

Module-5: Functional materials

- Classification based on heat response and conducting electricity, Polymers (ABS and BAKELITE)- synthesis and application,
- Conducting polymers- polyacetylene and effect of doping.
- Nano materials – introduction (classification and properties(Surface area effect and Quantum effect),
- Top-down and bottom-up approaches for synthesis (Ball mill and sol gel) - bulk vs nano (gold)

Introduction to Polymers

- Polymers are **encountered in everyday life** and are **used for many purposes**.
- Grocery bags, soda and water bottles, textile fibers, phones, computers, food packaging, auto parts, and toys all **contain polymers**.



Introduction to Polymers

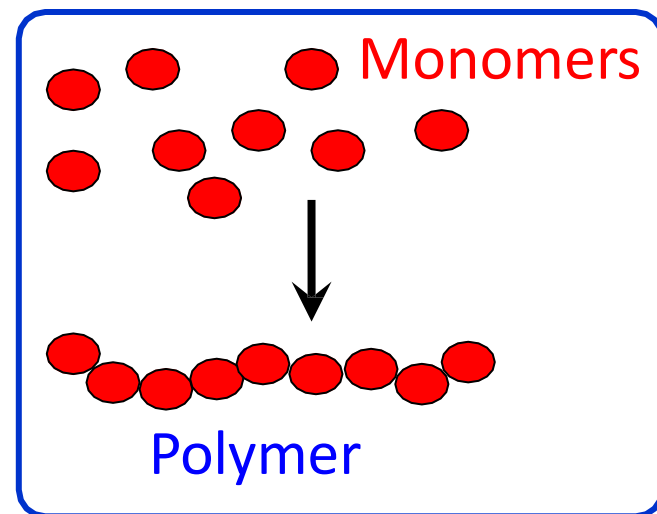
Polymers: Poly + mers

Poly means **many**

mers means **units** or **parts**

Polymers - **Many repeated parts**

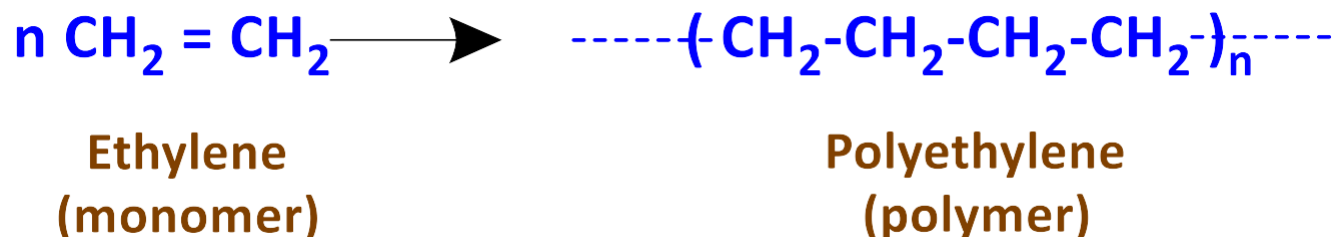
- or **many repeated units**



Definition of Polymer

Polymers are macromolecules (giant molecules of higher molecular weight) formed by the repeated linking of large number of small molecules called **monomers**.

Example:

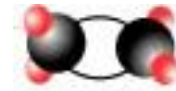


Definition

Polymers are materials made of long, repeating chains of molecules. The materials have unique properties, depending on the type of molecules being bonded and how they are bonded.

Terminology

Monomer : one unit (A)

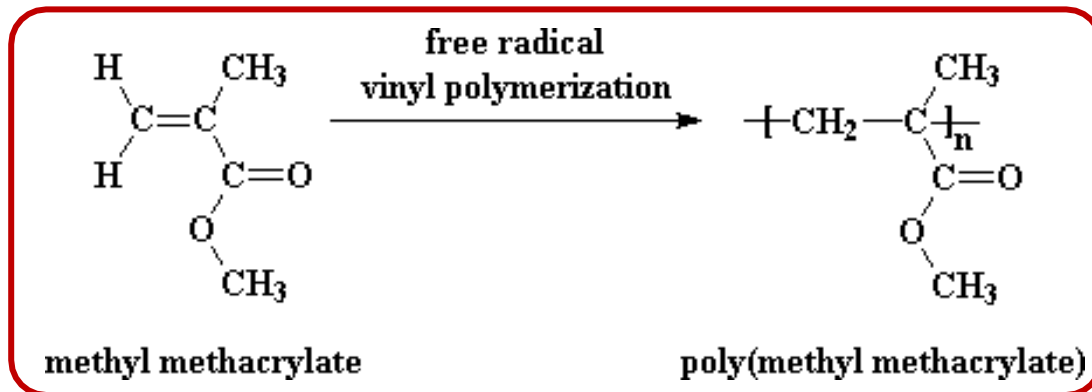


Dimer : two units (A-A)

Trimer : three units (A-A-A)

Tetramer : four units (A-A-A-A)

Polymer : many units $(-A-A-A-A-A-A-A-A-A-A-A-A-A-)_n$



Polymer – Classification

Polymers are classified based on different parameters

1. Based on “**Occurrence**”

- Natural polymers (e.g. Silk)
- Synthetic polymers (e.g. Nylon)
- Semi-synthetic polymers (e.g. vulcanized rubber)

2. Based on “**Type of polymerization**”

- Addition polymers (e.g. Polyethylene)
- Condensation polymers (e.g. Polyester)

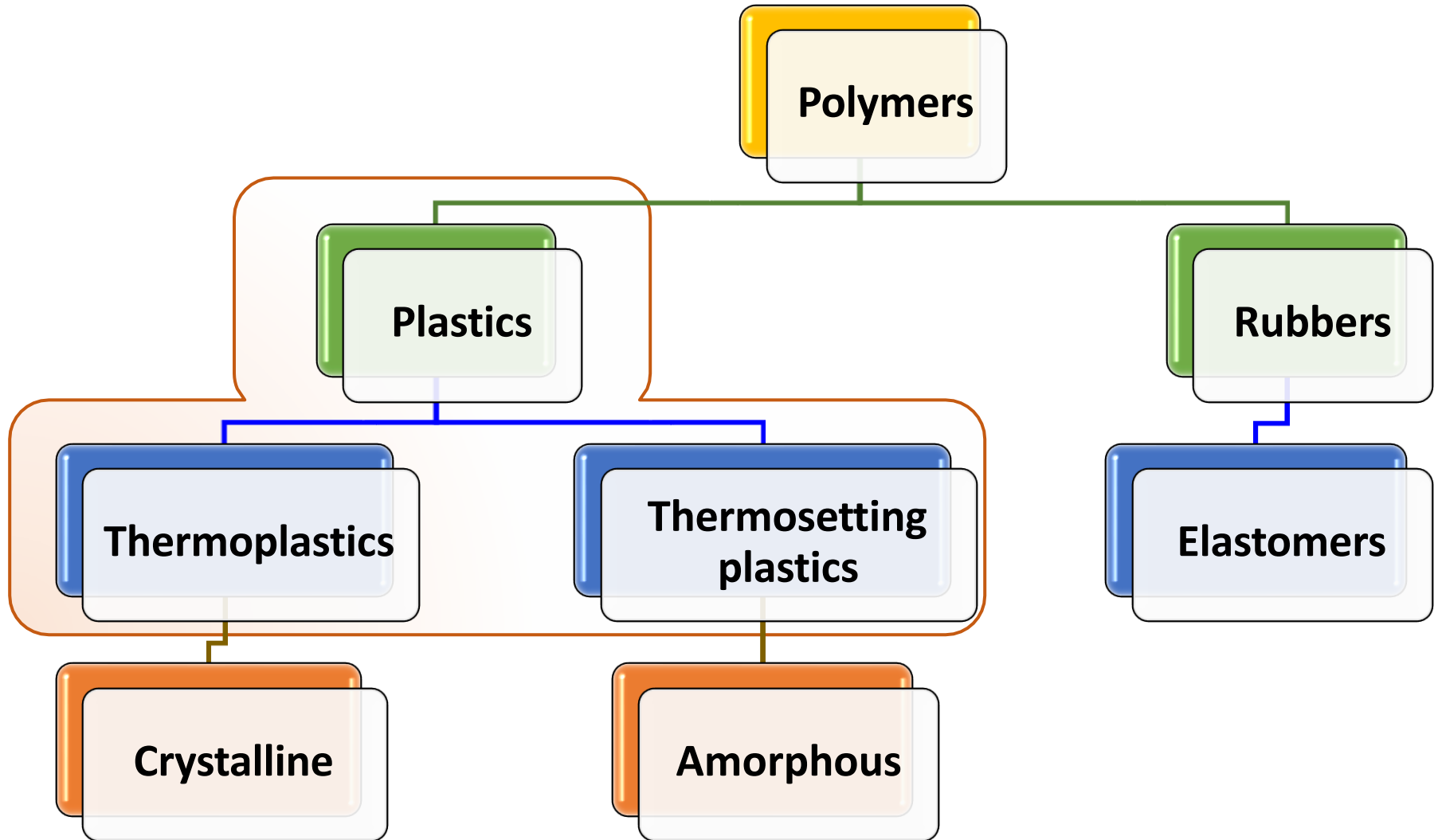
3. Based on “**Monomeric units**”

- ❖ Homopolymers (e.g. Polypropylene)
- ❖ Co-polymers (e.g. Styrene butadiene rubber)

4. Based on “**Thermal Effect**”

- ❖ Plastics (e.g. Polyvinyl chloride)
- ❖ Rubbers (e.g. Butyl rubber)

Classification – Thermal Effect



Plastics

- **Plastics** are **high molecular weight organic polymer materials**, that can be moulded into any desired shape by applying heat and pressure



- **Plastics or resins are classified into two types**
 - (A) Thermoplastics**
 - (B) Thermosetting plastics**

Types of Plastics

Plastics are classified into two types.....

1. Thermoplastic
2. Thermosetting resins

1. Thermoplastic

Thermoplastics are the plastics that do not undergo chemical change in their composition when heated and can be molded again and again.

- ✓ They are prepared by addition polymerisation.
- ✓ They are straight chain (or) slightly branched polymers and
- ✓ Various chains are held together by weak vanderwaal's forces of attraction.
- ✓ It can be softened on heating and hardened on cooling reversibly.
- ✓ They are generally soluble in organic solvents

Examples: Polyethylene, Polyvinylchloride

- ✓ Common thermoplastics range from 20,000 to 500,000 amu
- ✓ Each polymer chain will have several thousand repeating units.

They can be recycled and reused many times by heating and cooling process.

2. Thermosetting resins or Thermosets

- ✓ Thermosetting resins can melt and take shape once; after they have solidified, they stay solid.
- ✓ They are prepared by condensation polymerisation.
- ✓ Various polymer chains are held together by strong covalent bonds (cross links)
- ✓ These plastics get harden on heating and once harden, they cannot be softened again.
- ✓ They are almost insoluble in organic solvents.

Examples: Bakelite, Polyester

Thermoset Polymers whose individual chains have been chemically cross linked by covalent bonds and form a 3-D cross linked structure.

- Therefore, they resist heat softening and solvent attack.
- These are hardened during the molding process and once they are cured, they cannot be softened and they cannot be recycled and reused

Eg. Phenol-formaldehyde resins, urea-formaldehyde paints.

Difference between Thermoplastic and Thermosetting Polymers.....

Thermoplastic polymers	Thermosetting polymers
Consists of long-chain linear polymers with negligible cross-links.	Have 3-Dimensional network structures joined by strong covalent bonds.
Soften on heating readily because secondary forces between the individual chain can break easily by heat or pressure.	Do not soften on heating; On prolonged heating, they are charred.
By re-heating to a suitable temperature, they can be softened, reshaped and thus reused.	Retain their shape and structure even on heating. Hence, cannot be reshaped.
Usually soft, weak and less brittle.	Usually, hard, strong and brittle.
Can be reclaimed from wastes.	Cannot be reclaimed from wastes.
Usually soluble in some organic solvents.	Due to strong bonds and cross-linking, they are insoluble in almost all organic solvents.

Properties and engineering applications

Types of Thermoplastic resins:

Vinyl resins.. Examples:

- (i) PVC
- (ii) TEFLON or FLUON
- (iii) ABS (Acrylonitrile Butadiene Styrene)

Types of Thermosetting resins:

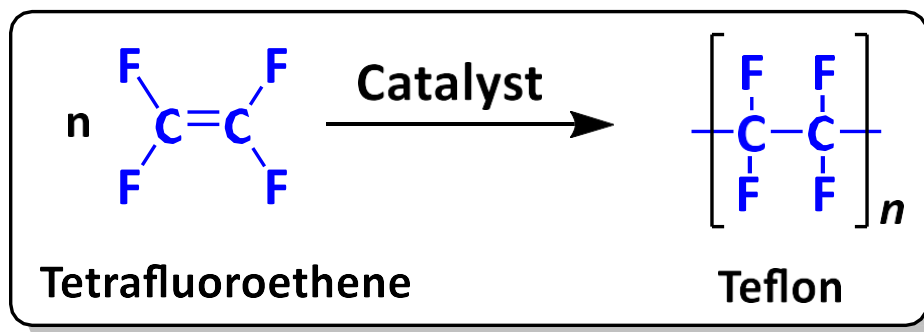
Phenolic resins or phenoplasts

- (i) Novolac
- (ii) Bakelite

i. TEFLON (or) PTFE – Preparation & Properties

TEFLON

- The trivial name of **PTFE (Polytetrafluoroethylene)** is **Teflon**.
- Teflon is made by the polymerization of tetrafluoroethene.



Properties of TEFLON

- This polymer is a **hard, strong, chemically resistant compound** with a **high melting point** and **very low surface friction**.
- **Hydrophobic** polymer
- **Lowest coefficient of friction** against any solids

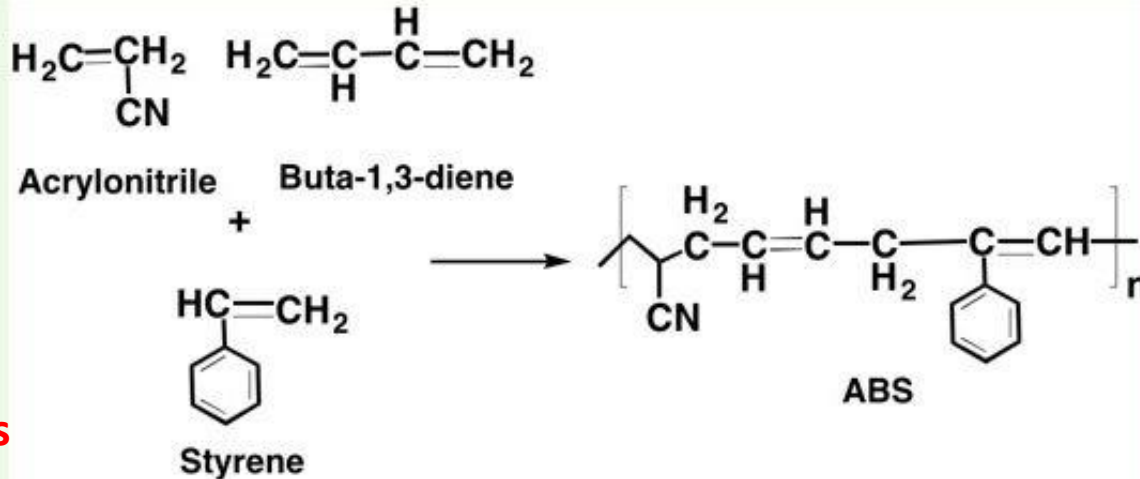
i. TEFLON (or) PTFE – Uses

Uses of TEFLON

- In motors, transformers coils, capacitors, pipes, tanks and storage of chemicals.
- Non-stick appliances.
- TEFLON is used as a lubricant, it reduces friction, wear and energy consumption of machinery.



Acrylonitrile-Butadiene-Styrene (ABS) Plastics



Properties

- ABS is an opaque thermoplastic and amorphous polymer.
- It can be easily recycled and relatively non-toxic.
- ABS has a strong resistance to corrosive chemicals and/or physical impacts.
- It is very easy to mold and has a low melting temperature making it particularly simple to use in injection molding manufacturing processes or 3D printing on an FDM machine.
- ABS is also relatively inexpensive.

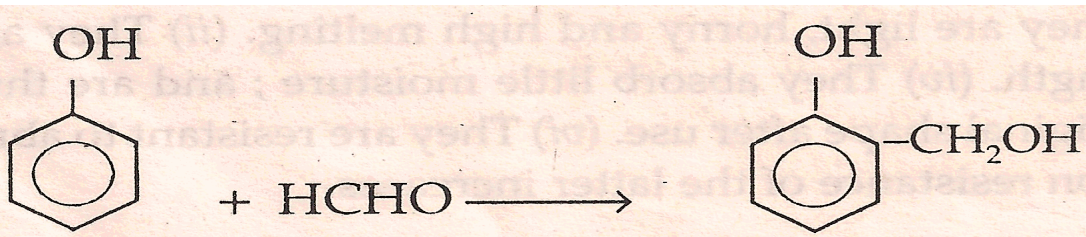
Applications

- Among the most widely identifiable are keys on a computer keyboard, power-tool housing, the plastic face-guard on wall sockets (often a PC/ABS blend), and LEGO toys.
- ABS is used for 3D Printing and Prototype Development.
- Also, it is used in camera housings, protective housings, and packaging.
-

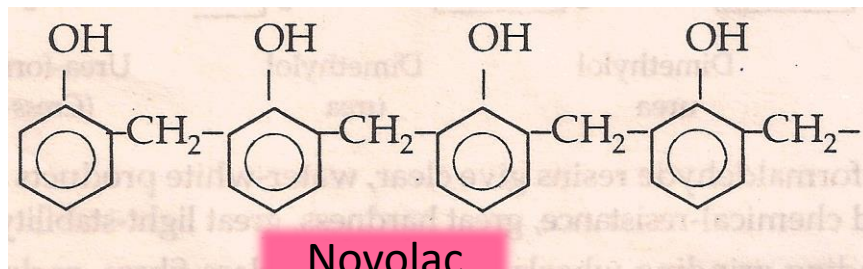
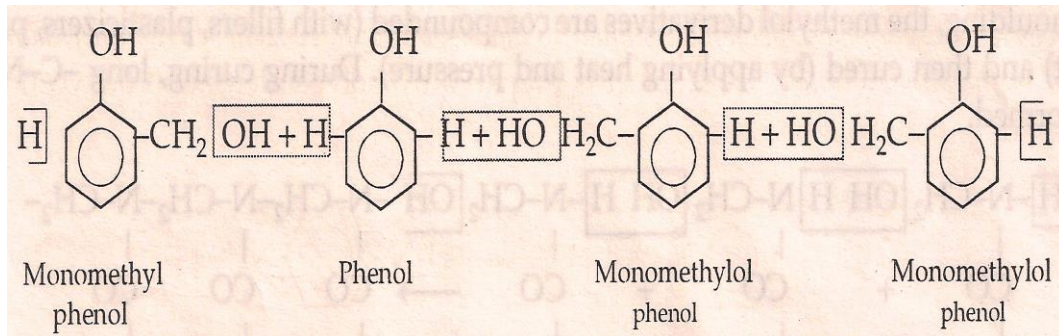
Thermosetting Plastics:

(a) Phenolic resins or Phenoplasts : Novolac and Bakelite

Phenolic resins are condensation polymerization products of phenol derivatives and aldehydes.



At first, Phenol reacts with Formaldehyde in presence of acidic / alkaline catalyst to form Monomethylol phenol.

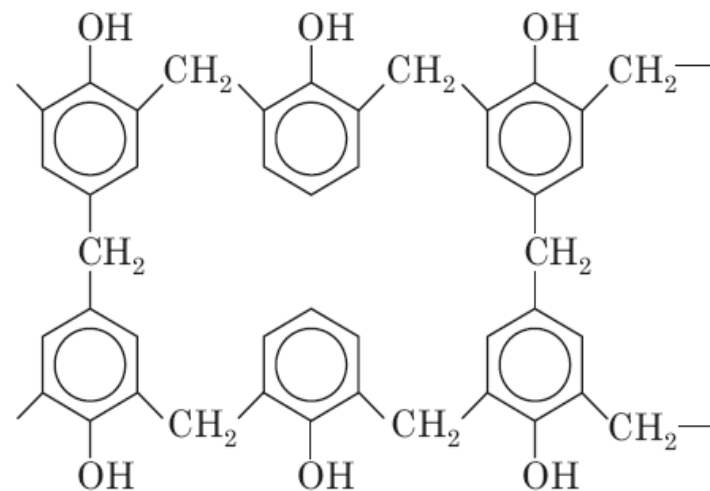


Monomethylol phenol further reacts with Phenol to form a linear polymer "Novolac".

Water is removed as the by-product.

Thermosetting Plastics: Bakelite

- ✓ Further addition of HCHO at high temperature and pressure converts Novolac (soft and soluble) into cross-linked “Bakelite” (hard and insoluble).



Bakelite

Properties : Phenolic resins (bakelite) set to rigid, hard, scratch-resistant, infusible, water-resistant, insoluble solids, which are resistant to non-oxidizing acids, salts and many organic solvents, but are attacked by *alkalis*, because of the presence of free hydroxyl group in their structures. They possess excellent *electrical insulating* character.

Uses : (1) For making *electric insulator parts* like switches, plugs, switch-boards, heater-handles, etc. (2) For making *moulded articles* like telephone parts, cabinets for radio and television. (3) For *impregnating* fabrics, wood and paper. (4) As *adhesives* (e.g., binder) for grinding wheels. (5) In paints and varnishes. (6) As *hydrogen-exchanger resins* in water softening. (7) For making *bearings*, used in propeller shafts for paper industry and rolling mills.

Bakelite

Properties:

- ✓ Bakelite is resistant to acids, salts and most organic solvents, but it is attacked by alkalis because of the presence of -OH groups.
- ✓ It possesses excellent electrical insulating property.
- ✓ As thermoset it is difficult to recycle.

Uses:

- ✓ Bakelite is used as an adhesive in plywood laminations & grinding wheels, etc
- ✓ It is also widely used in paints, varnishes,
- ✓ It is used for making electrical insulator parts like plugs, switches, heater handles, paper laminated products, thermally insulation foams etc.

Conducting Polymers

- Polymers, particularly those with a conjugated p-bond structure often show higher conductivity when doped with conductive materials.
- But the use of conductive polymers is limited since they have poor mechanical strength.
- Hence, a combination of mechanical and electrical properties can only find good applications in conductive polymers area.
- Sometimes, in a polymer blend, a bifunctional linker is doped to increase the conductivity of Polyaniline (PANI) (having conductivity) and polycaprolactum (PCL) (having mechanical strength) blend.
- Conductive polymers can be made using simple procedures like melt blending, solution blending etc., and can be used for antistatic and electromagnetic shielding applications.

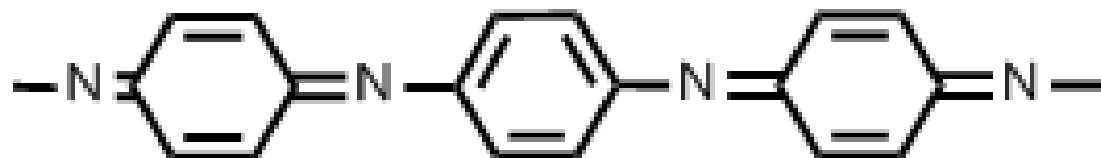
Some Examples of Conductive Polymers



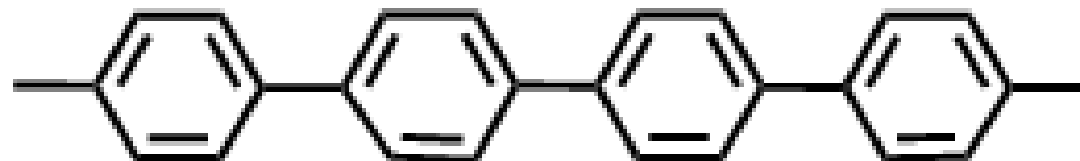
trans-polyacetylene



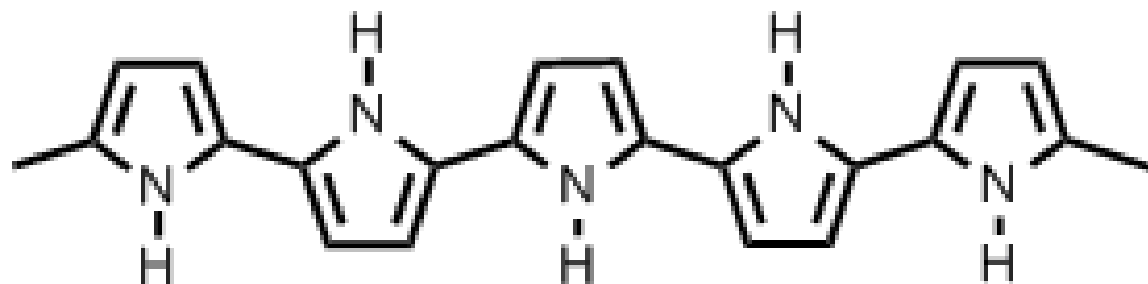
polythiophene



polyaniline

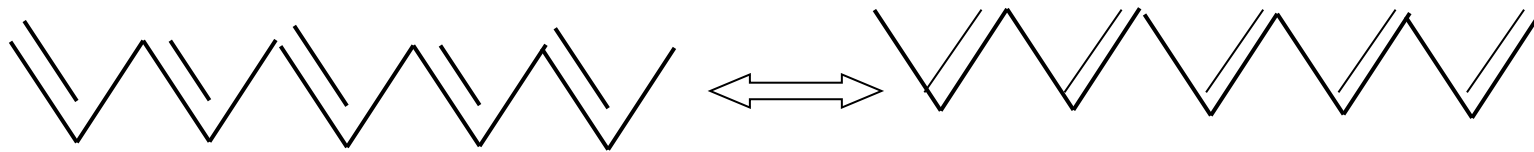


poly(p-phenylene)



polypyrrole

Mechanism of Conduction in Polymers



Conjugation of π -electrons

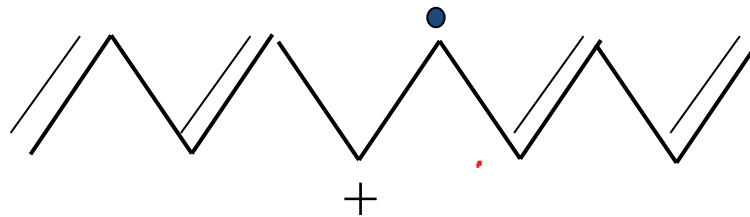
Undoped



Insulating



Doped



Conducting

A⁻

Dopant anion for charge neutrality

Different Types of Conducting Polymers:

1. Intrinsically conducting polymers (ICP)
2. Doped Conducting polymers
3. Extrinsically conducting polymers (ECP)

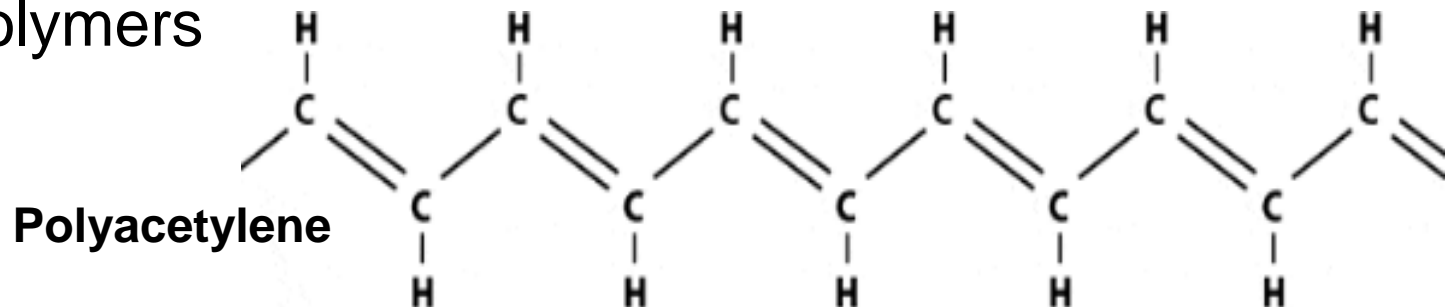
Factors that affect the conductivity:

1. Density of charge carriers
2. Their mobility
3. The direction
4. Presence of doping materials (additives that facilitate the polymer conductivity in a better way)
5. Temperature

1. Intrinsically Conducting Polymers (ICPs)

- Polymer consisting of alternating single and double bonds is called conjugated double bonds.
- In conjugation, the bonds between the carbon atoms are alternately single and double. Every bond contains a localised “sigma” (σ) bond which forms a strong chemical bond.
- In addition, every double bond also contains a less strongly localised “pi” (π) bond which is weaker.
- Conjugation of sigma and pi-electrons over the entire backbone, forms valence bands and conduction bands.

Eg: Poly-acetylene, poly-p-phenylene, polyaniline, polypyrrole polymers



Doped Conducting Polymers

- ICPs possess **low ionisation potential and high electron affinity**. So they can be **easily oxidised or reduced**.
- The conductivity of ICP can be increased by creating positive charges (oxidation) or by negative charges (reduction) on the polymer backbone.
- This technique is called **DOPING**.
- There are two types of doping:
 - p-doping achieved by oxidation
 - n-doping achieved by reduction

p-Doping

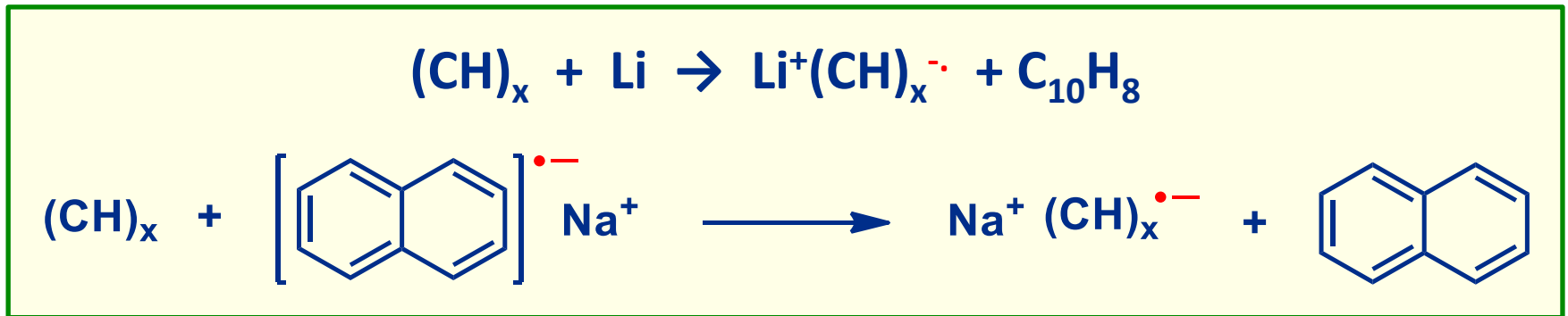
- p-doping is achieved by oxidation process. It is also known as the **oxidative doping**.
- It involves treatment of an polyacetylene with a Lewis acid or iodine which leads to oxidation process and positive charges on the polymer backbone are created.
- Some of the p-dopants are I_2 , Br_2 , AsF_5 , $FeCl_3$, $HClO_4$, PF_5 etc.



- This oxidation process or removal of one electron leads to the formation of delocalized radical ion called **polaron**
- A second oxidation of the polaron, followed by radical recombination generates two mobile positive charge carriers also known as **soliton**, which are responsible for conduction

n-Doping

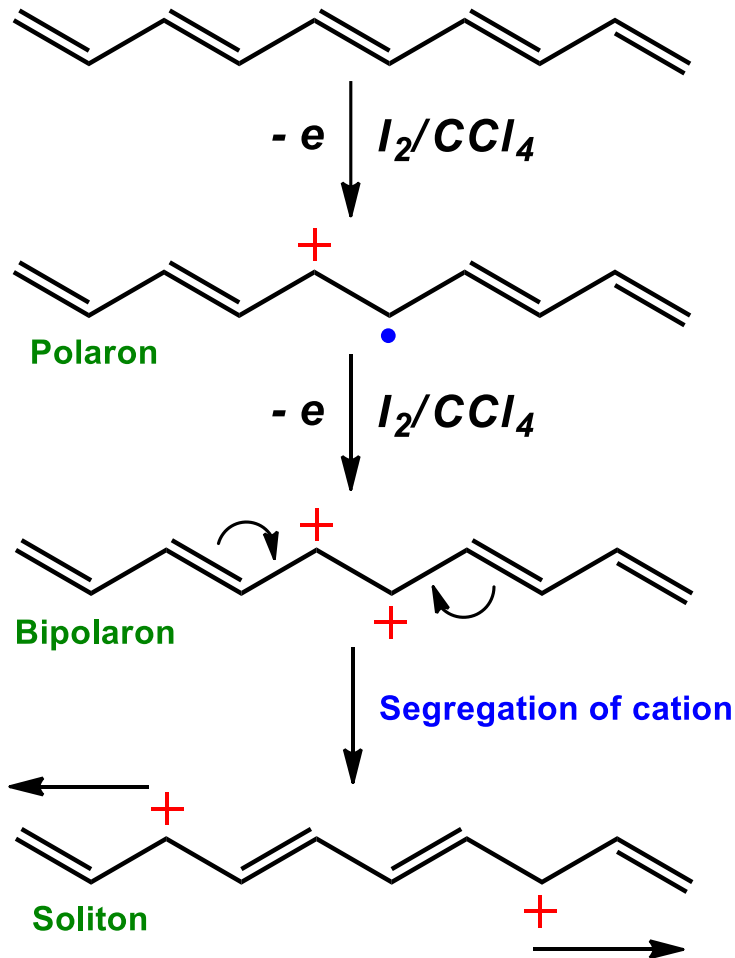
- n-doping is achieved by reduction process. It is also known as the **reductive doping**.
- It involves treatment of an polyacetylene with a Lewis base which leads to reduction process and negative charges on the polymer backbone are created.
- Some commonly available n-dopants are **Li, Na, Ca, sodium naphthalide**, etc.



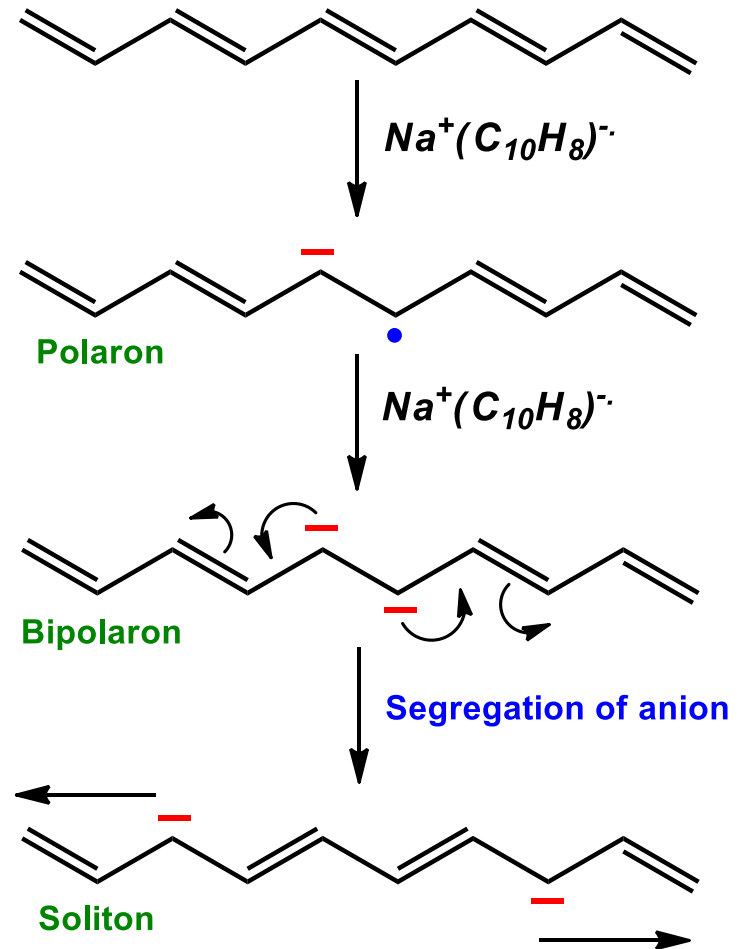
- This reduction process or the donation of one electron leads to the formation of **delocalized radical anion, an anionic polaron**
- Second reduction, followed by radical recombination generates negatively charged **soliton**

Doping in ICP

p-doping

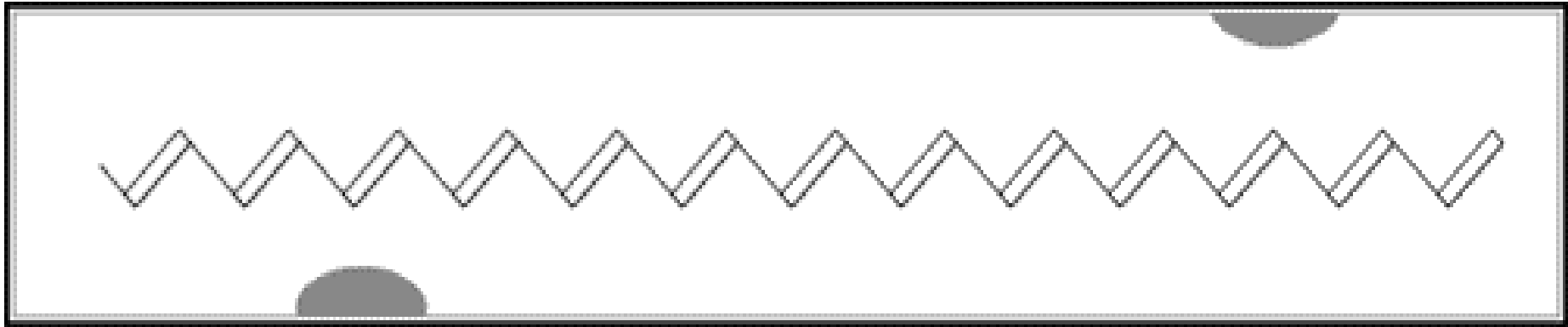


n-doping



- **What is a soliton?** The soliton is a charged or a neutral defect in the polyacetylene chain that propagates down the chain, thereby reducing the barrier for interconversion.

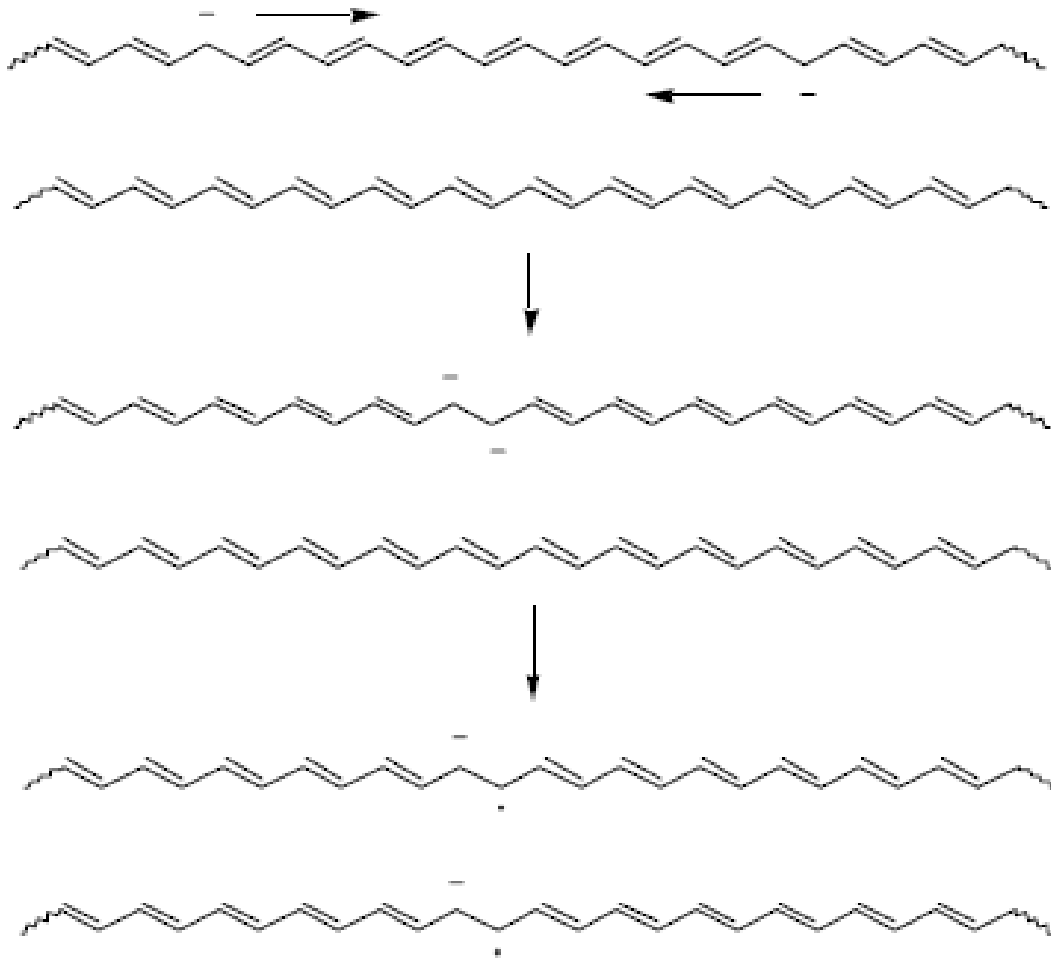
- In p-type doping, the dopant (Iodine, I_2) attracts an electron from the polyacetylene chain to form (I_3^-) leaving a positive soliton (**carbenium ion**) in the polymer chain that can move along its length.
- The lonely electron of the double bond, from which an electron was removed, can move easily.
- As a consequence, the double bond successively moves along the molecule, and the polymer is stabilized by having the charge spread over the polymer chain.



Doping in Trans-Polyacetylene

Conductivity Mechanism in Polyacetylene:

- The mechanism followed by **polyacetylene** for the transfer of charge from one chain to another is called **intersoliton hopping**.
- **What is a soliton?** The soliton is a charged or a neutral defect in the polyacetylene chain that propagates down the chain, thereby reducing the barrier for interconversion.



- ✱ In n-type doping (This can be done by dipping the film in THF solution of an alkali metal) soliton is a resonance-stabilized polyenyl anion of approximately 29-31 CH units in length, with highest amplitude at the centre of the defect.
- ✱ The solitons (**anions**) transfer electrons to a neutral soliton (**radical**) in a neighboring chain through an isoenergetic process.
- ✱ The charged solitons are responsible for making polyacetylene a conductor.²⁸

3. Extrinsically Conducting Polymers

These are those polymers whose conductivity is due to the presence of externally added ingredients in them.

Two types:

(1) Conductive element filled polymer:

- It is a resin/polymer filled with carbon black, metallic fibres, metal oxides etc. Polymer acts as a binder to those elements.
- These have good bulk conductivity and are low in cost, light weight, strong and durable. They can be in different forms, shapes and sizes.

(2) Blended Conducting Polymers:

- It is the product obtained by blending a conventional polymer with a conducting polymer either by physical or chemical change.
- Such polymers can be processed and possess better physical, chemical and mechanical strength.

Introduction - Nanomaterials

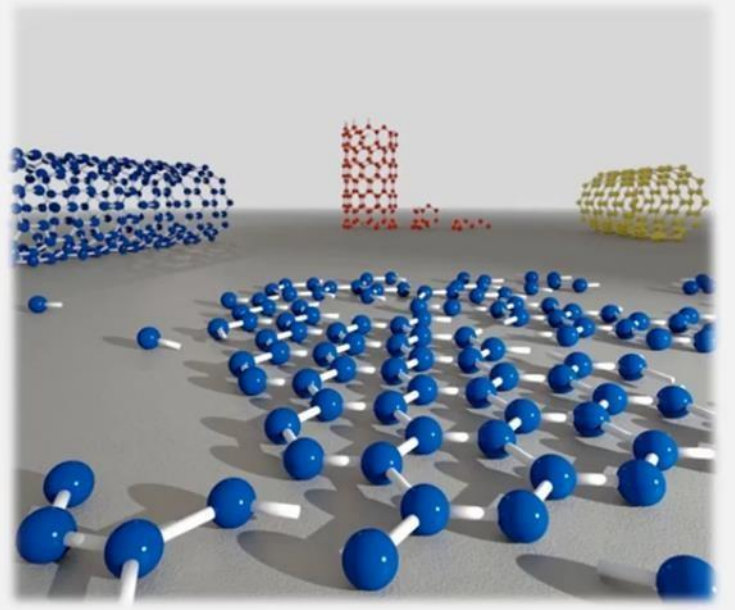
Nanomaterials can be defined as materials possessing, at minimum, one external dimension measuring 1-100nm.

NanoMaterials

Definition :

- If at least **one dimension of a material stands at the nanoscale, between 1 to 100 nm**, that material is counted as a Nanomaterials

$$1 \text{ nm} = 10^{-6} \text{ mm} = 10^{-9} \text{ m}$$



§ Introduction to Nanomaterials

A nanoparticle is an entity with a width of a few nanometers to a few hundred, containing tens to thousands of atoms. Their defining characteristic is a very small feature size in the range of 1-100 (nm).

•Nano size:

One nanometre is a millionth part of the size of the tip of a needle.

$$1 \text{ nm} = 10^{-6} \text{ mm} = 10^{-9} \text{ m}$$

Table 1. Some examples of size from macro to molecular

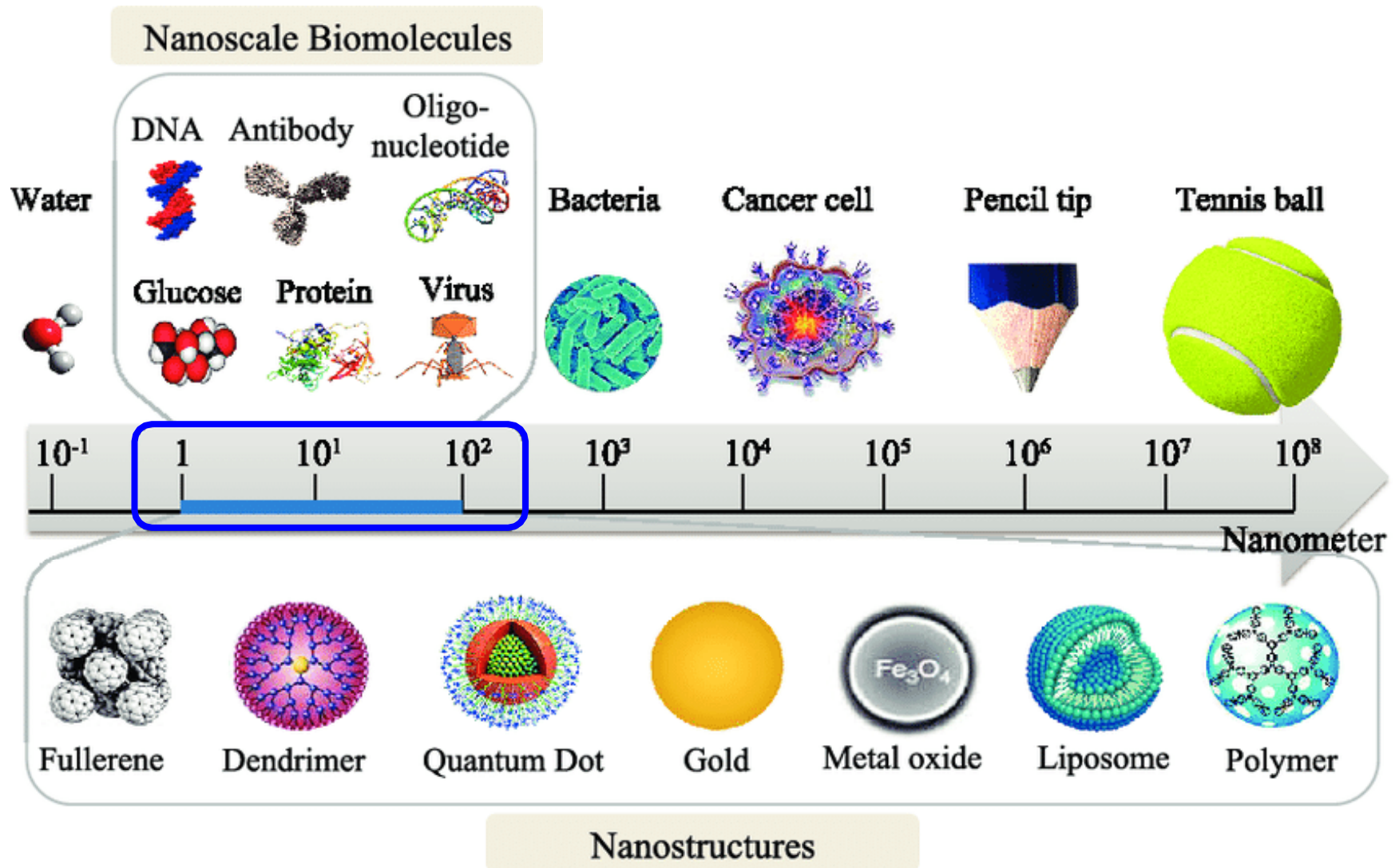
Size (nm)	Examples	Terminology
0.1-0.5	Individual chemical bonds	Molecular/atomic
0.5-1.0	Small molecules, pores in zeolites	Molecular
1-1000	Proteins, DNA, inorganic nanoparticles	Nano
10^3 - 10^4	living cells, human hair	Micro
$>10^4$	Normal bulk matter	Macro



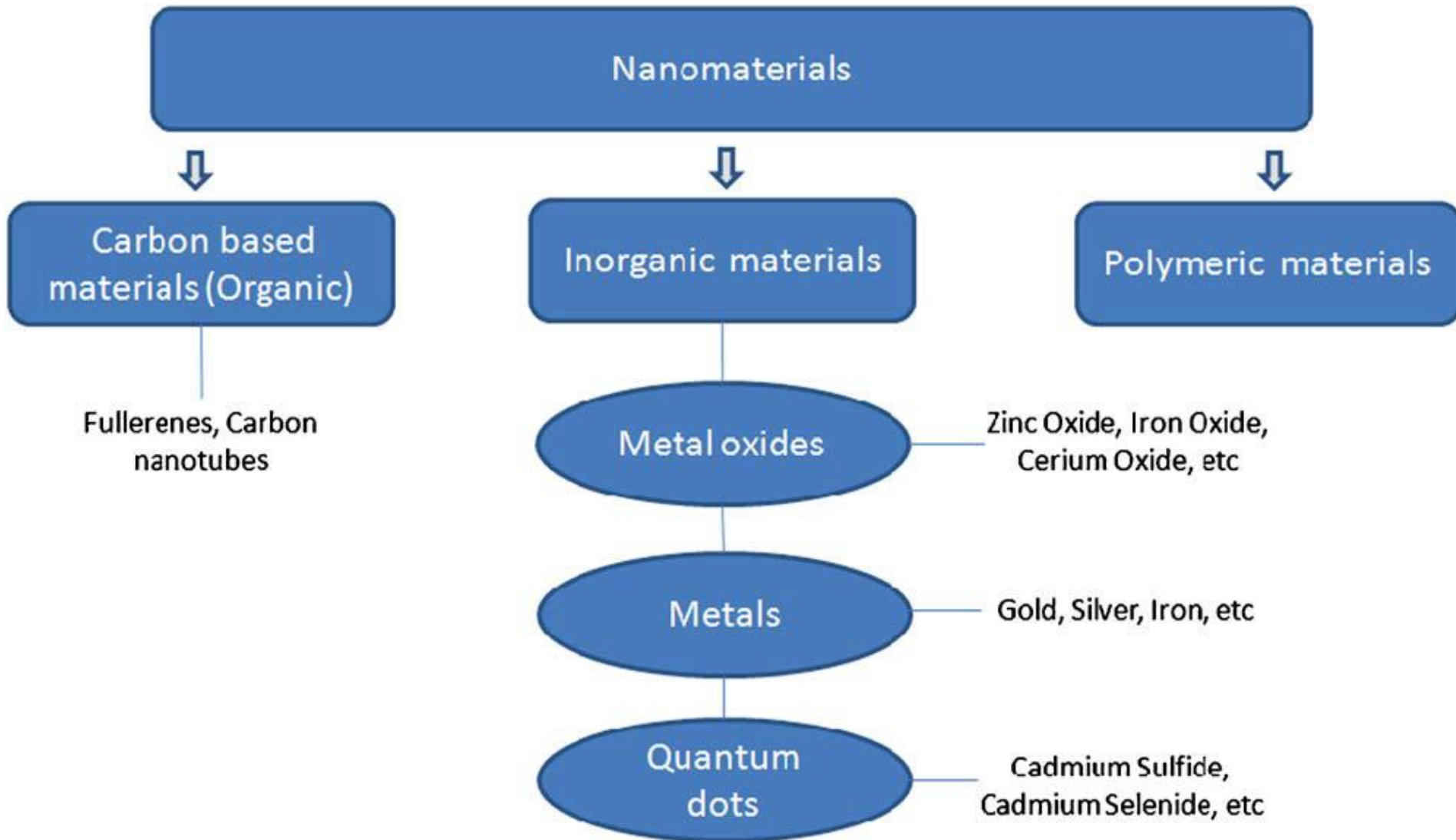
Bulk Gold

From: USDA's roadmap of nanotechnology.

Nanoscale



Categories of Nanomaterials



Why do nanoparticles behave differently? Two principal factors cause the properties of nanomaterials different from bulk materials.

1. Surface area effect

- Surface to volume ratio

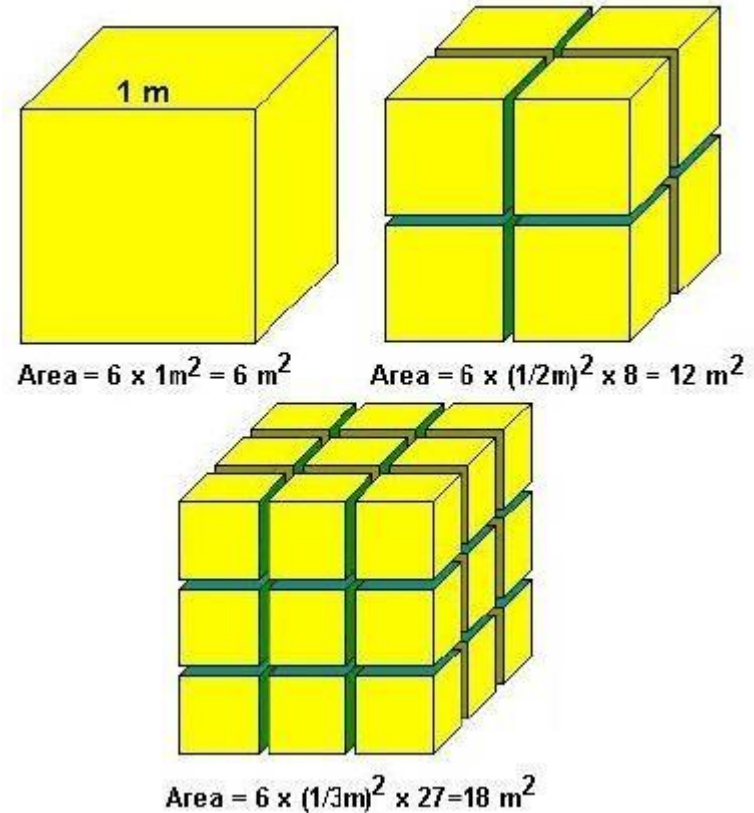
2. Quantum effect

- Quantum confinement

1. Surface area effect

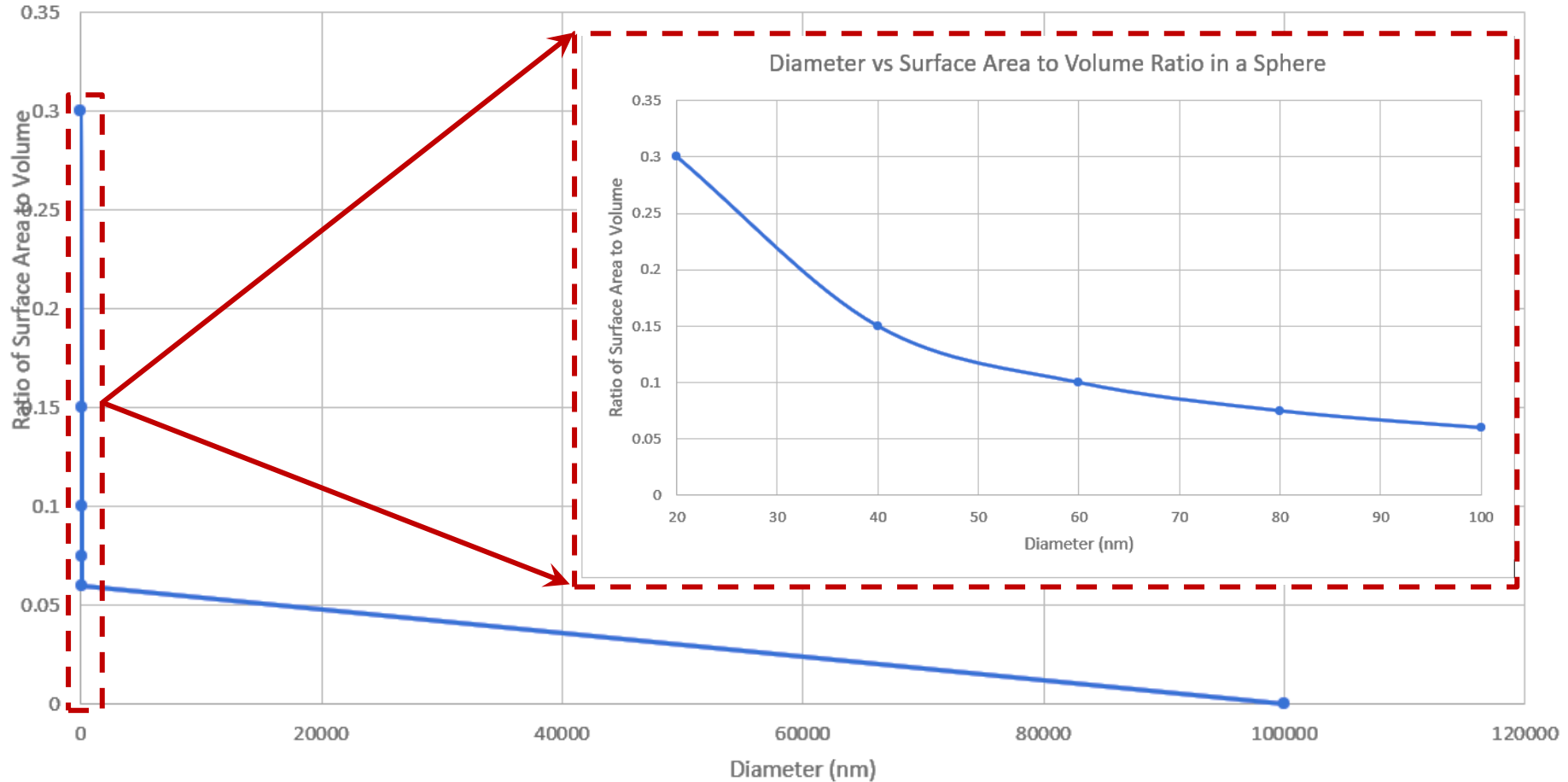
Surface to volume ratio

- By breaking the cube into multiple cubes the **amount of surface exposed increases**
- A greater amount of a substance **comes in contact with surrounding material**
- This results in **better reactivity**, since a greater proportion of the material is exposed for potential reaction.



1. Surface area effect

Diameter vs Surface Area to Volume Ratio in a Sphere

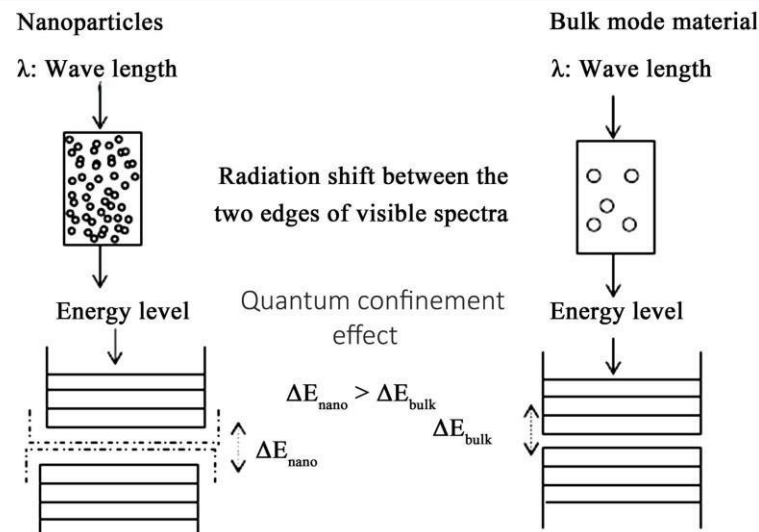


2. Quantum effect

The characteristics of **individual atoms** become **important** for materials at **nano scale**.

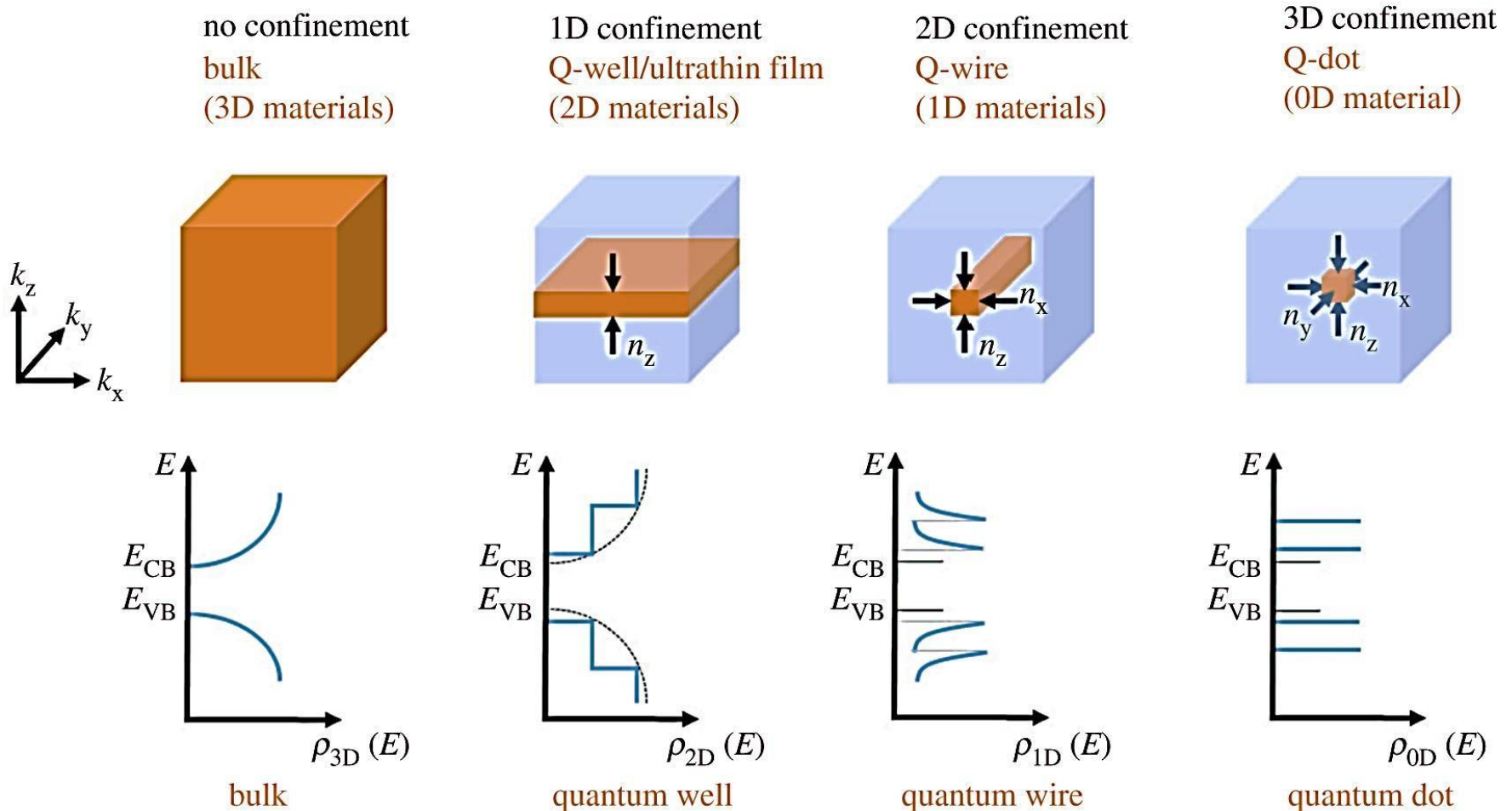
⇒ requires a new set of physics laws (**quantum mechanics**) to explain

Quantum mechanics also explains the very different **optical**, **electrical** and **magnetic** properties of **nano materials** from that of bulk materials.



2. Quantum effect

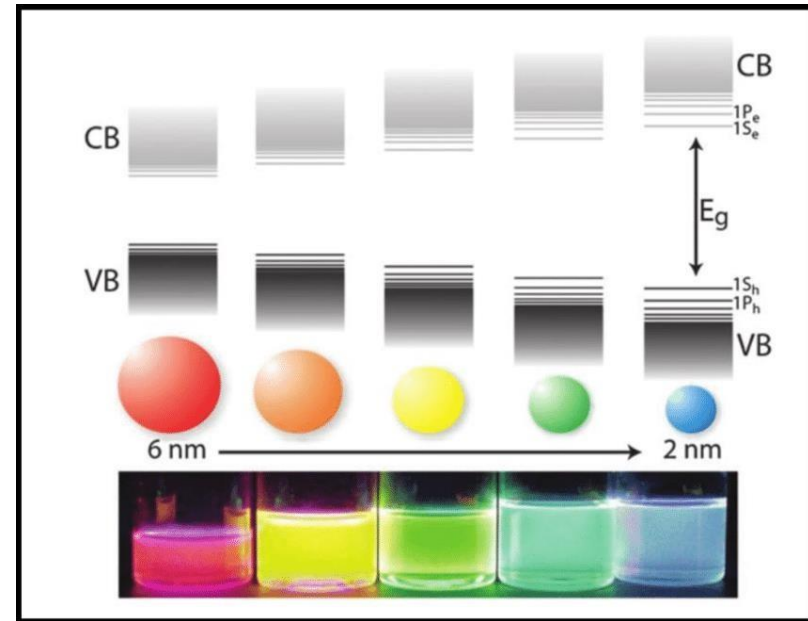
Quantum confinement



2. Quantum effect

Quantum confinement

- Quantum confinement is **change of electronic and optical properties** when the material sampled is of sufficiently small size - typically 10 nanometers or less.
- The **bandgap increases** as the **size of the nanostructure decreases**.



Size and shape dependent colors of Au and Ag nanoparticles

Gold NPs in Glass

**25 nm
Sphere
reflected**

Size*: 25 nm
Shape: sphere
Color reflected:



100 nanometers =
0.0001 millimeter

**50 nm
Sphere
reflected**

Size*: 50 nm
Shape: sphere
Color reflected:

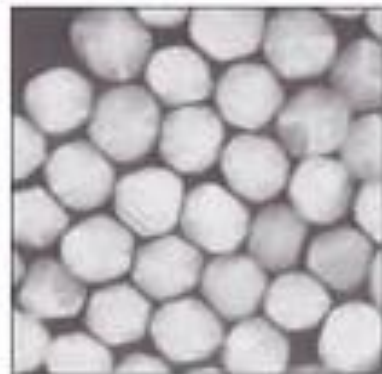
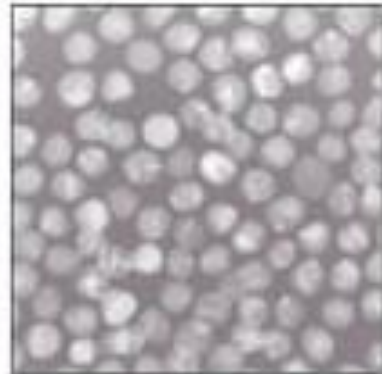
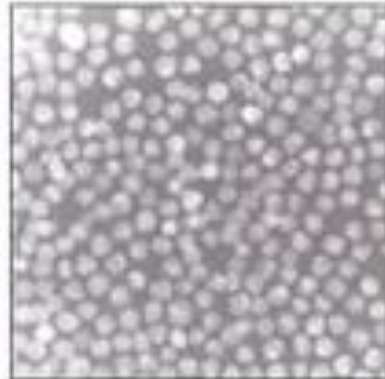


**100 nm
Sphere
reflected**

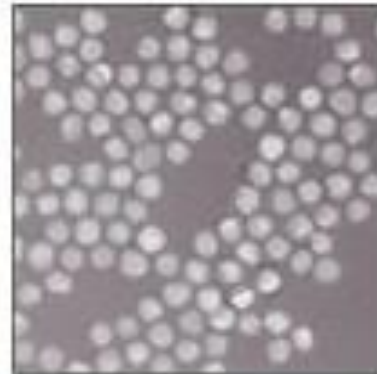
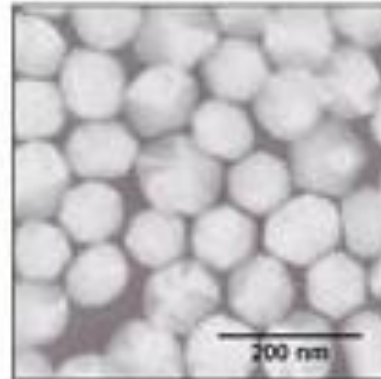
Size*: 100 nm
Shape: sphere
Color reflected:



Gold particles in glass



Silver particles in glass



Silver NPs in Glass

Size*: 100 nm
Shape: sphere
Color reflected:



**100 nm
Sphere
reflected**

Size*: 40 nm
Shape: sphere
Color reflected:



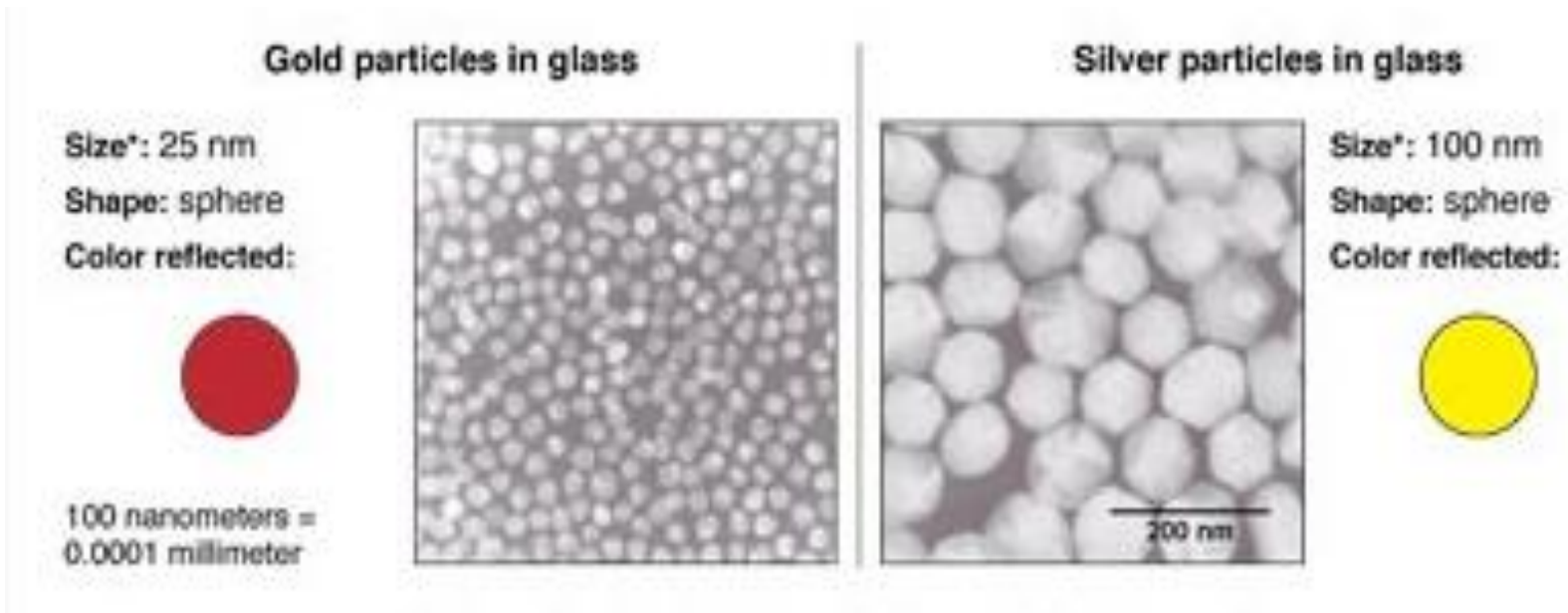
**40 nm
Sphere
reflected**

Size*: 100 nm
Shape: prism
Color reflected:



**100 nm
prism
reflected**

Size and shape dependent colors of Au and Ag nanoparticles



Note: **nanomaterials scatter visible light rather than absorb**

➤ Distance between particles also effects colour

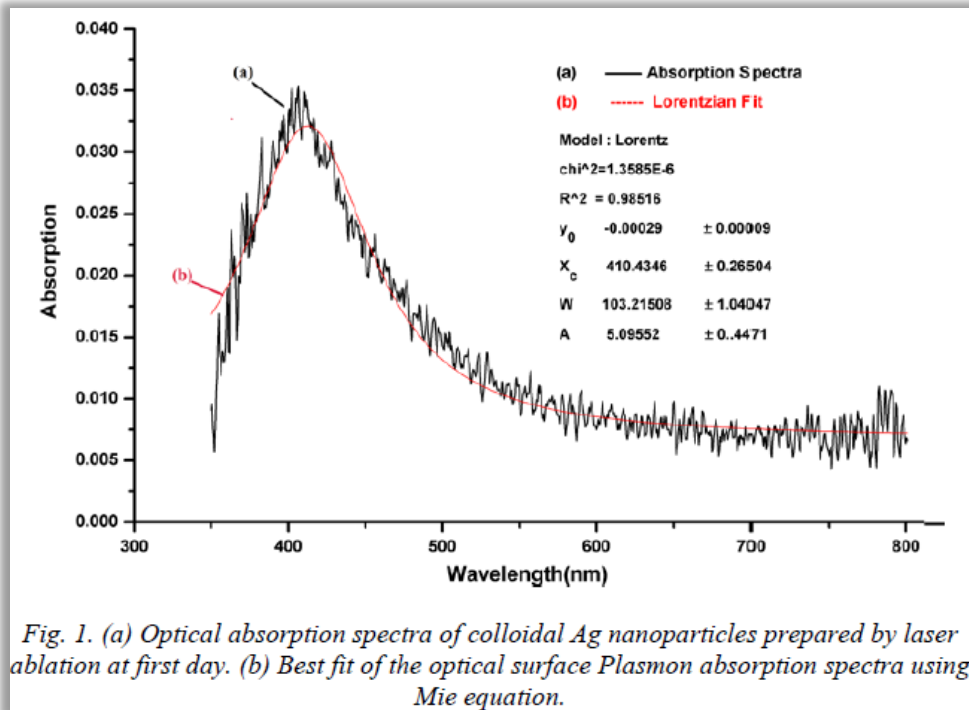
Surface plasmon resonance: Excitation of [surface plasmons](#) by light (visible or infra red) is denoted as a surface plasmon resonance

Localized surface plasmon resonance (LSPR) for nanometer-sized metallic structures

What are surface plasmons ?

- ✓ When an electromagnetic radiation interacts with metal nano particles (e.g. Au & Ag) present in a dielectric medium, it induces a collective oscillation of conduction electrons called surface plasmons.
- ✓ It can be studied by the UV-Visible spectrum of the nano particles

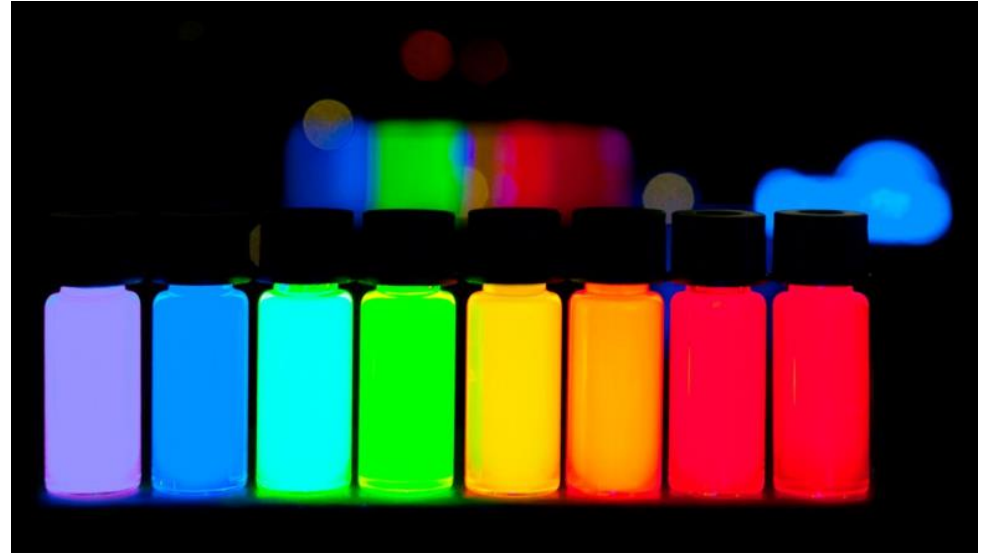
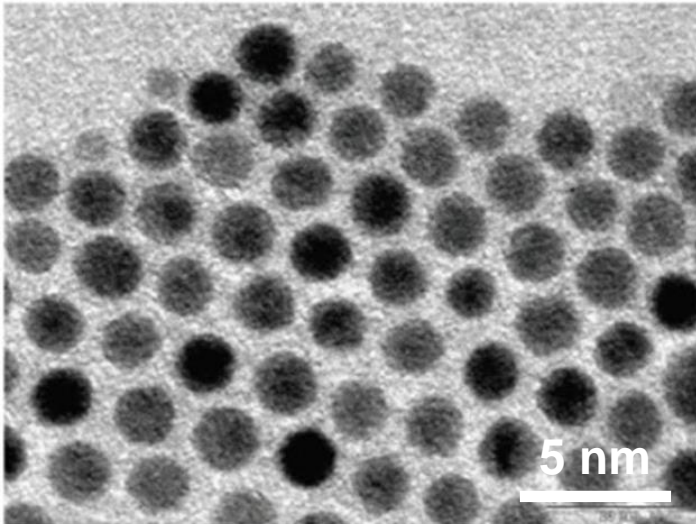
Applications: diagnostics and analysis of biomolecular interactions etc.



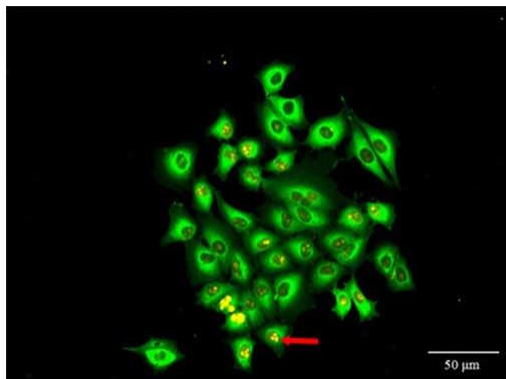
- ✓ Surface plasmon resonance spectrum can be simulated by Mie theory
- ✓ It helps to arrive at the particle size of the nano particles .
- ✓ The adjacent figure shows the experimental spectrum and the calculated one for Ag nano particles.

Quantum Dots and applications

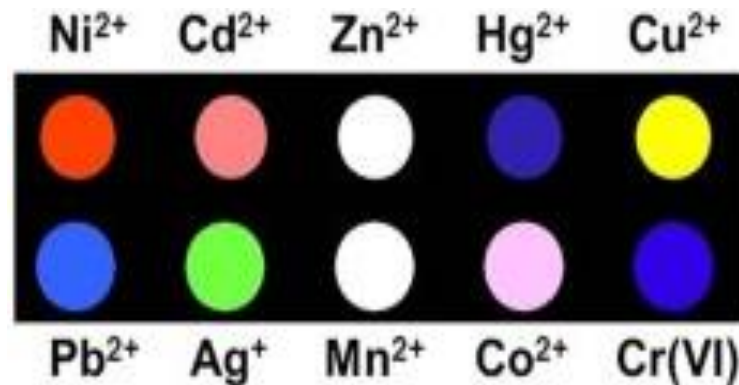
Quantum dots (QDs) are semiconductor particles of few nanometers (<10 nm) in size, having optical and electronic properties that differ from larger particles.



Cancer cell imaging



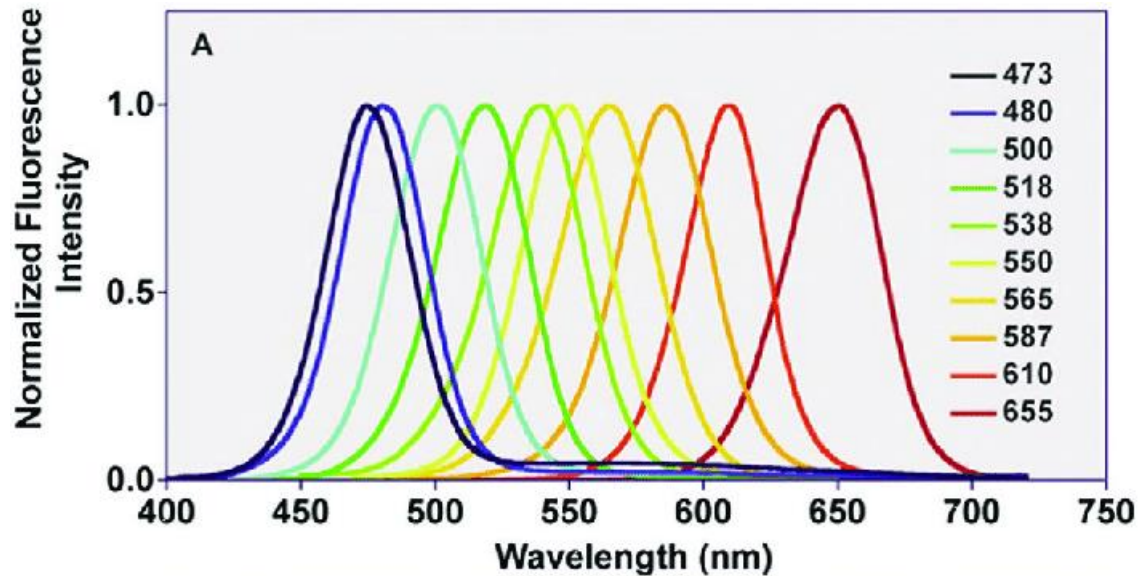
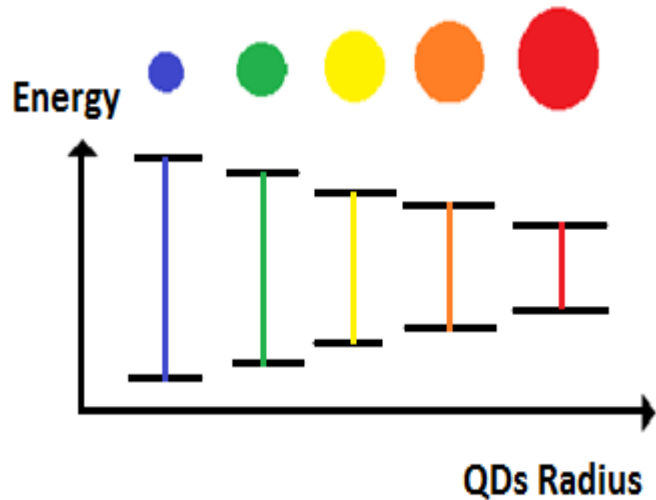
Metal ions sensing



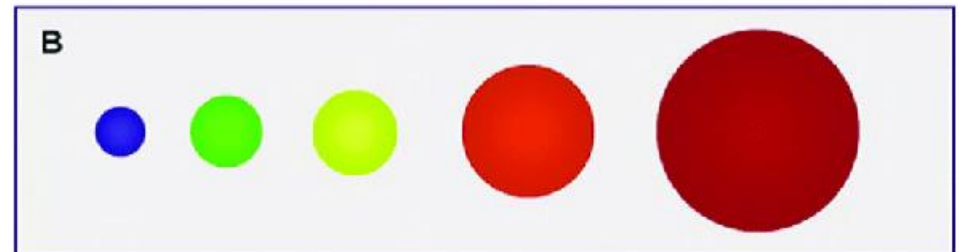
Light emitting diode



Emission properties of Quantum Dots



1. Band gap decreases as the QDs size increases
2. Emission wavelength becomes red shifted with increase in size of QDs



Synthetic Methods of Quantum Dots

1. High temperature synthesis
2. Hydrothermal synthesis
3. Microwave synthesis
4. Ultrasonication synthesis

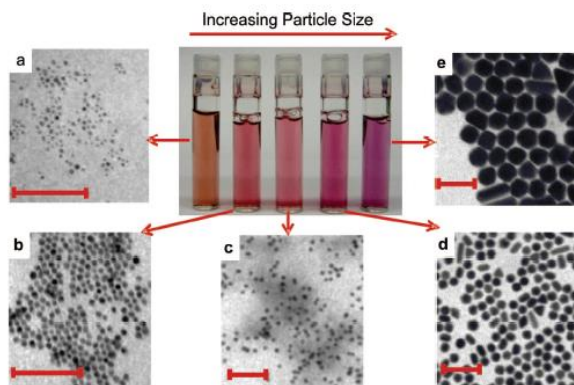
- **Nanomaterials show unusual**

- **Mechanical**
- **Electrical**
- **Optical**
- **Magnetic properties.**

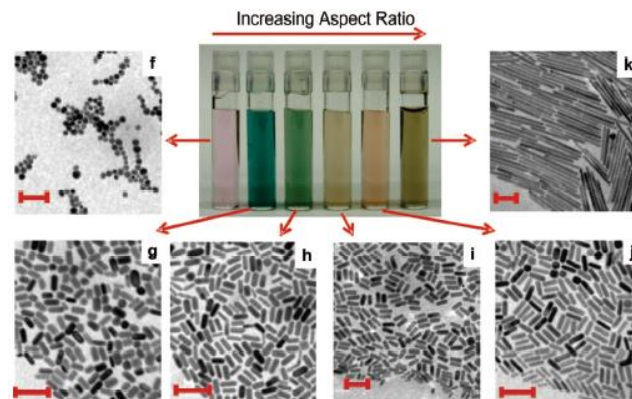
Hence it has potential **applications in**

- **Biomedical field**
- **Electronic applications**
- **For example, long lasting medical implants of biocompatible nanostructured ceramic and carbides,**
- **Biocompatible coating**
- **Drug delivery**
- **Protection coatings**
- **Composite materials**
- **Anti fogging coatings for spectacles and car windows, etc.**

- At the **nanomaterial level**, some material properties are affected by the laws of atomic physics, rather than behaving as traditional bulk materials.
- Nanomaterials can be metals, ceramics, polymeric materials, or composite materials.
- The beautiful ruby red color of some glass is due to gold nanoparticles (Au NPs) trapped in the glass matrix.
- The decorative glaze known as luster, found on some medieval pottery, contains metallic spherical nanoparticles dispersed in a complex way in the glaze.



Spherical AuNPs




Rod shaped nano Au

What makes these nanomaterials so different and so intriguing?

- Deviation from the reduced size and dimensionality of the nanometer-sized building blocks (crystallites), the numerous **interfaces between adjacent crystallites, grain boundaries and surfaces**
- These building blocks have different crystallographic orientation that may lead to **incoherent or coherent interfaces between them**
- Lead to **inherent heterogeneous structure** on a nanometer scale.
- Grain boundaries make up a major portion of the material at nanoscales, and strongly affect properties and processing.
- Surfaces and interfaces- half or more than half atoms near to interfaces
- Hence, surface properties such as **energy levels, electronic structure, and reactivity** are different from bulk materials

Gold : Bulk vs. Nano

	Bulk Gold	Nano Gold
1	Lustrous—they have a shiny surface when polished	Are never gold in colour but found in a range of colours
2	Malleable—they can be hammered, bent or rolled into any desired shape 	Size & Shape of the nanoparticles determines the colour
3	Ductile—they can be drawn out into wires	For example, Gold particles in glass 25 nm > red reflected 50 nm > green reflected 100 nm > orange reflected
4	Is metallic, with a yellow colour when in a mass	Are not “metals” but are semiconductors (Band gap energy = 3.4 eV)

5	Good conductors of heat and electricity	Are very good catalysts
6	Generally have high densities	
7	Have high melting point (~1080°C)	Melts at relatively low temp (~940° C)
8	Are often hard and tough with high tensile strength	
9	Having high resistance to the stresses of being stretched or drawn out	
10	Not easily breakable	
11	Inert-unaffected by air & most reagents	

Synthesis of nanomaterials

Two Different Approaches to Nanofabrication

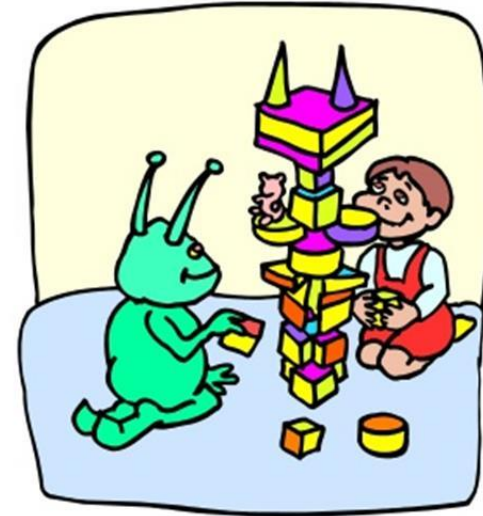
➤ Top ⇒ Down:

- Start with the bulk material and "cut away material" to make the what you want

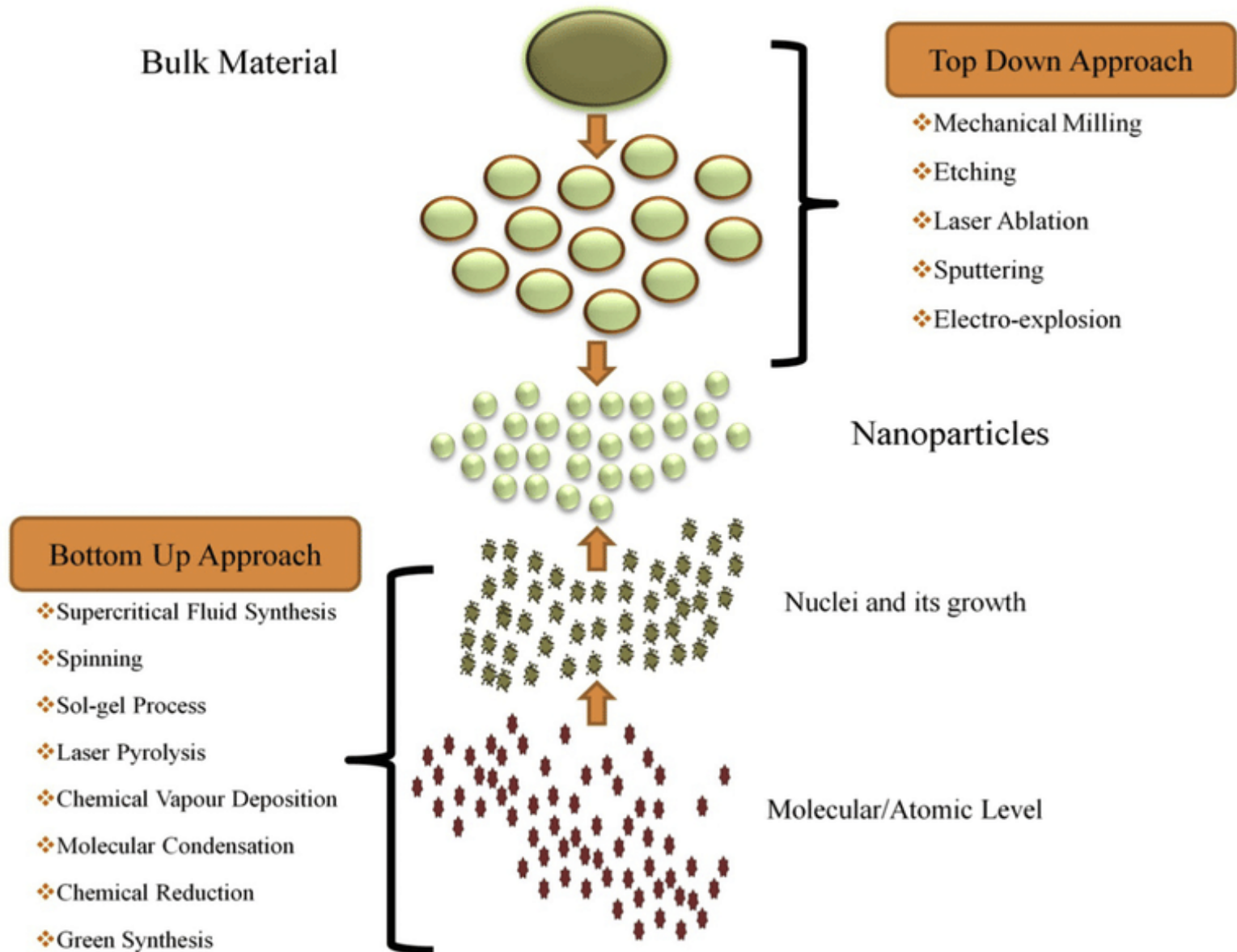


➤ Bottom ⇒ Up:

- Building what you want by assembling it from building blocks (such as atoms and molecules).
- Atom-by-atom, molecule-by-molecule, or cluster-by-cluster

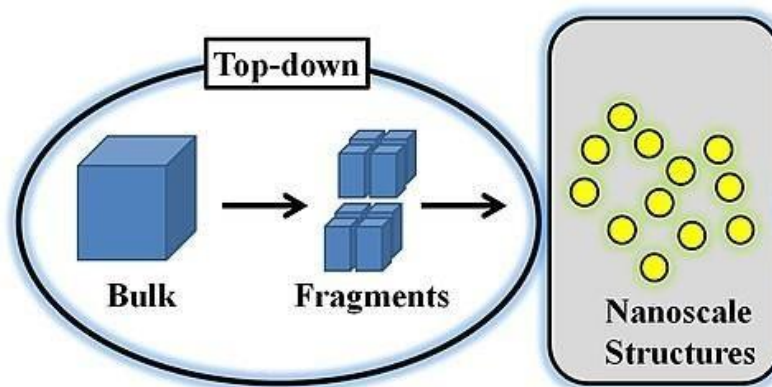


Synthesis of nanomaterials



Top down approach

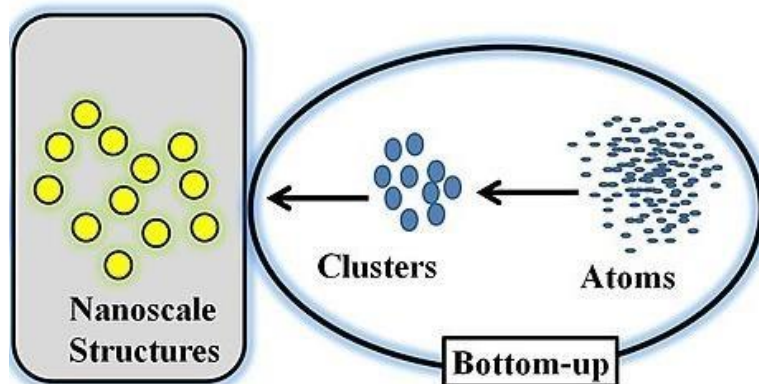
- Begins with a pattern generated on a larger scale, then reduced to nanoscale
- Relatively expensive and time consuming technique
- The approach use larger (macroscopic) initial structures
- The structures can be extremely-controlled in the processing of nanostructures



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

Bottom up approach

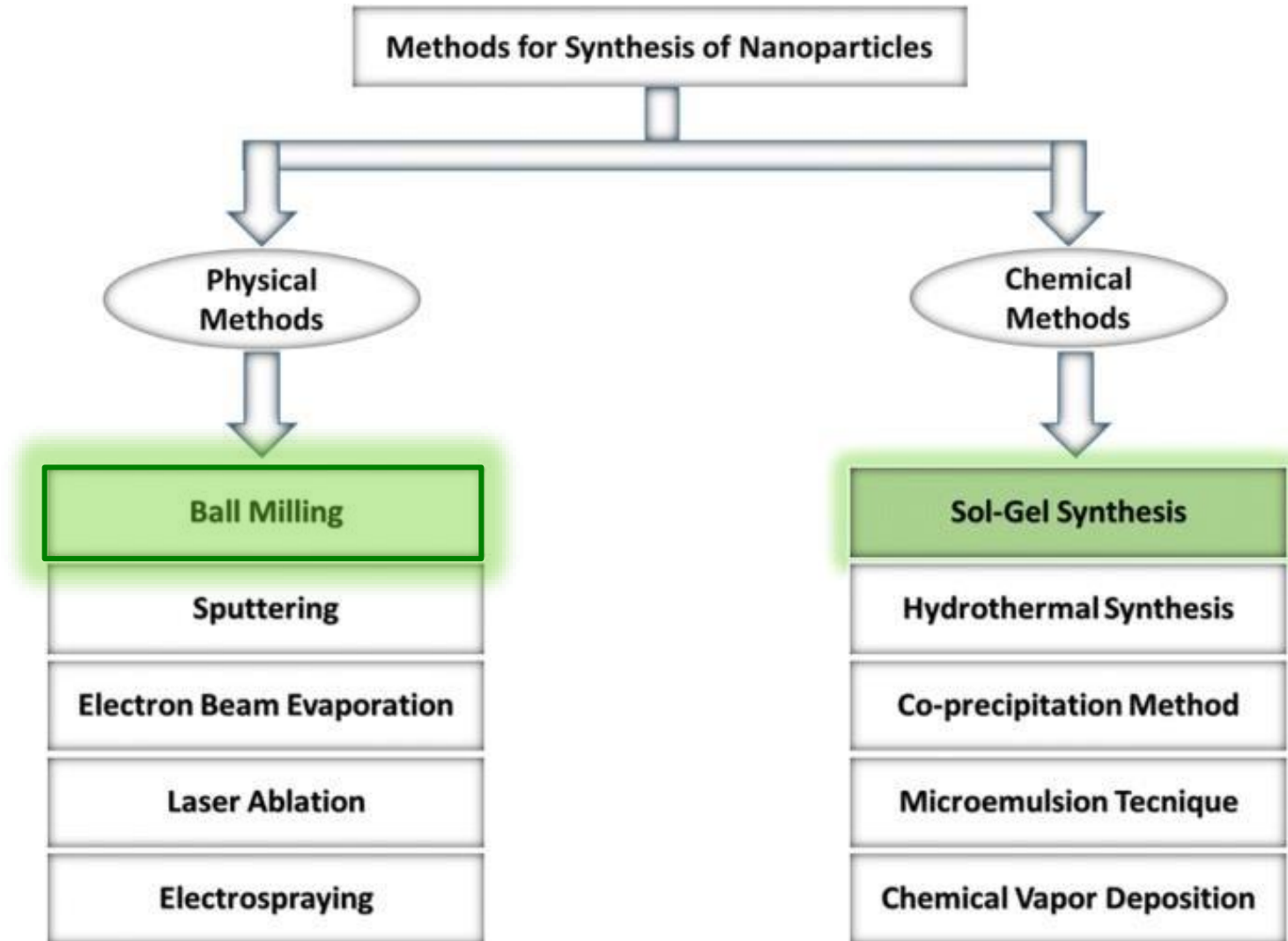
- Starts with atoms or molecules and build up to nanostructures
- Fabrication is much less expensive
- Includes the miniaturization of materials components (atomic level) leading to formation of nano structures
- During self assembly the physical forces operating at nanoscale are used to combine basic units into larger stable structure.



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

Synthesis & Characterization of nanoparticles

- Synthesis



Any fabrication technique should provide the followings:

- Identical size of all particles (also called mono sized or with uniform size distribution)
- Identical shape or morphology
- Identical chemical composition and crystal structure
- Individually dispersed or mono dispersed i.e., no agglomeration

Nanoparticles preparation:

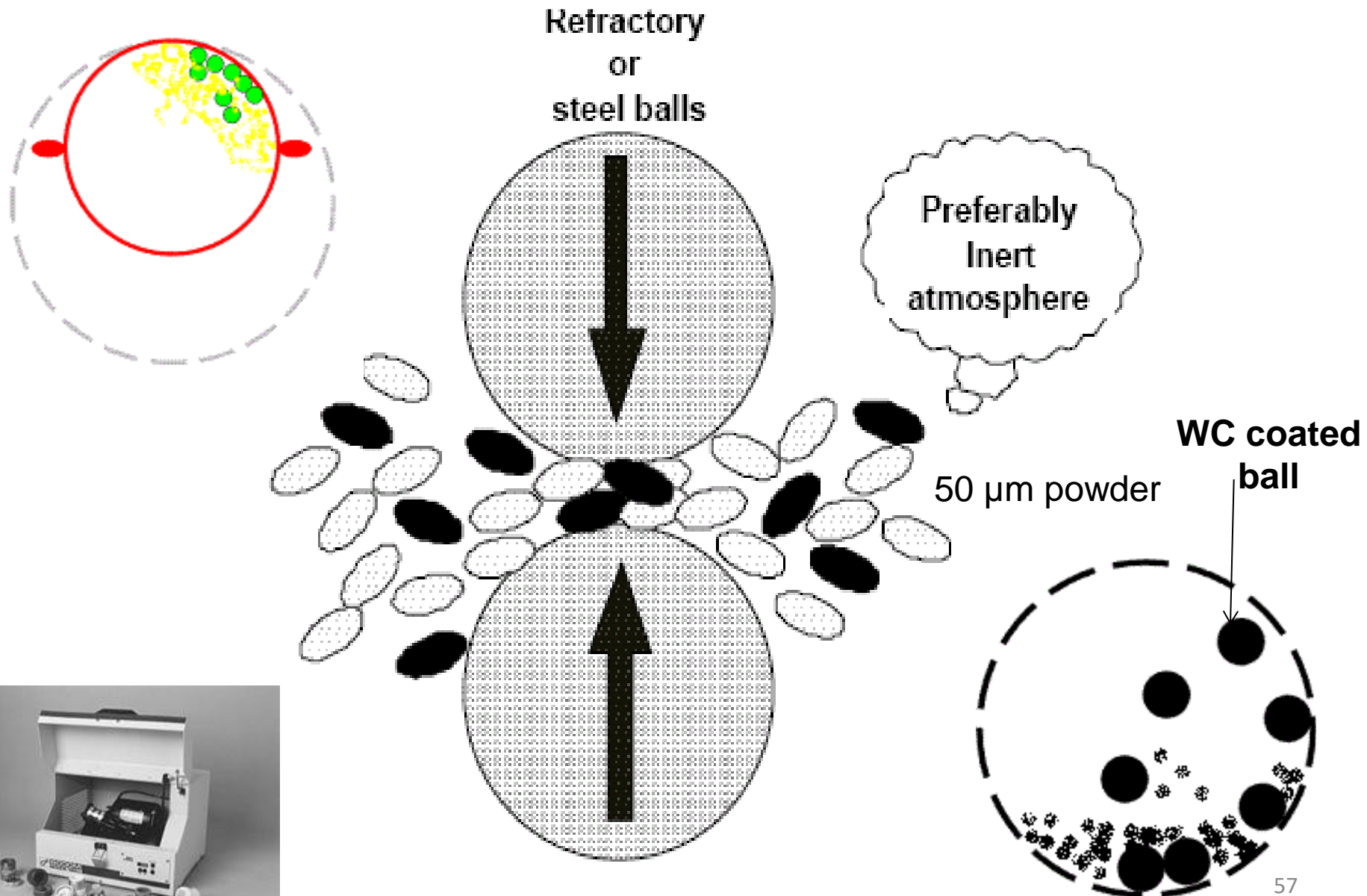
❖ Top-down approaches

- High-energy ball milling/Machining
- Chemical Oxidation Process (CNTs to QDs)
- Electrochemical Oxidation Process (Graphite rod to QDs)
- Lithography (photo- and electrochemical)
- Etching/Cutting
- Coating
- Atomization

❖ Bottom-up approaches

- Gas Condensation Processing (GCP)/Aerosol Based Processes
- Chemical Vapour Condensation (CVC)
- Atomic or Molecular Condensation
- Laser ablation
- Supercritical Fluid Synthesis
- Wet Chemical Synthesis of nanomaterials (Sol-gel process)
- Precipitation method
- Spinning
- Self-Assembly
- DNA Origami

Schematic representation of the principle of mechanical milling



Mineral, ceramic processing, and powder metallurgy industry

❖ Procedure of milling process

- Particle size reduction, solid-state alloying, mixing or blending, and particle shape changes
- Restricted to relatively hard, brittle materials which fracture and/or deform and cold weld during the milling operation
- To produce nonequilibrium structures including nanocrystalline, amorphous and quasicrystalline materials
- Users are tumbler mills, attrition mills, shaker mills, vibratory mills, planetary mills etc
- Powders diameters of about 50 μm with a number of hardened steel or tungsten carbide (WC) coated balls in a sealed container which is shaken or violently agitated. The most effective ratio for the ball to powder mass is 5 : 10.

- Shaker mills (e.g. SPEX model 8000) uses small batches of powder (approximately 10 cm³ is sufficient)

❖ Advantage: High production rates

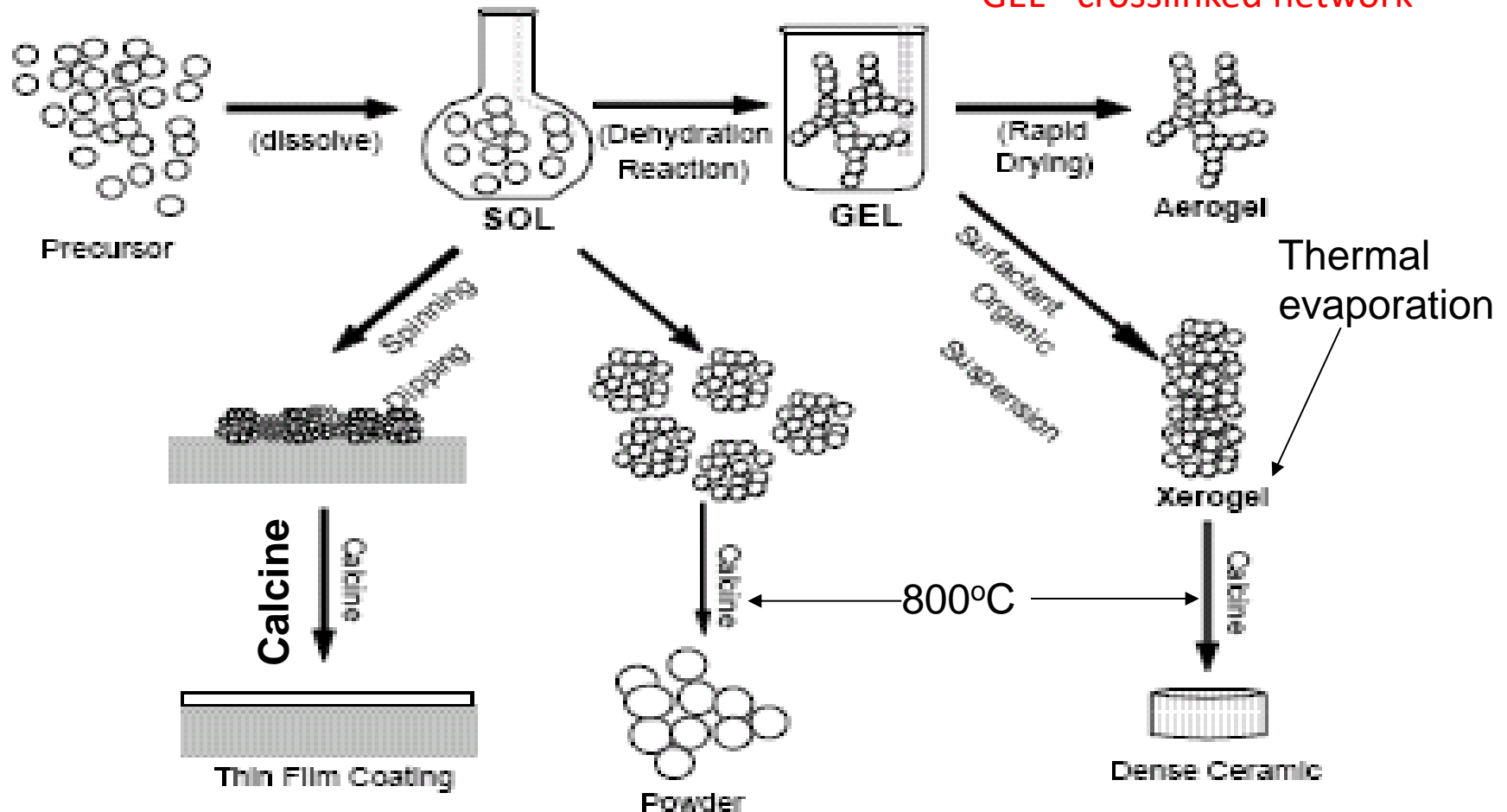
❖ Limitation

- Severe plastic deformation associated with mechanical attrition due to generation of high temp in the interphase, 100 to 200 °C.
- Difficulty in broken down to the required particle size
- Contamination by the milling tools (Fe) and atmosphere (trace elements of O₂, N₂ in rare gases) can be a problem (inert condition necessary like Glove Box)(Fe <1-2% and Trace elements<300 ppm)
- Protective coating to reduce milling tools contamination (MTC) increases cost of the process
- Working duration (>30 h) increases MTC (>10%)

Wet Chemical Synthesis of nanomaterials (Sol-gel process)

SOL - nanoparticle dispersion

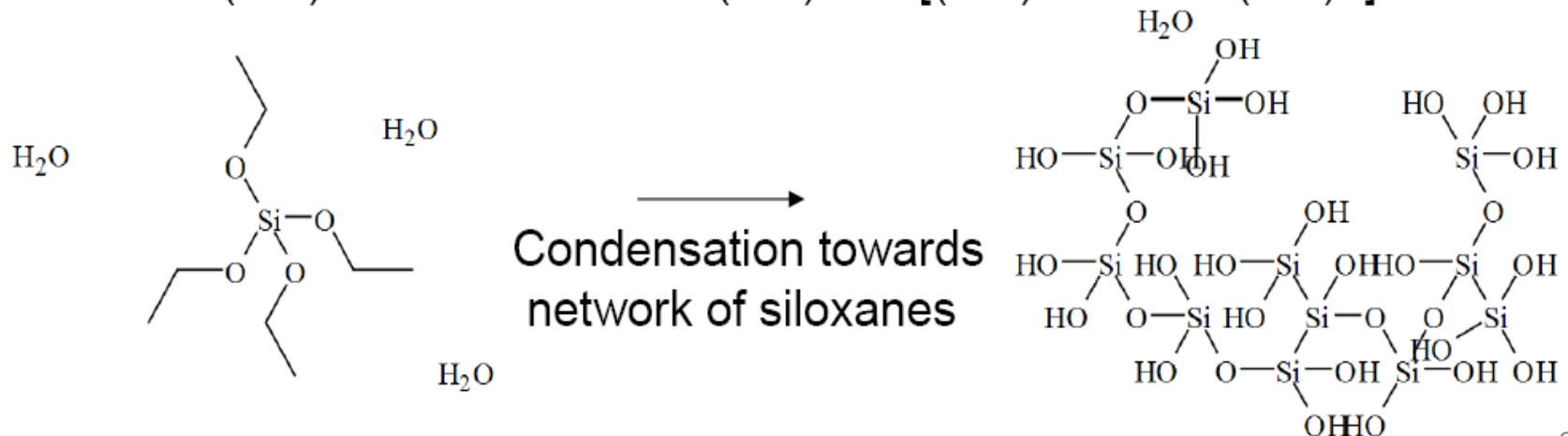
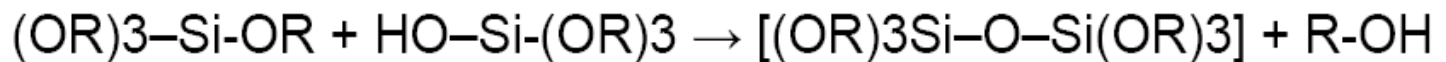
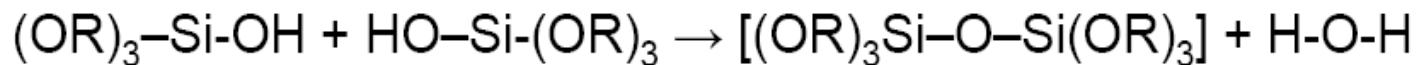
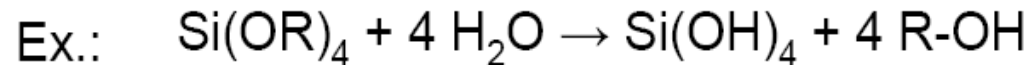
GEL - crosslinked network



Schematic representation of sol-gel process of synthesis of nanomaterials.

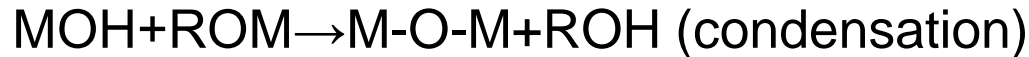
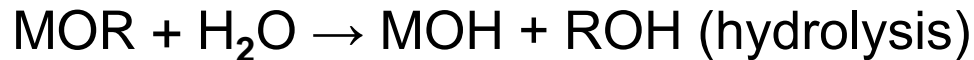
Sol-Gel Processing

- Creation of Sol (solid particles in solution)
- Followed by the following two generic sol-gel processes (assuming as a precursor a metal alkoxide MOR):



- **Overall Steps:**
- **Step 1:** Formation of different stable solutions of the alkoxide (the sol).
- **Step 2:** Gelation resulting from the formation of an oxide- or alcohol-bridged network (the gel) by a **polycondensation or polyesterification reaction**
- **Step 3:** Aging of the gel, during which the polycondensation reactions continue until the gel transforms into a solid mass, accompanied by contraction of the gel network and expulsion of solvent from gel pores.
- **Step 4:** Drying of the gel, when water and other volatile liquids are removed from the gel network.
 - If isolated by thermal evaporation, the resulting **monolith** is termed a **xerogel**.
 - If the solvent (such as water) is extracted under supercritical or near super critical conditions, the product is an **aerogel**.
- **Step 5:** Dehydration, during which surface- bound M-OH groups are removed, thereby stabilizing the gel against **rehydration**. This is normally achieved by calcining the monolith at temperatures up to 800°C.
- **Step 6:** Densification and decomposition of the gels at high temperatures ($T > 800^{\circ}\text{C}$). The pores of the gel network are collapsed, and remaining organic species are volatilized. The typical steps that are involved in sol-gel processing are shown in the schematic diagram above.

- Sol/gel transition controls the particle size and shape. Calcination of the gel produces the product (eg. Oxide).
- Sol-gel processing > hydrolysis and condensation of alkoxide-based precursors such as $\text{Si}(\text{OEt})_4$ (tetraethyl orthosilicate, or TEOS).
- The reactions are as follows:



- If the aging process of gels exceeds 7 days it is critical to prevent the cracks in gels that have been cast
- Steps are:

**Sol → Gel → Ageing → Drying → Dehydration
→ Densification & Decomposition → Product**

❖ Advantages

- Synthesizing nonmetallic inorganic materials like glasses, glass ceramics or ceramic materials at very low temperatures compared to melting glass or firing ceramics
- Monosized nanoparticles possible by this bottom up approach.

❖ Disadvantages

- Controlling the growth of the particles and then stopping the newly formed particles from agglomerating.
- Difficult to ensure complete reaction so that no unwanted reactant is left on the product
- Completely removal of any growth aids
- Also production rates of nanopowders are very slow by this process