Subject: **Physics of NanoMaterials** Code: Ph522

Course: M.Sc. Physics Semester: 4th Unit-I

Dr Suresh Kumar

Associate Professor

Department of Physics

Maharishi Markandeshwar University

Sadopur, Ambala

“I don't know how to do this on a small scale in a practical way, but I do know that computing machines are very large; they fill rooms. Why can't we make them very small, make them of little wires, little elements, and by little, I mean little?.”

Richard Feynman

PHYSICS OF NANO MATERIALS

Syllabus

UNIT I

Classification of nanomaterials: Quantum dots, wires and dots, Bulk Nanostructured Materials, Nanostructured Crystals, Biological Nanomaterials.

Methods of Synthesis: RF Plasma, Chemical Methods, Thermolysis, Pulsed Laser methods etc.

UNIT II

Size and dimensionality effects: Size effects, Conduction electrons and dimensionality, Fermi gas and density of states, Potential wells, Partial confinement, Properties dependent on density of states, excitons, single electron tunneling.

UNIT III

Properties of individual Nanoparticles: Metal nanoclusters, Magic Numbers, Bulk to nanotransition, Semiconducting Nanoparticles, optical properties, rare gas and molecular clusters, various types of clusters. Nanomachines and Nanodevices (MEMS and NEMS).

UNIT IV

Particle size and surface structure determination: Crystallography, Microscopy, Transmission Electron Microscopy, Field Ion Microscopy, Scanning microscopy, Spectroscopy: Infrared and Raman Spectroscopy, Photoemission and X-Ray spectroscopy, Magnetic Resonance, LEED and RHEED.

<u>UNIT I</u>

Classification of nanomaterials:

Quantum Dots, Quantum Wires and Quantum Well,

Bulk Nanostructured Materials,

Nanostructured Crystals,

Biological Nanomaterials.

Methods of Synthesis:

RF Plasma,
Chemical Methods,
Thermolysis,
Pulsed Laser methods
etc.

- **NanoScience and NanoTechnology**

NanoScience:
study of phenomenon & manipulation of materials at atomic and molecular scales.

NanoTechnology:
engineering which deals with the synthesis, design, characterization, production and application of structures, devices and systems in nanoscale

***NT** literally means any technology on a nanoscale that has applications in the real world.*

The word '**nano**' is derived from Greek word which means 'dwarf' or 'small'.

The prefix 'nano' means billionth (10^{-9}) part of a unit in general.

NanoMaterials

NanoStructures

NanoDevices

NanoTechnology

NanoScience

What do you mean by Nano-Particles?

Nano Particles are the particles of size between 1 nm to 100 nm

- 1 nm is only three to five ***atoms*** wide.
- ~40,000 times smaller than the width of an average human hair

Nanometer - One billionth (10^{-9}) of a meter

- **The size of Hydrogen atom 0.04 nm**
- **The size of Proteins ~ 1-20 nm**
- **Feature size of computer chips 180 nm**
- **Diameter of human hair ~ 10 µm**

At the nanoscale, the physical, chemical, and biological properties of materials differ in fundamental and valuable ways from the properties of individual atoms and molecules or bulk matter

Significance of the nanoscale:

When we go to nanoscale, nanomaterial exhibits extraordinary properties which differ significantly from their bulk counterparts.

Unique properties nanomaterials coz two reasons:

(i) relatively **large surface to volume ratio**
(ii) **quantum size effect**

First, Nanomaterials have a relatively **larger surface area** when compared to the same mass of material produced in a larger form.

Nano particles can make materials more **chemically reactive** and affect their strength or electrical properties.

Second, quantum effects can begin to dominate the behaviour of matter at the Nanoscale

Material	**property in BULK form**	**property in NANO form**
Copper	Opaque	Transparent
Platinum	Inert	Catalyst
Aluminum	Stable	Combustible
Silicon	Insulator or semiconductor	Conductor
Gold	Solid	Liquid

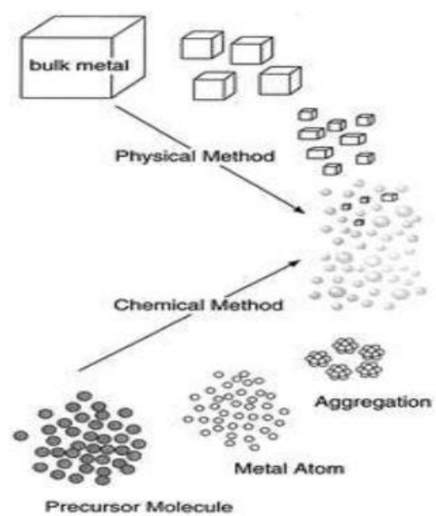
Nanotechnology” *synthesis and application of ideas from science & engineering towards the understanding & production of novel material & devices*

Techniques for NanoMaterial Synthesis:

Top-down approach	Bottom-up approach
Ball Milling	Chemical Solution
Laser Evaporation	Sol-Gel synthesis
Sputtering	Electrochemical
Chemical Vapor	SEM
Plasma Synthesis	Nanoscale Lithography

SYNTHESIS OF NANOMATERIALS

- Bottom up method
- Top bottom method



Methods of Synthesis:

RF Plasma,
Chemical Methods,
Thermolysis,
Pulsed Laser methods etc.

Tools to make NanoStructures

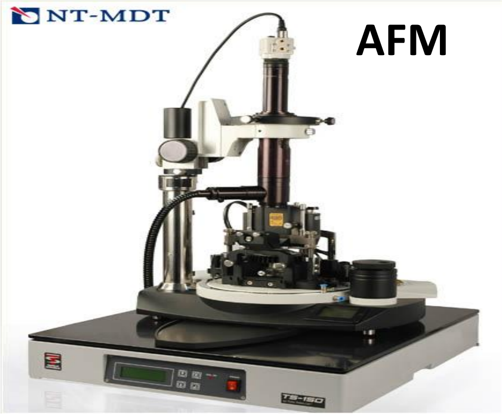
1. Scanning probe Instruments

Scanning Probe Lithography (SPL)

Scanning Tunneling Microscope (STM)

Atomic Force Microscopy (AFM)

Dip-Pen Nanolithography (DPN)



2. Nanoscale Lithography

Optical or Photo-lithography

X-ray Lithography (XL)

NanoImprint Lithography (NIL)

Scanning Probe Lithography (SPL)

Scanning Tunneling Microscope (STM)

Dip-Pen Nanolithography (DPN)

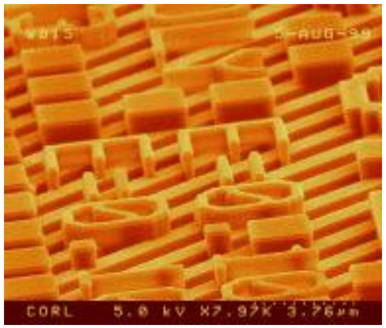
Atomic Force Microscopic Nanolithography (AFM)

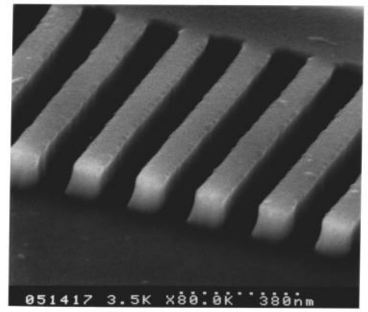
Thermochemical Nanolithography (TCNL)

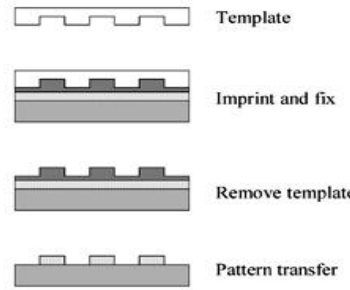
Magnetolithography

Laser Printing of Single Nanoparticles

3.Micro-Imprint lithography (MIL) and Nano-Imprint lithography (NIL)

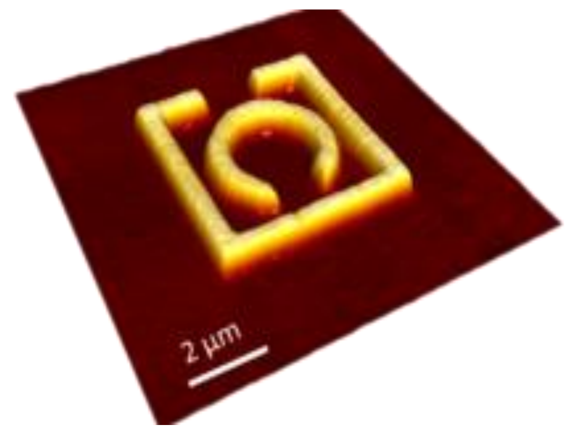






examples of imprinting over a planarized surface and block diagram

4. Dip-Pen Lithography (DPN):



. Gold on Si-metastructure fabricated with top-down DPN methods

5. E-beam Lithography (EBL):

Applications of NanoTechnology:

NanoMaterials can be classified primarily into different types

Natural nanomaterials:

Artificial nanomaterials:

Carbon Based: Spherical & ellipsoidal (**fullerenes)**, cylindrical (**carbon nanotubes)**.

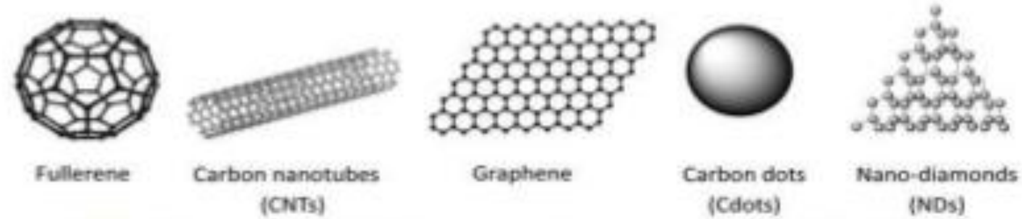
Metal Based:

Dendrimers: nanomaterials are nanosized polymers – drug delivery.

Composites: any combination of metal based, carbon based or polymer based nanomaterials with any form of metal, ceramic, or polymer bulk materials!

Types of nanomaterials

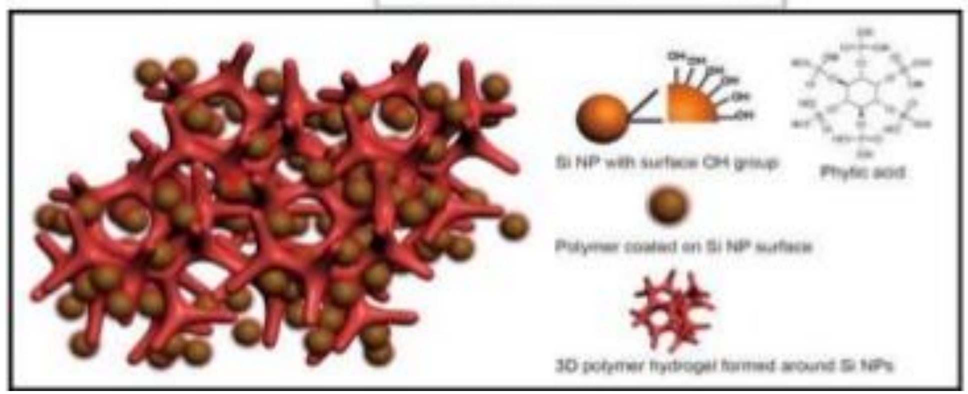
- Carbon based



- Metal based

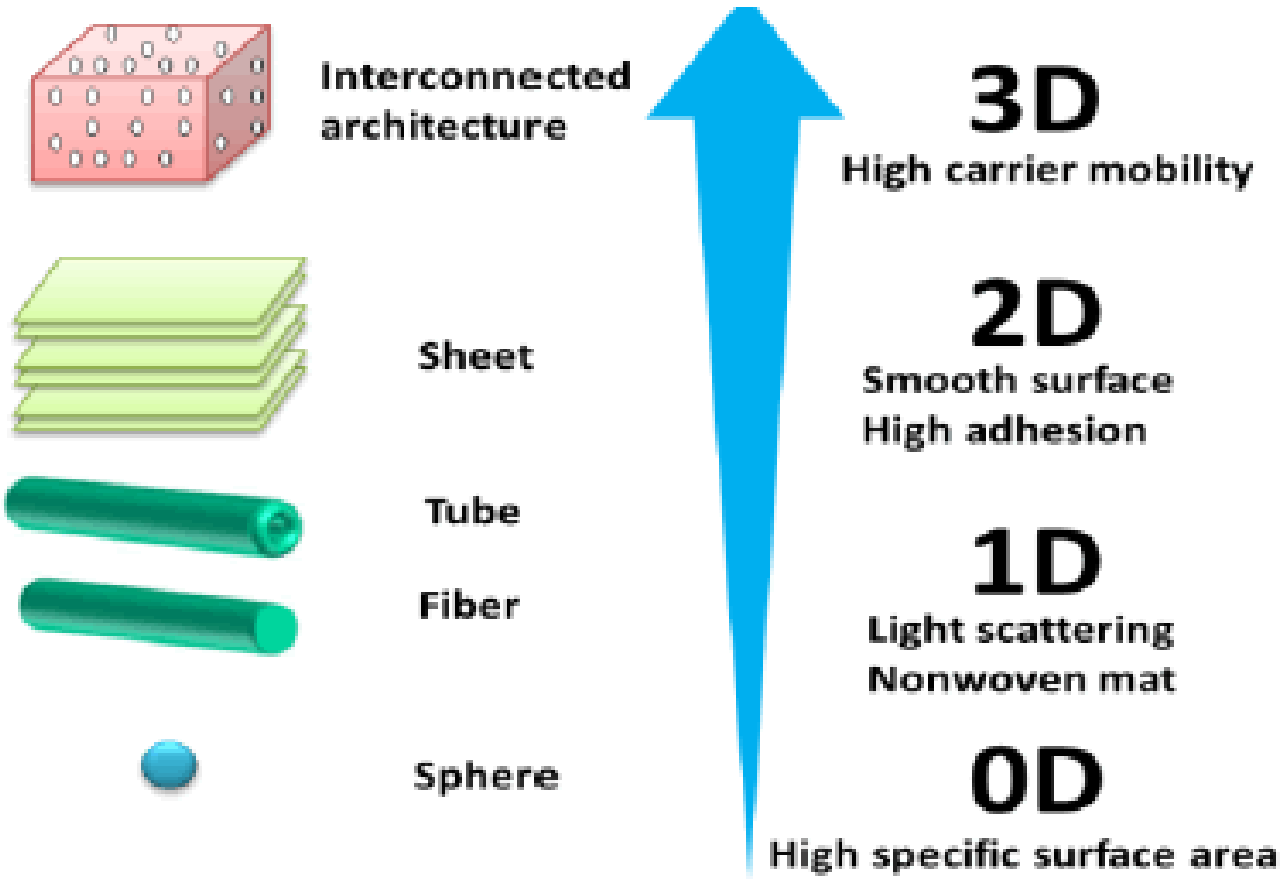
- Dendrimers

- Composites



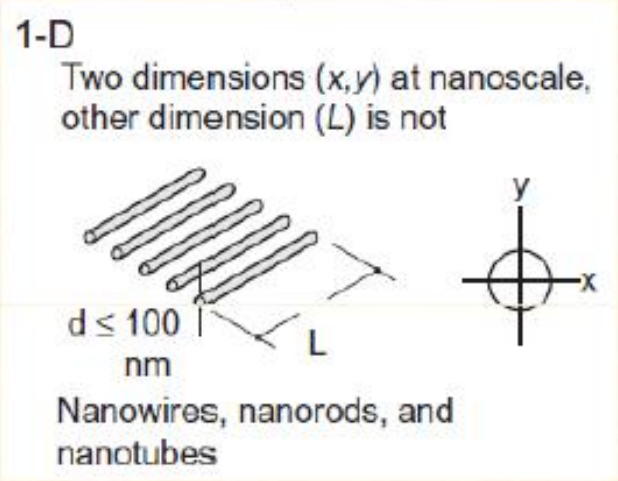
Some 'Nano' Definitions

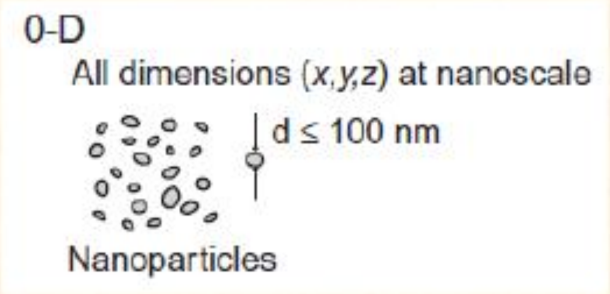
- Cluster
    - A collection of units (atoms or reactive molecules) of up to about 50 units
- Colloids
    - A stable liquid phase containing particles in the 1-1000 nm range. A colloid particle is one such 1-1000 nm particle.
- Nanoparticle
    - A solid particle in the 1-100 nm range that could be noncrystalline, an aggregate of crystallites or a single crystallite
- Nanocrystal
    - A solid particle that is a single crystal in the nanometer range

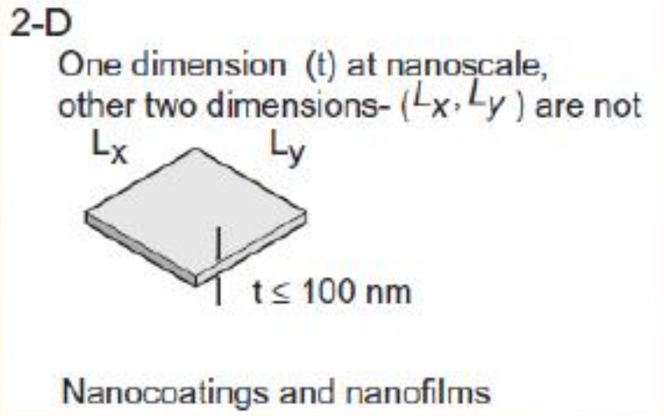

Interconnected architecture
Sheet
Tube
Fiber
Sphere
3D
High carrier mobility
2D
Smooth surface
High adhesion
1D
Light scattering
Nonwoven mat
0D
High specific surface area

Classification

- Classification is based on the number of dimensions, which are not confined to the nanoscale range (<100 nm).
- (1) zero-dimensional (0-D),
- (2) one-dimensional (1-D),
- (3) two-dimensional (2-D), and
- (4) three-dimensional (3-D).



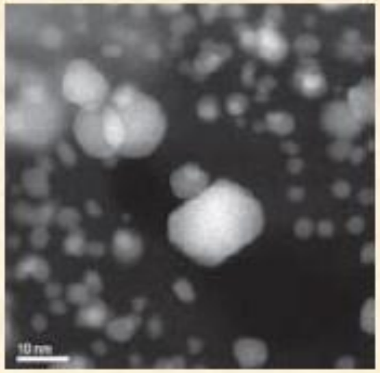




Zero-dimensional nanomaterials

- Materials wherein all the dimensions are measured within the nanoscale (no dimensions, or 0-D, are larger than 100 nm).
- The most common representation of zero-dimensional nanomaterials are **nanoparticles.**

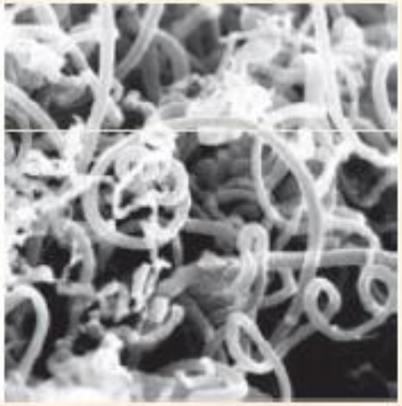
- **Nanoparticles** can:



- Be amorphous or crystalline
- Be single crystalline or polycrystalline
- Be composed of single or multi-chemical elements
- Exhibit various shapes and forms
- Exist individually or incorporated in a matrix
- Be metallic, ceramic, or polymeric

One-dimensional nanomaterials

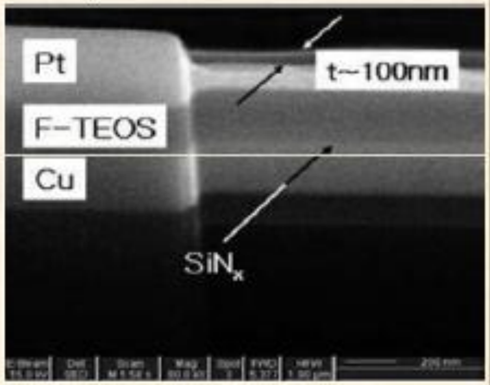
- One dimension that is outside the nanoscale.
- This leads to needle like-shaped nanomaterials.
- 1-D materials include **nanotubes, nanorods, and nanowires**.



- **1-D nanomaterials** can be
- Amorphous or crystalline
- Single crystalline or polycrystalline
- Chemically pure or impure
- Standalone materials or embedded in within another medium
- Metallic, ceramic, or polymeric

Two-dimensional nanomaterials

- Two of the dimensions are not confined to the nanoscale.
- 2-D nanomaterials exhibit plate-like shapes.
- Two-dimensional nanomaterials include **nanofilms, nanolayers, and nanocoatings.**



- **2-D nanomaterials** can be:
- Amorphous or crystalline
- Made up of various chemical compositions
- Used as a single layer or as multilayer structures
- Deposited on a substrate
- Integrated in a surrounding matrix material
- Metallic, ceramic, or polymeric

Three-dimensional nanomaterials

- **Bulk** nanomaterials are materials that are not confined to the nanoscale in any dimension. These materials are thus characterized by having three arbitrarily dimensions above 100 nm.
- Materials possess a nanocrystalline structure or involve the presence of features at the nanoscale.
- In terms of nanocrystalline structure, bulk nanomaterials can be composed of a multiple **arrangement of nanosize crystals**, most typically in different orientations.
- With respect to the presence of features at the nanoscale, **3-D nanomaterials** can contain dispersions of nanoparticles, bundles of nanowires, and nanotubes as well as multinanolayers.

Quantum well

- It is a two dimensional system
- The electron can move in two directions and restricted in one direction.

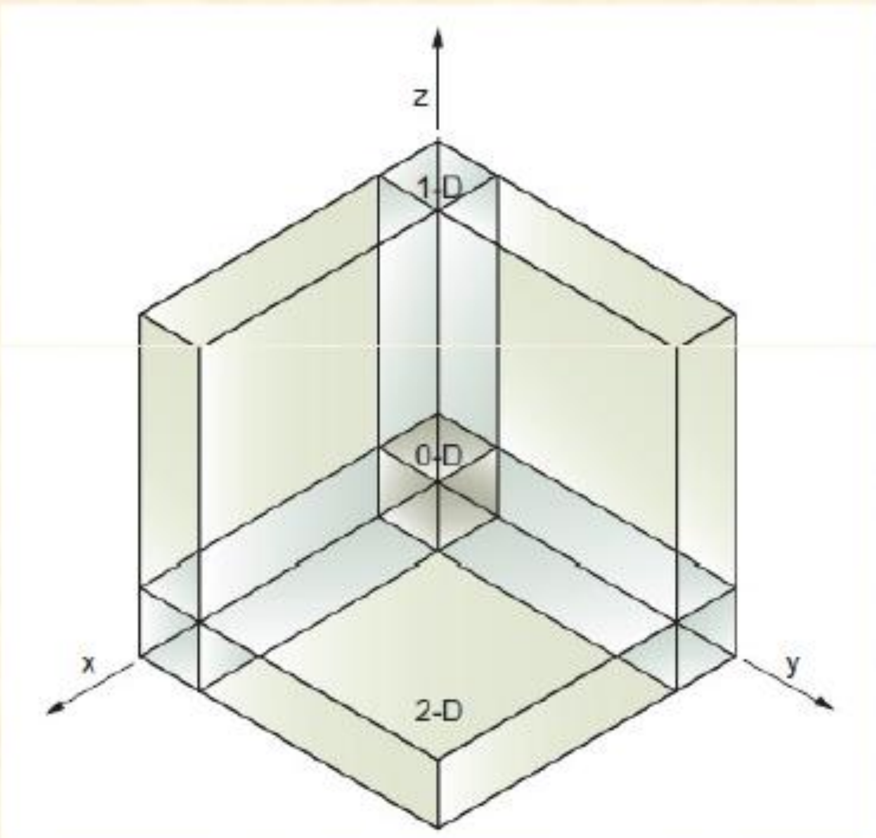
Quantum Wire

- It is a one-dimensional system
- The electron can move in one direction and restricted in two directions.

Quantum dot

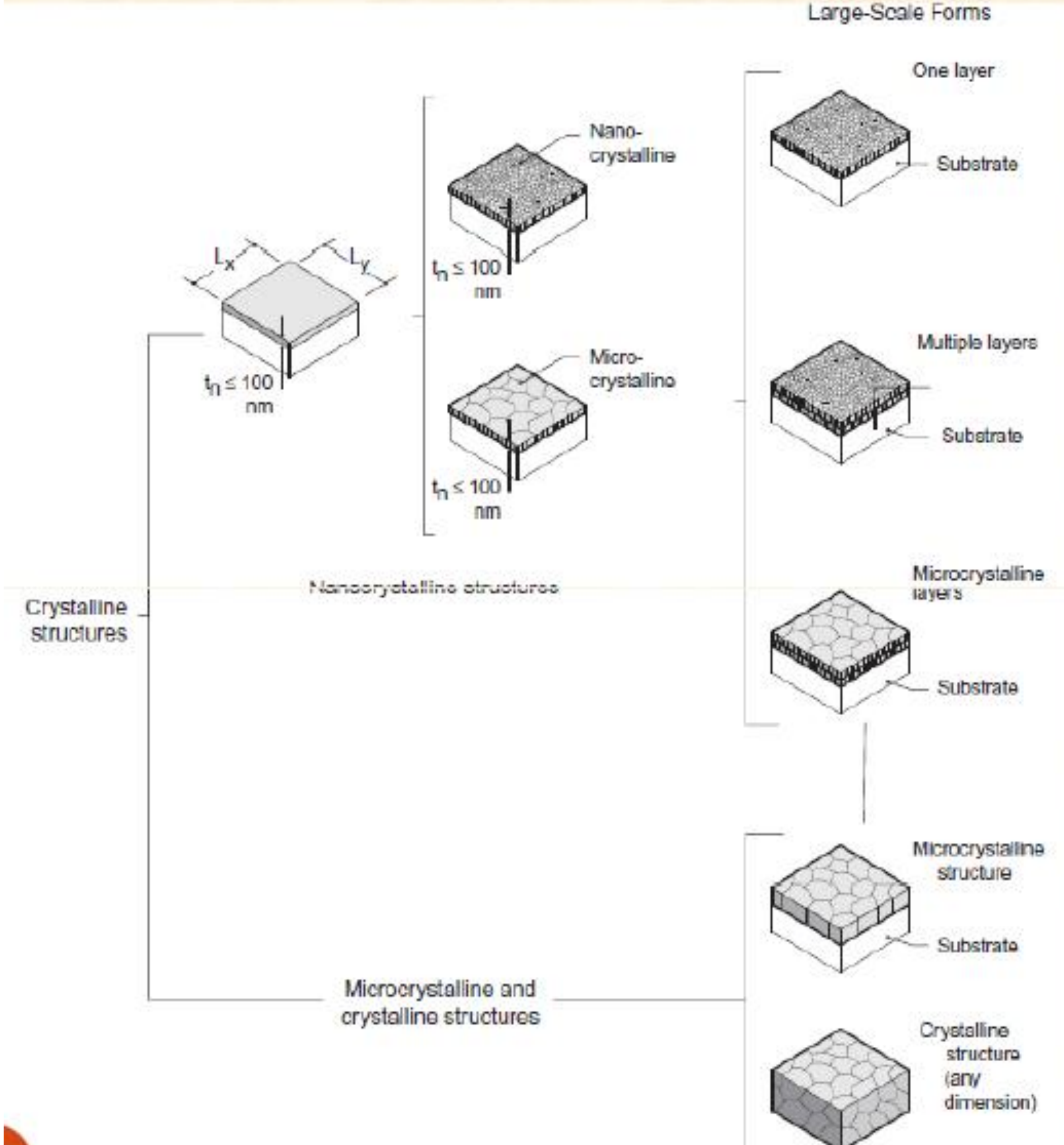
- It is a zero dimensional system
- The electron movement was restricted in entire three dimensions

Three-dimensional space showing the relationships among 0-D, 1-D, 2-D, and 3-D nanomaterials.



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

Summary of 2-D and 3-D crystalline structures



Quantum effects

- The overall behavior of bulk crystalline materials changes when the dimensions are reduced to the nanoscale.
- For **0-D nanomaterials**, where all the dimensions are at the nanoscale, an electron is confined in 3-D space. No electron delocalization (freedom to move) occurs.
- For **1-D nanomaterials**, electron confinement occurs in 2-D, whereas delocalization takes place along the long axis of the nanowire/rod/tube.
- In the case of **2-D nanomaterials**, the conduction electrons will be confined across the thickness but delocalized in the plane of the sheet.

Electrons confinement

- For **0-D nanomaterials** the electrons are fully confined.
- For **3-D nanomaterials** the electrons are fully delocalized.
- In **1-D and 2-D nanomaterials**, electron confinement and delocalization coexist.
- The effect of confinement on the resulting energy states can be calculated by quantum mechanics, as the **"particle in the box"** problem. An electron is considered to exist inside of an infinitely deep **potential well** (region of negative energies), from which it cannot escape and is confined by the dimensions of the nanostructure.

Quantum Confinement in Nanomaterials

In a bulk material: not confine **(3D) system**

$$E = \frac{\eta^2 k_x^2}{2m^*} + \frac{\eta^2 k_y^2}{2m^*} + \frac{\eta^2 k_z^2}{2m^*} \quad D(E) = \frac{1}{2\pi^2}\left(\frac{2m^*}{\eta}\right)^{\frac{3}{2}}\sqrt{E}$$

$$k = \frac{n\pi}{L}$$

In a nano material: **quantum-well (2D) system**

$$E_{n_z} = \frac{h^2}{8m^*}\left(\frac{n_z^2}{L_z^2}\right) + \frac{\eta^2 k_y^2}{2m^*} + \frac{\eta^2 k_x^2}{2m^*} \quad D(E) = \frac{m^*}{\pi\eta^2}$$

quantum-wire (1D) system

$$E_{n_z} = \frac{h^2}{8m^*}\left(\frac{n_z^2}{L_z^2} + \frac{n_y^2}{L_y^2}\right) + \frac{\eta^2 k_x^2}{2m^*} \quad D(E) = \frac{2m^*}{\eta^2}\frac{1}{\pi}\sqrt{E}$$

quantum-dot (1D) system

$$E_{n_z} = \frac{h^2}{8m^*}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right) \quad D(E) = 2\sum_{i=1}^{n} d_i \delta(E - E_i)$$

Energies

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

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

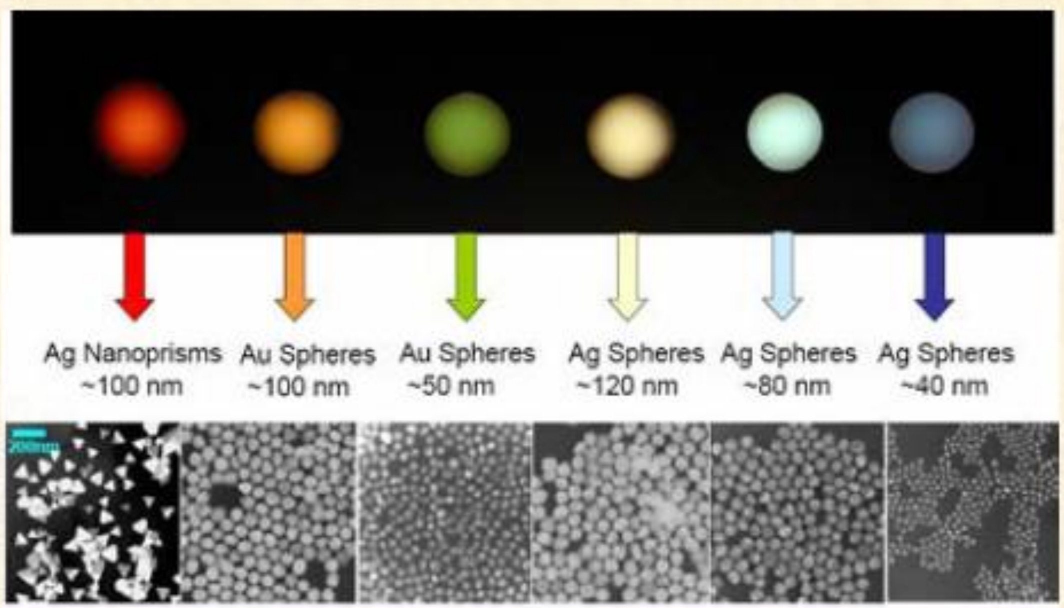
(2-D) $$E_n = \left[\frac{\pi^2\hbar^2}{2mL^2}\right]\left(n_x^2\right)$$

where $h^{-} \equiv h/2\pi$, h is Planck's constant, *m* is the mass of the electron, *L* is the width (confinement) of the infinitely deep potential well, and *nx, ny*, and *nz* are the principal quantum numbers in the three dimensions x, y, and z.

The **smaller** the dimensions of the nanostructure (smaller L), the **wider** is the separation between the energy levels, leading to a spectrum of **discreet energies**.

What's different at the nanoscale?

Each of the different sized arrangement of gold atoms absorbs and reflects light differently based on its energy levels, which are determined by size and bonding arrangement. This is true for many materials when the particles have a size that is less than 100 nanometers in at least one dimension.



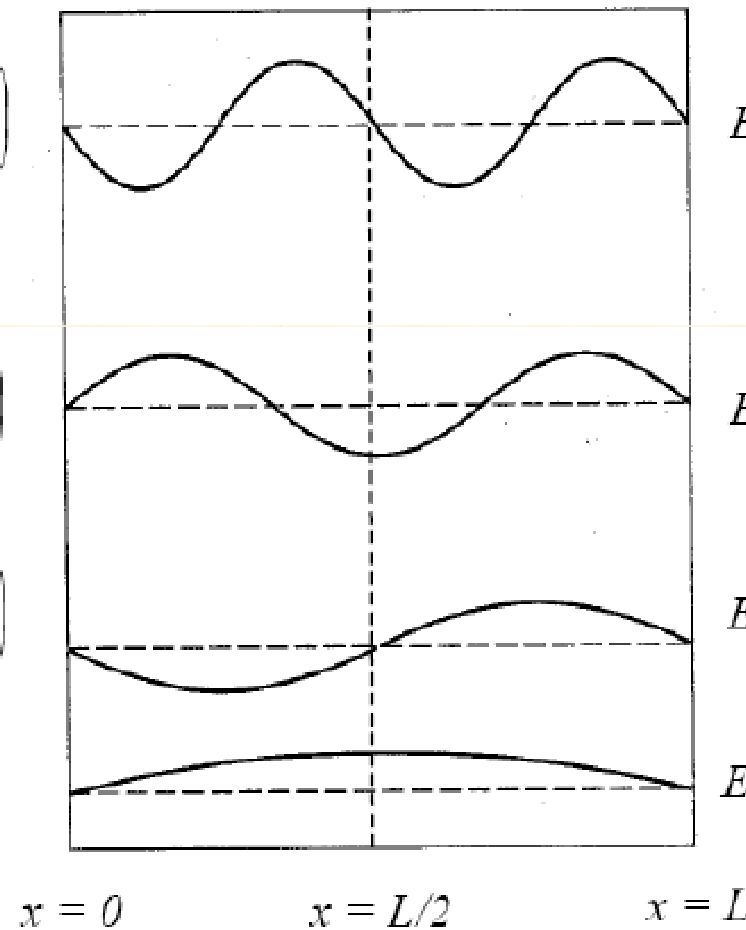
Energy levels in infinite quantum well

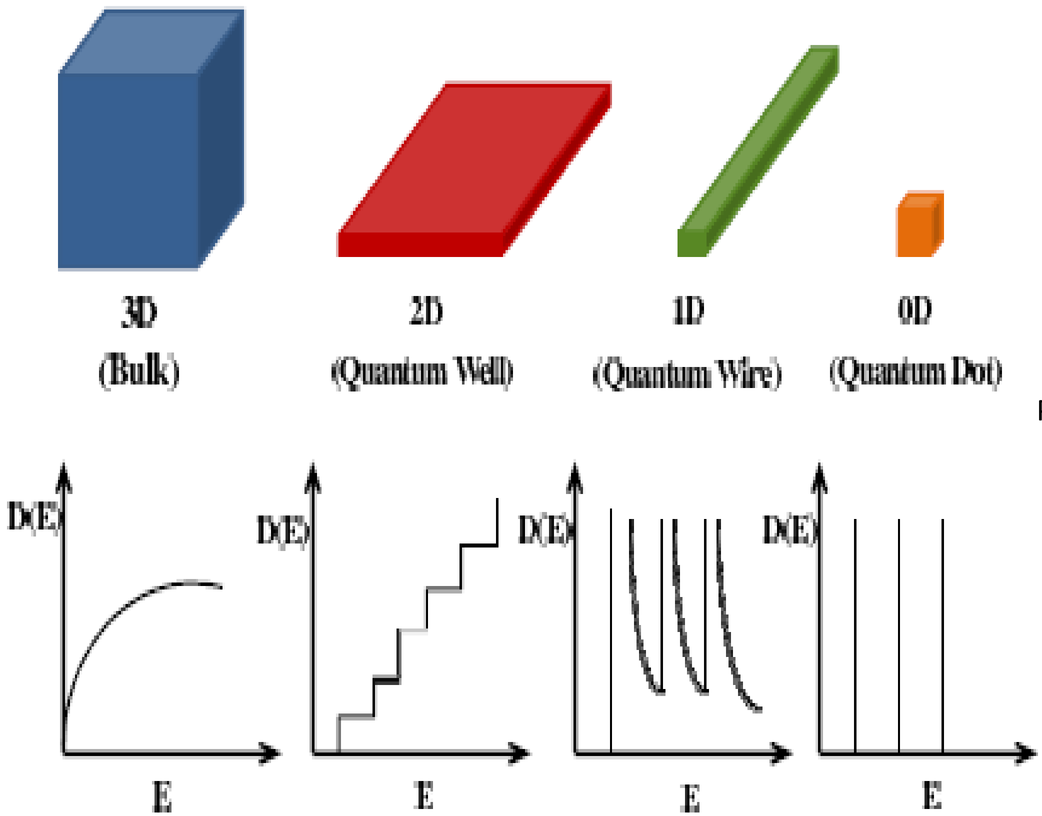
$$\psi_4(x) = A\sin\left(\frac{4\pi x}{L}\right) \qquad E_4 = \frac{\hbar^2}{2m}\frac{16\pi^2}{L^2}$$

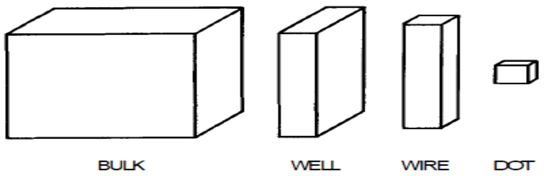
$$\psi_3(x) = A\sin\left(\frac{3\pi x}{L}\right) \qquad E_3 = \frac{\hbar^2}{2m}\frac{9\pi^2}{L^2}$$

$$\psi_2(x) = A\sin\left(\frac{2\pi x}{L}\right) \qquad E_2 = \frac{\hbar^2}{2m}\frac{4\pi^2}{L^2}$$

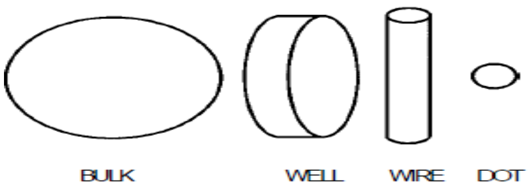
$$\psi_1(x) = A\sin\left(\frac{\pi x}{L}\right) \qquad E_1 = \frac{\hbar^2}{2m}\frac{\pi^2}{L^2}$$





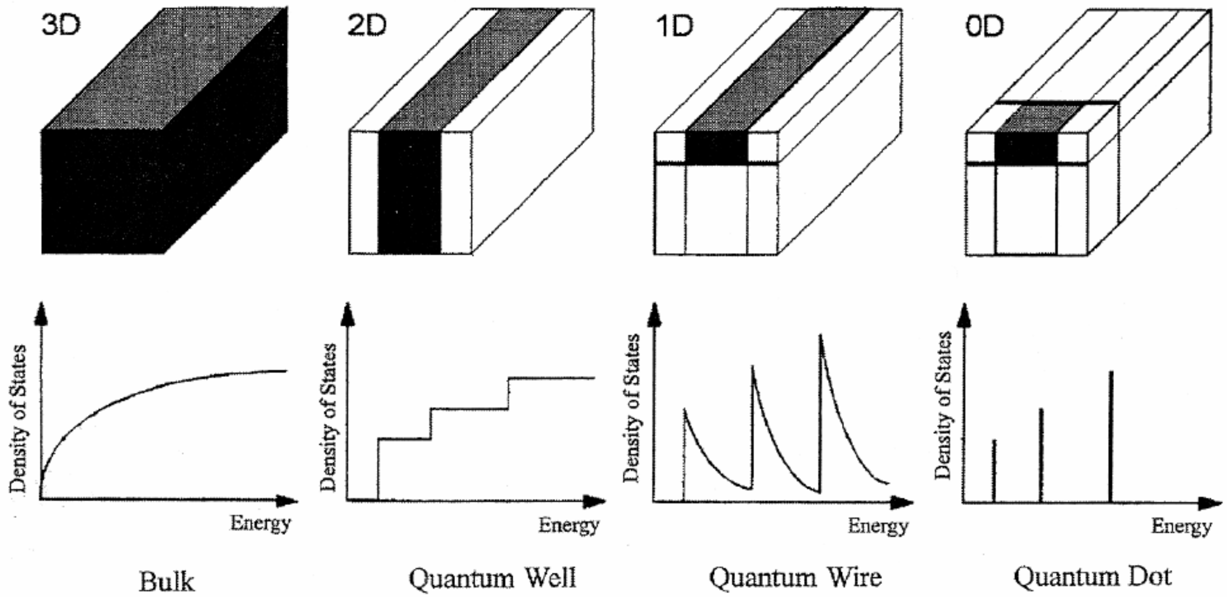


Progressive generation of rectangular nanostructures.



Progressive generation of c curvilinear nanostructures.

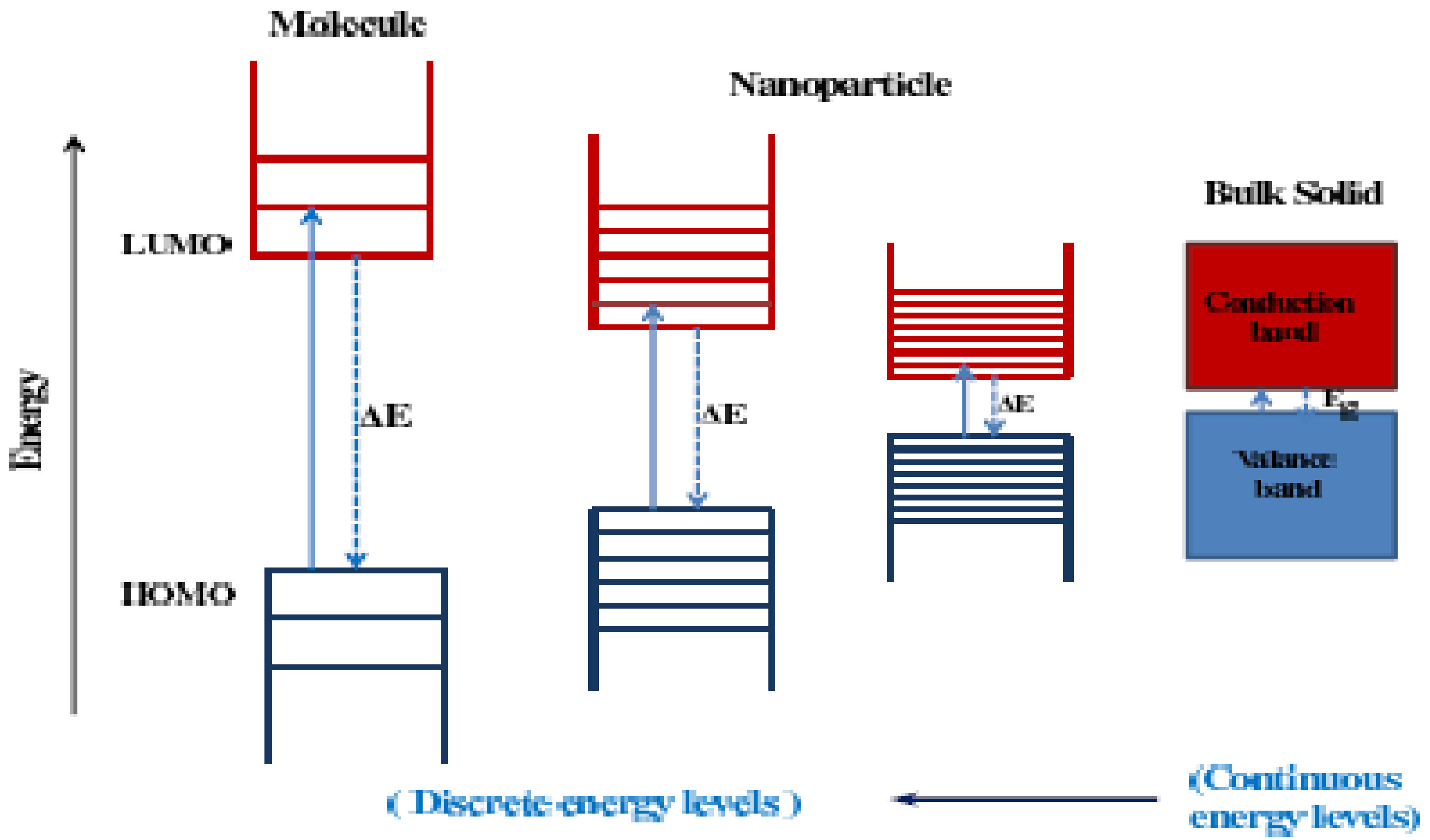
Dimension Variation ⇒ 3D → 2D → 1D → 0D



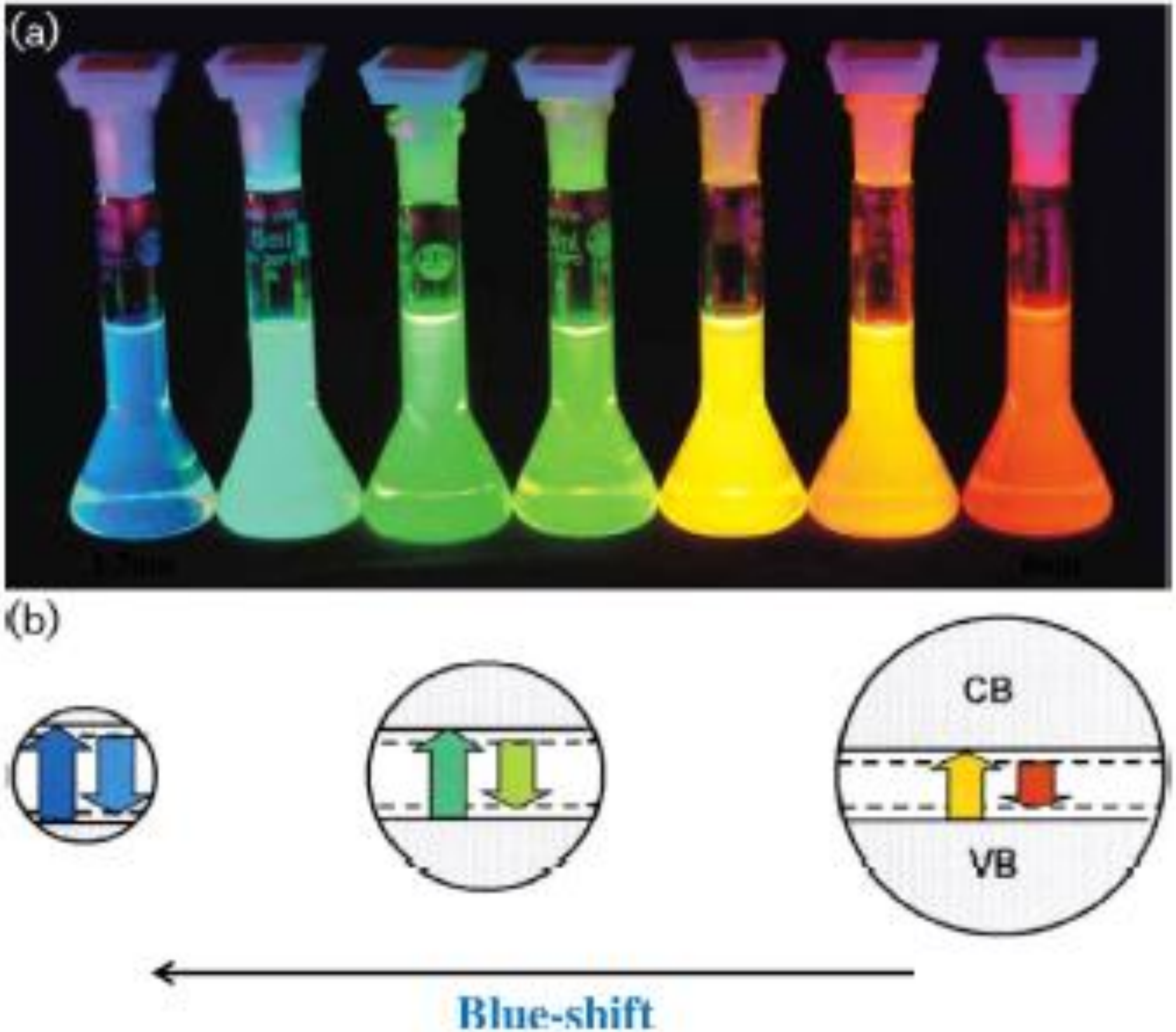
Source: Nanoscale Materials in Chemistry, Wiley, 2001

- If a bulk metal is made thinner and thinner, until the electrons can move only in two dimensions (instead of 3), then it is "2D quantum confinement."
- Next level is 'quantum wire
- Ultimately 'quantum dot'

Quantum confinement effect

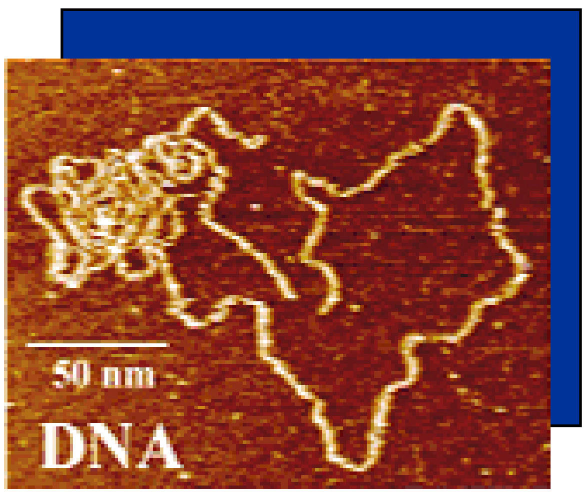


Widening of bang gap (discreteness) of a semiconductor with decreasing size

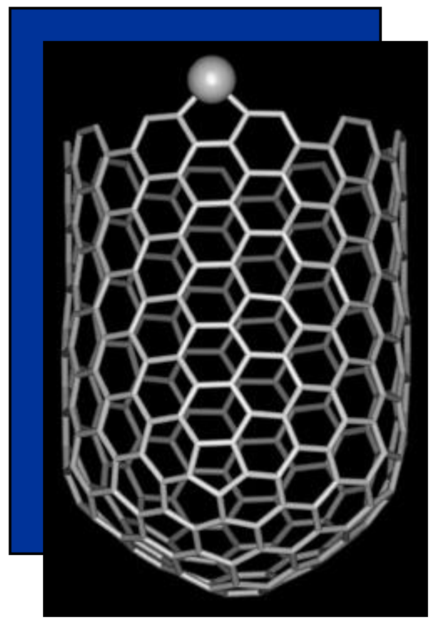

(a)
(b)
CB
VB
Blue-shift

Examples of Nanostructures

- Examples
  - Carbon Nanotubes
  - Proteins, DNA
  - Single electron transistors



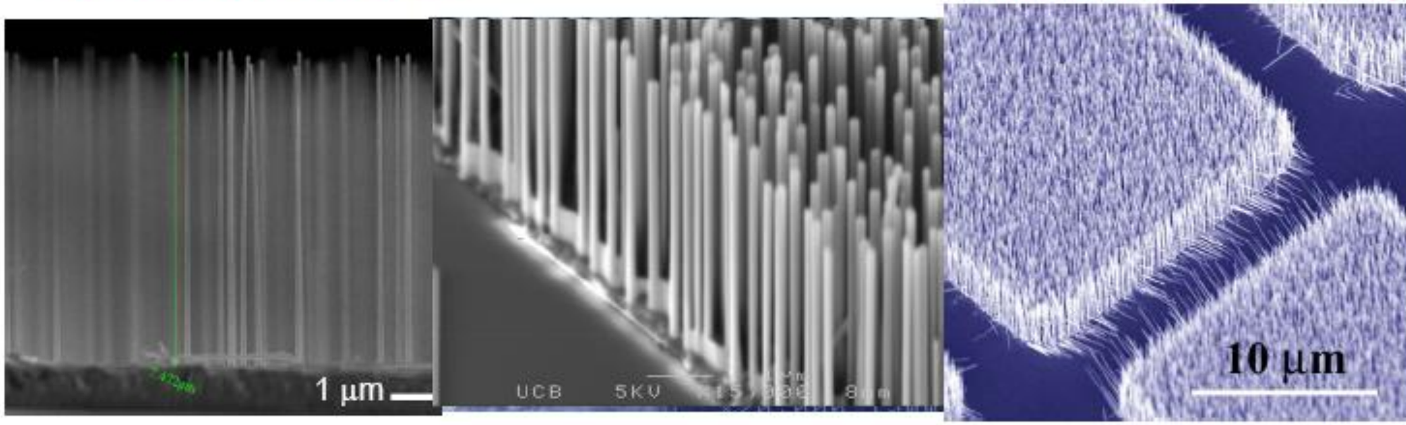
AFM Image of DNA



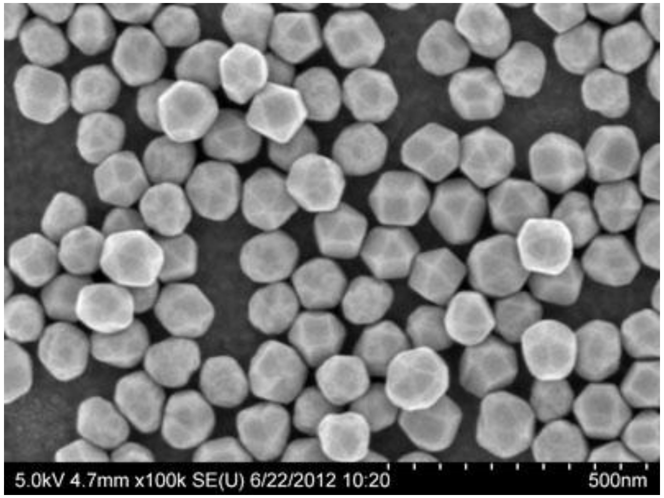
Carbon Nanotubes

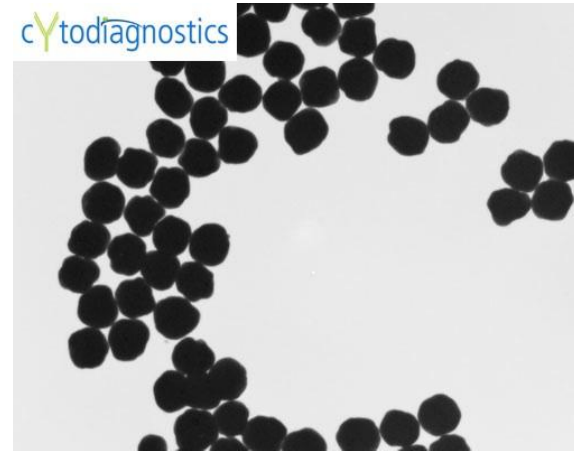
Si Nanowire Arrays

GaN Nanowire Arrays



ZnO Nanowire Arrays

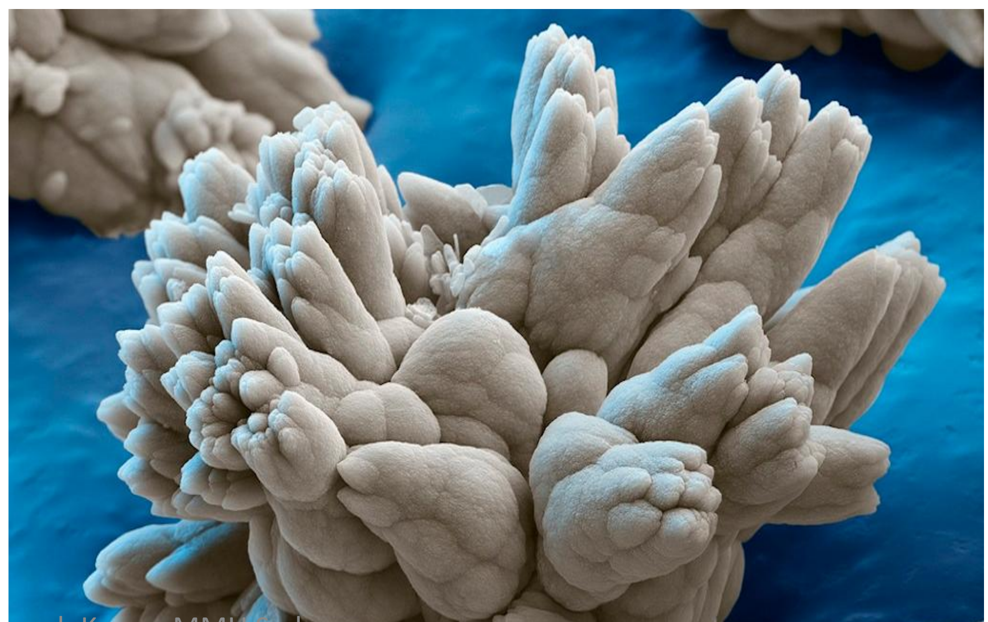




300nm Gold Nanoparticles (20ml)

In cancer treatments, use of materials (1 & 100 nm), National Cancer Institute.
(a flu virus is about 100 nm)

A microscopic view of a nanoparticle carrying a drug payload inside

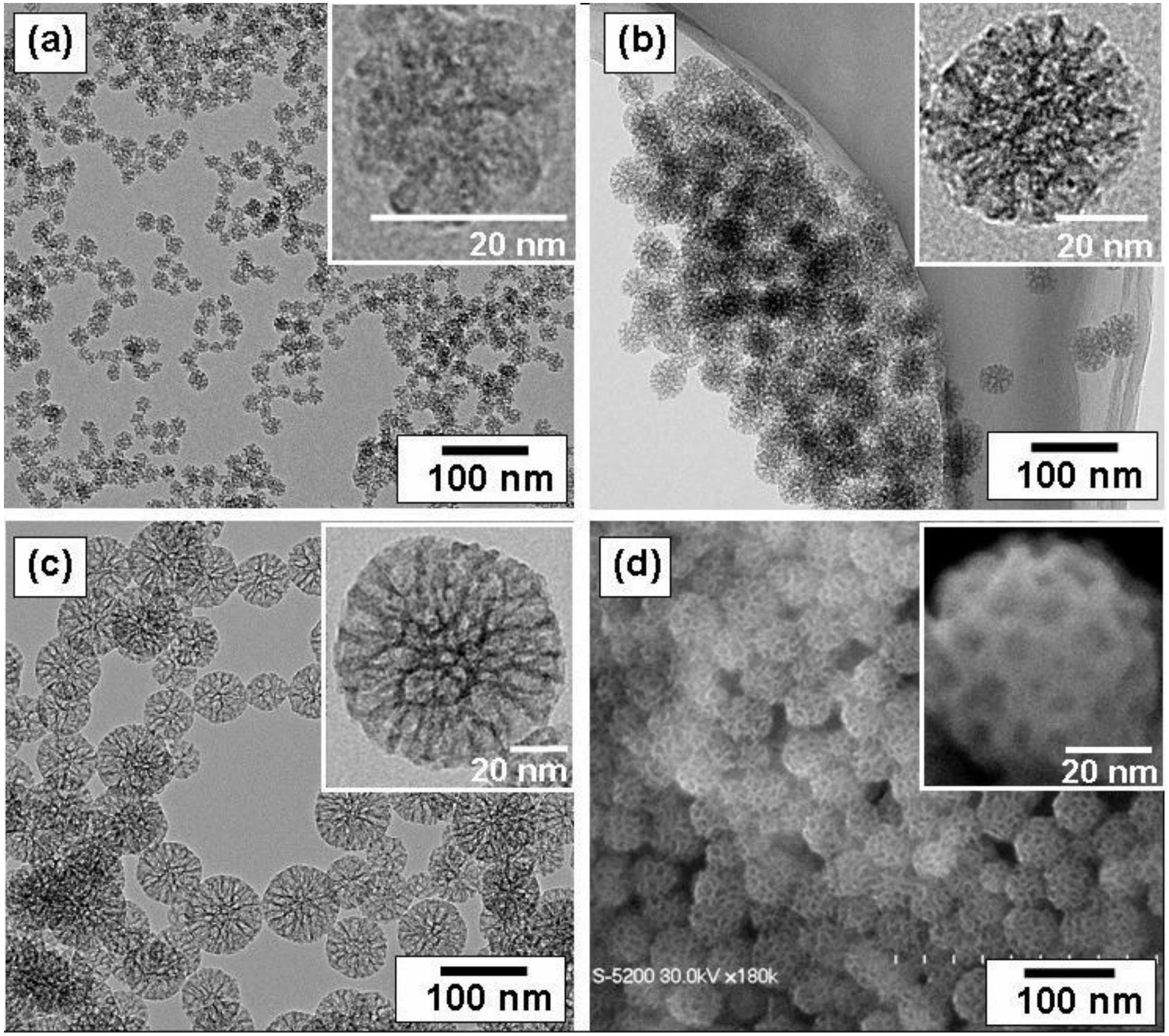


Nano-scale Effects on Properties

Properties	Examples
Catalytic	Better catalytic efficiency through higher surface-to-volume ratio
Electrical	Increased electrical conductivity in ceramics and magnetic nanocomposites, increased electric resistance in metals
Magnetic	Increased magnetic coercivity up to a critical grain size, superparamagnetic behaviour
Mechanical	Improved hardness and toughness of metals and alloys, ductility and superplasticity of ceramic
Optical	Spectral shift of optical absorbtion and fluorescence properties, increased quantum efficiency of semiconductor crystals
Sterical	Increased selectivity, hollow spheres for specific drug transportation and controlled release
Biological	Increased permeability through biological barriers (membranes, blood-brain barrier, etc.), improved biocompatibility

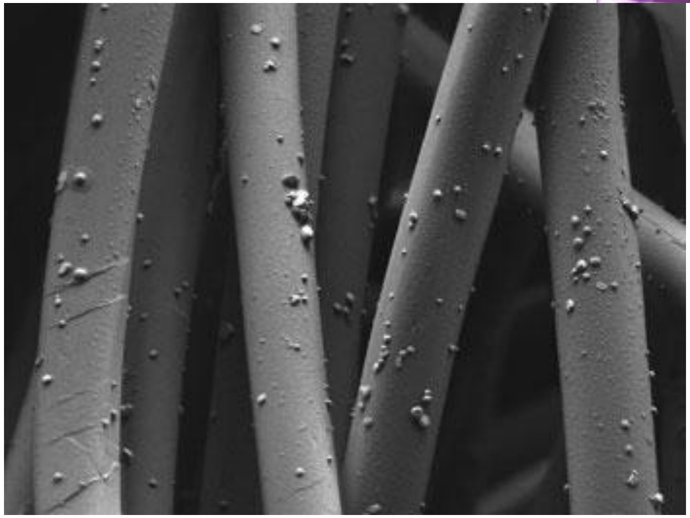
1kg of particles of $1mm^3$ has the same surface area as 1mg of particles of $1nm^3$

Silicon nanopowder



TEM (a, b, & c) images of prepared mesoporous silica nanoparticles with mean outer diameter: (a) 20nm, (b) 45nm, and (c) 80nm. SEM (d) image corresponding to (b). The insets are a high magnification of mesoporous silica particle.

Silver nanoparticles



Fibers coated in silver nanoparticles (those tiny dots) are used in germ-killing dressings for wounds.

This 92-year-old man used nose drops containing silver for many years. This use led to a condition called **argyria**, which permanently tinted his **skin blue**

Bulk Nanostructured Materials