Nanostructured materials

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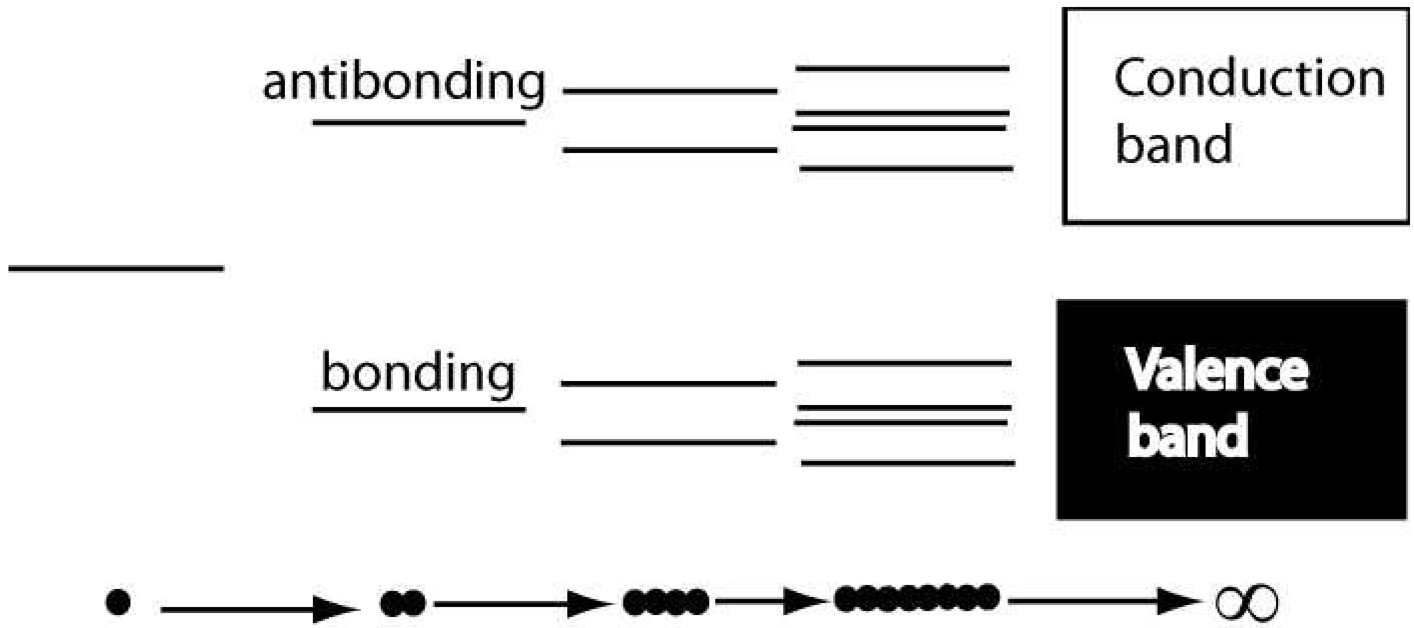
- **0D: quantum dots**
- **1D: Nanowires**
- **2D: superlattices and heterostructures**
- **Nano-Photonics**
- **Magnetic nanostructures**
- **Nanofluidic devices and surfaces**

- ***Nanostructured materials derive their special properties from having one or more dimensions made small compared to a length scale critical to the physics of the process.***

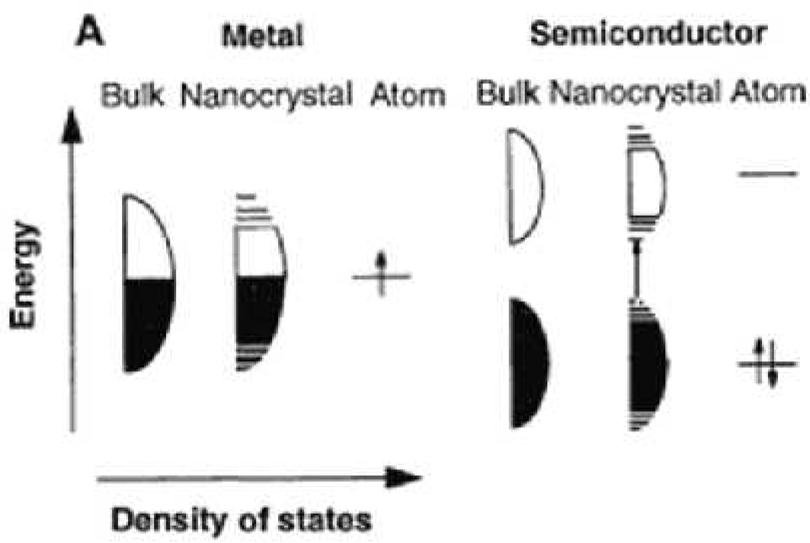
Phenomenon	Electronic Transport	Optical Interactions	Magnetic Interactions	Thermal	Fluidic Interactions
Physics	Fermi wavelength, λ_F Scattering length, ℓ	Wavelength of light in medium, $\lambda / 2n$	Range of exchange interactions, range of magnetic dipole interactions	Phonon mean free path	Boundary layers, molecular dimensions
Length scale	$\lambda_F \approx 1Å$ $\ell \approx$ 10-100 nm	100 – 300 nm	Exchange 1-100 Å, Dipolar ca. microns	Hundreds of nm at 300K to very large at low T	Always in the low Reynolds number limit: Radius of gyration for dissolved molecules.

Development of electronic properties as a function of cluster size

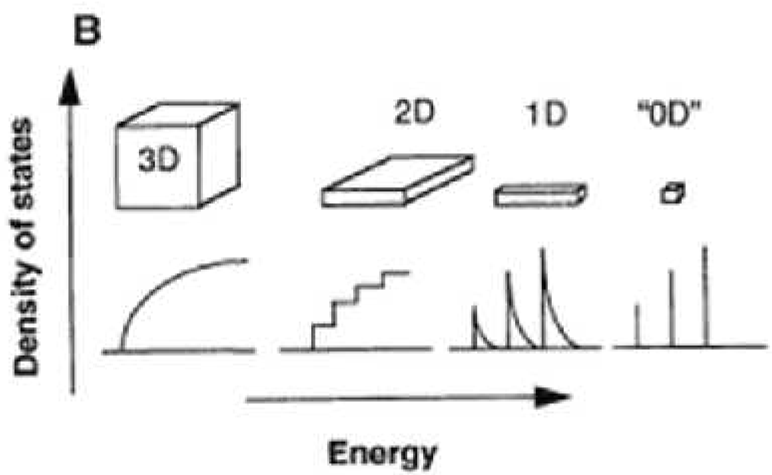


- *Each band has a width that reflects the interaction between atoms, with a bandgap between the conduction and the valence bands that reflects the original separation of the bonding ad antibonding states.*

Electronic Density of States (DOS) and Dimensionality



- *Size effects are most evident at band edges (semiconductor NPs).*

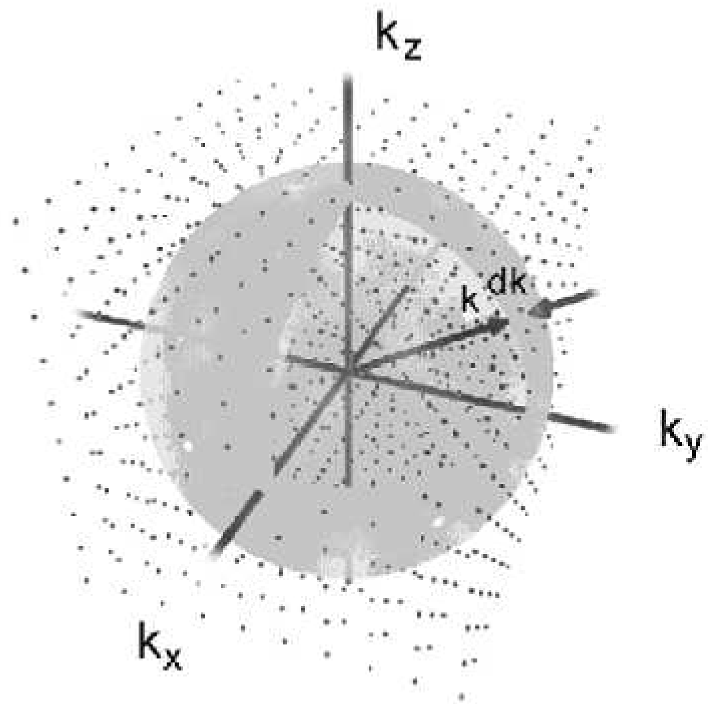


- *DOS (dn/dE) as a function of dimensionality.*

Size Dependence of DOS

- k-space is filled with an uniform grid of points each separated in units of 2π/L along any axis.

- The volume of k-space occupied by each point is: $\left(\frac{2®}{L}\right)^{3}$



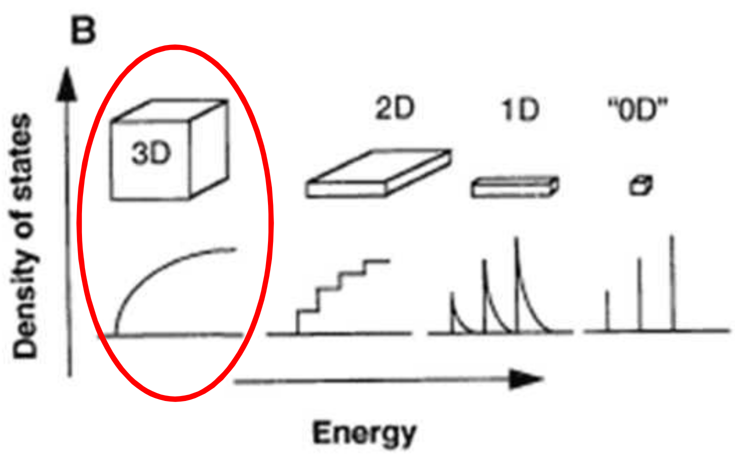
3D DOS

Density of states in a volume V per unit wave vector:

$$\frac{dn}{dk} = \frac{Vk^2}{2\circledR^2}$$

For a free electron gas: $E = \frac{\hbar^2 k^2}{2m}$ $\quad \frac{dE}{dk} = \frac{\hbar^2 k}{m}$

$$\frac{dn}{dE} = \frac{dn}{dk}\frac{dk}{dE} = \frac{Vk^2}{2\circledR^2}\frac{m}{\hbar^2 k} = \frac{Vm}{\hbar^2 2\circledR^2}\sqrt{\frac{2mE}{\hbar^2}} \propto E^{\frac{1}{2}}$$



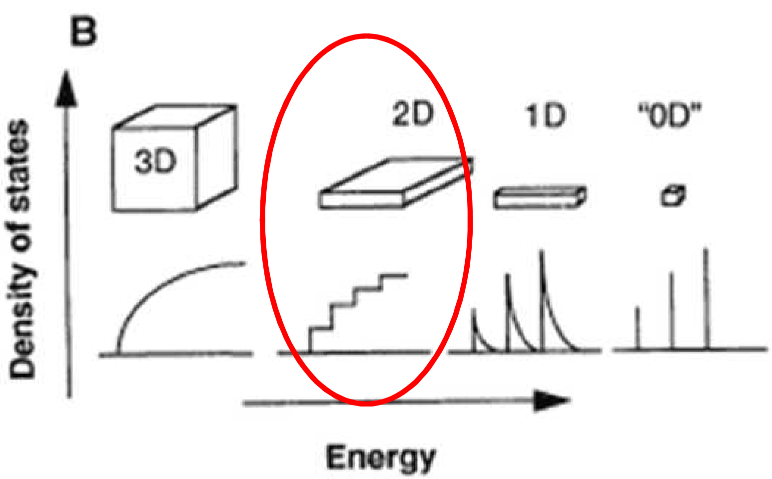
3D case is for free particles.

2D DOS

$$\frac{dn}{dk} = \frac{A2\pi k}{(2\pi)^2}$$

$$\frac{dE}{dk} = \frac{\hbar^2 k}{m}$$

$$\frac{dn}{dE} = \frac{dn}{dk}\frac{dk}{dE} = \frac{Am}{2\pi\hbar^2}$$



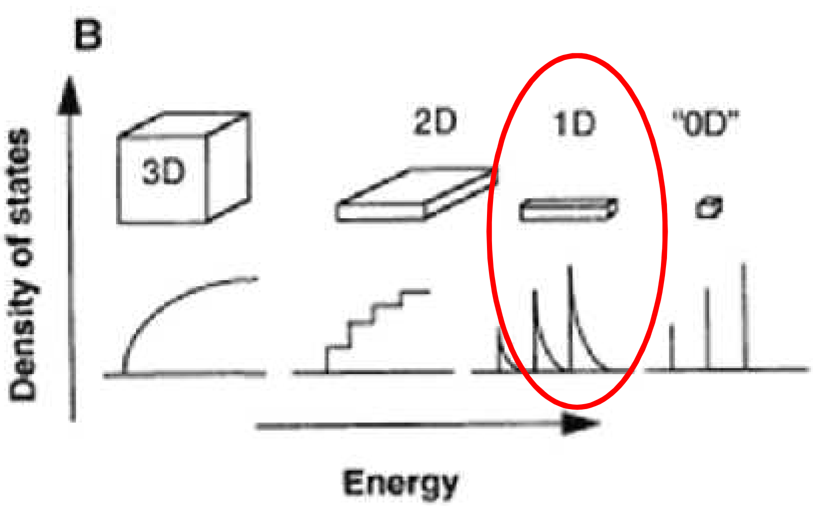
<u>Constant for each electronic band</u>

1D DOS

$$\frac{dn}{dk} = \frac{L}{2\text{®}}$$

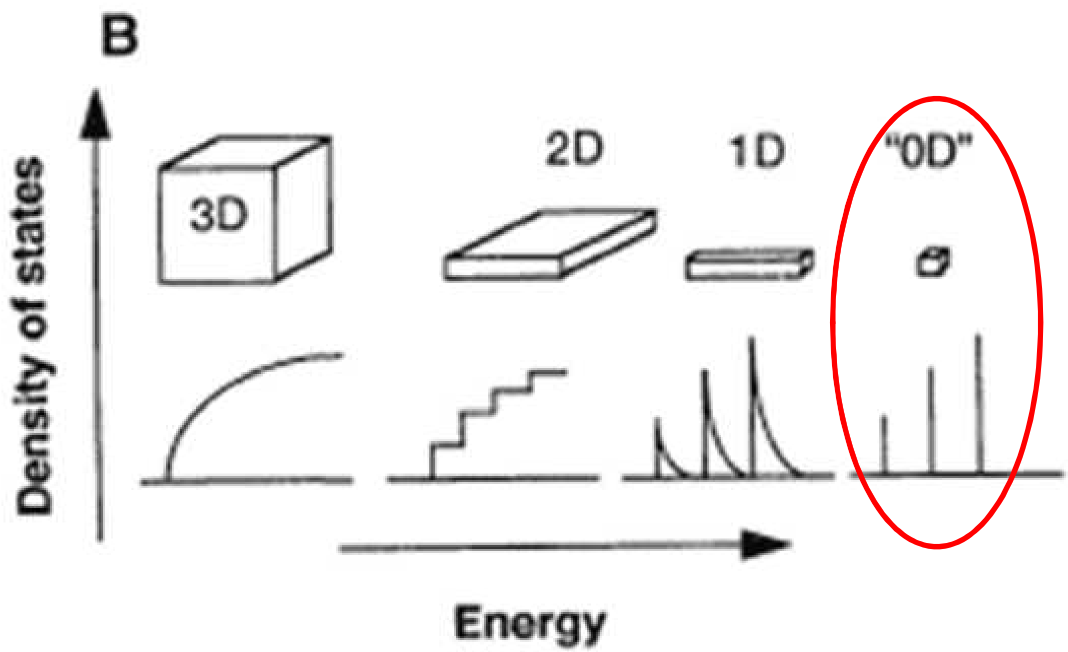
$$\frac{dE}{dk} = \frac{\hbar^2 k}{m}$$

$$\frac{dn}{dE} = \frac{Lm}{2\text{®}\hbar^2 k} \propto E^{-\frac{1}{2}}$$



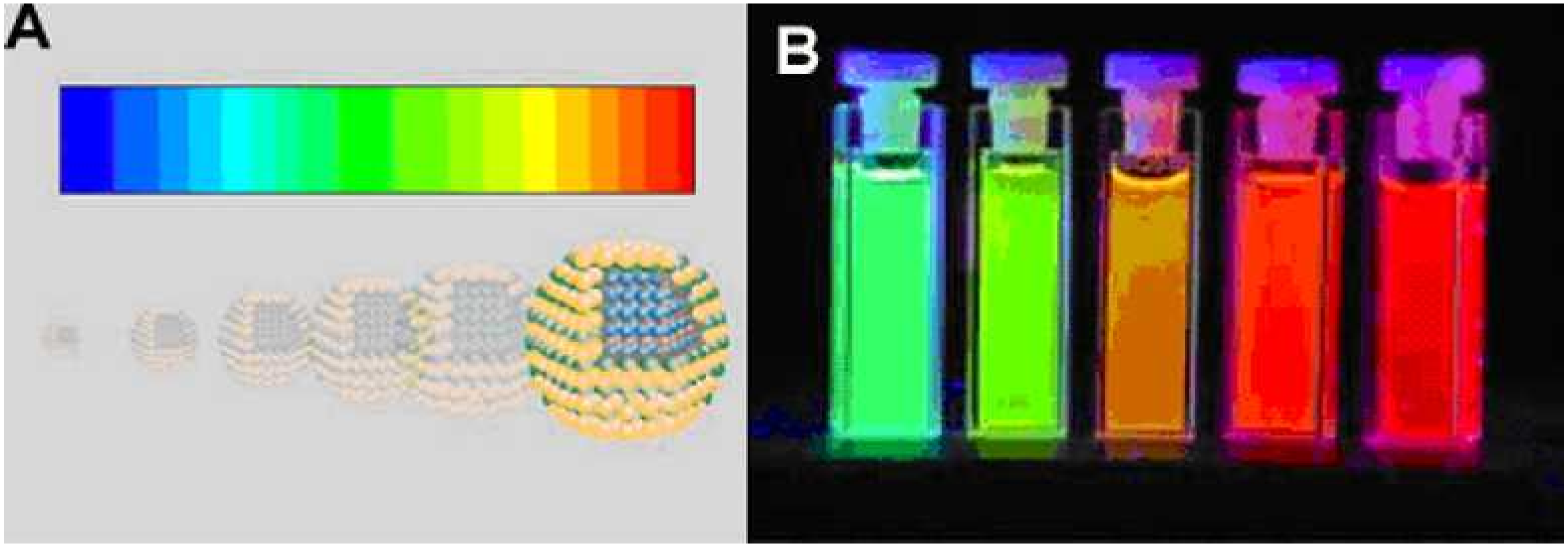
- ***At each atomic level, the DOS in the 1D solid decreases as the reciprocal of the square root of energy.***

0 D DOS



- ***In zero dimensions the energy states are sharp levels corresponding to the eigenstates of the system.***

0D Electronic Structures: Quantum Dots



- ***Electronic energy gap***

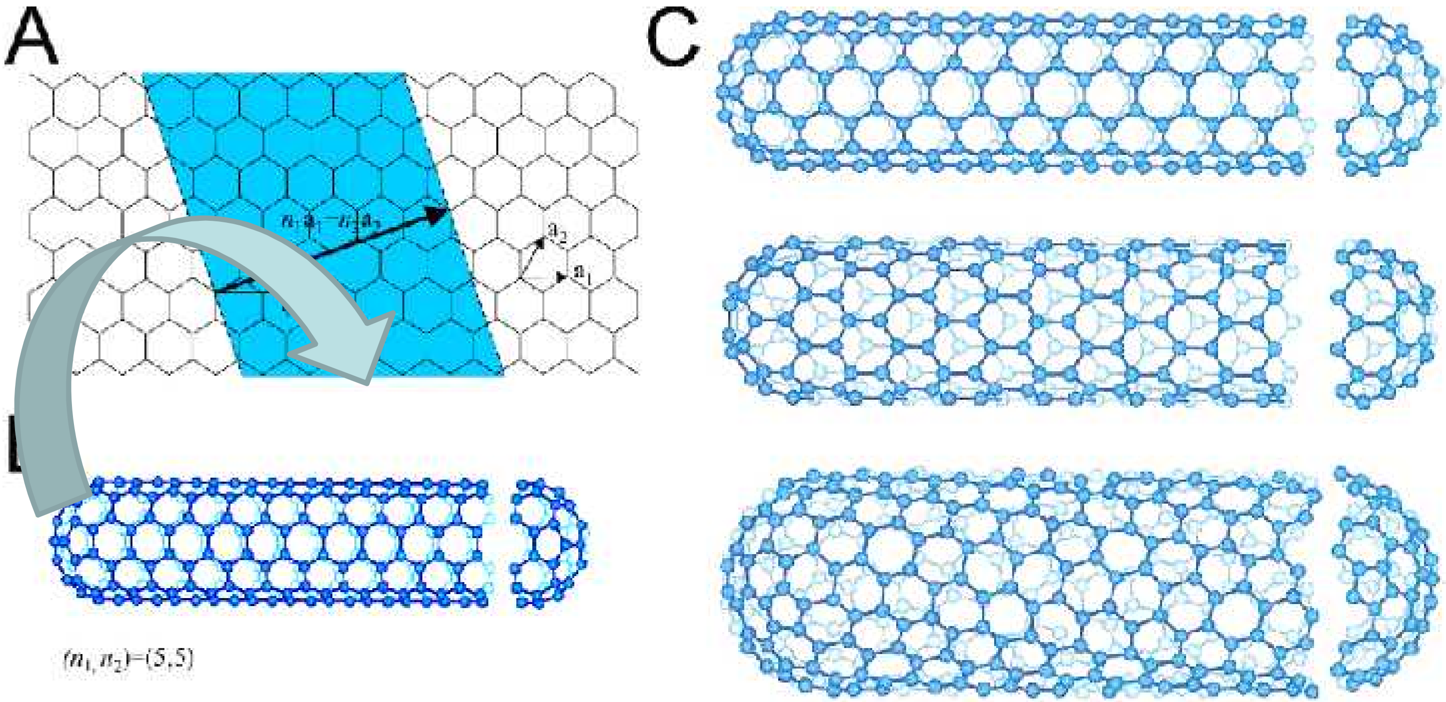
$$\text{a}E = \text{a}E^0 + \frac{\hbar^2 \text{®}^2}{2R^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - 1.8\frac{e^2}{\text{£}\ R}$$

Intrinsic band gap

NP radius

electrostatic correction

1-D Electronic Structures: Carbon Nanotubes



Wrapping vector: $\vec{n} = n_1\vec{a}_1 + n_2\vec{a}_2$

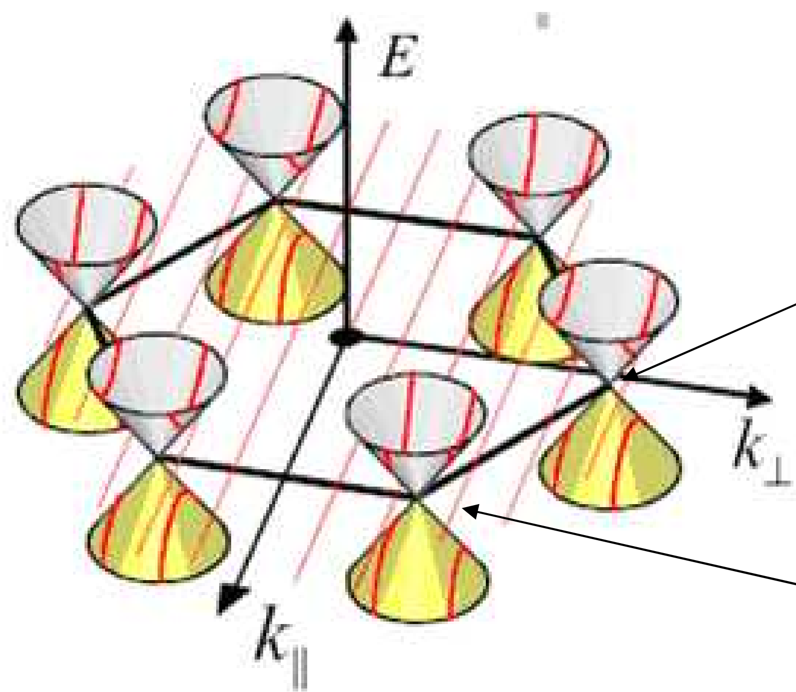
Diameter: $d = \sqrt{n_1^2 + n_2^2 + n_1 n_2}\ 0.0783\text{nm}$

- ***The folding of the sheet controls the electronic properties of the nanotubes.***

Conduction in CNTs

- p_z electrons hybridize to form π-π* valence and conduction bands that are separated by an energy gap of about 1V (semiconductor).

- For certain high simmetry directions (the K points in the reciprocal lattice) the material behaves like a metal.



- *Apex: at this point CB meets VB for graphene sheets (metal-like behavior)*

Allowed $k_\perp$ states

- The component of the wave vector perpendicular to the CNT long axis is quantized

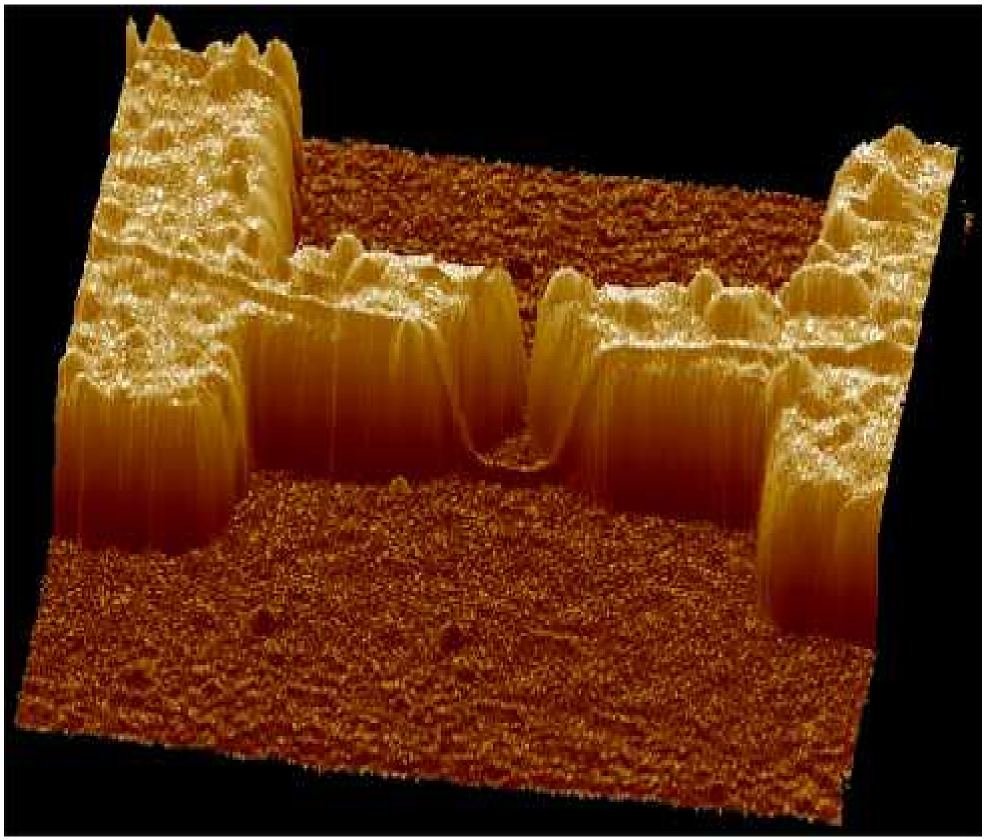
$$k_{\perp} = \frac{2n}{D}$$

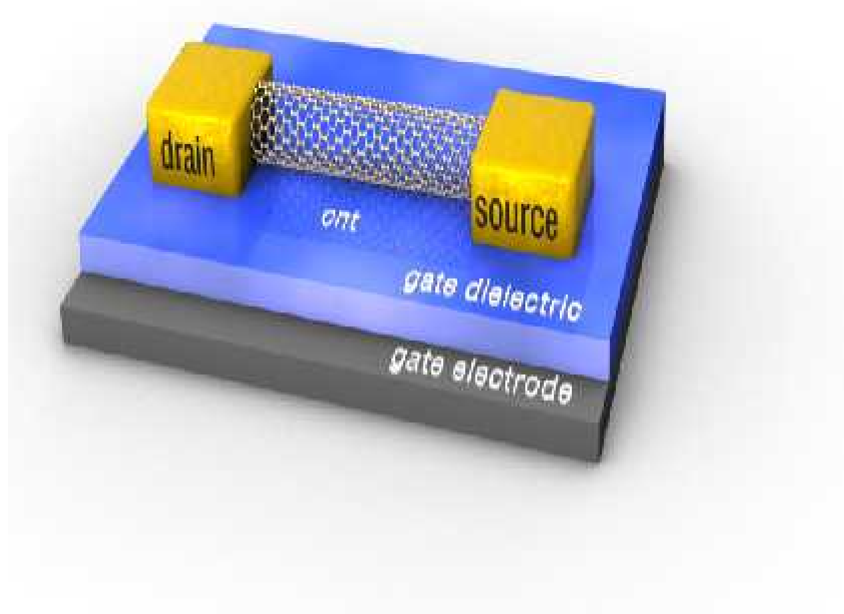
D = diameter of the nanotube

- Metallic behavior: the allowed values of $k_{\perp}$ intersect the k points at which the conduction and valence bands meet.

- ***<u>CNTs can be either metals or semiconductors depending on their chirality.</u>***

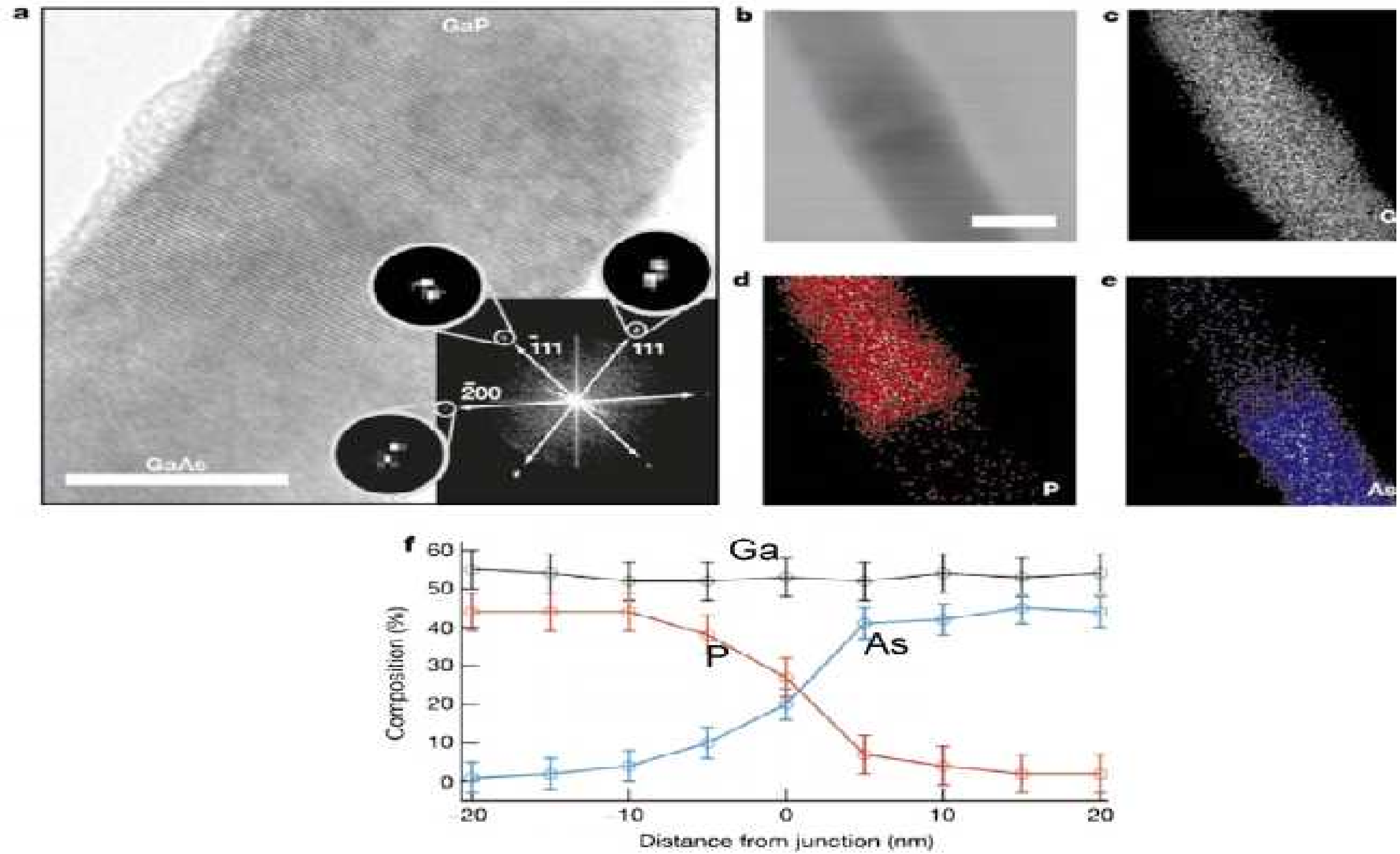
- Field effect transistor (FET) made from a single semiconducting CNT connecting source and drain connectors.





Semiconductor Nanowires

- **Ga-P/Ga-As p/n nanojunctions**

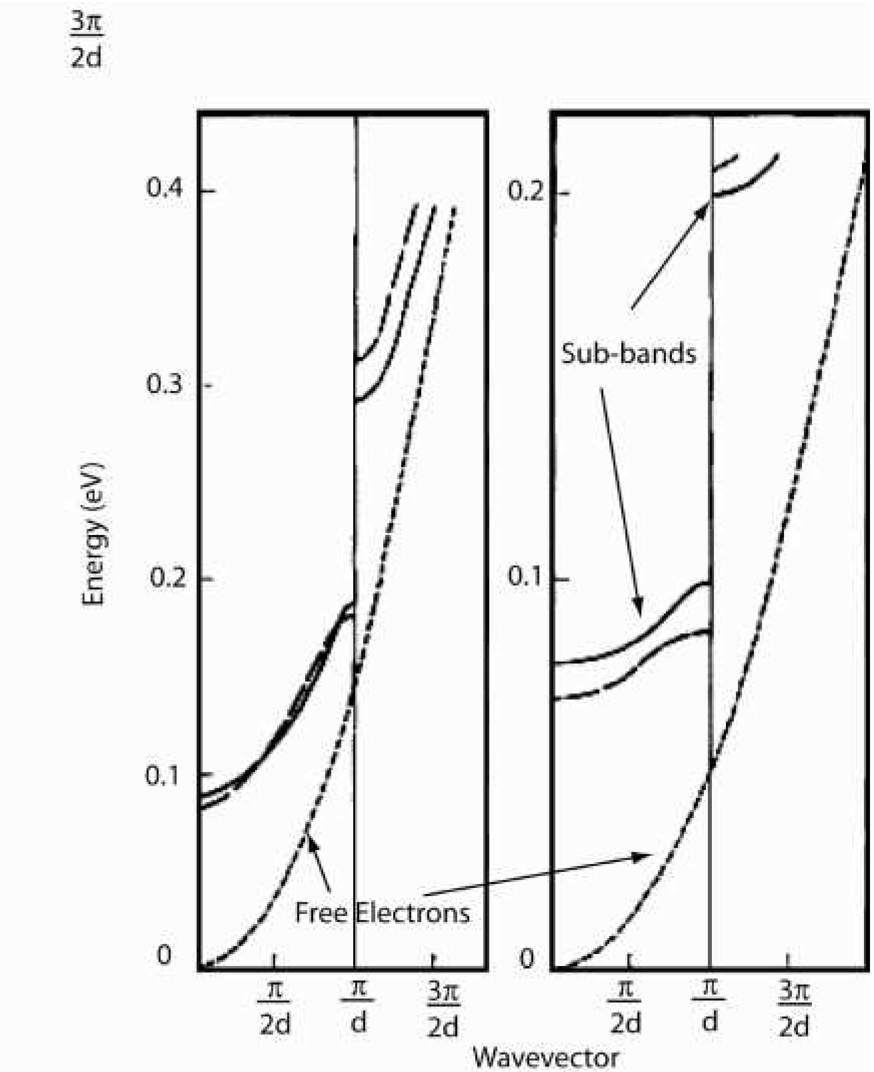


2D Electronic Structures: superlattices and heterostructures

Superlattice:

- Alternating layers of small bandgap semiconductors (GaAs) interdispersed with layers of wide bandgap semiconductors (GaAlAs).

- The thickness of each layer is considerably smaller than the electron mean free path.



Band splitting into sub-bands

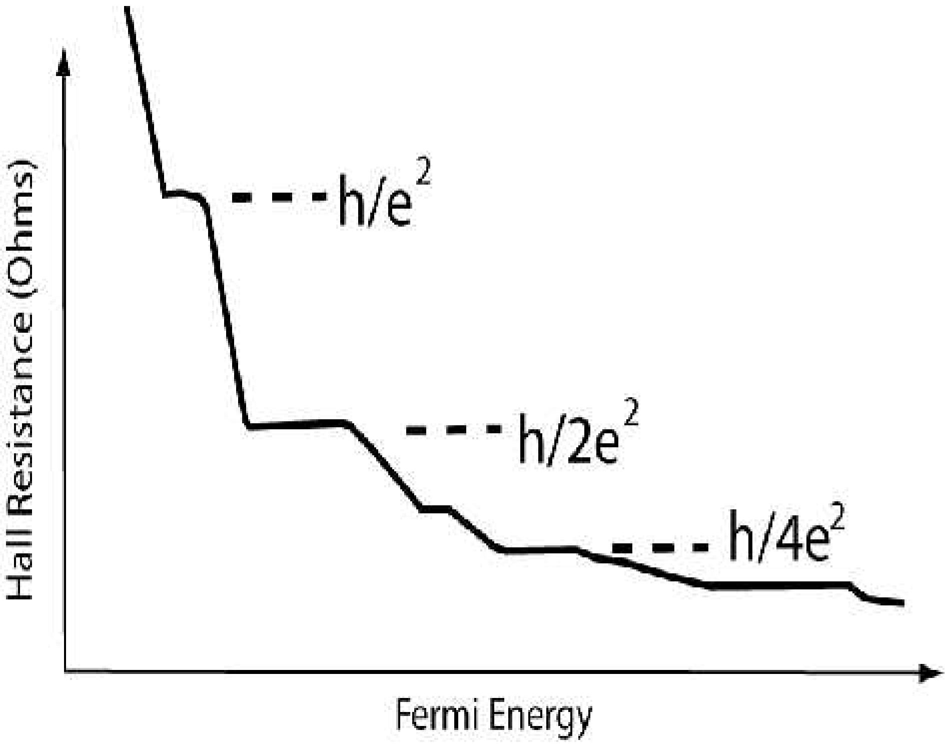
- Modulation of the structure on the length scale d (thickness of the layer in the superlattice) gives rise to the formation of new bands inside the original Brillouin zone .
- Electrons can pass freely from one small bandgap region to another without scattering.

Quantum Hall resistance of 2D electron gas

- Electrons in a layer are accelerated by an applied magnetic field (B) at a frequency:

$$\mu_C = \frac{eB}{m}$$

$$R_H = \frac{h}{ne^2}$$



Magnetic quantization in 2D electron gas.

Confinement on optical length scales Plasmonics

- Small metal particles exhibit a phenomenon called ***plasma resonance***, i.e. plasma-polariton resonance of the free electrons in the metal surface.

- A resonant metal particle can capture light over a region of many wavelengths in dimension even if the particle itself is only a fraction of a wavelength in diameter.

- Free electrons in metals polarize excluding electric fields from the interior of the metal showing a negative dielectric constant.
- The polarizability of a sphere of volume V and dielectric constant ε_r is:

$$\alpha = \varepsilon_0 3V \frac{\varepsilon_r - 1}{\varepsilon_r + 2}$$

When $\varepsilon_r \rightarrow -2$ $\quad \alpha \rightarrow \infty$

- For d<<λ the resonant frequency is independent on the particle size, but depends on particle shape.

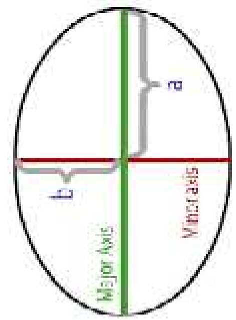
For a prolate spheroid of eccentricity e:

$$e^2 = 1 - \left(\frac{b}{a}\right)^2$$

$$\sim = \frac{\pounds_0 V}{L} \frac{1 - \pounds_r}{(1/L - 1) + \pounds_r}$$

where:

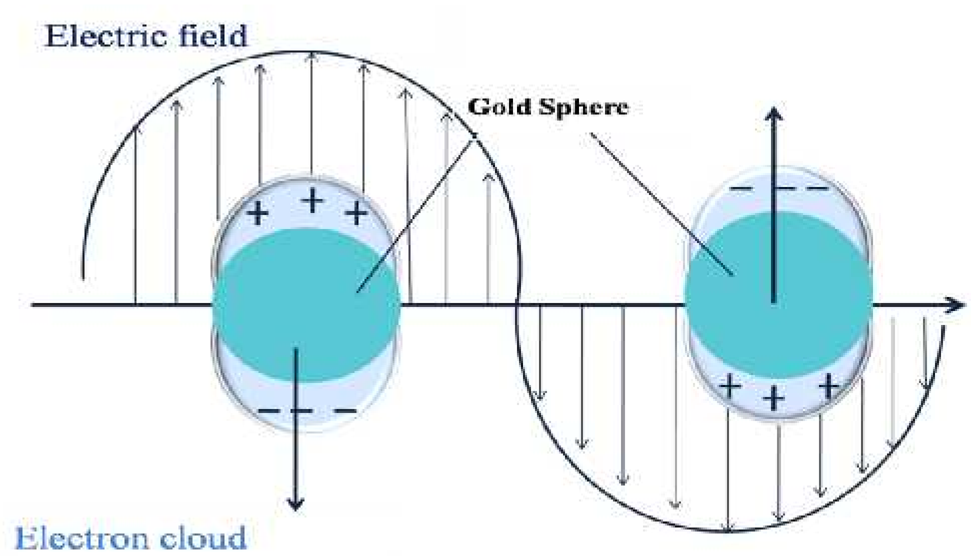
$$L = \frac{1 - e^2}{e^2}\left(-1 + \frac{1}{2e} \ln \frac{1+e}{1-e}\right) \approx \left(1 + \frac{a}{b}\right)^{-1.6}$$



Prolate Spheroid

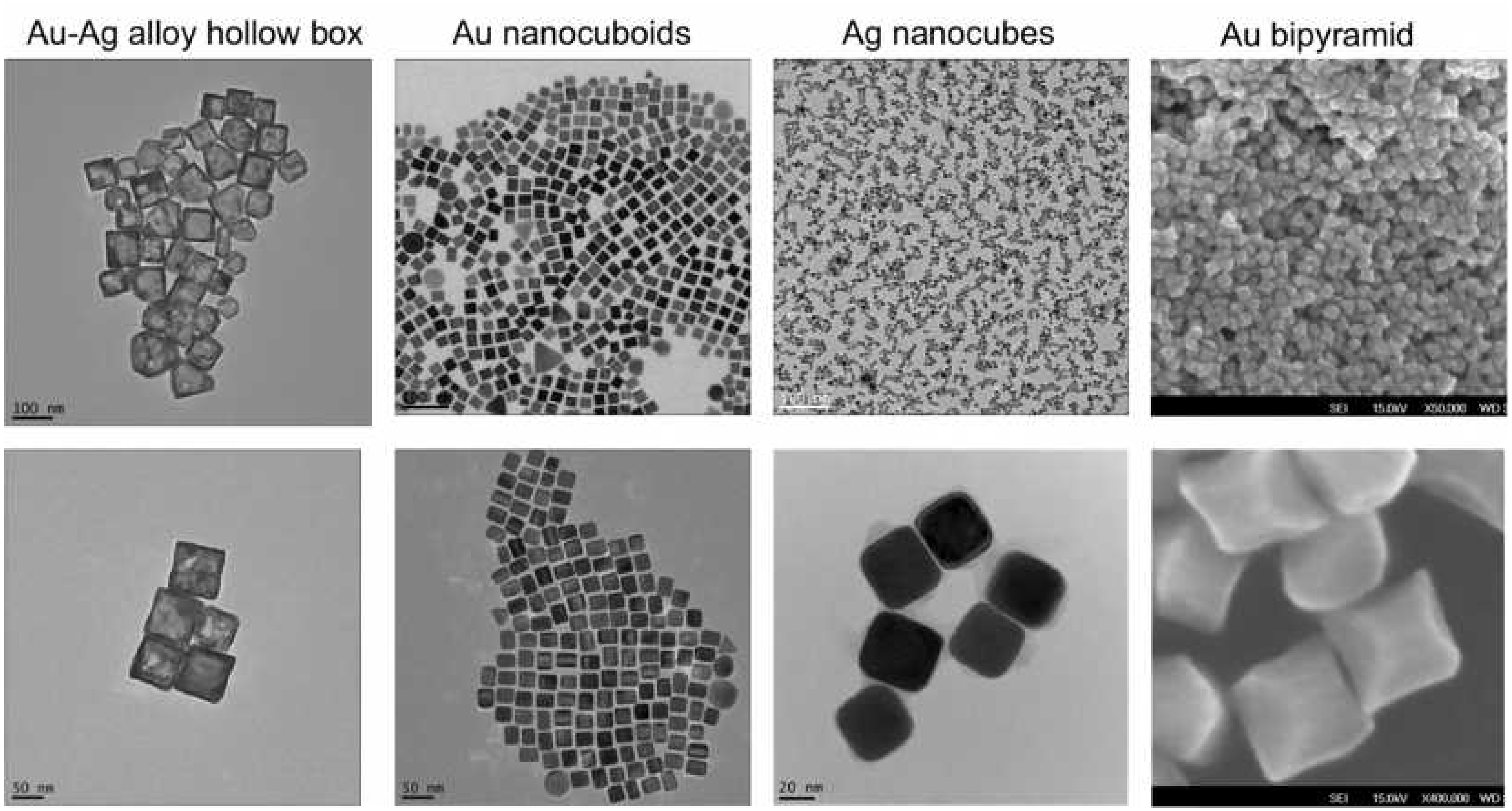
<u>The resonance is tunable throughout the visible by engineering the particle shape.</u>

Plasmon Enhanced Optical Absorption



Electric field surrounding a resonant nanoparticle ($E=E_z$)

Noble Metal Nanoparticles



Magnetic properties

• ***Diamagnetism***:

Zero-spin systems give rise to circulating currents that oppose the applied field.

• ***Paramagnetism***:

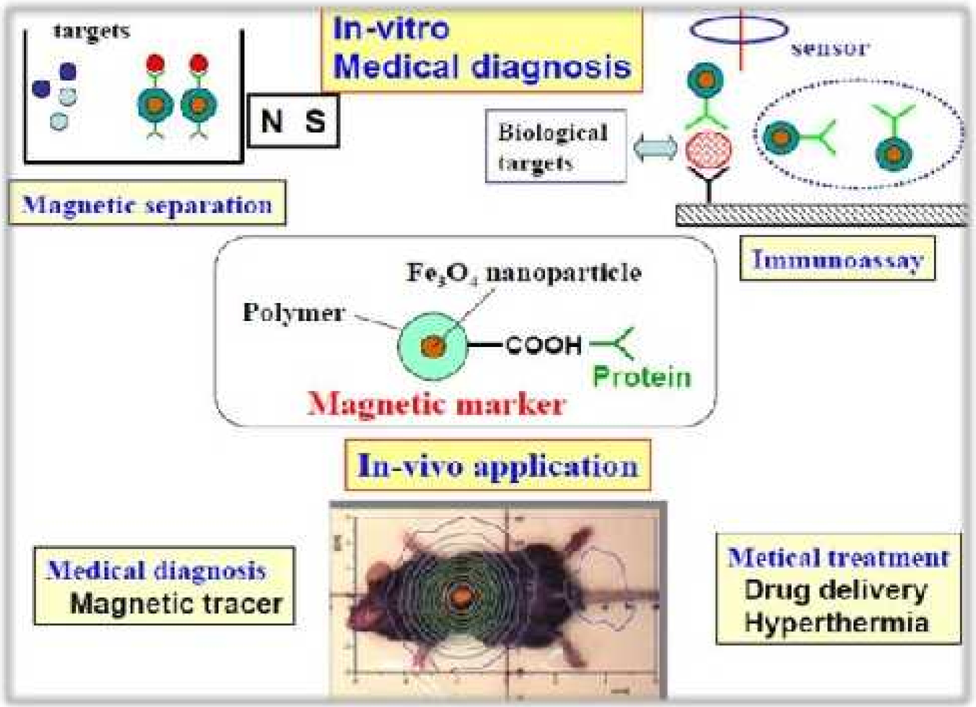
Free-electrons are magnetically polarized by an external magnetic field (*positive magnetic susceptibility*, Pauli paramagnetism).

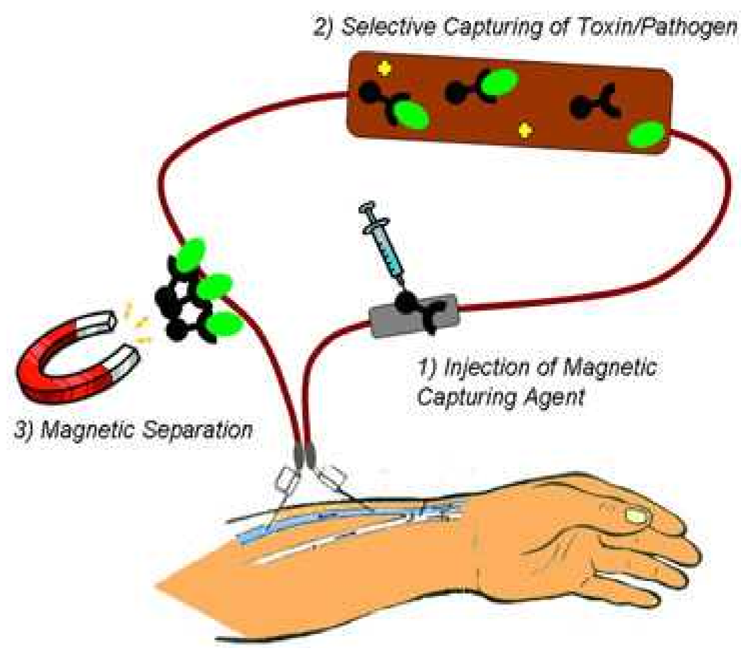
• ***Ferromagnetism***:

Spontaneous magnetic ordering due to electron-electron interactions.

Antiferromagnetism: polarization alternates from atom to atom.

Magnetic nano-particles could improve medical imaging





2D Nanostructures:
Super hydrophobic Surfaces

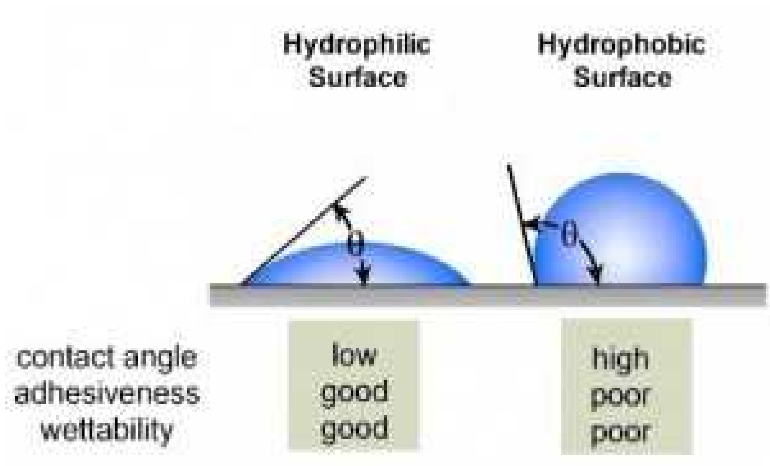
- The angle formed by a tangent to a flat surface of a drop of water at the point of contact (***contact angle***) is given in terms of the interfacial energies of the system by the Young equation:

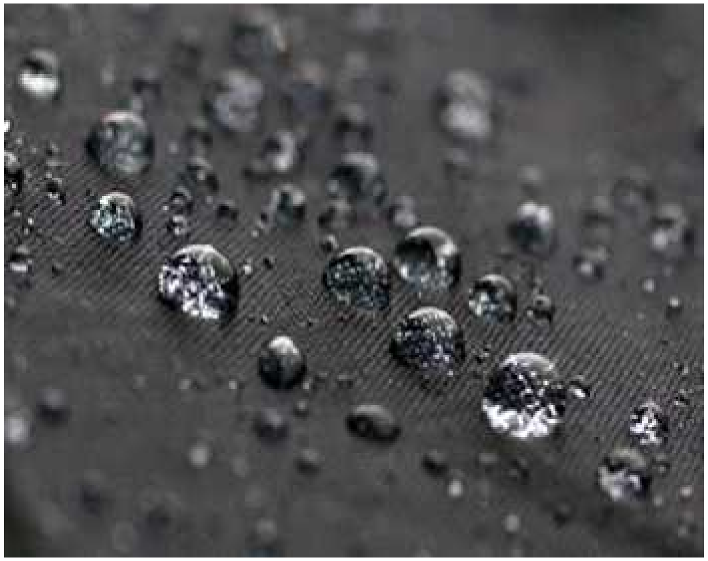
$$\cos\theta_c = \frac{\gamma_{AB} - \gamma_{AC}}{\gamma_{BC}}$$

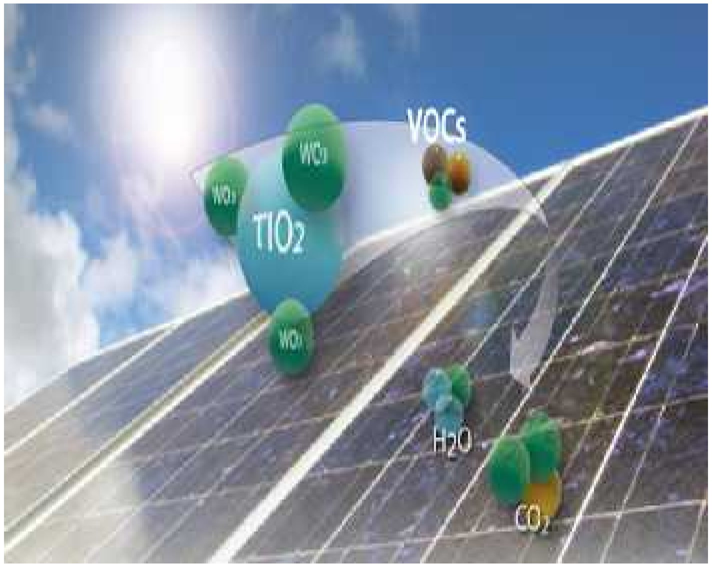
γ_{AB}= air/surface interfacial tension

γ_{AC}= water/surface interfacial tension

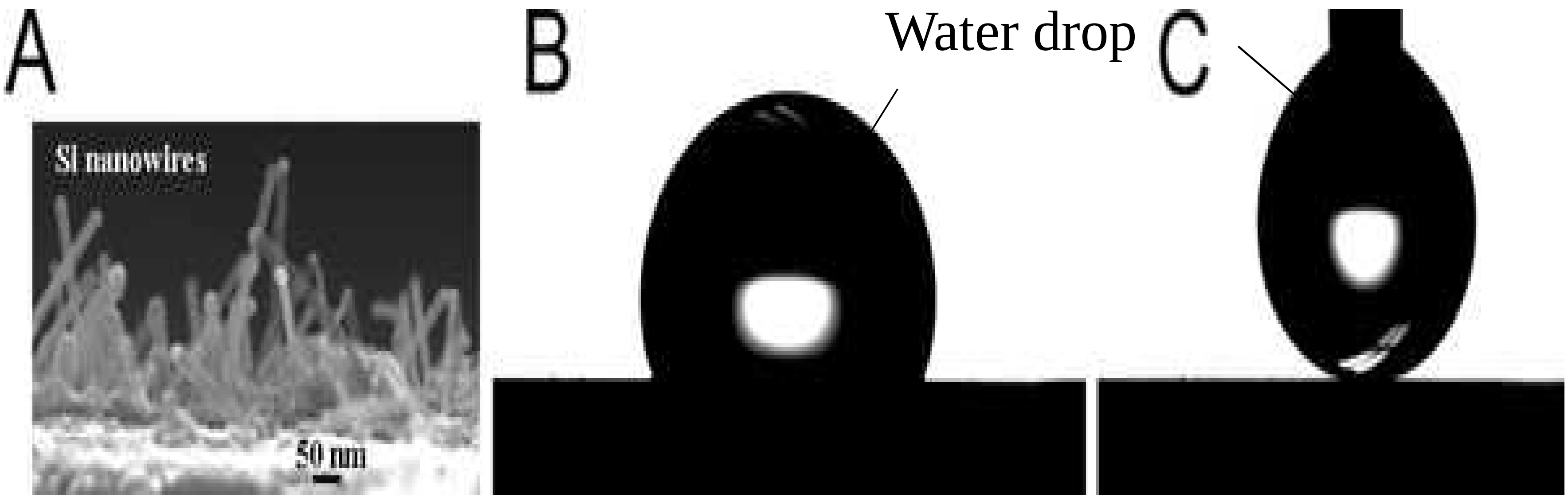
γ_{BC}= air/water interfacial tension


Hydrophilic Surface
Hydrophobic Surface
θ
θ
contact angle
adhesiveness
wettability
low
good
good
high
poor
poor




VOCs
TIO2
H2O
CO2

$cos\,\mathrm{g}_c < 1$ Water/surface repulsion (large interfacial tension)



Si Nanowires ***Coated Si surface (planar)*** ***Coated nanostructured surface (rough)***

Roughening on the nanoscale can greatly increase hydrophobicity.