



# Size-Dependent Properties of Nanomaterials and Applications (1)

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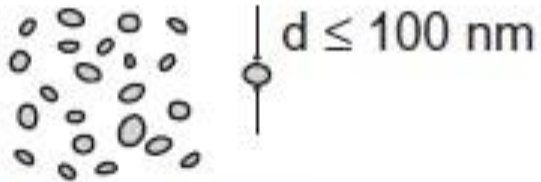
## Course objectives and outline:

1. Introduction to nanomaterials
  2. Why does size influence the material's properties?
  3. How does size influence the material's performance?
  4. Why are properties of nanoscale objects different than those of the same materials at the bulk scale?
  5. Some optoelectronic, photonic and magnetic applications
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# Classification of nanomaterials

0-D

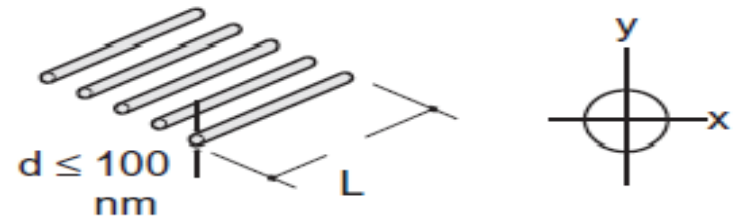
All dimensions (x,y,z) at nanoscale



Nanoparticles

1-D

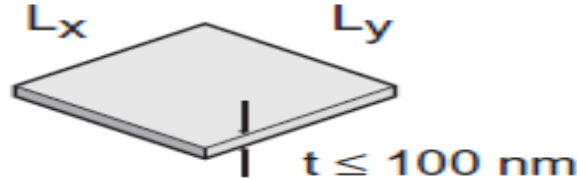
Two dimensions (x,y) at nanoscale, other dimension (L) is not



Nanowires, nanorods, and nanotubes

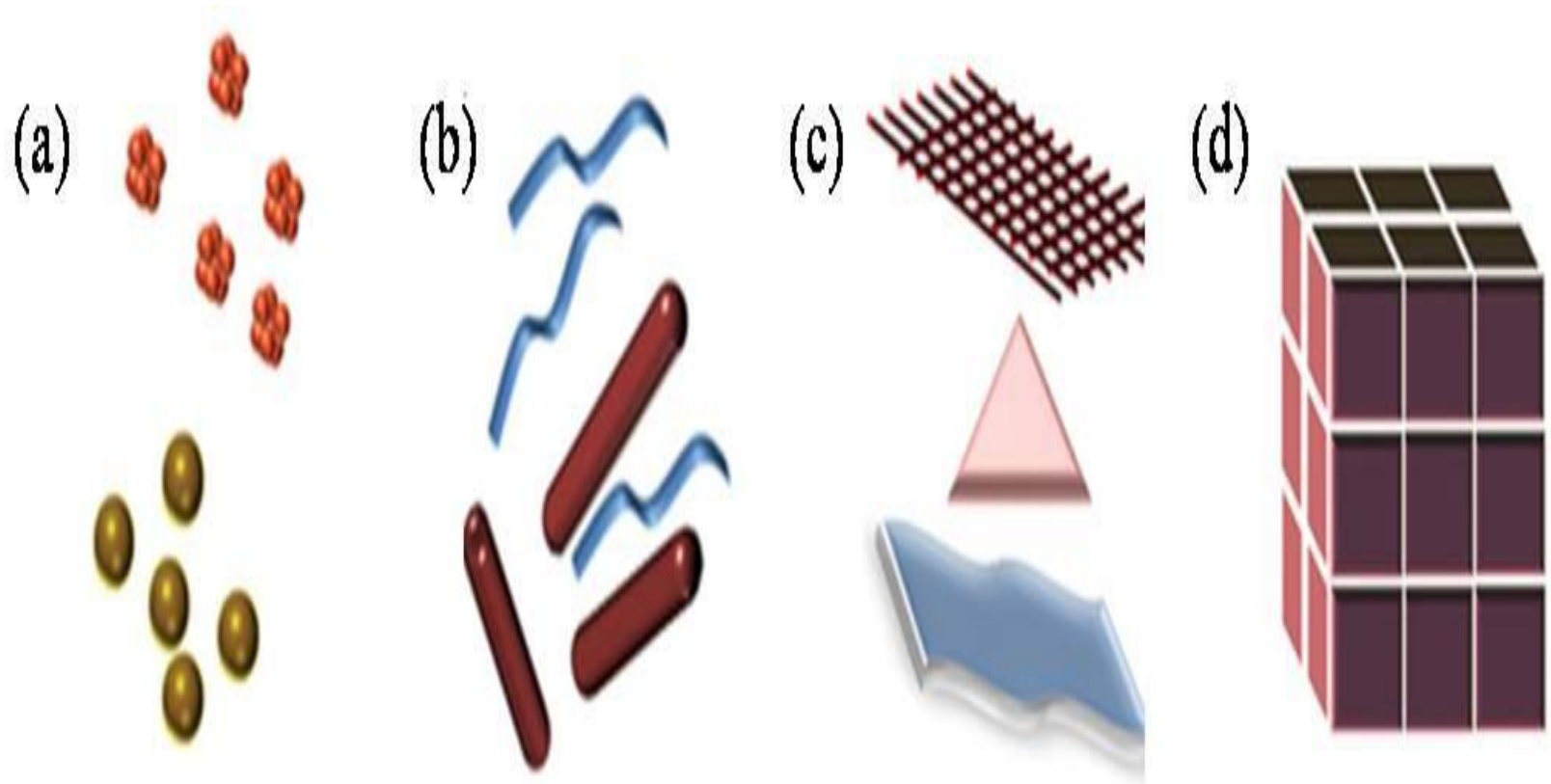
2-D

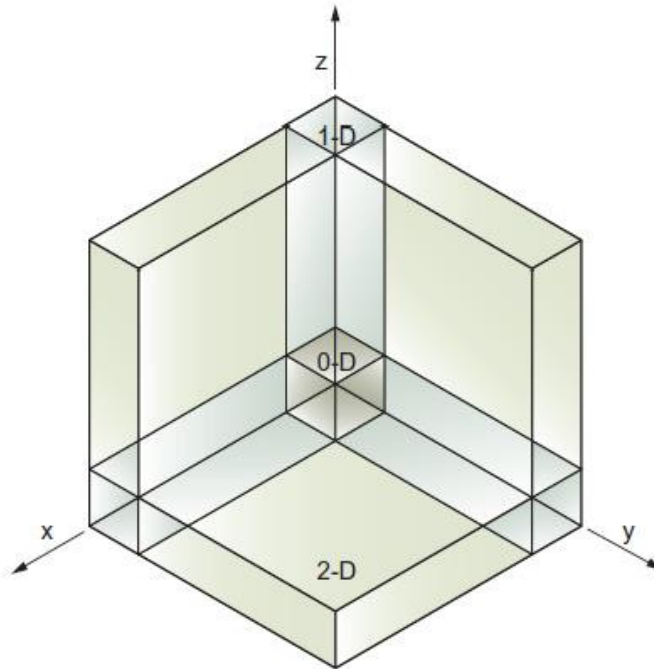
One dimension (t) at nanoscale, other two dimensions- ( $L_x, L_y$ ) are not



Nanocoatings and nanofilms

Type of nanomaterials according to Siegel





**0-D:** All dimensions at the nanoscale

**1-D:** Two dimensions at the nanoscale,  
one dimension at the macroscale

**2-D:** One dimension at the nanoscale,  
two dimensions at the macroscale

**3-D:** No dimensions at the nanoscale,  
all dimensions at the macroscale

# Size-dependent properties

**At the nanometer scale, properties become size-dependent.**

For example,

- (1) Chemical properties - reactivity, catalysis
- (2) Thermal properties - melting temperature
- (3) Mechanical properties - adhesion, capillary forces
- (4) Optical properties - absorption and scattering of light
- (5) Electrical properties - tunneling current
- (6) Magnetic properties - superparamagnetic effect



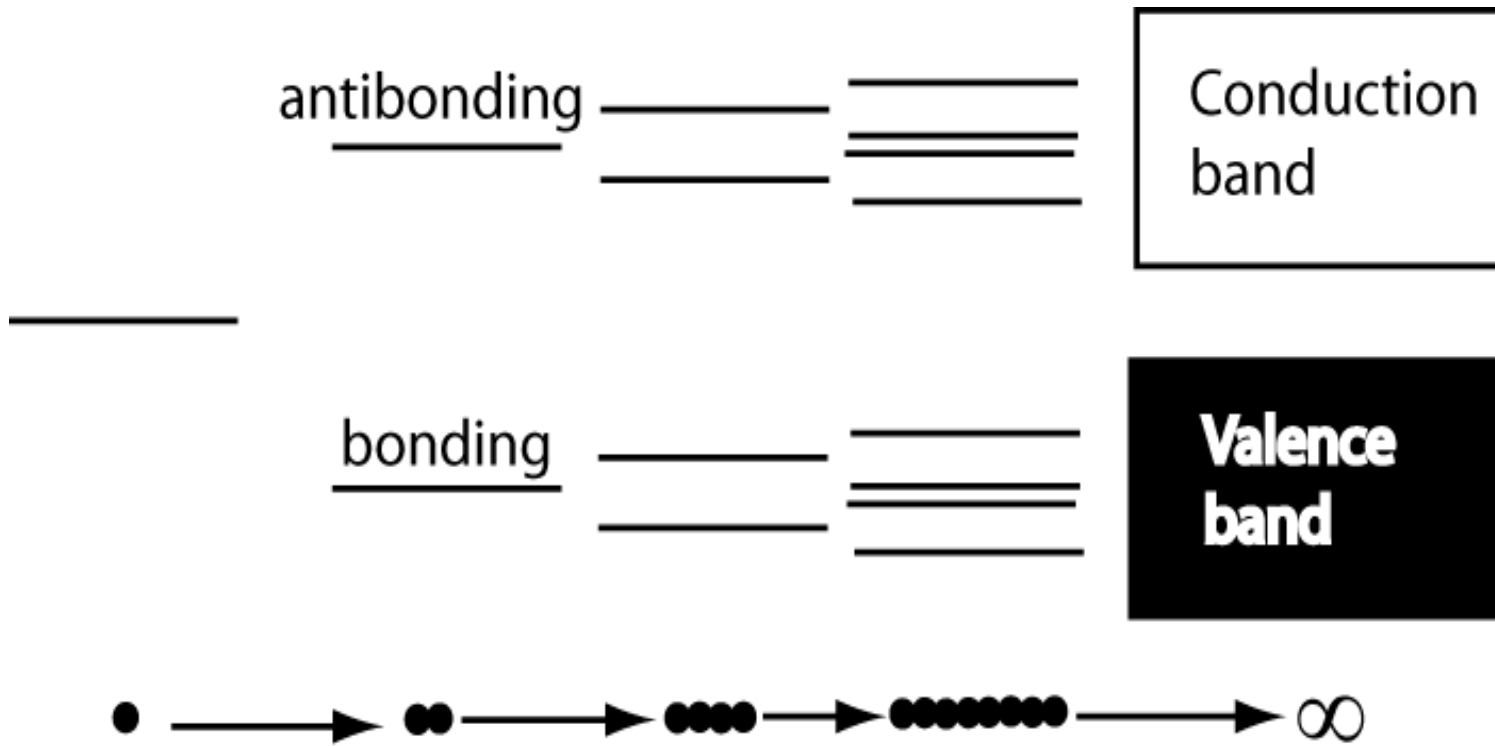
**New properties enable new applications**

## **The nanometer size of the materials render them having:**

- (i) Large fraction of surface atoms.**
- (ii) High surface energy.**
- (iii) Spatial confinement effect, which bring the quantum size effects.**
- (iv) Reduced imperfections. Nanomaterials favors of a self-purification process in that the impurities and intrinsic material defects will move to near the surface upon thermal annealing.**
- (v) Modified and quite differently energy band structure and charge carrier density from their bulk and in turn will modify the electronic and optical properties of the material.**

**This means that the physical and chemical properties of nanomaterials depend not only on their composition but also on the particle size and shape.**

# 1- Electronic properties of nanomaterials



Development of electronic properties as a function of cluster size (number of atoms)



- When several atoms are brought together into a molecule, their atomic orbitals split and produces a number of molecular orbitals proportional to the number of atoms.
  - In solids, there are so many atoms, the difference in energy between them becomes very small, so that forming bands of energy rather than the discrete energy levels, that is to say form nearly continuous bands of states.
  - 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 and antibonding states.
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# Energy bands



**Variation of band structure with the number of atoms**

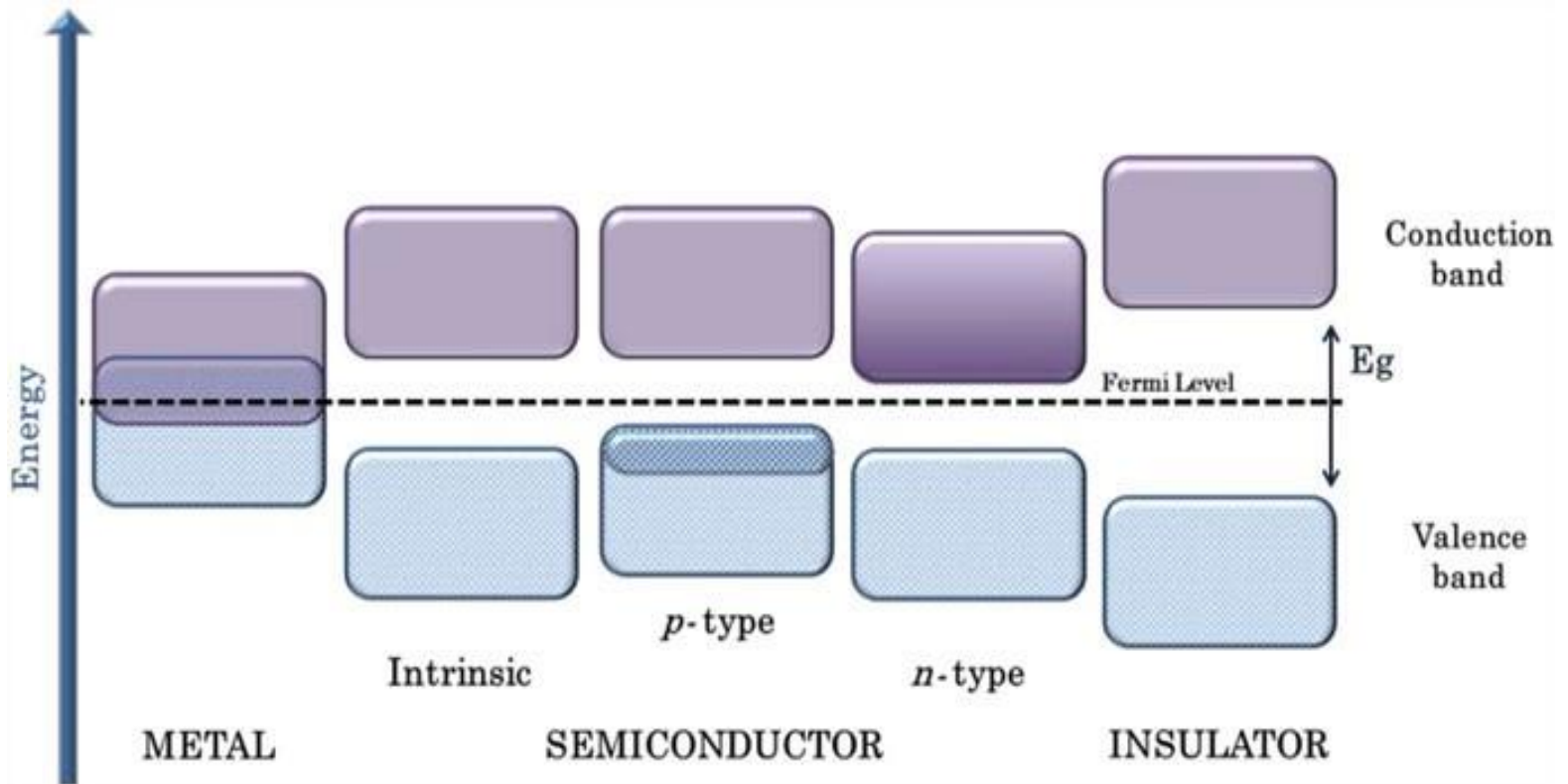
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## 1.1- Quantum confinement (size) effect

- Quantum Confinement is the spatial confinement of electron-hole pairs (excitons) in one or more dimensions within the material.
- This is due to changes in the atomic structure as a result of ultra-small length scale on the energy band structure.
- Quantum confinement is more prominent in semiconductors because they have an energy gap. Metals do not have a bandgap.
- The regime of quantum confinement length scale ranges from 2 to 25 nm for typical semiconductor groups of IV, III-V and II-VI.
- These “geometrical” constraints, electrons “feel” the presence of the particle boundaries and respond to changes in particle size by adjusting their energy. **11**

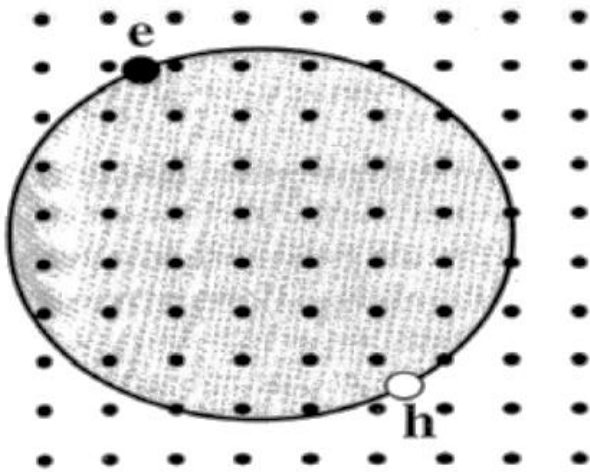
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**This phenomenon is known as the quantum-size effect.**



**Electronic band structures of metal, semiconductor, and insulator indicating the Fermi level**

## Exciton

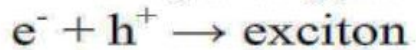


(a) Free exciton



(b) Tightly bound exciton

Binding energy and Bohr's radius



- free exciton  $E_b \approx 0.01 \text{ eV}$
- tightly bound exciton  $E_b > 0.1 \text{ eV}$

## Free and tight Excitons

Quantization effects become most important when the particle dimension of a semiconductor becomes near to or below Bohr exciton radius.

$$a_B = \varepsilon \frac{m}{m^*} a_0$$

Bohr radius of a particle

$\varepsilon$  is the dielectric constant of the material,

$m^*$  is the mass of the particle,

$m$  is the rest mass of the electron,

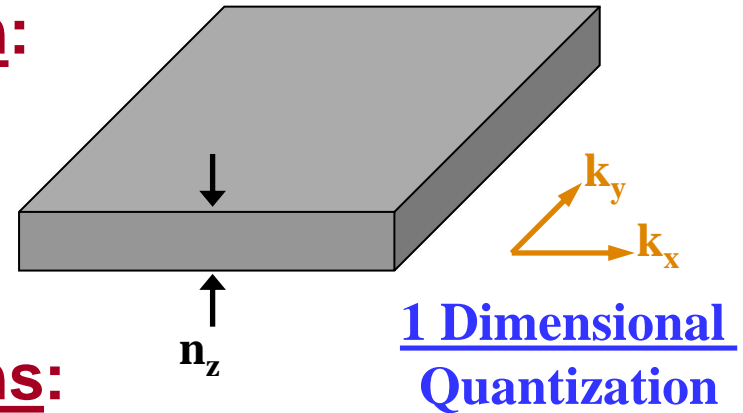
and  $a_0$  is the Bohr radius of the hydrogen atom.

# Quantum Confinement in Nanostructures

## Electrons Confined in 1 Direction:

Quantum Wells (thin films):

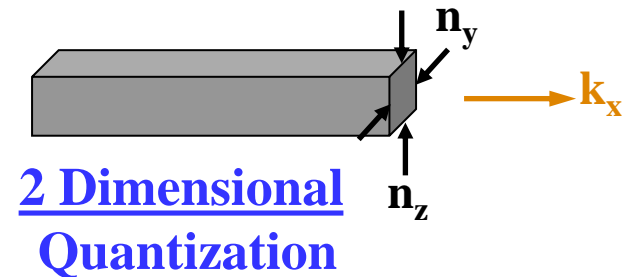
- **Electrons** can easily move in **2 Dimensions.**



## Electrons Confined in 2 Directions:

Quantum Wires:

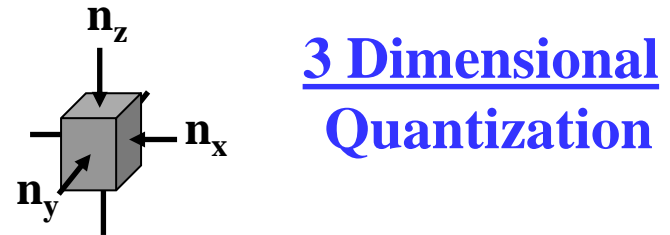
- **Electrons** can easily move in **1 Dimension.**

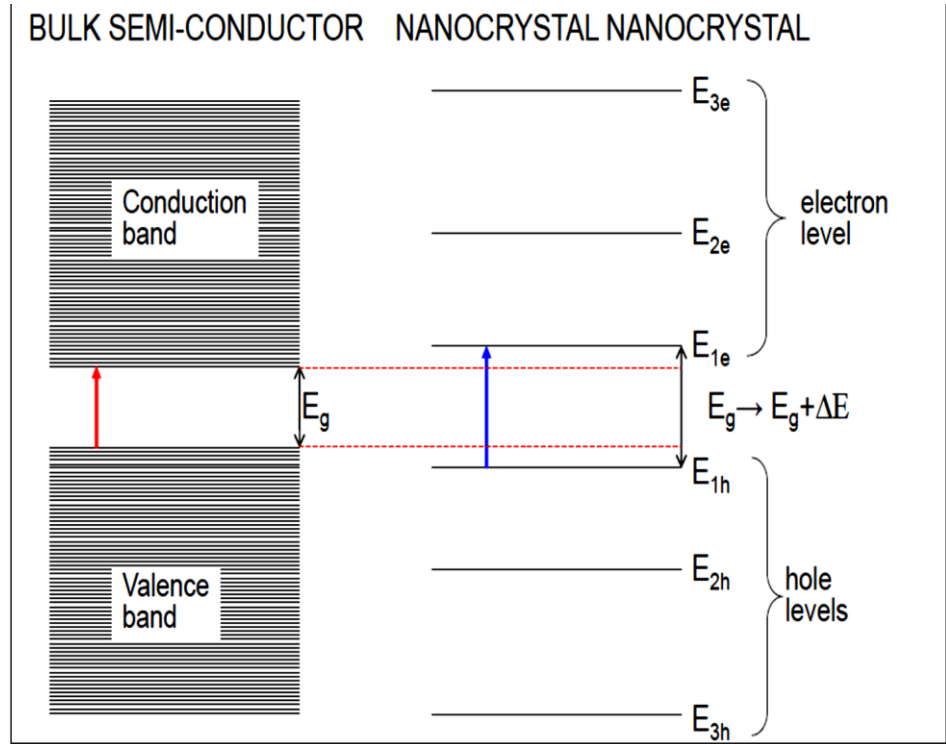
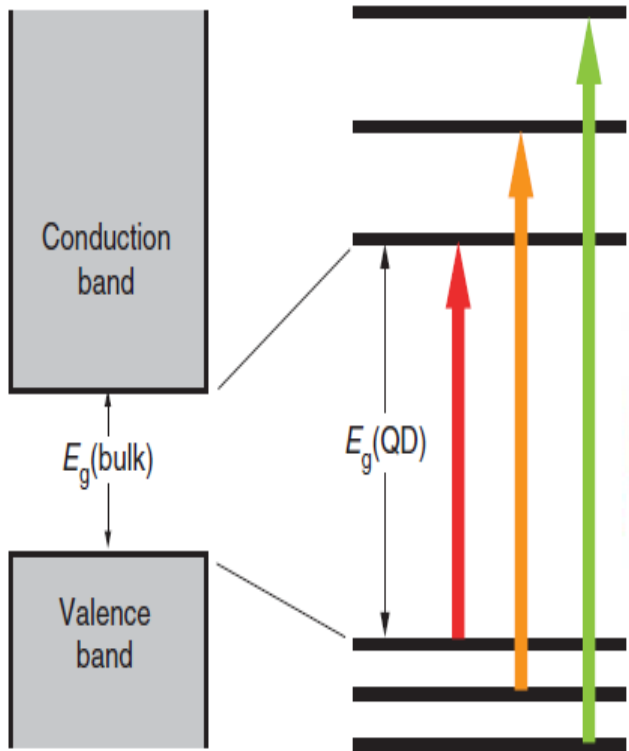


## Electrons Confined in 3 Directions:

Quantum Dots:

- **Electrons** can easily move in **0 Dimensions.**





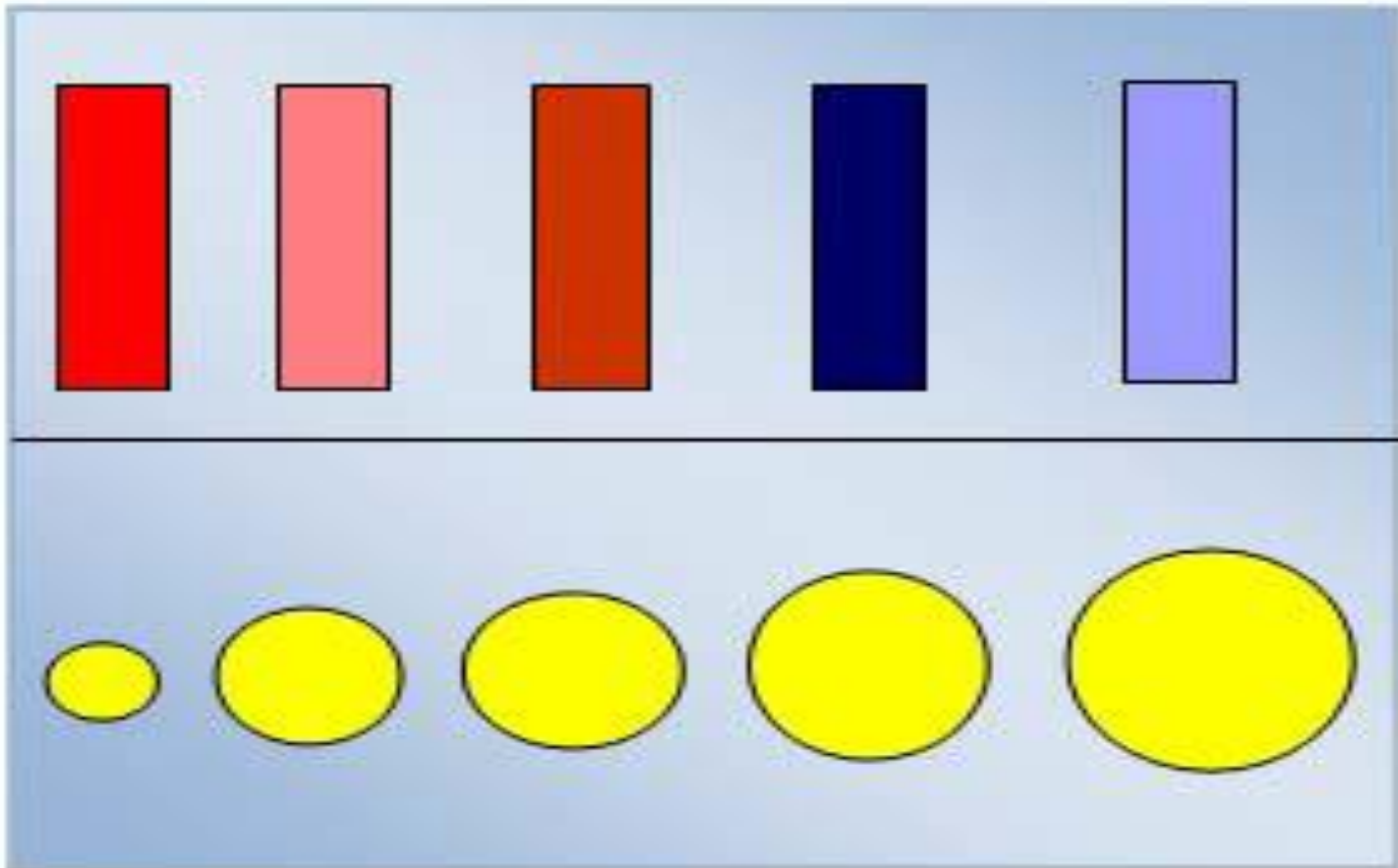
**A schematic of the discrete energy level of a semiconductor.**



1- The quantum confinement effect causes increasing of the excitonic transition energy and blue shift in the absorption and luminescence band gap energy.

- For example, 4.8 nm diameter PbSe NCs show an effective band gap of approximately 0.82 eV, exhibiting a strong confinement induced blue shift of >500 meV compared to the bulk PbSe band gap of 0.28 eV (the Bohr exciton radius in PbSe is 46 nm).

2- Quantum confinement leads to a collapse of the continuous energy bands of a bulk material into discrete, atomic like energy levels, so a discrete absorption spectrum, compared to the continuous absorption spectrum of a bulk semiconductor.

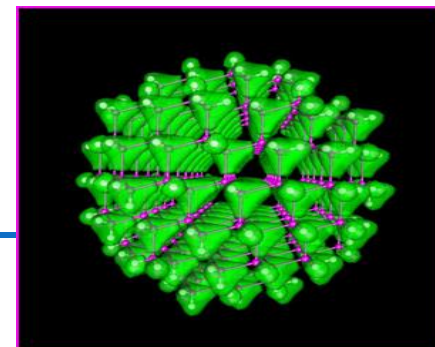


**Gold particle of difference size producing different color**

Quantum dots (QD) are nanoparticles/structures that exhibit 3 dimensional quantum confinement, which leads to many unique optical and transport properties.

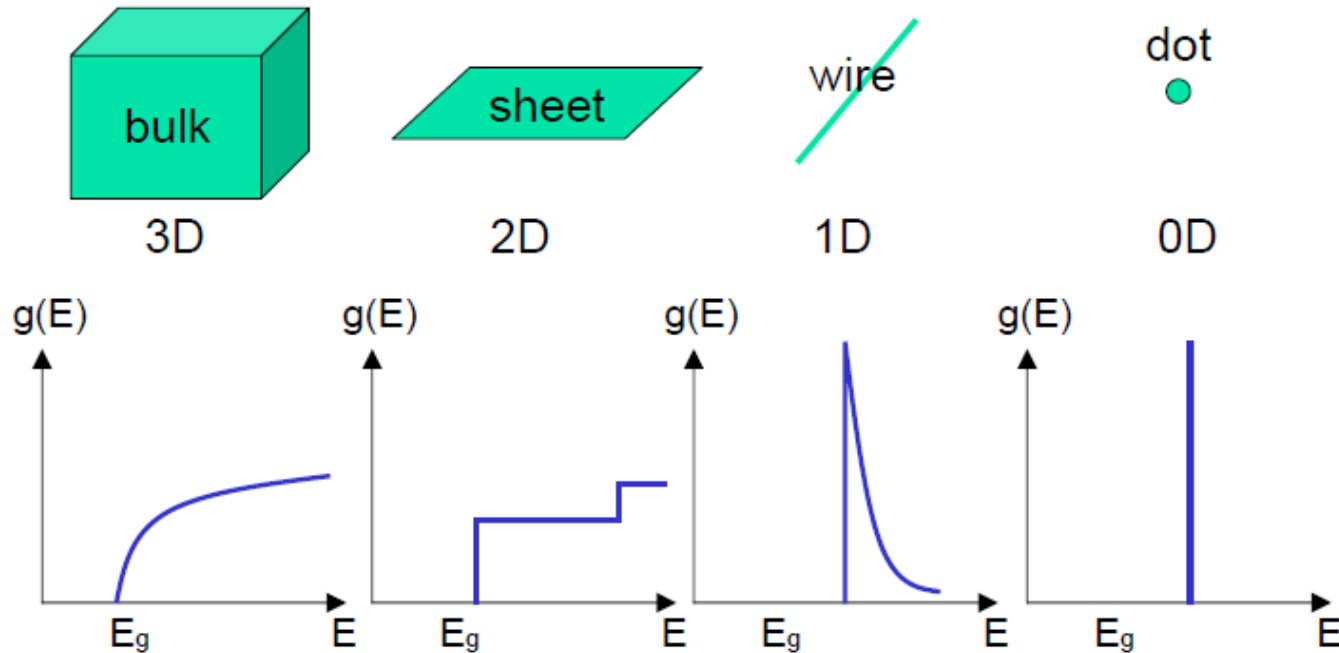
- Quantum dots are usually regarded as semiconductors by definition, in some cases it may be acceptable to speak about metal quantum dots.
- Typically, quantum dots are composed of groups II-VI, III-V, and IV-VI materials.
- QDs are bandgap tunable by size which means their optical and electrical properties can be engineered to meet specific applications.
- In QD, the optical absorption spectrum is roughly proportional to the density of states.

GaAs Quantum dot containing just 465 atoms.



# Density of electronic states

$g(E)$  = Density of states



Density of electron states in bulk, 2D, 1D and 0D semiconductor structure.

As more number of the dimension is confined, more discrete energy levels can be found.

$$\frac{dn}{dE} = \frac{Vm}{\hbar^2 2\pi^2} \sqrt{\frac{2mE}{\hbar^2}} \propto E^{\frac{1}{2}}, \quad \frac{dn}{dE} = \frac{Am}{2\pi\hbar^2}, \quad \frac{dn}{dE} = \frac{Lm}{2\pi\hbar^2 k} \propto E^{-\frac{1}{2}}$$

Density of electron states in bulk, 2D and 1D semiconductor structure

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

- For zero-dimensional quantum dots semiconductors, the excited electron-hole pairs are confined within a small volume, the density of states concentrate carriers in a certain energy range.

The quantum confinement of carriers converts the density of states to a set of discrete quantum levels.

- For two dimensions the density  $N(E)$  of states changes from a continuous dependence  $N(E) \sim E^{1/2}$  to a step like dependence.

The optical absorption edge for a quantum well is at a higher photon energy than for the bulk semiconductor, the spectrum is stepped rather than smooth the steps, at each step, sharp peaks appear corresponding to electron-hole (exciton) pair states.

$$(0\text{-D}) \quad E_n = \left[ \frac{\pi^2 \hbar^2}{2mL^2} \right] (n_x^2 + n_y^2 + n_z^2)$$

$$(1\text{-D}) \quad E_n = \left[ \frac{\pi^2 \hbar^2}{2mL^2} \right] (n_x^2 + n_y^2)$$

$$(2\text{-D}) \quad E_n = \left[ \frac{\pi^2 \hbar^2}{2mL^2} \right] (n_x^2)$$

The confined energy levels of nanostructures are predicted by solving Schrodinger equation assuming the barriers have an infinite confining potential.

$\hbar \equiv h/2\pi$ ,  $h$ ; Planck's constant,  $m$ ; electronic mass,  $L$ ; width of the infinitely deep potential well, and  $n_x$ ,  $n_y$ , and  $n_z$  principal quantum numbers in the three confining dimensions  $x$ ,  $y$ , and  $z$ .

The smaller the dimensions of the nanostructure (smaller  $L$ ), the wider is the separation between the energy levels, **23**

leading to a spectrum of discrete energies

## Weak confinement regime

- This regime is applicable to the case where **the particle size is small but still a few times larger than the exciton Bohr diameter.**
- The Coulomb energy is much larger than the confinement energy resulting in the quantization of exciton center-of-mass motion.

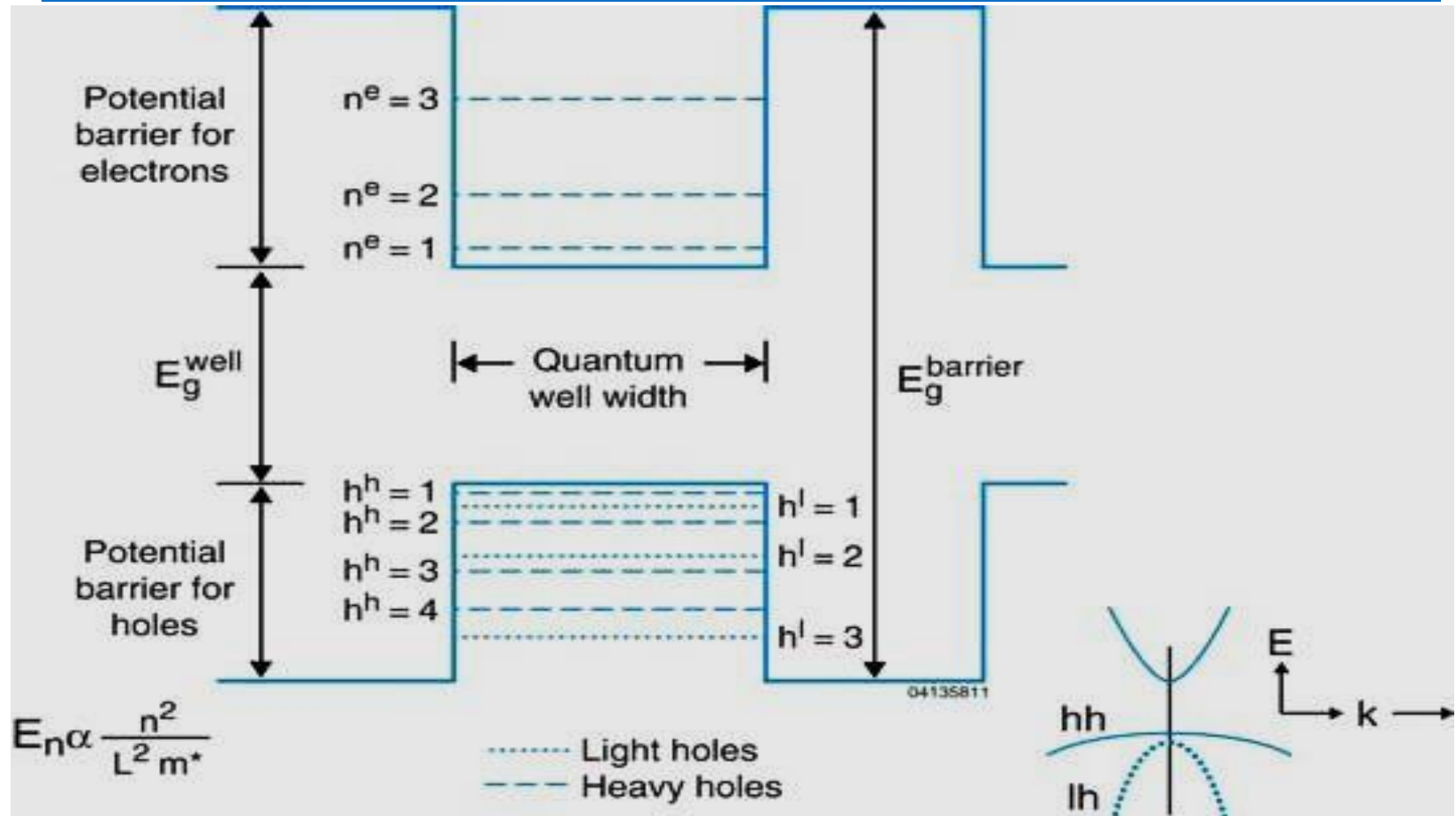
## Strong confinement regime

- This regime is applicable to the case where **the particle size is much smaller than the exciton Bohr diameter.**
- The Coulomb energy cannot be taken into consideration as it is negligible with respect to confinement energy.
- The movement of both electron and hole is independent and their confinements occur separately in the infinite spherical potential.



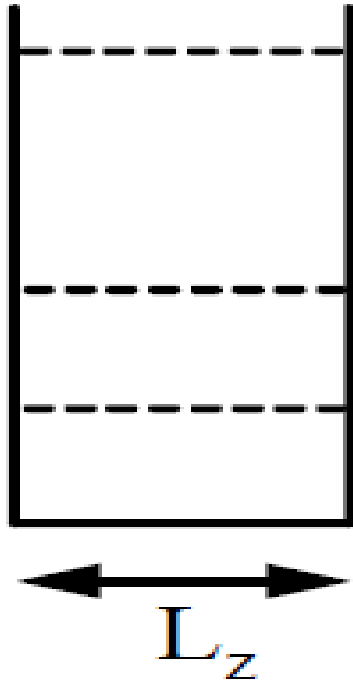
## 1.2- Quantum well structures and its properties

- A quantum well (QW) is a particular kind of heterostructure in which a single layer of material A (layer thickness  $L$ ), sandwiched between 2 macroscopically large layers of material B (usually, the bandgaps satisfy:  $E_{gA} < E_{gB}$ ).
- Both electrons and holes see lower energy in the "well" layer, hence the name by analogy with a "potential well".
- The layer in which both electrons and holes are confined, is so thin (typically about 100 Å or about 40 atomic layers) that we cannot neglect the fact that the electron and hole are both waves.
- only particular waves are standing waves, the system is quantized, hence the name "quantum well".



One-dimensionally confined quantum well created by a thin small-band gap semiconductor layer sandwiched between two larger band gap semiconductor layers.  $E_g^{\text{Well}}$  is the band gap of the well material and  $E_g^{\text{barrier}}$  that of the barrier material.

energy



$n=3$

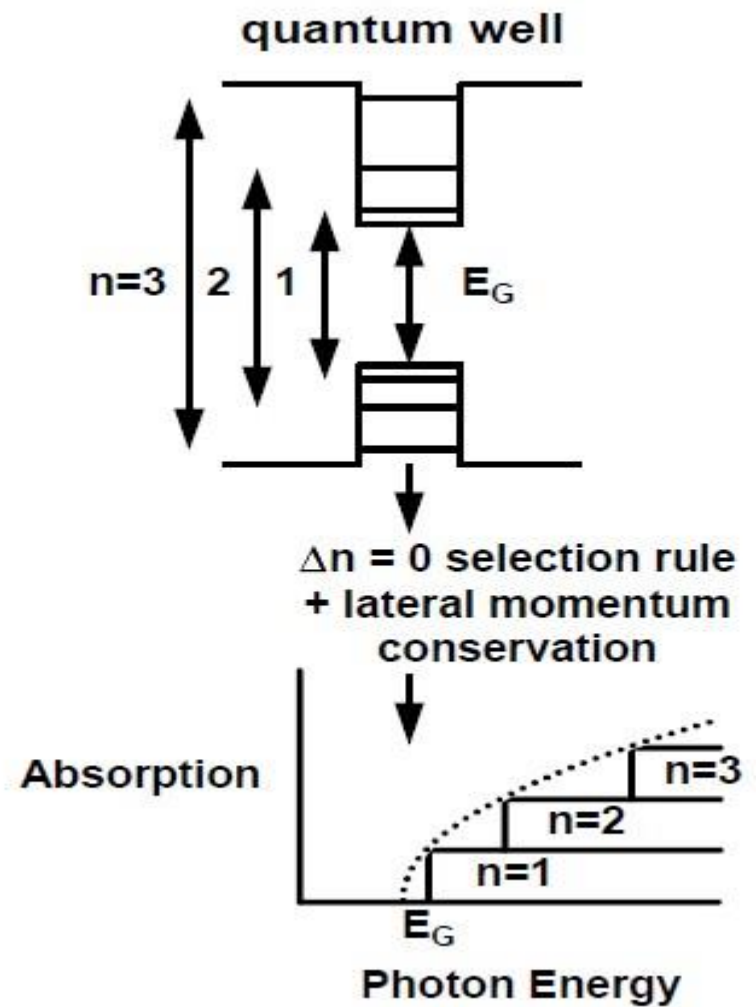
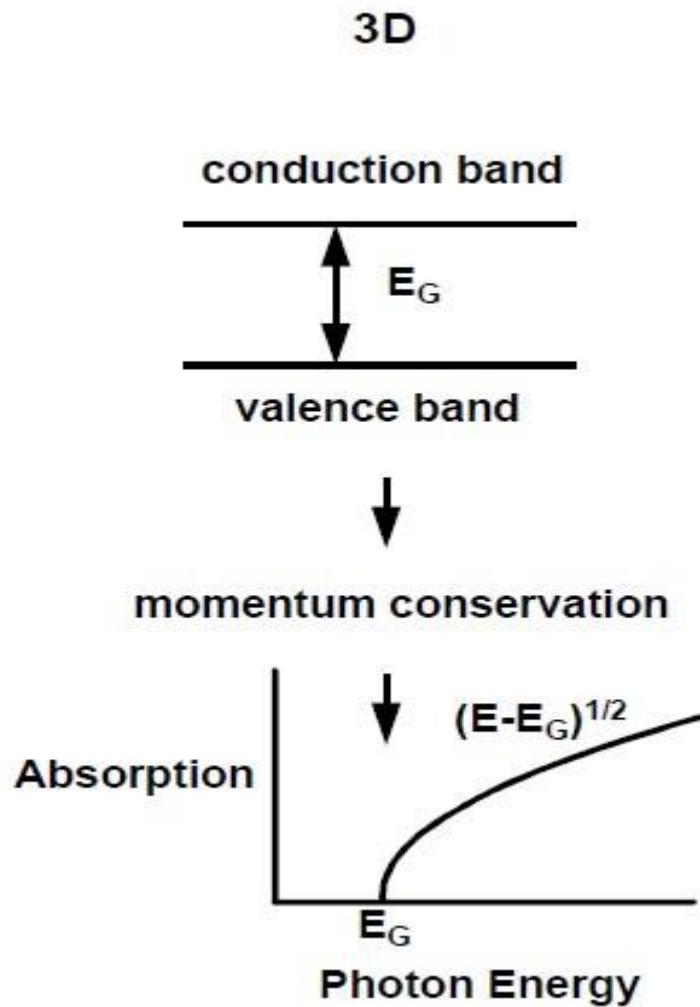
$n=2$

$n=1$

wavefunction



Infinite quantum well and associated wave functions.



*Optical absorption in bulk (i.e., 3D) semiconductors and in quantum wells.*

# Quantum Confinement Terminology

## Quantum Well $\equiv$ QW

= A single layer of material **A** (layer thickness  $L$ ), sandwiched between 2 macroscopically large layers of material **B**. Usually, the bandgaps satisfy:

$$E_{gA} < E_{gB}$$

## Multiple Quantum Well $\equiv$ MQW

= Alternating layers of materials **A** (thickness  $L$ ) & **B** (thickness  $L'$ ). In this case:

$$L' \gg L$$

So, the  $e^-$  &  $h^+$  in one A layer are independent of those in other A layers.

## Superlattice $\equiv$ SL

= Alternating layers of materials **A** & **B** with similar layer thicknesses.

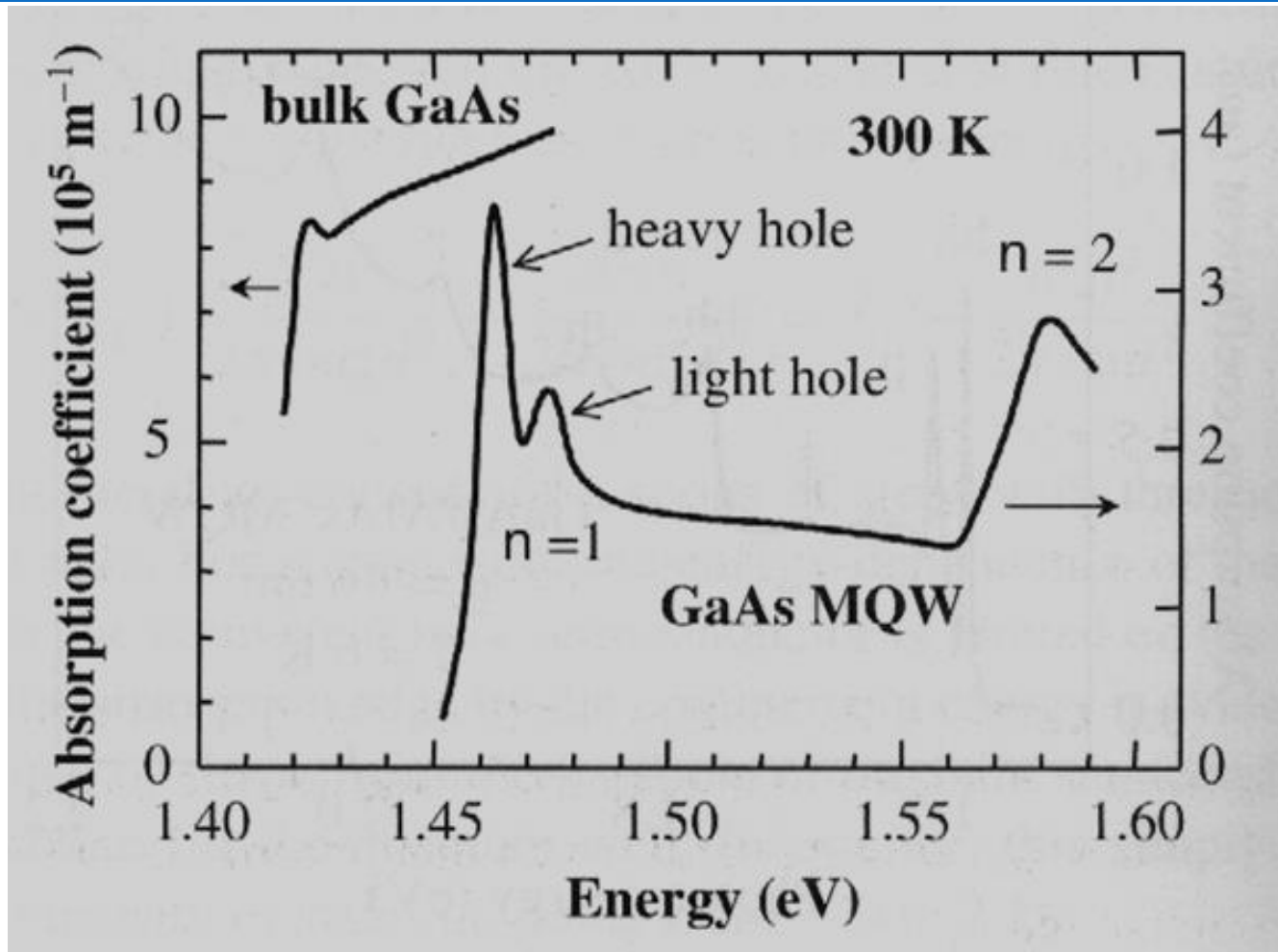
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## In bulk semiconductors;

- The simplest model for absorption is to raise an electron from the valence band to a state of essentially the same momentum in the conduction band (a "vertical" transition) by absorbing a photon.
- Such transitions have identical strength, although they will have different energies corresponding to the different energies for such vertical transitions.
- The optical absorption spectrum follows directly from the density of states in energy, so, an absorption edge that rises as the square root of energy.

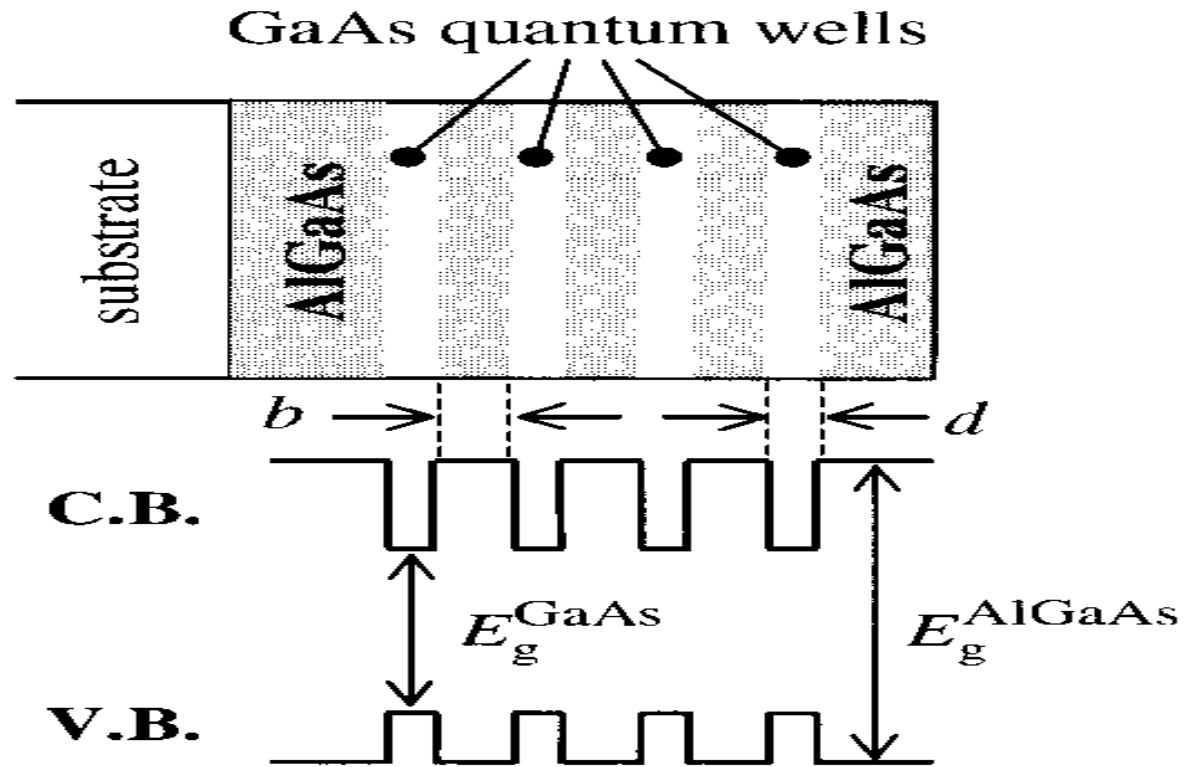
## In a quantum well;

- The electrons and holes are still free to move in the directions parallel to the layers.
- No really discrete energy states for electrons and holes in quantum wells; instead "sub-bands" that start at the energies calculated for the confined states.
- The electron in a given confined state have an amount of kinetic energy for its in-plane motion in the quantum well, and so have an energy greater than or equal to the simple confined-state energy for that sub-band.
- The density of states for motion in the plane of the quantum well layers turns out to be constant with energy, so the density of states for a given sub-band is a "step" that starts at the appropriate confinement energy.
- Optical transitions and the optical absorption in a quantum well is a series of steps, with one step for each quantum number,  $n$ .



Room temperature absorption spectrum of a GaAs/  $\text{Al}_{0.28}\text{Ga}_{0.72}\text{As}$  MQW structure containing 40 periods with 7.6 GaAs quantum well





Multiple Quantum Well (MQW) Alternating layers of materials A (thickness  $L$ ) & B (thickness  $L'$ ). In this case:  $L' \gg L$ . So, the  $e^-$  &  $e^+$  in one A layer are independent of those in other A layers.

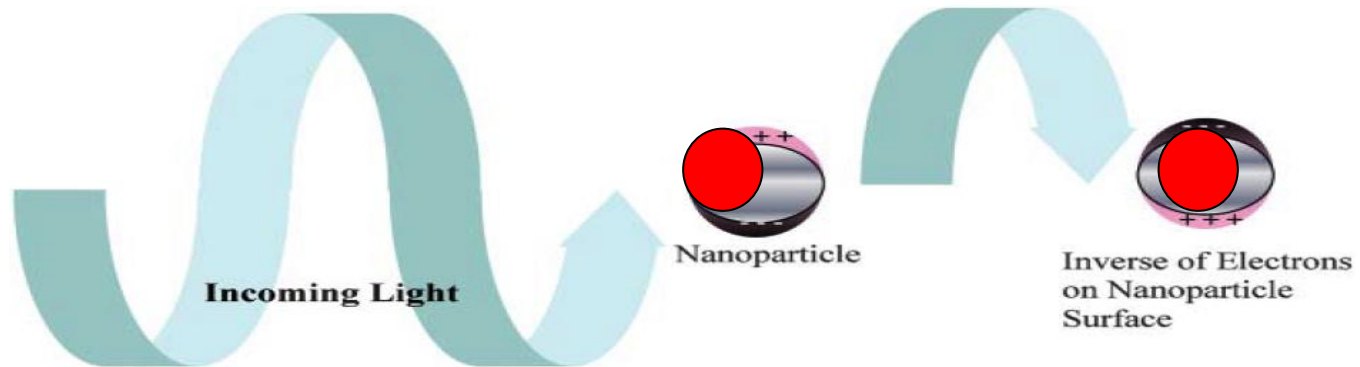
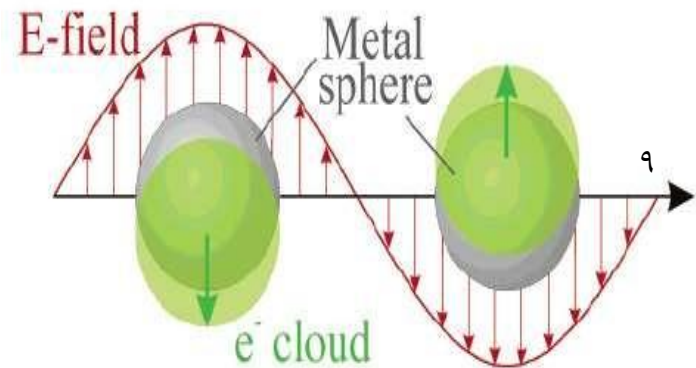
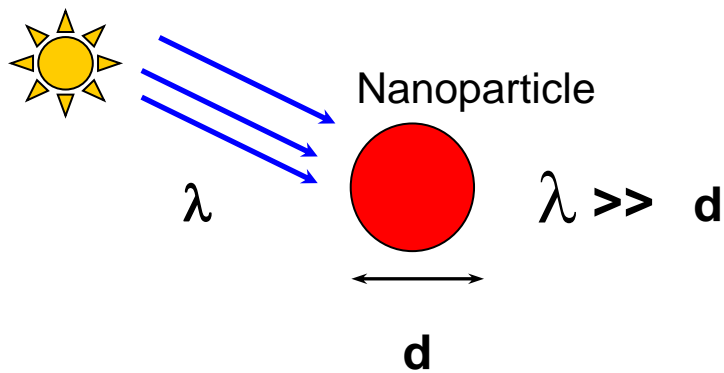
Superlattice (SL) Alternating layers of materials A & B with similar layer thicknesses.

## 2- Optical properties of nanomaterials

### 2.1- Origin of Surface Plasmon Resonance and Coloring in Metal nanoparticles


Surface Plasmons Resonance is;

- The oscillations of free electrons that are the consequence of the formation of a dipole in the material due to electromagnetic waves.
  - The electrons migrate in the material to restore its initial state, however, light in resonance causes the free-electrons in the metal to oscillate. As the wave front of the light passes, the electron density in the particle is polarized to one surface and oscillates in resonance with the light's frequency causing a standing oscillation.
  - This is referred to as the surface plasmon resonance, since it is located at the surface.
-



Schematic of plasmon oscillation for a sphere, showing the displacement of the conduction electron charge cloud relative to the nuclei. When the wavelength of light is much larger than the nanoparticle size it can set up standing resonance conditions

- The resonance condition is determined from absorption and scattering spectroscopy and is found to depend on the shape, size, and dielectric constants of both the metal and the surrounding material.
- As the shape or size of the nanoparticle changes, the surface geometry changes, causing a shift in the electric field density on the surface. This causes a change in the oscillation frequency of the electrons, generating different cross-sections for the optical properties including absorption and scattering.
- The free electrons in the metal (d electrons in silver and gold) are free to travel through the material. The mean free path in gold and silver is ~50 nm, therefore in particles smaller than this, no scattering is expected from the bulk.



The reduction of materials' dimension has pronounced effects on the optical properties. The size dependence can be generally classified into two groups;

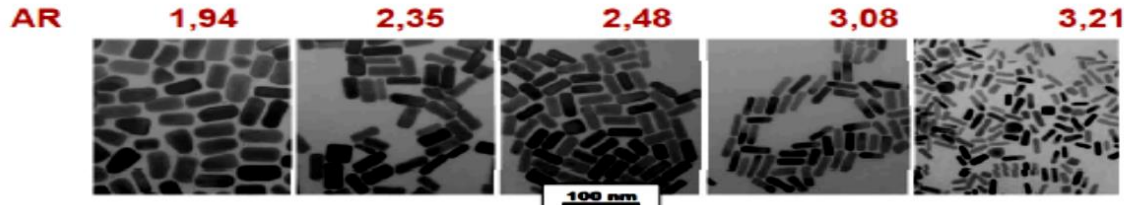
- One is due to the increased energy level spacing as the system becomes more confined,
- and the other is related to surface plasmon resonance.

# Different Geometries (Gold nanorods)

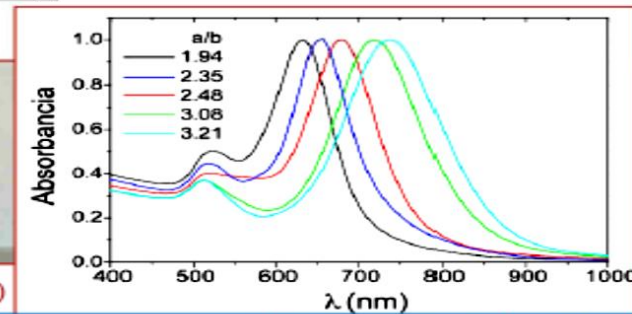
## Plasmons in metallic nanoparticles



### The colors of gold nanorods



J. Pérez-Juste *et al.*, *Appl. Surf. Sci.* (2004)



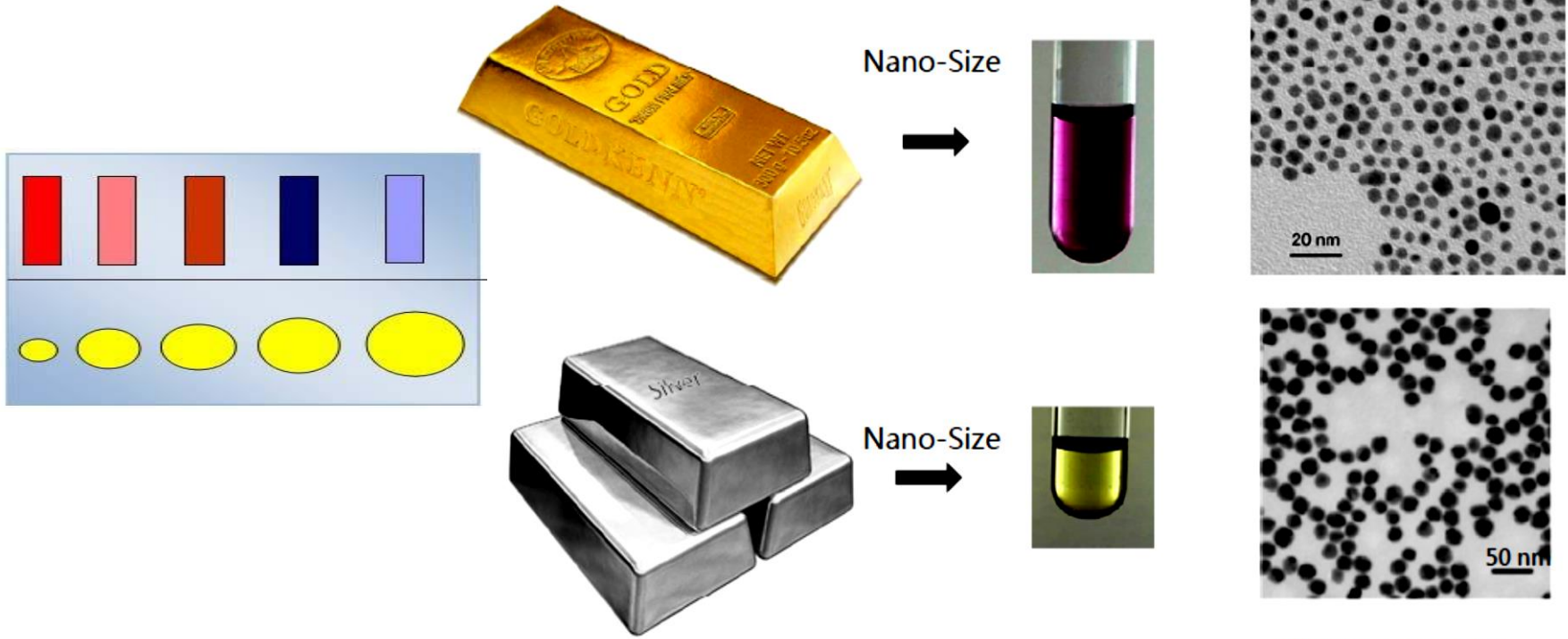
Localized plasmons and plasmons in nanoparticles

ORC Lecture – Southampton, January 17, 2011

The frequency of the SP depends on the dielectric function of the gold, and the shape of the nanoparticle. For a spherical particle, the frequency is about 0.58 of the bulk plasma frequency. Thus, although the bulk plasma frequency is in the UV, the SP frequency is in the visible (in fact, close to 520 nm),

# Surface plasmonic effect

Gold nanoparticcells



Silver nanoparticles

Colloidal solutions of gold nanoparticle have deep red colour which progressively becomes more yellow as a particle size increases, as a result of surface plasmon resonance occurring in low dimensional materials.

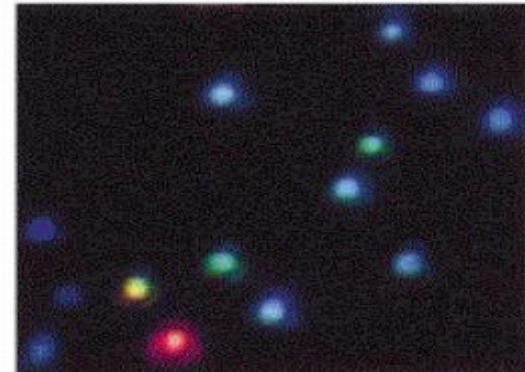
# Plasmon Confinement in Metal Nanoparticles

Mesoscopic oscillation and restoring force

Au and thin gold layers on silica.



... <http://www.ece.rice.edu/~halas/>



Mock et al, *J. Chem. Phys.* **116**, 6755 (2002)



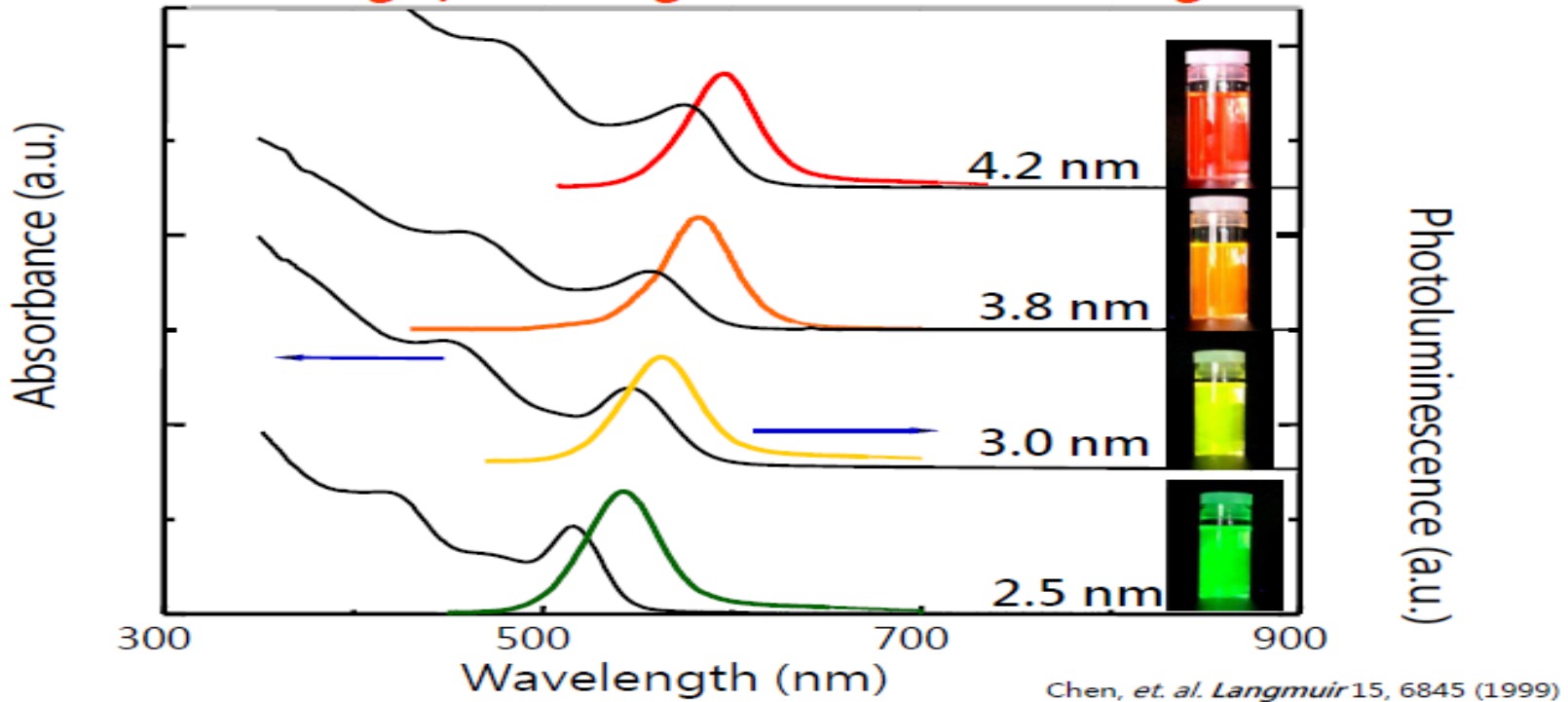
peak in the scattering efficiency corresponds to the excitation of a plasmon resonance in the sphere

<http://www.ifh.ee.ethz.ch/~martin/res50.en.html>



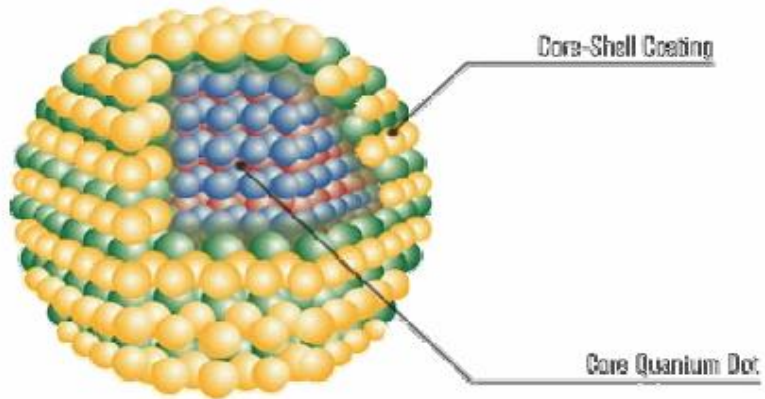
## Size-dependent optical properties of CdSe QDs

Band gaps change with their average sizes

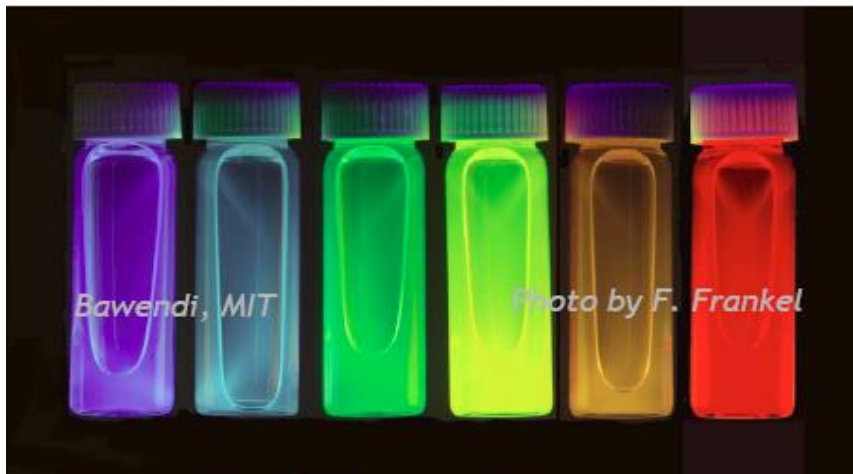
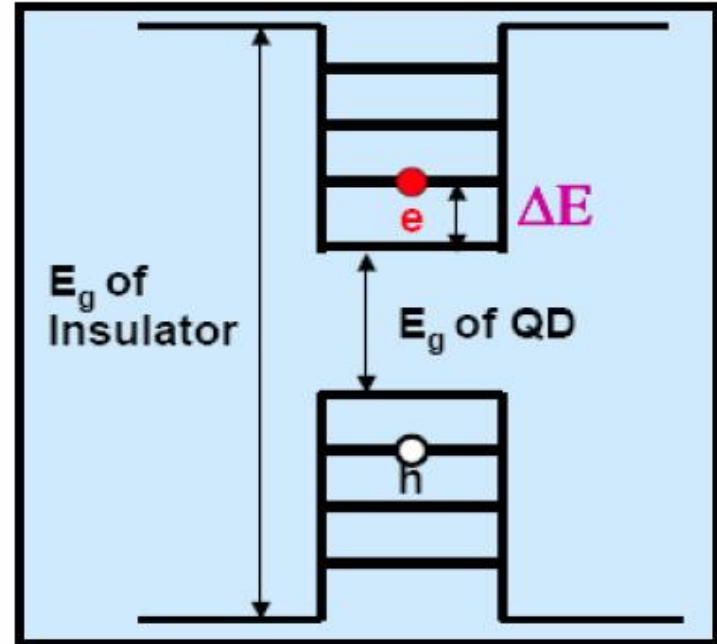


- Quantum dots are bandgap tunable by size, smaller QDs have a large bandgap. So, the absorbance and luminescence spectrums are blue shifted with decreasing particle size.
- We can engineer their optical and electrical properties.

# Colloidal Semiconductor Nanoparticles



Red: bigger dots!  
Blue: smaller dots!



# Spectral Range of Nanoshells



cosmetics & pigments

photonics & telecom

environmental sensing

biotechnology

solar energy applications

night vision, surveillance