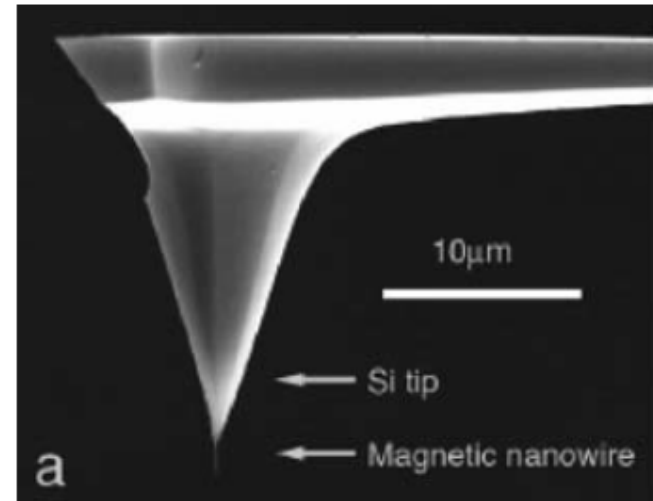
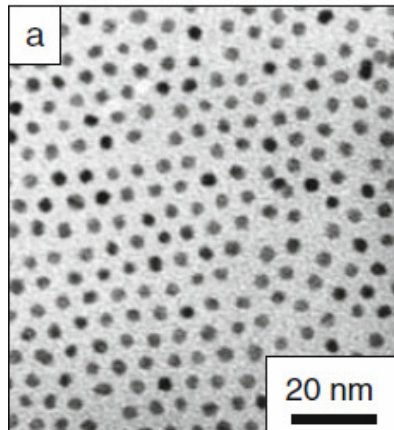
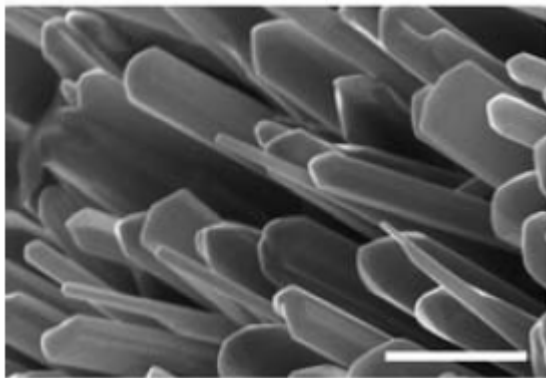
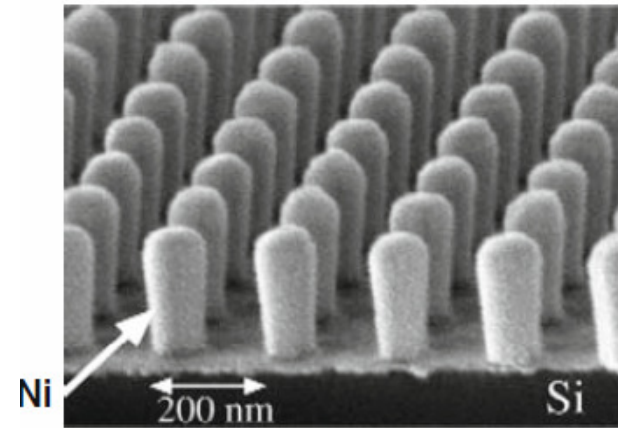
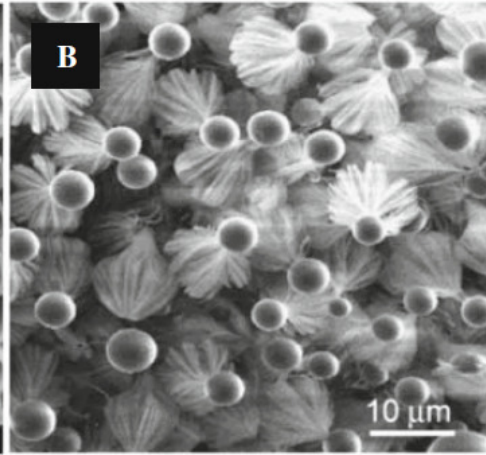
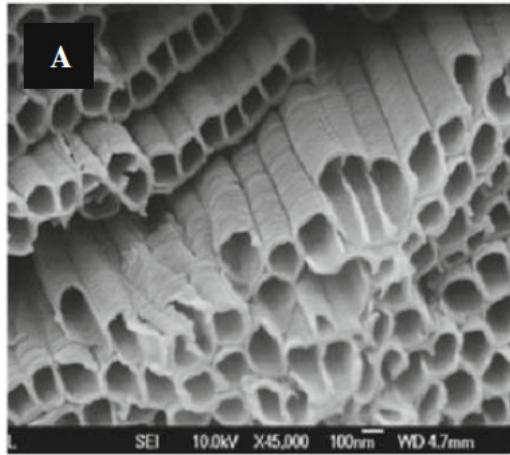


# Nanochemistry Lecture 1

Dr Charu Arora, Associate Professor, Department of Chemistry

# Nanostructures

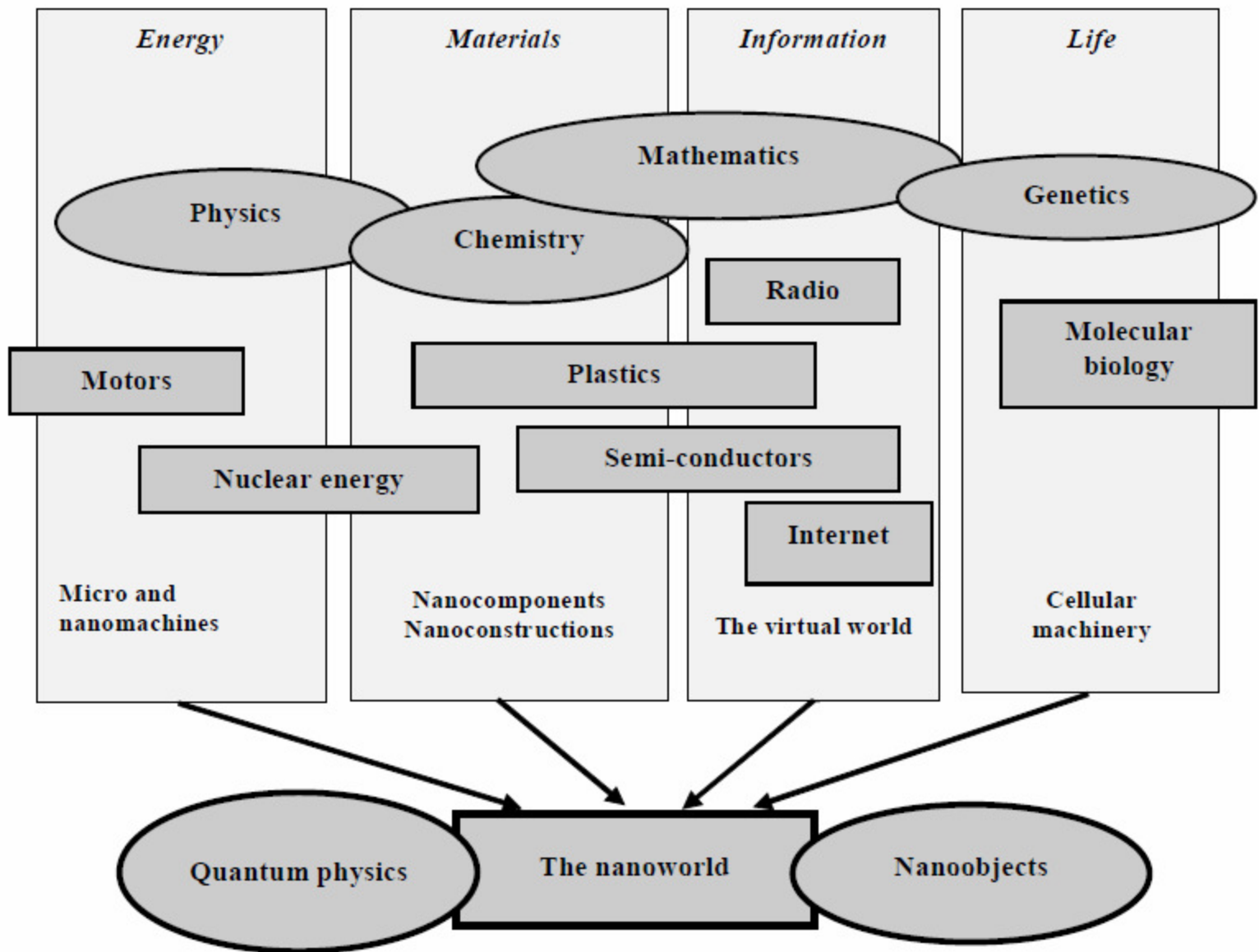


## Nanoscience and nanotechnology

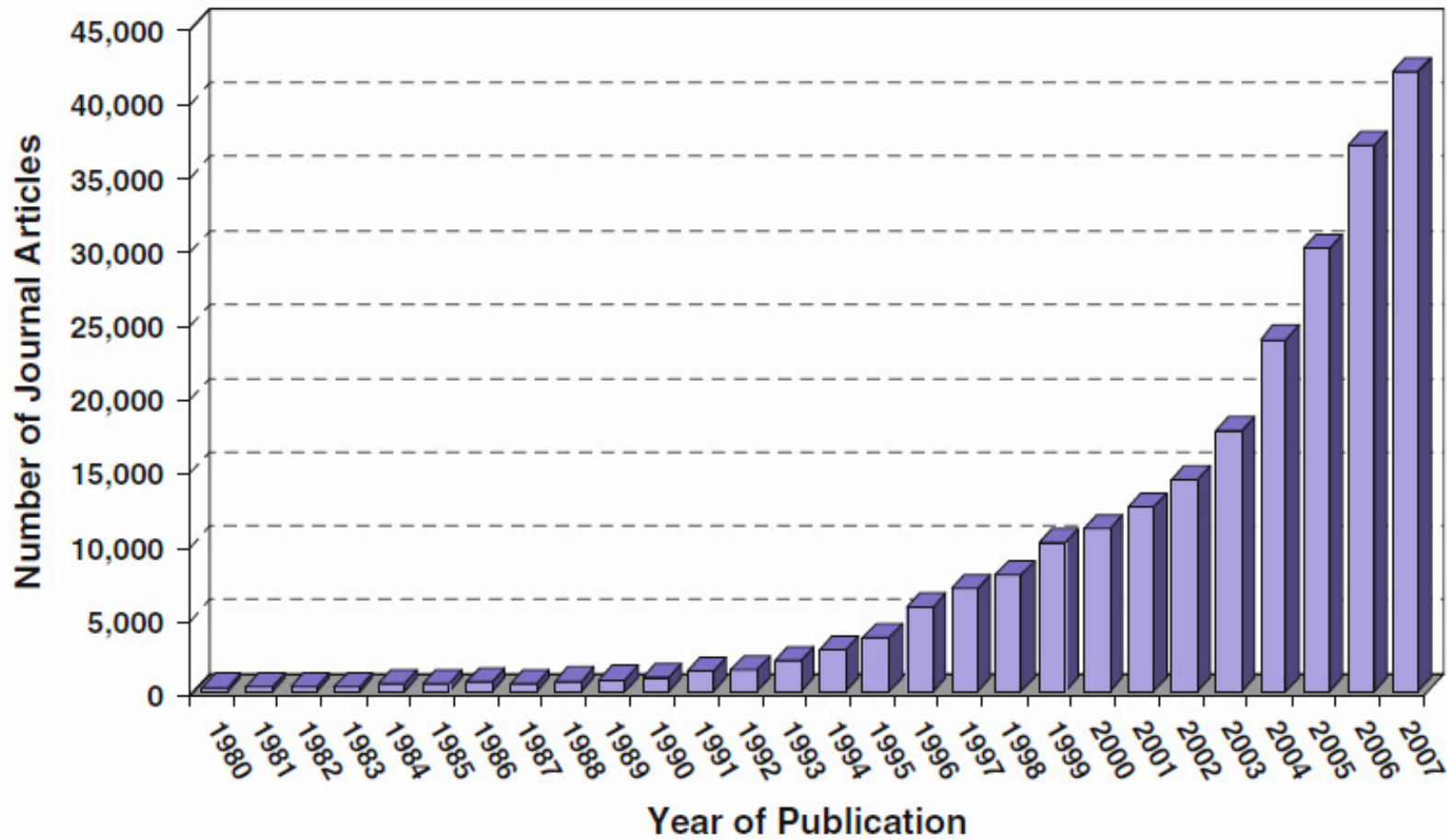
- ***Nanoscience*** deals with the scientific study of objects with sizes in the 1 – 100 nm range in at least one dimension.
- ***Nanotechnology*** deals with using objects in the same size range to develop products with possible practical application. It is usually based on nanoscience insights.

# Nanoscience and Nanochemistry

- Nanoscience is interesting in part of course because it by definition is new. But a more profound and important reason is that it deals with objects which are only slightly larger than an atom. This means that the properties of the objects can be influenced by direct manifestations of quantum mechanics.
- It is also possible that nanoscale objects do behave just like as expected from (semi)classical physics, but the downgrading in size opens up possible new applications.



# Research on nano



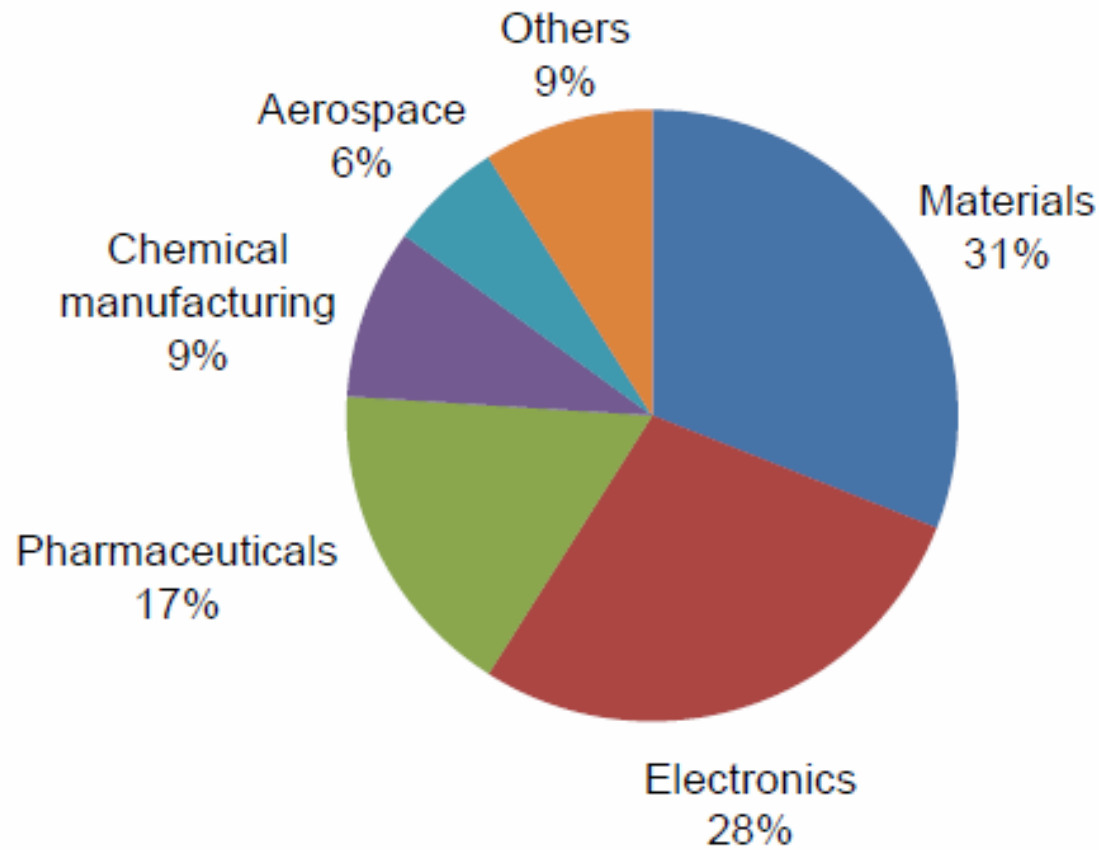
- **Nanotechnology** is the creation of functional materials, devices, and systems through control of matter on the nanometer (1 to 100 nm) length scale and the exploitation of novel properties and phenomena developed at that scale.
- A scientific and technical revolution has begun that is based upon the ability to systematically organize and manipulate matter on the nanometer length scale.

# Ancient nanotech.

- It is interesting to note that there has been use of what now would definitely be called nanoscience much before the advent of the word.
- - Vases used by old Greeks and Romans



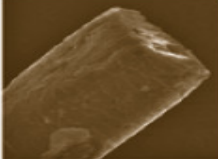
# Nanotechnology market



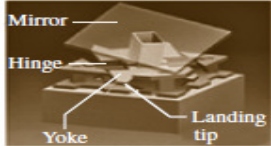
# Nanoscale

**MEMS:** Characteristic length less than 1 mm, larger than 100 nm

**NEMS:** Less than 100 nm



Human hair  
50–100  $\mu\text{m}$



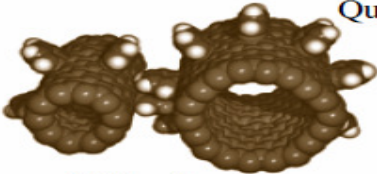
DMD 12  $\mu\text{m}$



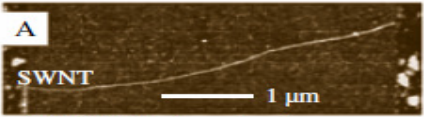
Quantum-dots transistor  
300 nm



Red blood cell  
8  $\mu\text{m}$



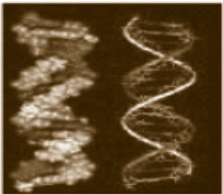
Molecular gear  
10–100 nm



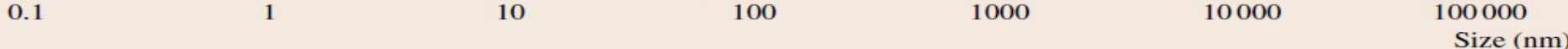
SWCNT chemical sensor  
2 nm



C atom  
0.16 nm



DNA  
2.5 nm

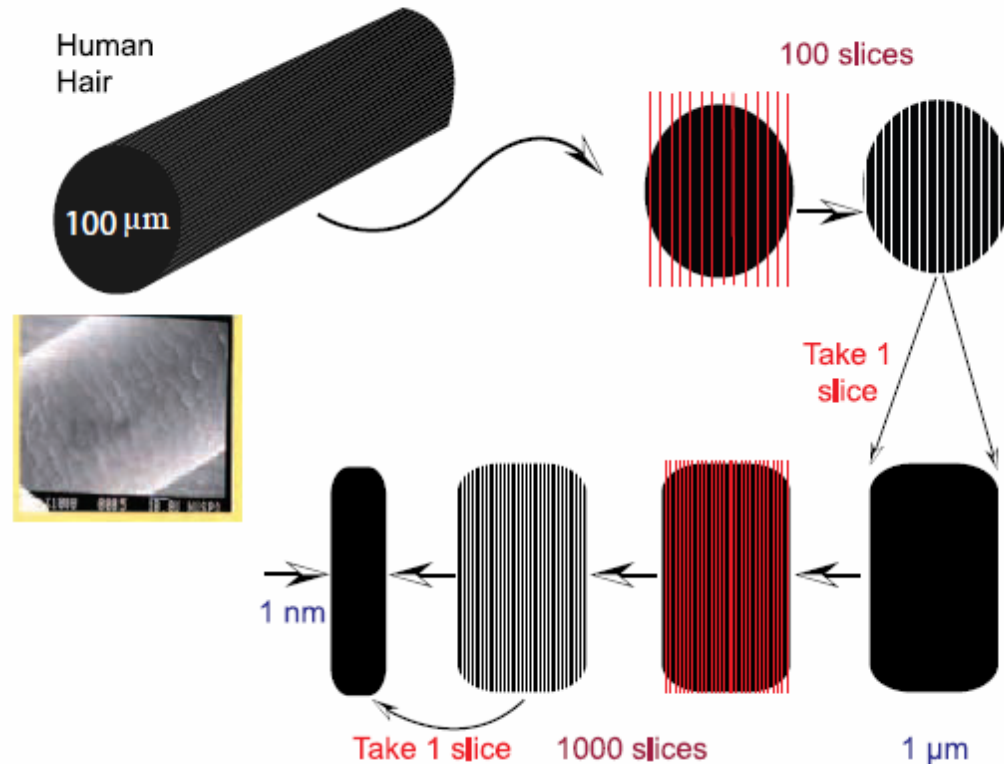


# Defining Nanoscale

Nano - Dwarf

Nano size:  $1 \text{ nm} = 10^{-6} \text{ millimeter (mm)} = 10^{-9} \text{ meter (m)}$  nm

Combination of atoms or molecules to form objects of nanometer scale



Cross section of human hair

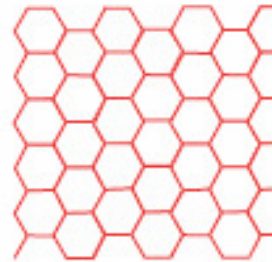
# Carbon nanostructures



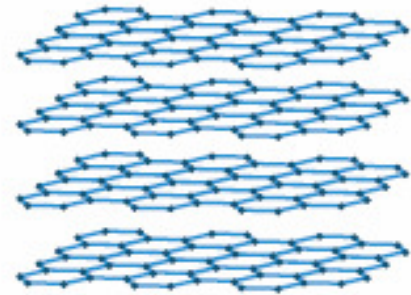
0D-Buckyball



1D-Nanotube



2D-Graphene



3D-Graphite

# Importance of nanoscale

- The wavelike properties of electrons inside matter are influenced by variations on the nanometer scale. By patterning matter on the nanometer length, it is possible to vary fundamental properties of materials (for instance, *melting temperature, magnetization, charge capacity*) without changing the chemical composition.
- The systematic organization of matter on the nanometer length scale is a key feature of biological systems. Nanotechnology promises to allow us to place artificial components and assemblies inside cells, and to make new materials using the self-assembly methods of nature.

# Importance of nanoscale

- Nanoscale components have *very high surface areas*, making them ideal for use in composite materials, reacting systems, drug delivery, and energy storage.
- The finite size of material entities, as compared to the molecular scale, determine an increase of the relative importance of *surface tension and local electromagnetic effects*, making *nanostructured materials harder and less brittle*.
- The interaction wavelength scales of various external wave phenomena become comparable to the material entity size, making materials *suitable for various opto-electronic applications*.

• **Nano-materials:** Used by humans for 100 of years, the beautiful ruby red color of some glass is due to gold Nano particles trapped in the glass (ceramic) matrix.

- The decorative glaze known as luster. Ruby Red glass pot (entrapped with gold nanoparticles)



### What's special with Nano?

The properties of nanomaterials deviate from those of single crystals or polycrystals (bulk). For example, the fundamental properties like electronic, magnetic, optical, chemical and biological Surface properties: energy levels, electronic structure, and reactivity are different for nano materials.

Exhibit size dependent properties, such as lower melting points, higher energy gaps etc. On the Surfaces and interfaces basics:

**Bulk.** In bulk materials, only a relatively small percentage of atoms will be at or near a surface or interface (like a crystal grain boundary).

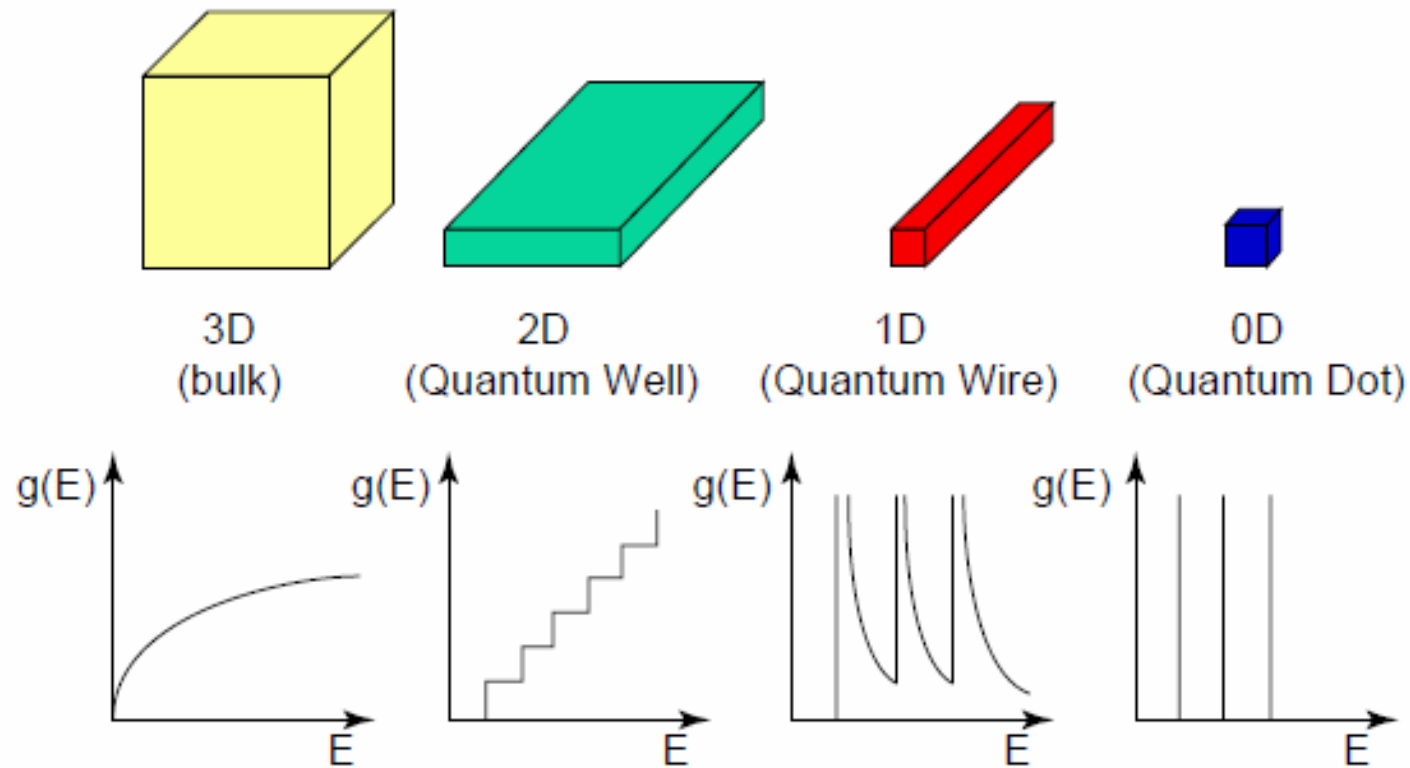
**Nano.** In nanomaterials, large no. of atomic features near the interface.

# Nanostructured materials

- Nanoparticles
- Nanowires
- Nanotubes
- Nanorods
- Nanoporous materials
- Other structures

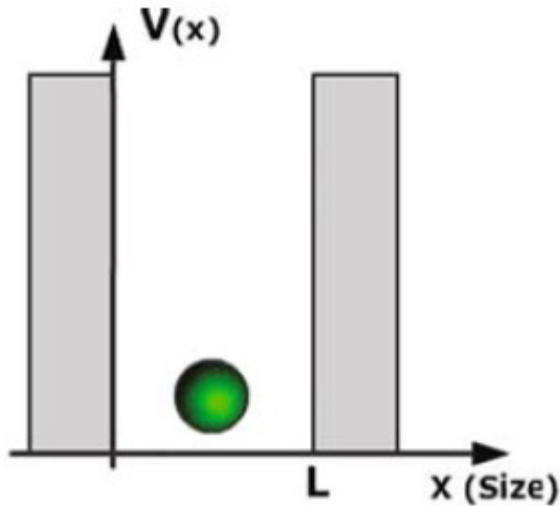


# Bulk and Nanoscale



Density of states for 3D, 2D, 1D, 0D showing discretization of energy and discontinuity of DOS

# Electrons in nanoparticles as particle in a box model



$$E_n = \frac{\hbar^2 \pi^2}{2mL^2} n^2$$

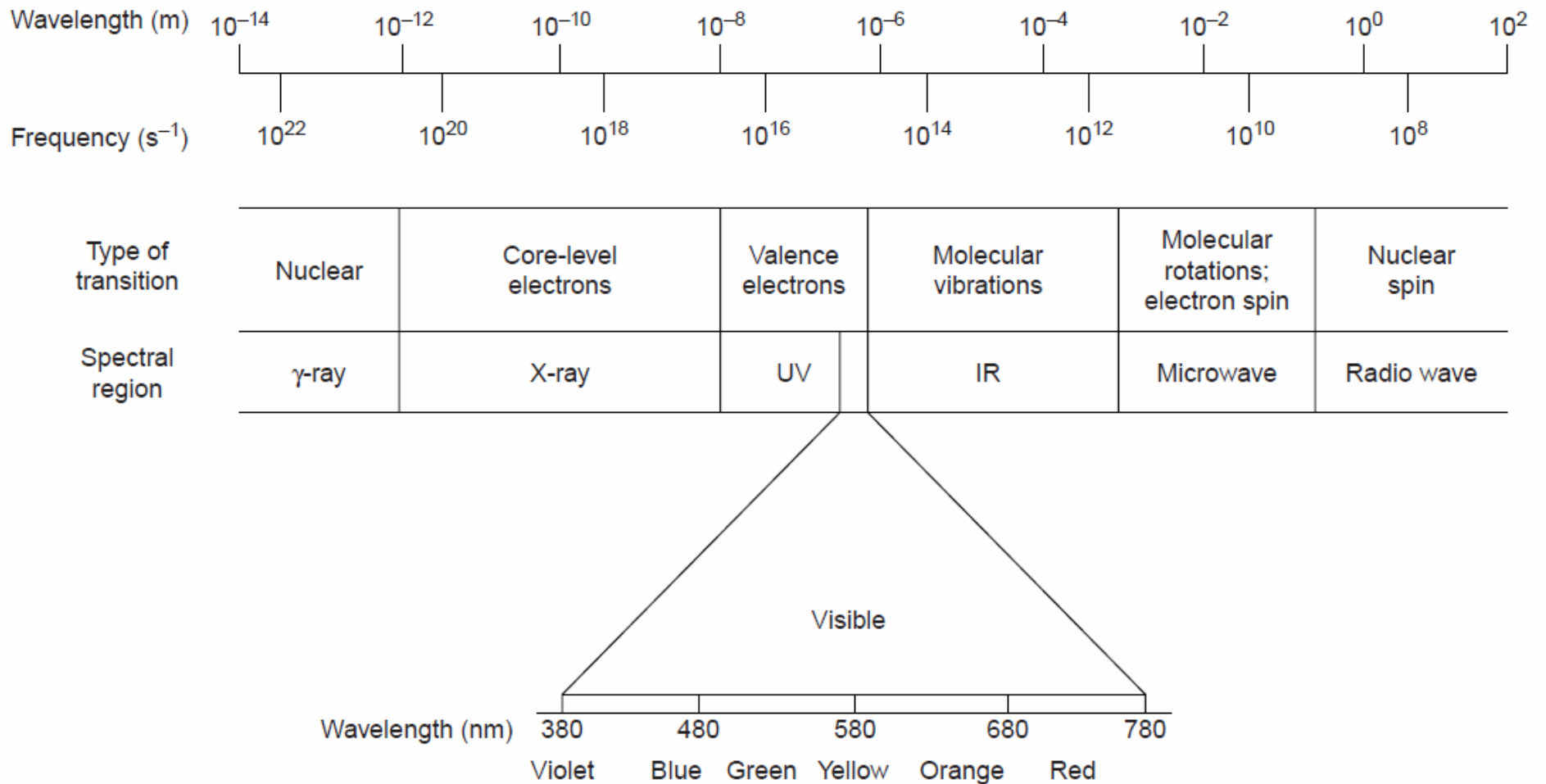
# Effects of Nano size

- Properties depends on size, composition and structure
- Nano size increases the surface area
- Change in surface energy (higher)
- Change in the electronic properties
- Change in optical band gap
- Change in electrical conductivity
- Higher and specific catalytic activity
- Change thermal and mechanical stabilities
- Different melting and phase transition temperatures
- Change in catalytic and chemical reactivities

# Bulk and Nanoscale

Bulk (eg. Gold)	Nano (eg. Gold)						
<ol style="list-style-type: none"> <li>1. <b>Lustrous</b>—Shiny surface when polished.</li> <li>2. <b>Malleable</b>—Can be hammered, bent or rolled→any desired shape.</li> <li>3. <b>Ductile</b>—Can be drawn out into wires</li> <li>4. Yellow colour when in a mass</li> <li>5. Heat &amp; electricity conductor</li> <li>6. High densities</li> <li>7. High melting point (1080°C)</li> <li>8. Tough with high tensile strength</li> <li>9. Inert-unaffected by air and most reagents</li> </ol>	<ol style="list-style-type: none"> <li>1. Vary in appearance depending on size &amp; shape of cluster.</li> <li>2. Are never gold in colour!</li> <li>3. Are found in a range of colours.</li> <li>4. Are very good catalysts.</li> <li>5. Are not “metals” but are semiconductors.</li> <li>6. Melts at relatively low temperature (~940° C).</li> <li>7. Size &amp; Shape of the nanoparticles determines the color.</li> <li>8. <u>For example</u>; Gold particles in glass:               <table style="margin-left: 20px; border: none;"> <tr> <td>25 nm</td> <td>—</td> <td>Red reflected</td> </tr> <tr> <td>50 nm</td> <td>—</td> <td>Green reflected</td> </tr> </table>               (Unexpected visible properties &amp; they are small enough to scatter visible light rather than absorb)             </li> </ol>	25 nm	—	Red reflected	50 nm	—	Green reflected
25 nm	—	Red reflected					
50 nm	—	Green reflected					

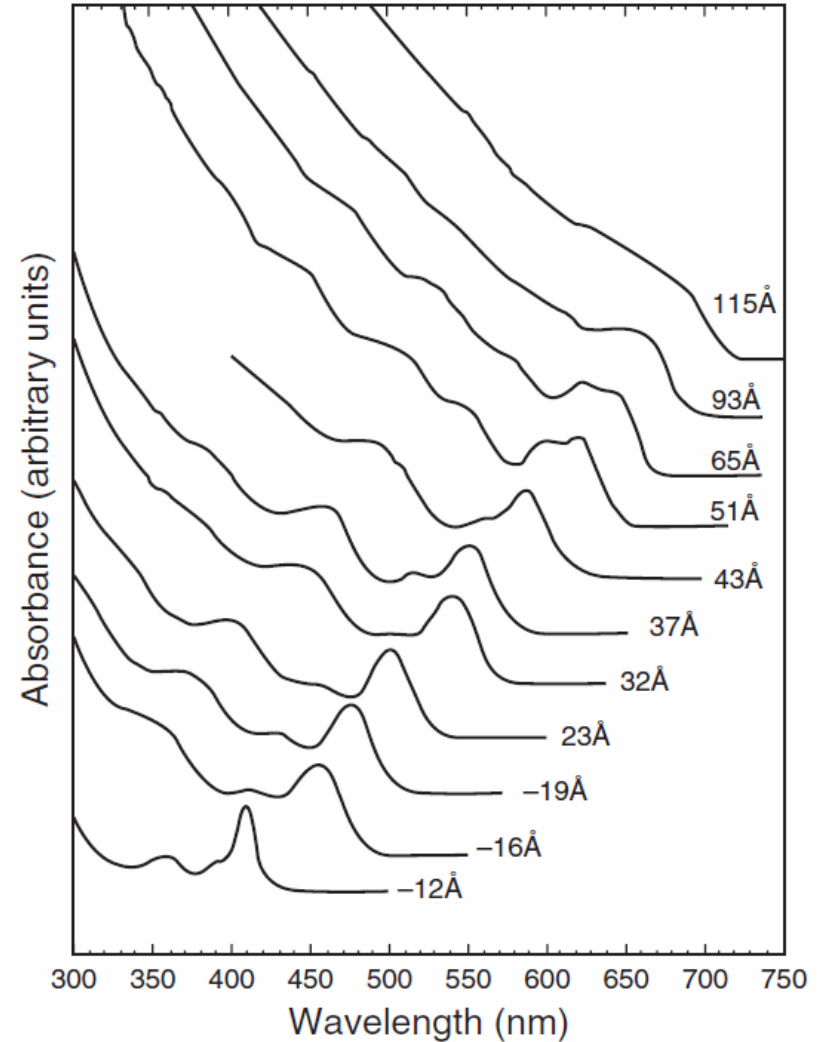
# Electromagnetic spectrum



# Size variation



Various size of CdSe nanoparticles and their solution. The bulk CdSe is black

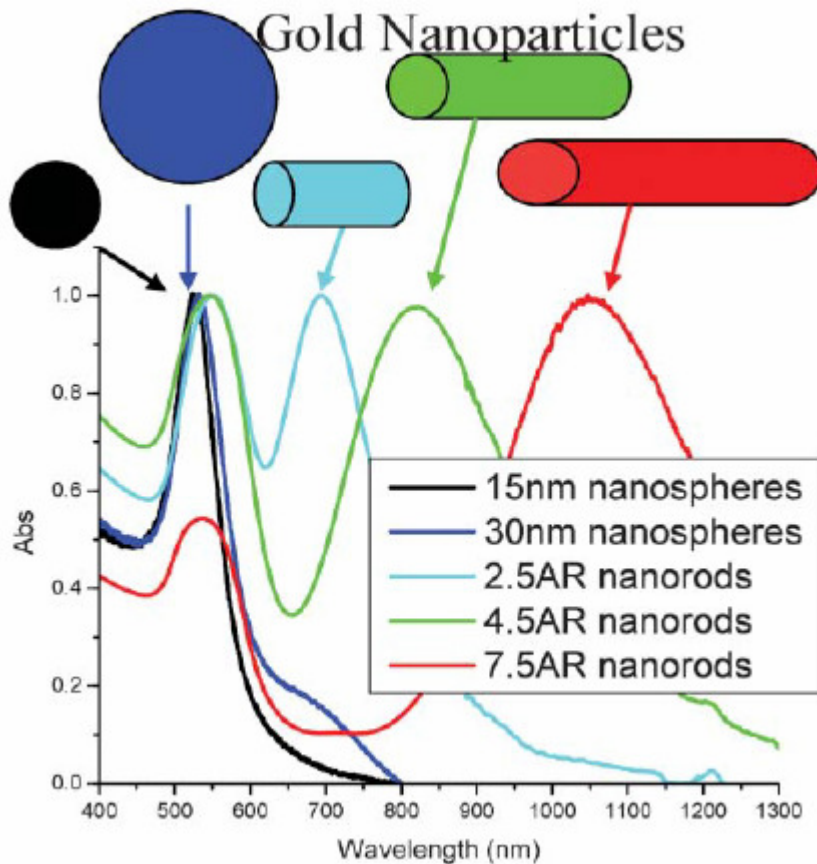


Room temperature optical absorption spectra of CdSe nanocrystallites dispersed in hexane and ranging in size from  $\sim 12$  to  $115 \text{ \AA}$

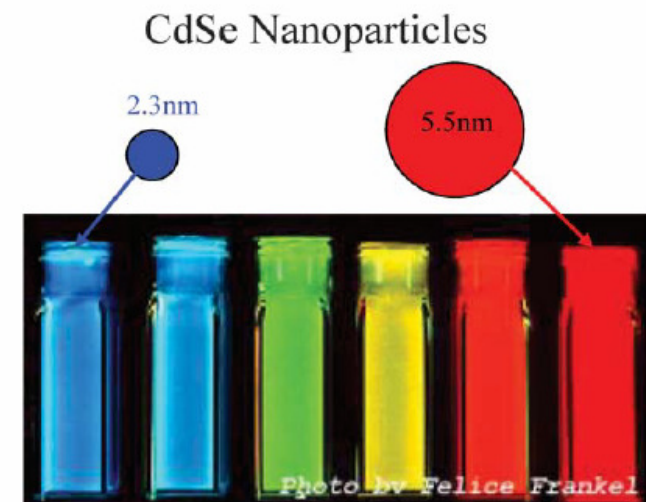
# Nanochemistry Lecture-2

Dr Charu Arora, Associate Professor, Department of  
Chemistry

# Optical properties of Gold NPs



Size, shape, change the optical properties of nano sized gold





# §4.1.1.1 Gold nanoparticles

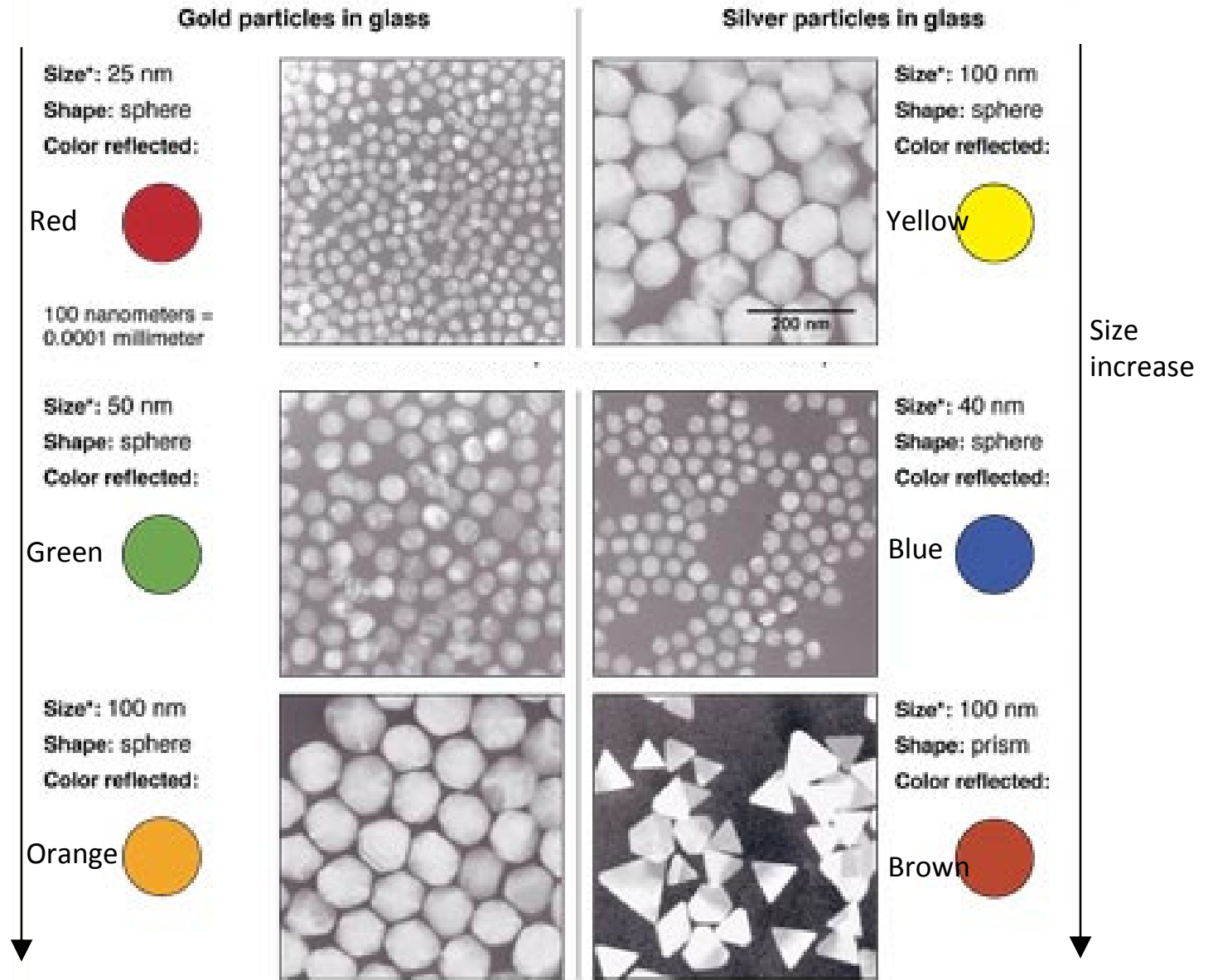
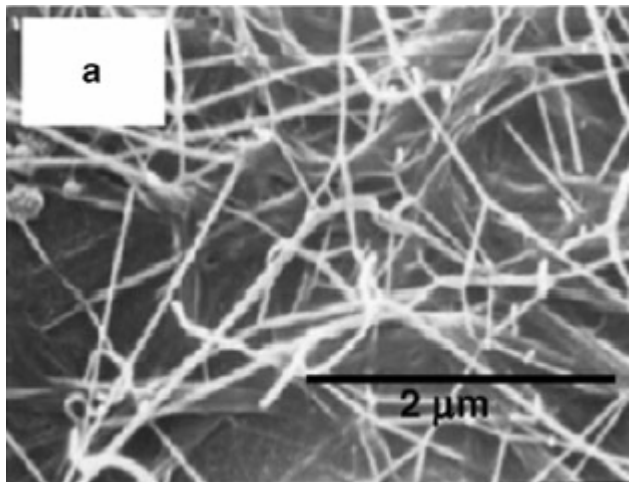


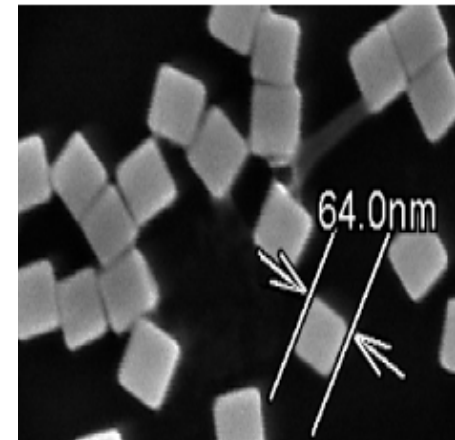
Fig 1. Size and shape dependent colors of Au & Ag nanoparticles

# Silver : Bulk - Nano

- In nano size not only the surface area increased the electronic properties are modified. This influence the optical, electrical, catalytic properties
- It improve the selectivity in catalysis

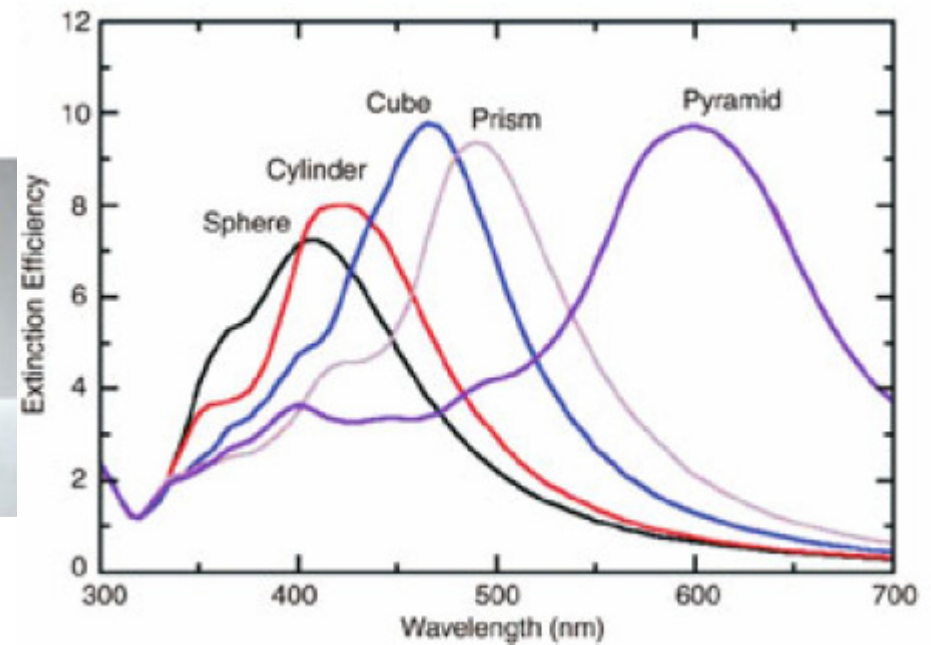
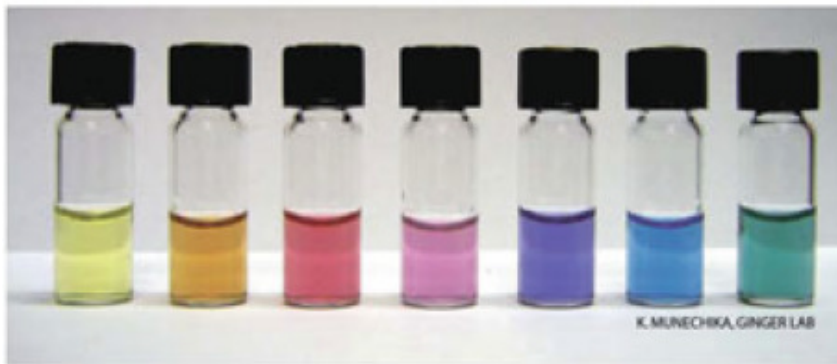


Silver nanowires



Silver nanocubes

# Silver nanoparticles



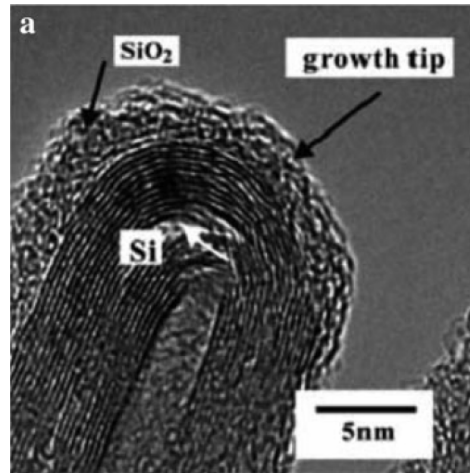
Change in shape and size shows the difference in the visible spectrum of Ag nanoparticles

The scattering or absorption is due to the localized surface plasmon resonance

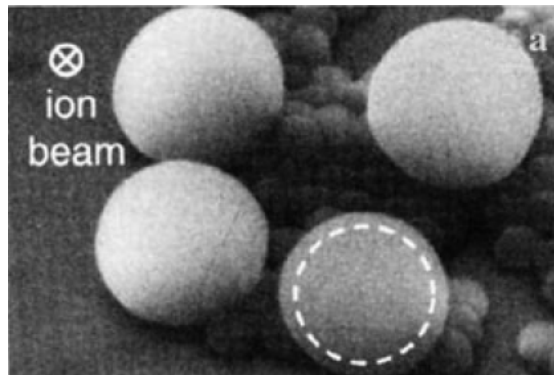
# SPR

- Surface plasmon resonance SPR: The collective oscillations of the electron gas at the surface of nanoparticles ( eg. 6s electrons of the conduction band for Au NPs) that is correlated with the electromagnetic field of the incoming light, i.e., the excitation of the coherent oscillation of the conduction band.
- SP band provides some information regarding NPs band structure
- ( see the notes for detailed information)

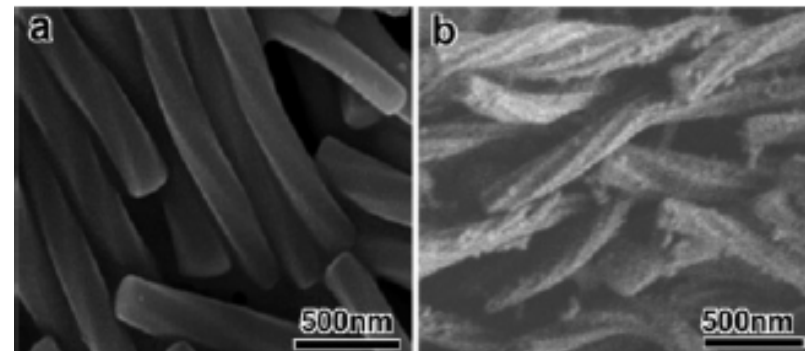
# Silicon



Si - SiO<sub>2</sub> - Nanotubes



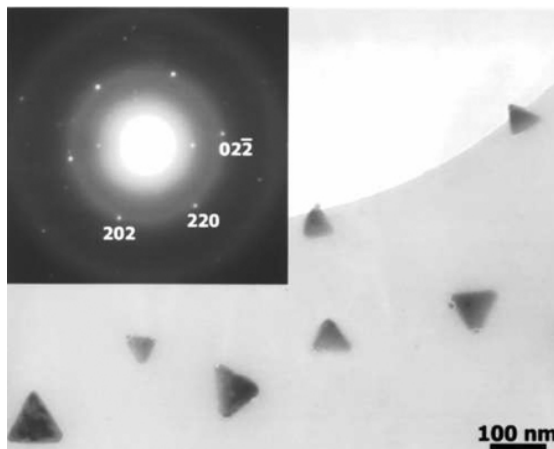
SiO<sub>2</sub> - Nanospheres



SiO<sub>2</sub> - Nanotubes

# Nano - Silicon

- Si nanostructures shows visible luminescence because of quantum confinement
- Surface modification and change in size of particles influences the luminescence wavelength and intensities



Alkyl passivated Si nanoparticles

# Nano characterization techniques

- Spectroscopy – UV-Vis, Surface enhanced Raman scattering, X-ray photoelectron spectroscopy, Nuclear magnetic resonance
  - Electrical conductivity measurement
  - Magnetic measurements
  - Microscopic techniques – Scanning electron microscopy, Transmission electron microscopy, Atomic force microscopy, Scanning tunneling microscopy
- uses- morphology, Surface force measurement, surface roughness, Imaging with atomic level resolution, lattice parameter,

# Issues

- Health hazard

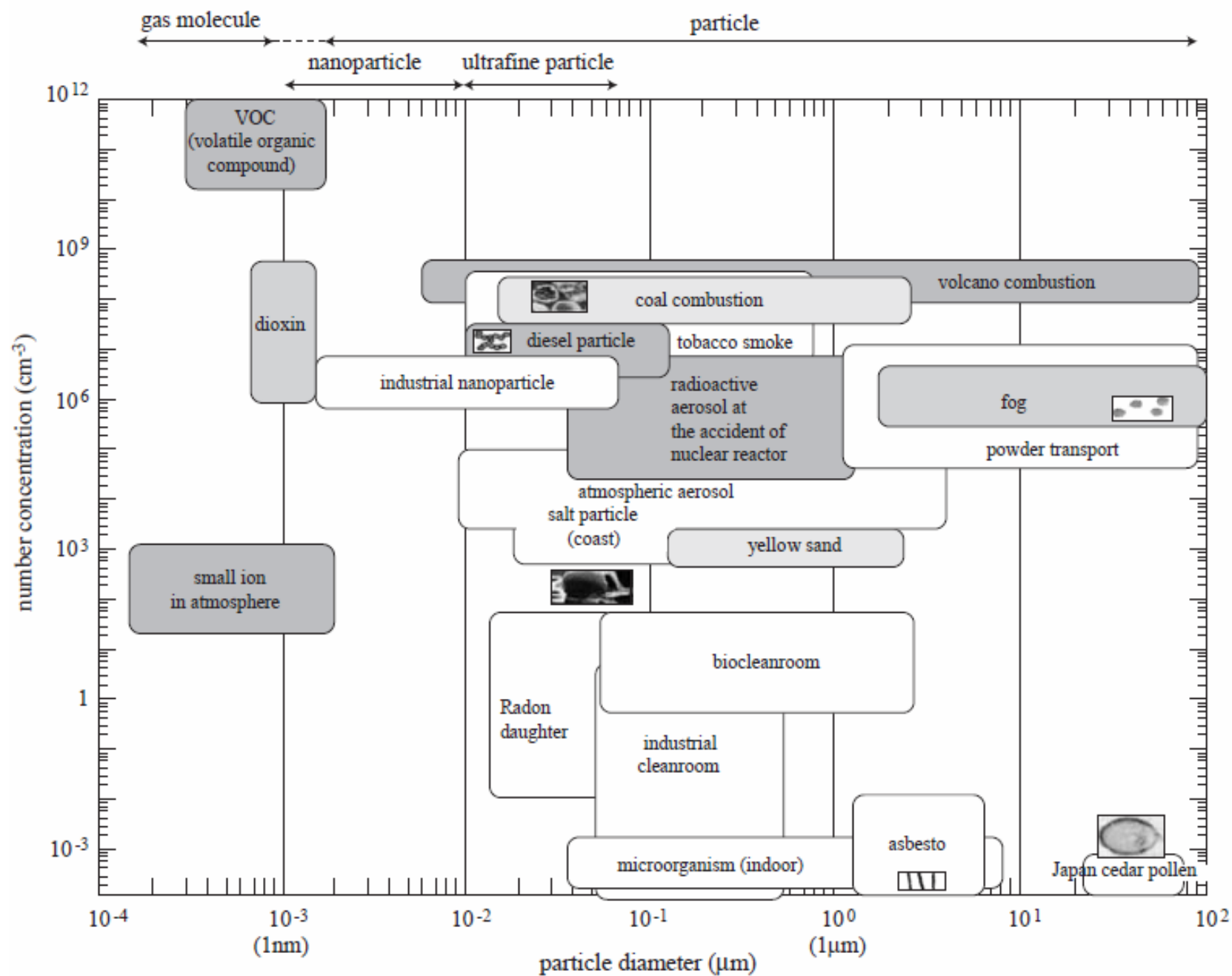
The greater specific surface area (surface area per unit weight) may lead to increased rate of absorption through the skin, lungs, or digestive tract and may cause unwanted effects to the lungs as well as other organs. However, the particles must be absorbed in sufficient quantities in order to pose health risks

- DNA damage iron oxide , Zinc oxide Titanium dioxide and Carbon nanotubes causes DNA damage at low levels. Copper oxide was found to be the worst offender, and was the only nanomaterial identified by the researchers as a clear health risk



# Issues

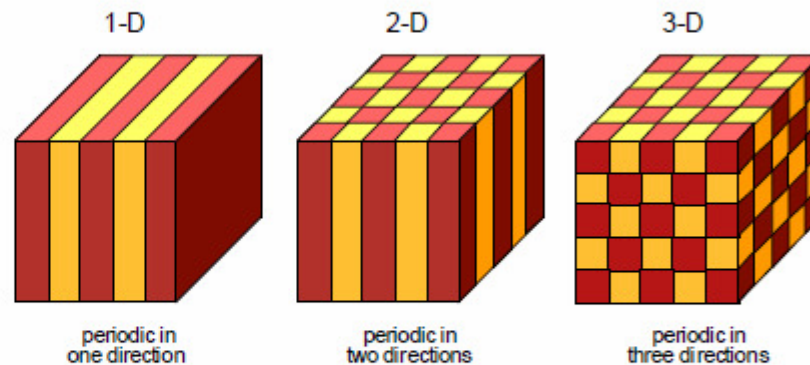
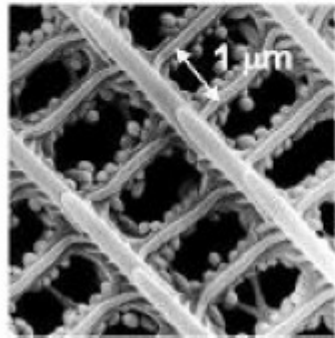
- Nanoparticles in water
- Nanoparticles in exhaust gases
- Nanoparticles in atmosphere



# Applications

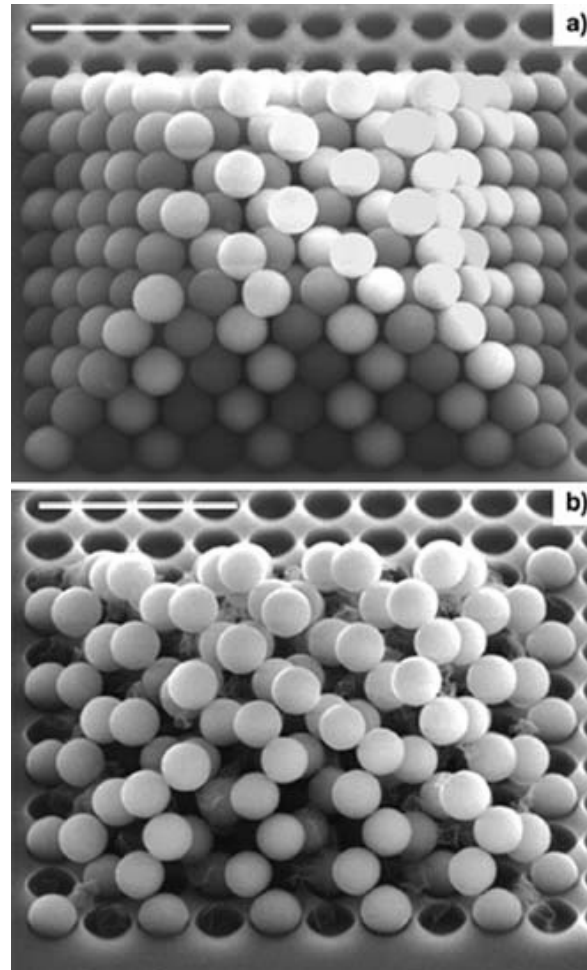
# Nanophotonics

- Photonic crystals are new types of optical materials, in which small dielectric cells with the size of optical wavelength (from several 100 nm to several 10  $\mu\text{m}$ ) are periodically arranged in two- or three-dimensions.



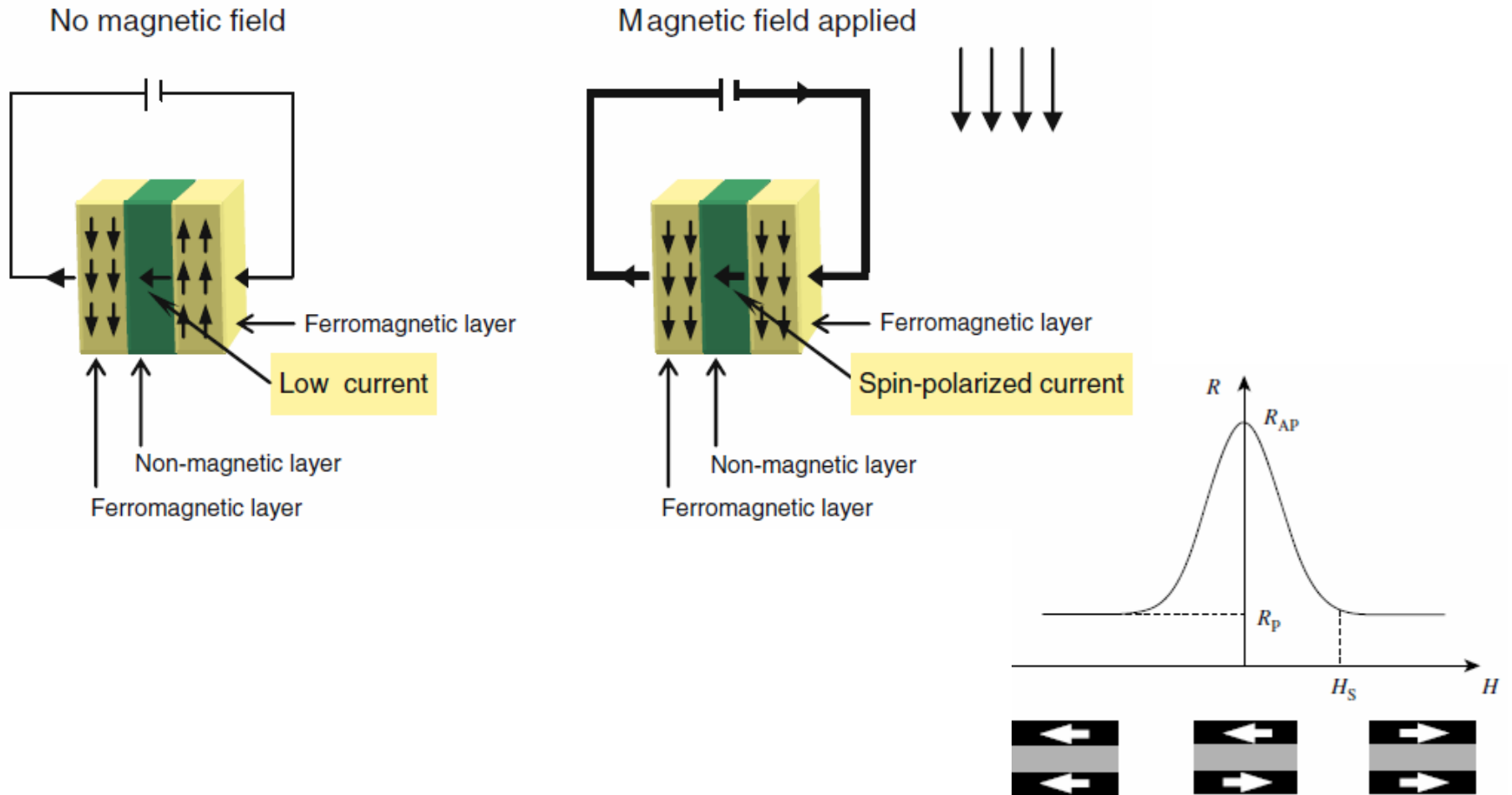
periodic electromagnetic media

# Nanophotonics



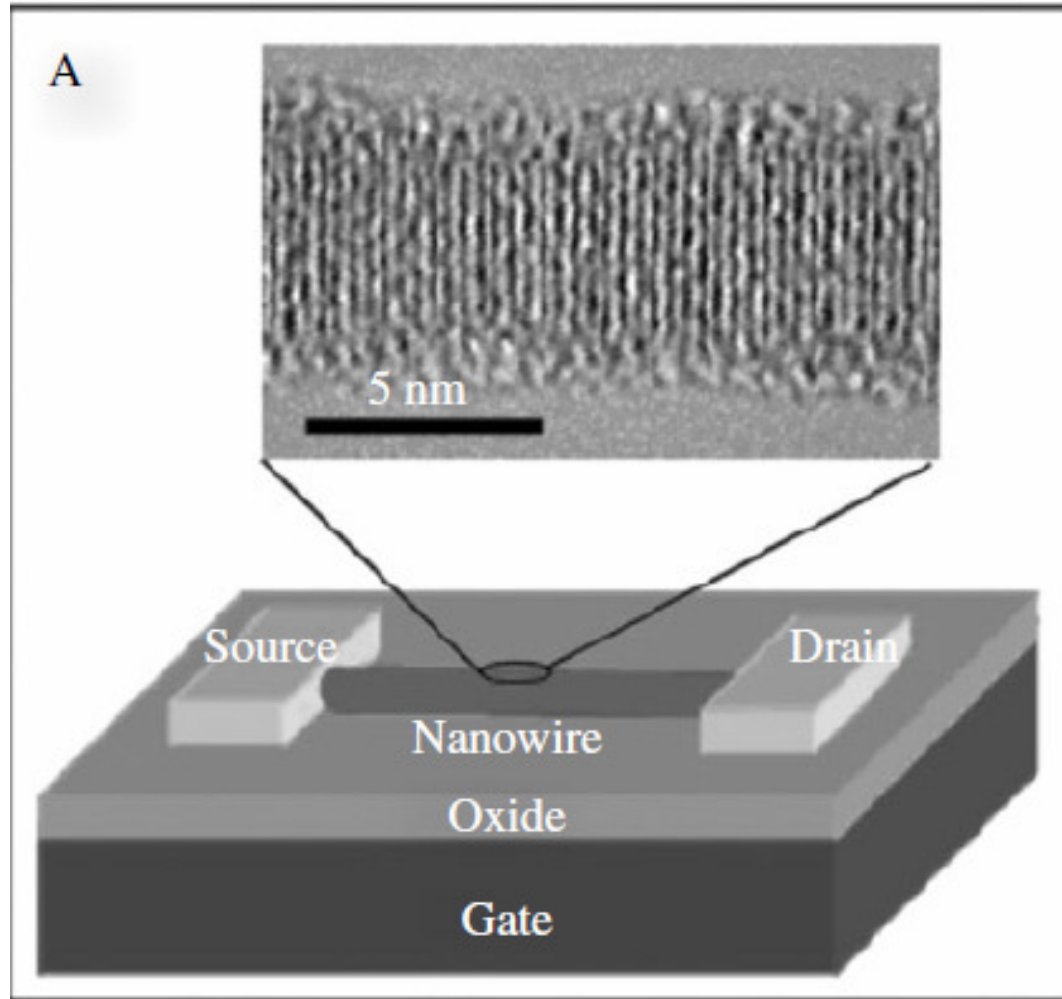
Photonic crystal with a diamond lattice.

# Nanospintronics - Giant magnetoresistance effect



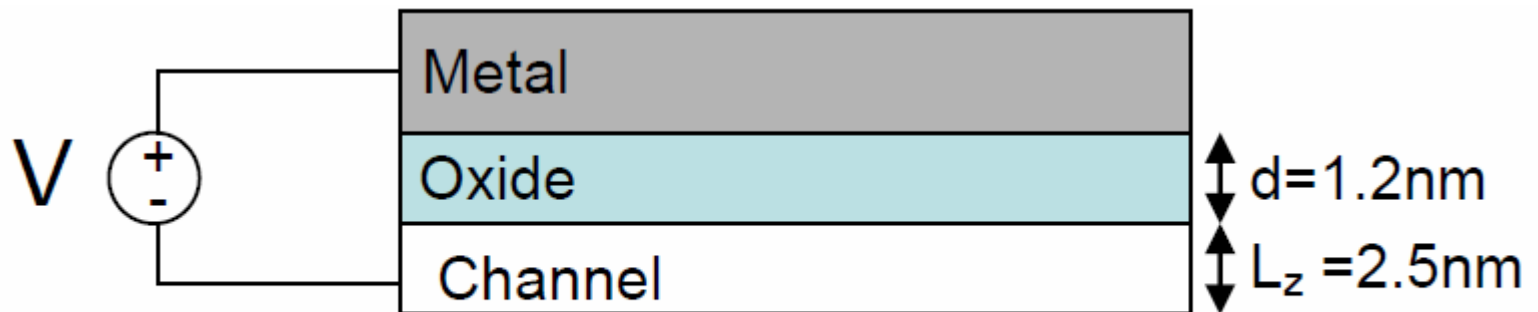
# Nanoelectronics

## Si nanowire Field effect transistor



# Single electron transistors

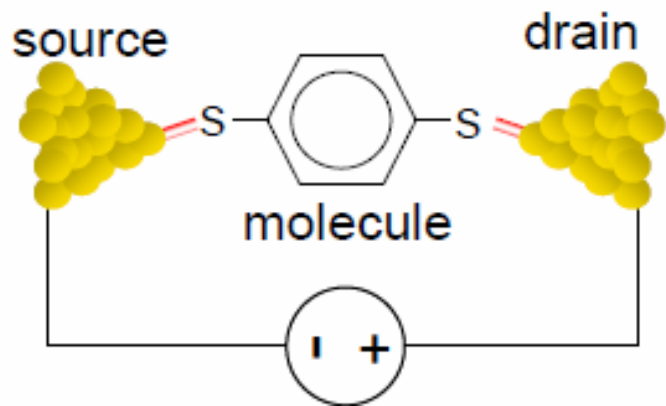
- Uses the coulomb blockade effect of reduced size of nanomaterials
- The scaling of such devices down to atomic scaling is expected to replace the customary semiconductor logic or analog devices. Due to the narrowing of the distance to several nanometers between isolated gate from the drain and source, tunneling current surmounts the conventional conduction currents readily



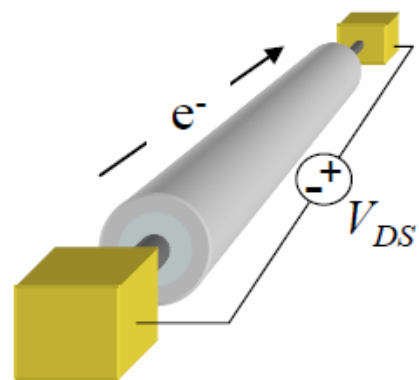
A simple model of a modern transistor.



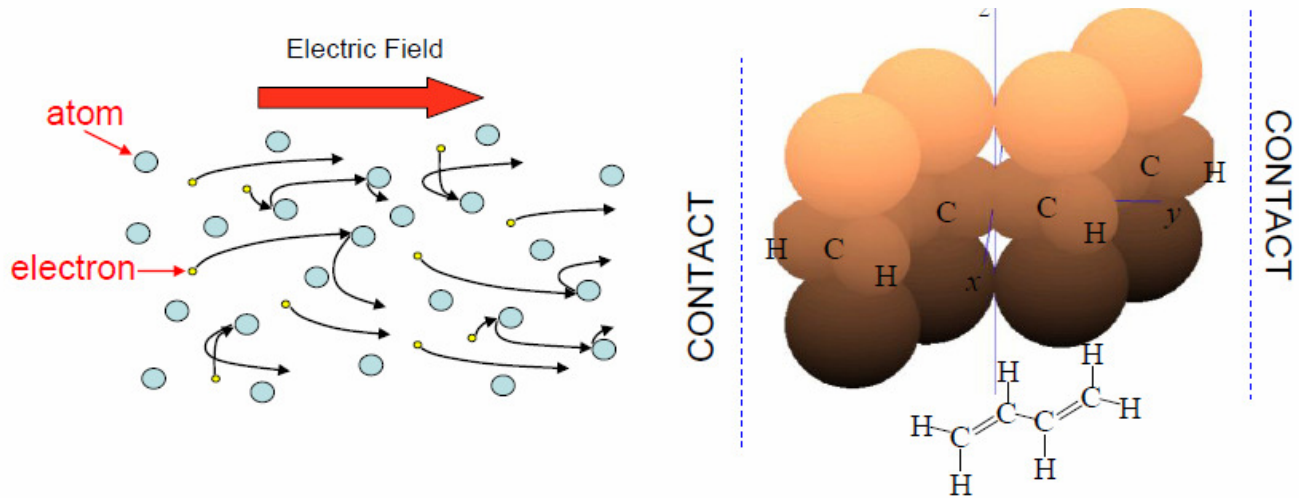
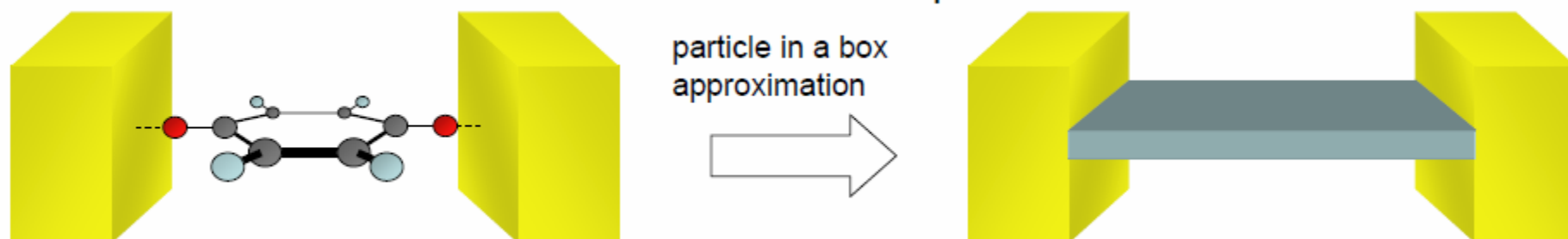
## Molecular electronics



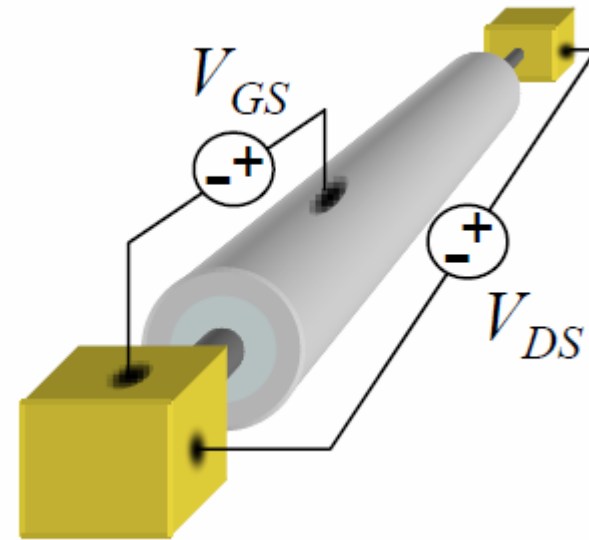
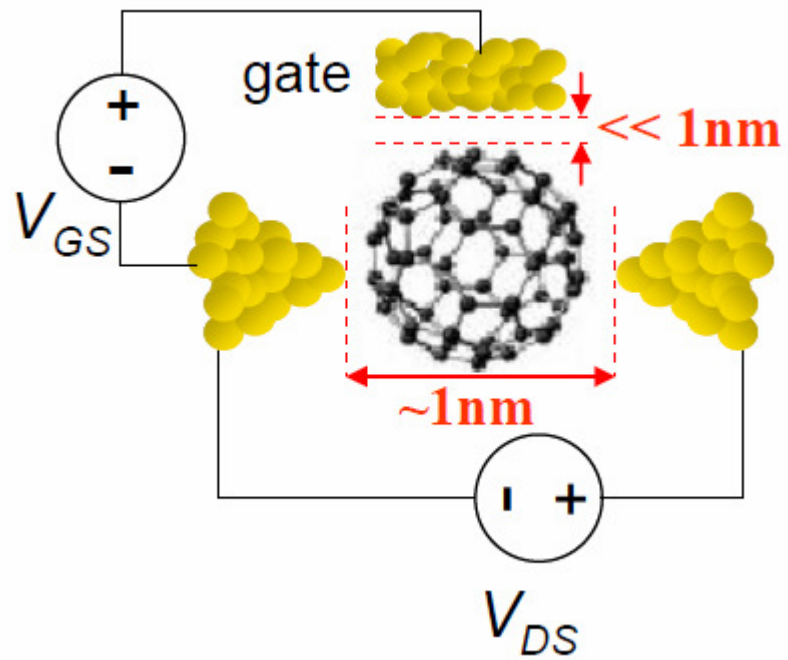
## Nanowire electronics



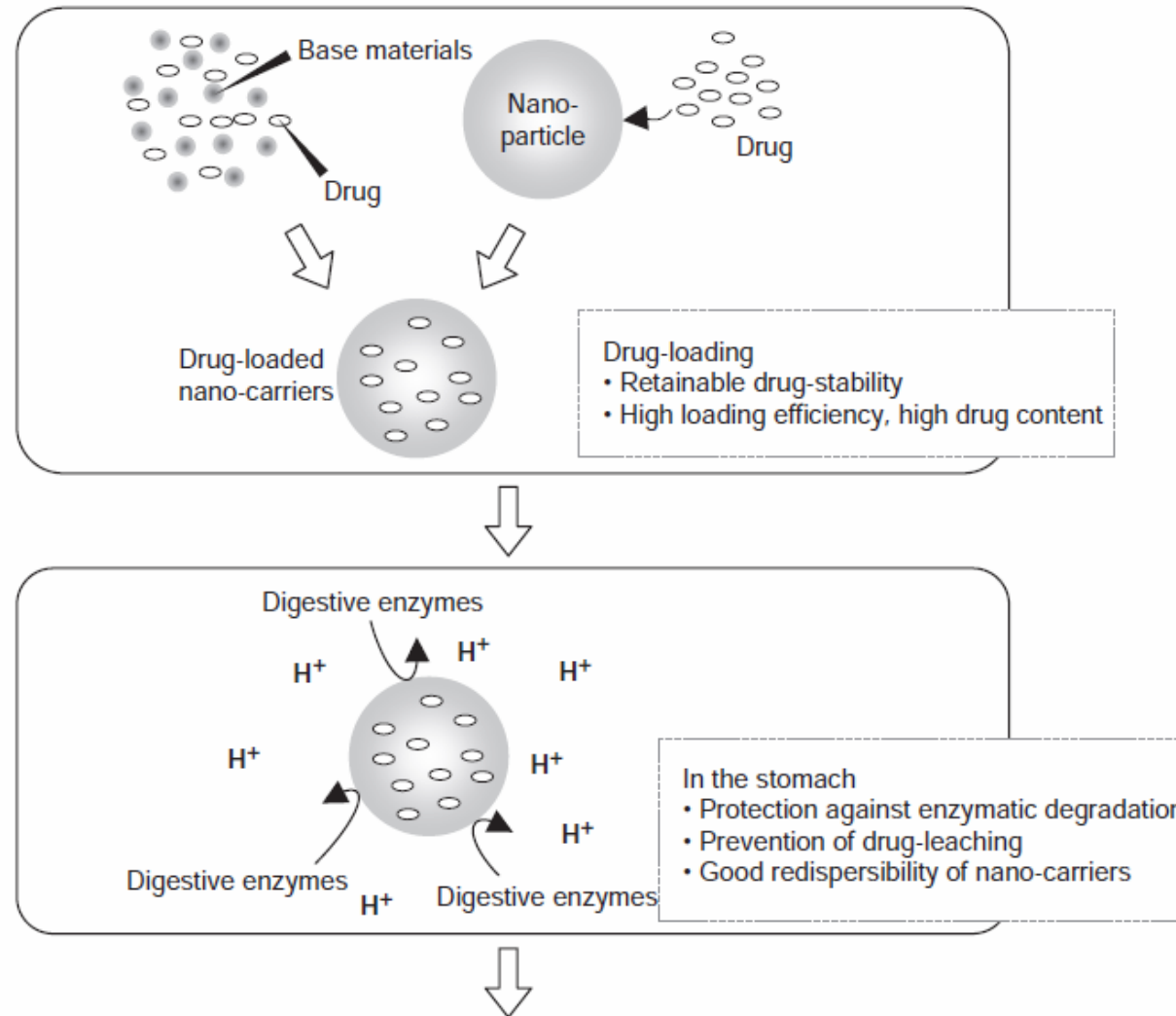
A two terminal device with a molecular/quantum dot conductor.

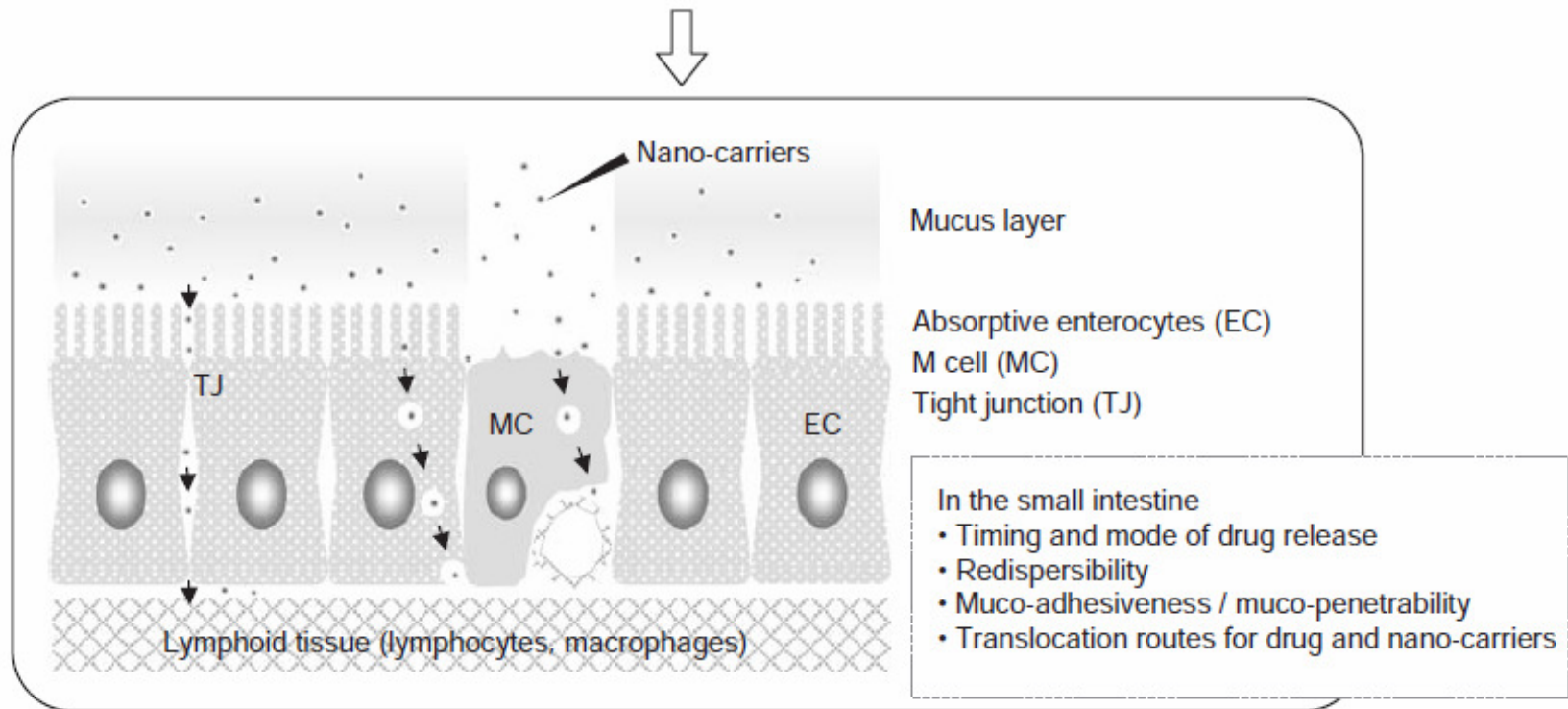


# Field effect transistor

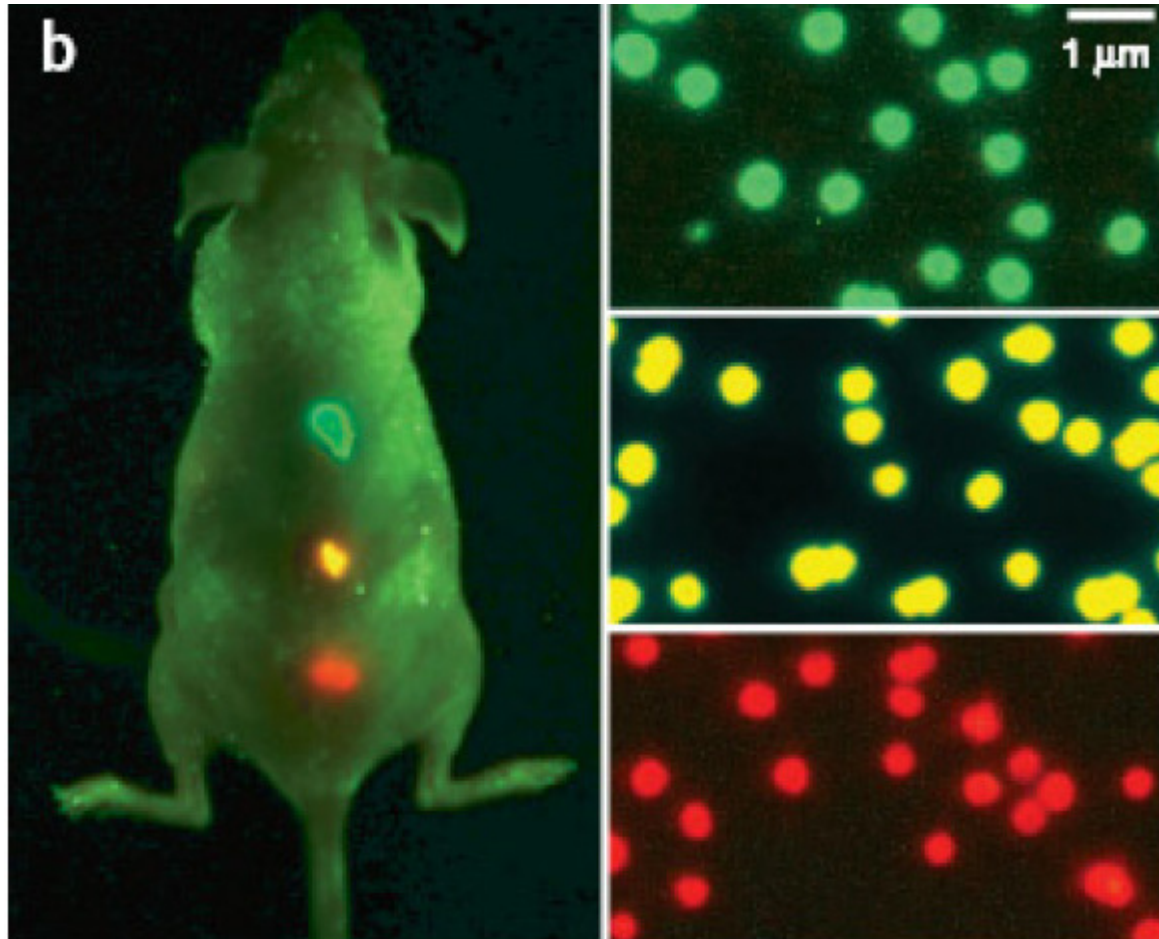


# Nanomedicine - Drug delivery



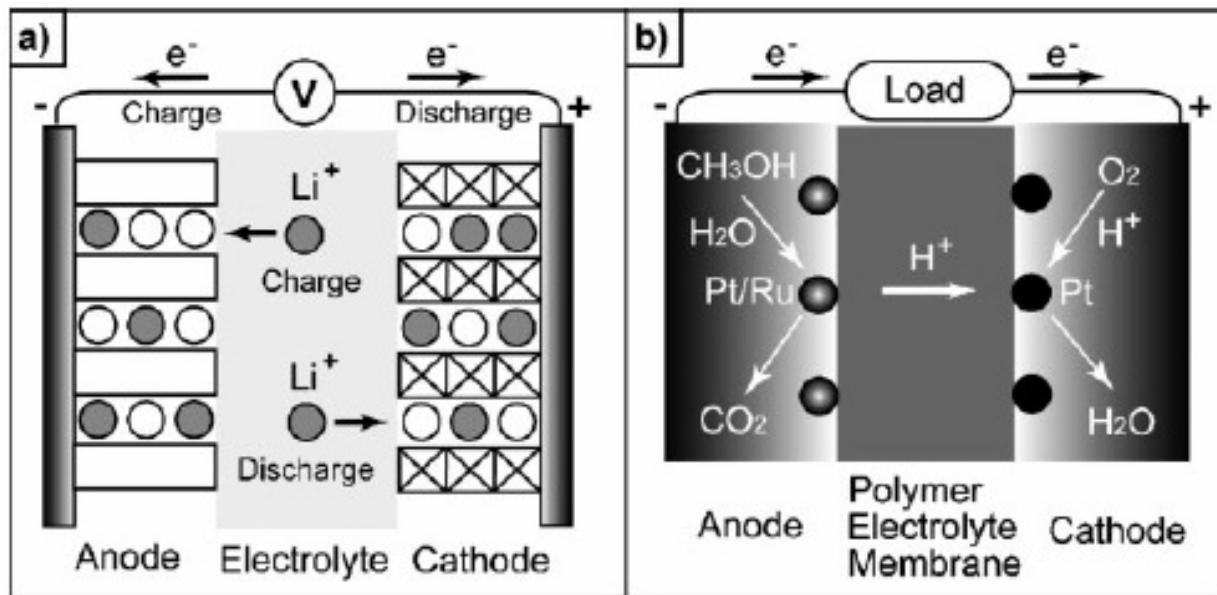


# Quantum dot imaging



# Energy conversion devices

- Nanomaterials have obtained considerable applications in electrochemical and solar energy conversion devices
- Nanosized electrocatalysts for fuel cell application
- Nanostructured materials for Li-ion batteries
- Nanomaterials in electrochemical double Layer supercapacitors



Schematic illustration of a) a lithium-ion battery and b) a direct methanol fuel cell.

