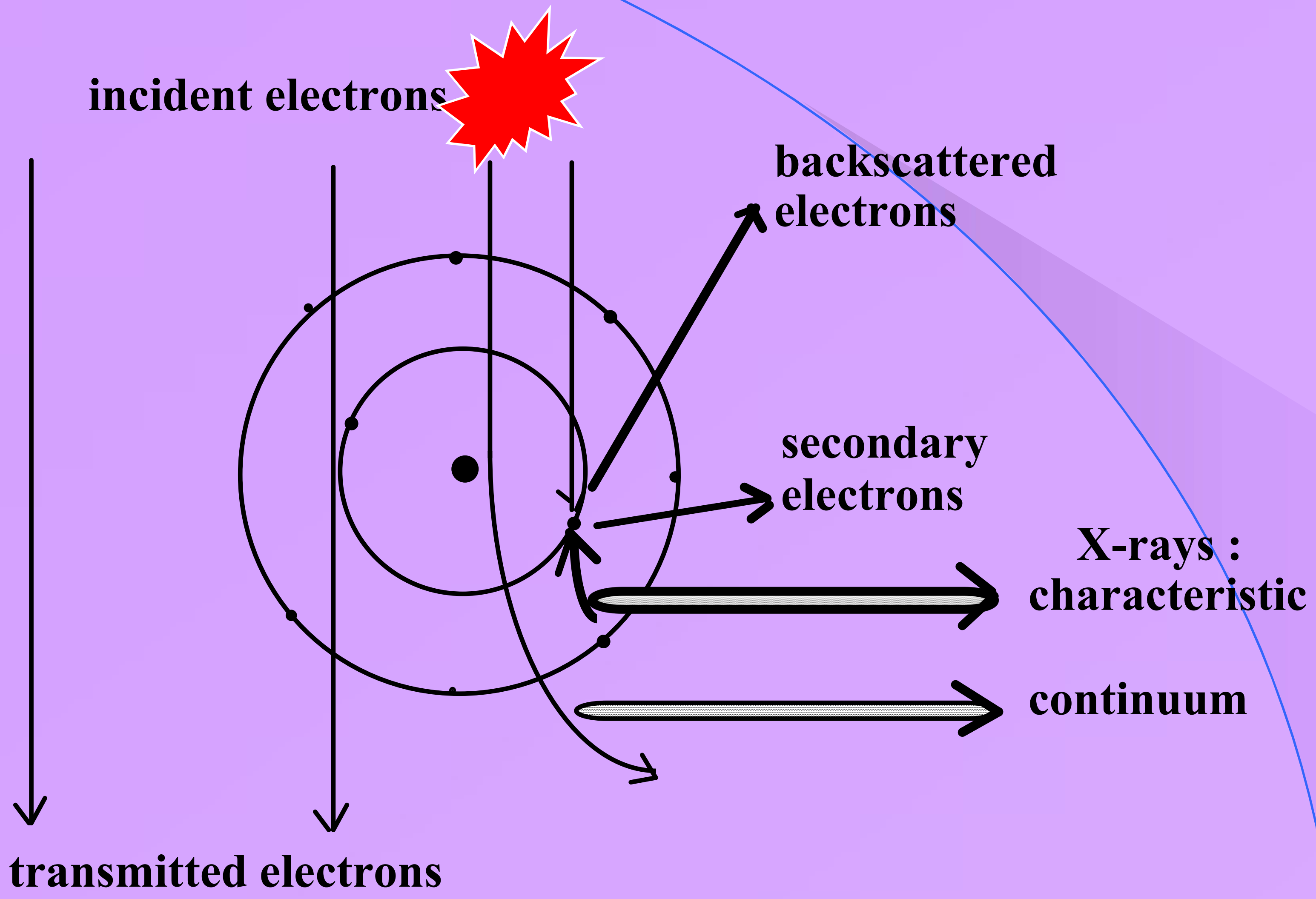
> the original high-energy electron is scattered

- known as a ‘back-scattered’ electron (SEM use)

> an outer-shell electron drops into the position formerly occupied by the ejected electron

> this is a *quantum process*, so a X-ray photon of precise wavelength is emitted - basis for *X-ray microanalysis*

when electrons hit matter ..



incident electrons

backscattered electrons

secondary electrons

X-rays : characteristic

continuum

transmitted electrons

when electrons hit matter ..

(2) they may collide or nearly collide with an atomic nucleus

> undergo varying degree ofdeflection (inelastic scattering)

> undergo loss of energy - again varying

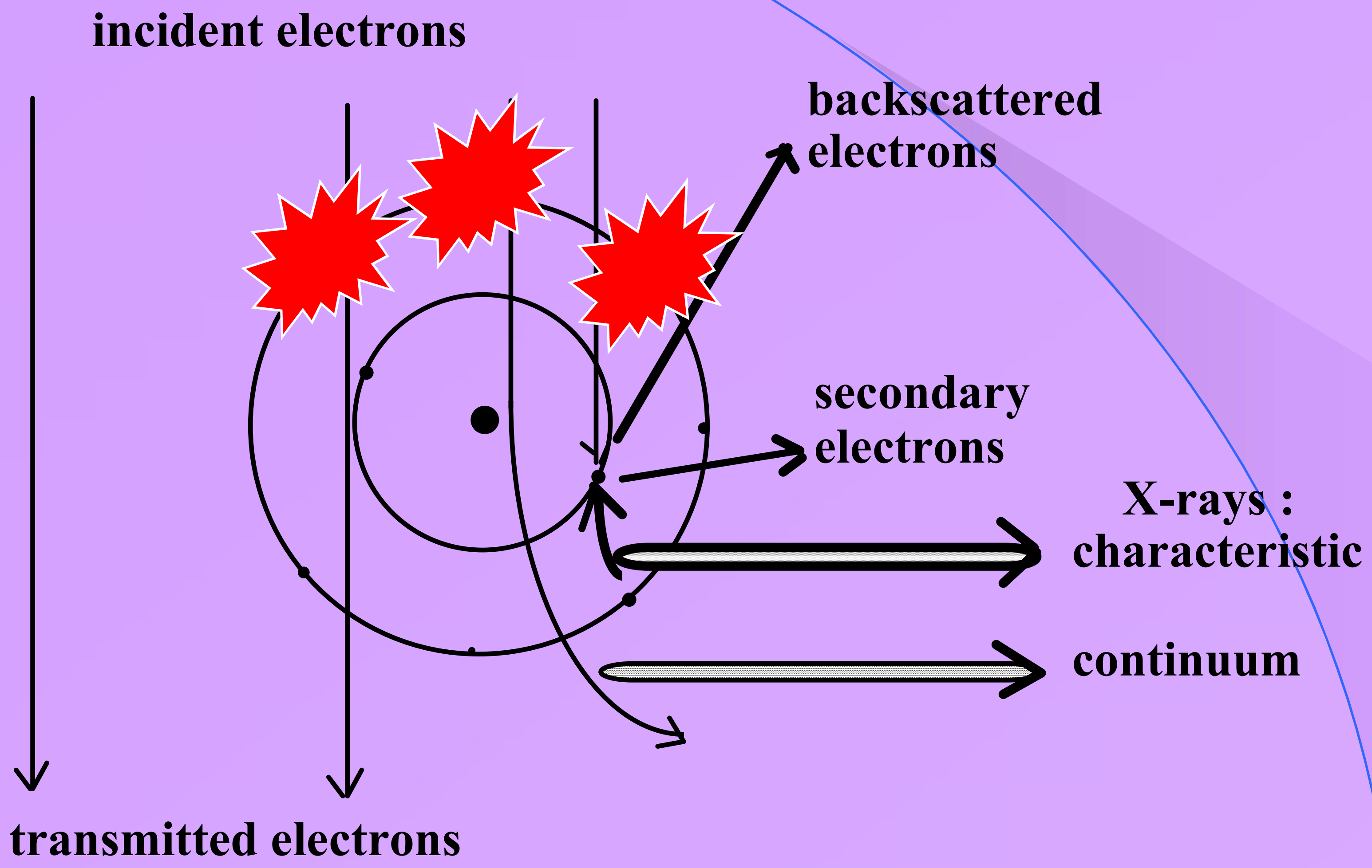
> lost energy appears as X-rays of *varying wavelength*

> this X-ray continuum is identical to that originating from
an X-ray source/generator (medical, XRC etc)

> original electrons scattered *in a forward direction* will
enter the imaging system, but with ‘wrong’ λ

> causes a ‘haze’ and loss of resolution in image

when electrons hit matter ..



incident electrons

backscattered electrons

secondary electrons

X-rays : characteristic

continuum

transmitted electrons

when electrons hit matter ..

(3) they may collide with *outer shell electrons*

> *either* removing *or* inserting an electron

> results in *free radical* formation

> this species is extremely chemically active

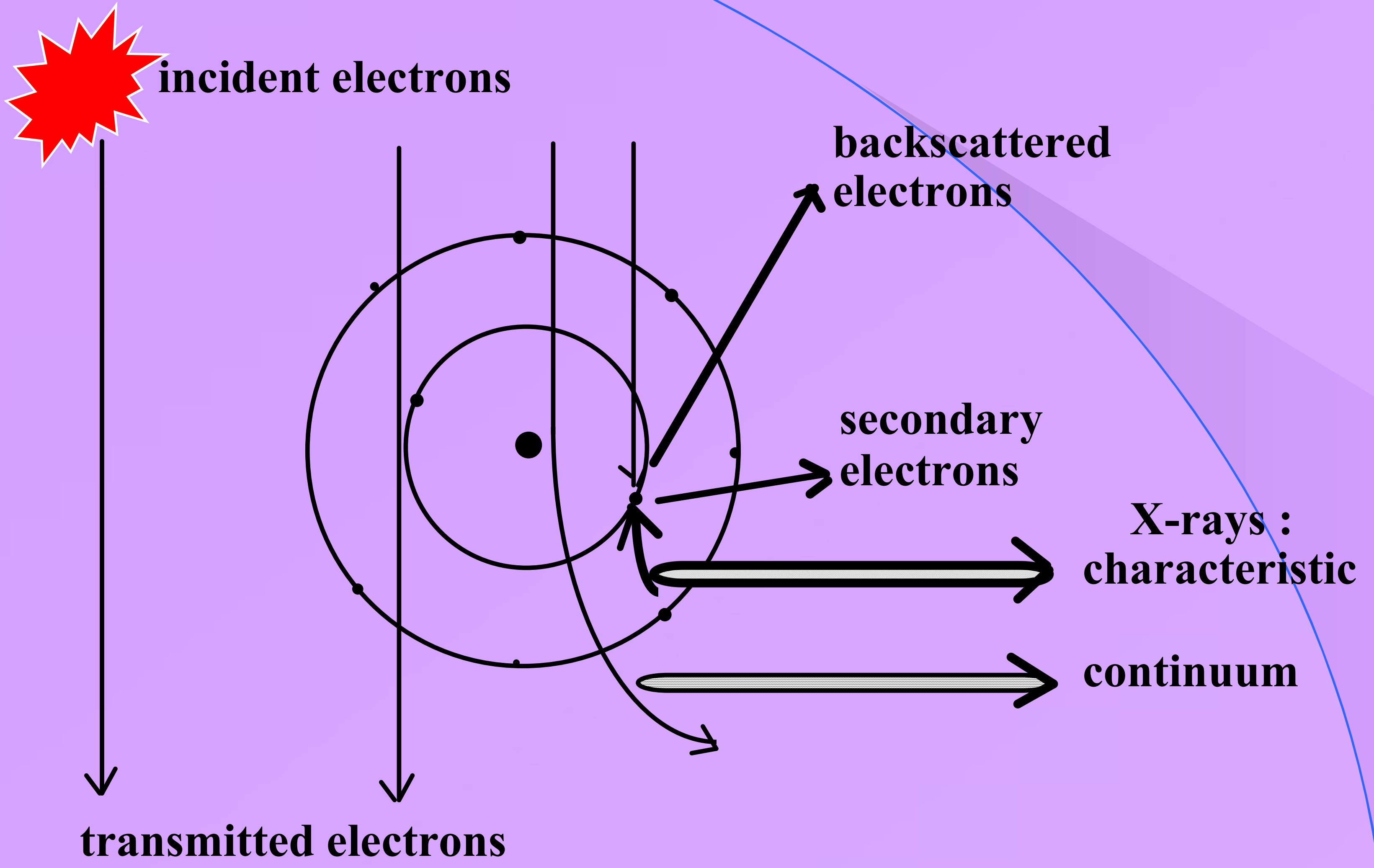
> reactions with neighbouring atoms induce massive change in the specimen, especially in the light atoms

> this *radiation damage* severely limits possibilities of EM

> examination of cells in the live state NOT POSSIBLE

> all examinations need to be as brief (low dose) as possible

when electrons hit matter ..



when electrons hit matter ..

(4) they may pass through unchanged

> these *transmitted electrons* can be used to form an image

> this is called imaging by *subtractive contrast*

> can be recorded by either

(a) TV-type camera (CCD) - very expensive

(b) photographic film - direct impact of electrons

Photographic film

> silver halide grains detect *virtually every electron*

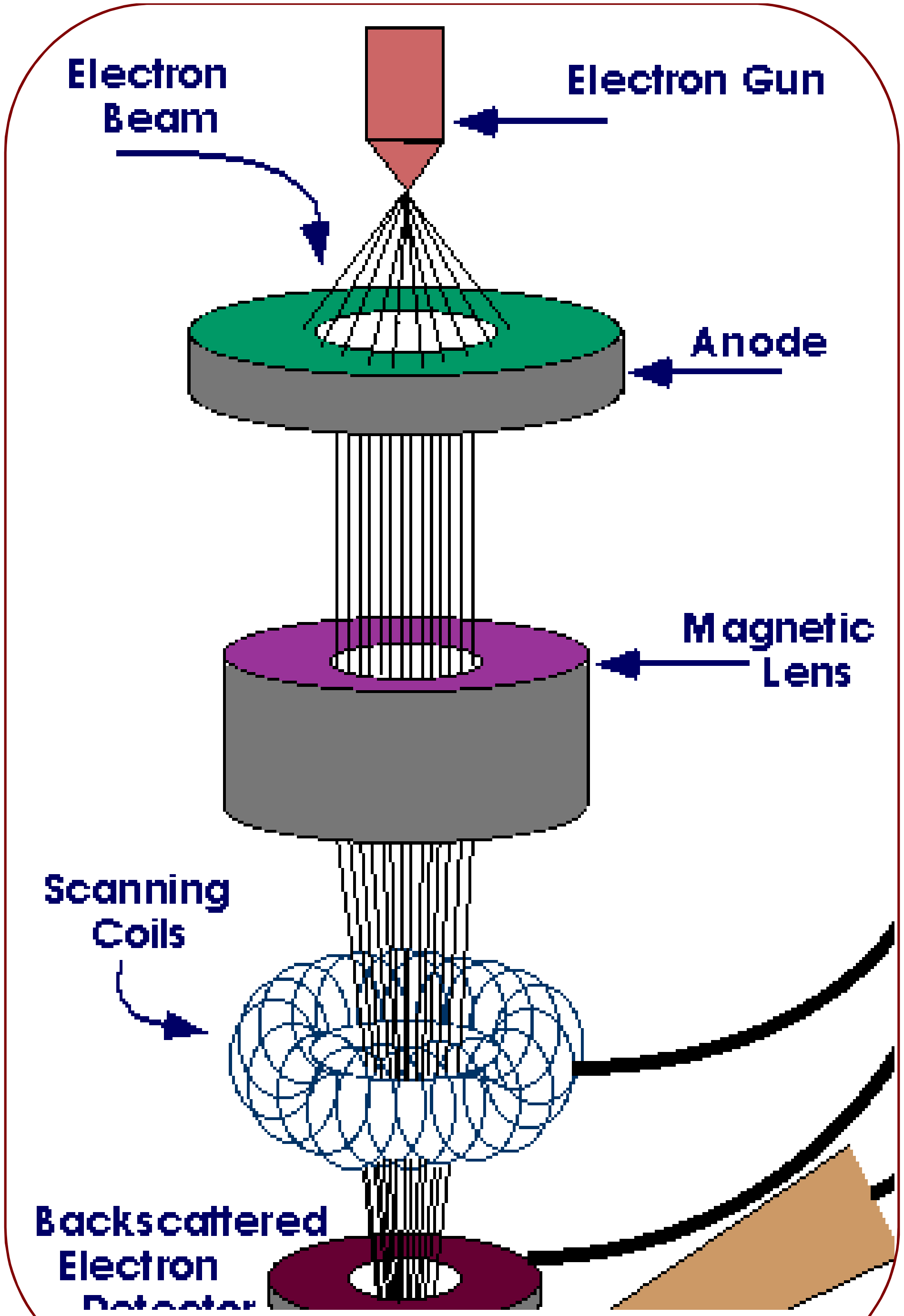
> at least *50x more efficient than photon capture !*

Scanning Electron Microscopy

- The **scanning electron microscope** (**SEM**) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity.
- Signals: From secondary electrons, back-scattered electrons

The Scanning Electron Microscope

- uses electrons reflected from the surface of a specimen to create image
- produces a 3D image of specimen’s surface features


Electron Beam
Electron Gun
Anode
Magnetic Lens
Scanning Coils
Backscattered Electron Detector

Strength and Limitations Of SEM

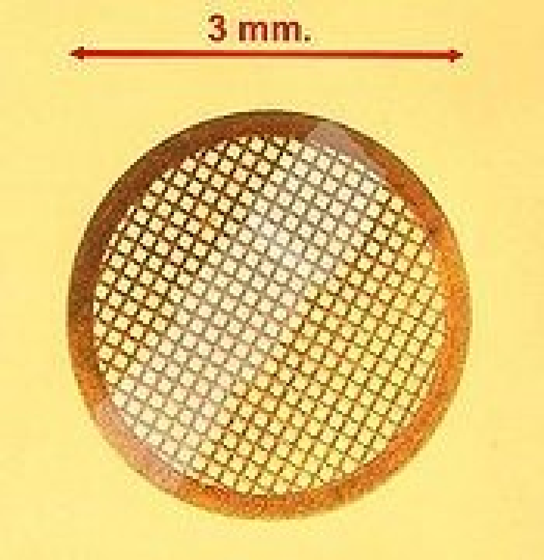
- Low vacuum ~ 10^{-5} torr
- User Friendly
- Wet samples also
- Elemental analysis (EDS)

- Insulating samples cannot be analyzed

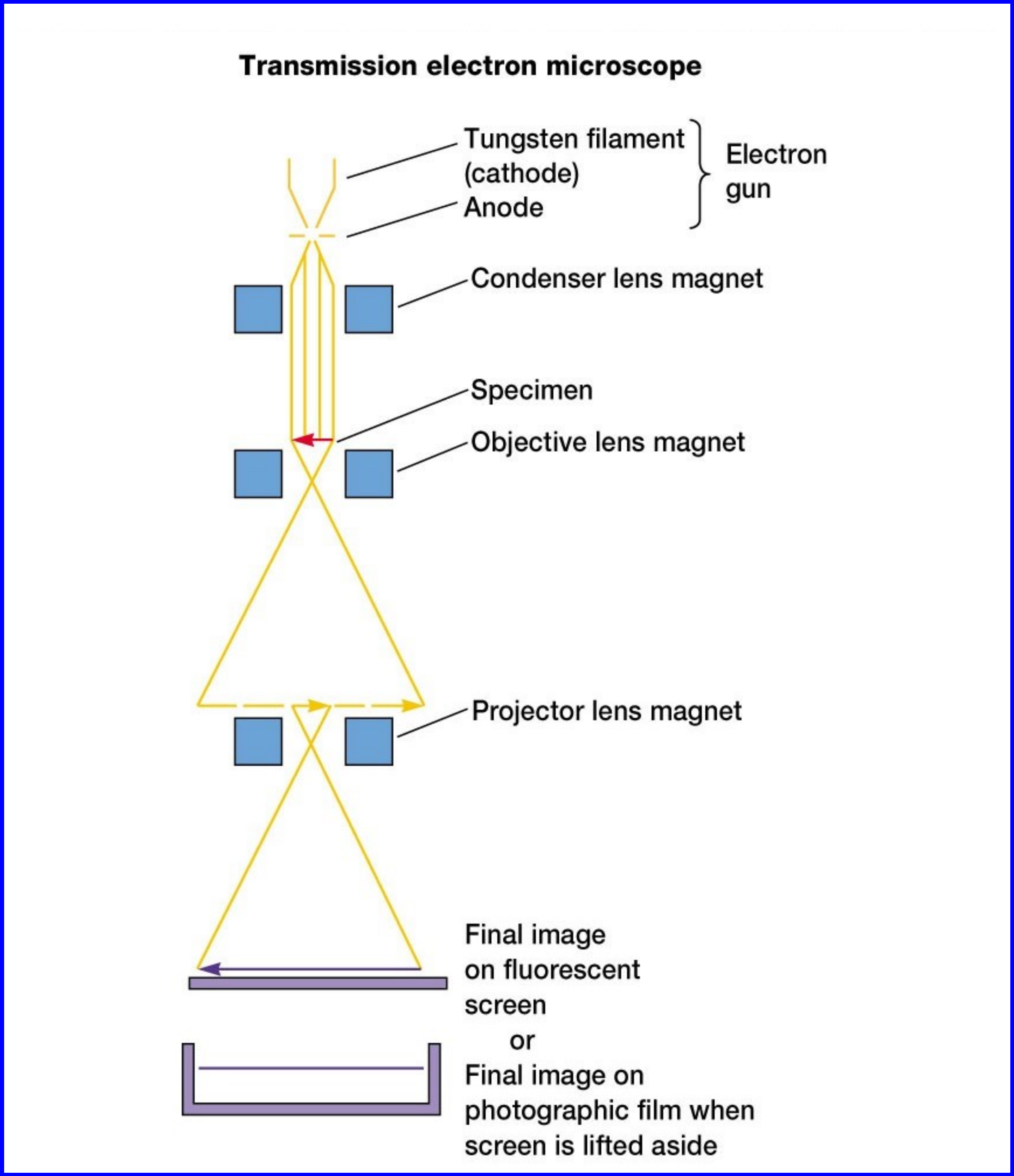
-

The Transmission Electron Microscope

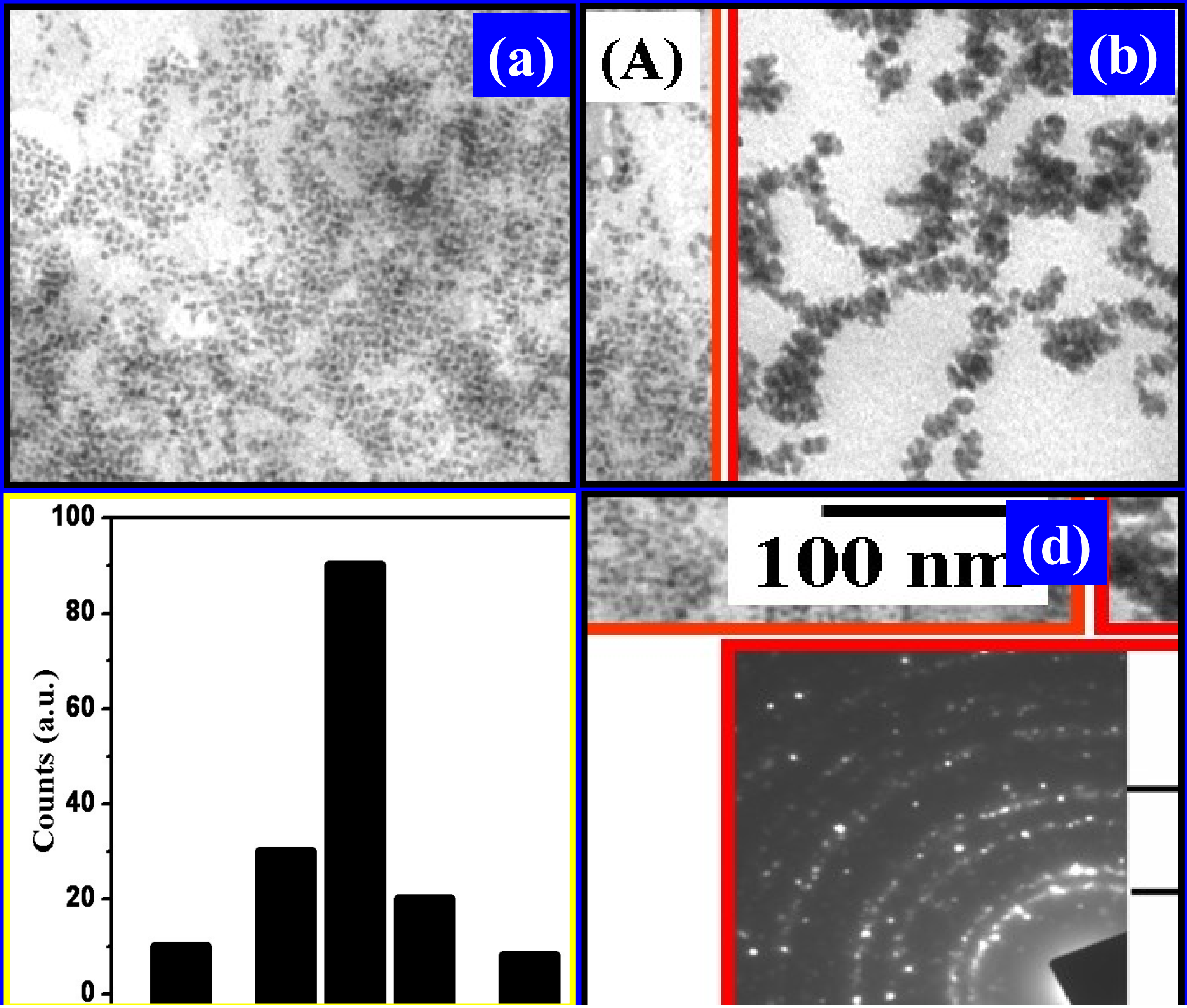
- electrons scatter when they pass through thin sections of a specimen
- transmitted electrons (those that do not scatter) are used to produce image
- denser regions in specimen, scatter more electrons and appear darker

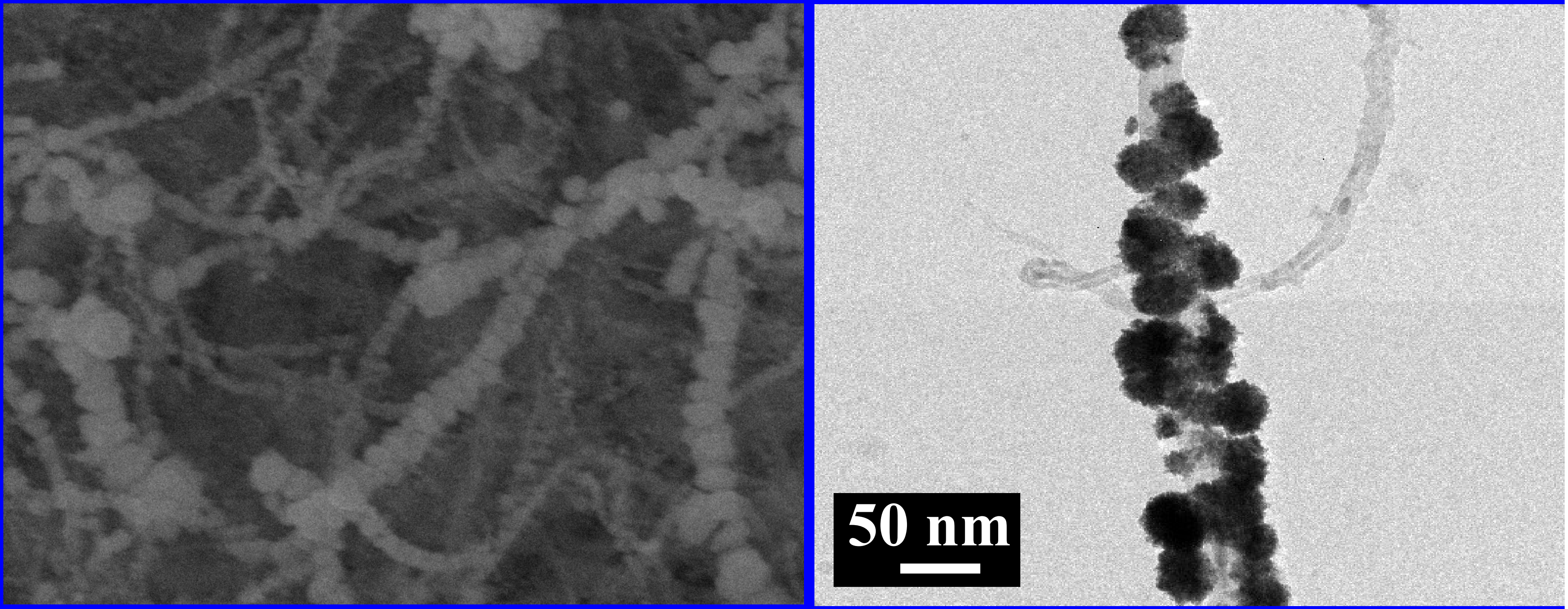


Cu Grid


Transmission electron microscope

TEM (Image and ED)




50 nm

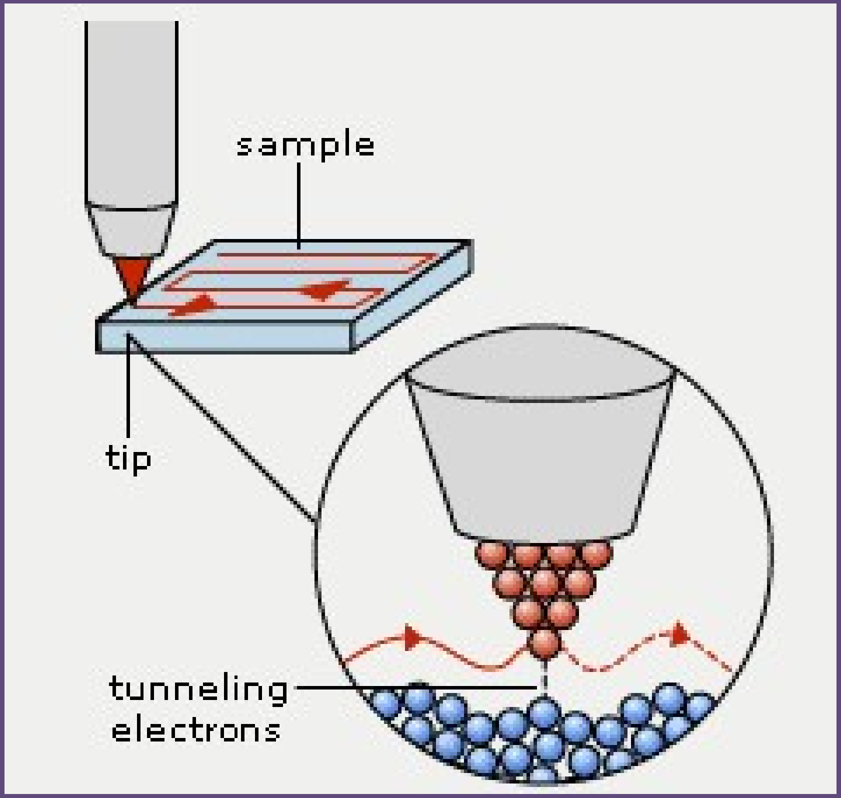
Scanning Probe Microscopy

Scanning Probe Microscopy

- Sharp tip of a metal is scanned across a sample surface
- To produce the images of samples even at subatomic level
- First SPM :- STM- 1982 by Binning and Roher- Nobel Prize in 1986
- AFM and MFM (magnetic force microscope)
- To overcome limitations of individual spectroscopy and microscopes
- Chemical nature/Electronic Structure, Material studies (mechanical, thermal, optical, magnetic and so on)
- No special preparation, Vacuum is not necessary
- Not only insulating, Live biological and even liquid samples can analyse
- Tip materials : Si, Pt-Ir, Pt-Rh……………

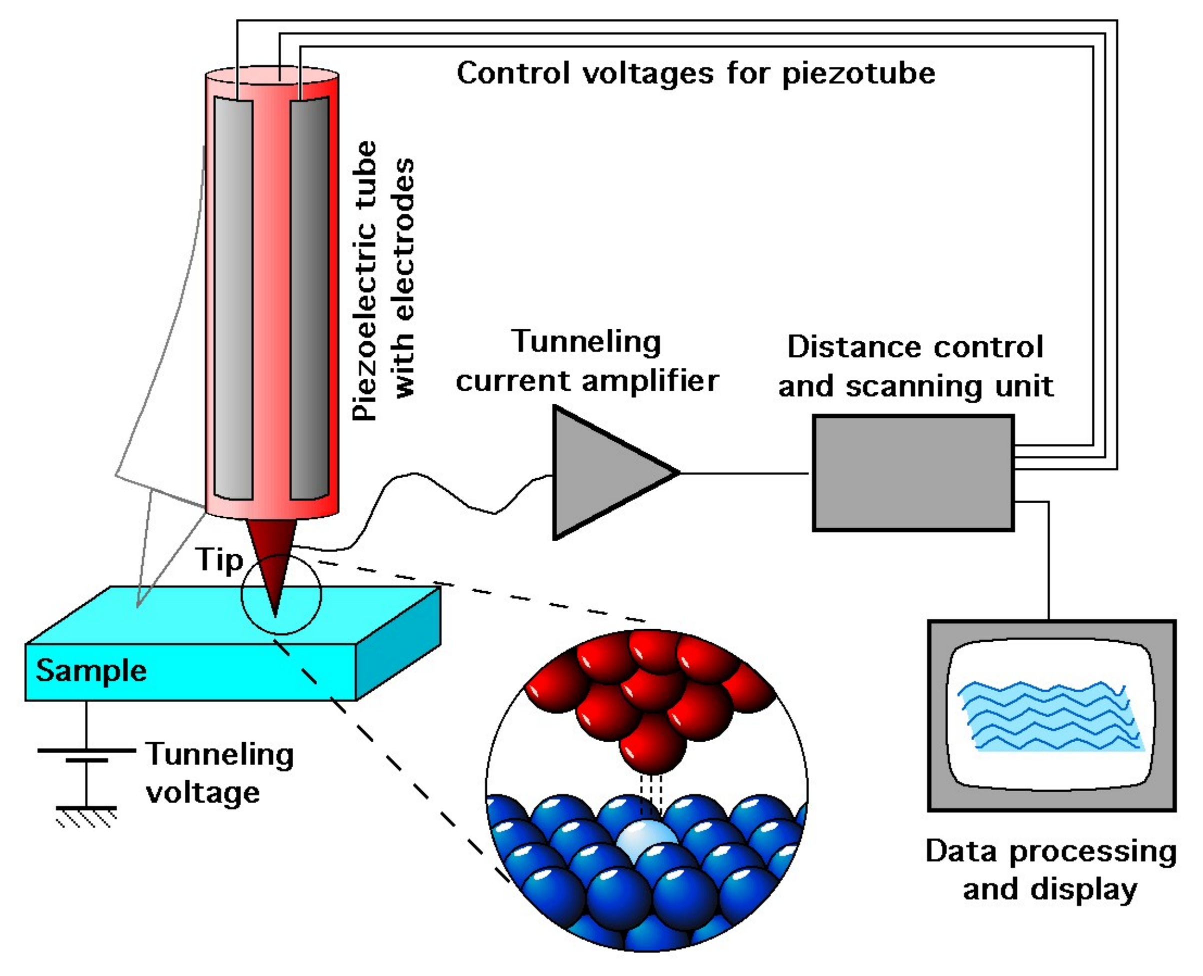
The Scanning Tunneling Microscope (STM)

The STM is an electron microscope that uses a single atom tip to attain atomic resolution.

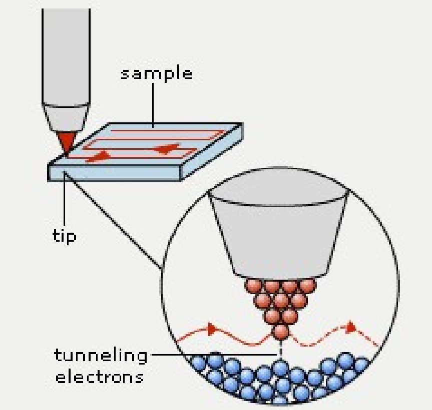


History

The scanning tunneling microscope was developed at IBM Zürich in 1981 by Gerd Binning and Heinrich Rohrer who shared the Nobel Prize for physics in 1986 because of the microscope.



General Overview



- An extremely fine conducting probe is held
- about an atom’s diameter from the sample.

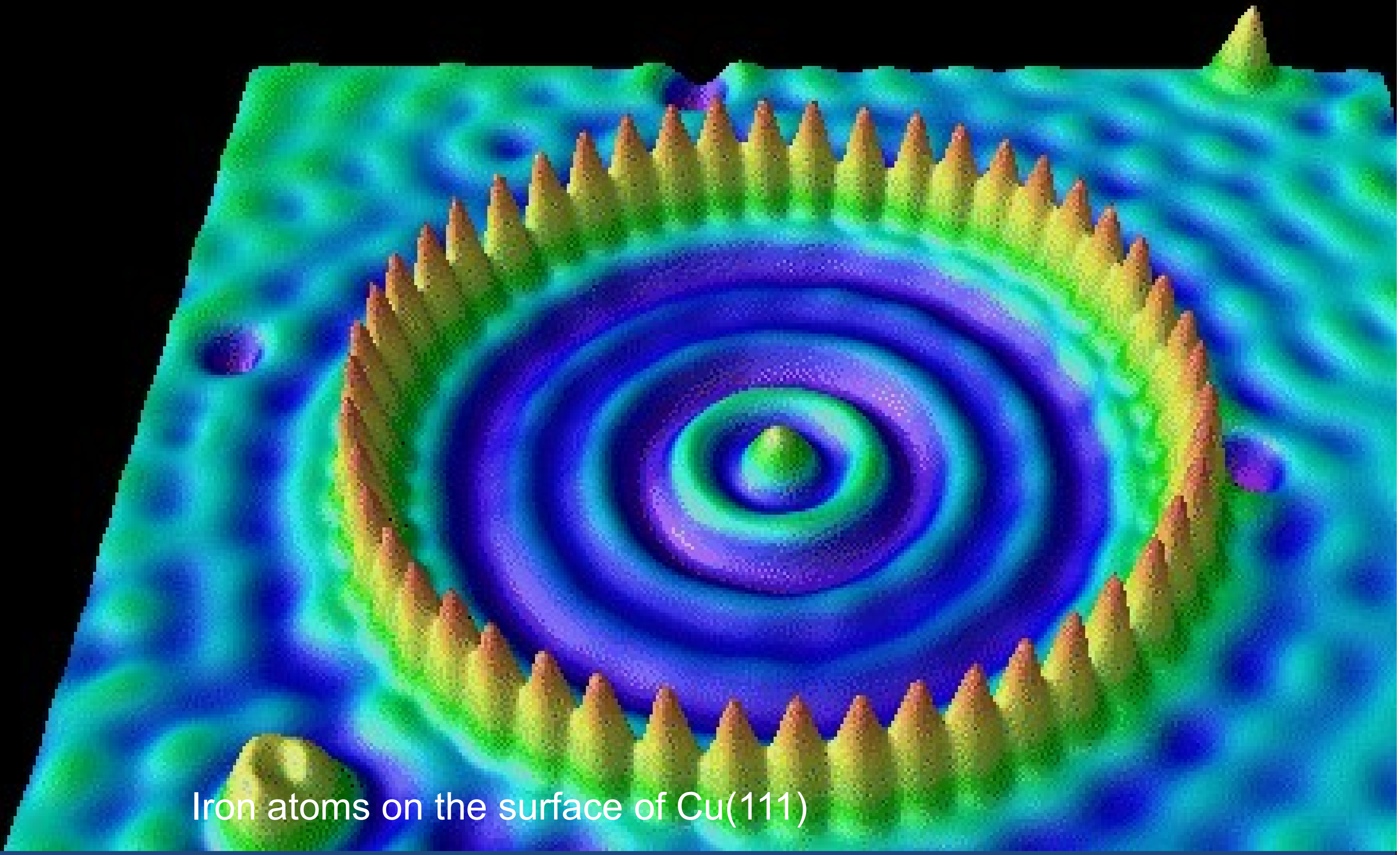
- Electrons tunnel between the surface and the tip, producing an electrical signal.

- While it slowly scans across the surface, the tip is raised and lowered in order to keep the signal constant and maintain the distance.

- This enables it to follow even the smallest details of the surface it is scanning.

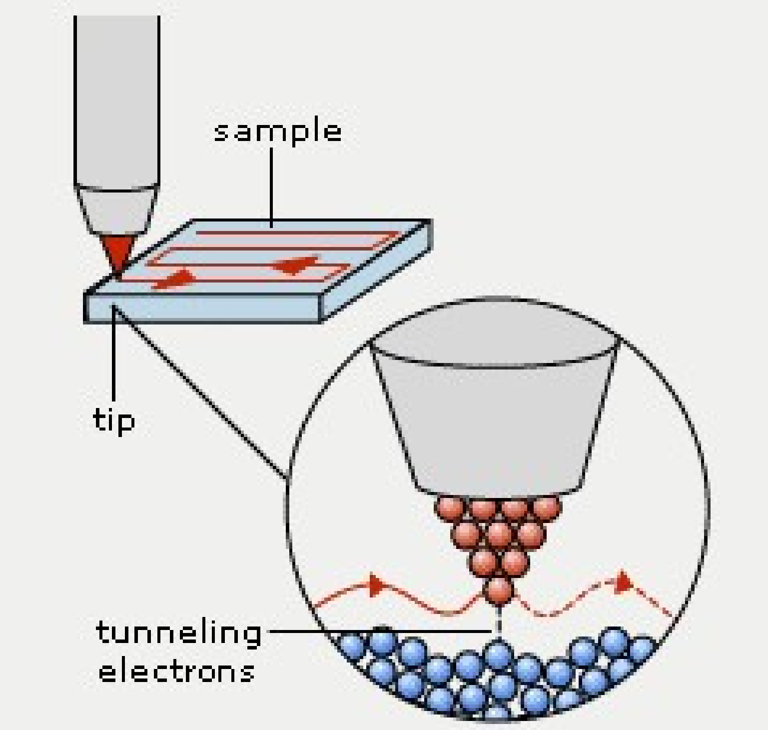
- Depends on work functions of metals

Image from an STM



Iron atoms on the surface of Cu(111)

The Tip



As we will see later, is very important that the tip of the probe be a single atom.

Tungsten is commonly used because you can use Electro-chemical etching techniques to create very sharp tips like the one above.

Quantum Tunneling

So if you bring the tip close enough to the surface,
you can create a tunneling current,
even though there is a break in the circuit.

The size of the gap in practice is on the order
of a couple of Angstroms (10^{-10} m)!

As you can see, the current is VERY sensitive to the gap distance.

STM Operation Modes

Constant Current Mode

Constant Height Mode

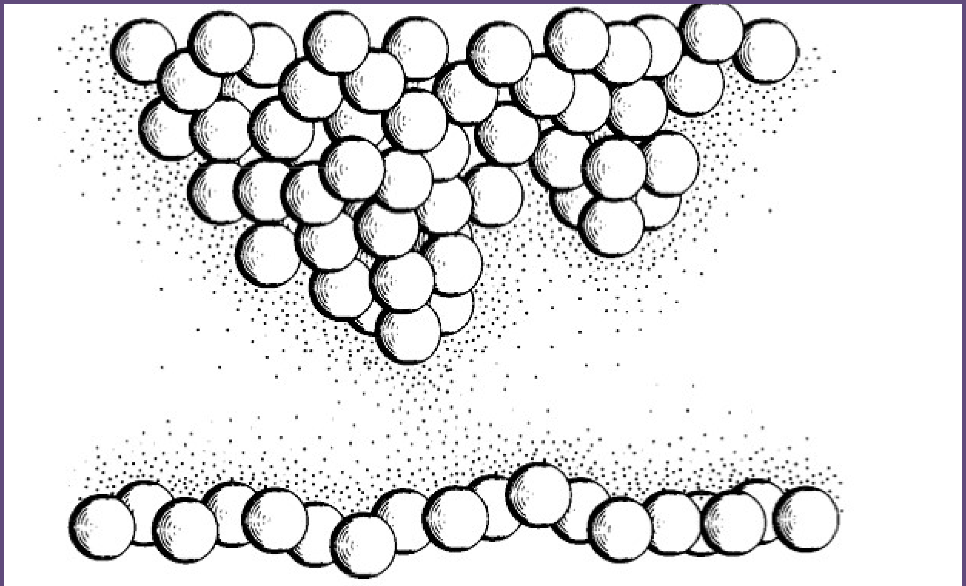
Constant Current Mode

- Sample remains constant and tip is slowly moved on the surface
- In order to maintain constant Current between the tip and sample, the distance between the tip and the atoms of sample needs to kept const
- Controlled by proper feed back loop

Constant Height Mode

- Tip moved on the surface at const height (~0.5 nm)
- Tip can move faster and requires less time as compared to earlier one
- Needs to keep away from the surface
- Results into loss in sensitivity

Problems with Tip



The second tip shown above is recessed by about two atoms and thus carries about a million times less current. That is why we want such a fine tip. If we can get a single atom at the tip, the vast majority of the current will run through it and thus give us atomic resolution.

Note

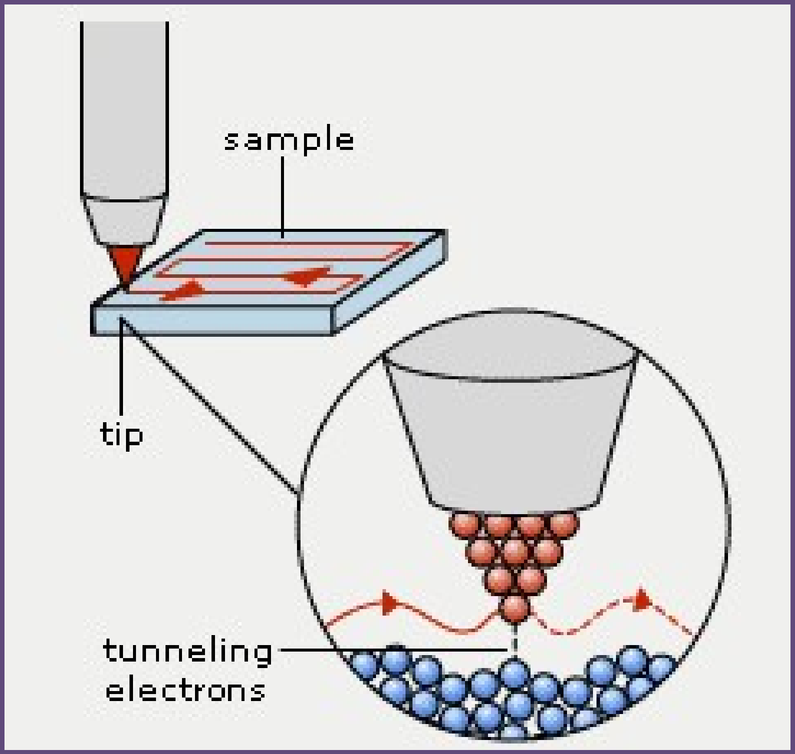
A STM does not measure nuclear position directly.

Rather it measures the electron density clouds on the surface of the sample.

In some cases, the electron clouds represent the atom locations pretty well, but not always.

Small Movements

To get the distance between the tip and the sample down to a couple of Angstroms where the tunneling current is at a measurable level, STMs use feedback servo loops and converse piezoelectricity.



Problems and Solutions

- Bringing the tip close to the surface and scanning the surface
    - **Feedback Servo Loops**
- Keeping the tip close to the surface
    - **Converse Piezoelectricity**
- Creating a very fine tip
    - **Electro-chemical etching**
- Forces between tip and sample
    - **Negligible in most cases**
- Mechanical vibrations and acoustic noise
    - **Soft suspension of the microscope within an ultra high vacuum chamber (**10^{-11} Torr)
- Thermal length fluctuations of the sample and especially the tip
    - **Very low temperatures**

- The sample has to be able to conduct electricity
    - **There is no way around this, try using an AFM**

Different STM Ideas

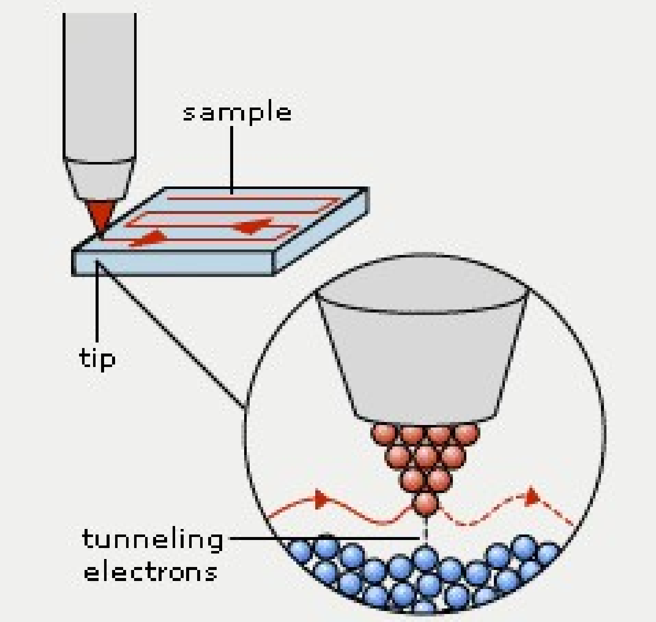
You could decide not to use piezoelectricity to keep the distance between the tip and the surface equal at all times, and instead use the current measurements to determine the surface of a sample.

Pros:

- You can scan much faster

Cons:

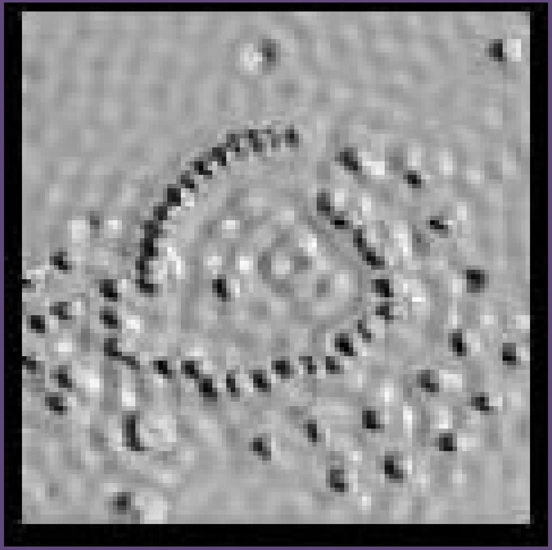
- The surface must not have cavities more than a few Angstroms deep (an atom or two) because of tunneling



Different STM Ideas

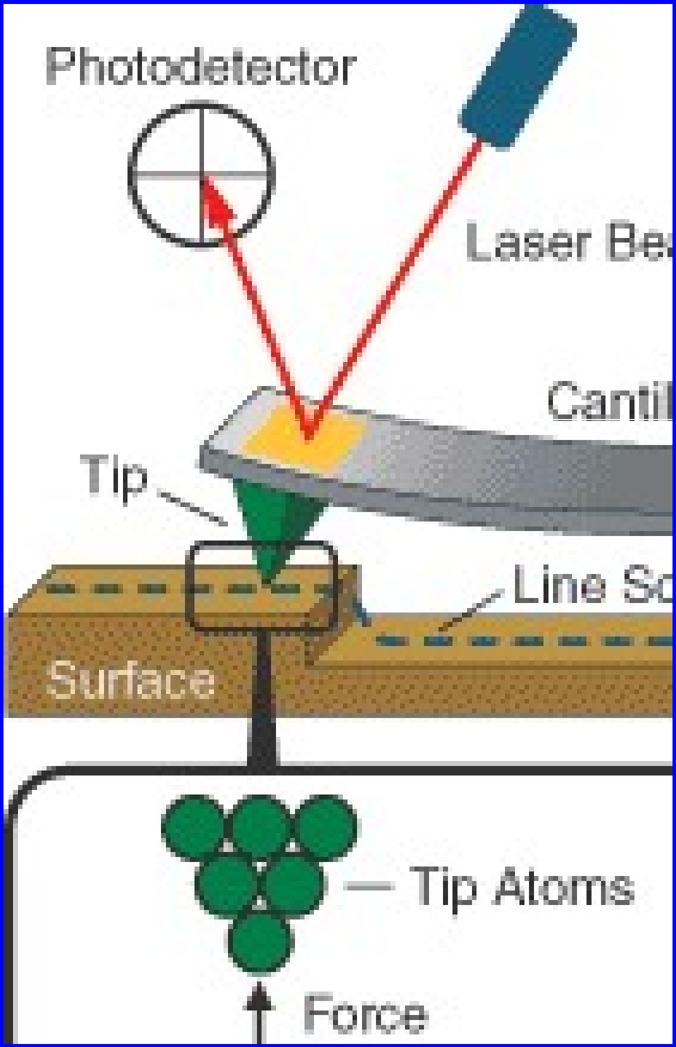
Imagine increasing the tunneling current when you are on top of an atom by lowering the tip a little. The attractive force between the tip and the atom would then increase, allowing you to “drag” atoms around.

IBM imagined this. Iron atoms were first physisorbed (stuck together using intermolecular forces, aka Van Der Waals forces) on a Cu surface. The iron atoms show up as bumps below.



Atomic Force Microscopy

How It Works



http://www.molec.com/what_is_afm.html

- Invented in 1986
- Cantilever
- Tip
- Surface
- Laser
- Multi-segment photodetector

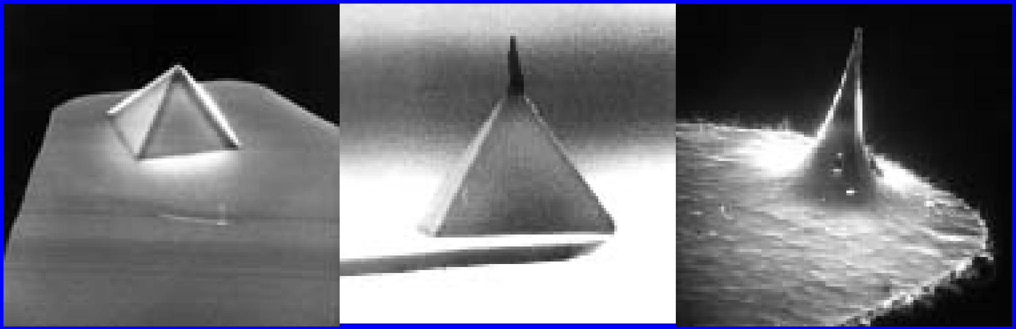
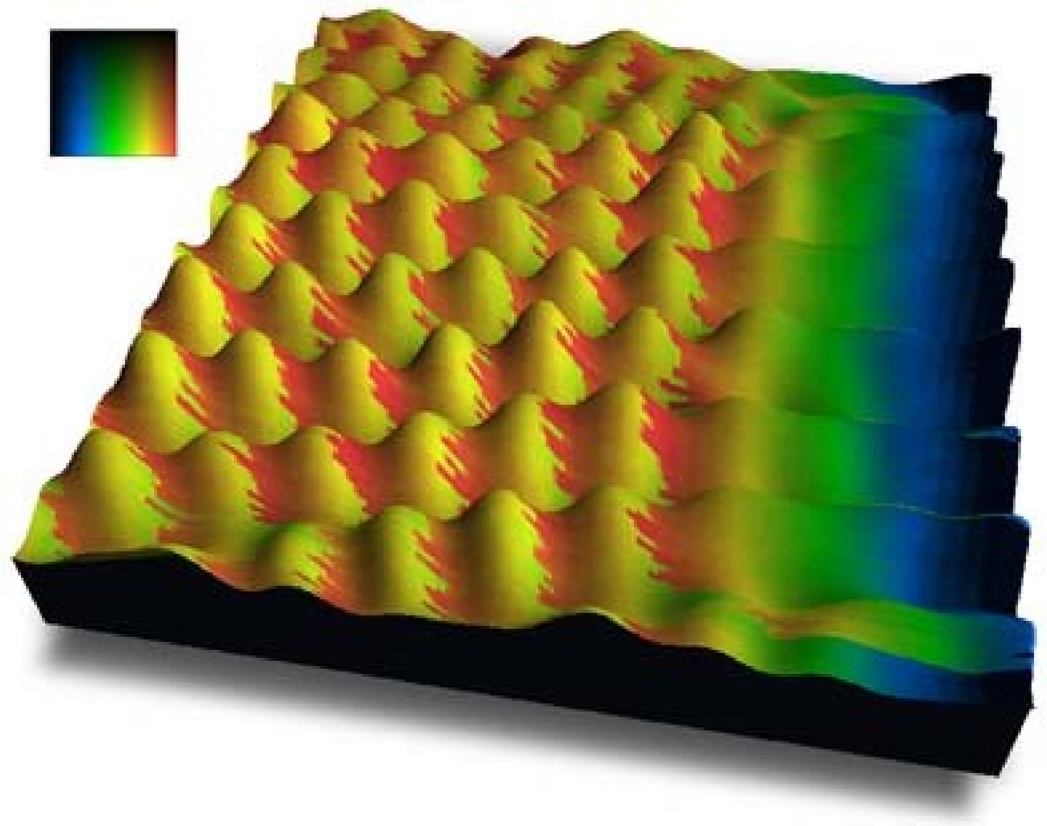


Figure 4. Three common types of AFM tip. (a) normal tip (3 µm tall); (b) supertip; (c) Ultralever (also 3 µm tall). Electron micrographs by Jean-Paul Revel, Caltech. Tips from Park Scientific Instruments; supertip made by Jean-Paul Revel.

http://stm2.nrl.navy.mil/how-afm/how-afm.html#imaging%20modes

Topography

- Contact Mode
  - High resolution
  - Damage to sample
  - Can measure frictional forces
- Non-Contact Mode
  - Lower resolution
  - No damage to sample
- Tapping Mode
  - Better resolution
  - Minimal damage to sample



2.5 x 2.5 nm simultaneous topographic and friction image of highly oriented pyrolytic graphic (HOPG). The bumps represent the topographic atomic corrugation, while the coloring reflects the lateral forces on the tip. The scan direction was right to left

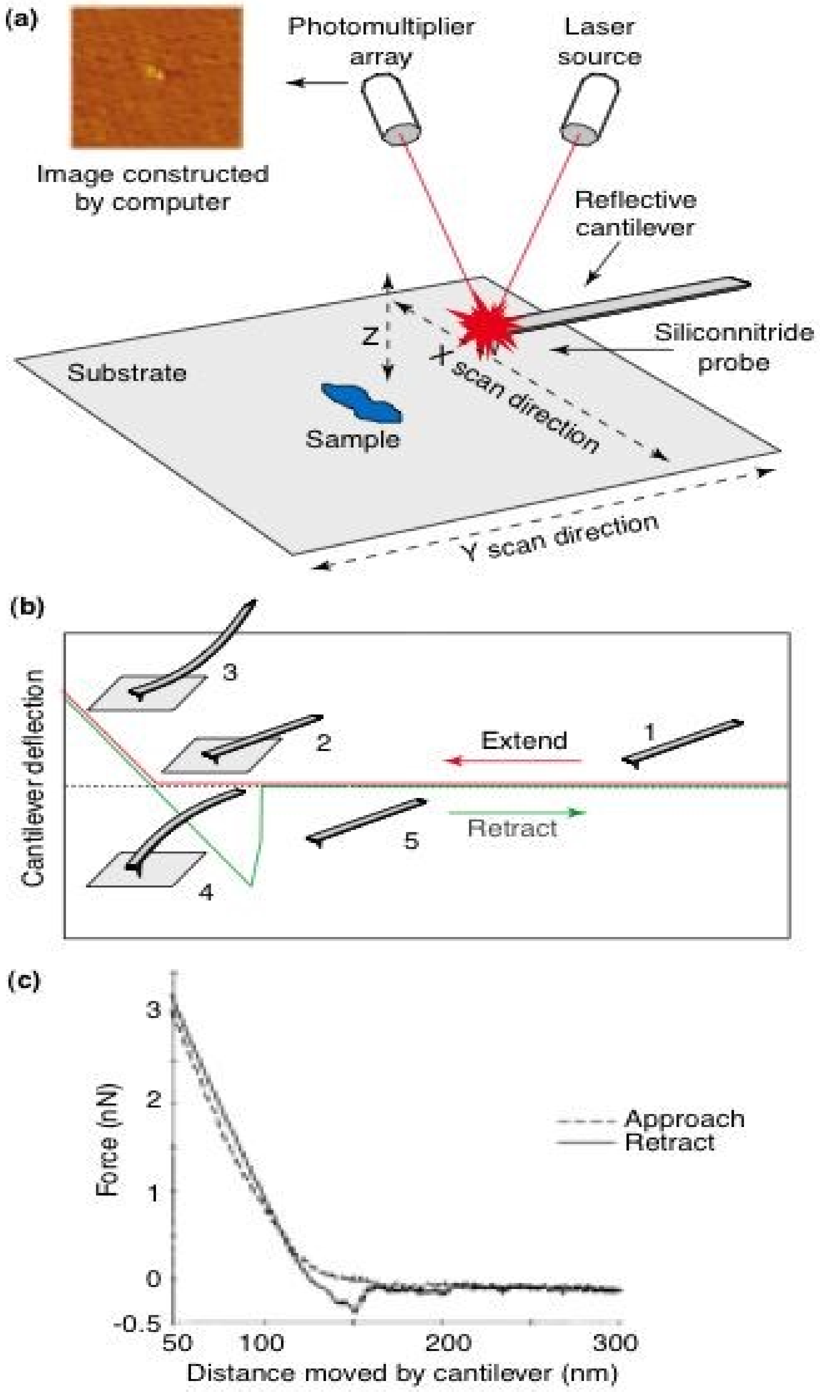
http://stm2.nrl.navy.mil/how-afm/how-afm.html#imaging%20modes

Approach

- In the approach the tip is not yet in contact with the surface
- Attractive forces maybe
- Repulsive forces definitely
  - Due to contact
  - Gives information about the elasticity or stiffness of sample

Retraction

- Attractive forces again during the retraction phase
  - Chemical and/or electrostatic
- Break of attractive forces due to retraction of the tip > characteristic “jump” in force curve



Drug Discovery Today

Figure 1. Operation of the atomic force microscope. **(a)** The principle of AFM. A fine pyramidal silicon nitride tip at the end of a reflective cantilever is scanned back and forth over the substrate in a raster pattern. As the tip is deflected by the sample, the cantilever also deflects, and the magnitude of the deflection is registered by the change in direction of a laser beam that is reflected off the end of the cantilever and detected by a photomultiplier array. In this way, a topological map of the surface is constructed. **(b)** The principle of the force curve. The tip is held stationary over the substrate and then oscillated up and down ('extended' and 'retracted'). At point '1' the tip is not in contact with any substrate and so no deflection is registered. At '2' the probe meets the substrate, and at '3' it is advanced further downwards onto the substrate and so the cantilever bearing the probe is deflected. This is shown in the 'y' axis of the curve. The piezo drivers then begin to withdraw the probe upwards ('retract'). Because the probe and substrate are physically attracted, they maintain contact '4', even when the probe has been withdrawn before the point where it originally made contact with the substrate. At point '5', the probe loses contact with the substrate and jumps back to its original position, as does the 'retract' curve. The measure of the force of attraction between tip and substrate is given broadly by the size and shape of the triangle lying below the dotted line in the diagram. **(c)** The measurement of the force between a biotinylated AFM tip and a streptavidin-coated substrate. The 'retract' trace shows the breakage of the attachment between streptavidin and biotin and the force measured is approximately 300 pN. Part **(c)** of this figure is adapted from Reference [5].

J Michael Edwardson and Robert M. Henderson

DDT Vol. 9, No. 2 January 2004

AFM Operation Modes

Contact Mode

Non-contact Mode

Tapping Mode

Who Needs It

- Vacuum, Air, Aqueous Medium - Mimic Biological Environment
- Sub-nanometer resolution
- Manipulate Surface with Molecular Precision
- Real Time Direct Structure-Function Studies

- 3-D Surface Topography
- Force Measurements in pico-Newton - nano-Newton range
- May Be Combined Simultaneously With Other Techniques
  - AFM with Flourescence
  - AFM with Patch-Clamp

Applications

- Study Unfolding Of Proteins
- Imagining Of Biomolecules
- Force Measurements In Real Solvent Environments
- Antibody-Antigen Binding Studies
- Ligand-Receptor Binding Studies
- Binding Forces Of Complimentary DNA Strands
- Study Surface Frictional Forces
- Ion Channel Localization

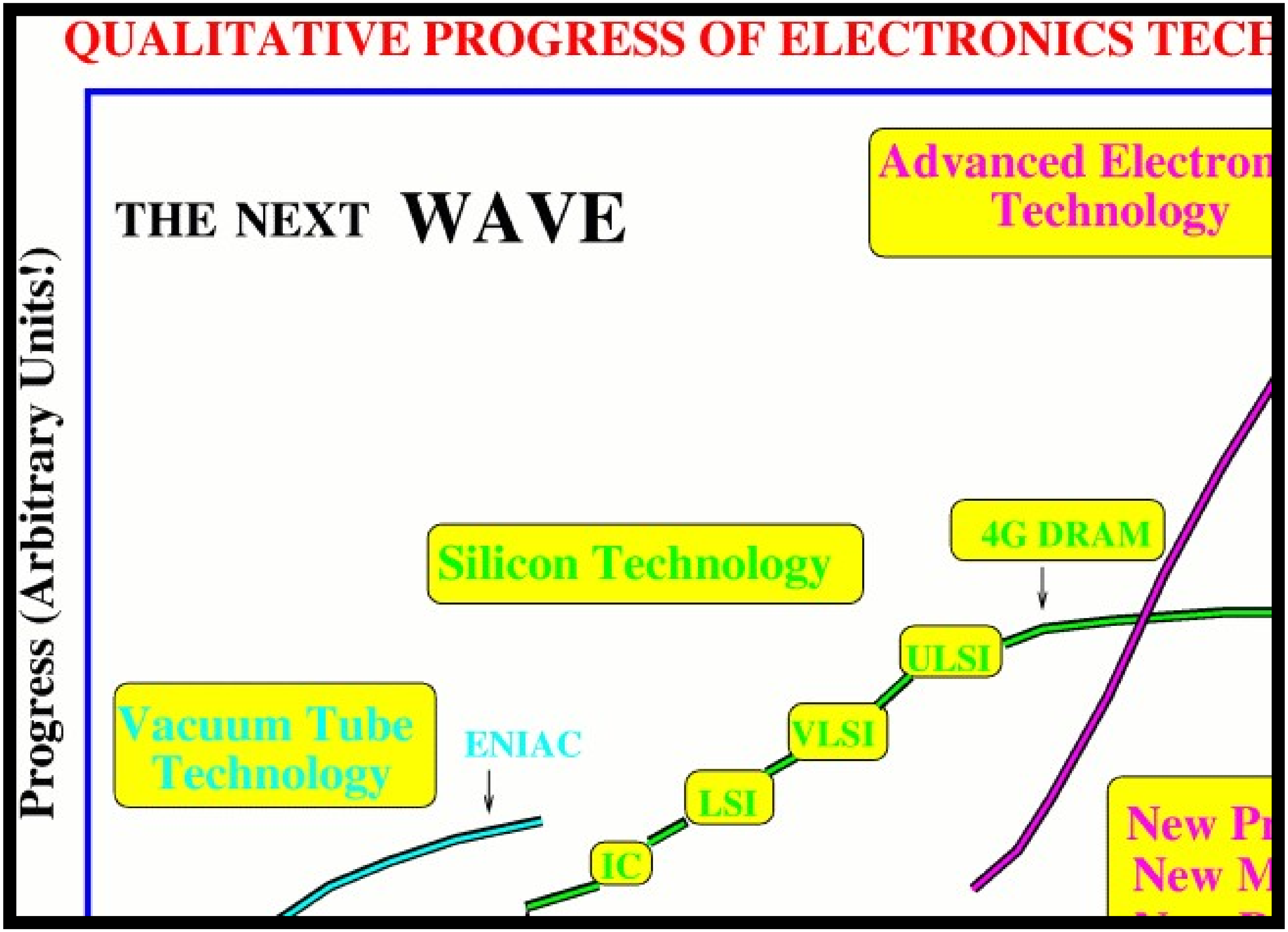
Properties of Nanomaterials

Mechanical Properties

- Depends on composition of bonds between the atoms
- Presence of impurities affect on properties Like (O, N, C, P, S)
- Single nanoparticle study is difficult …..Study on nanocrystalline materials is possible

Electrical Properties

Moor’s Law



Larger grain boundaries

Good candidate for the energy/storage

What is the reason for interesting Electrical behavior?

- MPCs are tiny capacitor (10^{-18} F).

- Single Electron charging at RT.

- Charge transport is possible, if,
  $E_c >> K_B T$.

- $E_c \approx e^2/2C$; where, C= Capacitance of the MPC

How does the Capacitance of MPC's can be calculated?

- **Spherical Shell Capacitor Model**

MPCs can be viewed as a spherical capacitor covered by a dielectric thin shell.

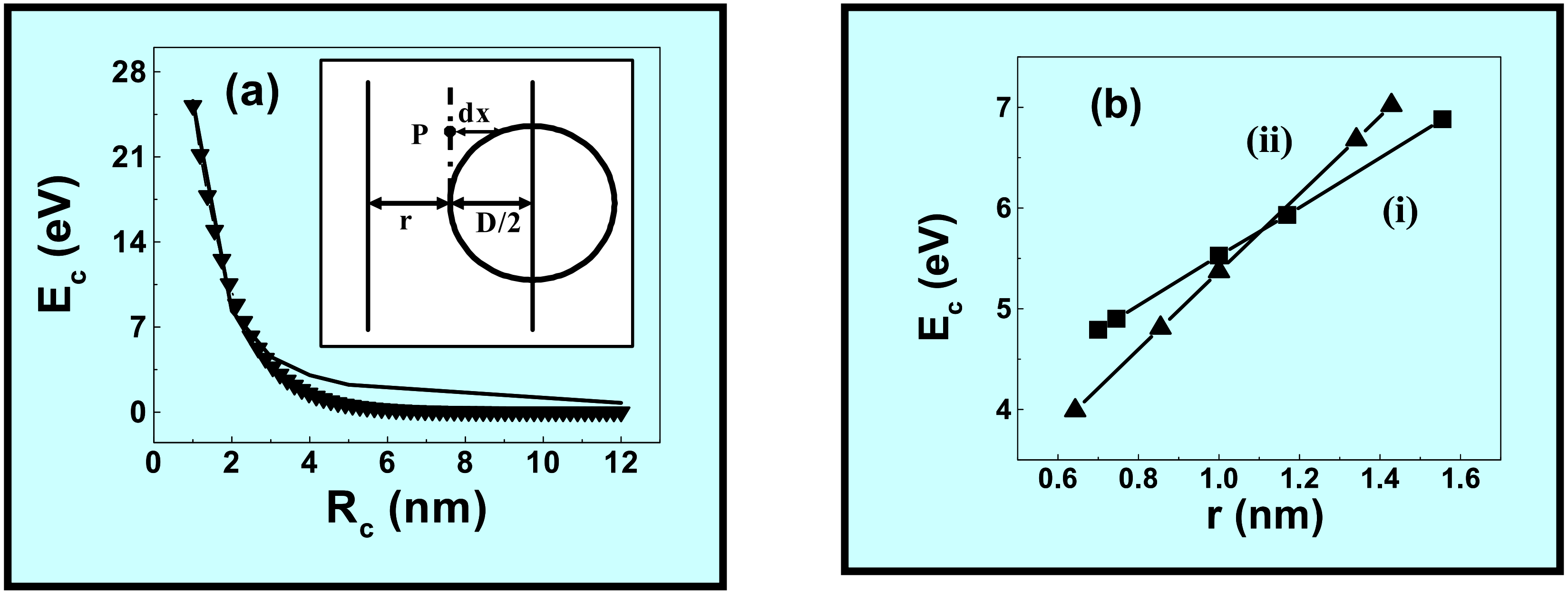
Accordingly,

$$\mathbf{C = 4\pi\varepsilon_o\varepsilon_r rR/R\text{-}[r(1\text{-}\varepsilon_r)] ,}$$

&

$$\mathbf{E_c = e^2 [D_c -(r(1- \varepsilon_r))] /8\pi\varepsilon_o\varepsilon_r rD_c}$$

How E_c depends on the length of the capping molecules and size of the clusters?

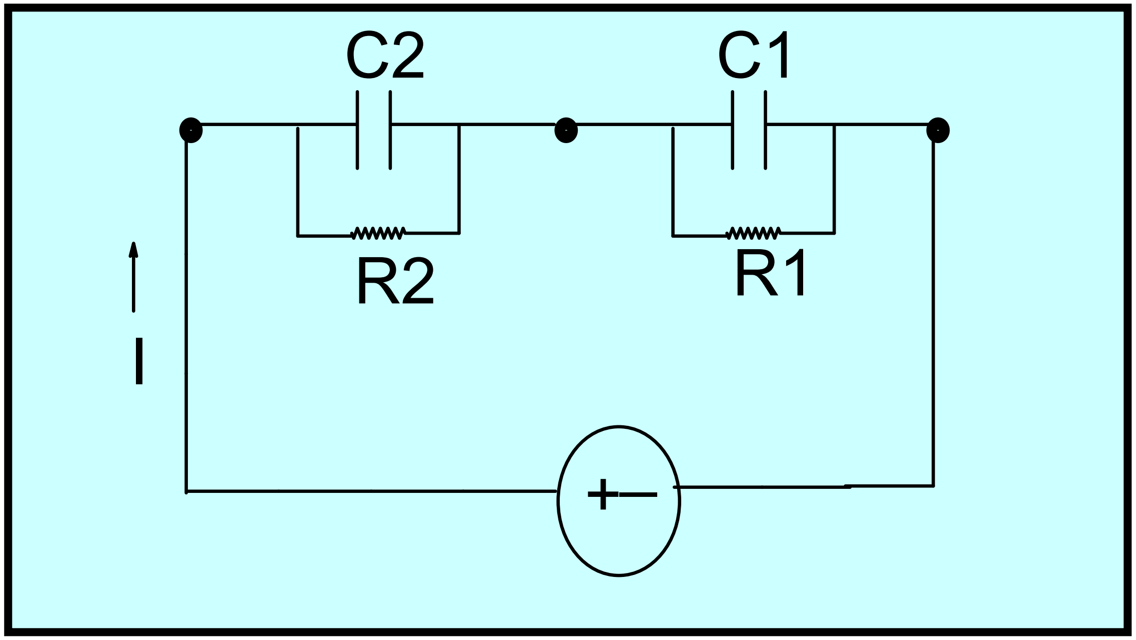


Variation of E_c with (a) size of MPCs and (b) with the length of the capping molecule by two different approximation (i) Curved metallic surface embedded in dielectric media (ii) Spherical shell model.

How to Measure Electrical property?

- **Creation of a Metal-Insulator-Metal junction (MIM) junction**
- **Applying a bias Voltage from an external Voltage source.**
- **A Double Barrier Tunnel Junction (DBTJ) is formed during I-V measurement**
- **I-V of single particle measured by STM.**
- **Electrical conductivity of nanomaterials, polycrystalline materials ; always greater than single crystal materials: Grain size effects**

What is the Double Barrier Tunnel Junction structure?



C_1 & C_2 = Capacitance

R_1 & R_2 = Resistance

Why Single Electron Transfer?

- MPCs are surrounded by thin dielectric media, thus creating Quantum Well structure.

- Small capacitive natures (10^{-18} F) allows them to charge with a single electron.

- SET can be visualized in I-V measurements as Coulomb Blockade behavior at RT, provided particle size is small (< 10 nm).

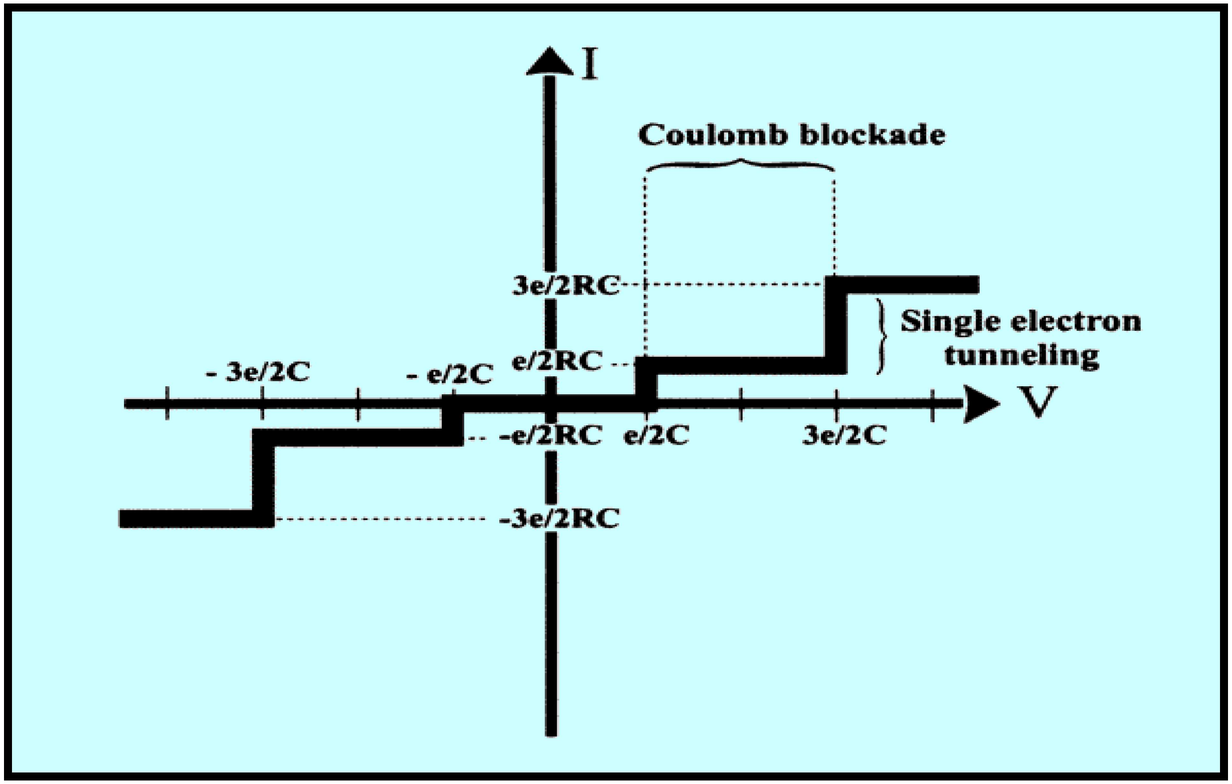
What is the Coulomb Blockade Behavior?

- The columbic interaction between electrons can prohibit their transport around a circuit; occurs in system when

$$E_c >> K_BT \ \& \ R_T >> h/e^2.$$

- Current steps are observed by voltage plateaus in I-V curve, when MIM junction is biased by an external voltage source.
- Voltage plateaus are known as Coulomb Blockade.
- Coulomb Blockade width is depends on size of the MPCs and intercluster spacing.

Ideal Coulomb Blockade Behavior of a DBTJ



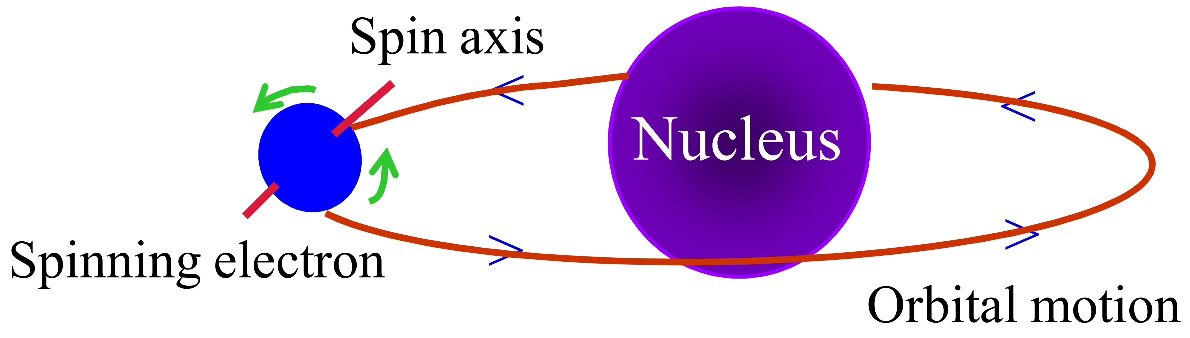
Current step are observed due to addition of one e to the MPC, which can be seen ideally after a successive Δ V corresponding to e/c.

Magnetic Properties

Magnetic Moments of Electrons

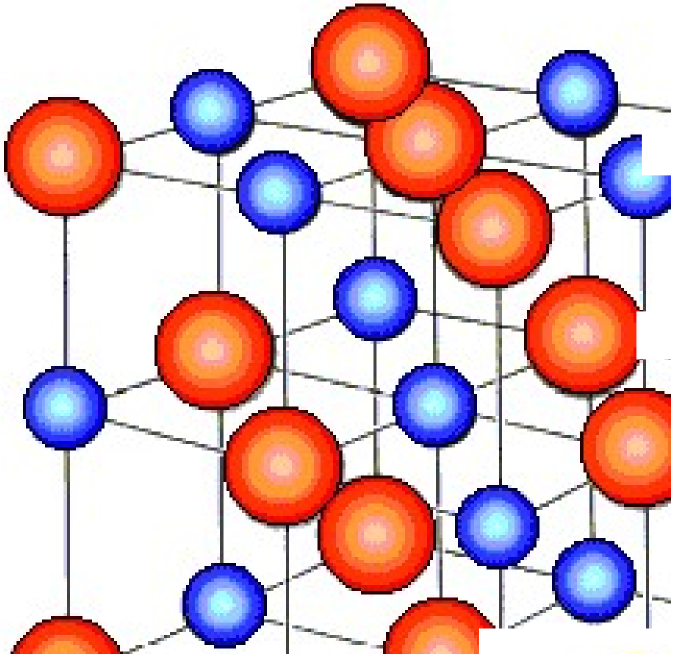
- Orbital motion
- Spin motion

Each has a magnetic moment

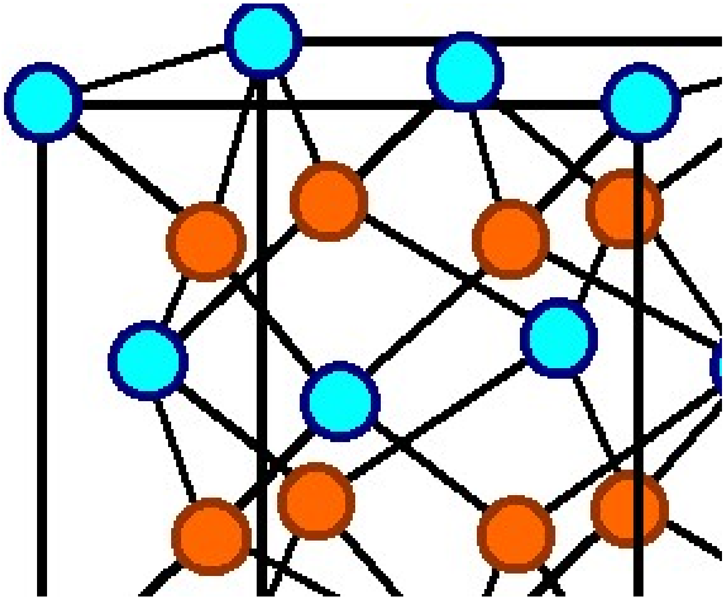


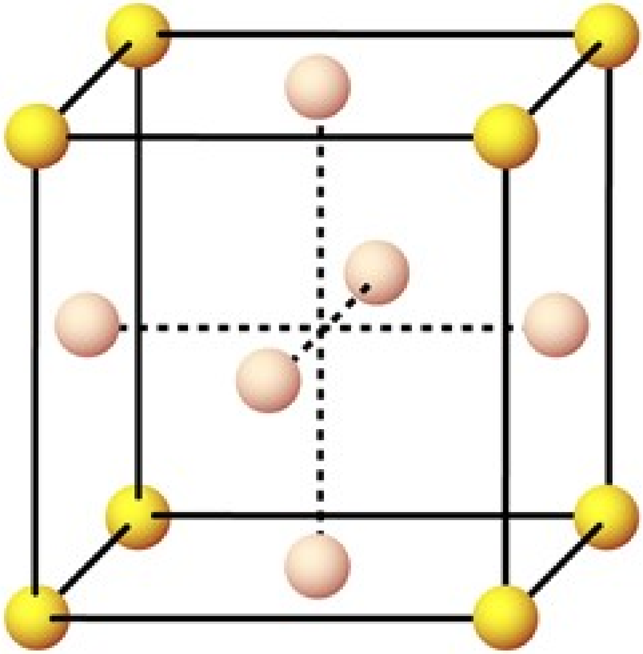
Magnetism due to unpaired electrons

d-block and f-block elements

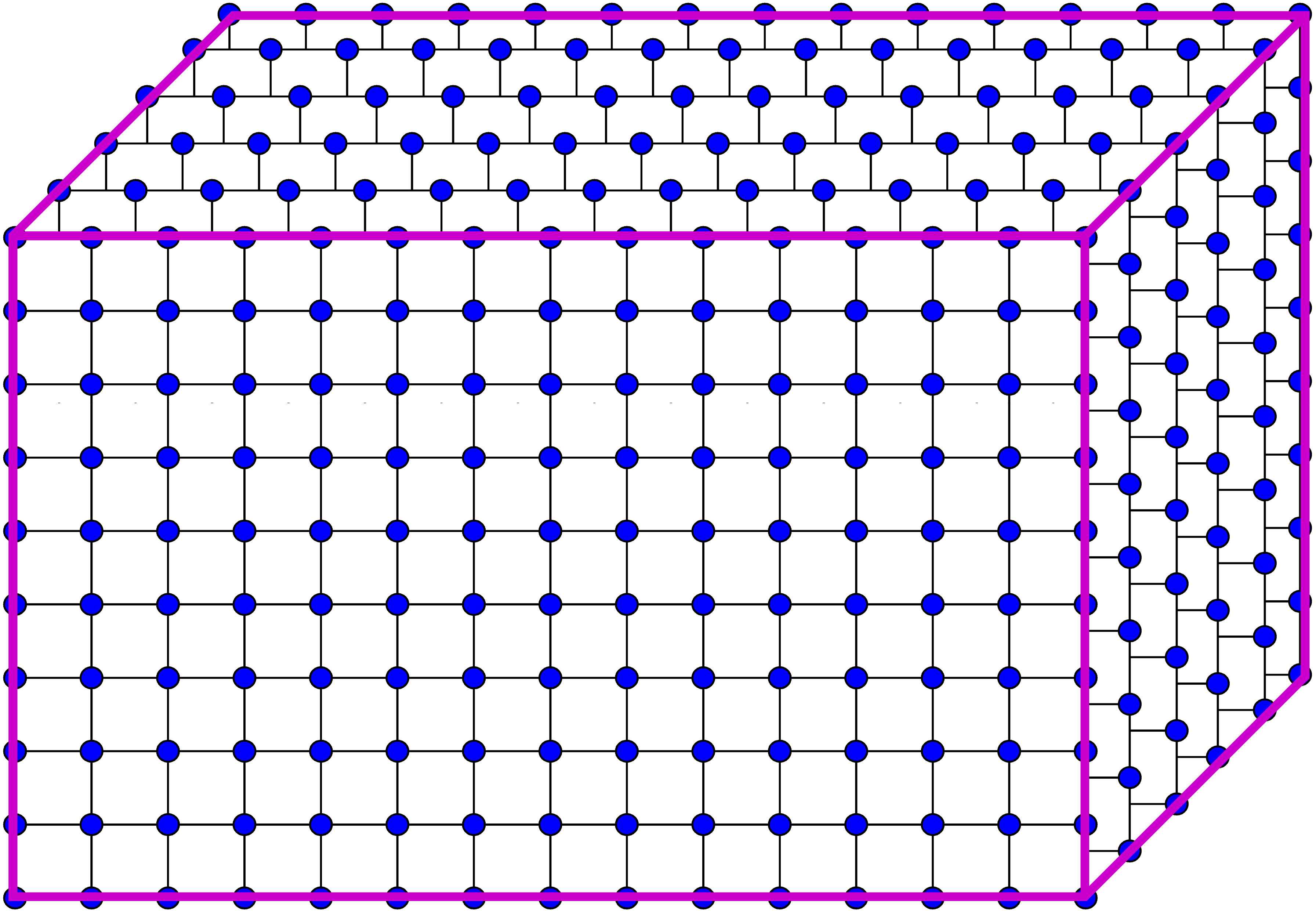


Solids

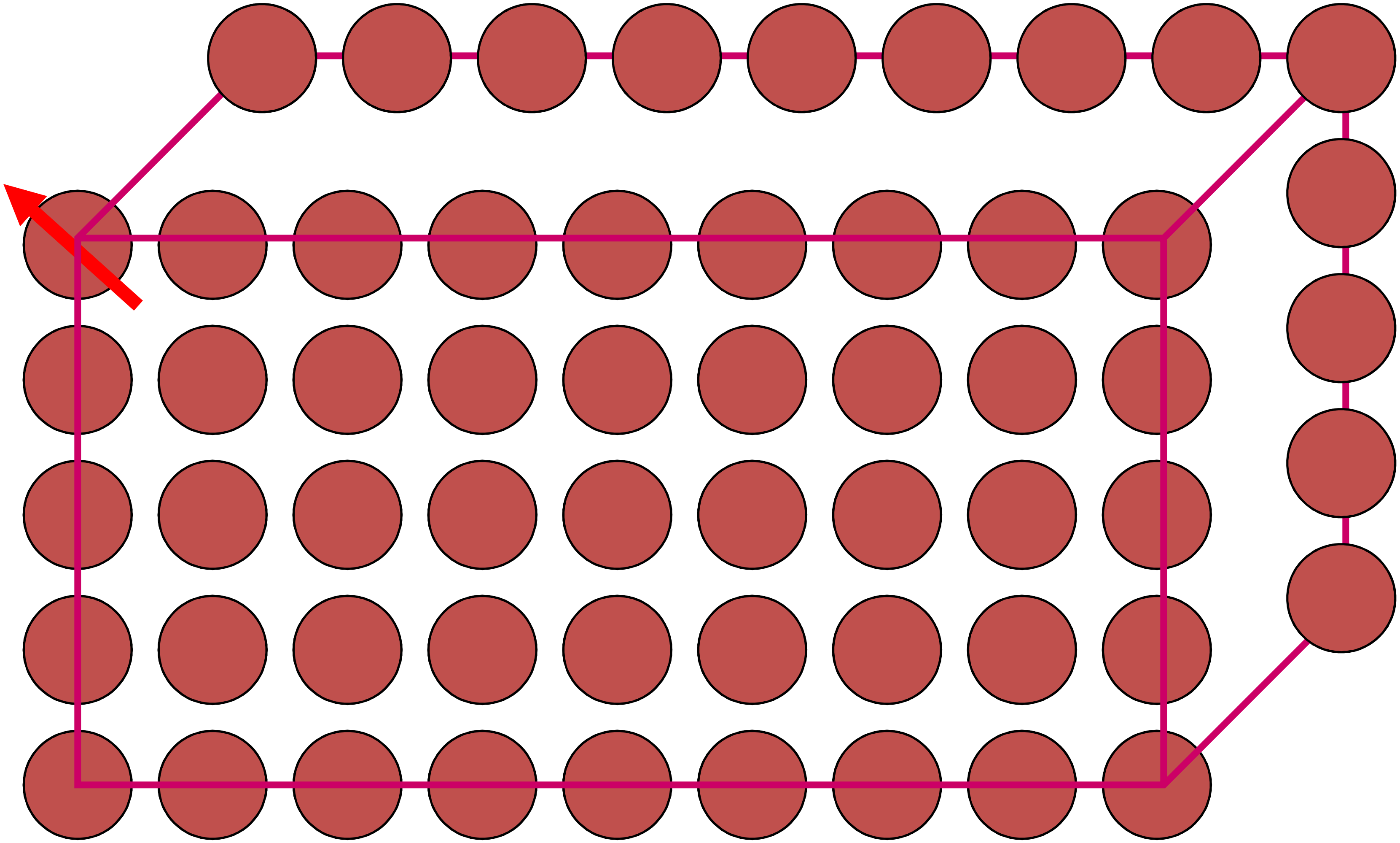




Solids – array of atoms in 3 dimension

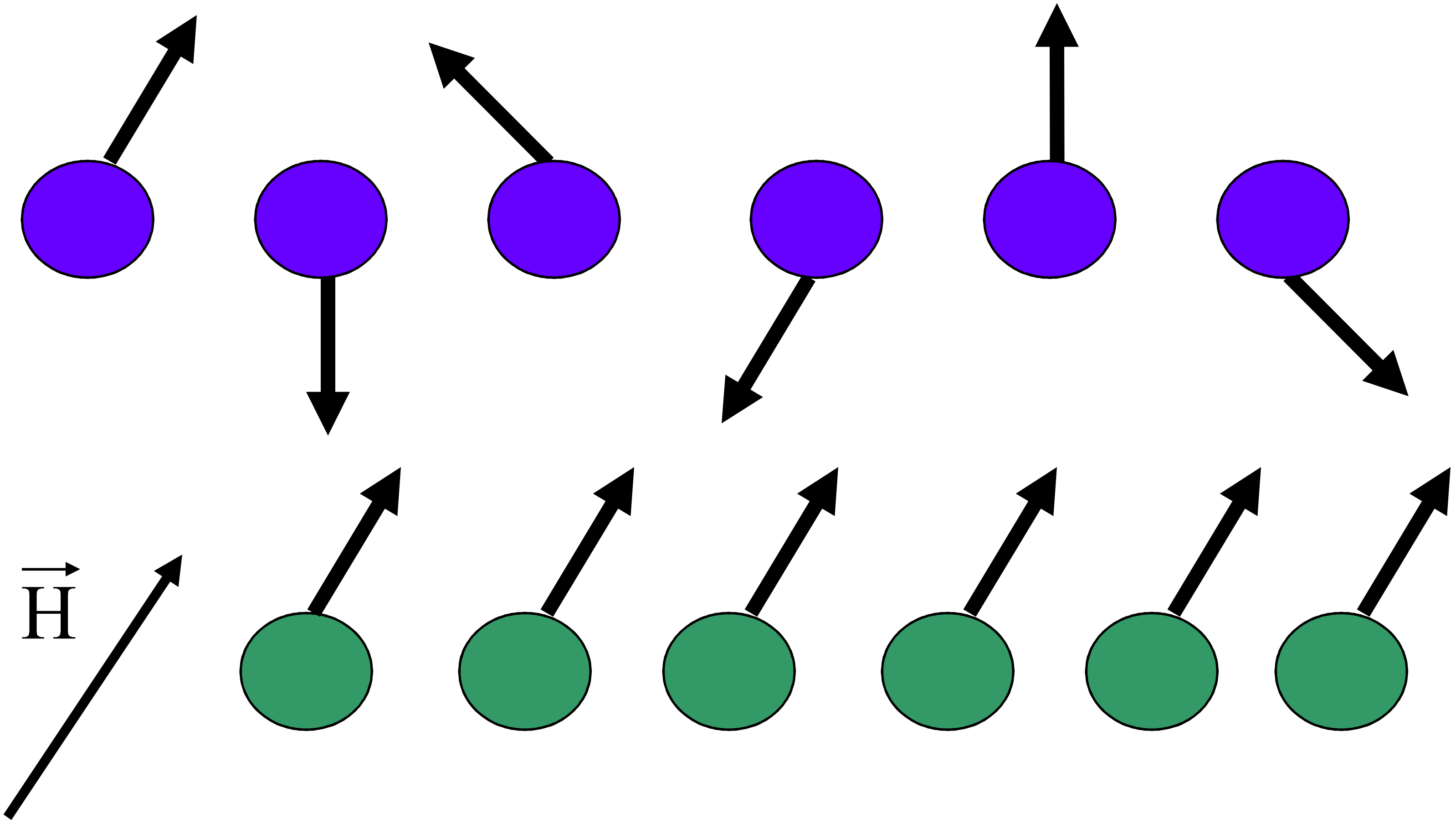


Magnetism in Solids

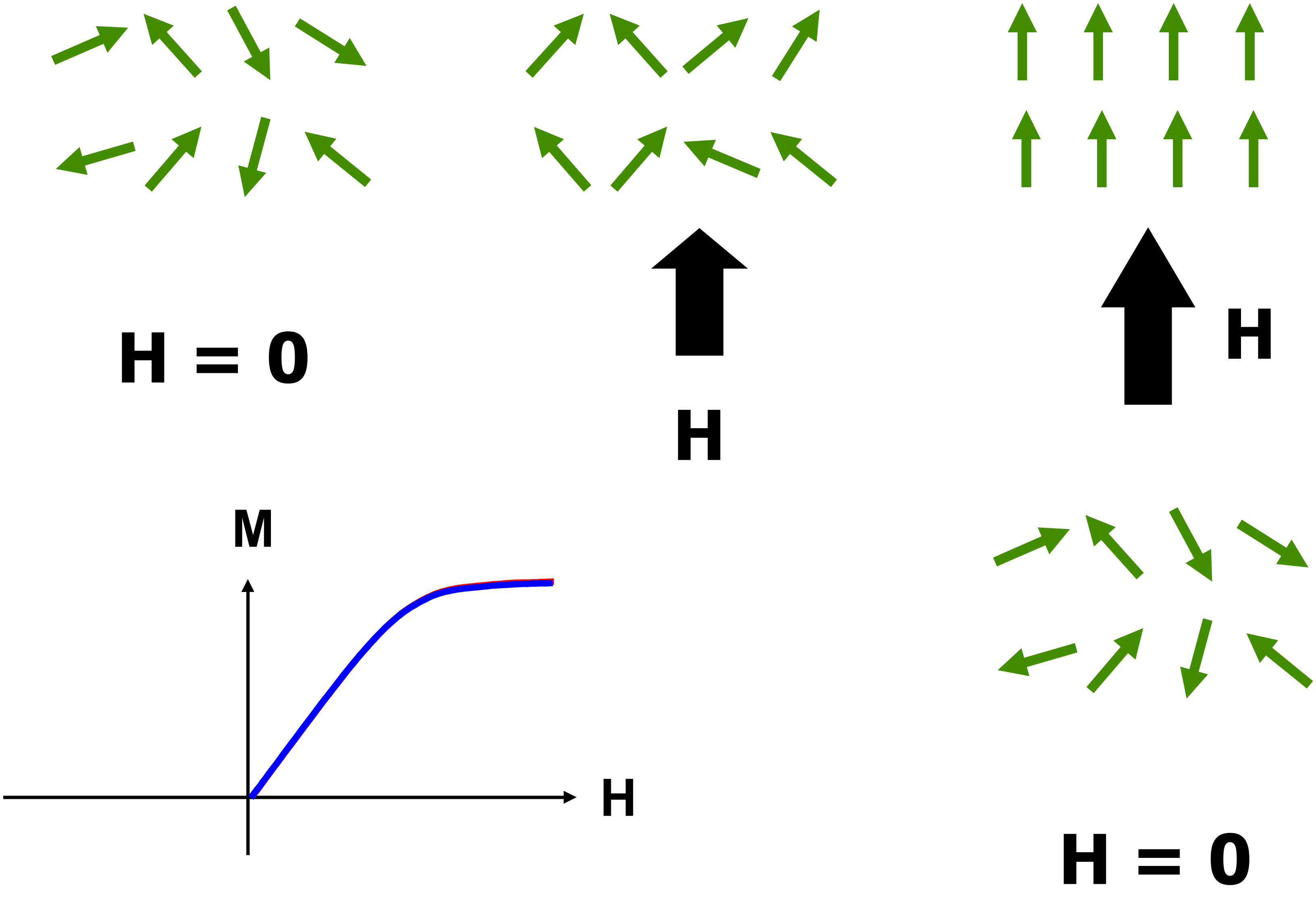


Orientation of magnetic moments in individual atoms/ions in a solid

Paramagnetism

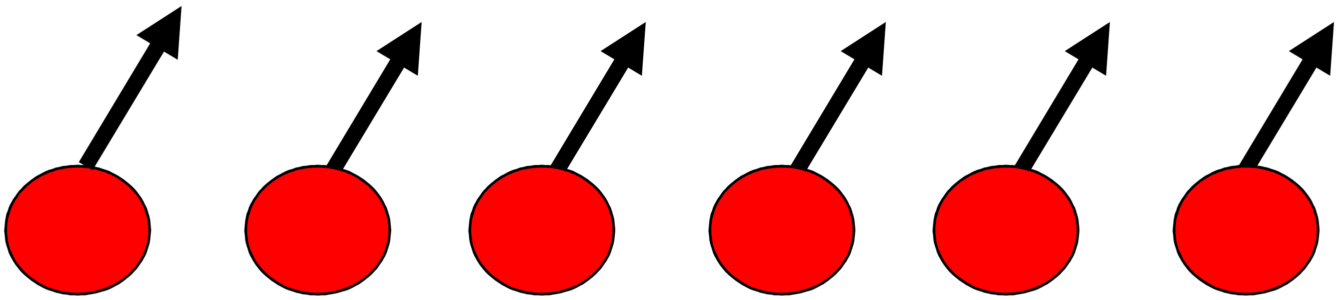


Paramagnetism

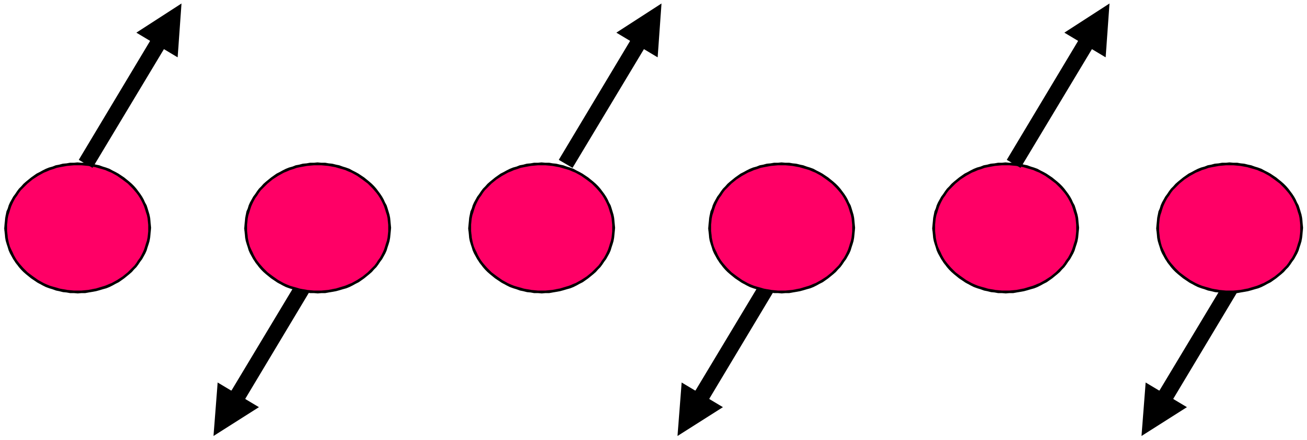


Spontaneous Magnetization (H=0)
Long Range Ordered Magnetism

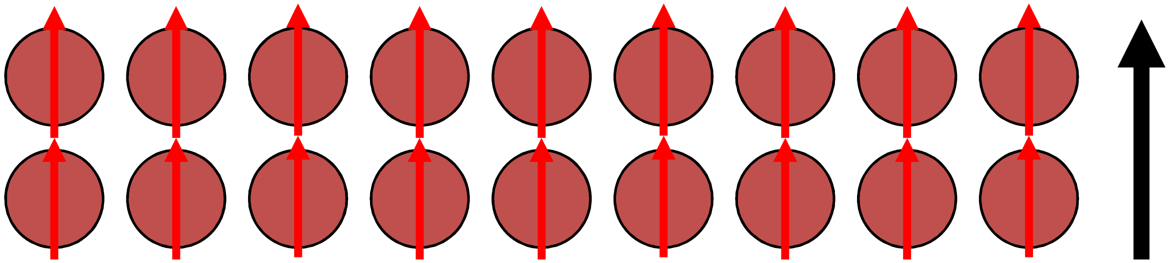
Ferromagnetism



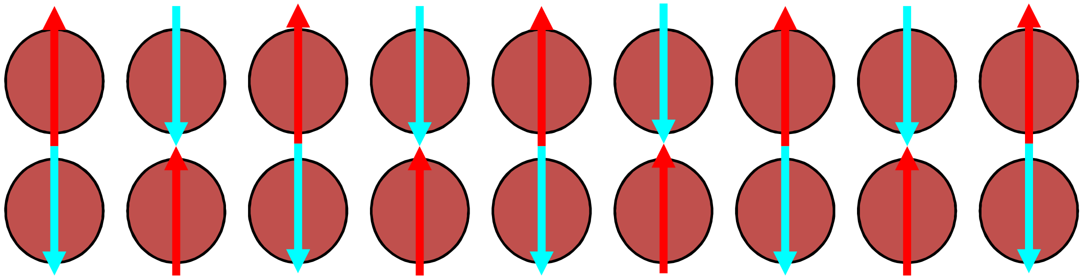
Antiferromagnetism



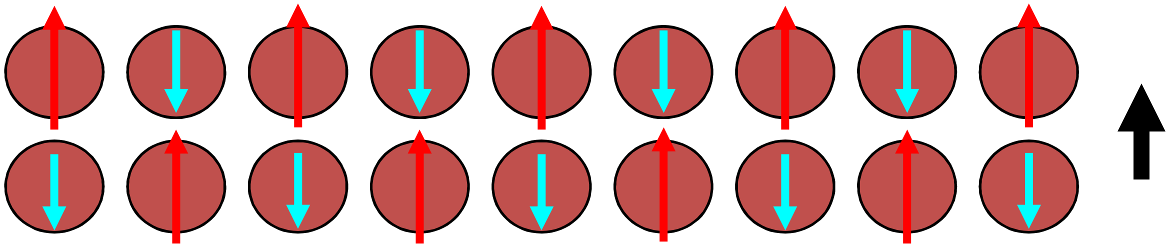
Different forms of ordered magnetism



Ferromagnetism

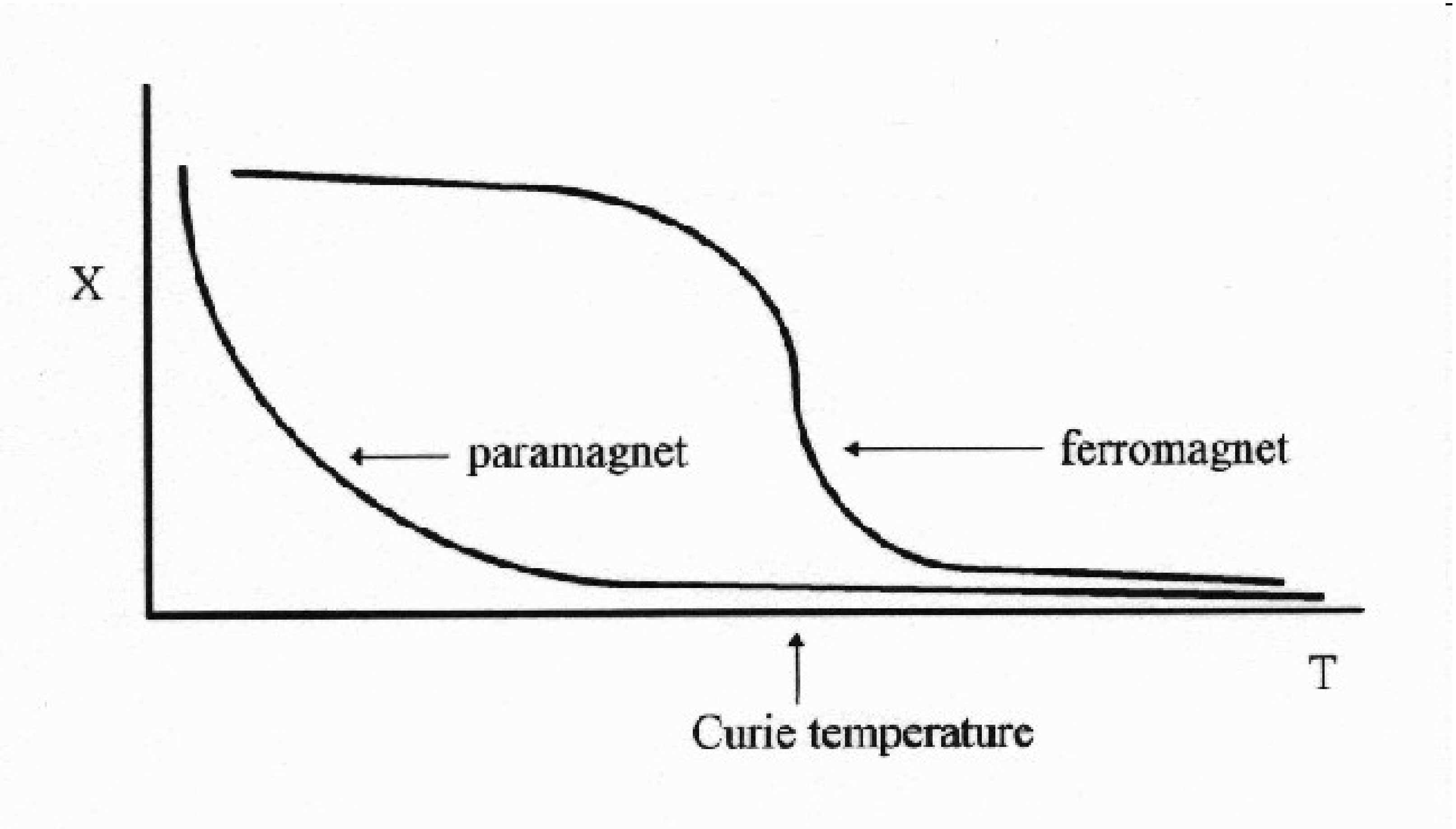


0 Antiferromagnetism

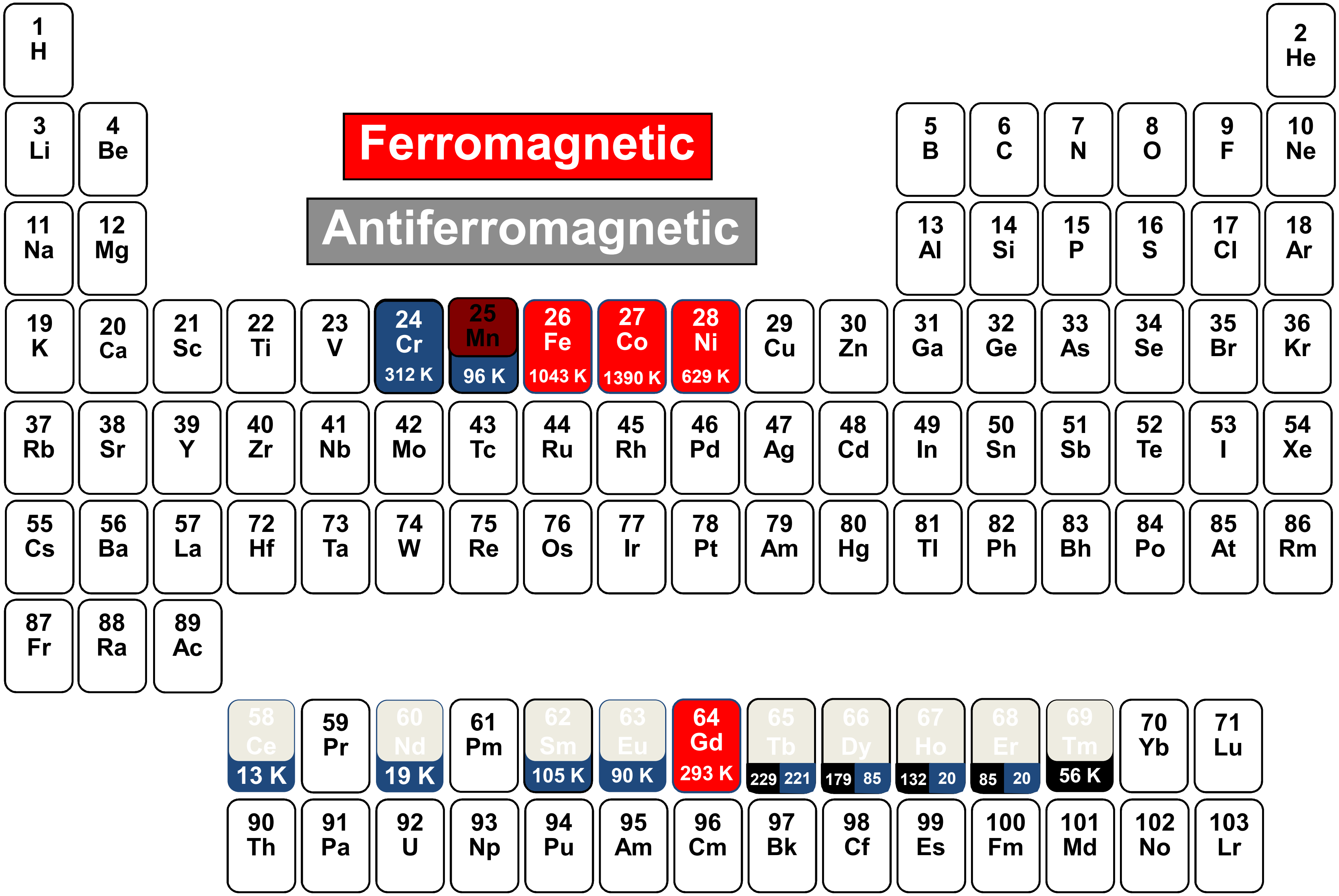


Ferrimagnetism

Effect of Temperature (Ferro, Ferri)



Magnetic Periodic Table

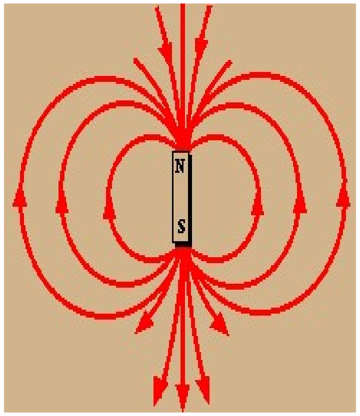


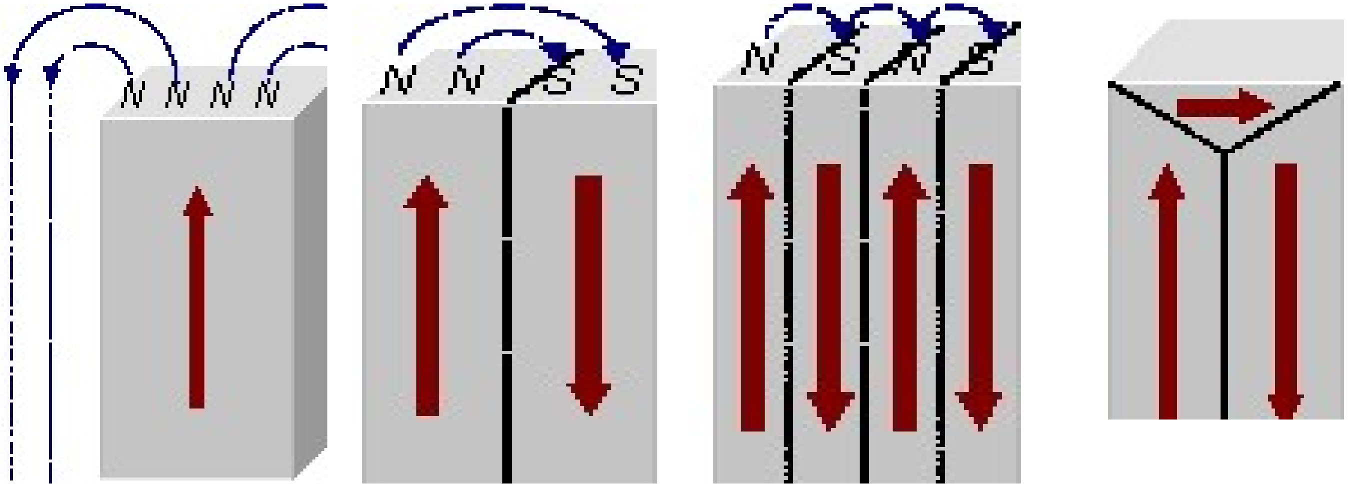
Ferromagnetic

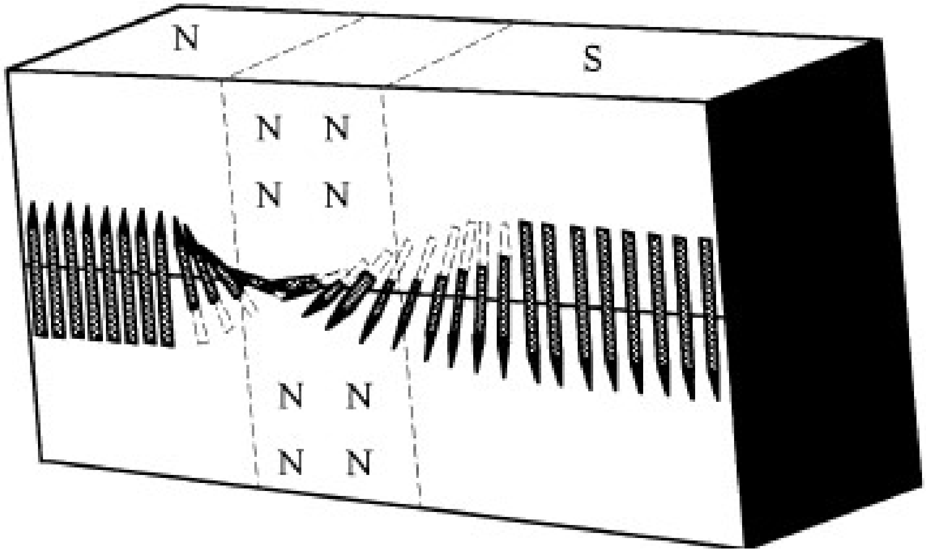
Antiferromagnetic

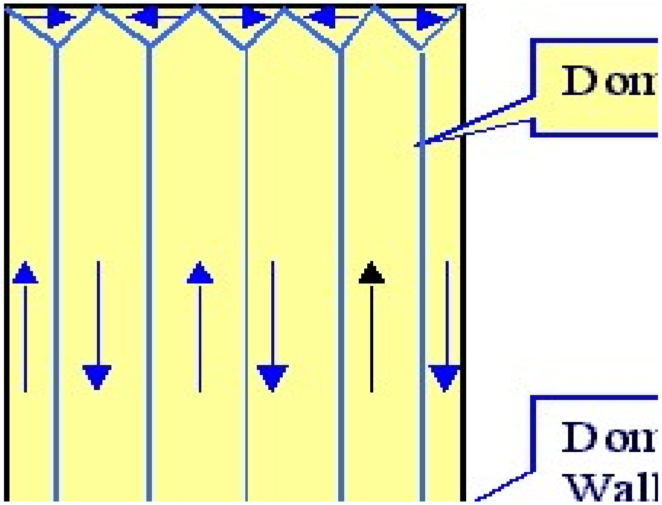
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr 312 K	25 Mn 96 K	26 Fe 1043 K	27 Co 1390 K	28 Ni 629 K	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Am	80 Hg	81 Tl	82 Ph	83 Bh	84 Po	85 At	86 Rm
87 Fr	88 Ra	89 Ac															
			58 Ce 13 K	59 Pr	60 Nd 19 K	61 Pm	62 Sm 105 K	63 Eu 90 K	64 Gd 293 K	65 Tb 229 221	66 Dy 179 85	67 Ho 132 20	68 Er 85 20	69 Tm 56 K	70 Yb	71 Lu	
			90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

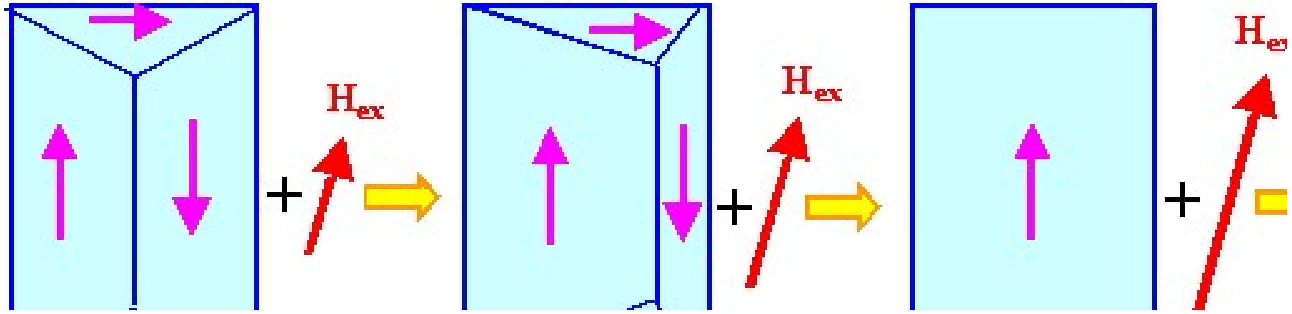
Magnetic Domains

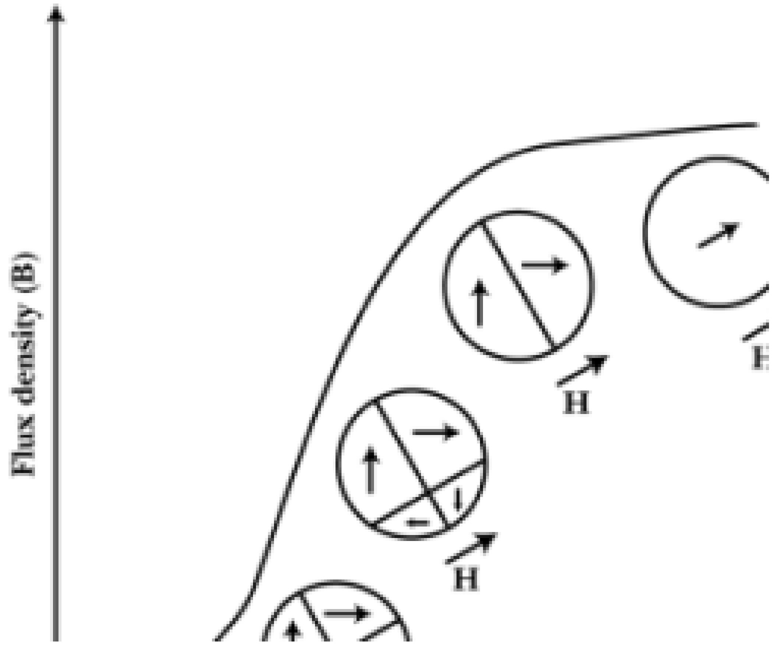


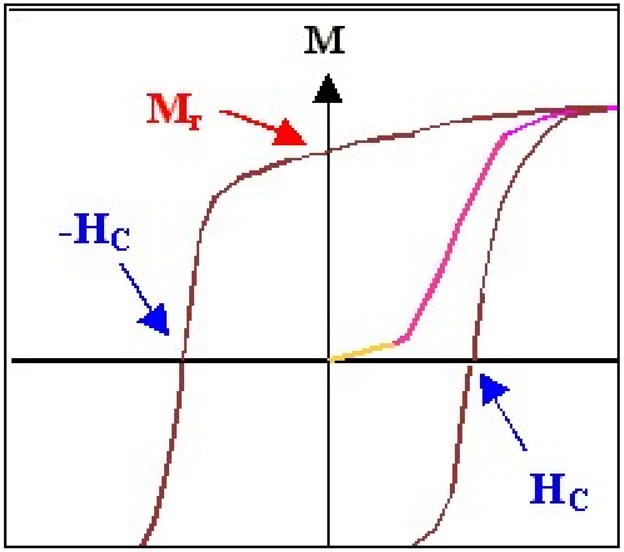






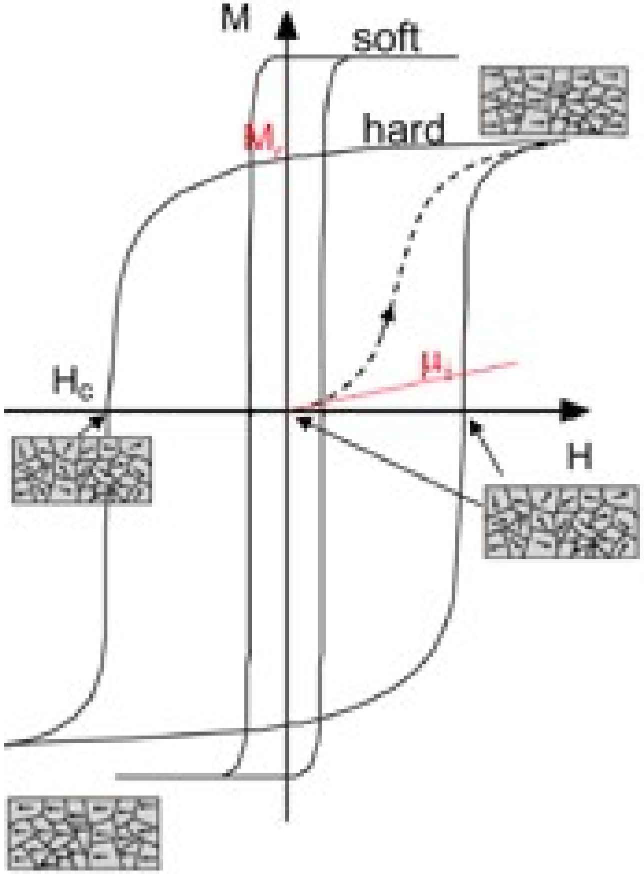

H_ex
+
H_ex
+
H_e
+

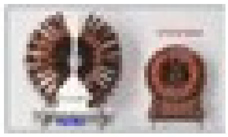

Flux density (B)
H
H
H


M
M_r
-H_C
H_C


Domains Before Magnetization
Magnetic field

Hard and soft magnetic materials





Soft magnetic materials

Easily magnetized, easily demagnetized

Inductor and transformer cores, recording head

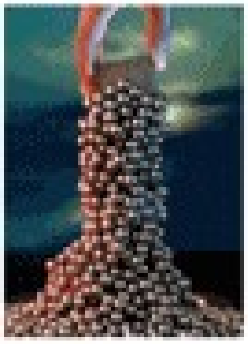
- High saturation magnetization M_s
- Low coercivity H_c
- High permeability μ
  - Low magnetocrystalline anisotropy K_u
  - Low magnetostriction λ_s
- Low core loss
  - High resistivity

Hard magnetic materials

Difficult to magnetize, difficult to demagnetize

Permanent magnets, recording media

- High saturation magnetization M_s
- Low coercivity H_c
  - High magnetocrystalline anisotropy K_u
- High maximum energy product $(BH)_{max}$



Hard

- Compass, magnetometers
- Holding devices
- Magnetic filtration
- Drives and couplings
- Switches
- Magnetic clutches
- Magnetic tools

- Travelling-wave tube
- Electron microscope
- Klystron
- Magnetron
- Mass spectrometer

- Loudspeakers
- DC motors
- Synchronous motors
- Brushless motors
- Hysteresis motors
- Computer peripherals
- Measuring instruments
- Telephone receivers

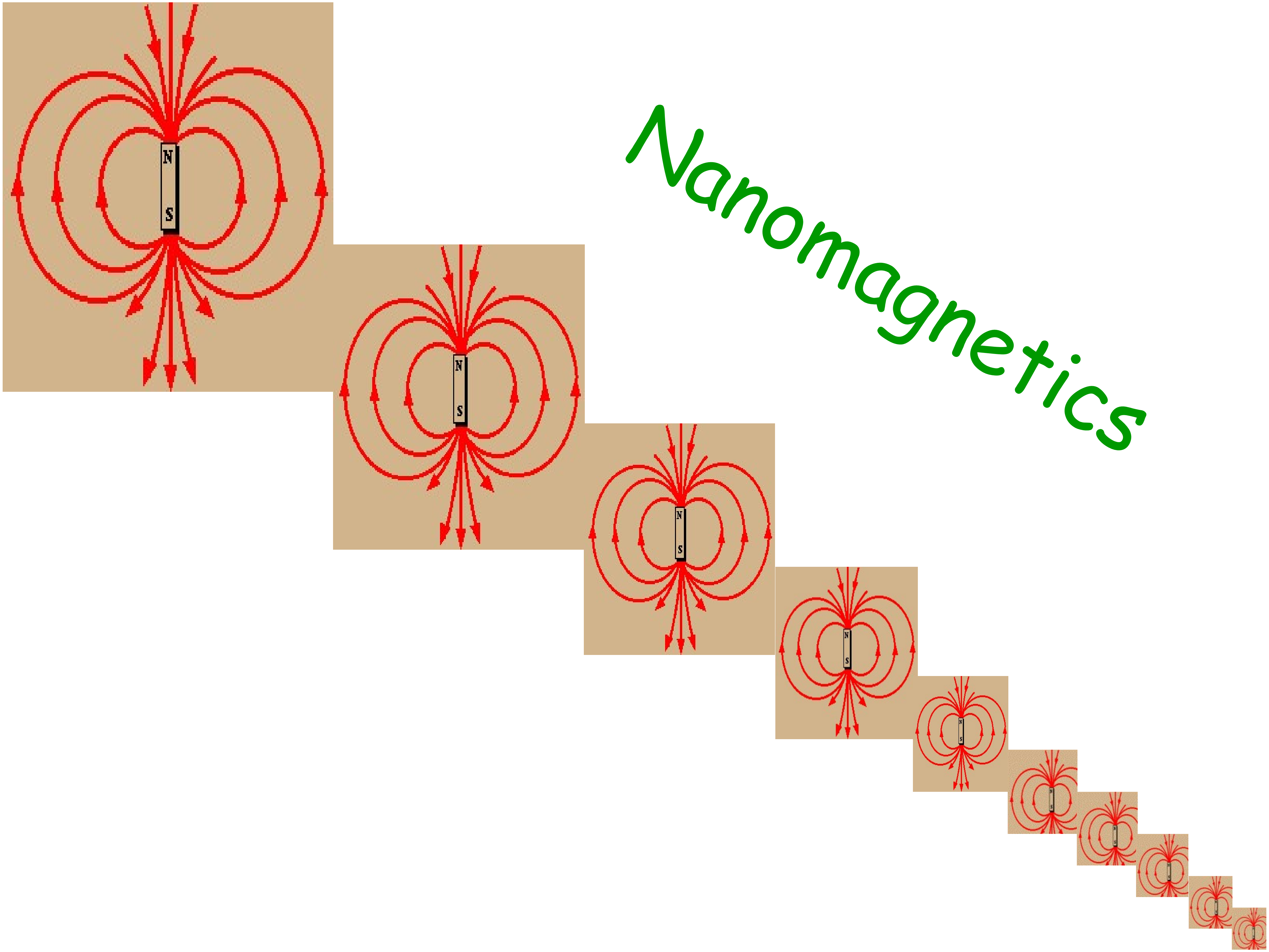
- Generators
- Microphones
- Brakes
- Speedometers

Soft

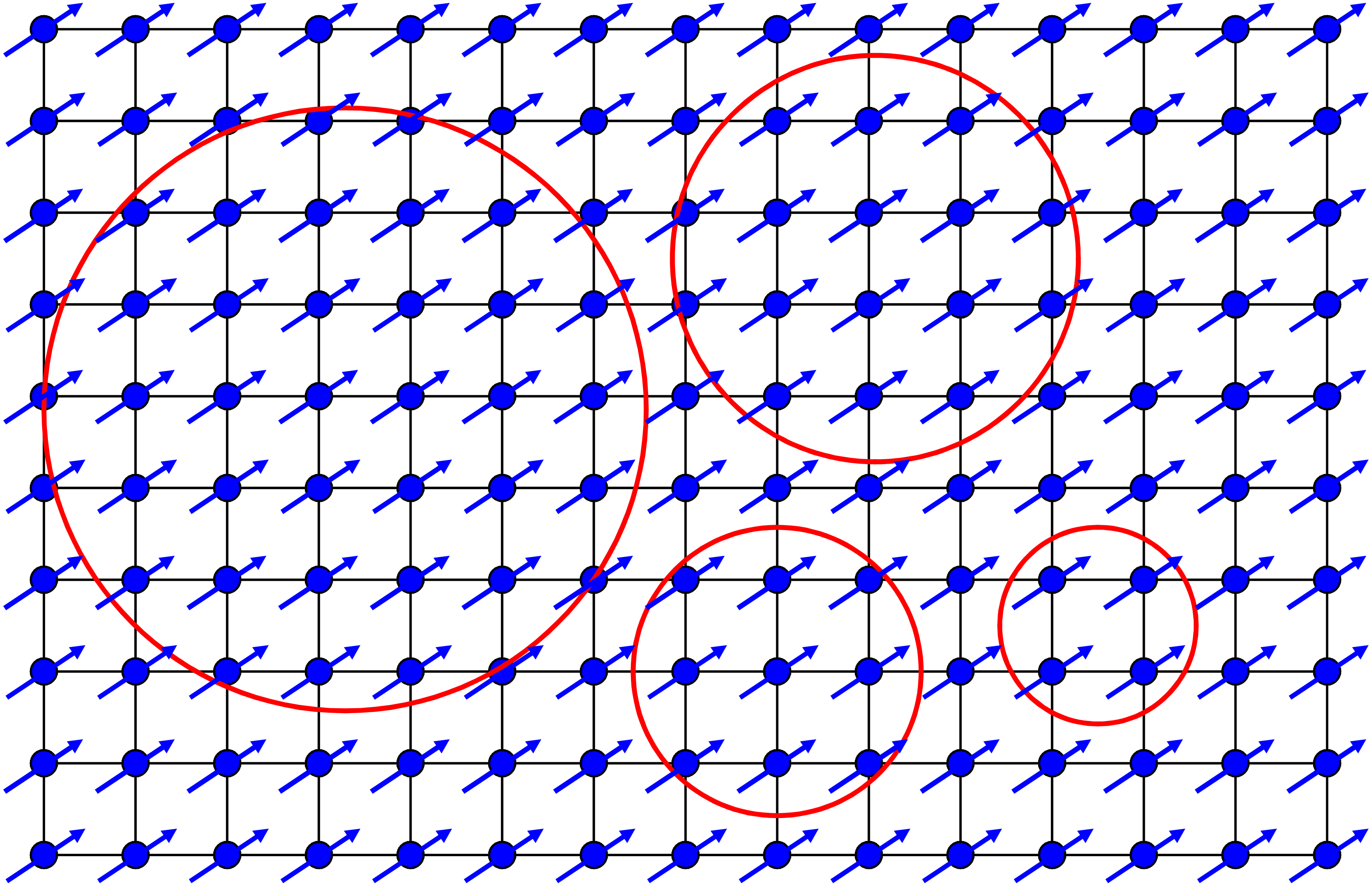
- Electromagnets and yokes
- Relays
- Magnetic shields
- Electrical measuring devices
- Magnetic amplifiers

- Transformers
- Motors and generators
- Signal transmitters and receivers

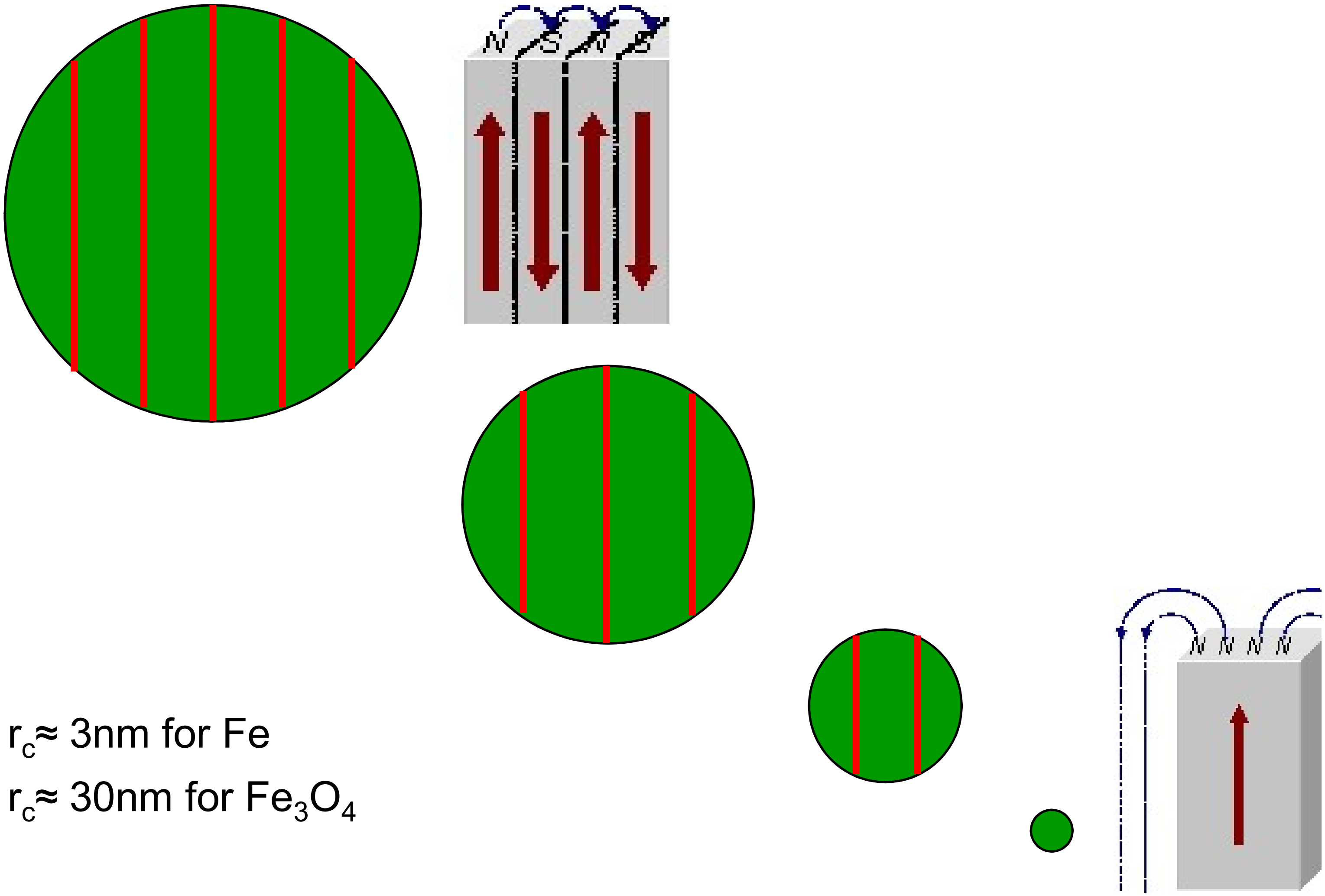
Nanomagnetics



Bulk and Nanomagnetic materials



Multi-domain

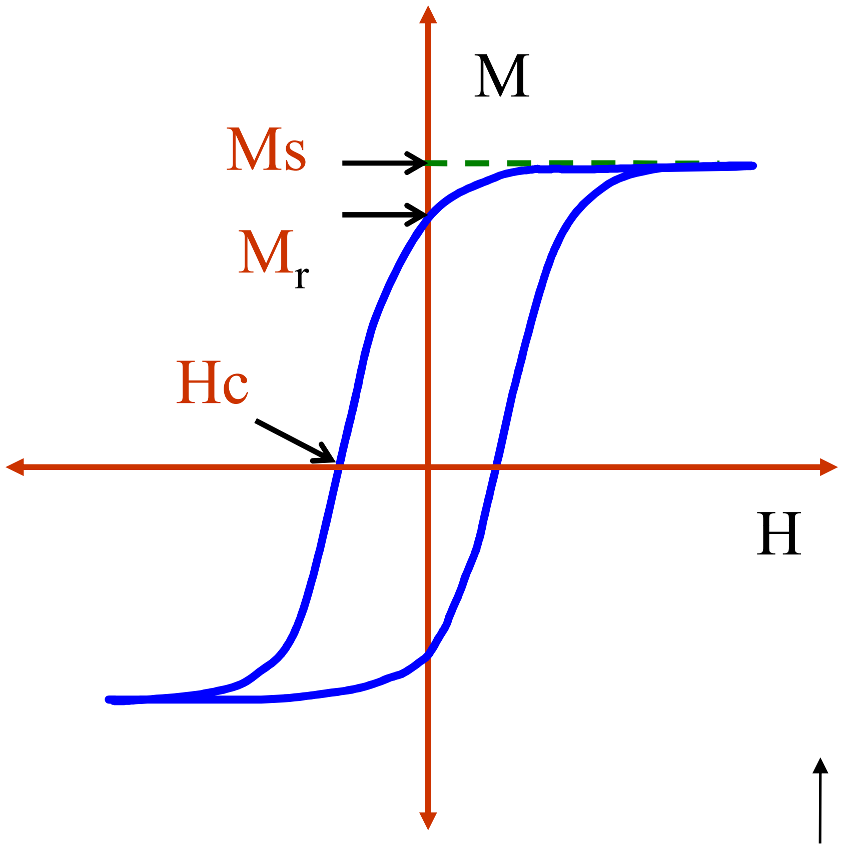


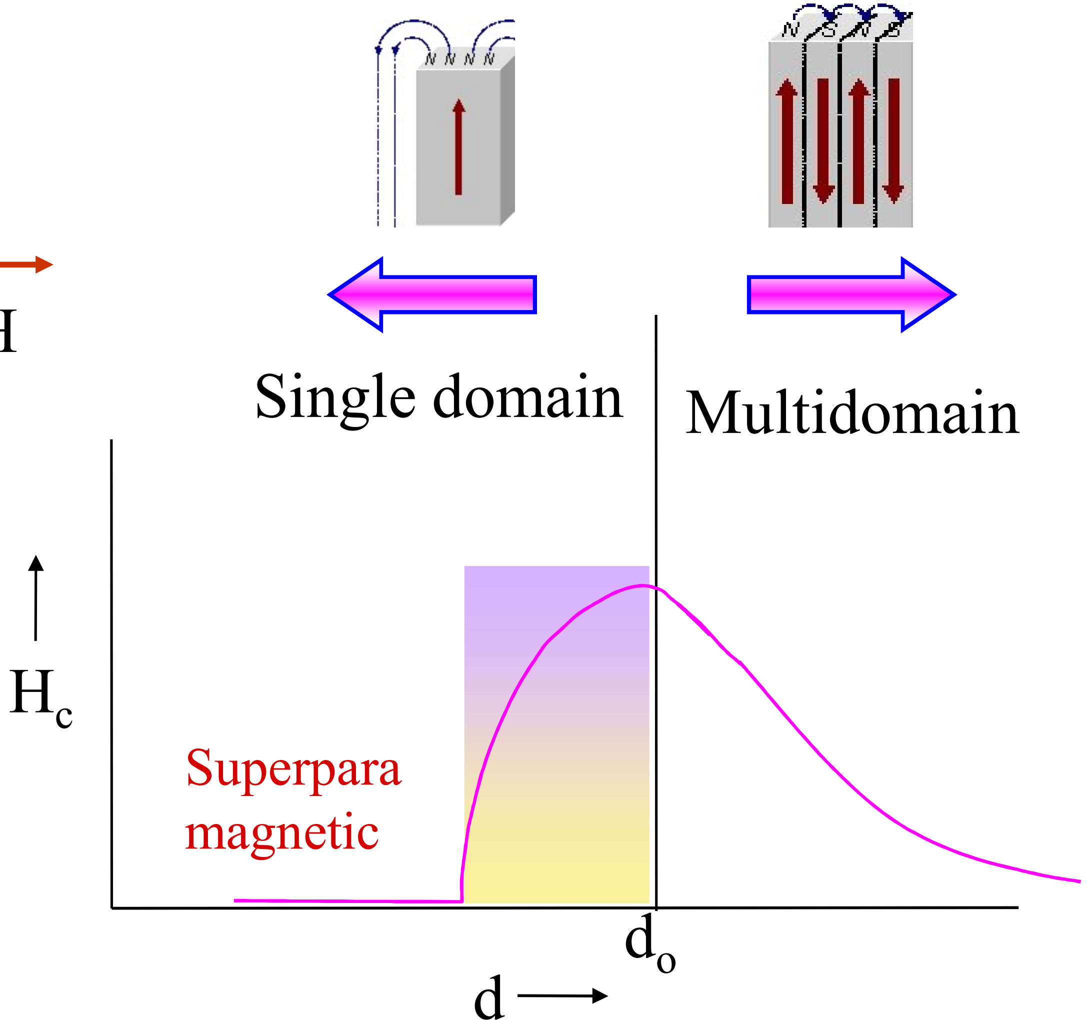
r_c≈ 3nm for Fe

r_c≈ 30nm for Fe_3O_4

Single-domain

Effect of Finite Dimension

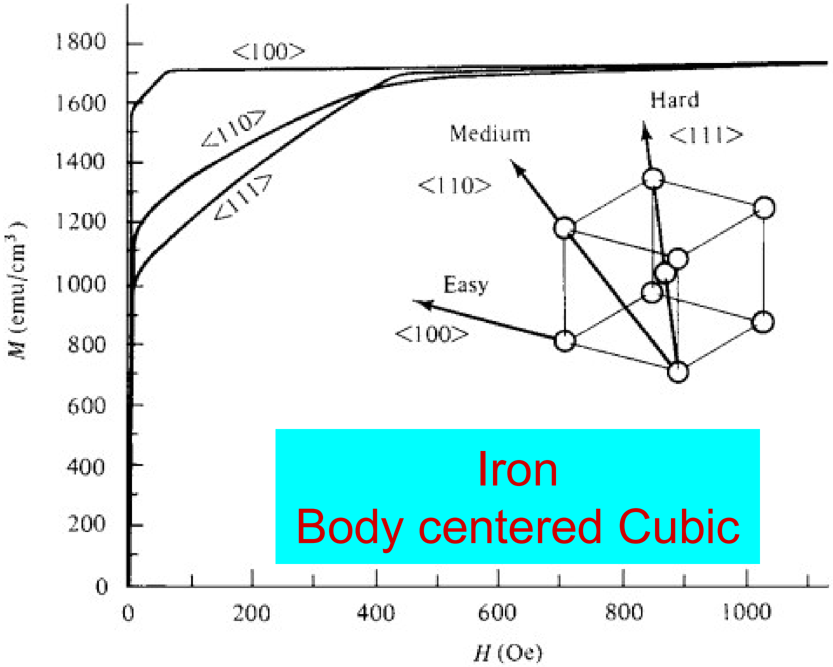




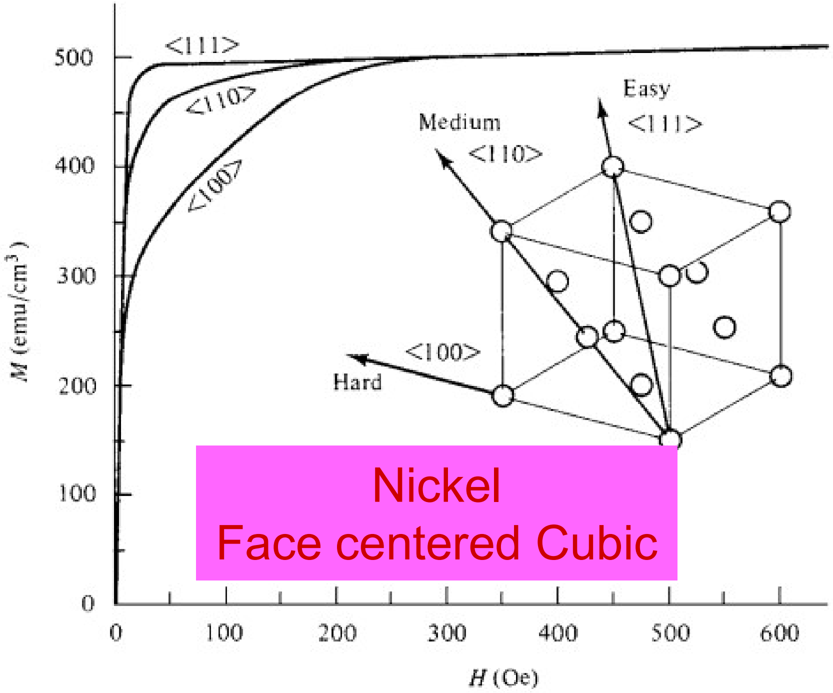
Magnetic anisotropy

Dependence of magnetic properties on a preferred direction in a solid

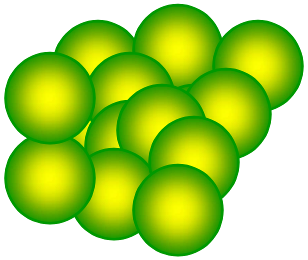
Magnetocrystalline - crystal structure (spin-orbit coupling)
Shape - grain shape
Stress - applied or residual stresses



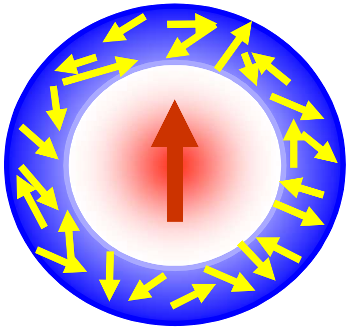
Iron
Body centered Cubic



Nickel
Face centered Cubic

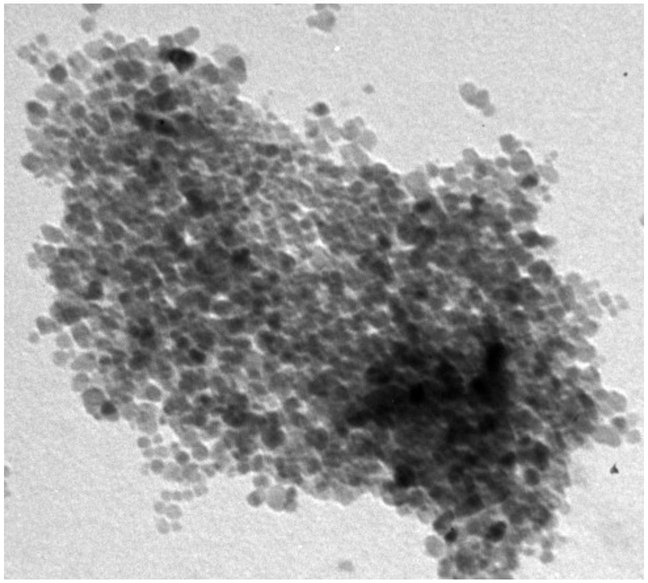


Magnetic nanoparticles



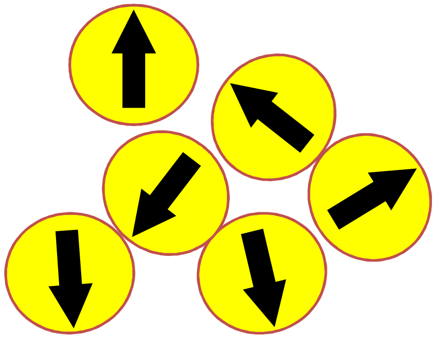
- Magnetocrystalline anisotropy
- Shape anisotropy
- Surface contributions to anisotropy
- Inter-particle interactions
    - Dipolar
    - Magnetic Exchange

Superparamagnetism

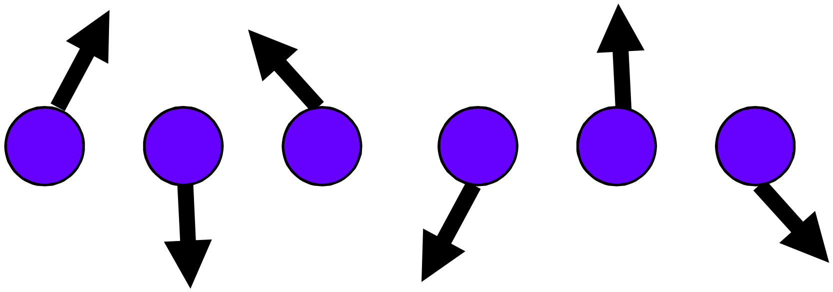


$$KV \approx 25\ k_BT$$

K – Anisotropy
V – Volume of a particle
k_B – Boltzmann's constant
T – Temperature

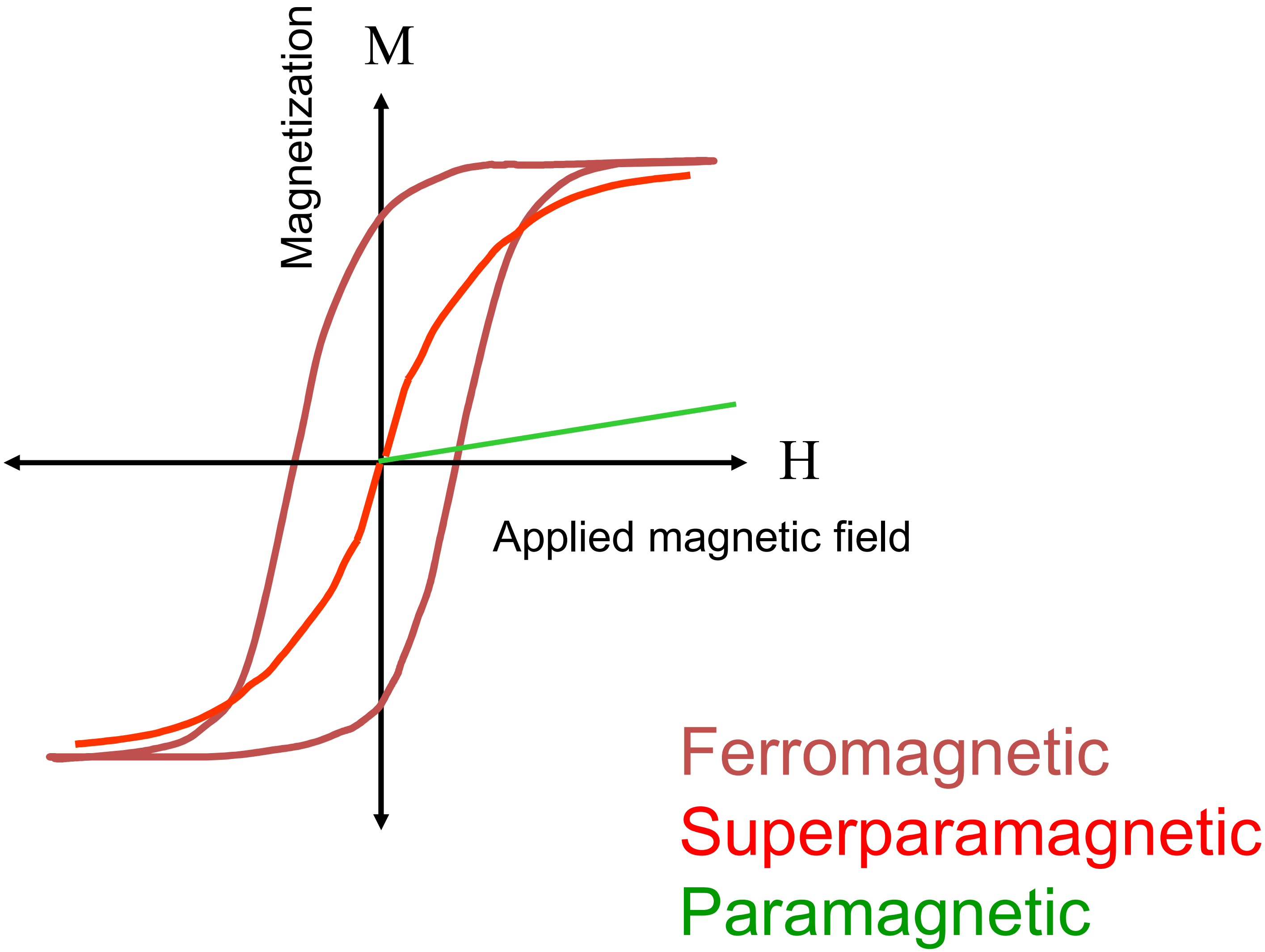


Super-Paramagnetic

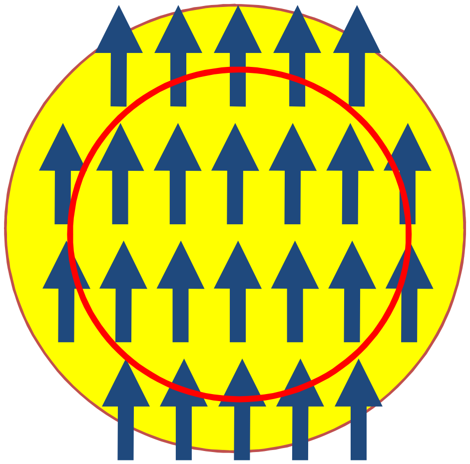


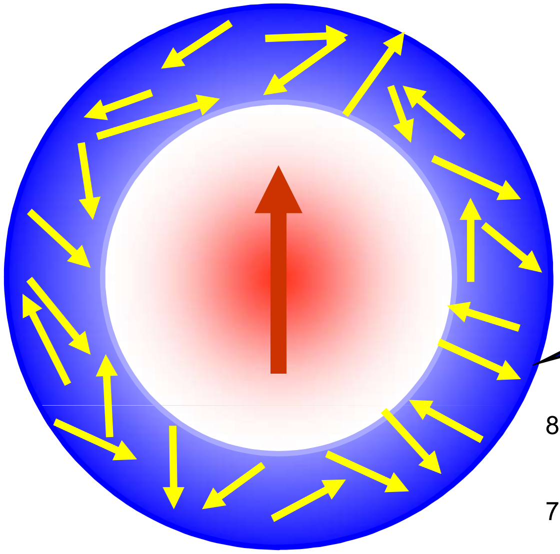
Paramagnetic

Nanomagnetic Materials

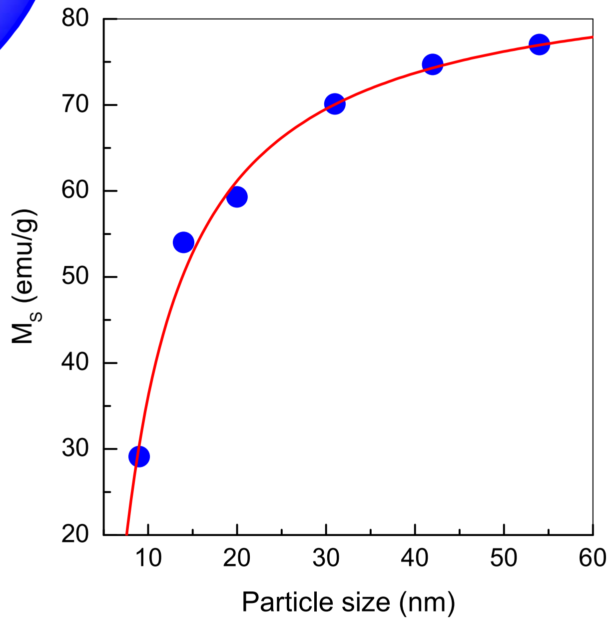


Magnetic Core-Shell Structure





Magnetically dead layer of thickness *t*



$$M_s^d = M_s^{bulk}\ 1-\frac{6t}{d}$$

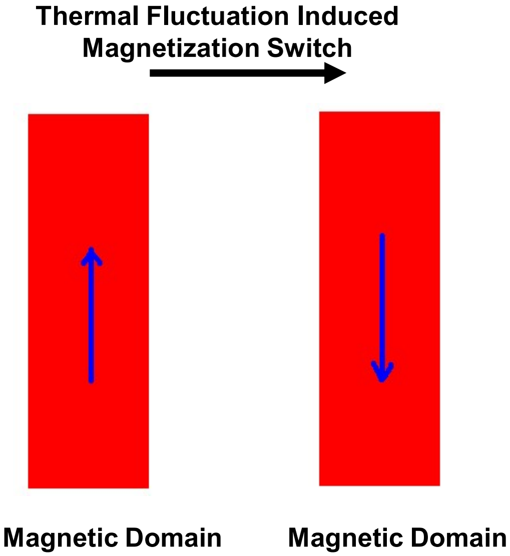
t ≈ 1 unit cell dimension

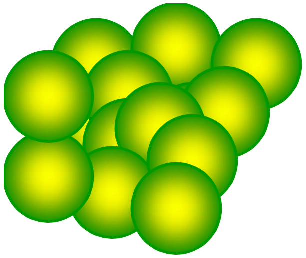
d – diameter of a particle

Thermal Stability Issue

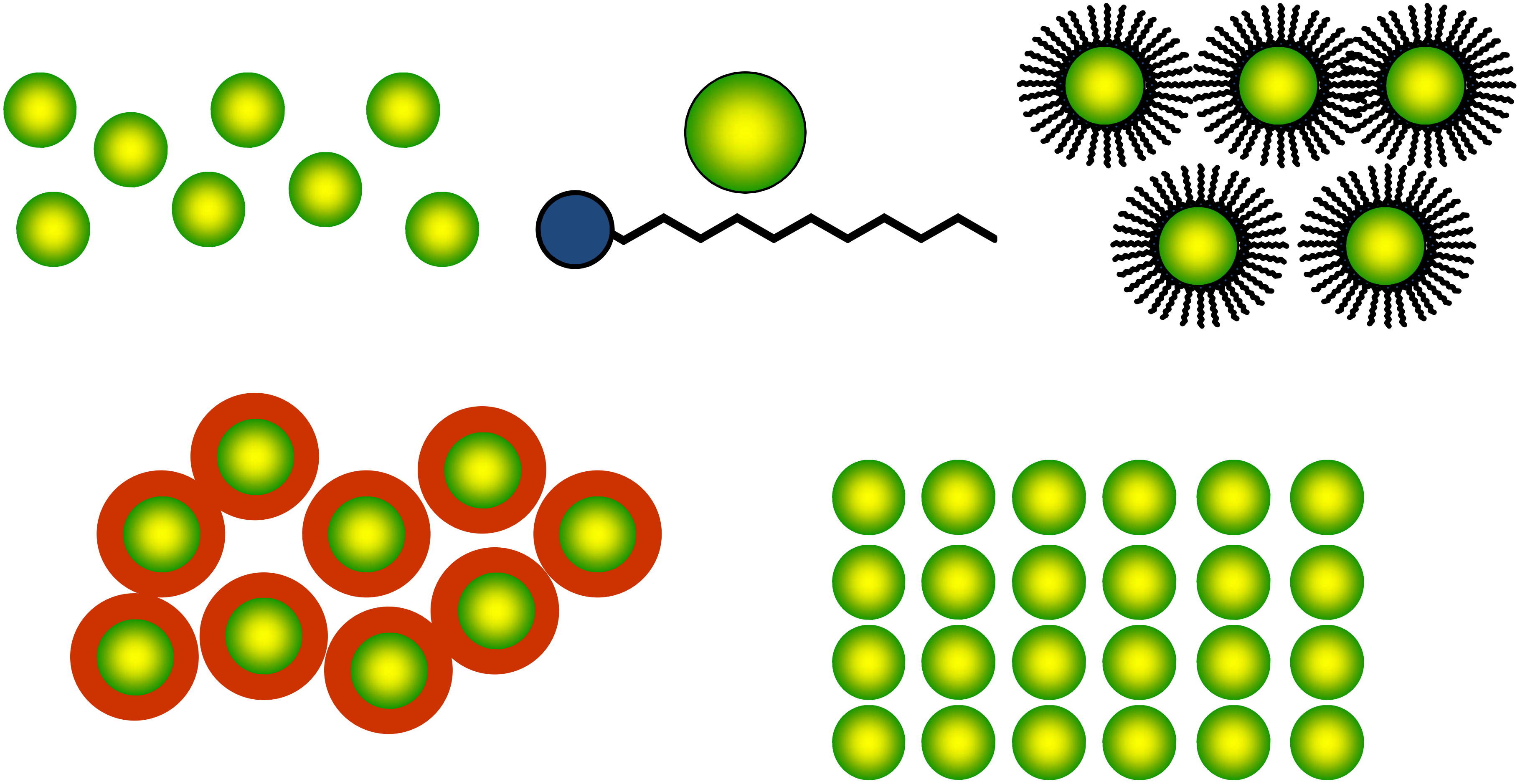
$KV \approx 25\ k_BT$

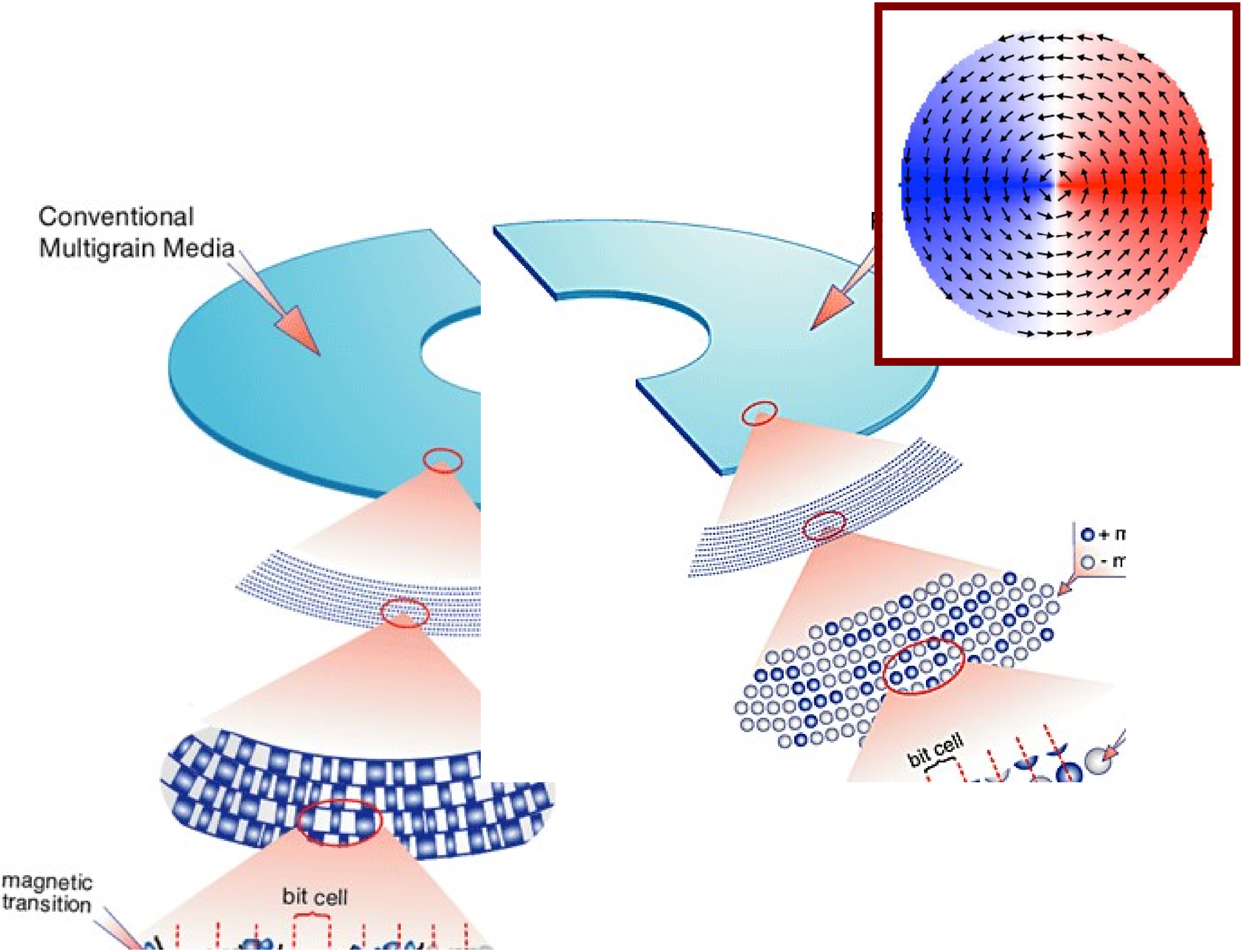
- Average Thermal Energy is
  k_BT (K_B is the Boltzmann's constant)
  T normally is room temperature, ~ 300K
- Energy barrier to switch a domain is
  KV(V is the volume of the domain;
  K is the anisotropy constant of the material. Higher K means higher writing magnetic field)
- KV/k_BT demtermines the thermal stability.
  Normally it should be larger than 60.





Magnetic Interactions




Conventional
Multigrain Media
magnetic
transition
bit cell
bit cell

Magnetic Nanomaterials

- Single Domains
- Superparamagnetism
- Thermal Effects
- Magnetic Core-Shell Structure
- Surface Contributions
- Inter-particle Interactions
- Particle size and distribution
- Technological Applications
- Biocompatibility
- Medical Applications

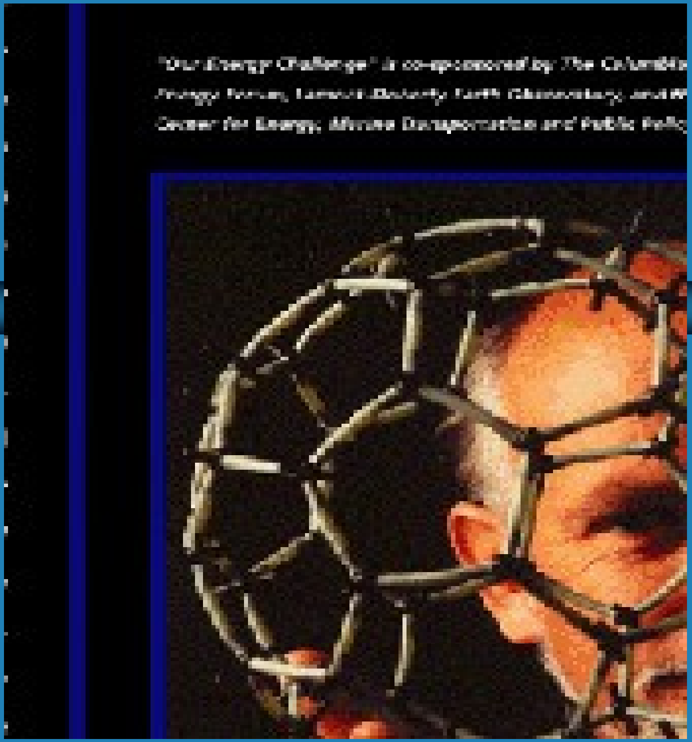
Some special Nanomaterials

Carbon-Nanotubes:

Synthesis, Characterization and Applications

Overview

- Introduction
- Types of CNTs
- Double Walled Carbon Nanotubes
- Synthetic Approaches
- Characterization Techniques
- Electronic Properties, Applications
- Conclusions

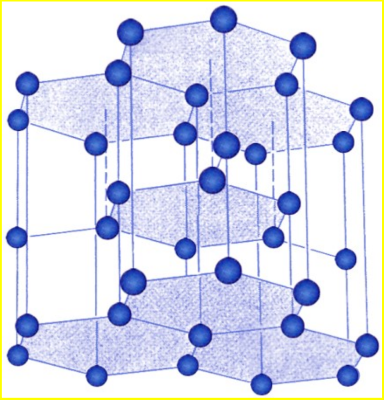


Nobel Prize 1996

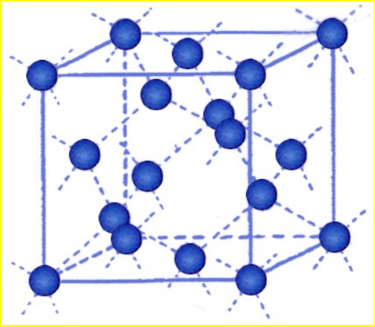
“Nanotechnology holds the answers, to the extent there are answers, to most of our pressing materials needs in energy, food, health, communication, transportation, water etc.”

- Richard Smalley

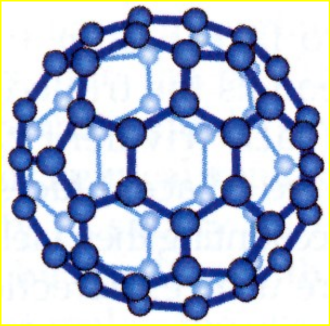
Ordered Carbon Structures



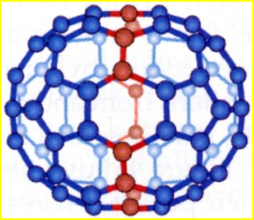
Graphite



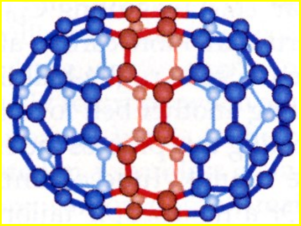
Diamond



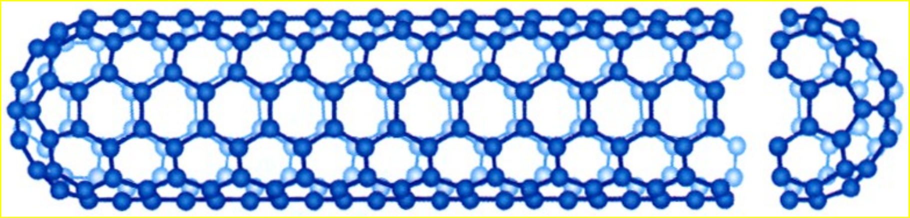
C_{60}



C_{70}

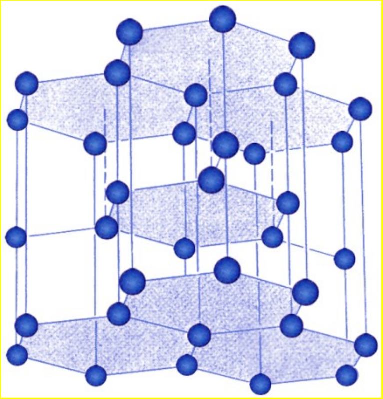


C_{80}



CNT

Ordered Carbon Allotropes



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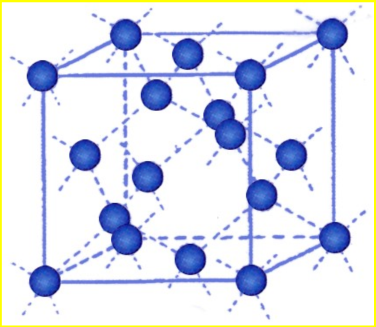
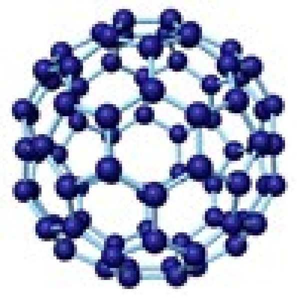
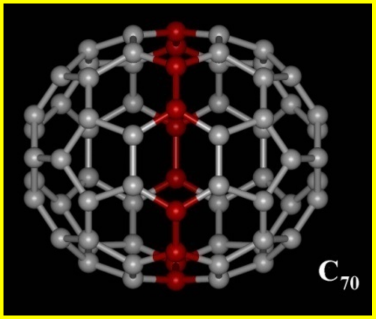


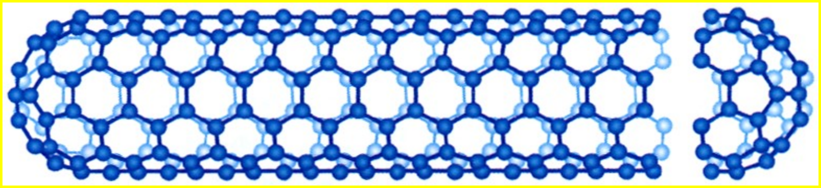
Diamond



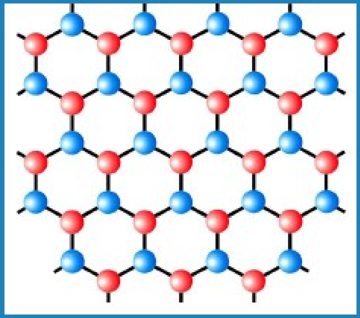
C_{60}



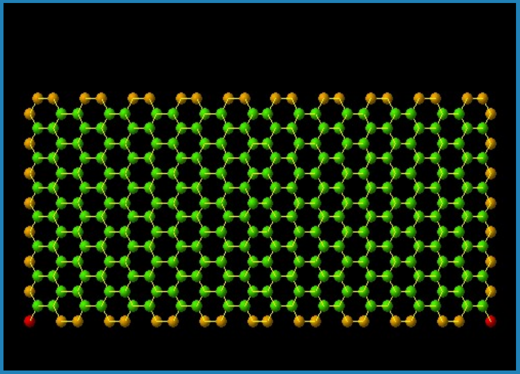
C_{70}



CNT



Graphene



Graphene-CNT

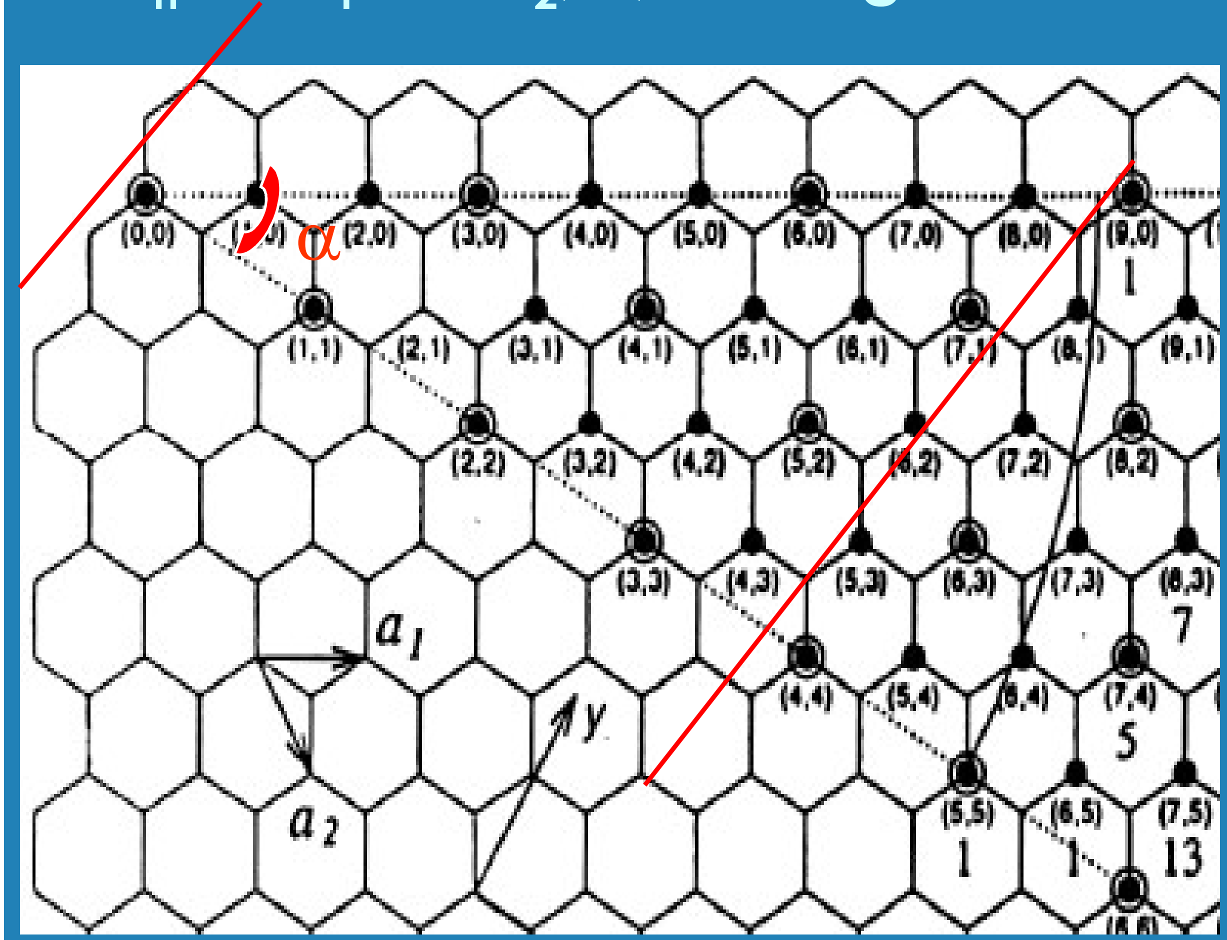
"Although other elements may form complex, covalently bonded structures, none has the rich molecular variety of carbon"

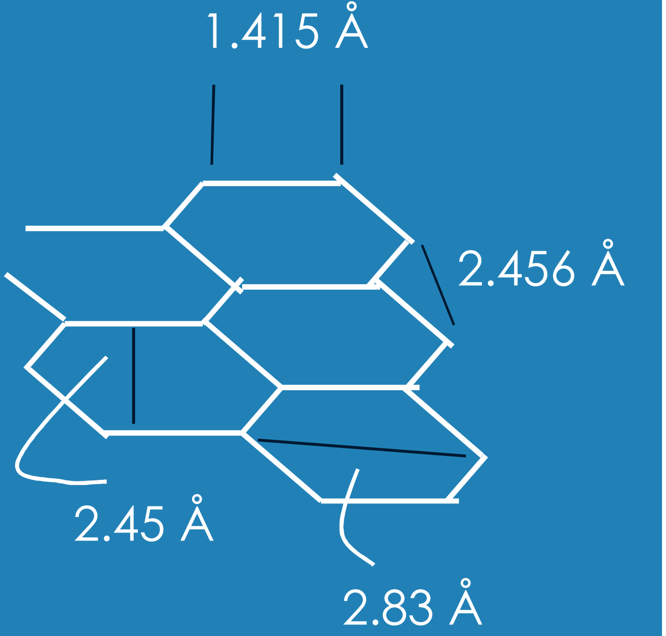
Carbon One-dimensional Structures

- **Discovered by S. Iijima in 1991**
- **Unique material properties**
- **Fundamental laboratory for quantum confinement physics**
- **SWNTs/MWNTs**
- **Nanoelectronics, Hydrogen storage, Gas sensors, Supercapacitors**

Structure

$C_h = na_1 + ma_2$; n, m integer



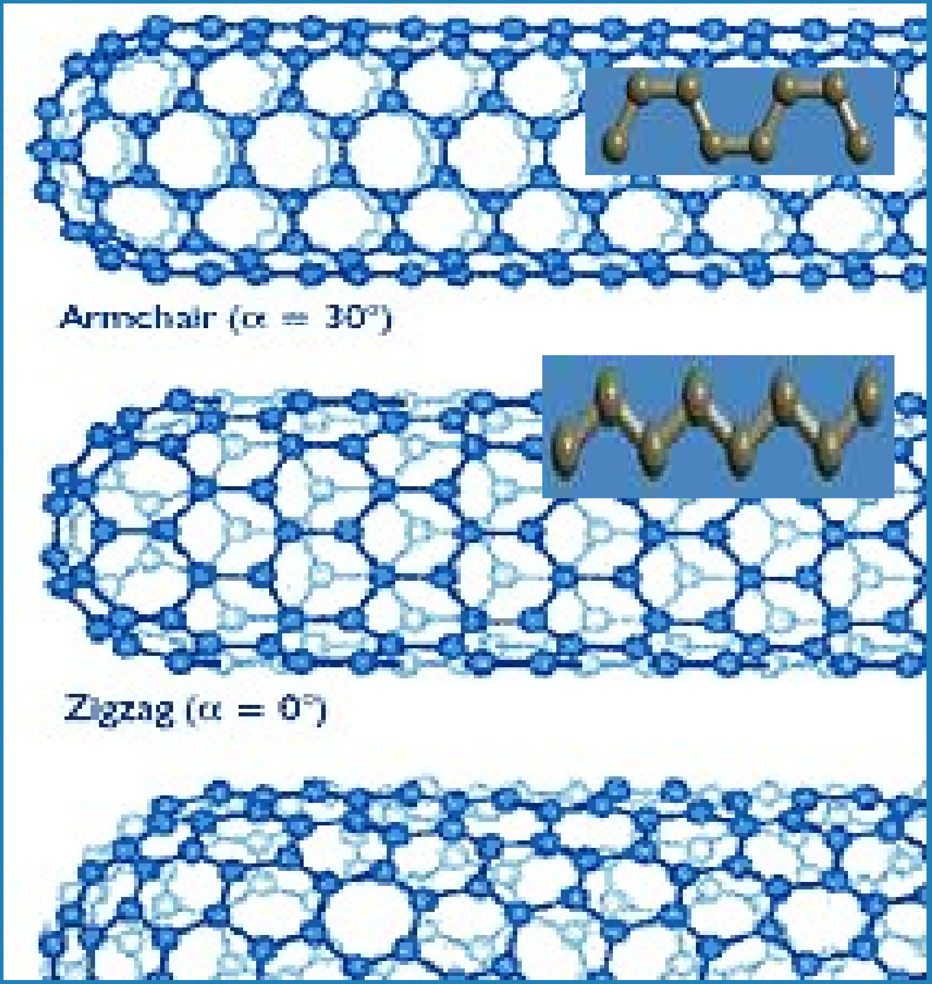


Richard E. Smalley et al. *Nature* **391**, 6662, 59-62 (1998)

Fundamental Gap

- **(n= m) CNTs are metals**
  Armchair ($\alpha = 30^0$)
- **(n,m) CNTs with n-m = 3j; tiny gap semiconductors or metals**
  Zigzag ($\alpha = 0^0$)
- **All others are large-gap (> 0.5 eV) semiconductors**

Chiral ($0 < \alpha < 30^0$)

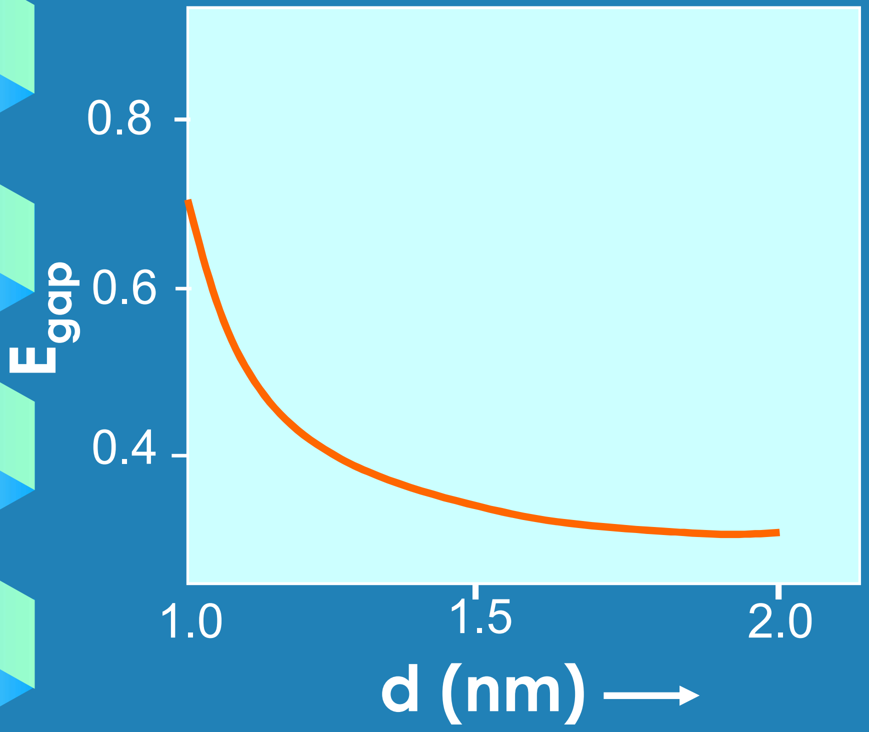


$d = (n^2 + m^2 + nm)^{1/2} 0.0783\ nm$

d = diameter,

(n,m) chiral parameters

Band Gap vs Diameter



$E_{gap} = 2\, y_0\, a_{cc} / d$

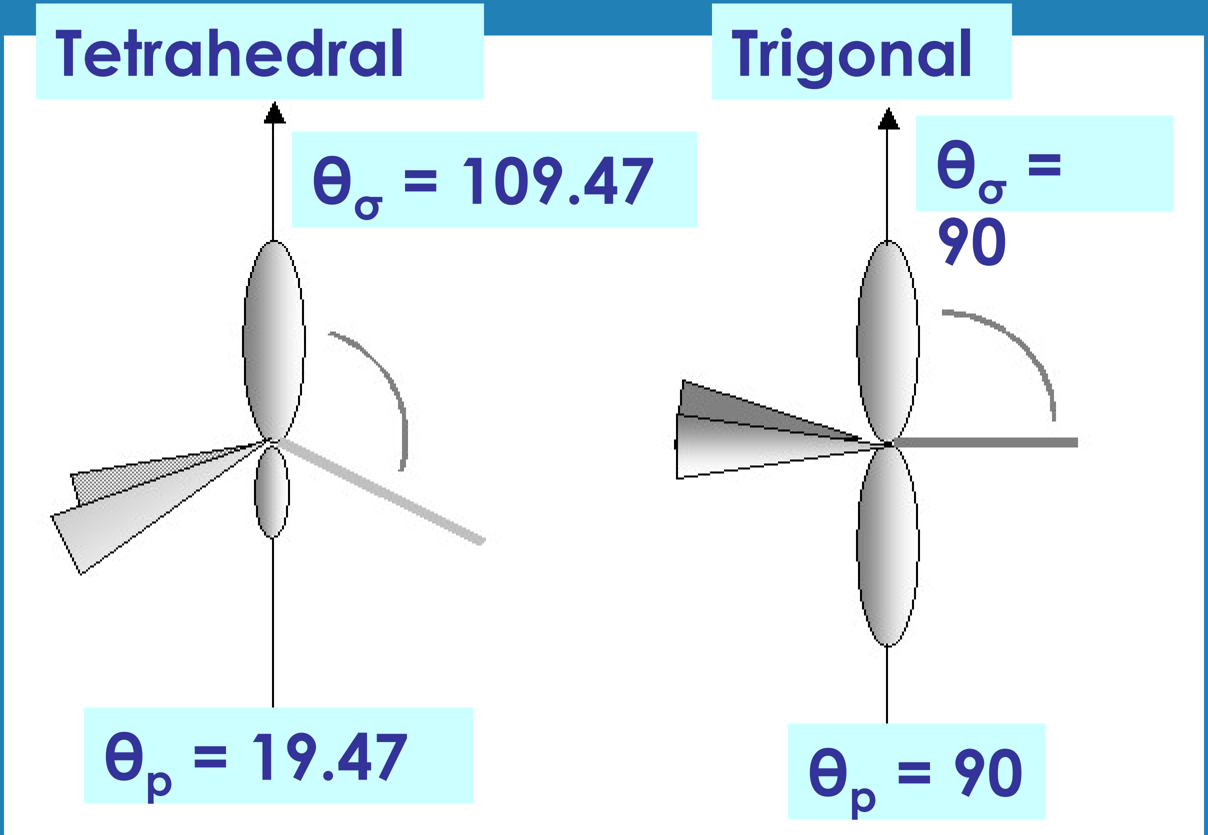
y_0 =C-C tight bonding overlap energy (2.7 eV)

a_{cc} =C-C distance (0.142 nm), and

d = diameter

Richard E. Smalley Nature 391, 6662, 59-62 (1998

Reactivity of CNTs



Tetrahedral

$\theta_\sigma = 109.47$

$\theta_p = 19.47$

Trigonal

$\theta_\sigma = 90$

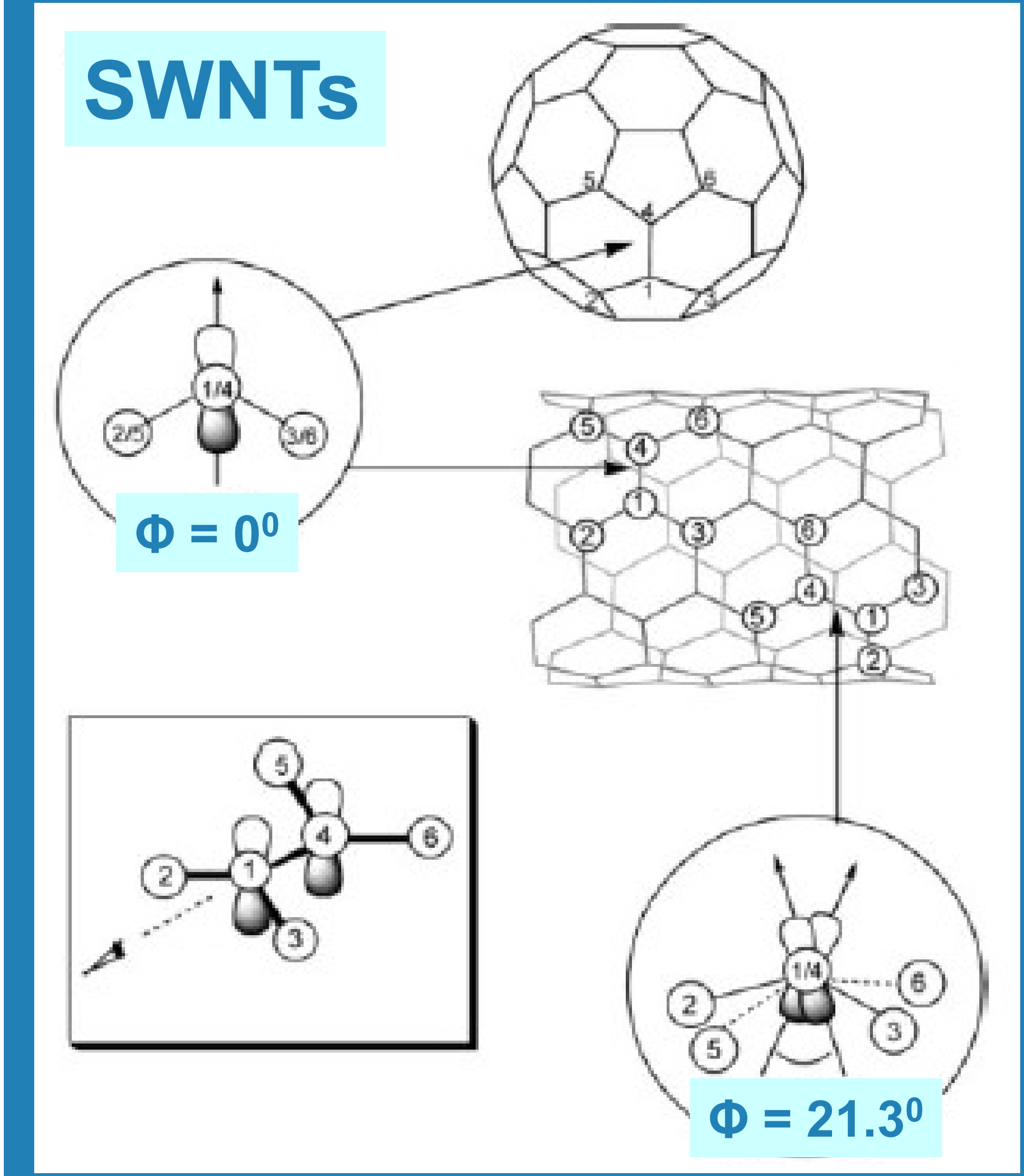
$\theta_p = 90$

Pyramidalization Angle

$\theta_p = (\theta_\sigma - 90)^0$

Release of Pyramidalization Strain- Energy Results in Addition Reactions Energetically Favorable

Sidewall Functionalization



π-Orbital Misalignment is More Important Than The Pyramidalization Angle

Smaller Diameter Tubes are More Reactive

Loss of Intrinsic Electronic Structure

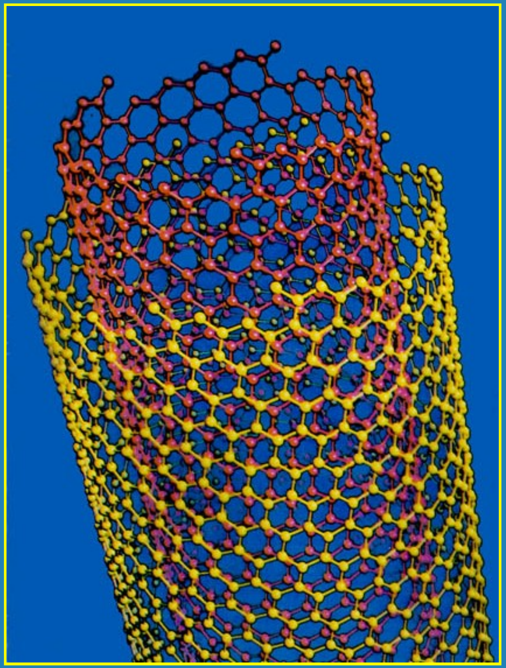
Excellent Material Properties

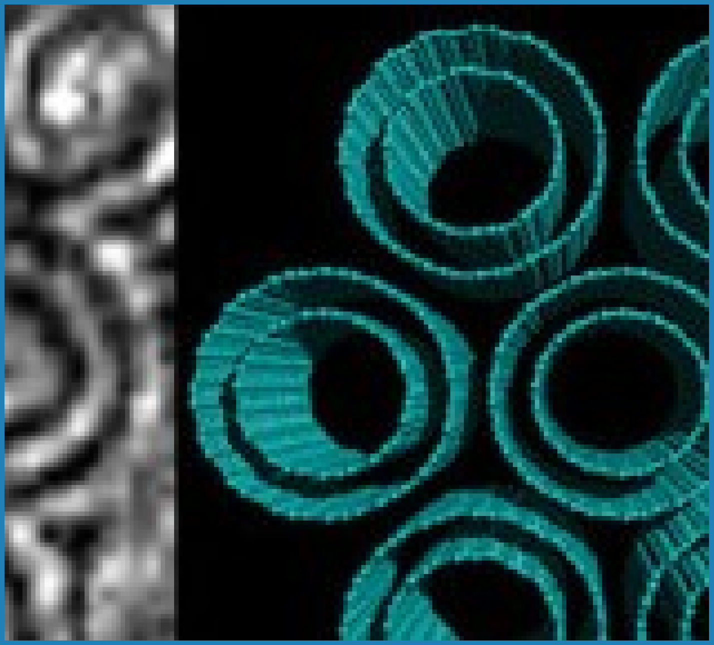
- **Large Aspect Ratio(>1000)**
- **Atomically Sharp Tips**
- **High Thermal and Chemical Stability**
- **High Electrical and Thermal Conductivity**

Material	*Young's Modulus (GPa)*	*Tensile Strength (GPa)*	*Density (g/cm^3)*
SWNT	1054	150-200	1.33
MWNT	1200	150	2.6
DWNT	1000-2000	300	0.77
Steel	208	0.4	7.8
Epoxy	3.5	0.005	1.25
Wood	16	0.008	0.6

Double Wall Carbon Nanotubes; Stronger Carbonaceous Material

The coaxial structure contains two concentric graphene cylinders

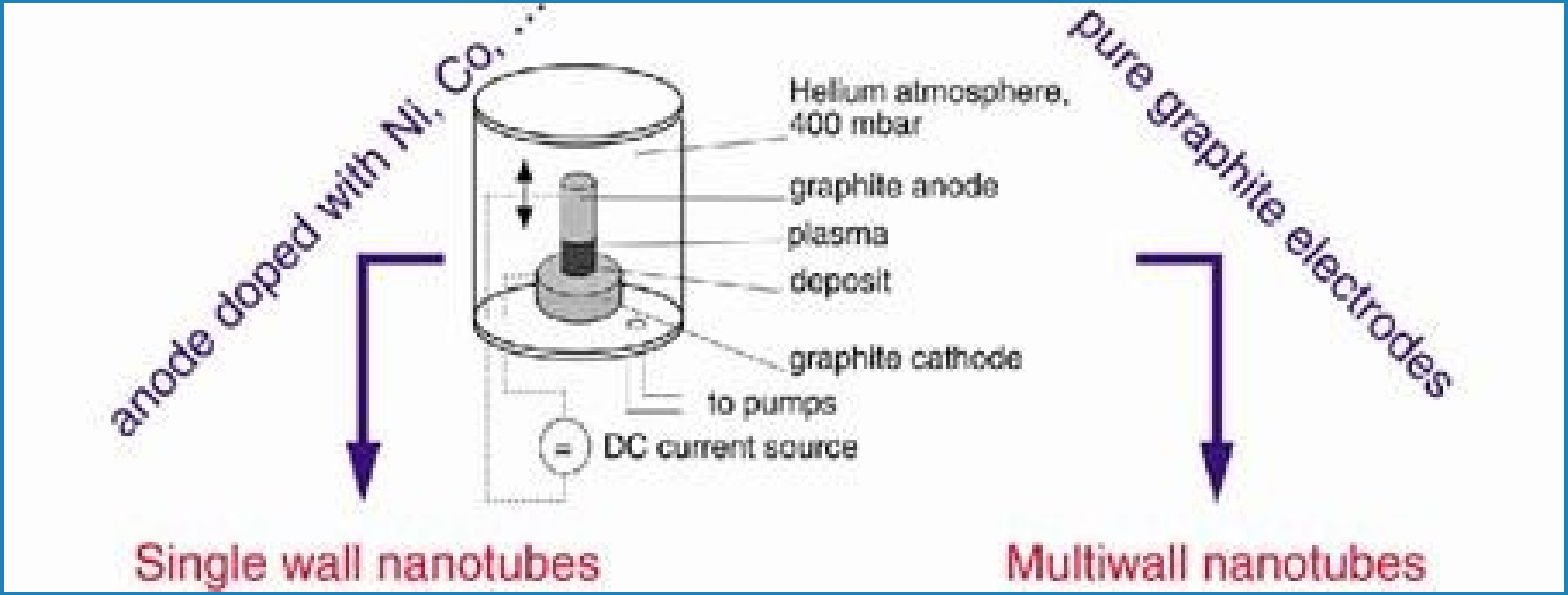




Commonly Adopted Synthetic Methods

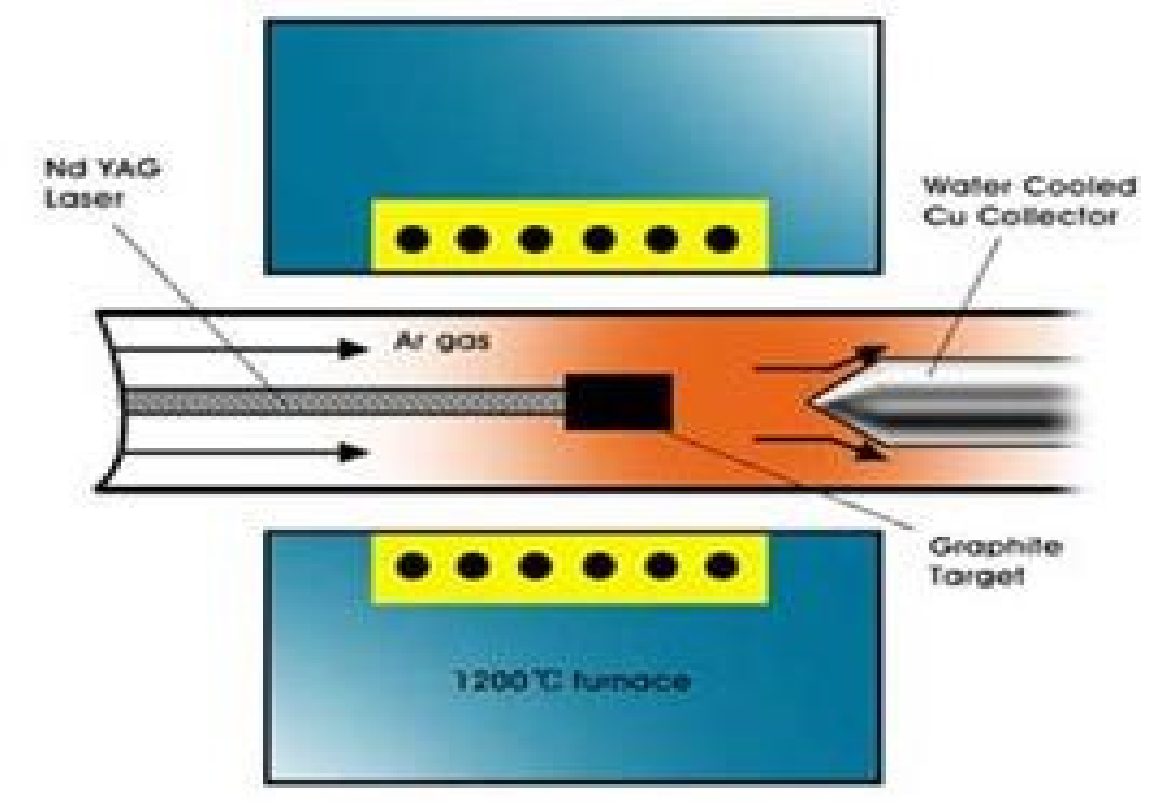
- Arc Discharge Synthesis
- Laser Ablation
- Chemical Vapor Deposition (CVD)

Arc Discharge Synthesis



- 100 A, 25-35 V dc for discharge
- Helium gas: Coolant, homogeneous deposition
- Catalysts: Y, Ni

Laser Ablation (PLV)

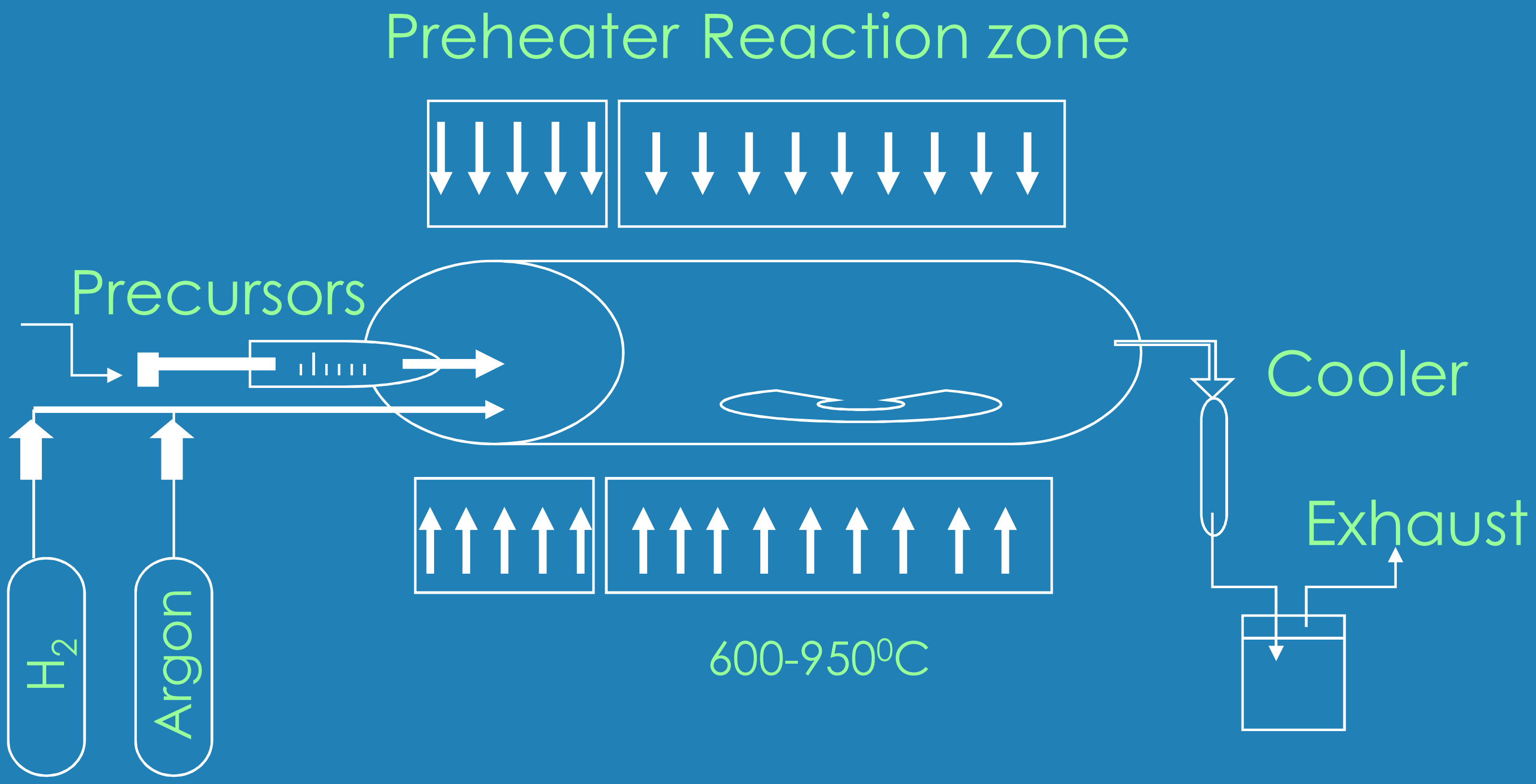


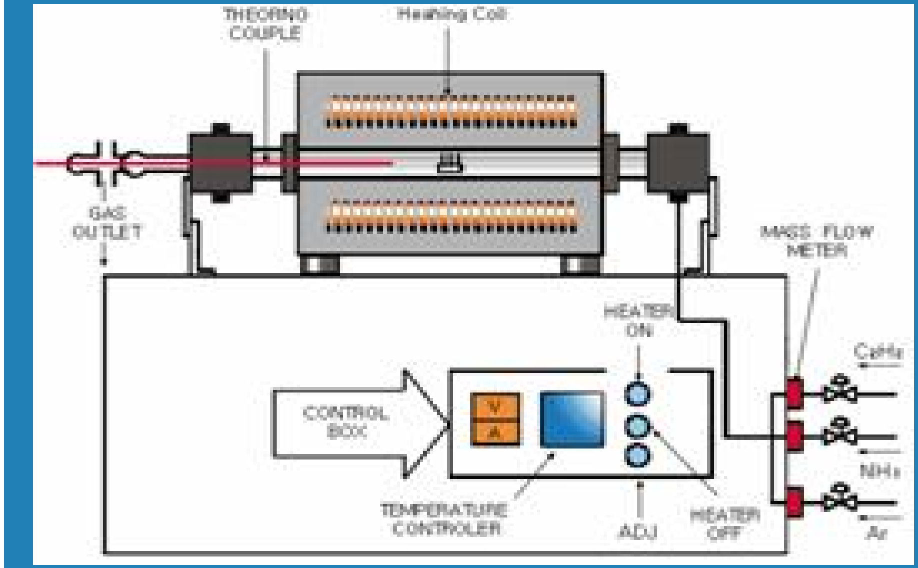
- ➢Avoids usage of electric field
- ➢ Lasers: Nd, YAG pulsed
- ➢ Frequency of pulse: 60 Hz (very fast)
- ➢ Target ablated by 5 cm beam at 500 watt in an oven of 1200^0C
- ➢ CNT deposition rate 0.3-0.4 g/hr

Chemical Vapour Deposition (CVD)

- Plasma enhanced chemical vapour deposition
- Thermal chemical vapour deposition
- Alcohol catalytic chemical vapour deposition (550^0C)
- Vapour phase growth (metallocene)
- Aero gel-supported chemical vapour deposition
- Laser-assisted thermal chemical vapour deposition
- CoMoCat process
- High pressure CO disproportionation process (HiPCO)

Chemical Vapor Deposition

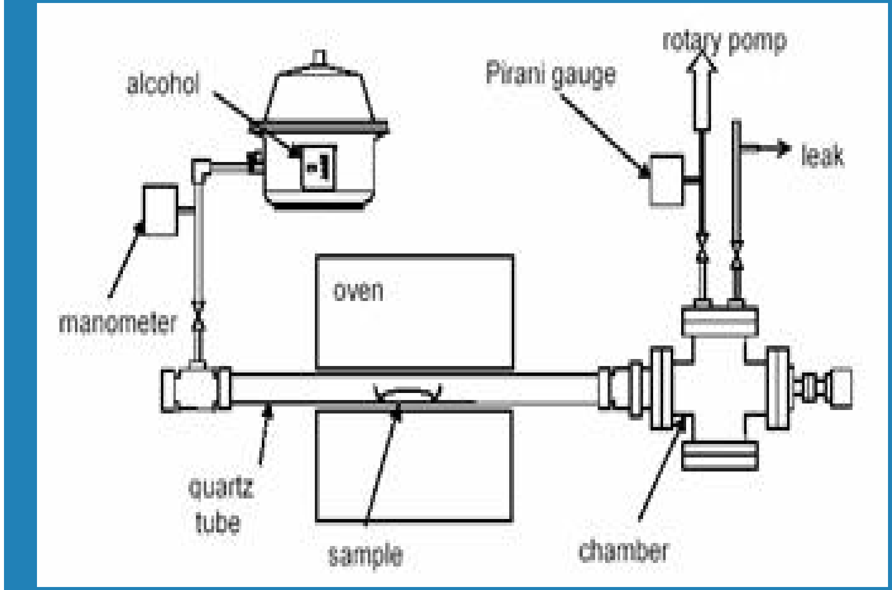




Thermal CVD

Fe, Ni, Co or an alloy as catalyst

750 to 1050° C

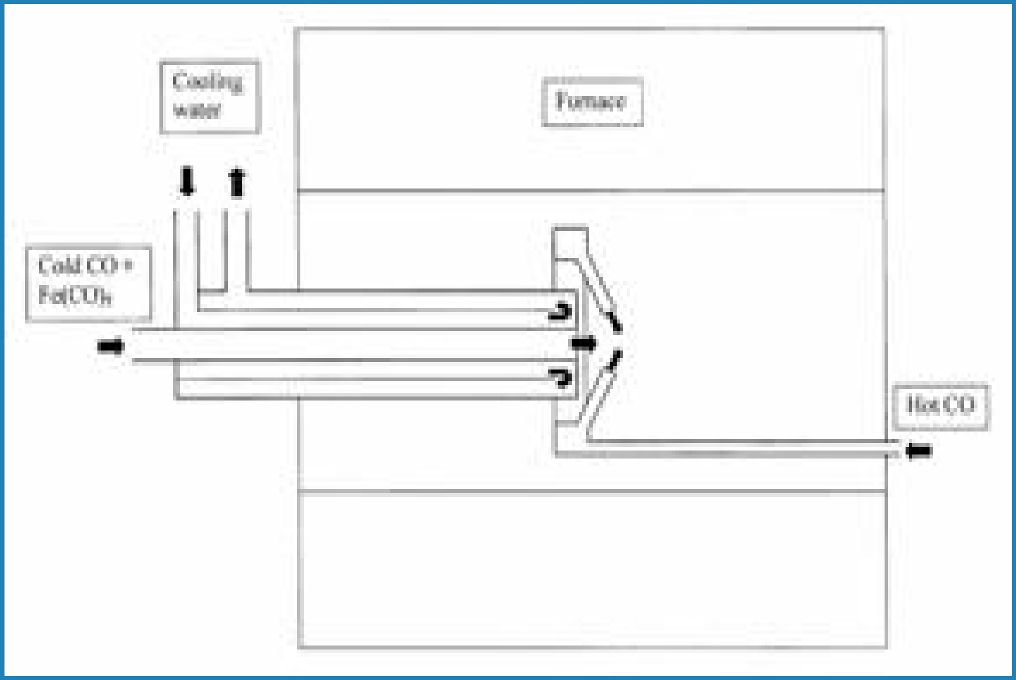


Alcohol catalytic CVD

Fe, Co particles supported with zeolite

Above 550^{0}C

High yield of SWNTs/DWNT mixture



HiPCO

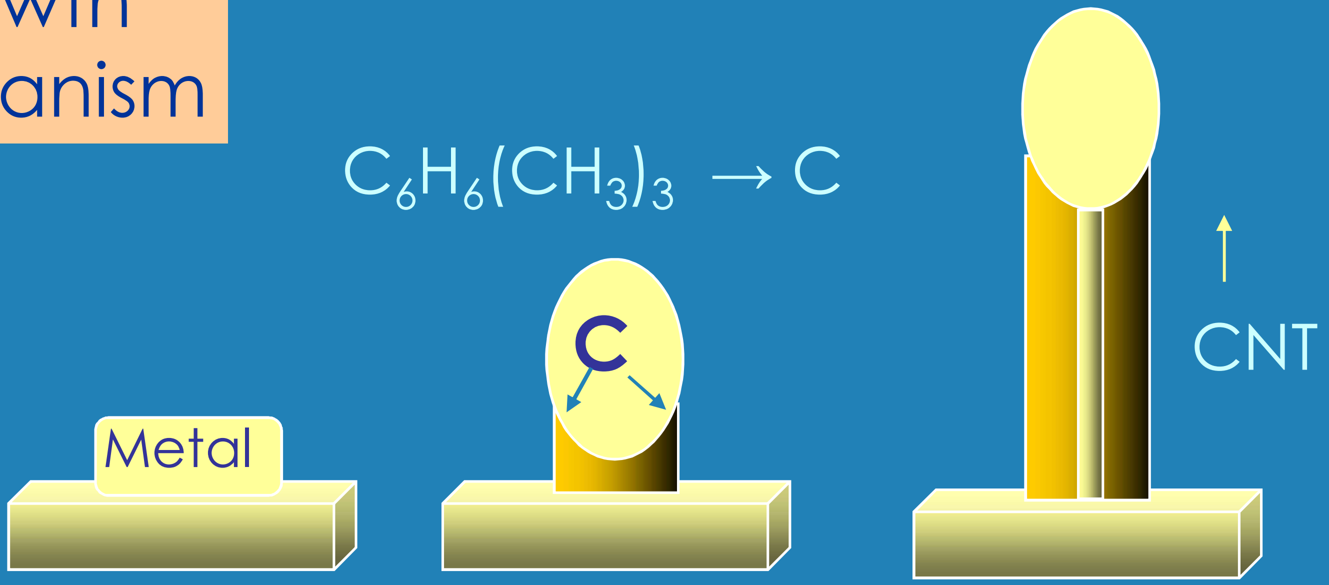
Flowing CO, along with $Fe(CO)_5$ through a heated reactor

Purity of 97% at rates of 450 mg/h

Thermal CVD set-up “First Nano”

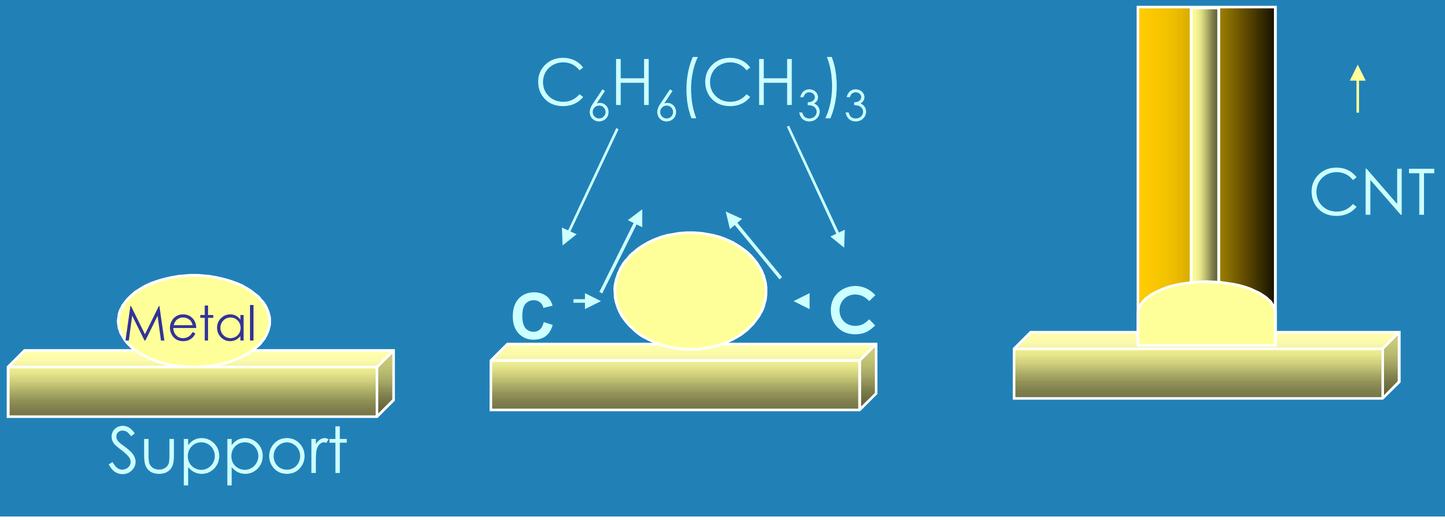
Growth Mechanism

Tip Growth Mechanism



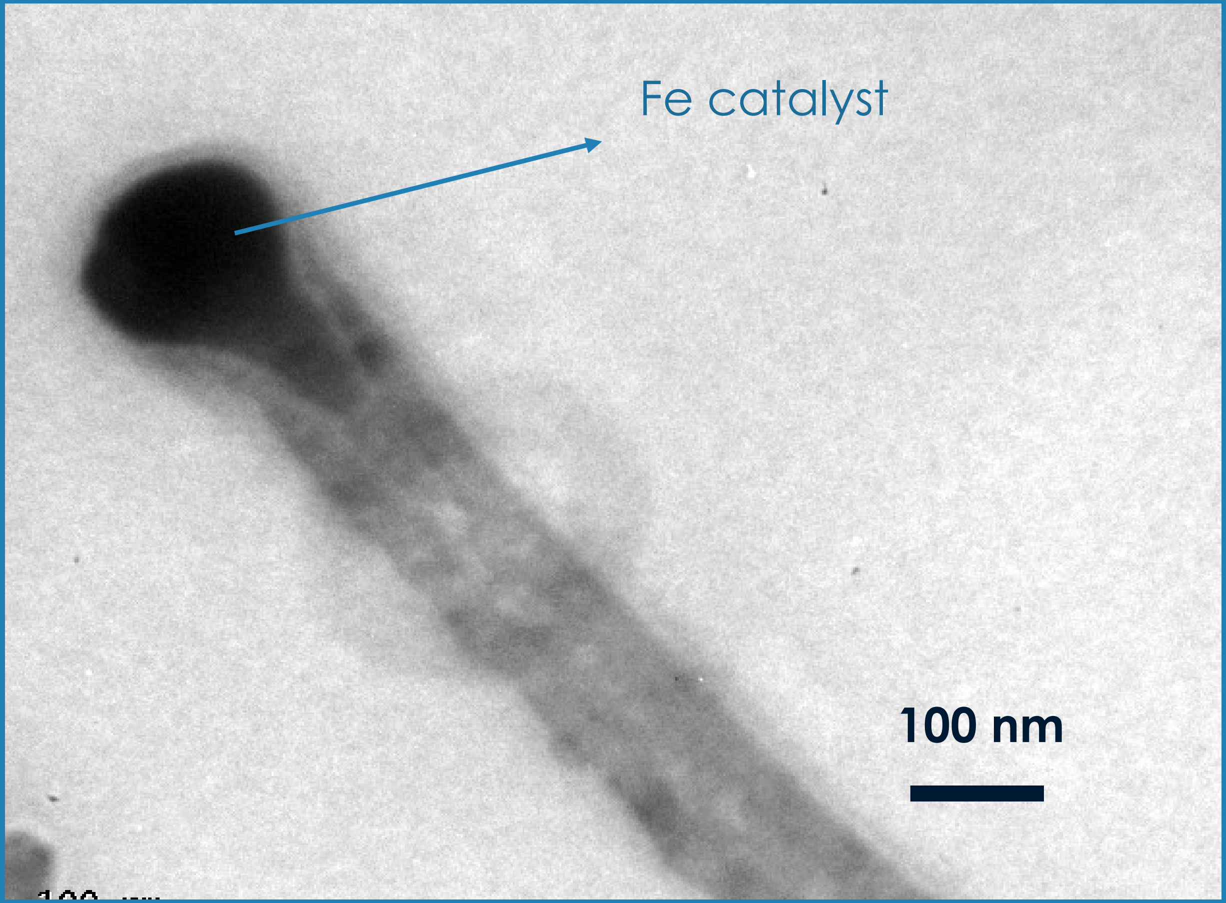
$C_6H_6(CH_3)_3 \rightarrow C$

Root Growth Mechanism



$C_6H_6(CH_3)_3$

“Tip Growth” mechanism



Purification Strategies

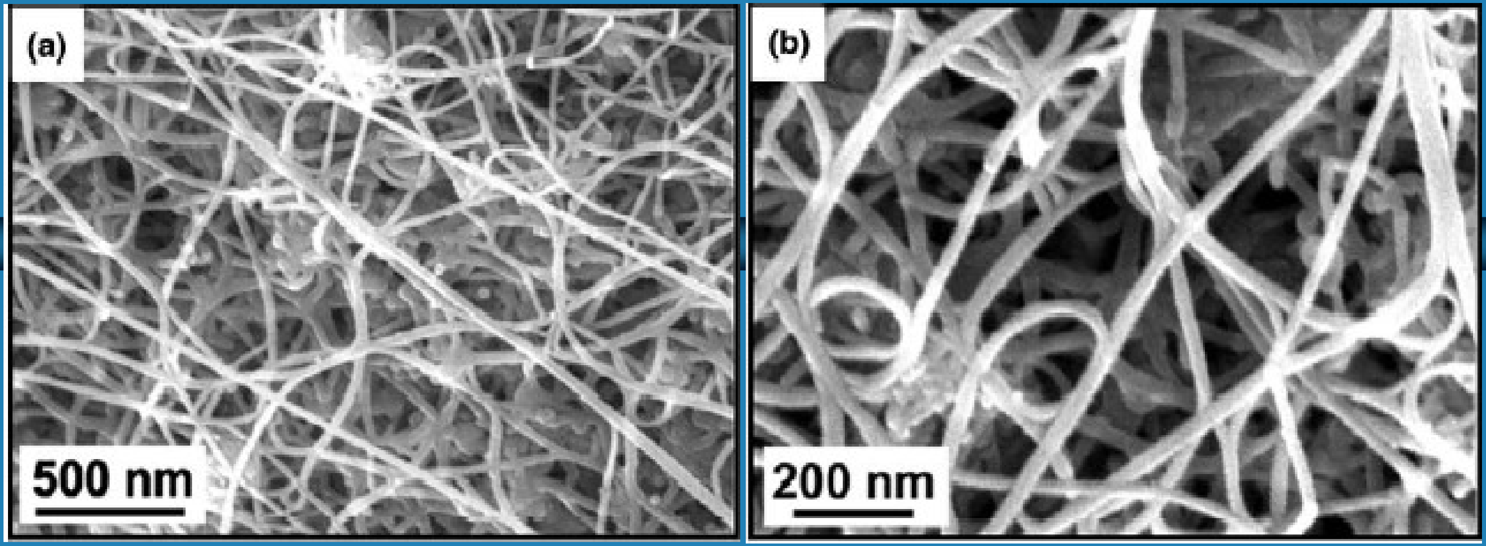
Acid Treatment : (a) H_2O_2 / H_2SO_4
(b) HNO_3 / H_2SO_4
(c) Conc. HCl

Ultrasonication, Refluxing at 100^0C-120^0C
Micro/nano Membrane Filtration
Annealing / Burning in Air at 400^0C
Microwave Heating
Heat treatment at 1000^0C-1100^0C in H_2 atmosphere

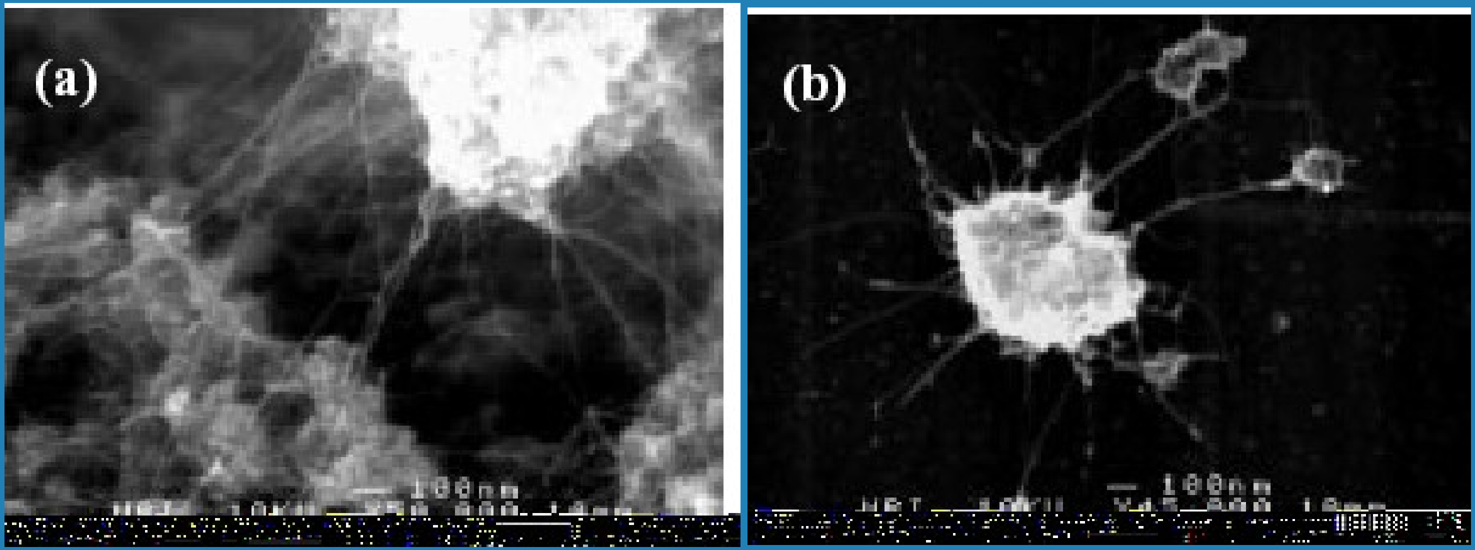
Characterization Techniques

- SEM: Structural Growth Patterns, Alignment
- TEM: CNT Types-SWNT/MWNT, Defects
- X-Ray Diffraction (XRD): Extent of graphitization
- EDX: Element Identification, Binding Energy
- Raman Spectroscopy: Defects, Radial geometry
- IR: Oxygenated Surface Functionalities
- AFM/ STM: Coulomb Blockade, SET property

Scanning Electron Microscopy

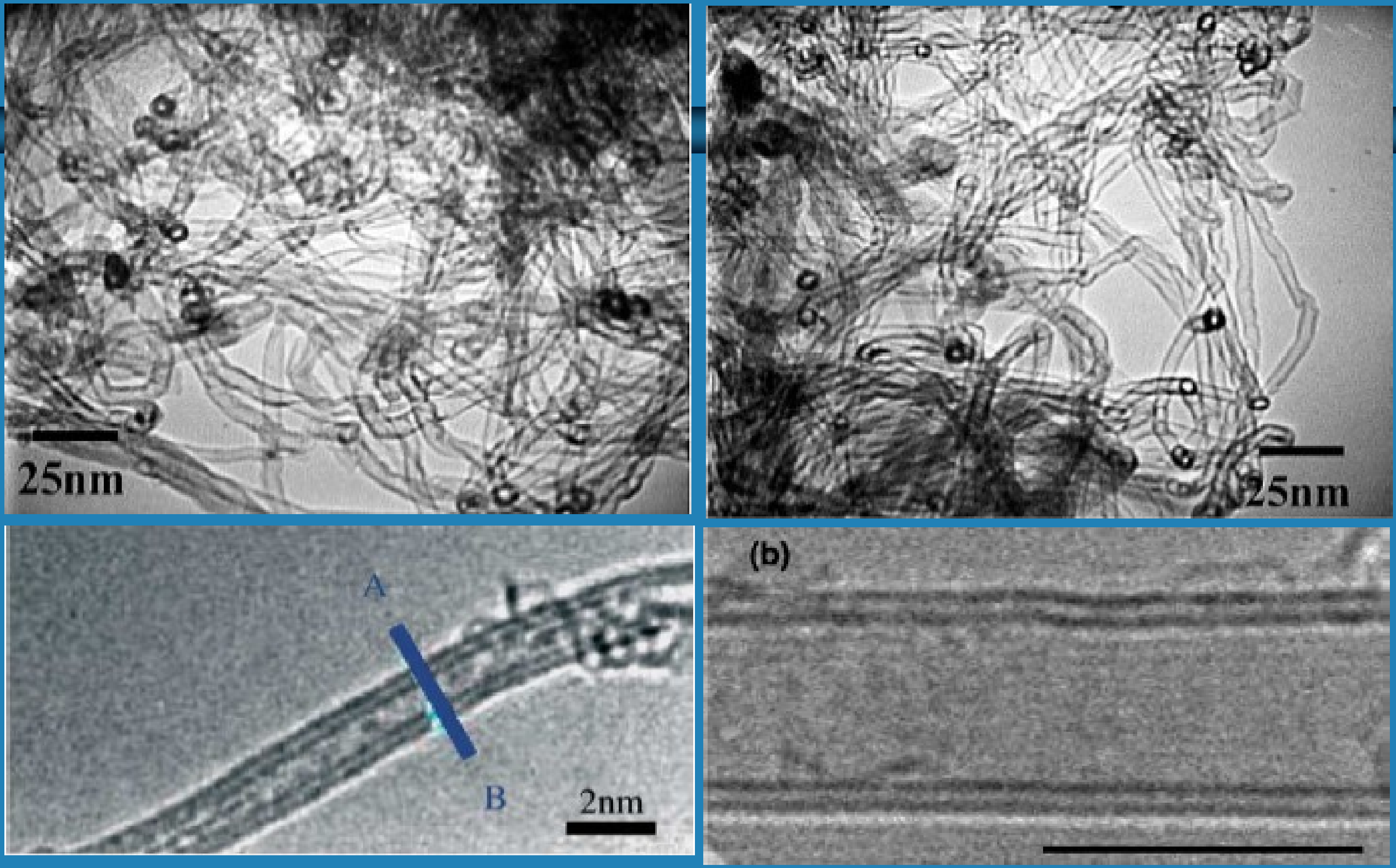


High-resolution SEM of bundles of DWNTs



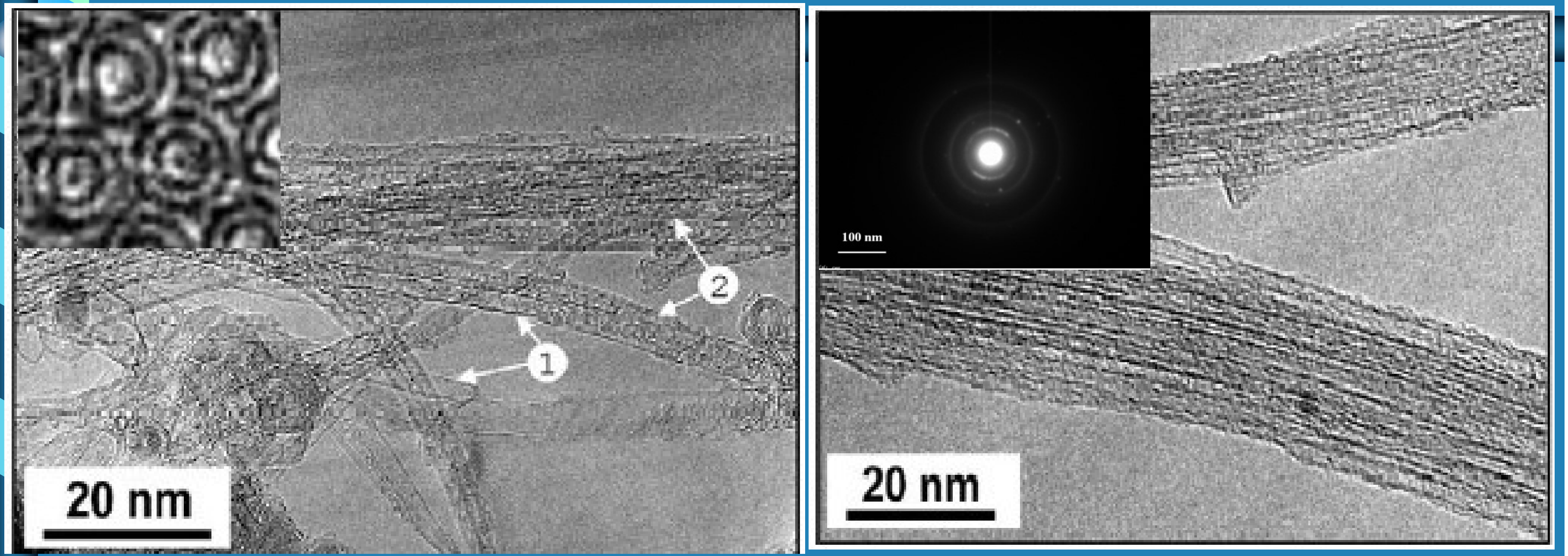
High-resolution SEM of SWNTs

Transmission Electron Microscopy



Catalytic decomposition of C_2H_2 over Fe-Co mixture at 900^0C

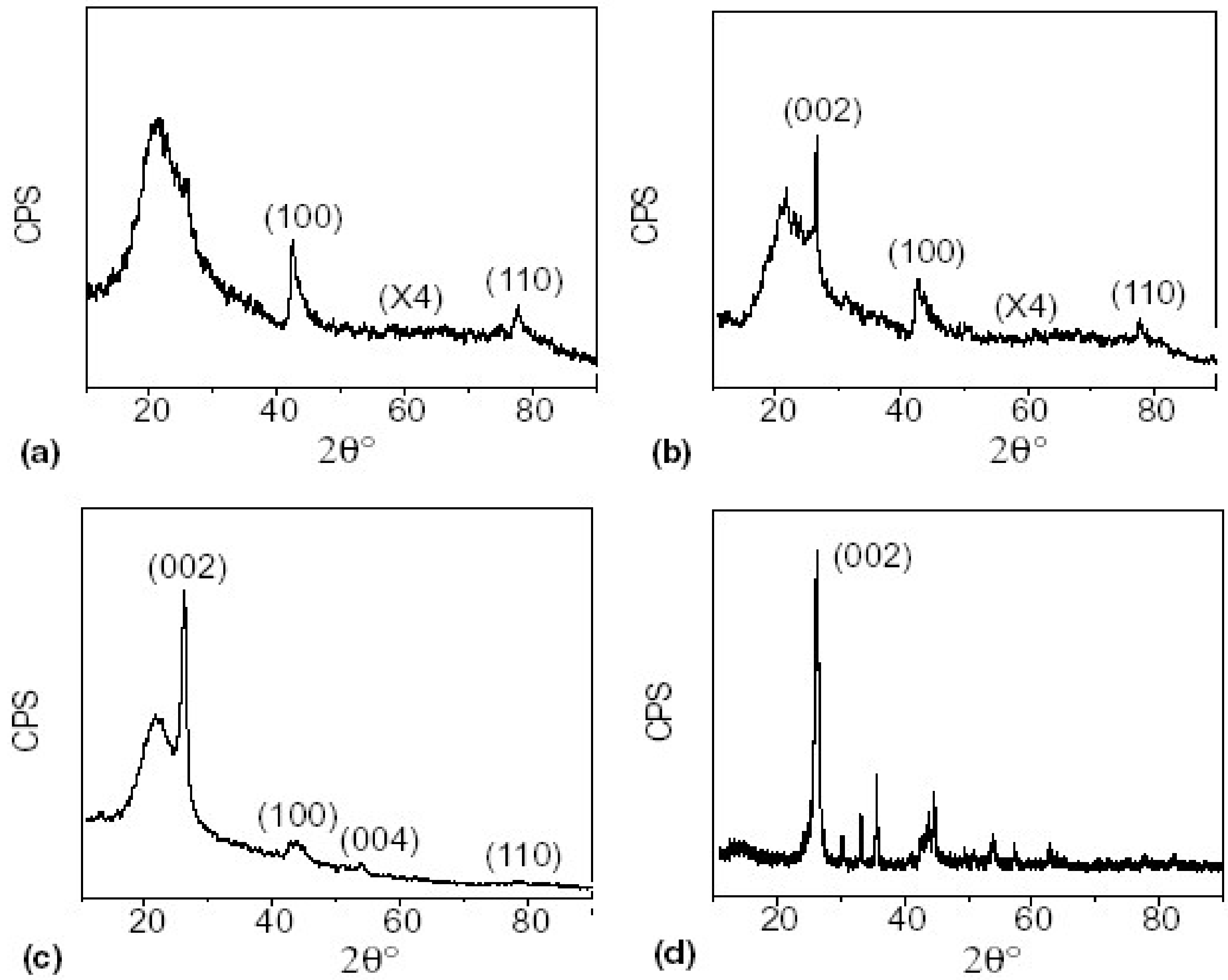
CPL 382 (2003) 679-685



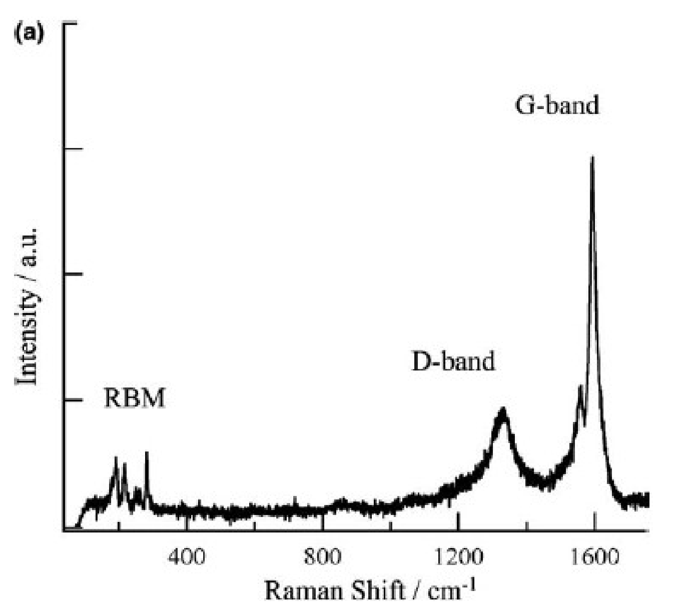
Catalytic decomposition of CH_4 over Fe-Mo/Al_2O_3

CPL 373 (2003) 475-479

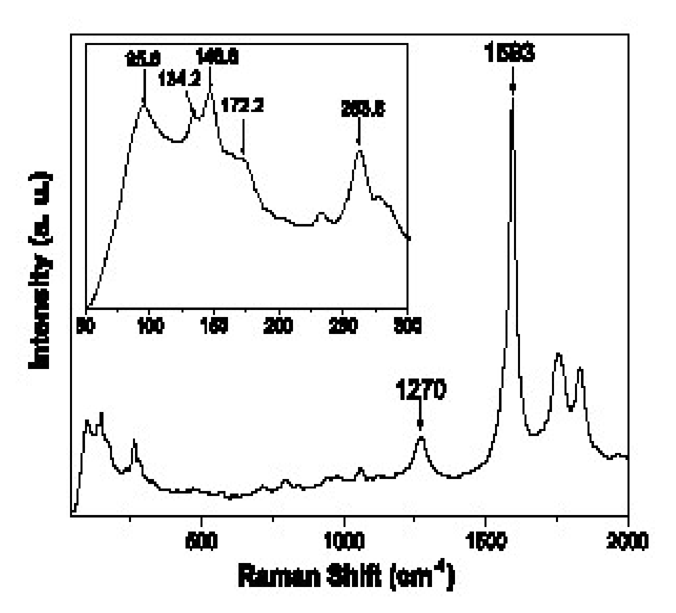
X-Ray Diffraction



Raman Studies



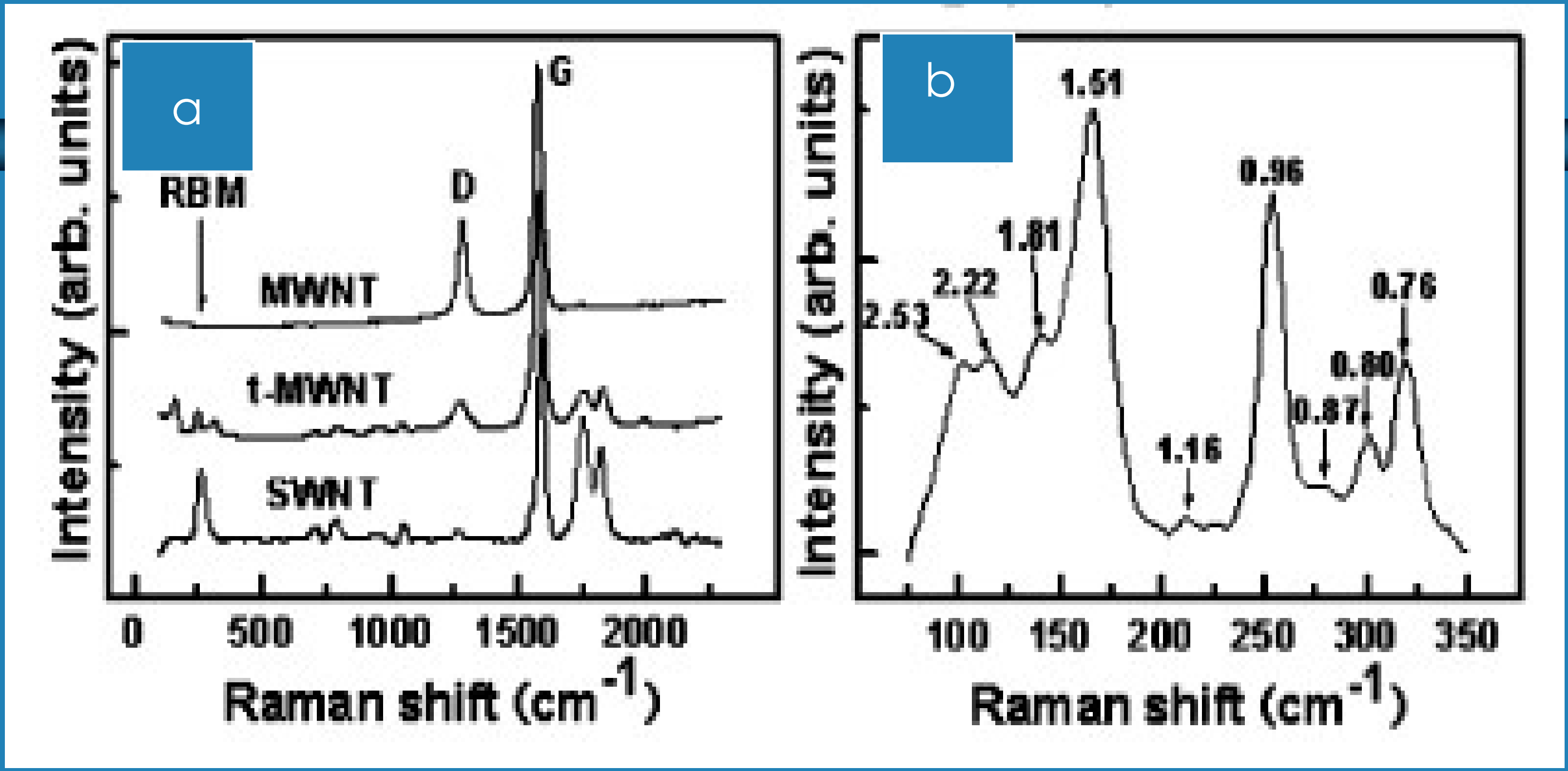
CCVD of C_2H_2 over Fe-Co mixture at 900^0C



CCVD of CH_4 over Fe-Mo/Al_2O_3
at 950^0C

RBM frequency ω_R (cm^{-1}) = 6.5+223.75/d (nm) …..Van der waal
= 248/d (nm)……..pure SWNT

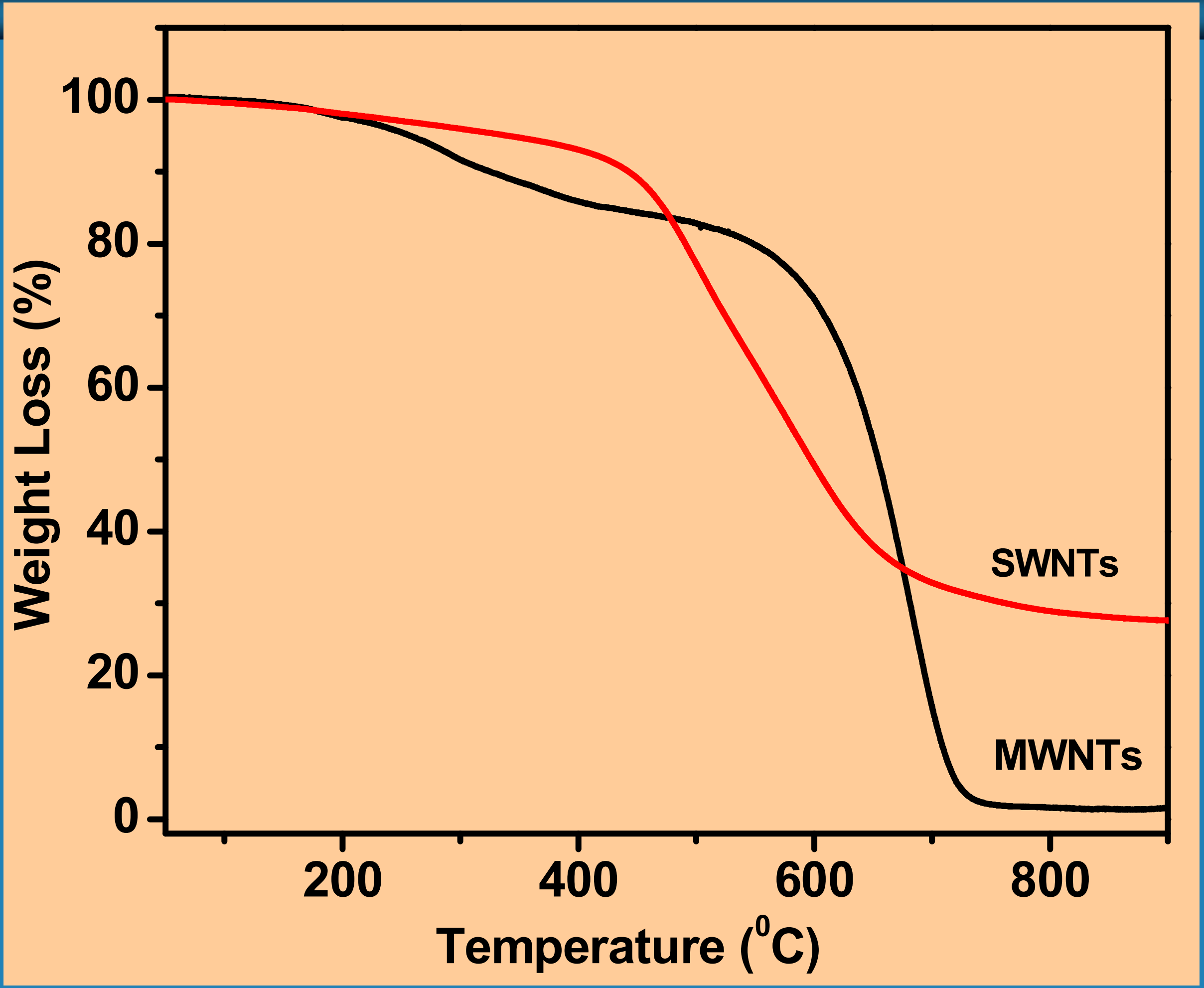
The nucleation of the inner tube should occur after the growth of the outer tube



(a) Raman spectra of MWNT, thin-MWNT and SWNT
(b) RBM of the thin-MWNT

J. Phys. Chem. B, Vol. 108, No. 46, 200

TGA



Weight Loss (%)
100
80
60
40
20
0
200
400
600
800
Temperature (^{0}C)
SWNTs
MWNTs

The Route Towards Applications

Molecular perfection and high aspect ratio promise not only to transform existing technologies but also to enable new ones. It opens incredible applications in materials, chemical processing, electronics, biology, medicine, transportation, and energy management

- Fuel cells, Batteries, Supercapacitors
- Hydrogen Storage
- Reinforcing composite
- Electronic devices

B. Gao, Chem. Phys. Lett. 327, 69 (200
A C Dillon et al. Nature, 386, 377 (1997)

Fuel cells, Batteries, Supercapacitors

Intrinsic characteristics
High surface area (1000 m^2/g)
Good electrical and thermal conductivity
Linear geometry

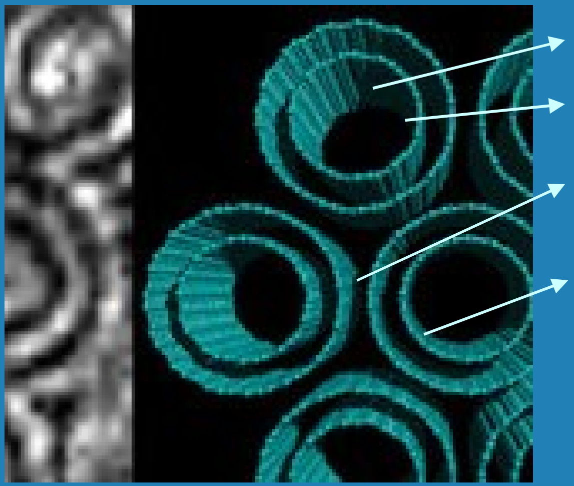
Currently 50% of all Li- batteries incorporate CNFs which Doubles their energy capacity
CNT shows tenfold improvement in the performance of fuel cells

A tiny fuel cell for mobile terminals using carbon nanotubes as electrodes

Hydrogen Storage

Hydrogen is an Energy carrier with great potential to become a major fuel for both mobile and stationary power generation

Major hurdles is storage: less cost effective,
compactness and safety



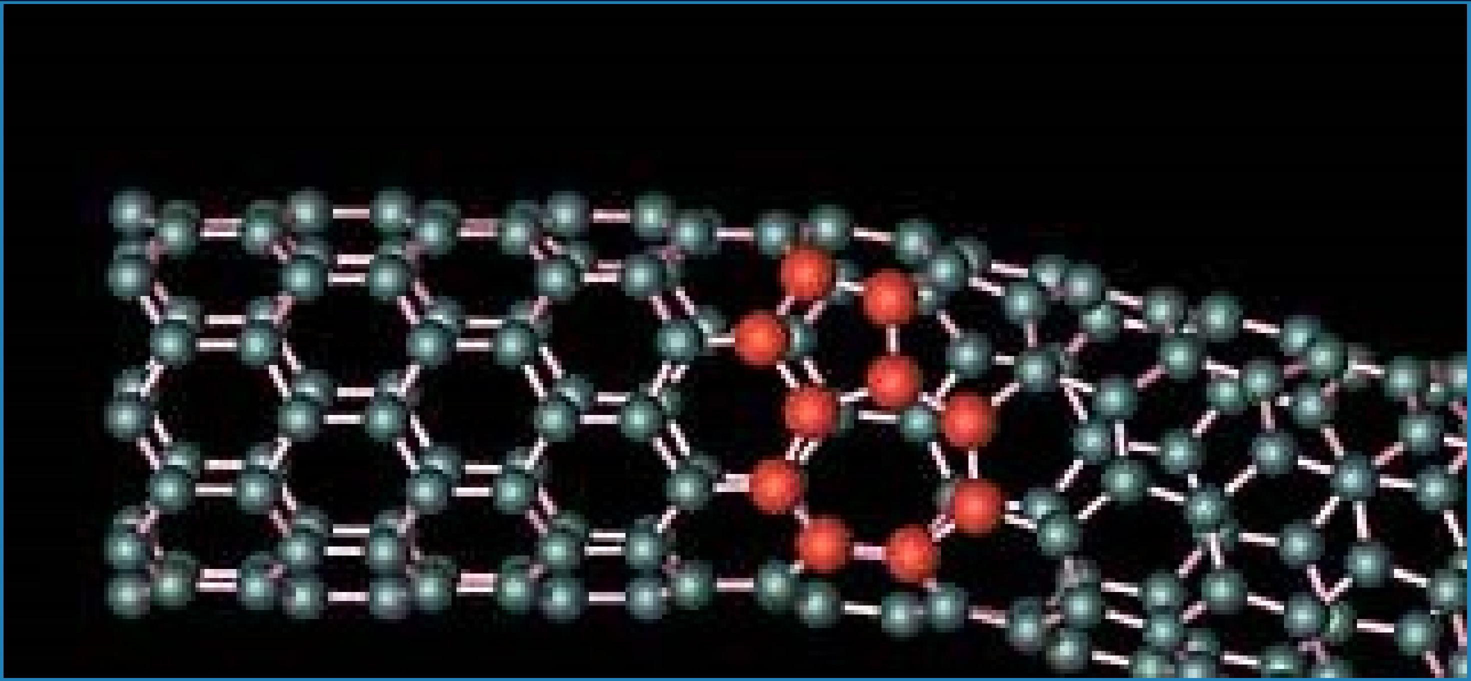
Composites; Superhard, Superstrong

Hot-drawn nanotube/PVA fibers

Bulletproof vests
Protective textiles
Helmets

Nano Lett. 2005

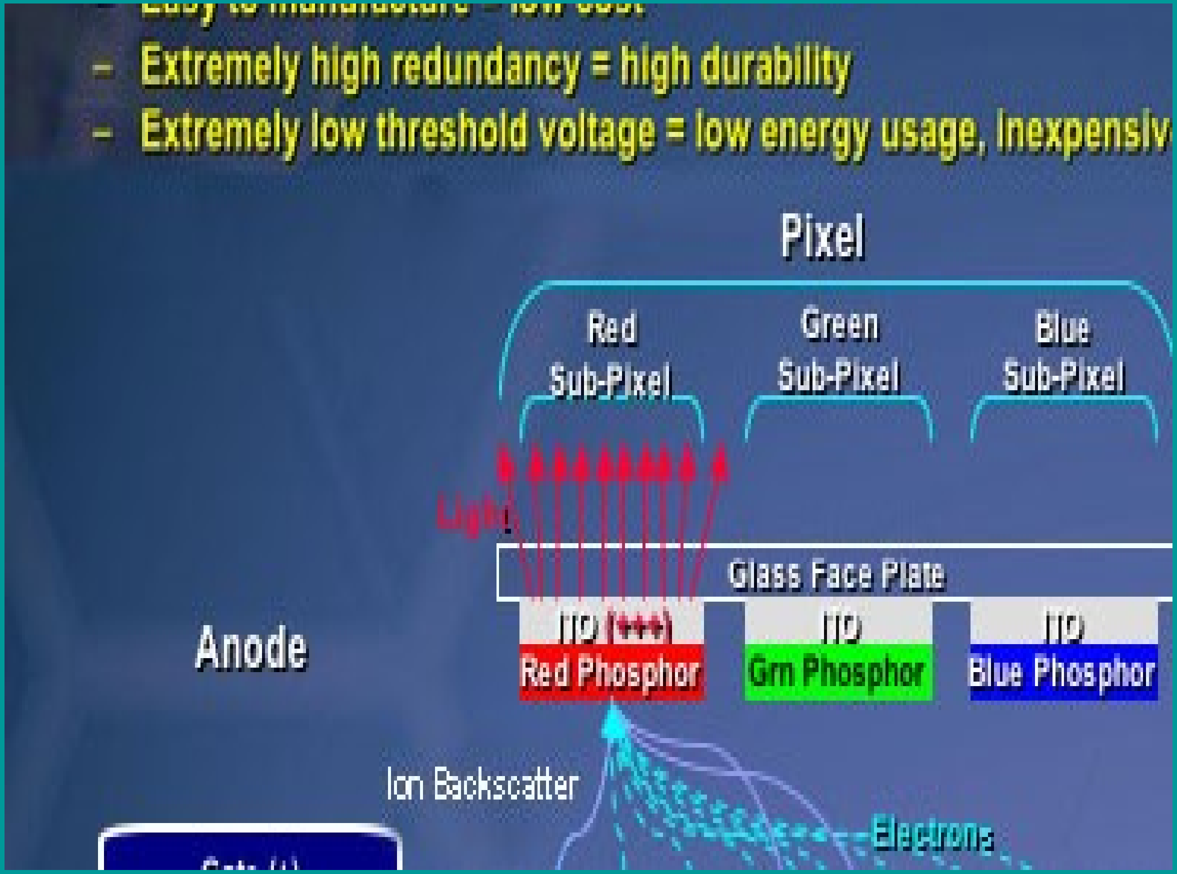
A CNT diode ?



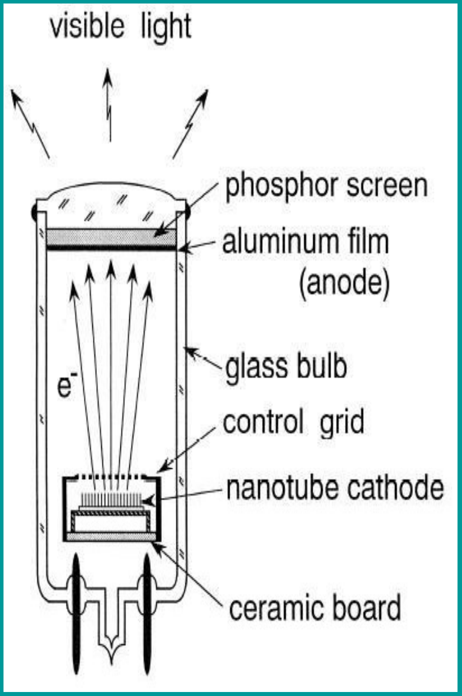
A diode can be formed by joining two nanoscale carbon tubes with different electronic properties

GE has succeeded to make CNT multifunctional diode (Dr. Ji-Ung Lee)

How Far Away from Reality ?



- Easy to manufacture = low cost
- Extremely high redundancy = high durability
- Extremely low threshold voltage = low energy usage, inexpensiv



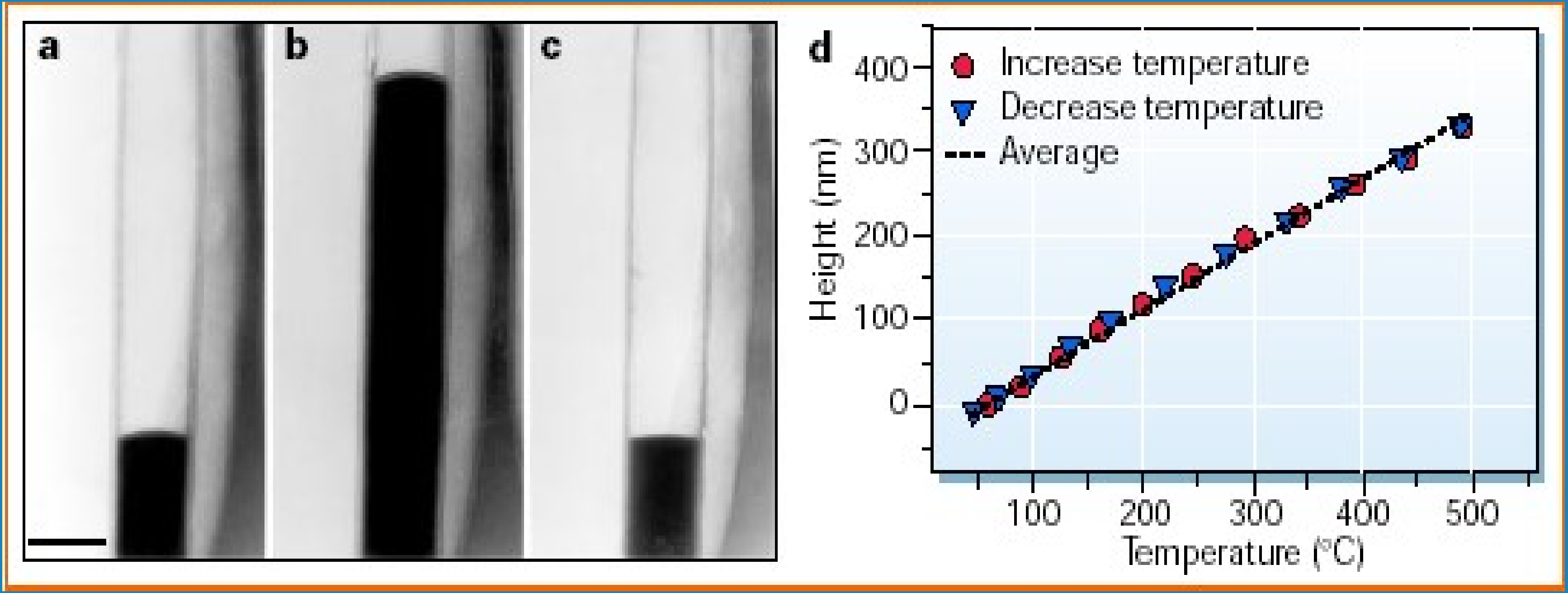
SDNT Field Emission Displays
2004 38" SWNT FED prototype
Expected Launch 2006-2007

SDNT Advantages
Size and Conductivity make them the ideal field emitter
Easy to manufacture= low cost
High durability
Low threshold voltage= low energy usage, inexpensive electronics

Space and Defence Applications

Faster, Better, Cheaper Space Transportation with Nanotubes

Gallium containing Carbon nanothermometer



58^{0}C 490^{0}C 45^{0}C

Macroscopic properties of Gallium are retained in this miniaturized nanodevice

Here lies the Future

"In 1900, nylon, polyester, polypropylene, Kevlar and other modern fibers and their composites did not exist, but life today seems to depend on them,"

"The rate at which technology is changing, is increasing so much, more dramatic changes can be expected in the next 100 years. Every major polymer fiber company in the world is now paying attention to the potential impact of carbon nanotubes."

Challenges

Less cost effective synthetic procedures

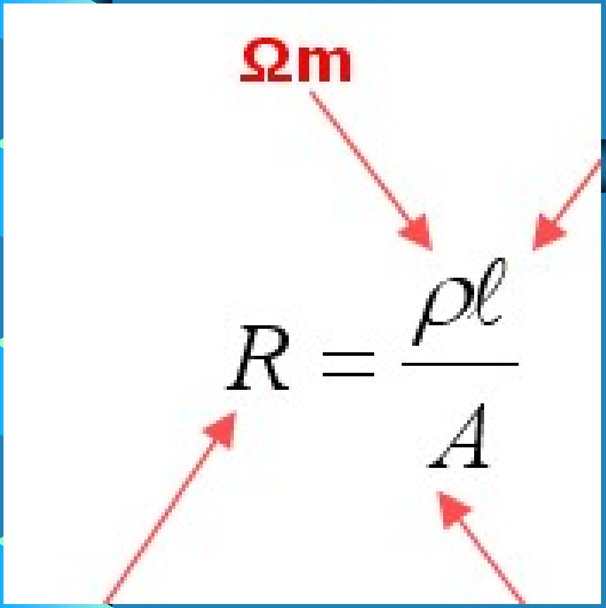
Polydispersity in nanotube type

Tedious separation methods

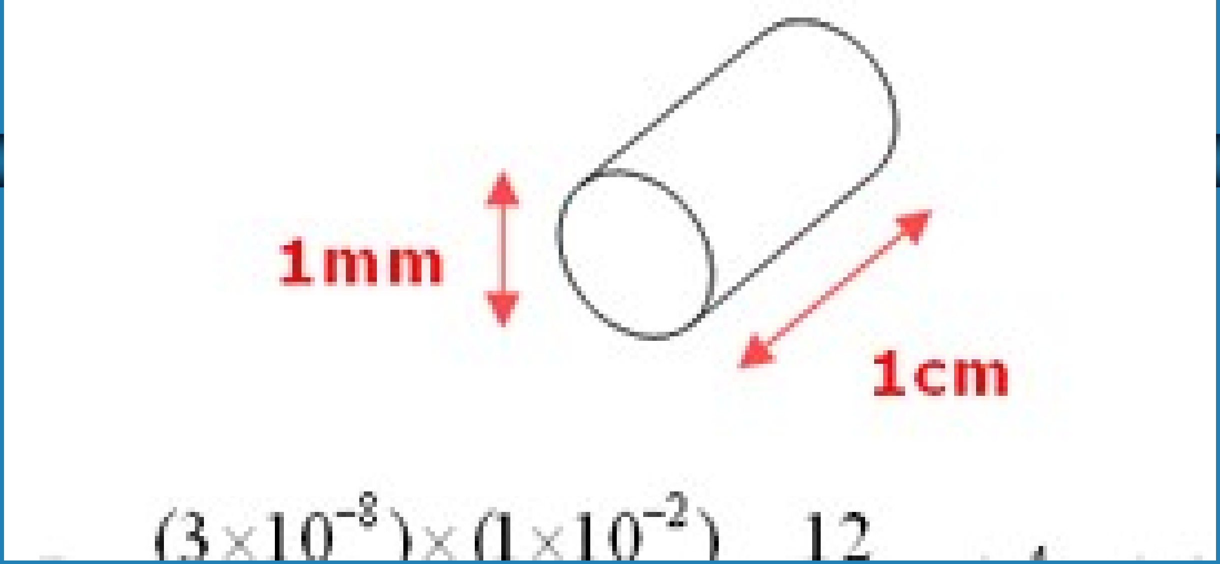
Limitations in processing and assembly in device

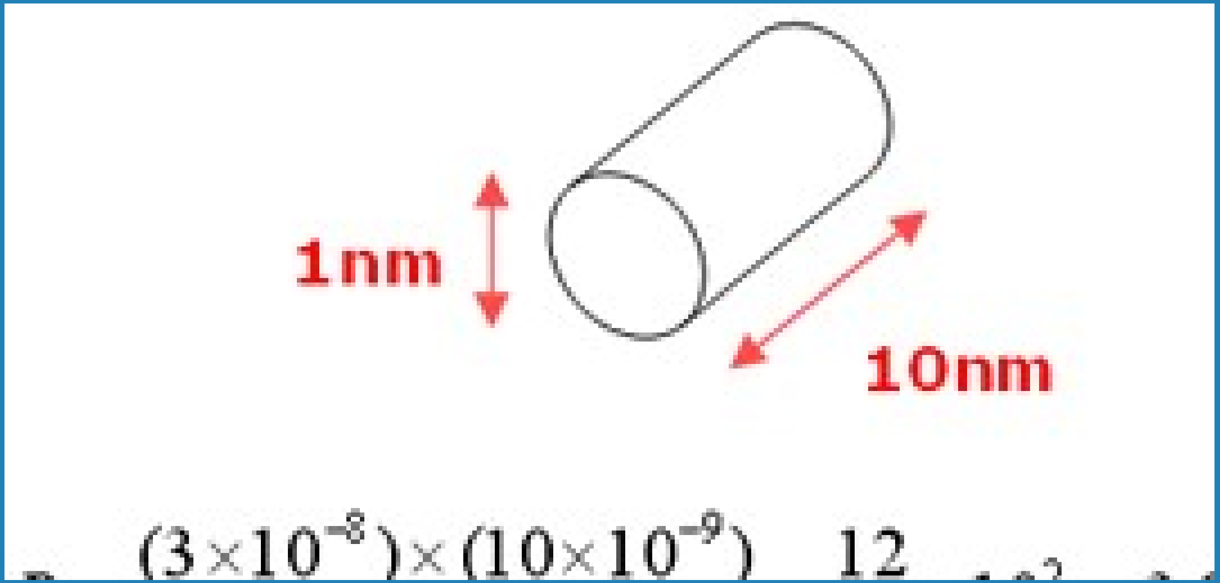
Little knowledge about growth mechanism

Failure in Nano-size ?

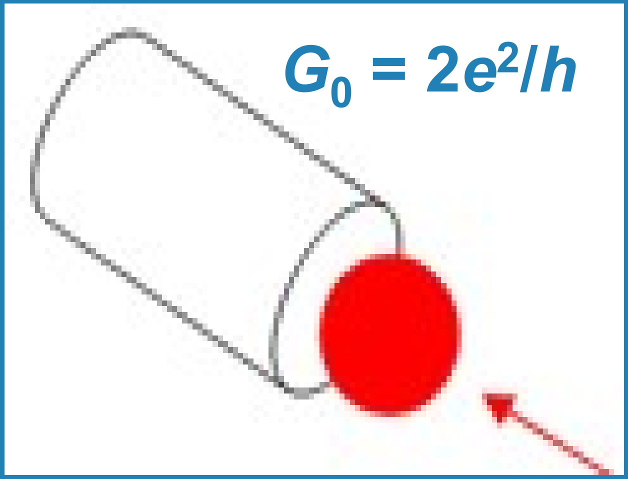


$$R = \frac{\rho \ell}{A}$$

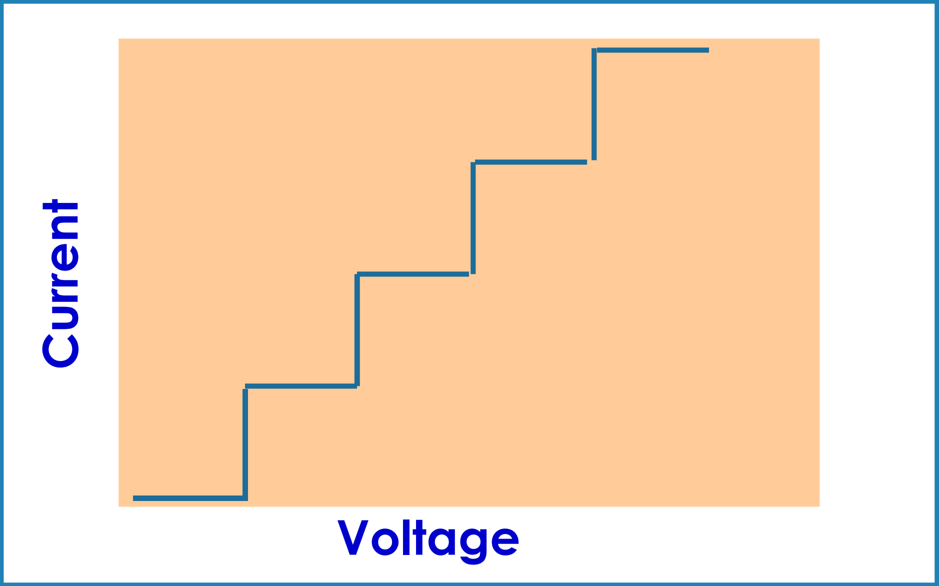


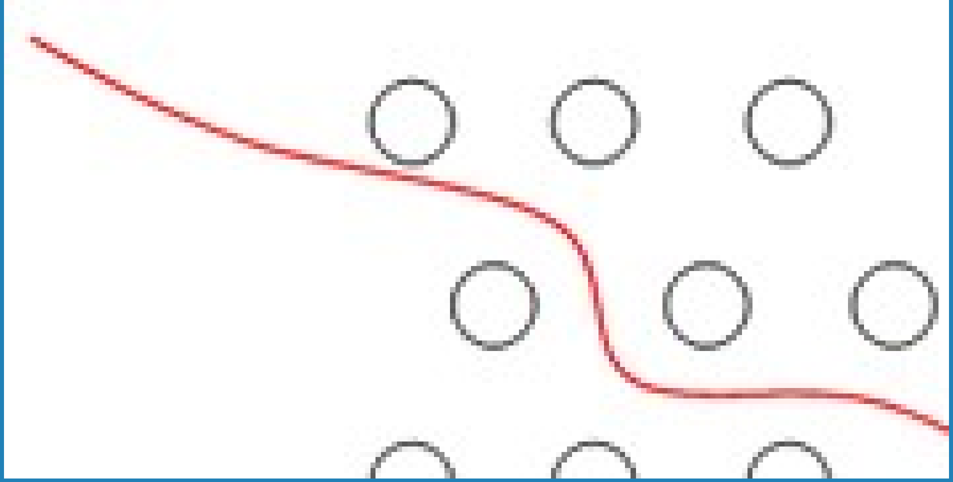


CNT Can solve this problem !



Conduct High Currents !

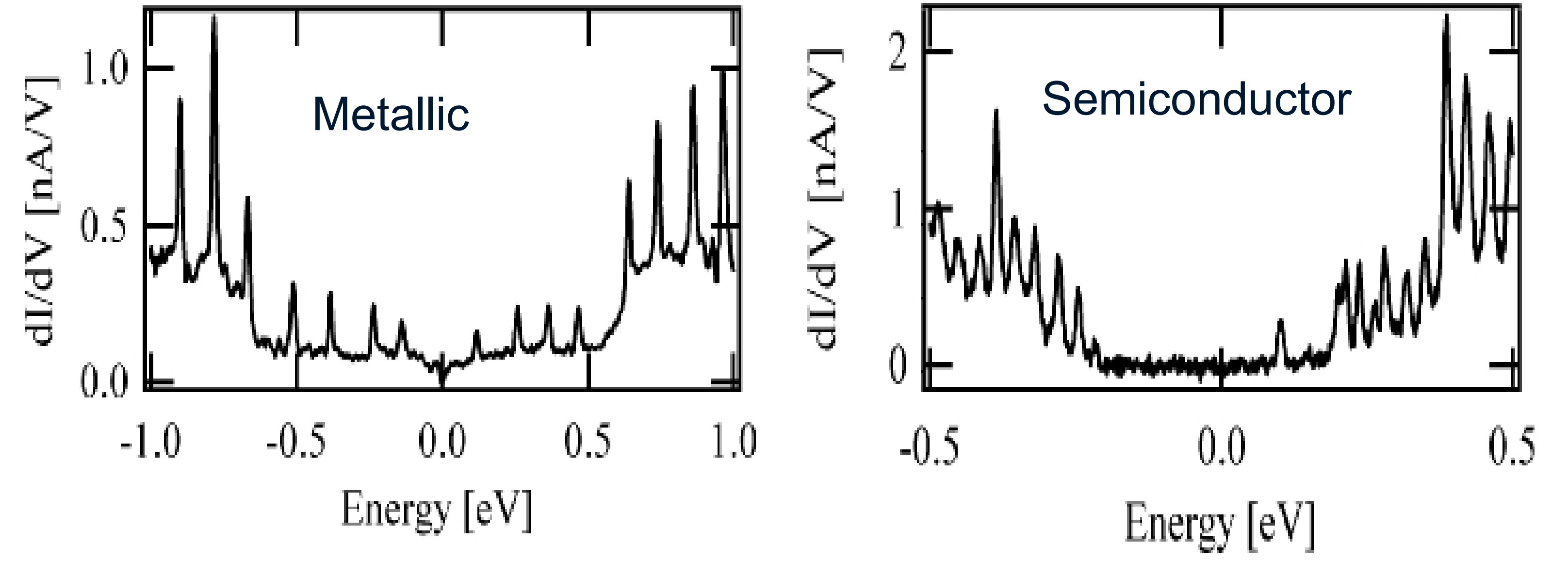


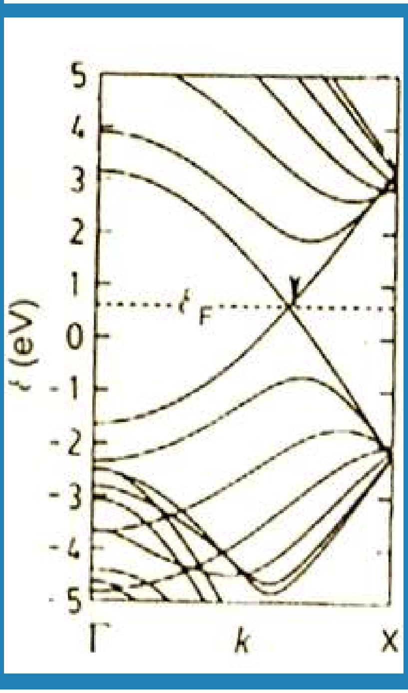


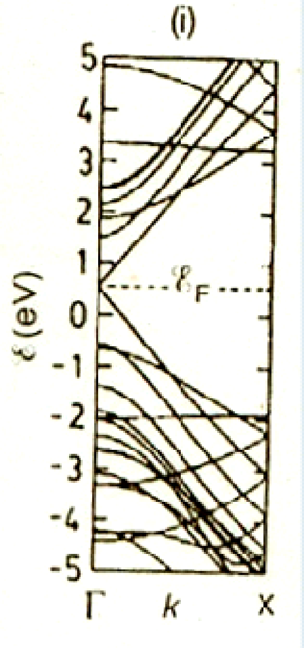
Handle High Current Densities
Faster and Smaller Chips !

Contact Problem ?

Coulomb blockade







Energy required to add/remove an e-
$\propto$ 1/ Capacitance

Bibliography

A number of sources were used for the presentation, including books, magazines, newspapers, journals. Those sources are listed wherever possible and images are also acknowledged

i. *Chem. Rev.* P. M. Ajayan **1999,** *99,* 1787–1799

ii. ‘*The Chemistry of Nanomaterials-Synthesis, Properties and Applications*’ vol. 1 C. N. R. Rao, *et. al.*

iii. ‘Physical Properties of Carbon Nanotubes’ R. Saito, G. Dresselhaus, M. S. Dresselhaus; Imperial College Press: London (1998)

Silicon Chemistry

- Semiconductor-electronic Industry
- Doping, Polishing, Etching, Stable oxide and good metal –Si contact
- Microelectronic Industry
- (FETs, MOSFETs, ICs, MEMs, LED………………………

Porous Silicon

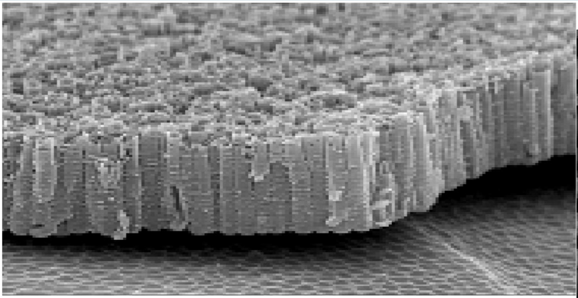
- 1990 Caham (Discovery of porous Si
- Photoluminescence (Visible Range)
- Nanocrystallites, Pore size: Decides wavelength of emission
- Tunable optical and electrical properties
- breakthrough for Si industry as optoelectronic materials

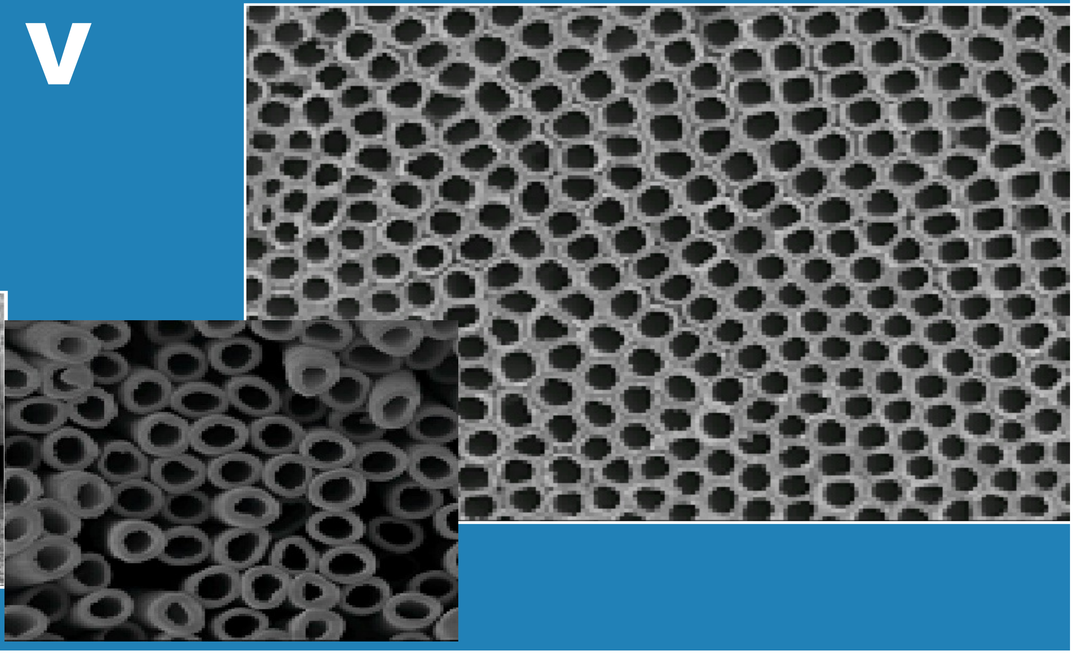
How to make Si Porous ?

- Ion irradiation
- Spark Erosion
- Chemical Etching
- Electrochemical Etching
  [HF + HNO_3 Mixture]
- Concentration of HF, surface structure (roughness), temperature, time of exposure and doping level, effect of light, current density, type of doping]

Electrochemical Etching

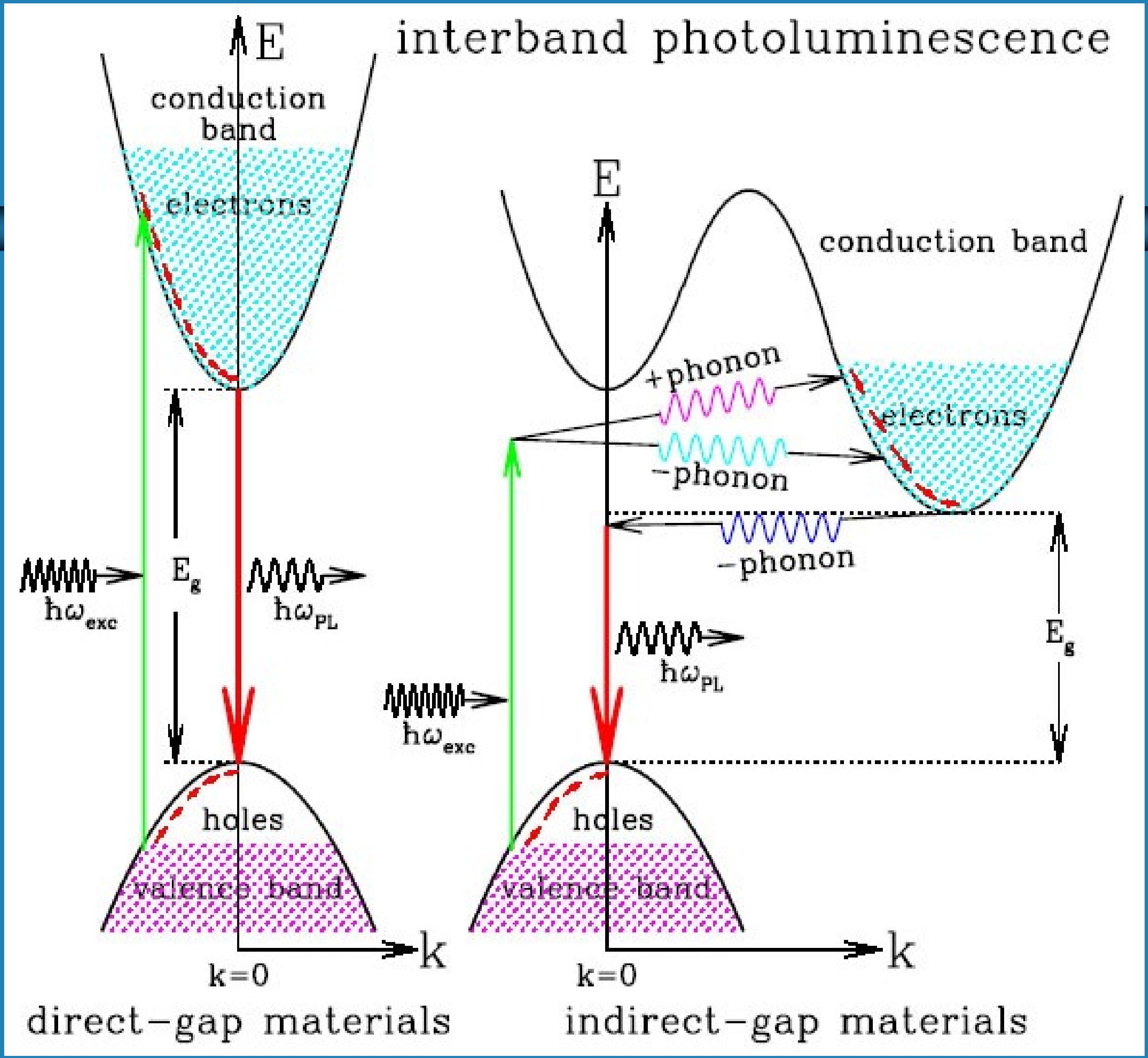
- Substrate: p-Si (111) B doped
- Current: 30 mA
- Solution: HF+ Ethanol+ water
- Voltage: 24 V





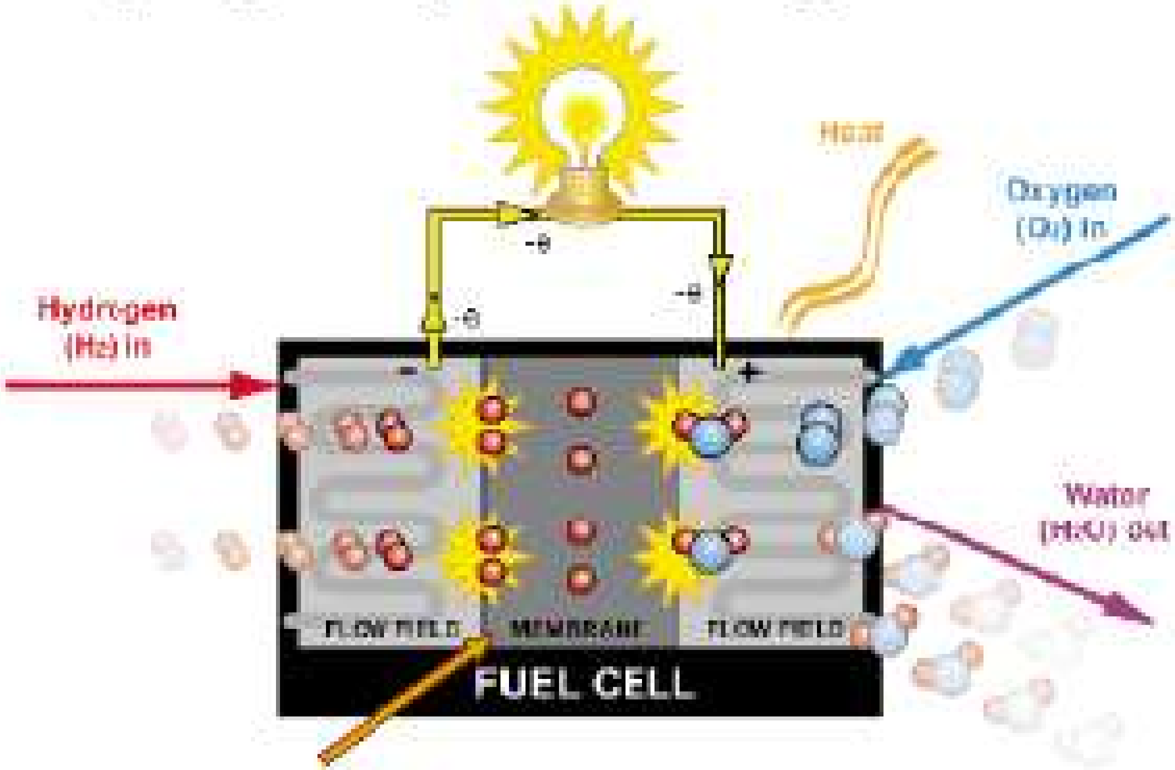
Properties of Porous Si

- Morphology: Nanopores, different shapes based on substrate nature
- Structure: Complex Amorphous
- Chemical Nature: Depends on synthesis parameters, F, O, H makes properties variations
- Electronic Structure: Indirect and Direct Band structure


interband photoluminescence
E
conduction band
electrons
E_g
$\hbar\omega_{exc}$
$\hbar\omega_{PL}$
holes
valence band
k
k=0
direct−gap materials
E
conduction band
+phonon
electrons
−phonon
−phonon
$\hbar\omega_{PL}$
$\hbar\omega_{exc}$
E_g
holes
valence band
k
k=0
indirect−gap materials

Fuel Cell and Batteries

$2H_2 + O_2 \rightarrow 2H_2O$ + electrical power + heat



Membrane conducts protons from anode to cathode
proton exchange membrane (PEM)

Automobiles

Sports and Toys

Cosmetics

Biomedical Applications

Environmental

Space and Defense