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RV College of Engineering®, Bengaluru-59**

**Materials Science for Engineers – ME232TB  
Unit V**

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## Nanomaterials -----7 Hours

**Synthesis of nanomaterials:** ball milling, sol-gel, vapour deposition growth, pulse laser, magnetron sputtering, lithography.

**Nano porous materials:** zeolites, mesoporous materials, carbon nanotubes, graphene, nano FRPs, nano fabrics, bioresorbable and bio-erodable materials, nano ceramic, nano glasses, nano biomaterials, nano implant associated materials.

**Characterisation of nanostructures,** spectroscopic techniques, atomic force microscopy



# Nanomaterials

**Nanomaterial - A material with any external dimension in the nanoscale (the length ranging from approximately 1 nm to 100 nm) or having internal structure or surface structure in the nanoscale.**

Materials that have at least one dimension in the size range of approximately 1 nanometers (nm) to 100 nm and certain materials that otherwise exhibit related dimension-dependent properties and phenomena

Nanomaterials can exhibit unique optical, mechanical, magnetic, conductive, and sorptive properties different than the same chemical substances in a large size.

**Nanoscience** – is the study of nanomaterials, their properties and related phenomena.

**Nanotechnology** – is the application of nanoscience to produce devices and products.

**Nanoparticle** - Nanoparticle is any material having at least one of its dimensions in the range of 1-100 nm

A nanometer is one billionth of a meter ( $10^{-9}$  m)

## What is Nanomaterial ?

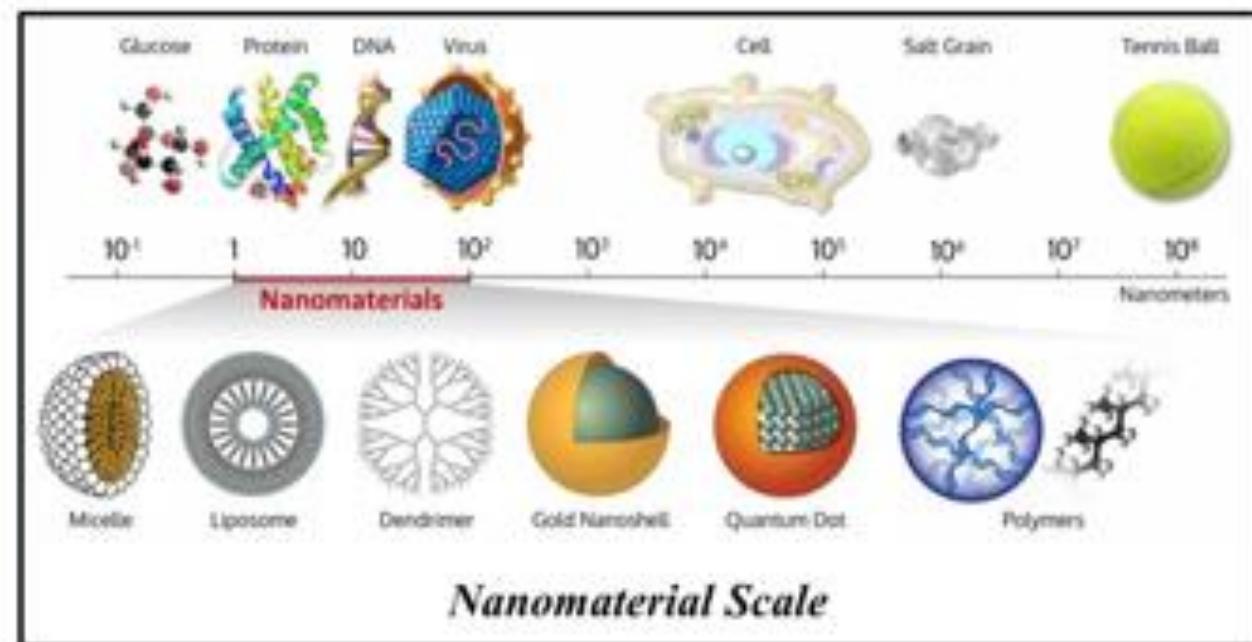
- Nanomaterials are materials with an average grain size less than 100 nanometers.
- Nanometer is the unit of length in metric, equals to one billionth of a meter ( $10^{-9}$ ).

### Nanoparticles

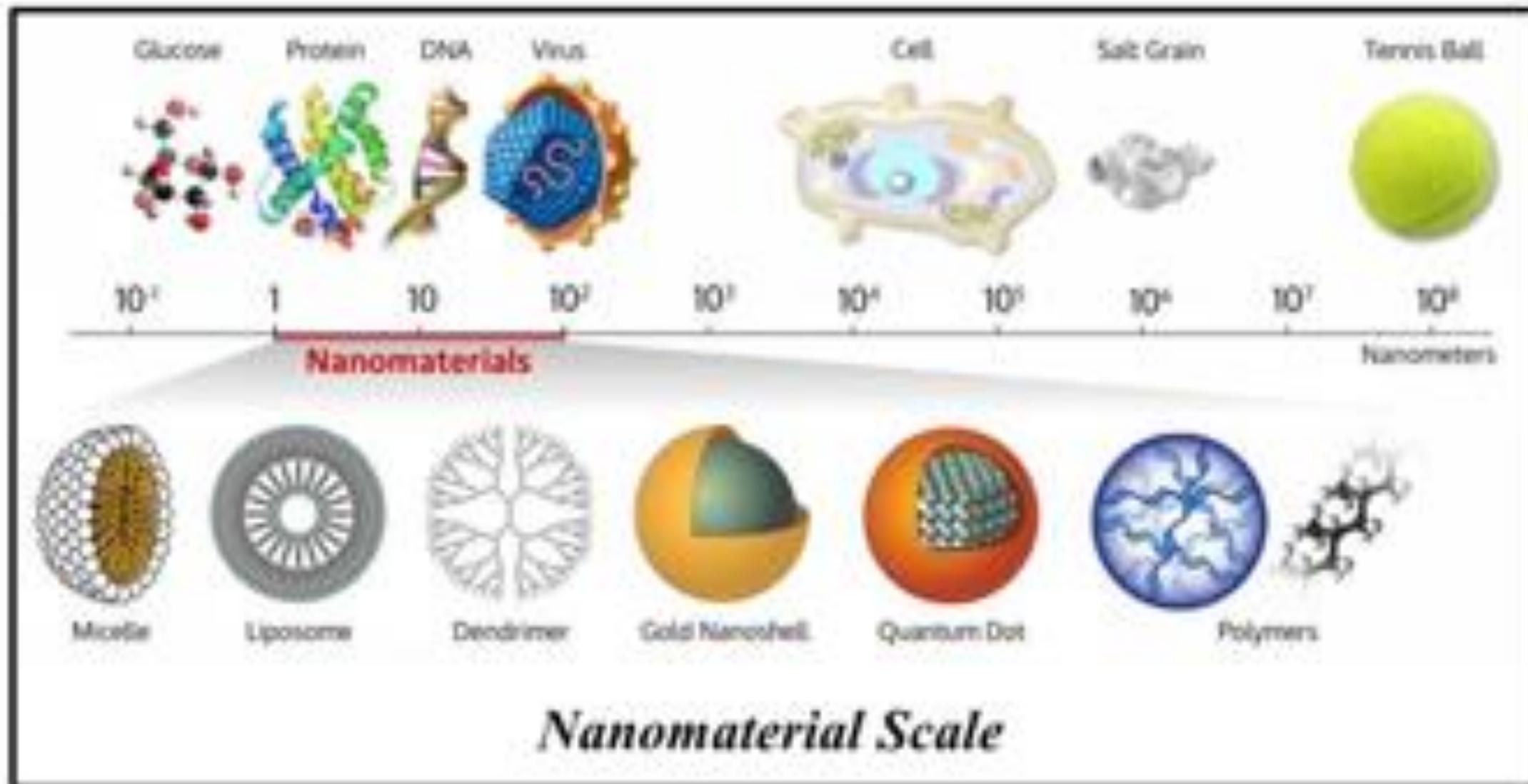
*1 Nanometer =  $10^{-9}$  meter =  $10 \text{ \AA}$   
(extremely small)*

**Particle = Small piece of matter**

Nanoparticles are objects with all three external dimensions at the nanoscale.



- Shape, structure and aggregation of particles at nanoscale influences the properties of material at macro level.



## Why Nanomaterials ?

- Nanotechnology exploits benefits of ultra small size, enabling the use of particles to deliver a range of important benefits.

**Small particles are invisible:**

- ✓ Transparent coating/films are attainable.

**Small particles are very weight efficient:**

- ✓ Surface can be modified with minimal material.

- Behavior of nanomaterials may depend more on surface area than particle composition itself.

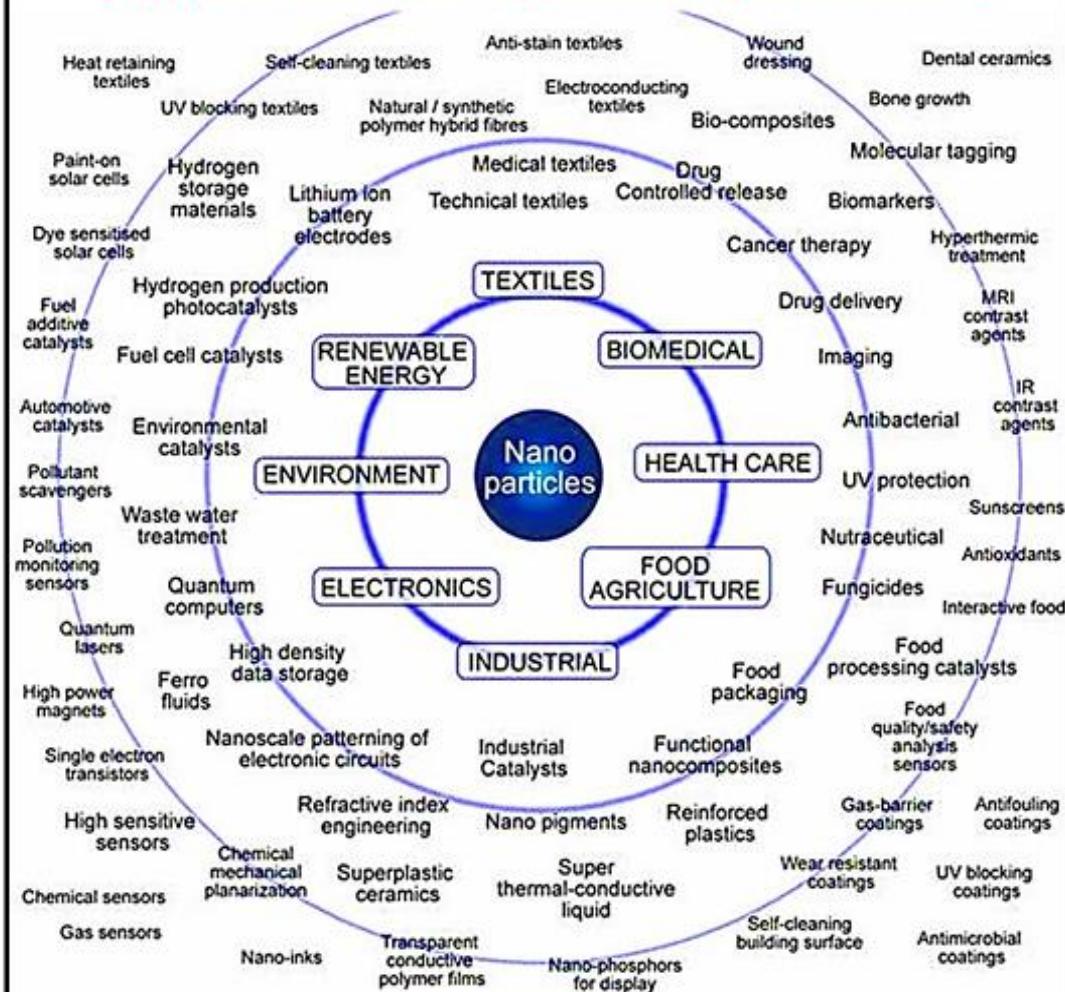
***Relative Surface Area***

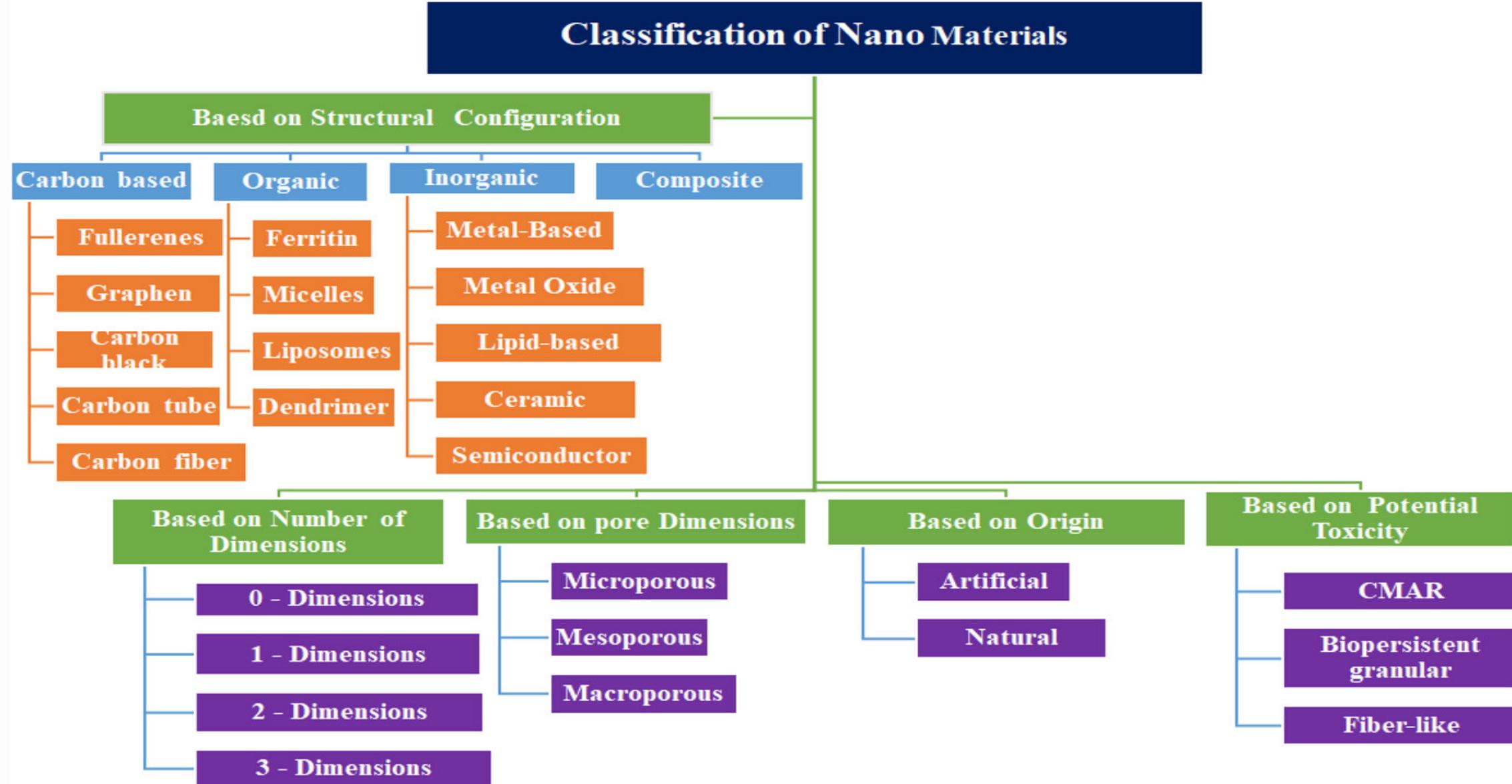
One of the principal factor that enhance its reactivity, strength and electrical properties.

## Properties:

- ✓ Increased surface area to volume ratio due to small particle size.
- ✓ High strength, hardness, formability and toughness.
- ✓ Exhibit super plasticity, even at lower temperature.
- ✓ Size of grain controls the mechanical, electrical, optical, chemical & magnetic properties.
- ✓ Melting point of nanomaterials get reduced on reducing the grain size.
- ✓ Magnetization and coercivity are higher.

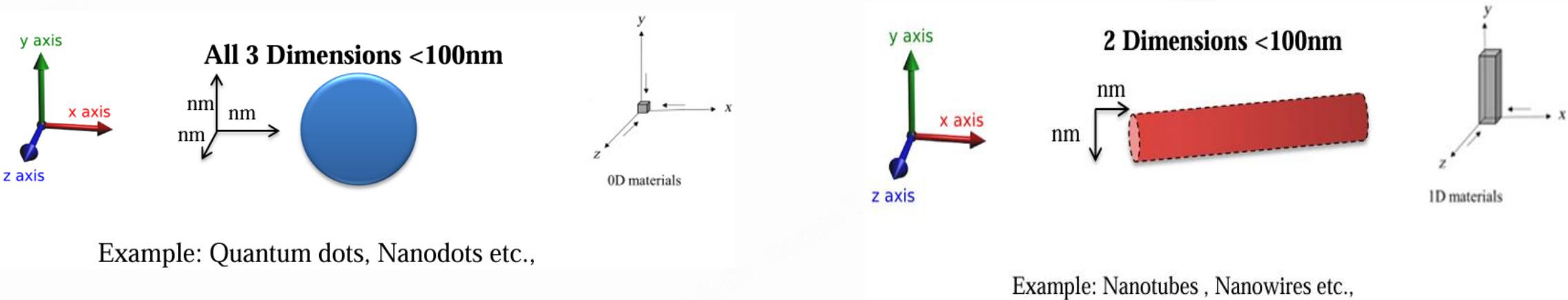
## Applications of Nanoparticles:





## Classification of nanoscale dimensions

**Zero dimension (0D)** -Materials having all the dimensions (x, y, z) within nanoscale (less than 100 nm), where quantum confinement follows.

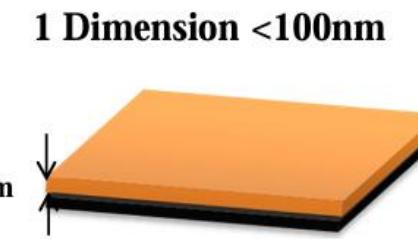
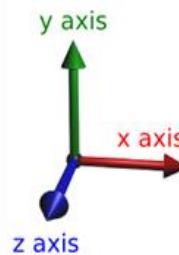


**One dimensions (1D)-** It has two dimensions at nanoscale and the remaining one dimension is larger than 100 nm.

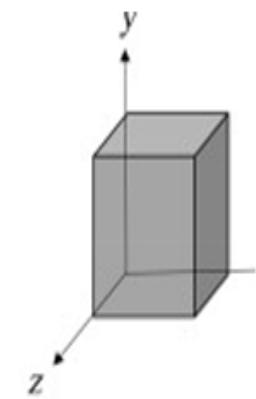
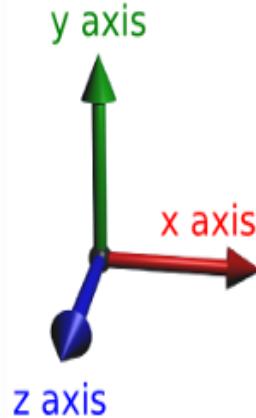
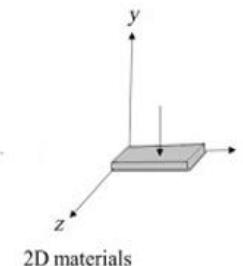
**Two dimension (2D)** – It has only one dimension at nanoscale and the remaining two dimensions are larger than 100 nm.

## 3D materials are NOT Nanomaterials

**Three dimension (3D)** – None of the dimensions are at nanoscale (i.e. all the three dimensions are larger than 100 nm).

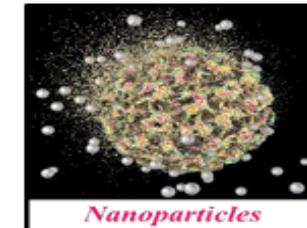


Example: nanofilms , nanocoatings etc.,



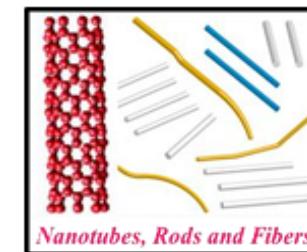
## Zero Dimensional (0-D):

- All dimensions at the nanoscale.
- Example: Nanoparticles, quantum dots.



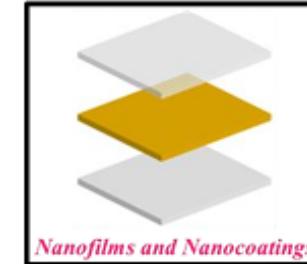
## One Dimensional (1-D):

- Two dimensions at the nanoscale, one dimension at the macroscale.
- Example: Nanorods, nanowires, and nanotubes.



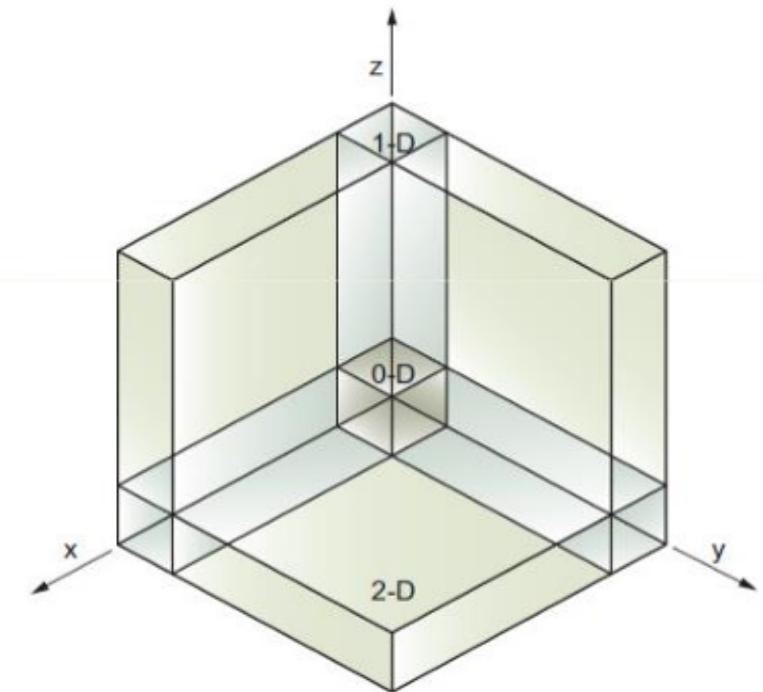
## Two Dimensional (2-D):

- One dimension at the nanoscale, two dimensions at the macroscale.
- Example: Nanofilms, nanolayers and nanocoatings.

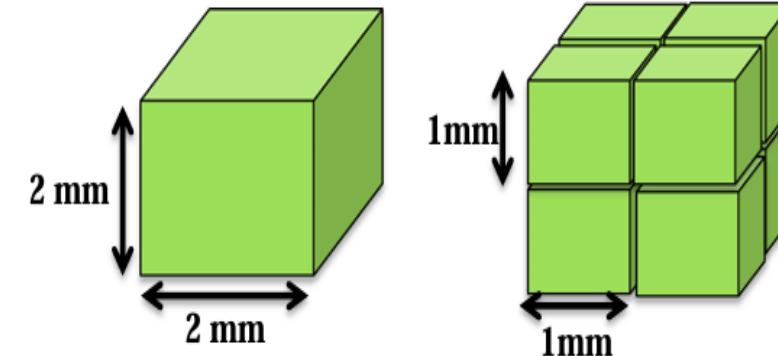


## Three Dimensional (3-D):

- No dimensions at the nanoscales. All dimensions at the macroscale.
- Example: Nanocrystalline structure.

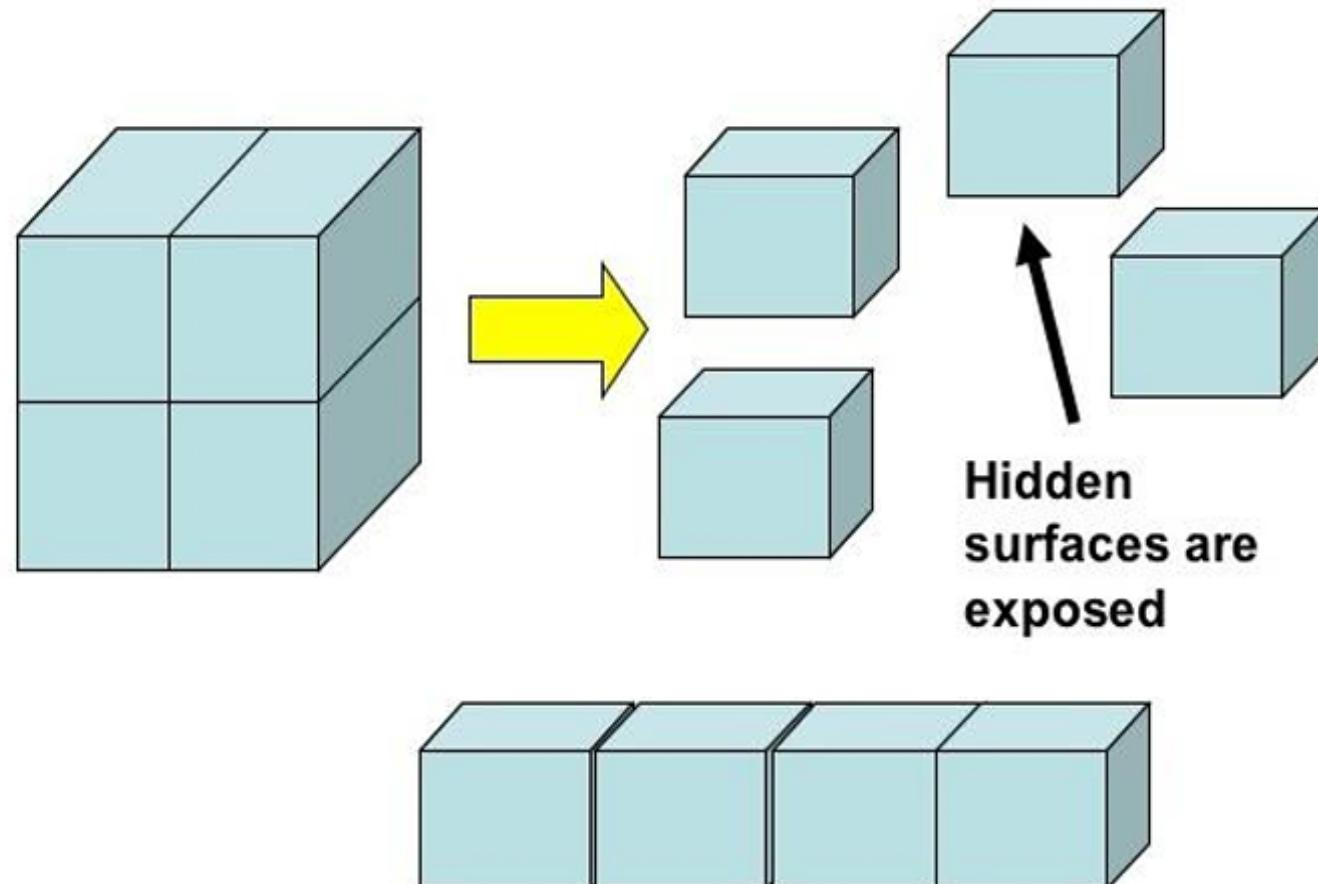


## Surface area-to-volume ratio



Surface Area (mm)	Surface area= Height x Width x No. of sides x No. of cubes	24 (2x2x6x1)	48 (1x1x6x8)
Volume (mm)	Volume=Height x Width x Length x No. of cubes	8 (2x2x2x1)	8 (1x1x1x8)
Surface Area/Volume ratio	Surface area/Volume	3 (24:8)	6 (48:8)

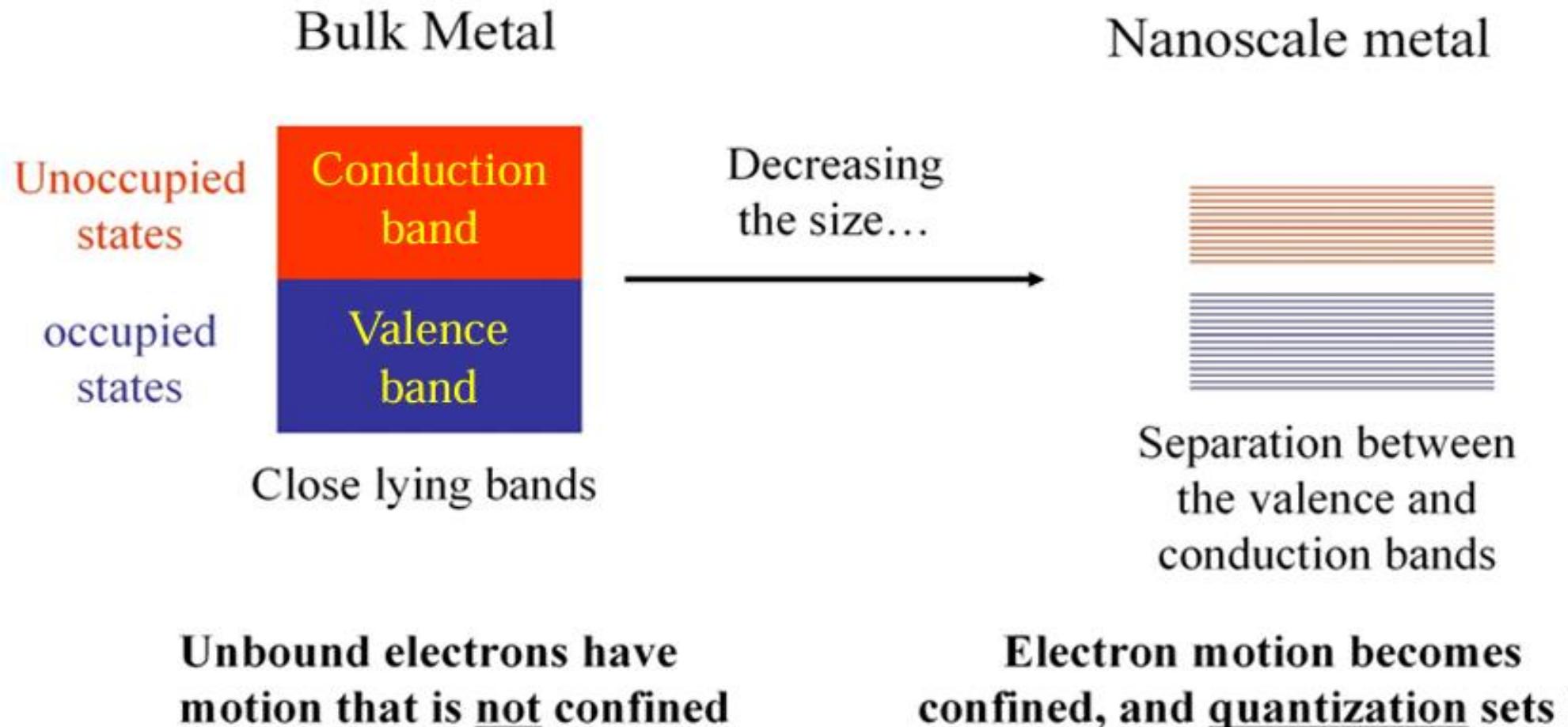
- As surface to volume ratio increases
- A greater amount of a substance comes in contact with surrounding material
- This results in better catalysts, since a greater proportion of the material is exposed for potential reaction



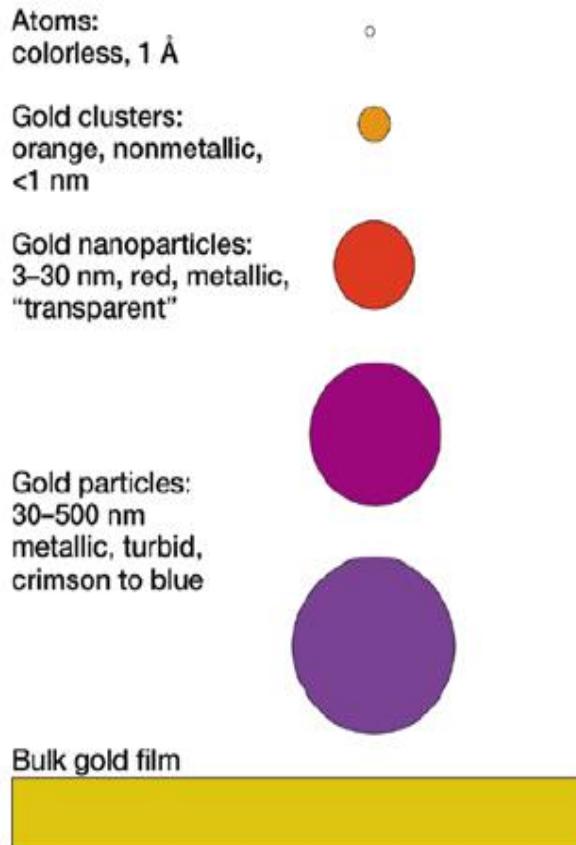
## Nanomaterials properties

- The properties of materials can be different at the Nanoscale for two main reasons:
- **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.
- A bulk material should have constant physical properties regardless of its size but at the nanoscale this is often not the case.
- Size-dependent properties are observed such as quantum confinement in semiconductor particles, and superparamagnetism in magnetic materials, etc..

## Origin of the properties



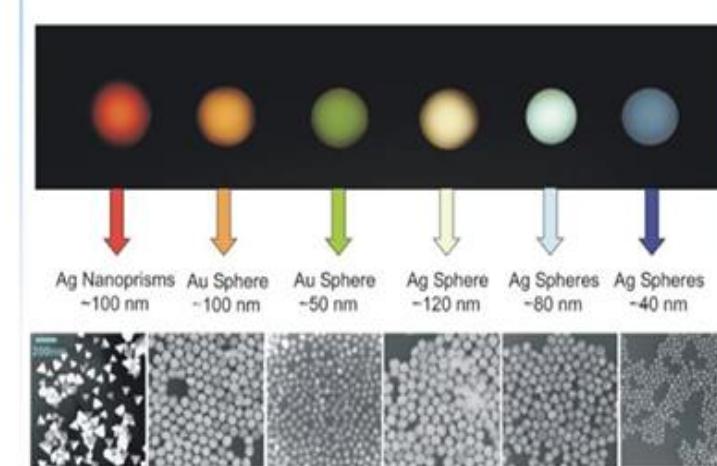
## Material properties vary with size of material



- (Bulk) Gold is a shiny yellow metal
- Gold (Au) nanoparticles appears red
- Bulk gold does not exhibit catalytic properties
- Au nanoparticle is an excellent low temperature catalyst

## Nanoscale size effect

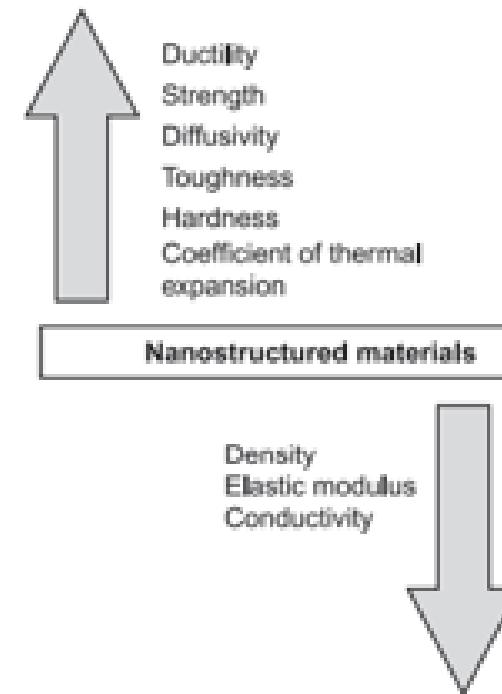
- Manifestation of novel phenomena and properties, including changes in:
  - Physical Properties (e.g. melting point)
  - Chemical Properties (e.g. reactivity)
  - Electrical Properties (e.g. conductivity)
  - Mechanical Properties (e.g. strength)
  - Optical Properties (e.g. light emission)



\* The scale bar is the same for all the images.

## Nano size and properties

Figure shows that nearly all properties like hardness, strength, ductility, elastic modulus, melting point, density, thermal conductivity, thermal expansion coefficient, diffusivity, and so on, change for nanomaterials.



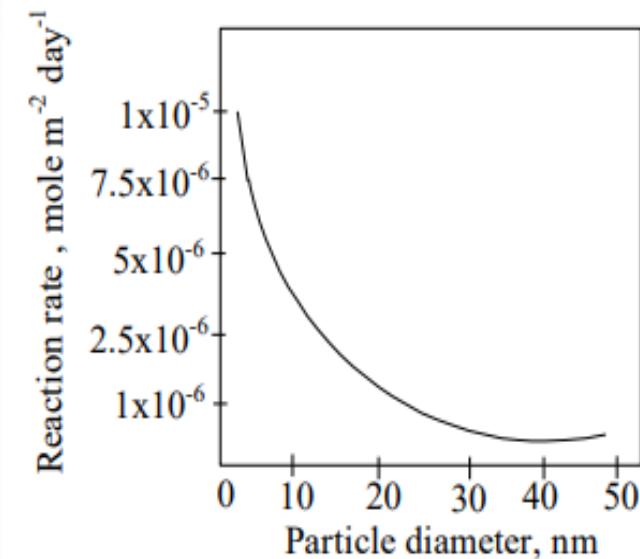
## SIZE DEPENDENT PROPERTIES OF NANOMATERIALS

The various properties, which get tremendously altered due to the size reduction in at least one dimension are:

- a) **Chemical properties:** Reactivity; Catalysis.
- b) **Thermal property:** Melting point temperature.
- c) **Electronic properties:** Electrical conduction.
- d) **Optical properties:** Absorption and scattering of light.
- e) **Magnetic properties:** Magnetization.

## Chemical Properties

- Based on the surface area to volume effect, nanoscale materials have:
  - a) Increased total surface area.
  - b) Increased number of atoms accessible on the surface.
  - c) Increased catalytic activity of those large number surface atoms.
  - d) Different/tunable surface catalytic properties by the change in shape, size and composition.
- Hence, nanoscale catalysts can increase the rate, selectivity and efficiency of various chemical reactions.



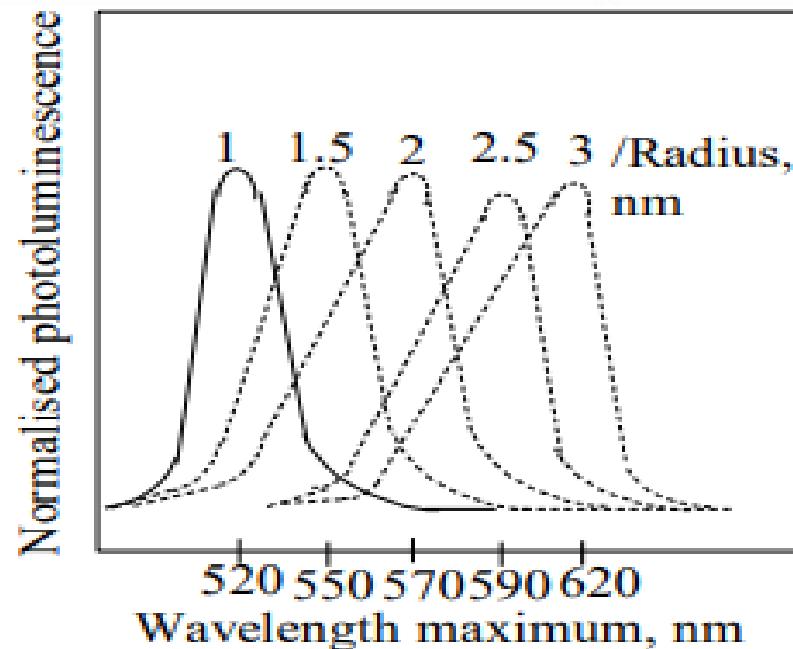
**Effect of Particle Size on the Reaction Rate**

## Electronic Properties

- In bulk materials, conduction of electrons is delocalized, that is, electrons can move freely in all directions.
- When the scale is reduced to nanoscale, the quantum effect dominates. For zero dimensional nanomaterials, all the dimensions are at the nanoscale and hence the electrons are confined in 3-D space. Therefore no electron delocalization (freedom to move) occurs.
- For one dimensional nanomaterials, electrons confinement occurs in 2-D space and hence electron delocalization takes place along the axis of nanotubes/nanorods/nanowires.
- Due to electron confinement, the energy bands are replaced by discrete energy states which make the conducting materials to behave like either semiconductors or insulators.

## Optical Properties

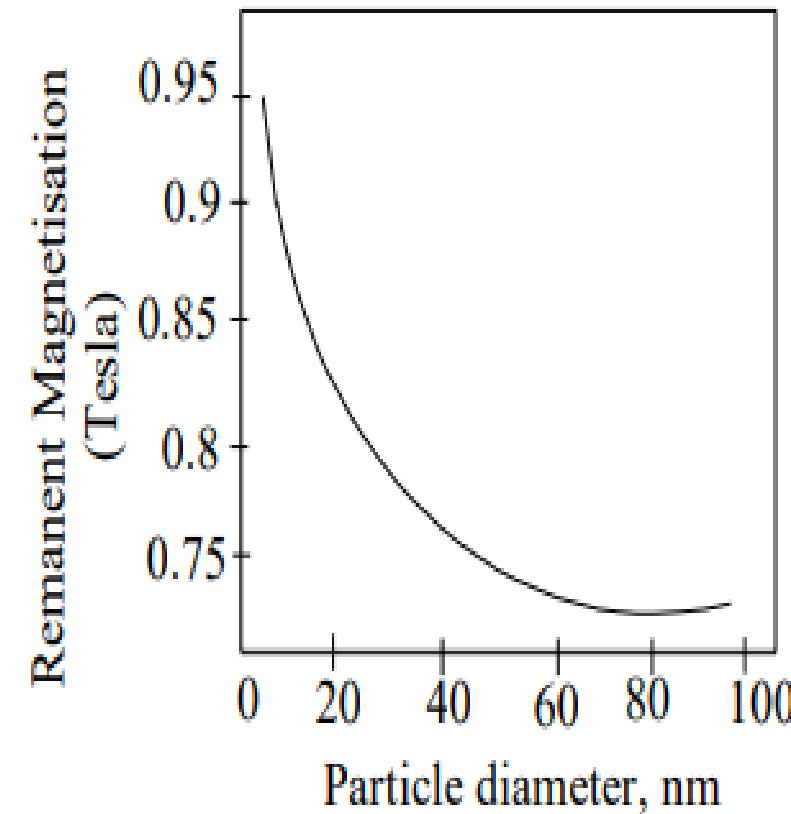
Because of the quantum confinement in nanomaterials, the emission of visible light can be tuned by varying the nanoscale dimensions. It is observed that the size reduction in nanomaterials shifts the emission of peak towards the shorter wavelength (blue shift).



**Effect of particle size on photoluminescence**

## Magnetic Properties

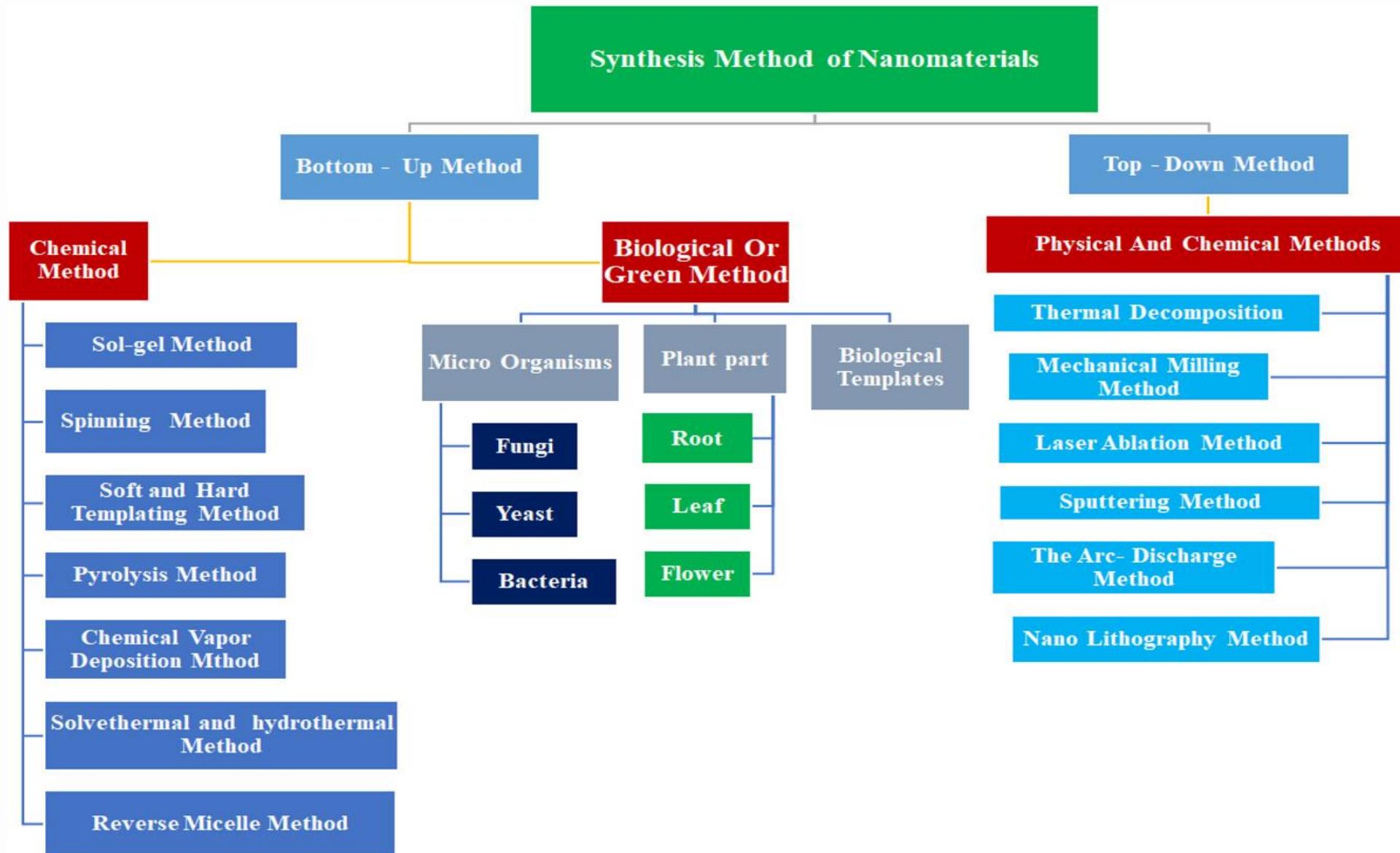
- The size of magnetic nanoparticles also influences the value magnetization. The figure illustrates the effect of particle size on the saturation magnetization of zinc ferrite.
- The magnetization increases significantly below a grain size of 20nm.
- Hence, by decreasing the particle size of a granular magnetic material it is possible to improve the quality of magnets fabricated from it.



**Effect of Particle Size on the Saturation Magnetization**



# Synthesis of Nanomaterials



## Bottom-up

Building something by assembling smaller components (like building a car engine), atom by atom assembly.

In nanotechnology: self-assembly of atoms and molecules, as in chemical and biological systems

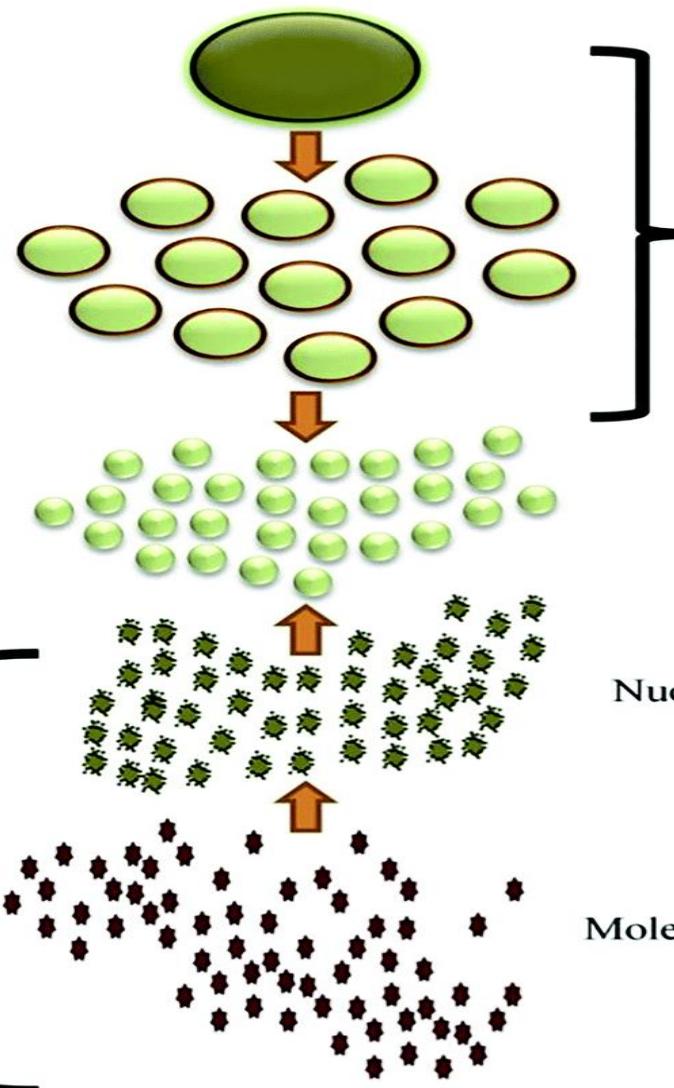


Brick



Building

Bulk Material



Top Down Approach

- ❖ Mechanical Milling
- ❖ Etching
- ❖ Laser Ablation
- ❖ Sputtering
- ❖ Electro-explosion

Nanoparticles

Bottom Up Approach

- ❖ Supercritical Fluid Synthesis
- ❖ Spinning
- ❖ Sol-gel Process
- ❖ Laser Pyrolysis
- ❖ Chemical Vapour Deposition
- ❖ Molecular Condensation
- ❖ Chemical Reduction
- ❖ Green Synthesis

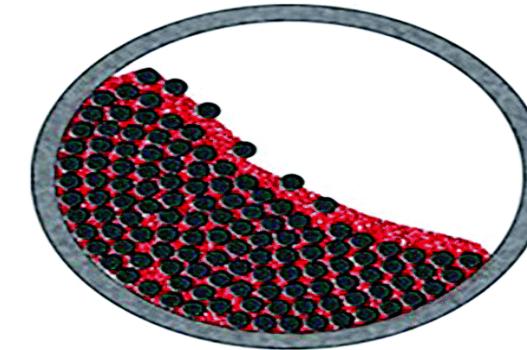
Nuclei and its growth

Molecular/Atomic Level

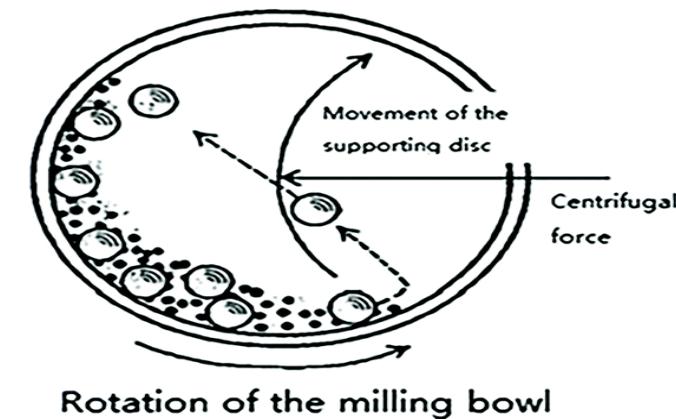
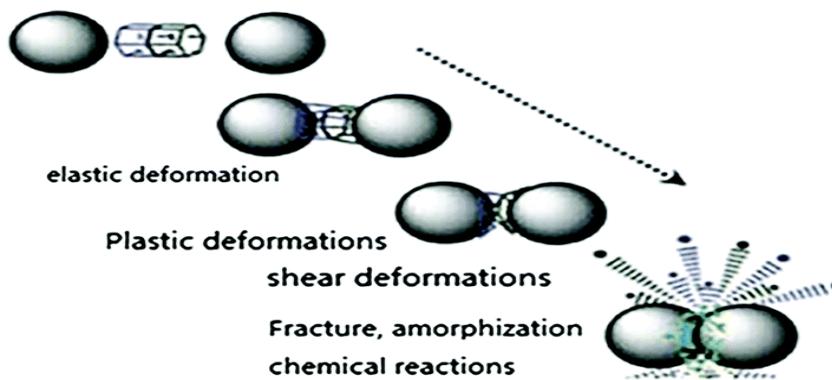
## TOP-DOWN APPROACHES

In top-down approaches, bulk materials are divided to produce nanostructured materials. Top-down methods include mechanical milling, laser ablation, etching, sputtering, and electro-explosion.

**Mechanical milling.** Mechanical milling is a cost-effective method for producing materials at the nanoscale level from bulk materials. Mechanical milling is an effective method for producing blends of different phases, and it is helpful in the production of nanocomposites. The principle of the ball milling method is shown in **Fig.** Mechanical milling is used to produce oxide- and carbide-strengthened aluminum alloys, wear-resistant spray coatings, aluminum/nickel/magnesium/copper-based nanoalloys, and many other nanocomposite materials. Ball-milled carbon nanomaterials are considered a novel class of nanomaterial, providing the opportunity to satisfy environmental remediation, energy storage, and energy conversion demands.



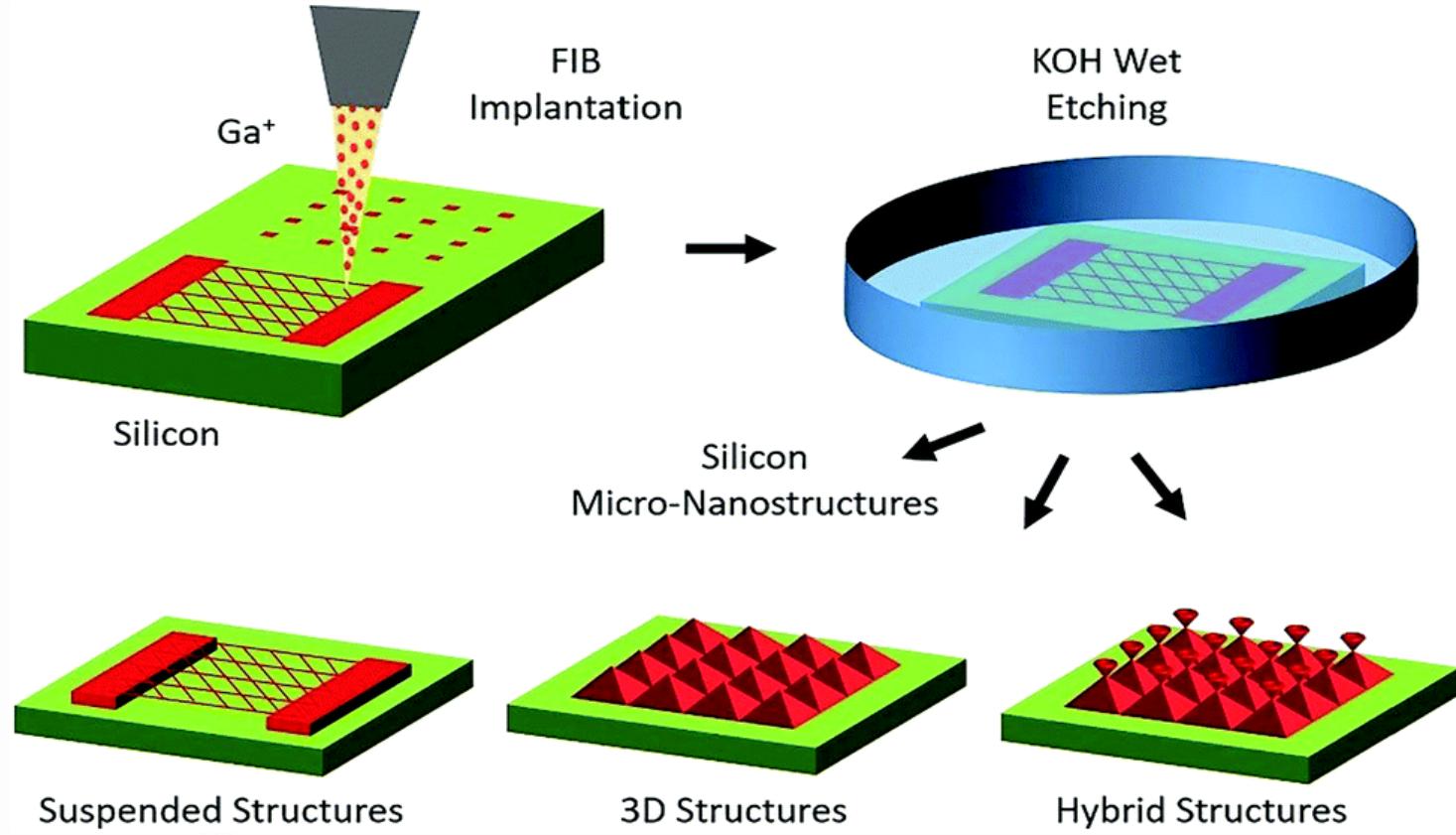
Horizontal section



Rotation of the milling bowl

## Lithography

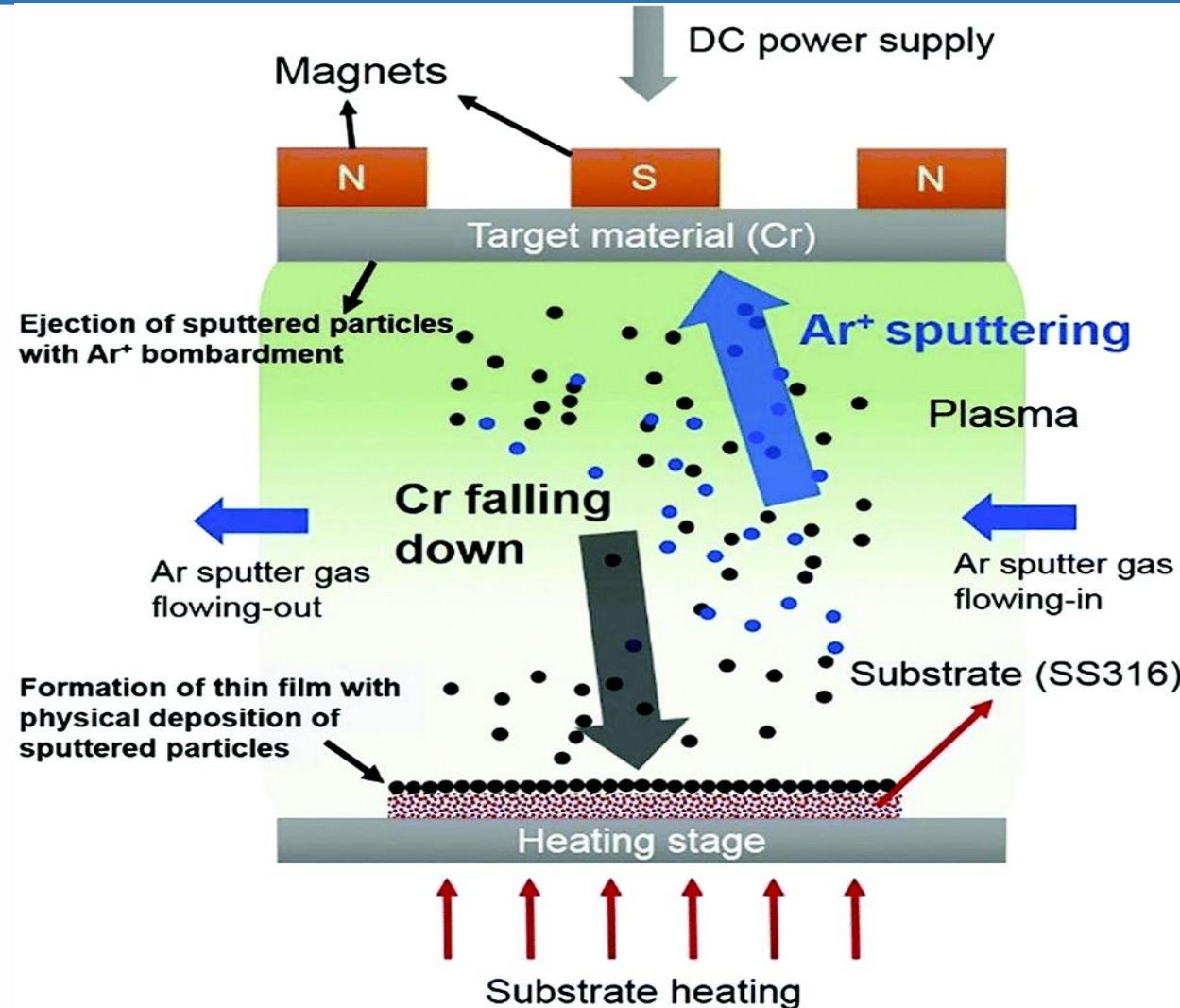
Lithography is a useful tool for developing nanoarchitectures using a focused beam of light or electrons. Lithography can be divided into two main types: masked lithography and maskless lithography.<sup>31</sup> In masked nanolithography, nanopatterns are transferred over a large surface area using a specific mask or template. Masked lithography includes photolithography, nanoimprint lithography, and soft lithography. Maskless lithography includes scanning probe lithography, focused ion beam lithography, and electron beam lithography. In maskless lithography, arbitrary nanopattern writing is carried out without the involvement of a mask. 3D freeform micro-nano-fabrication can be achieved *via* ion implantation with a focused ion beam in combination with wet chemical etching, as shown in Fig.



**Fig.** A schematic diagram of the fabrication of 3D micro-nanostructures with an ion beam through bulk Si structuring. This involves implantation in Si through Ga FIB lithography and mask-writing at nanometer resolution, subsequent anisotropic wet etching in KOH solution, and the fabrication of Si micro-nanostructures *via* the selective removal of the unimplanted region.

**Magnetron Sputtering** - Sputtering is a process used to produce nanomaterials *via* bombarding solid surfaces with high-energy particles such as plasma or gas. Sputtering is considered to be an effective method for producing thin films of nanomaterials. In the sputtering deposition process, energetic gaseous ions bombard the target surface, causing the physical ejection of small atom clusters depending upon the incident gaseous-ion energy (**Fig.**). The sputtering process can be performed in different ways, such as utilizing magnetron, radio-frequency diode, and DC diode sputtering. In general, sputtering is performed in an evacuated chamber, to which the sputtering gas is introduced. A high voltage is applied to the cathode target and free electrons collide with the gas to produce gas ions. The positively charged ions strongly accelerate in the electric field towards the cathode target, which these ions continuously hit, resulting in the ejection of atoms from the surface of the target. **Magnetron sputtering** is used to produce WSe<sub>2</sub>-layered nanofilms on SiO<sub>2</sub> and carbon paper substrates. The sputtering technique is interesting because the sputtered nanomaterial composition remains the same as the target material with fewer impurities, and it is cost-effective compared with electron-beam lithography

# Magnetron Sputtering



**Fig.** A schematic diagram of the DC magnetron sputtering process.

## BOTTOM – UP APPROACHES

### **SYNTHESIS OF NANOPOROUS MATERIALS BY SOL-GEL PROCESS**

#### **Sol-Gel Process:**

“Formation of an oxide network through polycondensation reactions of a molecular precursor in a liquid”.

#### **Precursors**

The precursor used in sol-gel process for the synthesis of nanoporous materials are metal alkoxides  $M(OR)_n$ . They readily react with water to form gels.

#### **Examples**

- Tetra methoxy silane  $[Si(O_3CH_4)]$
- Tetra ethoxy silane  $[Si(O_2C_2H_5)_4]$
- Tetra butoxy titanate  $[Ti(O_4C_9 H_4)]$

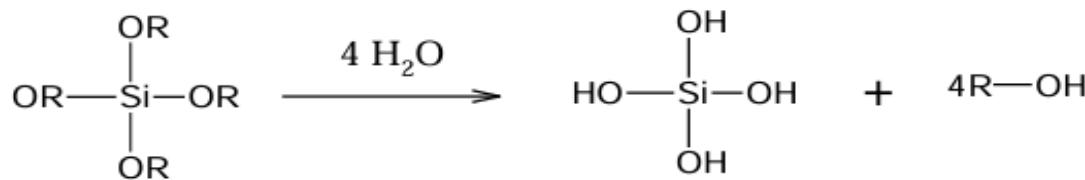
## Process (Synthesis of silica aerogel)

This process consists of four main steps.

1. Hydrolysis of precursors
2. Condensation followed by polycondensation
3. Gelation
4. Supercritical drying

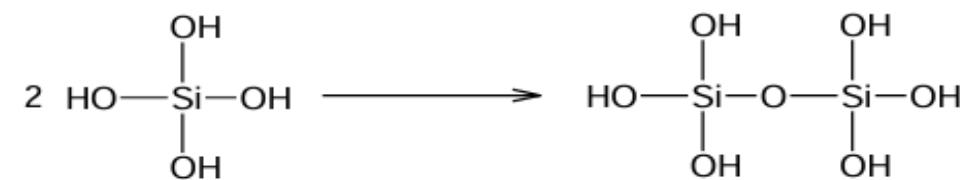
### 1. Hydrolysis

It occurs by the addition of water to any one of the precursor material to form silanol ( $\text{Si}-\text{OH}$ ) particles.



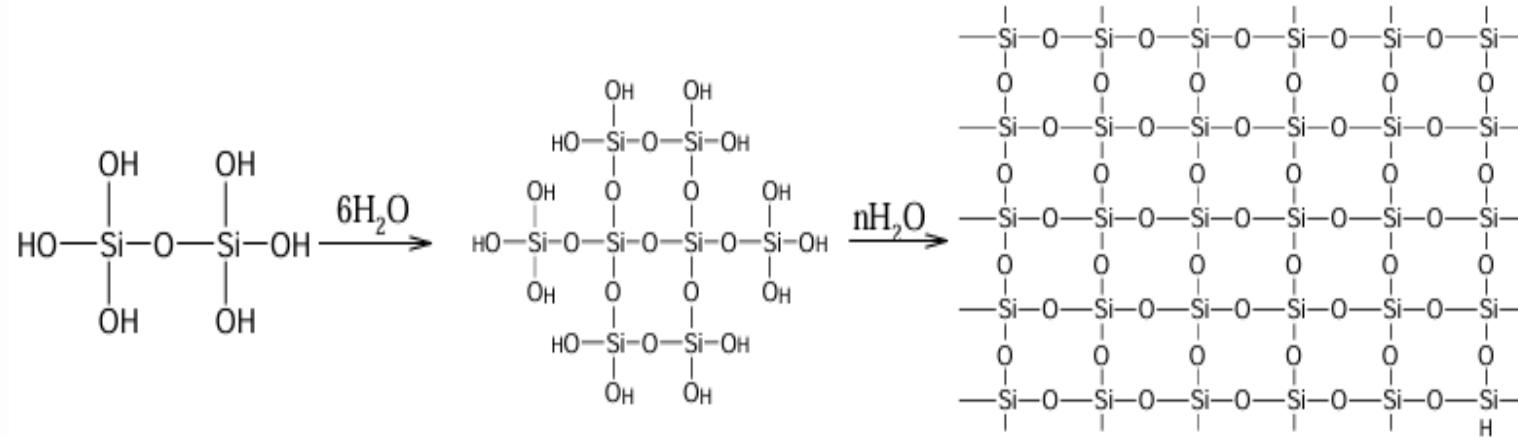
### 2. Condensation

The self condensation of silanol groups produces siloxane linkages filled with by products of water and alcohol.



### 3. Polycondensation

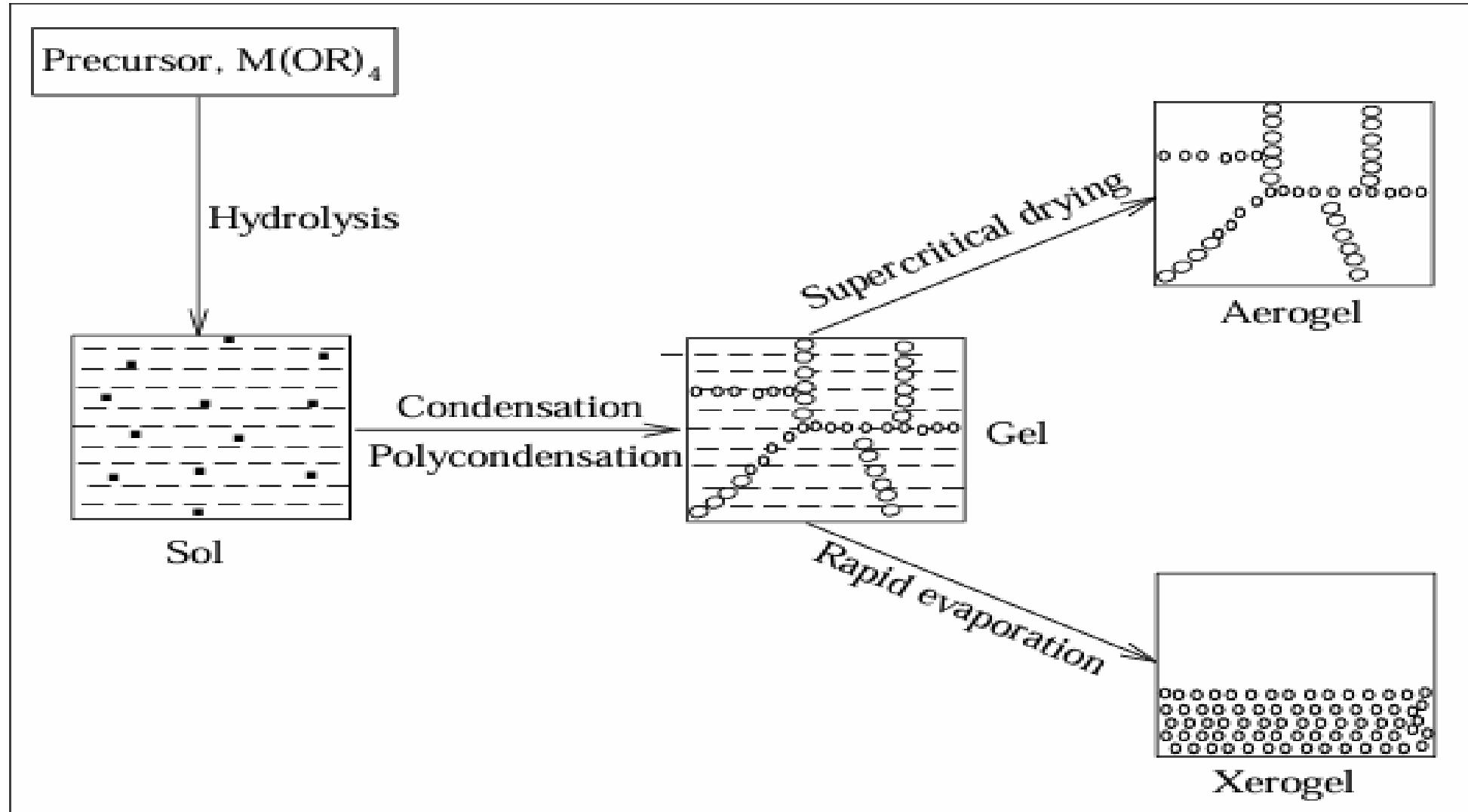
The condensation process continues to form poly condensed silica gel with Si-O-Si linkages.



## 4. Drying

The gels are subjected to super critical drying in an autoclave.

The critical pressure and critical temperature used are 78 bar and 294°C respectively in order to remove liquid from silica gel to form the network structure of silica aerogel.



**Fig. : Sol-gel process**

## Advantages of Sol-gel process

- It produces thin bond-coating to provide excellent adhesion between the metallic substrate and the top coat.
- It produces thick coating to provide corrosion protection performance.
- It easily shapes materials into complex geometries in a gel state.
- It has low temperature sintering capability, usually 200-600°C.
- It provides a simple, economic and effective method to produce high quality coatings.

## Applications of Sol-gel process

- It can be used in ceramics manufacturing processes as an investment casting material or as a means of producing very thin films of metal oxides for various purposes.
- Sol-gel derived materials have diverse applications in optics, electronics, energy, space, (bio) sensors, medicine (e.g. controlled drug release) and separation (e.g. chromatography) technology.
- One of the more important applications of sol-gel processing is to carry out zeolite synthesis.
- Other elements (metals, metal oxides) can be easily incorporated into the final product and the silicalite sol formed by this method is very stable.
- Other products fabricated with this process include various ceramic membranes for microfiltration, ultrafiltration, nanofiltration and reverse osmosis.

## SYNTHESIS OF NANOMATERIALS BY CHEMICAL VAPOUR DEPOSITION (CVD)

**Principle** - Chemical vapour deposition (CVD) method involves a transport of reactant gases towards the substrate kept at some temperature where reactants crack into different products which diffuse on the surface and undergo certain chemical reactions at appropriate site nucleate and grow to form desired films, coatings, wires and tubes.

### CVD Reactions

#### Precursors

The common precursors used in CVD reactions are

- o Metal hydrides –  $\text{SiH}_4$  ,  $\text{GeH}_4$
- o Metal halides- $\text{TiCl}_4$  ,  $\text{TaCl}_5$  ,  $\text{WF}_6$
- o Metal organics-  $\text{AlMe}_3$  ,  $\text{AlBu}_3$  ,  $\text{Fe}(\text{CO})_5$  ,  $\text{Ni}(\text{CO})_4$

#### (i) Thermal Decomposition (Pyrolysis):

Silicon deposition from  $\text{SiH}_4$  at  $650^\circ\text{C}$

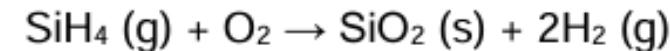


#### (ii) Reduction: W-deposition at $300^\circ\text{C}$



#### (iii) Oxidation:

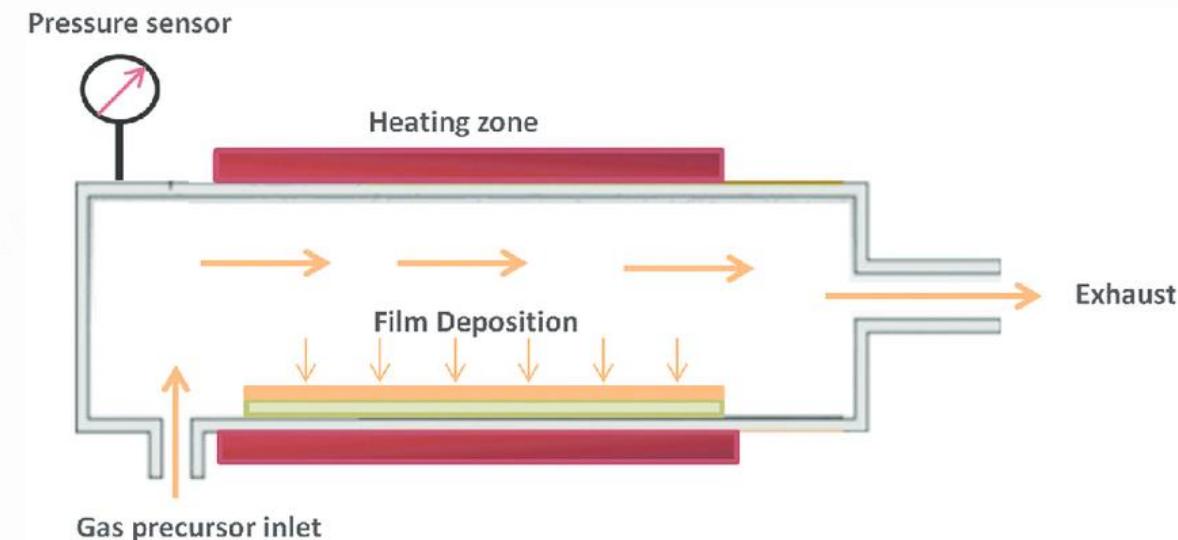
$\text{SiO}_2$  deposition at  $450^\circ\text{C}$



## Mechanism

The system follows a five step mechanism for any type of CVD.

- a) Transport of precursors into the reactors
- b) Absorption and diffusion of precursors on the substrate
- c) Chemical reactions at the substrate
- d) Deposition and growth of film
- e) Transport of unreacted precursors and by-products



## Advantages of CVD

- a) Versatile- CVD can deposit any element or compound.
- b) CVD produces high dense films.
- c) Economical in production since many products can be coated at a time.
- d) Used for coatings or freestanding structures
- e) Fabricates net or near-net complex shapes
- f) Self-cleaning—extremely high purity deposits (>99.995% purity)
- g) Conforms homogeneously to contours of substrate surface
- h) Controllable thickness and morphology
- i) Forms alloys
- j) Coats internal passages with high length-to-diameter ratios
- k) Simultaneously coat multiple components
- l) Coats powders

## Applications of CVD

- a) CVD can be used for the synthesis of nanotubes and nanowires.
- b) CVD can be used for hard coatings and metal films which are used in microelectronics.
- c) CVD can also be used for preparing semiconducting devices, dielectrics, energy conversion devices etc.
- d) CVD processes are used on a surprisingly wide range of industrial components from aircraft and land gas turbine blades, timing chain pins for the automotive industry, radiant grills for gas cookers and items of chemical plant to resist various attacks by carbon, oxygen and sulphur.
- e) Surface modification to prevent or promote adhesion.
- f) Photoresist adhesion for semiconductor wafers Silane/substrate adhesion for microarrays (DNA, gene, protein, antibody, tissue).
- g) BioMEMS and biosensor coating to reduce "drift" in device performance.
- h) Promote biocompatibility between natural and synthetic materials Copper capping Anti corrosive coating

## SYNTHESIS OF NANOMATERIALS BY PHYSICAL VAPOUR DEPOSITION (PVD)

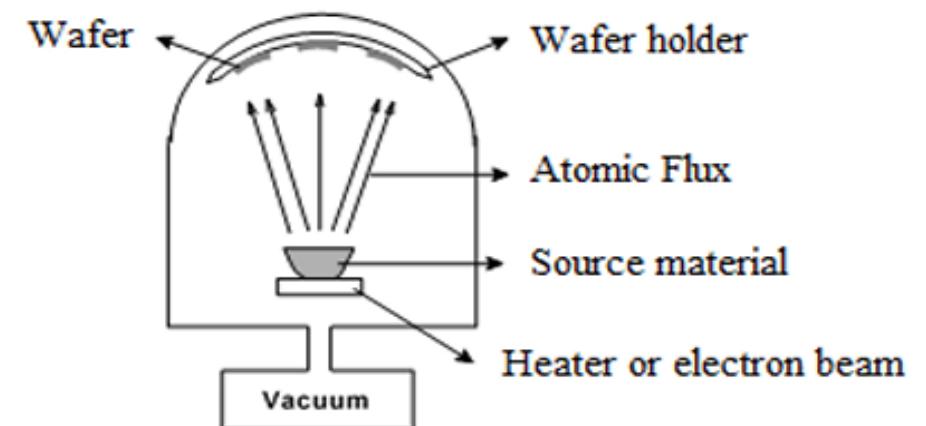
Nanomaterials in the form of thin films, multilayer films, nanoparticles and nanotubes can be produced by physical vapour deposition methods.

### Definition

Physical vapour deposition (PVD) is a technique by which a metal, ceramic or a compound can be converted into gaseous form and then deposited on the surface of a substrate. In general, PVD methods are subdivided into:

- 1. Evaporation**
- 2. Sputtering**
- 3. Pulsed Laser Deposition or Laser Ablation**

**EVAPORATION** - The source materials used in this process are generally refractory metals such as W, Ta, Mo etc. In evaporation technique, both substrate and source materials (to be deposited) are placed inside the vacuum chamber ( $10^{-6}$  to  $10^{-7}$  torr). The vacuum is required to allow the molecules to evaporate and to move freely in the chamber. An electron gun (e-gun) is used to produce electron beam of 10 keV. This beam is directed at the source material in order to develop sufficient vapour so as to produce deposits on wafer or substrates. **Figure.**, shows the schematic diagram of evaporation equipment.



Schematic diagram of evaporation equipment

**SPUTTERING** - The source materials used in this process are generally an alloy, ceramic or a compound. In sputtering technique, a high energy atom in ionized form usually  $\text{Ar}^+$  is used to hit the surface atoms of the targeted source material. Then the knocked out atoms in vapour form are deposited on the surface of the substrate to produce a uniform coatings.

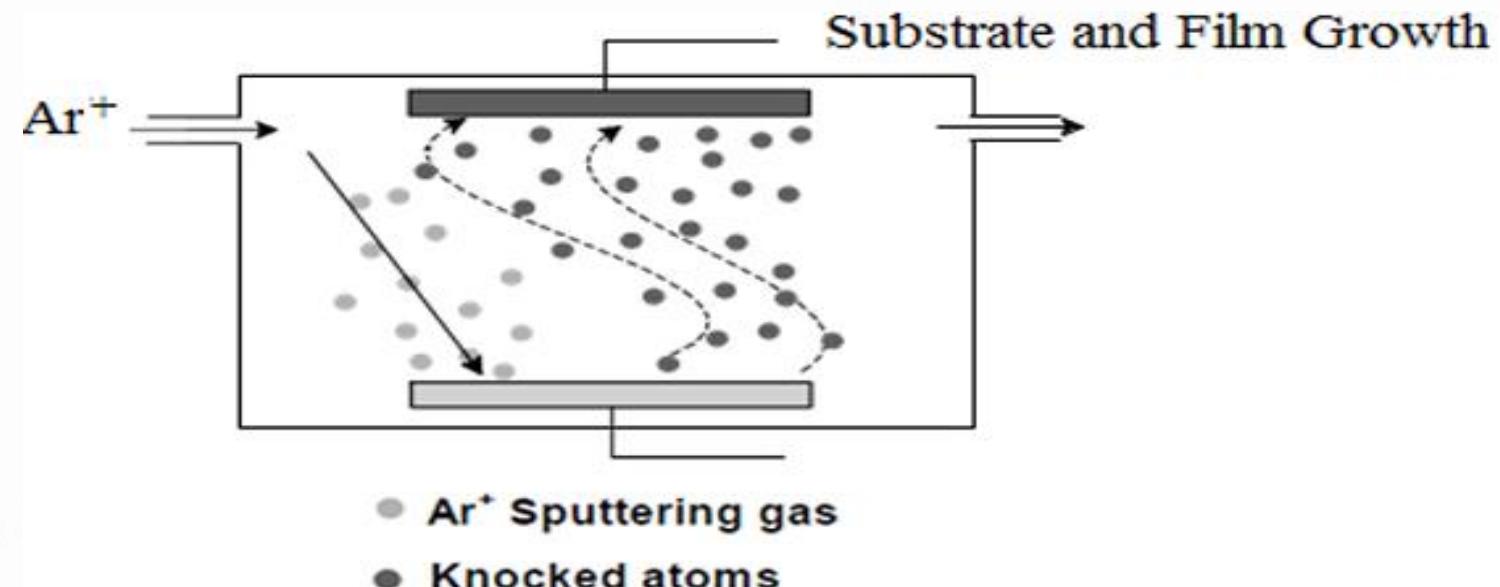


Fig. . Schematic diagram of sputtering equipment

**PULSED LASER DEPOSITION OR LASER ABLATION** - Pulsed Laser Deposition (PLD) is a thin film deposition technique that is used to deposit materials on substrates. A base system consists of a target, substrate carrier which is mounted in a vacuum chamber. An excimer laser is used to energize the surface of a target to produce a deposition plume. The plume is typically directed towards the substrate where a thin-film is deposited. Since each shot of the laser is directly related to the amount of material ablated, the deposition rate can be calibrated and controlled very precisely. **Figure.**, shows the schematic diagram of pulsed laser deposition.

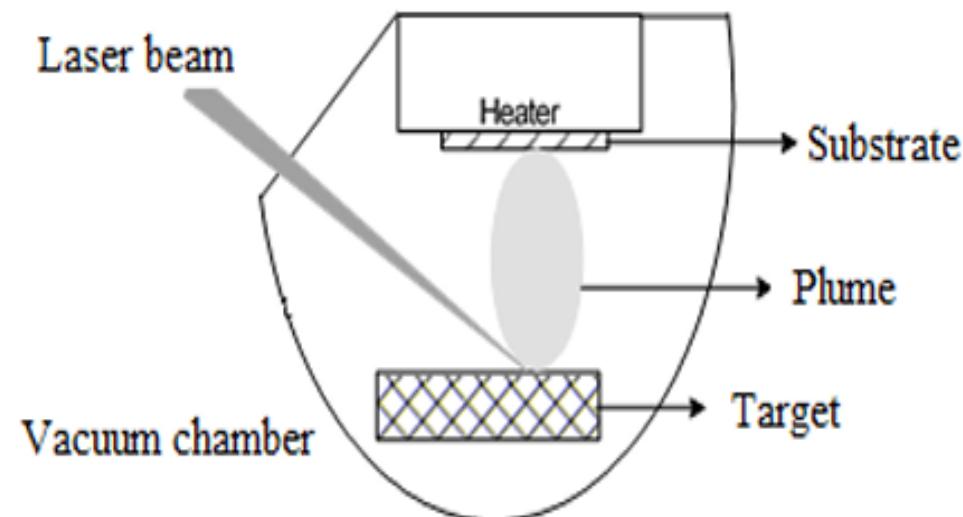


Fig.: Schematic diagram of Pulsed Laser Deposition

## Advantages of PVD

- • Ultrapure films or particles can be produced by PVD since it uses a vacuum environment.
- • PVD can provide good structural control by careful monitoring of the processing conditions.
- • Materials can be deposited with improved properties compared to the substrate material.
- • Almost any type of inorganic material can be used as well as some kinds of organic materials.
- • The process is more environmentally friendly than processes such as electroplating.

## Disadvantages of PVD

- • Since PVD operates in a low pressure range, it increases the complexity of deposition and cost of production.
- • It is a line of sight technique meaning that it is extremely difficult to coat undercuts and similar surface features.
- • High capital cost.
- • Some processes operate at high vacuums and temperatures requiring skilled operators.
- • Processes requiring large amounts of heat require appropriate cooling systems.
- • The rate of coating deposition is usually quite slow.

## Applications

- PVD is used to produce the deposit of various metals, alloys or compounds in the form of coatings or films for: Optics (Ex: Antireflection coatings) Electronics (Ex: Metal contacts) Mechanics (Ex: hard coatings on tools) etc.
- PVD coatings are generally used to improve hardness, wear resistance and oxidation resistance.
- PVD coatings use in a wide range of applications such as: Aerospace, Automotive, Surgical/Medical, Dies and moulds for all manner of material processing, Cutting tools, Fire arms 3030.

**NANOPOROUS MATERIALS** - Nanoporous materials are materials with nano-sized pores that have a large surface area to volume ratio and a high degree of porosity.

They have properties, include high surface area to volume ratio, High permeability, Good selectivity, Good heat and sound resistance, and Extreme sensitivity to environmental changes.

Nanoporous materials are used in a wide range of applications, which include catalysts, Separating and removing contaminants, Sensors, Membranes, Insulating materials, Drug delivery, Biosensing, and Bioimaging.

Some examples of nanoporous materials include:

**Zeolites** - Used in chemical production, CO<sub>2</sub> capture, biomass conversion, and automotive exhaust remediation

**Carbon-based materials** - Such as carbon nanotubes and graphene oxide, which are used in biomedical applications

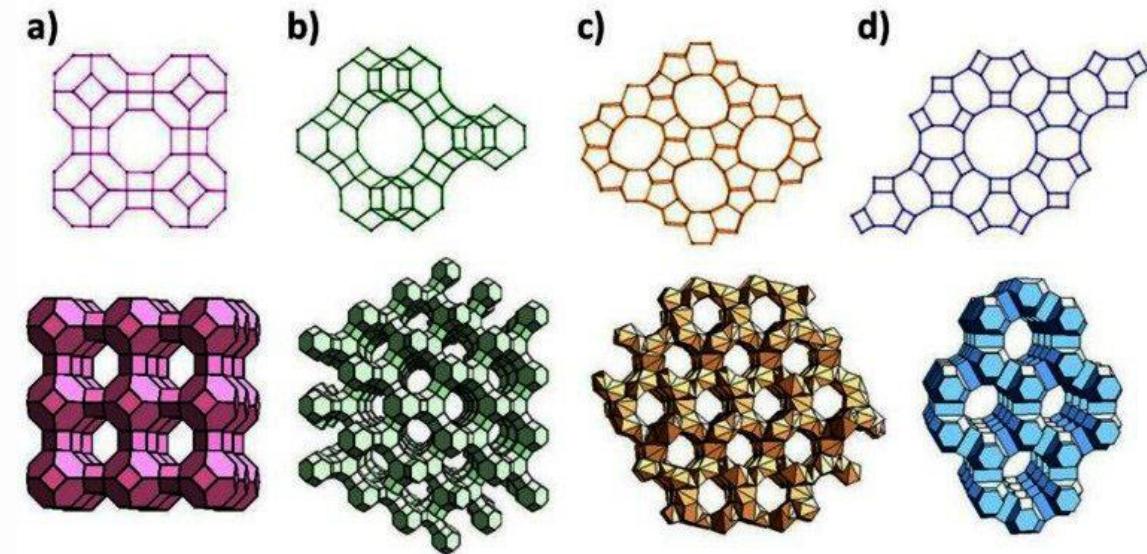
**Mesoporous silicas** - Used for molecule adsorption

**Activated carbon** - Can be made from a wide range of raw materials, including agricultural waste, wood, petroleum coke, and industrial biomass

## ZEOLITES: NANOPOROUS MATERIALS WITH VERSATILE APPLICATIONS

### What are Zeolites?

Zeolites are a class of microporous, aluminosilicate minerals that have a crystalline structure with a framework of interconnected tunnels and cages. They are naturally occurring but can also be produced synthetically. The term "zeolite" comes from the Greek words "zeo" (to boil) and "lithos" (stone), referring to their ability to release water when heated.



**Fig.** Representative zeolite frameworks, (with pore openings).  
(a) zeolite A (3D, 4.2 Å); (b) zeolite Y (3D, 7.4 Å); (c) Zeolite L (1D, 7.1 Å); (d) ZSM-5 (silicalite) (2D,  $5.3 \times 5.6$  Å,  $5.1 \times 5.5$  Å)  
D—dimensions of channel system.

## Structure and Composition

Zeolites have a three-dimensional framework structure composed of  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra connected by shared oxygen atoms. The presence of aluminum in the framework creates a negative charge, which is balanced by positively charged cations (such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ) located within the pores. The general chemical formula of a zeolite is:



where M is the cation with valence n, x and y are the total number of tetrahedra per unit cell, and z is the number of water molecules.

## Properties of Zeolites

**High Porosity and Surface Area** - The high surface area and nanoscale pores make zeolites excellent adsorbents and catalysts.

**Ion-Exchange Capacity** - This property is exploited in applications such as water softening, purification, and heavy metal removal.

**Thermal and Chemical Stability** - Zeolites are thermally stable and can withstand temperatures up to 1000 °C without significant structural changes. They are also chemically stable in both acidic and basic environments. This stability makes zeolites suitable for high-temperature catalytic reactions and harsh chemical processes.

**Shape Selectivity** - The regular pore structure of zeolites allows them to act as molecular sieves, selectively adsorbing molecules based on their size and shape. This shape selectivity is crucial in catalytic applications, where zeolites can control the access of reactants to active sites and the diffusion of products, leading to improved selectivity and yield.

## Applications of Zeolites

**Catalysis** - Zeolites are widely used as heterogeneous catalysts in various industrial processes, such as **fluid catalytic cracking (FCC) in oil refining, hydrocracking, isomerization, and alkylation reactions**. Their shape selectivity, high surface area, and acid sites make them efficient catalysts for hydrocarbon processing and fine chemical synthesis.

**Adsorption and Separation** - Zeolites are excellent adsorbents for gas and liquid separations. They are used in processes such as **air separation, natural gas purification, and the removal of volatile organic compounds (VOCs)**. Zeolites are also used in pressure swing adsorption (PSA) processes for **hydrogen purification and carbon dioxide capture**.

**Ion Exchange** - The ion-exchange properties of zeolites are exploited in **water softening and purification** applications. Zeolites can remove hardness ions ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) from water by exchanging them with sodium ions. They are also used in the **removal of heavy metals and radioactive ions from wastewater and nuclear waste**.

## Applications of Zeolites

**Detergents and Soaps** - Zeolites are used as builders in detergents and soaps, replacing phosphates, which can cause eutrophication in water bodies. Zeolites enhance the cleaning performance by softening the water and preventing the redeposition of dirt on the cleaned surfaces.

**Agriculture** - Zeolites are used as soil amendments and slow-release fertilizers. They can improve soil properties, enhance nutrient retention, and reduce the leaching of fertilizers. Zeolites are also used in animal feed as adsorbents to remove toxins and improve feed efficiency.

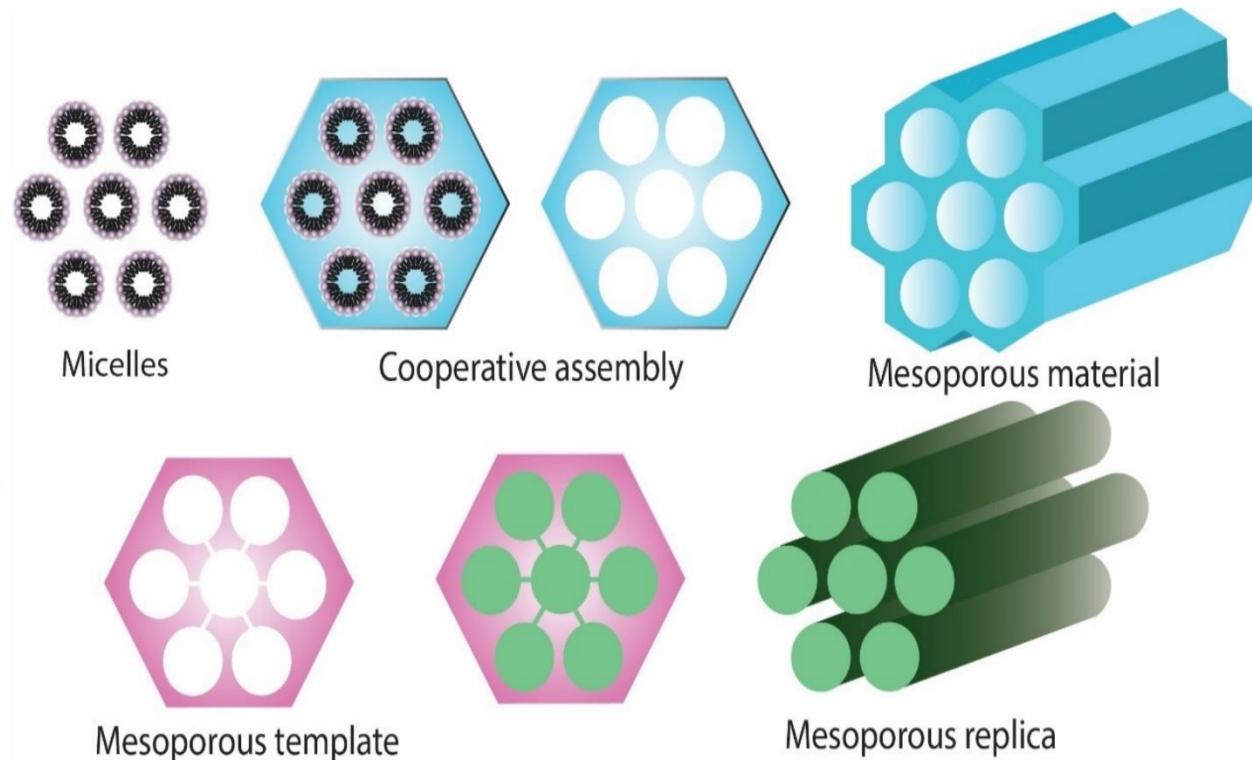
## Zeolites in Nanotechnology

- Zeolites can be used as hosts for the synthesis of metal nanoparticles and nanoclusters, providing size and shape control.
- Zeolite membranes with precise pore sizes can be used for molecular sieving and selective separations at the nanoscale.
- Zeolites can be used as templates for the synthesis of ordered mesoporous materials and carbon nanostructures.
- Nanozeolites with enhanced properties, such as higher surface area and improved diffusion, can be synthesized for catalytic and adsorption applications.

# Mesoporous materials

Go, change the world

**MESOPOROUS MATERIALS :** Mesoporous materials are a class of nanomaterials characterized by their highly ordered porous structure with pore sizes ranging from 2 to 50 nanometers. These materials possess large surface areas, tunable pore sizes and shapes, and high pore volume, making them attractive for a wide range of applications in catalysis, adsorption, separation, drug delivery, and energy storage



## Properties

**High Surface Area:** Mesoporous materials have large specific surface areas, typically ranging from 500 to 1500 m<sup>2</sup>/g, due to their nanoscale pores and high pore volume. This high surface area provides abundant active sites for catalysis, adsorption, and other surface-dependent processes.

**Tunable Pore Size and Shape:** The pore size and shape of mesoporous materials can be precisely controlled by adjusting the synthesis conditions and the choice of template. This tunability allows for the optimization of pore structure for specific applications, such as size-selective catalysis or controlled drug release.

**Diverse Composition:** Mesoporous materials can be synthesized from a wide range of inorganic and organic precursors, enabling the development of materials with various chemical compositions and functionalities. Examples include mesoporous silica, alumina, titania, carbon, and metal-organic frameworks (MOFs).

## Applications of Mesoporous Materials

**Catalysis** - They can enhance the activity, selectivity, and stability of catalytic processes by providing easy access to reactants and controlling the diffusion of products. Examples include mesoporous silica-supported metal catalysts for hydrogenation, oxidation, and coupling reactions.

**Adsorption and Separation** – They act as excellent adsorbents for the removal of pollutants, such as heavy metals, dyes, and volatile organic compounds, from water and air. They can also be used for the separation of gases and liquids based on size exclusion or specific interactions with the pore surface.

**Drug Delivery** - Mesoporous materials, particularly mesoporous silica nanoparticles (MSNs), have shown great potential as drug delivery vehicles. The porous structure allows for the loading of drug molecules, while the surface can be functionalized with targeting ligands or stimuli-responsive groups for controlled release.

**Energy Storage and Conversion** - used in various energy-related applications, such as lithium-ion batteries, supercapacitors, and fuel cells. They can serve as electrode materials or electrolyte additives, enhancing the charge transport, ionic conductivity, and electrochemical stability of the devices. Mesoporous carbons, in particular, have shown promise as high-performance electrode materials for supercapacitors.

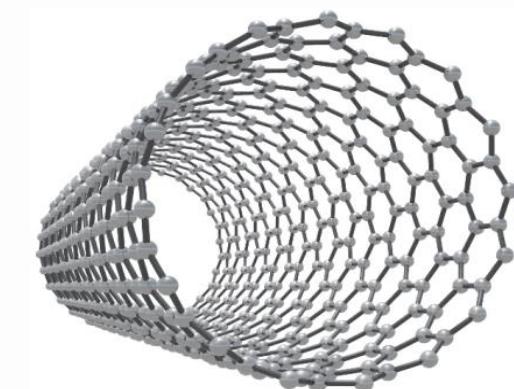
**CARBON NANOTUBES** - A carbon nanotube is a tube-shaped material, made of carbon, having a diameter measuring on the nanometer scale. It can be imagined as a rolled up sheet of graphene, which is a planar-hexagonal arrangement of carbon atoms distributed in a honeycomb lattice. A single layer of graphite sheet is called graphene.

**Types** - Single wall carbon nanotubes (SWCNT) and Multi wall carbon nanotubes (MWCNT)

**Single wall carbon nanotubes (SWCNT):** Single-wall nanotubes (SWNT) are tubes of graphite that are normally capped at the ends. They have a single cylindrical wall. The structure of a SWNT can be visualized as a layer of graphite, a single atom thick, **called graphene**, which is rolled into a seamless cylinder.

Most SWNT typically have a diameter of close to 1 nm. The tube length, however, can be many thousands of times longer. SWNT are more pliable yet harder to make than MWNT. They can be twisted, flattened, and bent into small circles or around sharp bends without breaking.

They have exceptional strength, and distinct electrical characteristics, and are effective heat conductors



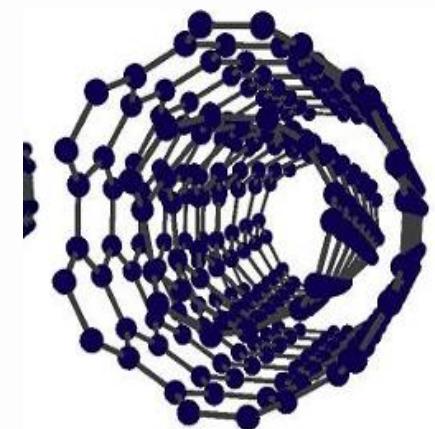
**Multi wall carbon nanotubes (MWCNT):** There are two structural models of multi wall nanotubes. In the Russian Doll model, a carbon nanotube contains another nanotube inside it (the inner nanotube has a smaller diameter than the outer nanotube).

In the Parchment model, a single graphene sheet is rolled around itself multiple times, resembling a rolled up scroll of paper. The simplest representative of a MWNT is a double walled carbon nanotube (DWNT).

Multi wall carbon nanotubes have similar properties to single wall nanotubes, yet the outer walls on multi wall nanotubes can protect the inner carbon nanotubes from chemical interactions with outside materials.

Multi wall nanotubes also have a higher tensile strength than single wall nanotubes. The diameters of MWNT are typically in the range of 5 nm to 50 nm. The interlayer distance in MWNT is close to the distance between graphene layers in graphite, around 3.39Ao.

MWNT are easier to produce than SWNT. However, the structure of MWNT is less well understood because of its greater complexity and variety. Regions of structural imperfection may diminish its desirable material properties.



Multi wall CNT

## Properties of carbon nanotubes

- CNTs have high mechanical strength such as high elastic modulus and hih tensile strength
- CNTs have high electrical conductivity
- CNTs have high thermal conductivity
- CNTs aspect ratio
- CNTs have very high stiffness and hardness
- CNTs are very elastic ~18% elongation to failure
- CNTs are highly flexible — can be bent considerably without damage
- CNTs have a low thermal expansion coefficient
- CNTs are good electron field emitters
- CNTs are stronger than steel and as rigid as a diamond.
- CNTs are have a very high melting point.
- The carbon nanotubes' density is one-fourth that of steel.
- They are exceptionally resistant to corrosion as, like graphite, they are highly chemically stable and can withstand almost any chemical reaction unless they are subsequently exposed to high temperatures and oxygen.

## Application of carbon nanotubes

Because of their unique characteristics, carbon nanotubes offer a wide range of possible applications. They can be utilized in a variety of applications, including electronics, textiles including water- and abrasion-resistant fabric, thermal conductivity-based sensors, and many more. They are excellent candidates for a variety of applications due to their superior thermal and electrical conductivity qualities. Some of the remarkable applications are discussed below:

- Attractive characteristics of carbon nanotubes (CNTs) include their high surface-to-volume ratios, improved conductivity & strength, biocompatibility, simplicity of functionalization, optical features, and more.
- CNTs have been employed successfully in pharmacy and healthcare to adsorb or synthesize a variety of therapeutic and diagnostic drugs attributed to their large surface area.
- Carbon nanotubes are used in thin-film electronics, actuators, coatings, water filters, automobile components, boat hulls, sporting goods, and electromagnetic shields.
- CNTs are attractive as drug delivery and biosensing operating systems due to their unique size, and chemical, optical, electrical, and structural properties, which have made them useful in the treatment of a wide range of diseases.

## Application of carbon nanotubes

- Nanotubes are utilized in aerospace and airplanes to reduce the overall load on the system as a whole.
- Due to their exceptional mechanical, electronic, thermal, barrier, and chemical properties, carbon nanotube-mediated nanocomposites have gained a lot of attention as promising replacements for more traditional composite materials.
- For a variety of electrochemical research as well as applications involving chemical and biological sensing, carbon nanotubes are frequently utilized as electrodes.
- Carbon nanotubes are highly attractive for catalysis due to their extraordinarily high surface area.

**GRAPHENE:** Graphene is the name for a single layer (monolayer) sheet of carbon atoms that are bonded together in a repeating pattern of hexagons. This sheet is only one atom thick. Monolayers of graphene stacked on top of each other form graphite. Since a typical carbon atom has a diameter of about 0.33 nanometers, there are about 3 million layers of graphene in a 1 mm thick sheet of graphite.

The extraordinary characteristics of graphene originate from the 2p orbitals, which form the  $\pi$  state bands that delocalize over the sheet of carbons that constitute graphene.

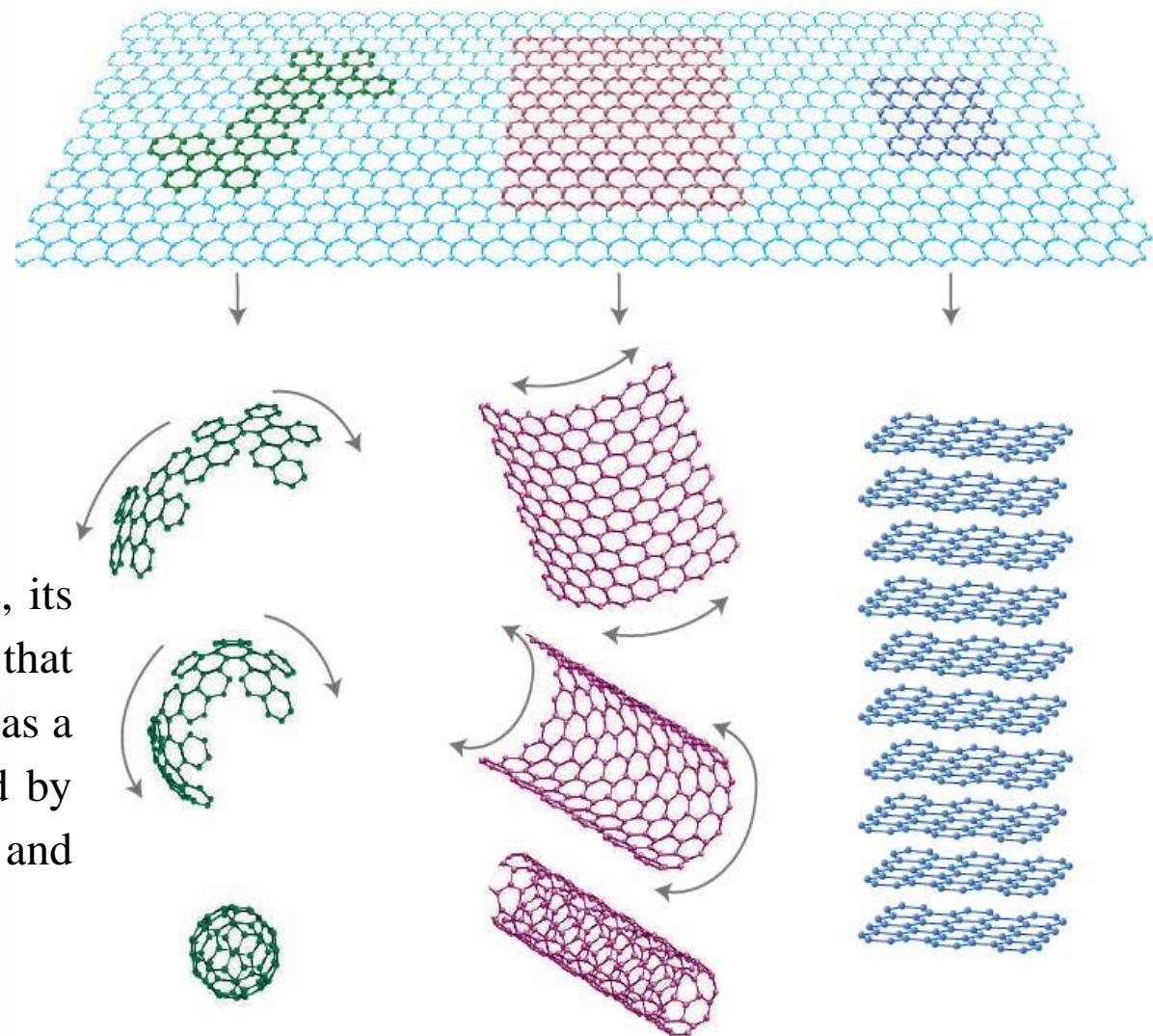
Harder than diamond yet more elastic than rubber; tougher than steel yet lighter than aluminum – graphene is the strongest known material.

Graphene represents a conceptually new class of materials that are only one atom thick, so-called two-dimensional (2D) materials (they are called 2D because they extend in only two dimensions: length and width; as the material is only one atom thick, the third dimension, height, is considered to be zero). And it is only at this single- or few-layer state that graphene's amazing properties appear.

Graphene is the basic building block for other graphitic materials like carbon nanotubes

**Fig.** Graphene sheets are building blocks for other graphitic materials. **Left:** Cut and folded into a spherical shape they make a C<sub>60</sub> fullerene molecule. **Middle:** rolled up they make a carbon nanotube. **Right:** Bonded on top of each other they make the bulk material graphite.

The impressive intrinsic mechanical properties of graphene, its stiffness, strength and toughness, are one of the reasons that make graphene stand out both as an individual material and as a reinforcing agent in graphene composites. They are caused by the stability of the sp<sup>2</sup> bonds that form the hexagonal lattice and oppose a variety of in-plane deformations.



**Electronic properties of graphene** - It is one of the best electrical conductors on Earth. The unique atomic arrangement of the carbon atoms in graphene allows its electrons to easily travel at extremely high velocity without the significant chance of scattering, saving precious energy typically lost in other conductors.

Scientists have found that graphene remains capable of conducting electricity even at the limit of nominally zero carrier concentration because the electrons don't seem to slow down or localize. That means that graphene never stops conducting. It was also found that they travel far faster than electrons in other semiconductors.

**Stiffness** - The breaking force obtained experimentally and from simulation was almost identical and the experimental value of the second order elastic stiffness was equal to  $340 \pm 50 \text{ N m}^{-1}$ . This value corresponds to a Young's modulus of  $1.0 \pm 0.1 \text{ TPa}$ , assuming an effective thickness of 0.335 nm.

**Strength** - Defect-free, monolayer graphene is considered to be the strongest material ever tested with a strength of  $42 \text{ N m}^{-1}$ , which equates to an intrinsic strength of 130 GPa.

**Toughness** - Research groups worldwide are working on the development of industrially manufacturable graphene sheets that have high strength and toughness in all sheet directions for diverse applications as graphene-based composites for vehicles, optoelectronics and neural implants.

**Nano-FRP** - Nano-FRP (Nano Fiber-Reinforced Polymer) innovations represent a cutting-edge field that combines nanotechnology with fiber-reinforced composites. These innovations leverage nanoscale materials and structures to enhance the performance, strength, and versatility of FRP composites. Here, are some examples of Nano-FRP innovations:

**Nanomaterial Reinforcements** - Integration of nanomaterials, such as carbon nanotubes, graphene, and nanoclays, into FRP composites. These reinforcements at the nanoscale level enhance mechanical properties, electrical conductivity, and thermal performance.

**Self-Healing Nanocomposites**: Development of self-healing Nano-FRP composites that utilize nanocapsules or nanoparticles to repair damage autonomously. Learn how these materials offer extended service life and reduced maintenance needs.

**Nanosensors and Structural Health Monitoring**: Incorporation of nanosensors into Nano-FRP structures for real-time structural health monitoring. Explore their use in detecting stress, strain, and damage to ensure early intervention and improved safety.

**Manufacturing Processes for FRPs** : Manufacturing processes for Fiber-Reinforced Polymers (FRPs) are at the heart of producing composite materials with tailored properties for diverse applications.

**NANO FABRICS** - Exploring the types of **nanomaterials** used in textiles reveals a fascinating array of substances that enhance fabric properties in remarkable ways.

One of the most versatile nanomaterials is **silver nanoparticles**. Known for their excellent **antimicrobial properties**, they help create fabrics that resist bacteria and odor, making them ideal for sportswear and medical textiles.

Another key player is **titanium dioxide**, which offers **self-cleaning** and **UV-protection capabilities**. These nanoparticles can be integrated into fabrics to break down dirt and provide sun protection, enhancing the longevity and usability of the garments.

**Carbon nanotubes (CNTs)** are also remarkable. They improve fabric strength and elasticity, making textiles more durable and flexible. This is particularly beneficial for high-performance and protective clothing.

Additionally, **silica nanoparticles** contribute to **fabric modification** by imparting water and stain resistance, ensuring that your clothes stay clean and dry.

**Advantages of Nanofabrics** - Nanotechnology's impact on fashion is transforming the industry by enabling the creation of smart, functional, and stylish garments. Nanotechnology allows designers to innovate in ways that align with consumer preferences for sustainable production and eco-friendly designs. The fashion industry is embracing these advancements to offer products that aren't only chic but also environmentally responsible. Here are some of the advantages of Nano Fabrics

- Self-cleaning fabrics
- UV protection
- Odor control
- Color retention
- Enhanced Durability
- Stain Resistance
- Environmental Impact
- Cost Effectiveness
- Longevity
- Versatility
- Durable Water Repellency
- Easy Cleaning Process

Bioresorbable means something can be broken down and absorbed by the body over time. The term is often used to describe materials used in medical devices, such as stents and stitches, that are designed to disappear after a certain amount of time.

Bioresorbable materials are also used in other applications, such as:

- **Bioresorbable electronics**

These include inorganic and organic transistors, resistors, inductors, antennas, capacitors, and diodes. They can be used in biomedical applications, such as antibacterial therapy, or to complement active components in more complex circuits.

- **Bioresorbable scaffolds**

These can be made from magnesium, zinc, and manganese to have similar mechanical properties to stainless steel stents.

- **Bioresorbable neurostimulators**

These can be used to treat compression peripheral nerve injury and CMT1A (hereditary peripheral neuropathy). The body can absorb, metabolize, and discharge the end products of bioresorbable materials without any abnormal responses.

Bioerodible materials are materials that break down through biological processes and are absorbed into surrounding tissue. They are often used in controlled drug delivery approaches. Here are some examples of biodegradable materials:

- **Polyanhydrides** - A synthetic polymer that is biocompatible and has a low toxicity profile. It is used in ocular drug delivery because of its unique biodegradation properties.
- **Polylactic acid (PLA)** - A bioplastic derived from renewable resources like corn starch or sugarcane. It is used in a variety of applications, including bone tissue engineering.
- **Polyphosphazenes** - A hybrid polymer with a backbone of alternating phosphorus and nitrogen atoms.

**Other examples** of biodegradable materials include – Wood, Wool, Cotton, Animal waste, Beeswax, Biodegradable athletic footwear, Biodegradable polythene film, BioSphere Plastic  
Biodegradable materials break down into carbon dioxide and water when exposed to sufficient water, oxygen, nutrients, and temperature.

**Nano ceramics** - Nanoceramics consist of ceramic materials composed of structural microscopic units, with at least one dimension in the nanoscale range (less than 100 nm). These structural units may include nanoparticles, nanotubes, nanorods, or nanoscale thin films. Nanoceramics have superior mechanical properties, such as high strength, excellent toughness, and fatigue resistance.

The **sol-gel process** is a key method for creating nanostructured ceramic materials, enabling the development of advanced materials with tailored properties for various applications. This process involves controlled hydrolysis and polycondensation of silica and alkoxides, resulting in nanoscale particles that form a nanoporous network after gelation. Depending on the aging and drying conditions, the process can yield either dense ceramic composites or nanoporous materials.

## Properties

- Superior strength, excellent toughness, fatigue resistance, electro-optical capabilities, and piezoelectric properties
- Poor ductility and machinability

## Applications of Nanoceramics

**Medical** – Nanoceramics are among the most widely utilized advanced materials used in biomedical applications. In regenerative medicine, particularly in **nanofiber scaffolding** and the modification of nanotopography in nanoparticles and scaffolds.

**Bioactive glass nanoceramics** (n-BGC), exhibit superior osteointegration properties highly effective for implants. Their topographical features and surface chemistry promote bone healing by facilitating extracellular matrix (ECM) secretion at injury sites. Additionally, nanoceramics with smaller pore structures facilitate osteochondral formation.

**Bioresorbable nanoceramics** - primarily based on calcium phosphate (CaP) can be shaped to fit different needs and release calcium and phosphate ions in biological fluids, regulating osteogenic cell functions. Doping these materials with ions like  $Mg^{2+}$  further enhances osteogenesis and remodeling by reducing crystallinity.

**Bio-inert nanoceramics**, including materials based on titanium, alumina, and zirconia, are valued for their bio-inertness, fracture toughness, and high mechanical strength in biological environments. Titanium and its alloys are particularly significant in bone tissue reconstruction due to their excellent corrosion resistance.

## Applications of Nanoceramics

A specialized form of nanoceramics - zirconia–yttria ceramics, also known as Tetragonal Zirconia Polycrystals (TZP) or Yttria-stabilized zirconia (YSZ), is crucial in **bone tissue engineering**. These materials are widely used as artificial bone fillers in dental crowns, prostheses, joint heads for knees and hips, tibial plates, and temporary supports.

Nanoceramics are also significant in tissue engineering, bioimaging, and drug delivery, where their structure and chemistry can be customized to control degradation rates, matching the pace of tissue growth. Often, these materials are combined with polymers to create nanocomposites with enhanced mechanical properties and improved biological performance.

Nanoglasses are a new class of noncrystalline solids that have a microstructure similar to polycrystals. They are made by consolidating nanometer-sized glassy clusters to create a solid material with a high density of interfaces between glassy regions.

Nanoglasses have a number of unique properties, which includes :

- **Different atomic and electronic structure** - Nanoglasses have a different electronic structure and a reduced number of nearest-neighbor atoms and density compared to melt-quenched glasses.
- **New properties** - Nanoglasses can have new properties, such as being more ductile, biocompatible, and catalytically active than melt-quenched glasses.
- **Composition and size** - The properties of nanoglasses can be modified by controlling the size of the glassy regions and/or by varying their chemical composition.

**Synthesis** - Nanoglasses can be synthesized by thermal evaporation inert gas condensation (IGC). IGC can produce near-bulk sample sizes, but the sizes are limited to the powder yield.

**Characterization** - Nanoglasses can be characterized using a variety of techniques, including X-ray diffraction (XRD), transmission electron microscopy, and Mössbauer spectroscopy.

Nanobiomaterial is defined as a nonviable material used in a medical device that is intended to interact with biological systems. The high-surface area, nano-sized (1-100 nm) biomaterial particles find many applications in tissue engineering, cancer therapy, drug and gene delivery, medical imaging and many more in biomedical field.

Nanobiomaterials have been widely accepted as potential drug delivery agents over the past decade. A wide variety of materials have been utilized as drug delivery carriers for various diseases like Cancer, Alzheimer's etc. Being the leading cause of death worldwide, effective drug delivery to cancer cells by using nanomaterials has become the most fascinating and dynamic regions of research. The decreased size of these materials increased permeability through physiological barriers, and increased cell to cell interactions are the properties that are highly suitable for drug delivery applications.

Biocompatibility and biodegradability are added advantages of using nano biomaterials as drug delivery systems

Nano implant-associated materials are a fascinating area of research, especially in the field of biomedical engineering. These materials are engineered at the nanoscale to enhance the performance, biocompatibility, and longevity of implants. Here are some key points about nano implant-associated materials:

**Nanoparticles:** These are used to improve the surface properties of implants, promoting better cell adhesion, proliferation, and differentiation. For example, silver nanoparticles are known for their antimicrobial properties, which help reduce the risk of infections.

**Nanocoatings:** These coatings can be applied to implants to provide sustained antimicrobial activity, inhibit bacterial colonization, and promote faster healing.

**Bioactive Coatings:** These coatings enhance osseointegration (the integration of the implant with bone) and reduce the risk of implant-associated complications.

**Biodegradable Materials:** These materials are used for temporary implants, as they can be absorbed by the body over time, eliminating the need for secondary surgeries to remove the implant.

Nano implant-associated materials offer unique characteristics such as high surface area-to-volume ratios and tunable physicochemical properties, making them highly effective for various biomedical applications.

# Characterization of Nanomaterials

## Characterization of Nanomaterials:

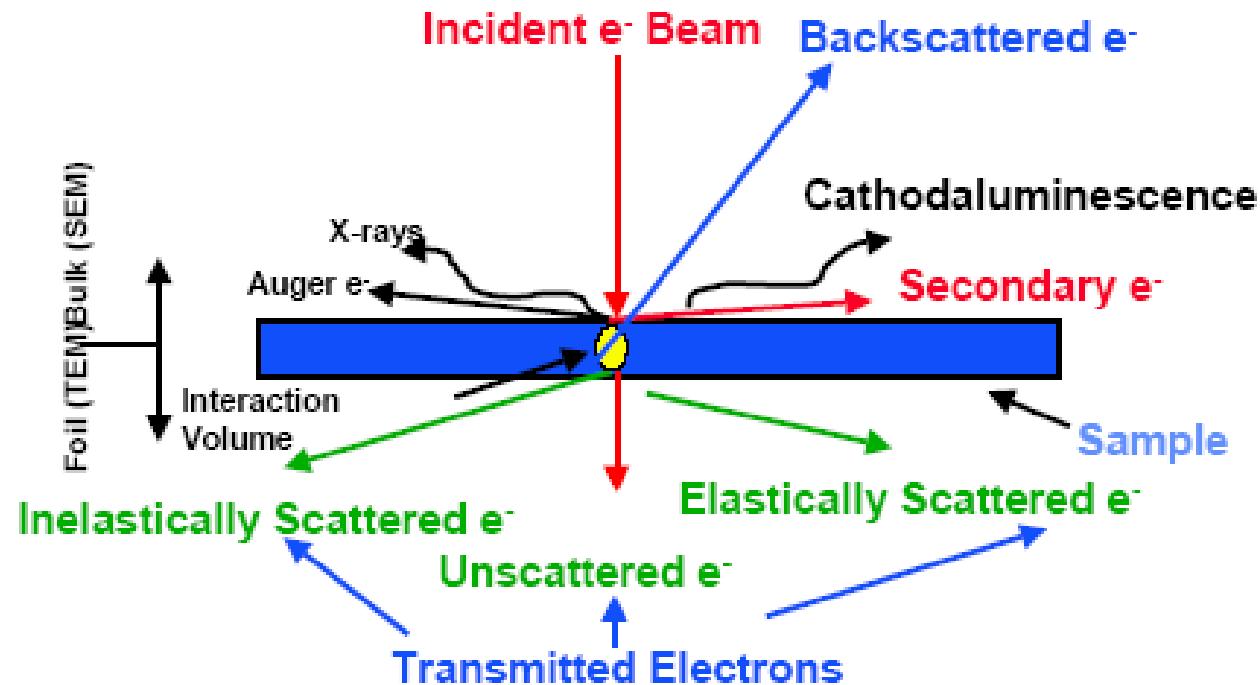
- ❖ Characterization refers to the study of materials features such as its composition, structure.
- ❖ Characterization of nanomaterials involve determining the structural, optical, electrical, magnetic, and mechanical properties, depending on their applications.
- ❖ **Structural characterization involves:**
  - ✓ Determining the morphology (shape and size) of nanomaterials.
  - ✓ Arrangement of atoms (crystal structure).
  - ✓ Material composition of nanomaterials.
- ❖ **Optical characterization involves:**
  - ✓ Determining the light emission and light absorption characteristics of the structures.

## Electron Probe Characterization Techniques:

Acronym	Technique	Utility
<b>SEM</b>	Scanning Electron Microscopy	Raster Imaging / Topology and Morphology
<b>TEM</b>	Transmission Electron Microscopy	Imaging / Particle Size-Shape
<b>HRTEM</b>	High Resolution Transmission Electron Microscopy	Imaging Structure Chemical Analysis
<b>STEM</b>	Scanning Transmission Electron Microscopy	Biological Samples
<b>EPMA</b>	Electron Probe Microanalysis	Particle Size / Local Chemical Analysis
<b>LEED</b>	Low Energy Electron Diffraction	Surface / Adsorbate Bonding

## 2.1 Electron-Solid Interactions

When an electron beam strikes a sample, a large number of signals are generated.

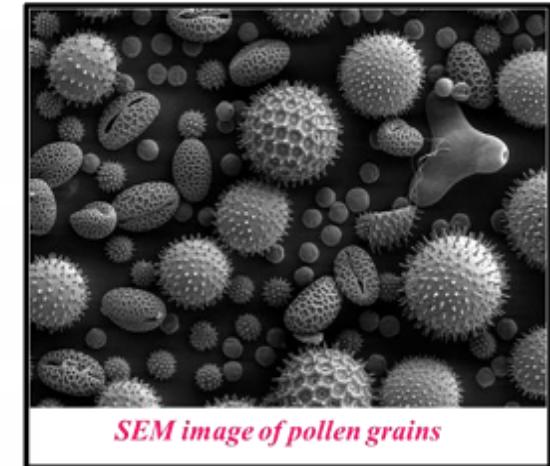


We can divide the signals into two broad categories:

- a) electron signals, b) photon signals

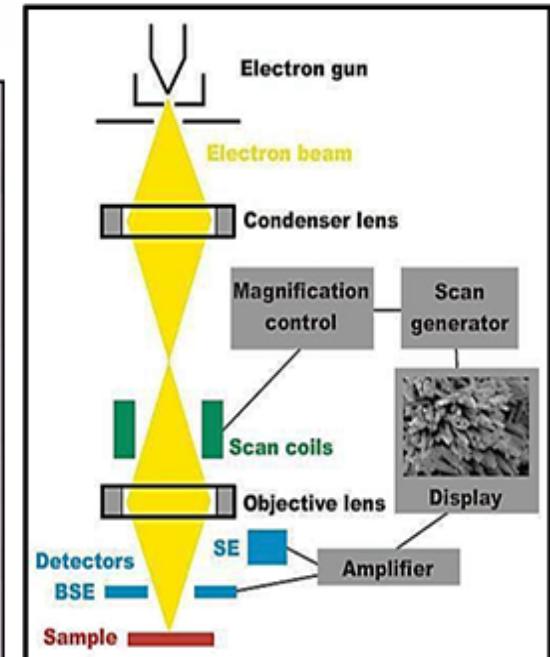
## Three Modes of Operation:

- Primary**
  - High resolution (1-5nm).
  - Secondary electron imaging.
- Secondary**
  - Generates characteristic X-rays.
  - Identification of elemental composition of sample by EDX technique.
- Tertiary**
  - Generates back-scattered electronic images.
  - Clues to the elemental composition of sample.



SEM image of pollen grains

- Electronic devices are used to detect & amplify the signals & display them as an image on a cathode ray tube in which the raster scanning is synchronized with that of microscope.
- In SEM, beam passes through pairs of scanning coils or pairs of deflector plates in the electron column to the final lens, which deflect the beam horizontally & vertically.
- The image displayed is therefore a distribution map of the intensity of the signal being emitted from the scanned area of the specimen.

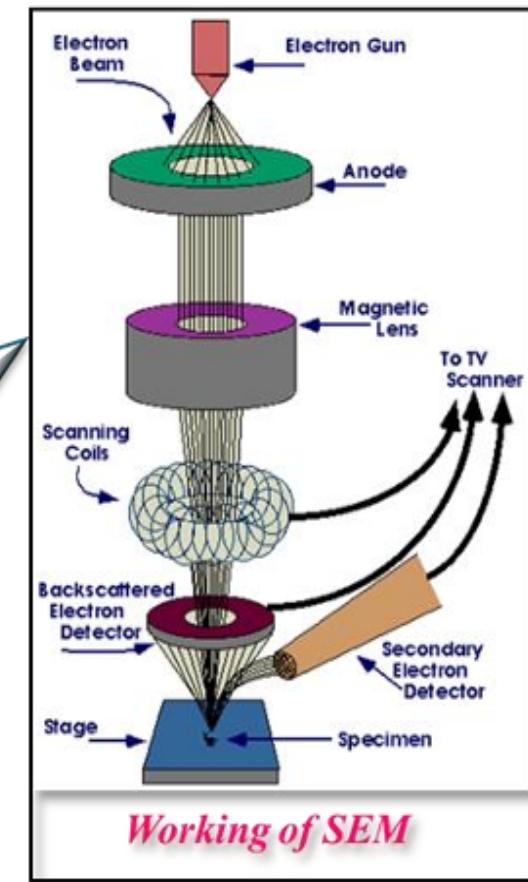


## Scanning Electron Microscopy (SEM):

SEM is a type of electron microscope that images a sample by scanning it with a high energy beam of electrons in a raster scan pattern.

### Basic Principle:

When beam of electrons strikes the surface of specimen & interacts with the atoms of sample, signals in the form of secondary electrons, back scattered electrons & characteristic X-rays are generated that contain information about the samples' surface topography, composition etc.



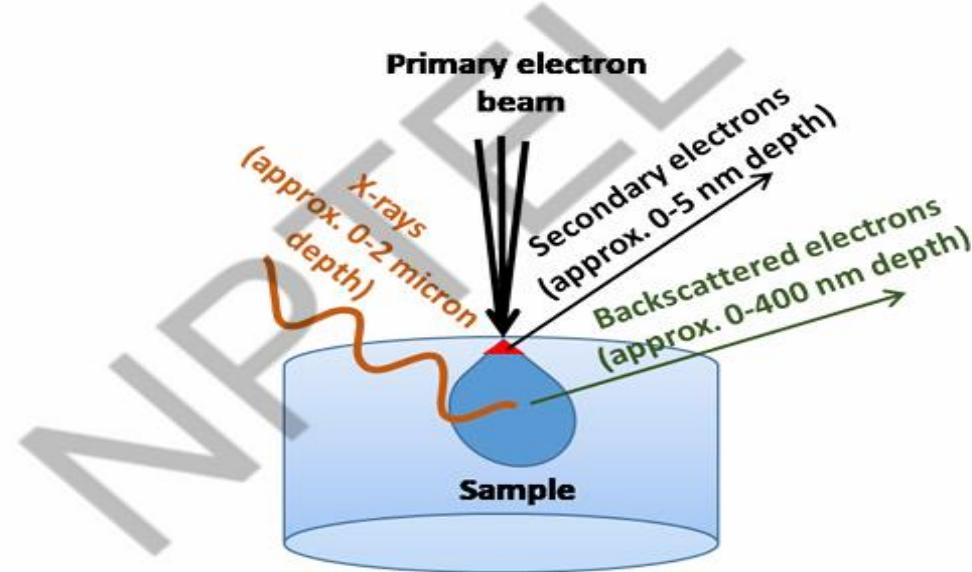
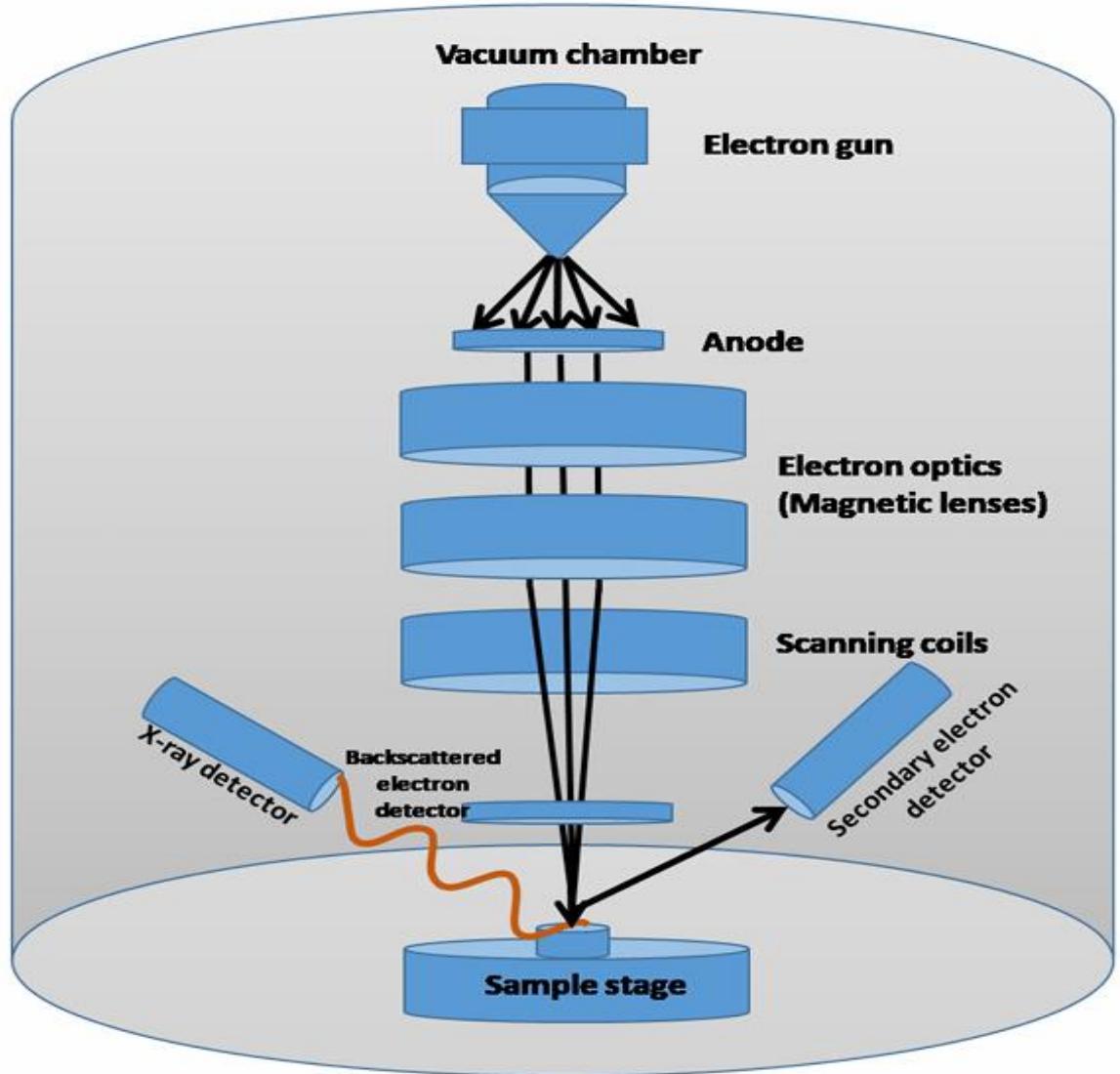
### What we can see with SEM?

- **Topography:** Texture/surface of a sample.
- **Morphology:** Size, shape, order of particles.
- **Composition:** Elemental composition of sample.
- **Crystalline Structure:** Arrangement present within sample.



# Scanning Electron Microscopy (SEM)

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**Secondary electron imaging (SEI): mainly topography contrast**

**Backscattered electron imaging (SEI): mainly material contrast**

**Energy-dispersive X-ray spectroscopy (EDX): elemental analysis**

## Principle:

- In the scanning electron microscope (SEM) electrons are made to fall on the sample and the scattered or generated electrons are detected. The SEM is usually operated with an acceleration voltage of 1K V to 40 K V for the electrons.
- The incoming electrons interact with the sample on a depth of  $\sim 1\mu\text{m}$ .
- This electron beam generates a number of different types of signals, which are emitted from the area of the specimen where the electron beam is impinging.
- The induced signals are detected and the intensity of one of the signals (at a time) is amplified and used to as the intensity of a pixel on the image on the computer screen.
- The electron beam then moves to next position on the sample and the detected intensity gives the intensity in the second pixel and so on.
- This produces an image with depth-of-field which is usually 300-600 times better than that of an optical microscope, and also enables a three-dimensional image to be obtained.

**Construction:** A schematic of typical SEM is shown in the figure.

- Electrons thermionically emitted from a tungsten filament (cathode) are drawn to an anode and focused by two successive magnetic lenses into a beam with a very fine spot size that is typically  $10\text{\AA}$  in diameter.
- Pairs of scanning coils located at the objective (magnetic) lens deflect the beam either linearly or in raster fashion over a rectangular area of the specimen surface.
- Upon impinging on the specimen, the primary electrons decelerate and several processes such as elastic scattering *viz.*, forward scattering and backscattering of the incoming electrons and inelastic scattering *viz.*, generation of secondary electrons, Auger electrons, bremsstrahlung, characteristic x-rays, electron-hole pairs (in insulators and semiconductors), long-wavelength electromagnetic radiation.
- A number of different types of signals, which are emitted from the area of the specimen where the electron beam is impinging, is as shown in slide no 86.
- Various SEM techniques are differentiated on the basis of what is subsequently detected and imaged, and the principle images produced in the SEM are of three types:
- i) Secondary electron images ii) Backscattered electron images and iii)- Elemental X-ray maps.

- The secondary electrons are the electrons which are generated from the surface of the specimen when it is bombarded by high energy primary electrons. These electrons are collected by detector which creates a pattern of light and dark areas in CRT corresponding to the emission of secondary electrons from the specimen. As the number of electrons produced at any given point can be related directly to the topography of the specimen with respect to the detector, the patterns created on the viewing screen represent the surface topography of the specimen.
- Backscattered electrons are the high energy electrons that are elastically scattered and essentially possess the same energy as the incident or primary electrons. The probability of backscattering increases with the atomic number of the sample material. Therefore the primary electrons arriving at a given detector position can be used to yield images containing information on both topology and atomic composition.
- An additional electron interaction in the SEM is that the primary electron collides with and ejects a core electron from an atom in the sample. The excited atom will decay to its ground state by emitting either a characteristic X-ray photon or an Auger electron. By analyzing energies of characteristic of the x-ray photon the atoms can be identified. Further the concentration of atoms in the specimen can be determined by counting the number of X-rays emitted.

## Advantages:

- ✓ Bulk-samples can be observed and larger sample area can be viewed.
- ✓ Generates photo-like images.
- ✓ Very high-resolution images are possible.
- ✓ SEM can yield valuable information regarding the purity as well as degree of aggregation.

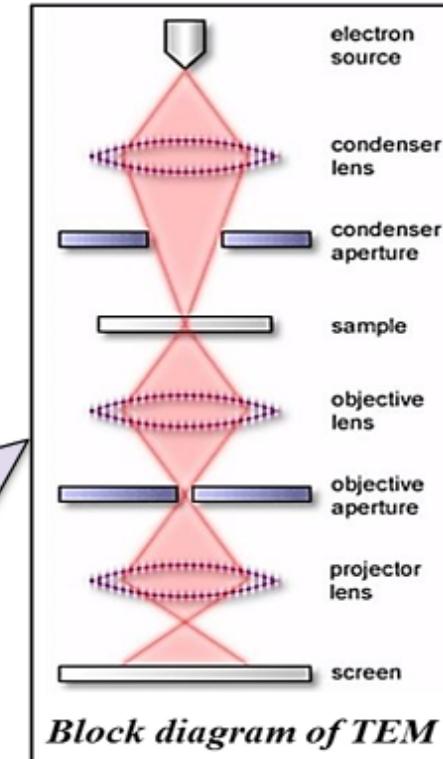
## Disadvantages:

- ✓ Samples must have surface electrical conductivity
- ✓ Non-conductive samples need to be coated with a conductive Layer
- ✓ Time consuming & expensive.
- ✓ Sometimes it is not possible to clearly differentiate nanoparticle from the substrate.
- ✓ SEM can't resolve the internal structure of these domains.

## Transmission Electron Microscopy (TEM):

### Principle:

- Crystalline sample interacts with electron beam mostly by diffraction rather than absorption.
- Intensity of diffraction depends on the orientation of planes of atoms in a crystal relative to electron beam.
- High contrast image can be formed by blocking deflected electrons which produces a variation in electron intensity that reveals information on the crystal structure.
- This generate both bright or light field & dark field images.



**What can  
be seen with  
TEM ?**

### Morphology:

- Shape, size, order of particles in sample.

### Crystalline Structure:

- Arrangement of atoms in sample & defects in crystalline structure.

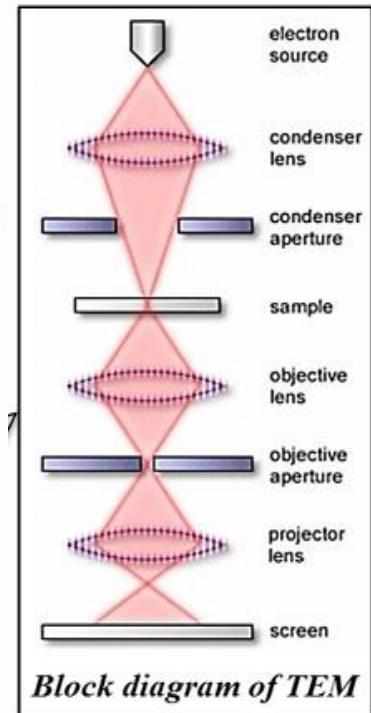
### Composition:

- Elemental composition of the sample.



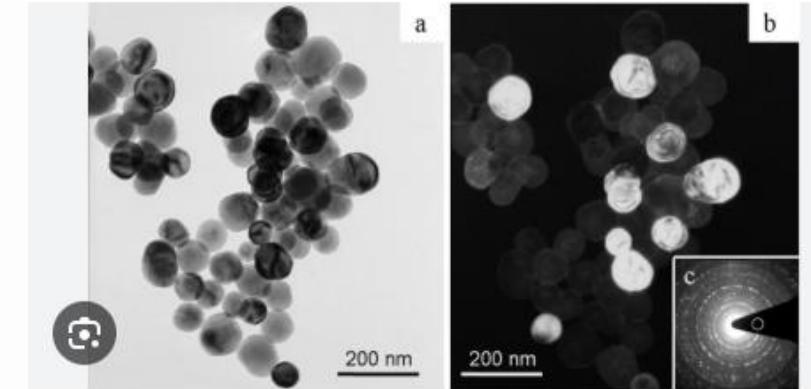
## Principle :

- Transmission Electron Microscopy (TEM) is a technique where an electron beam interacts and passes through a specimen. The electrons are emitted by a source and are focused and magnified by a system of magnetic lenses. The geometry of TEM is shown in figure.
- The electron beam is confined by the two condenser lenses which also control the brightness of the beam, passes the condenser aperture and “hits” the sample surface.
- The electrons that are elastically scattered consist the transmitted beams, which pass through the objective lens.
- The objective lens forms the image display and the following apertures, the objective and selected area aperture are used to choose of the elastically scattered electrons that will form the image of the microscope.
- Finally the beam goes to the magnifying system, consisted of three lenses, the first and second intermediate lenses which control the magnification of the image and the projector lens. The formed image either on a fluorescent screen or in monitor or both and is printed on a photographic film.



**Operation** - The operation of TEM requires an ultrahigh vacuum and a high voltage.

- The first step is to find the electron beam, so the lights of the room must be turned off. Through a sequence of buttons and adjustments of focus and brightness of the beam, we can adjust the settings of the microscope so that by shifting the sample holder find the thin area of the sample.
- Then tilting of the sample begins by rotating the holder. This is a way to observe as much areas as we can, so we can obtain as much information.
- Different types of images are obtained in TEM, using the apertures properly and the different types of electrons. Diffraction patterns are shown due to the scattered electrons.
- If the unscattered beam is selected, we obtain the **Bright Field Image**.
- Dark Field Images** are attained if diffracted beams are selected by the objective aperture. In transmission microscopy, we can actually see the specimen's structure and its atomic columns, thus compositional and crystallographic information is attained.
- However, is a very expensive technique, expertise is needed and the sample preparation phase is too difficult so that very thin samples are achieved.

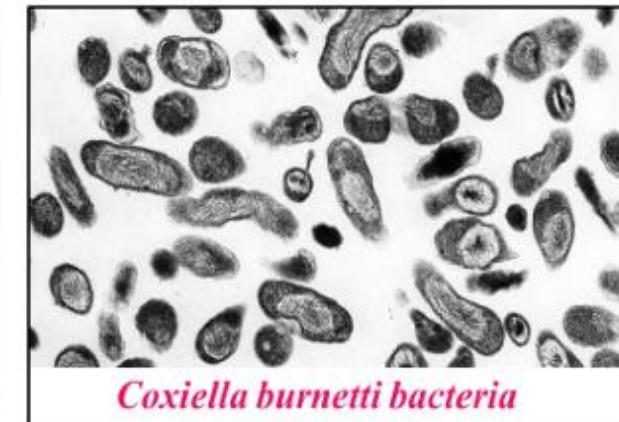


a) Bright-field and (b) dark-field TEM

[Visit >](#)

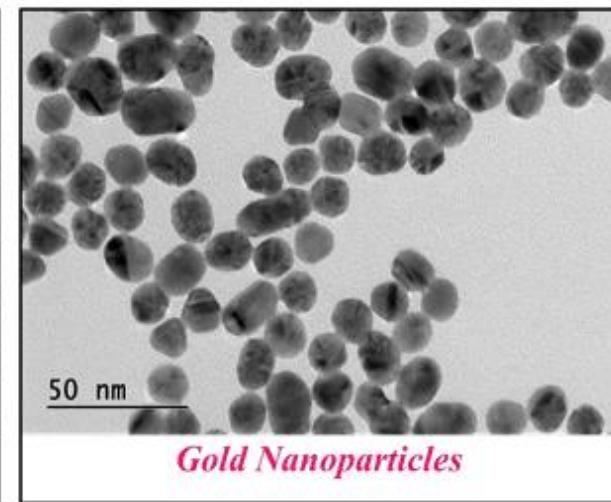
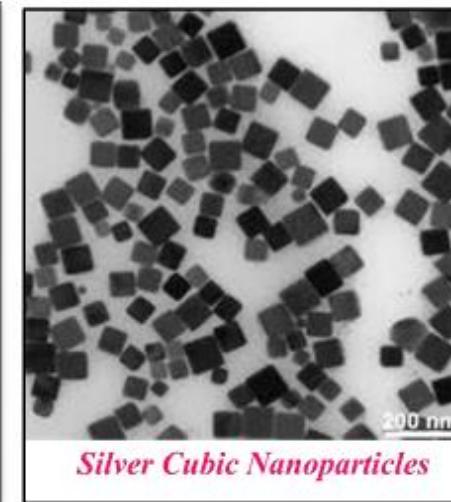
## Advantages:

- ✓ High **magnification** (*ability to enlarge an image*) & **resolution** (*ability to distinguish two very close object as separate images*).
- ✓ Provide information about internal ultrastructure of cells.
- ✓ Images are high quality and detailed.



## Disadvantages:

- ✓ TEMs are large and very expensive.
- ✓ Laborious sample preparation.
- ✓ Operation and analysis requires special training.
- ✓ Sample are limited to those that are electron transparent.
- ✓ TEMs require special housing and maintenance.
- ✓ Images are black and white.

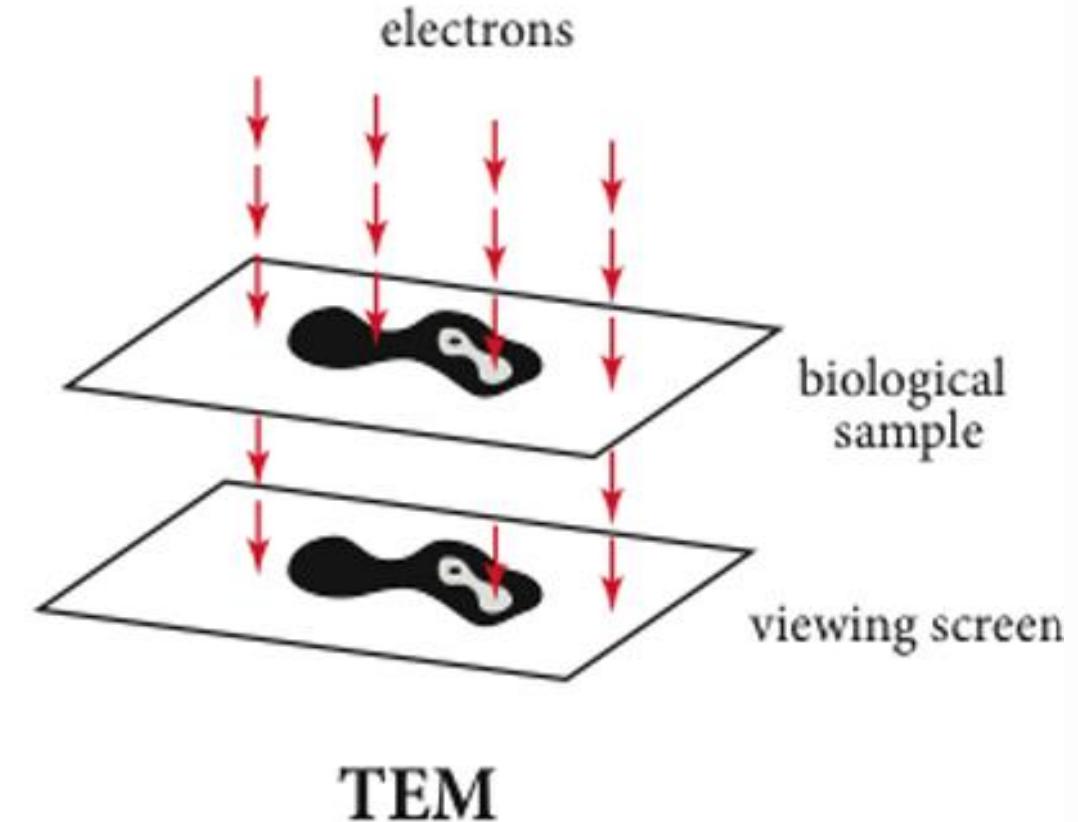
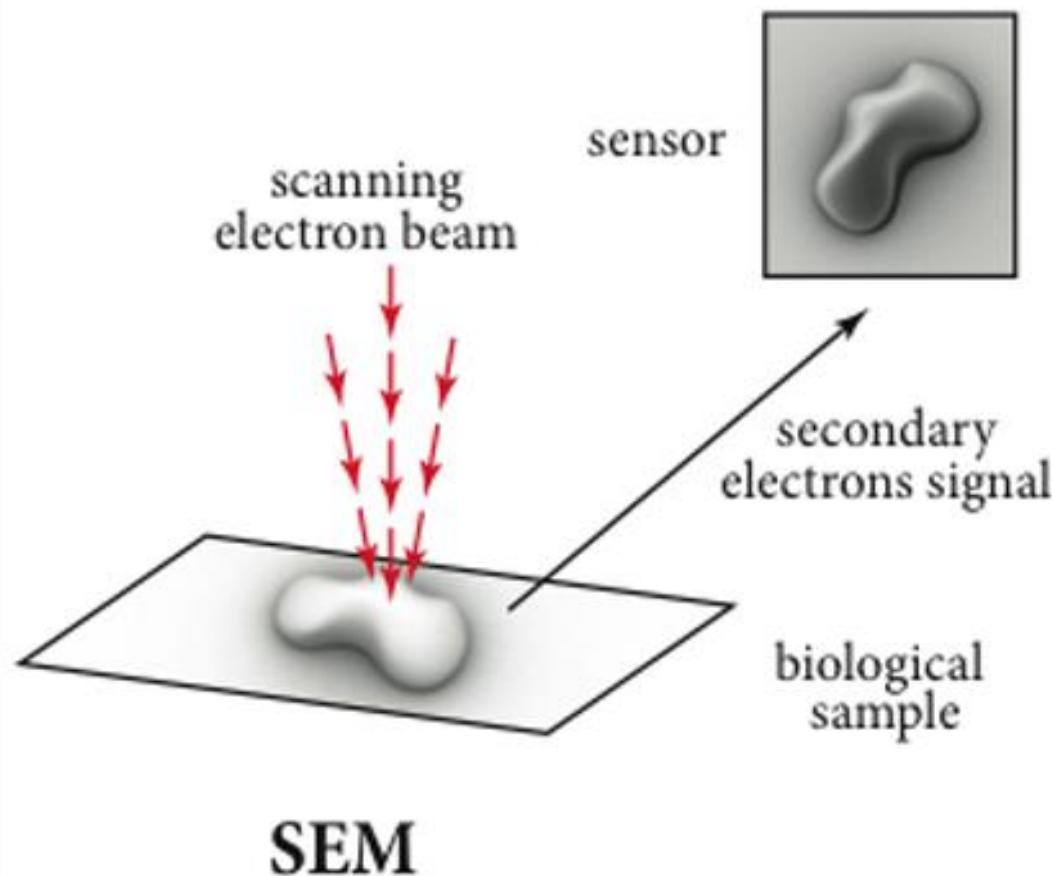


## Different TEM Images

# TEM vs SEM

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	TEM	SEM
<b>Beam voltage</b>	100-400 kV	1- 30 kV
<b>Focus of analysis</b>	Internal or beyond surface	Surface of sample
<b>Modes</b>	Broad beams and scanning probe	Scanning probe
<b>Smallest probe</b>	0.5 nm (5 Å) using STEM	~ 1 nm (10 Å)
<b>Best resolution</b>	0.14 nm (1.4 Å) lattice imaging	~ 1 nm (10 Å)
<b>Contrast</b>	Forward scattered electrons	Secondary emission and backscattered electrons
<b>Insulators</b>	No charging	Charging effects
<b>Sample thickness</b>	10-200 nm (100-2000 Å)	1-10 mm
<b>Sample diameter</b>	< 3 mm across	Full wafers
<b>Minimum preparation time</b>	~ 4 hours	< 1 min
<b>Image presentation</b>	2-D	3-D
<b>Display of image</b>	On TV monitor	On fluorescent screen



**Atomic Force Microscopy (AFM)** - The Atomic Force Microscope (AFM) is being used to solve processing and materials problems in a wide range of technologies affecting the electronics, telecommunications, biological, chemical, automotive, aerospace, and energy industries.

The materials being investigating include thin and thick film coatings, ceramics, composites, glasses, synthetic and biological membranes, metals, polymers, and semiconductors.

The AFM is being applied to studies of phenomena such as abrasion, adhesion, cleaning, corrosion, etching, friction, lubrication, plating, and polishing.

By using AFM one can not only image the surface in atomic resolution but also measure the force at nano-newton scale. The force between the tip and the sample surface is very small, usually less than  $10^{-9}$  N. Monitoring such small forces is very crucial and important.

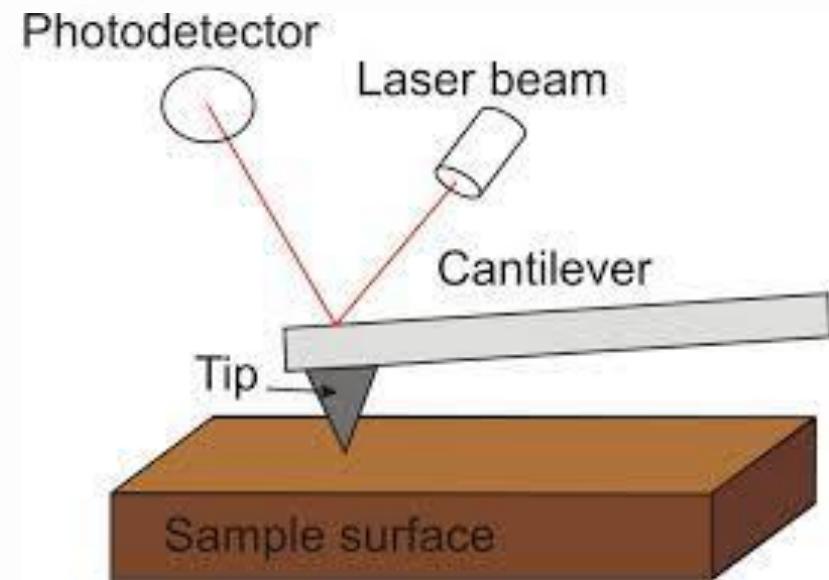
The detection system does not measure force directly. It senses the deflection of the micro cantilever. This is a sensitive system where a change in spacing of 1 Å between tip and cantilever changes the tunneling current by an order of magnitude.

It is straightforward to measure deflections smaller than 0.01 Å.

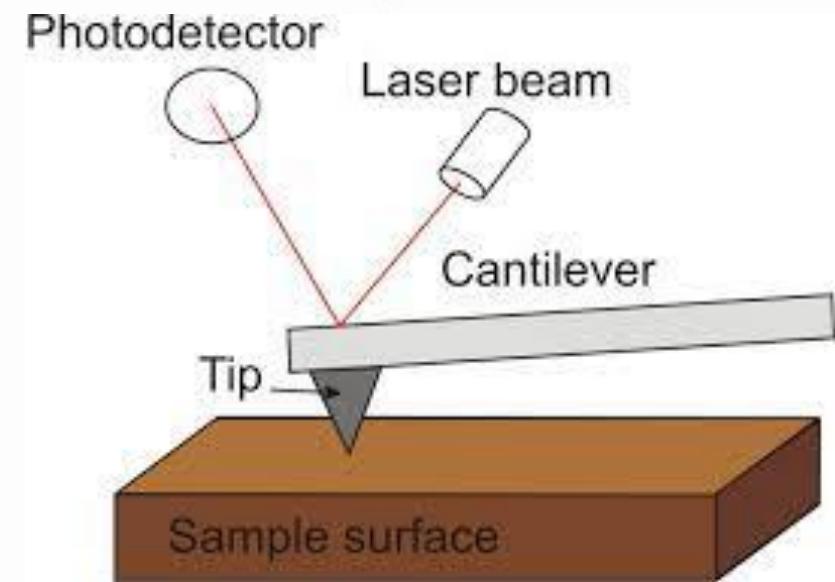
Principle : Subsequent systems were based on the optical techniques. In this system an optical beam is reflected from the mirrored surface on the back side of the cantilever onto a position-sensitive photo detector. In this arrangement a small deflection of the cantilever will tilt the reflected beam and change the position of beam on the photo detector. It is straightforward to measure deflections smaller than  $0.01 \text{ \AA}$ .

**Operation** - The principles on how the AFM works are very simple.

- An atomically sharp tip is scanned over a surface with feedback mechanisms that enable the piezo-electric scanners to maintain the tip at a constant force (to obtain height information), or height (to obtain force information) above the sample surface.
- Tips are typically made from  $\text{Si}_3\text{N}_4$  or Si, and extended down from the end of a cantilever.
- The Nano scope AFM head employs an optical detection system in which the tip is attached to the underside of a reflective cantilever.

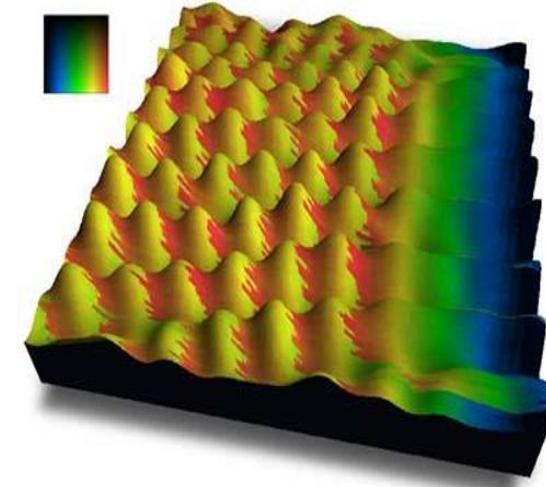


- A diode laser is focused onto the back of a reflective cantilever.
- As the tip scans the surface of the sample, moving up and down with the contour of the surface, the laser beam is deflected off the attached cantilever into a dual element photodiode.
- The photo detector measures the difference in light intensities between the upper and lower photo detectors, and then converts to voltage.
- Feedback from the photodiode difference signal, through software control from the computer, enables the tip to maintain either a constant force or constant height above the sample.
- In the constant force mode the piezo-electric transducer monitors real time height deviation is recorded .
- In the constant height mode the deflection force on the sample is recorded.



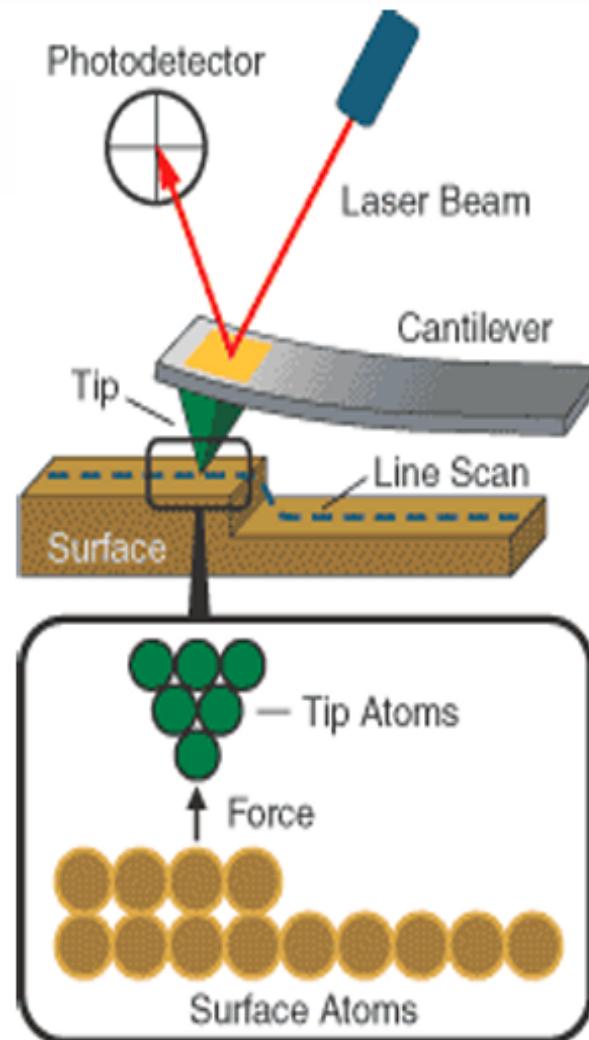
The latter mode of operation (Constant height) requires calibration parameters of the scanning tip to be inserted in the sensitivity of the AFM head during force calibration of the microscope.

- Some AFM's can accept full 200 mm wafers.
- The primary purpose of these instruments is to quantitatively measure surface roughness with a nominal 5 nm lateral and 0.01nm vertical resolution on all types of samples.
- Depending on the AFM design, scanners are used to translate either the sample under the cantilever or the cantilever over the sample.
- By scanning in either way, the local height of the sample is measured. Three dimensional topographical maps of the surface are then constructed by plotting the local sample height versus horizontal probe tip position.

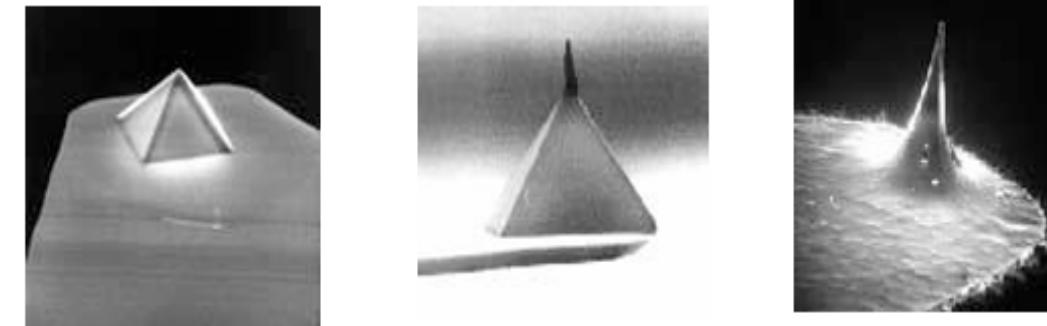


2.5 x 2.5 nm simultaneous topographic and friction image of highly oriented pyrolytic graphite (HOPG). The bumps represent the topographic atomic corrugation, while the coloring reflects the lateral forces on the tip. The scan direction was right to left

## How it works?



- Cantilever
- Tip
- Surface
- Laser
- Multi-segment photodetector



Three common types of AFM tip. (a) normal tip (3  $\mu\text{m}$  tall); (b) supertip; (c) Ultralever (also 3  $\mu\text{m}$  tall). Electron micrographs by Jean-Paul Revel, Caltech. Tips from Park Scientific Instruments; supertip made by Jean-Paul Revel.

[http://www.molec.com/what\\_is\\_afm.html](http://www.molec.com/what_is_afm.html)

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



The End