

Module 5

Functional Materials

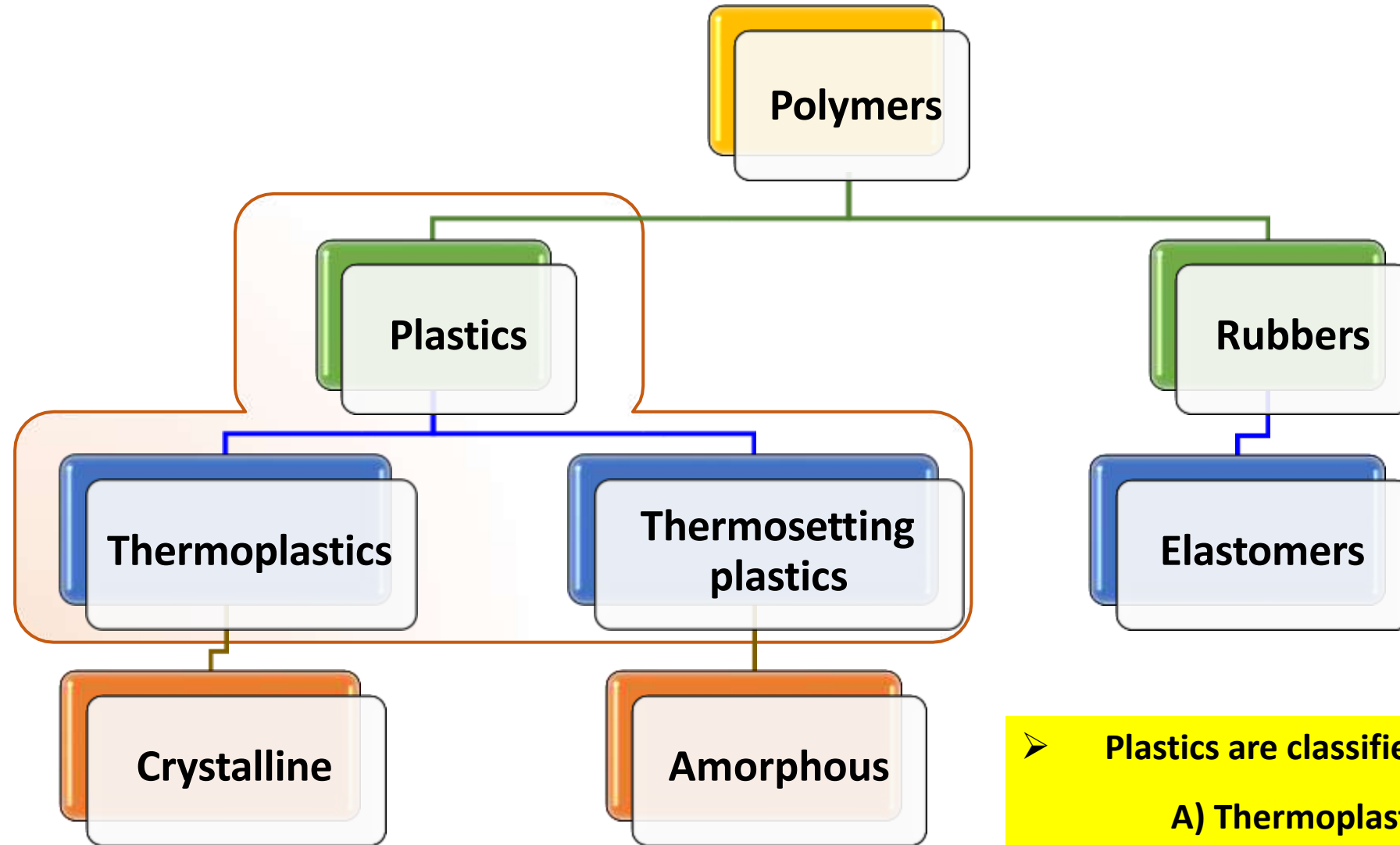
- ❖ Polymers – ABS & BAKELITE– synthesis and application
- ❖ Conducting polymers- polyacetylene and effect of doping
- ❖ Nanomaterials – introduction, bulk vs. nano (quantum dots)
- ❖ Top-down and bottom-up approaches for synthesis, and
- ❖ Properties of nano Au.

Introduction to Polymers

- Polymers are high molecular weight organic materials, that can be moulded into any desired shape by the application of heat and pressure in the presence of a catalyst
- 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**.



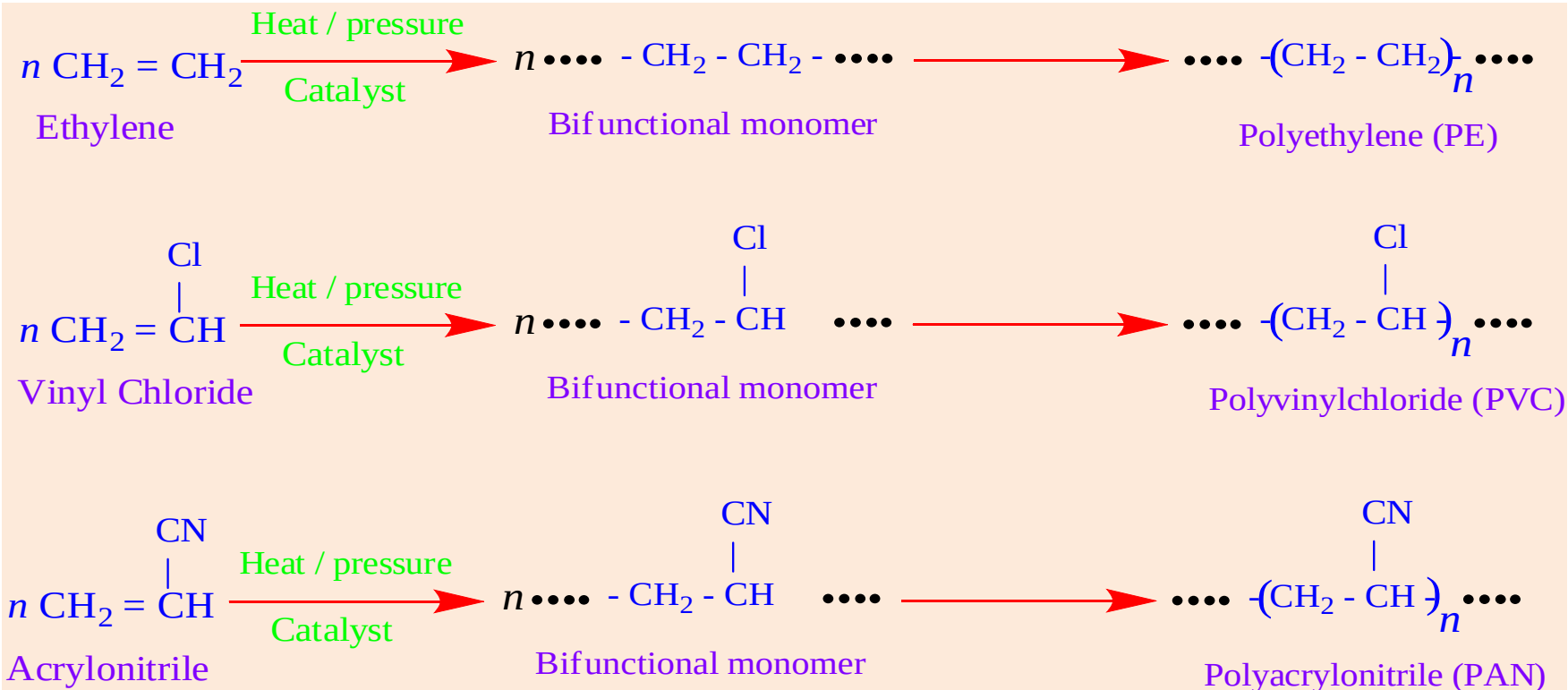
Classification



- **Plastics are classified into two types**
 - A) Thermoplastic resins**
 - B) Thermosetting resins**

1) Thermoplastic resins

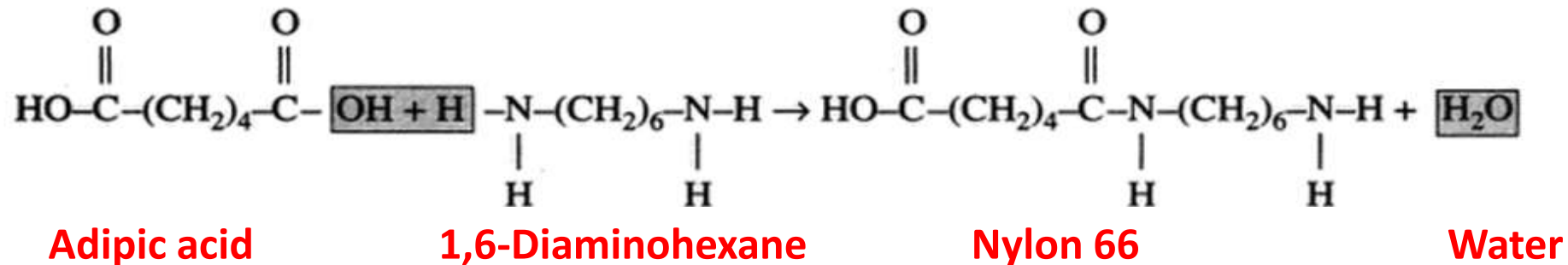
- They are prepared by **addition polymerisation**.
- They are **straight chain (or) slightly branched polymers** and various chains are held together by **weak vanderwaal's forces of attraction**.
- Thermoplastics can be softened on heating and hardened on cooling.
- They are generally **soluble in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

- Thermosetting resins (or) Thermosets
- They are prepared by condensation polymerisation
- Various polymer chains are held together by strong covalent bonds (cross links)
- Thermosetting plastics get harden on heating and once harden, they cannot be softened again
- They are almost insoluble in organic solvents.
- Examples: Bakelite, Polyester, Nylon 66

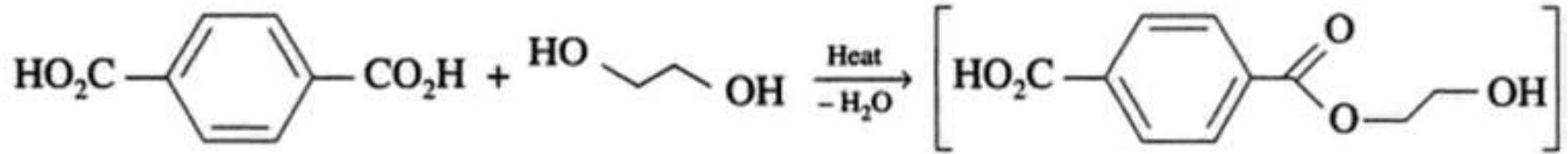


Thermoset Polymers whose individual chains have been chemically cross linked by covalent bonds and form a 3-D cross linked structure.

- 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

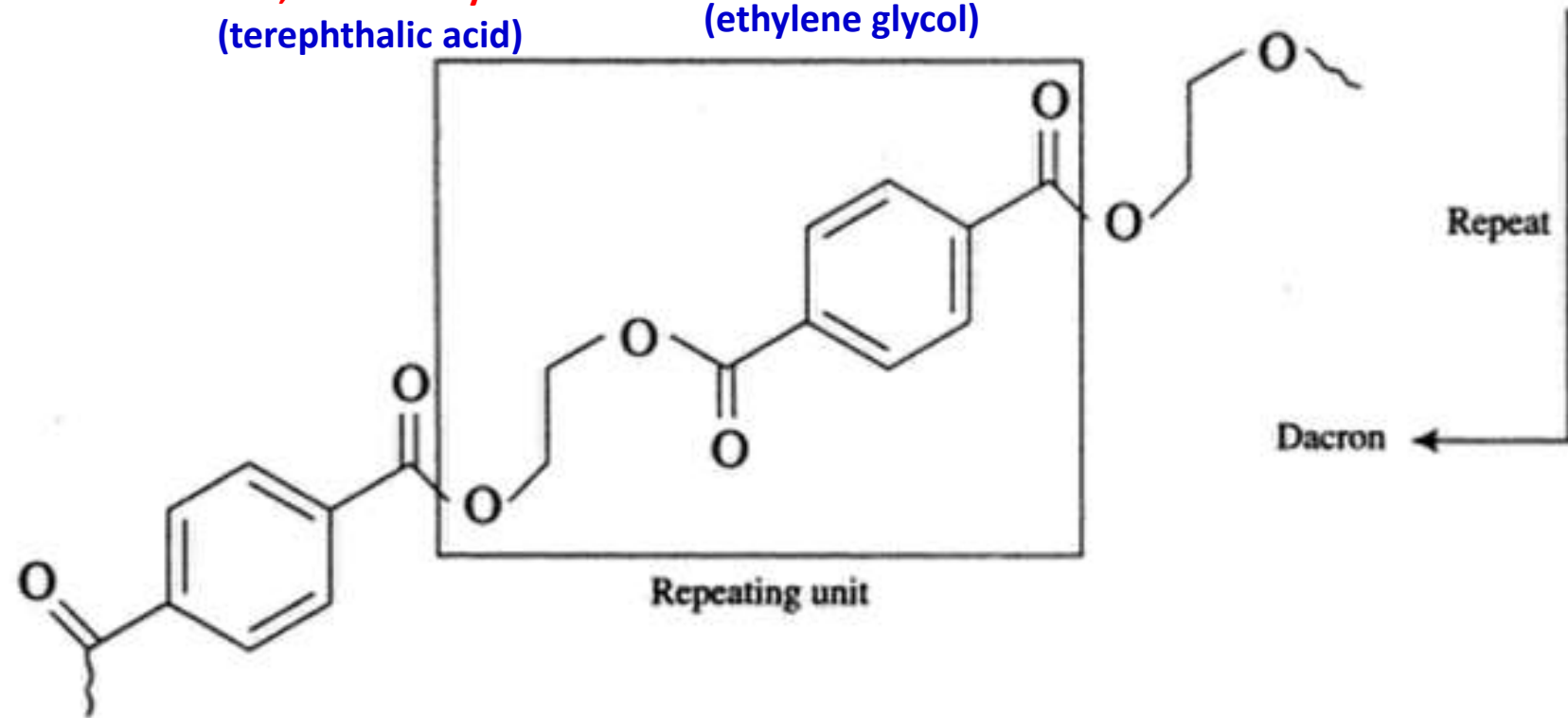
Eg. Phenol-formaldehyde resins, urea-formaldehyde paints.

1. Polyester



Benzene-1,4-dicarboxylic acid
(terephthalic acid)

Ethane-1,2-diol
(ethylene glycol)

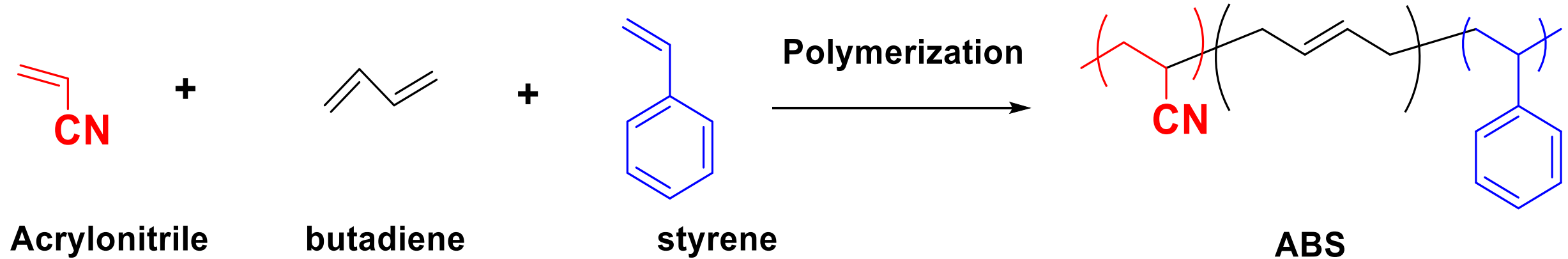


S.No.	Thermoplastic resins	Thermosetting resins
1	They are formed by addition polymerisation	They are formed by condensation polymerisation
2	They consist of linear long chain polymers	They consist of three dimensional network structure
3	All the polymer chains are held together by weak vanderwaals forces	All the polymer chains are linked by strong covalent bonds
4	They are weak, soft and less brittle	They are strong, hard and more brittle
5	They soften on heating and harden on cooling	They do not soften on heating
6	They can be remoulded	They cannot be remoulded
7	They have low molecular weights	They have high molecular weights
8	They are soluble in organic solvents	They are insoluble in organic solvents
9	Examples: PE, PVC	Examples: Bakelite, Polyester

Engineering applications of Plastics

i. Acrylonitrile butadiene styrene (ABS)

- ❖ ABS is a ter-polymer
- ❖ It is polymerized by the polymerization of *acrylonitrile, butadiene and styrene*



- ❖ It is an amorphous and thermoplastic polymer

Properties of ABS:

- Cost effective
- Good Impact Strength
- Good Chemical Resistance
- High Gloss Surface Finish
- Good Flexural Properties
- Can prepare in different grades as per the requirement

ABS can be recycled

Applications of ABS:

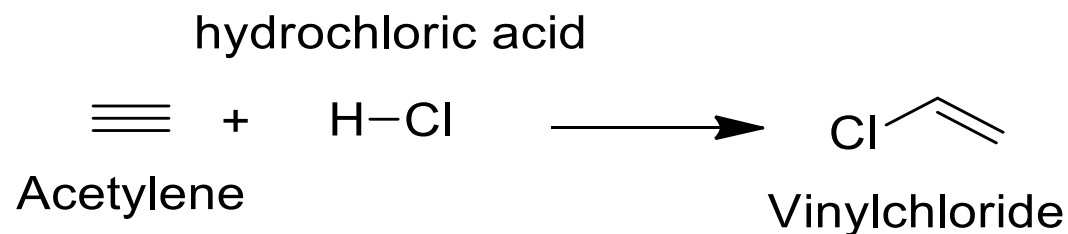
- Musical instruments (recorders, plastic clarinets, and piano movements)
- Automotive trim components, automotive bumper bars
- Medical devices for blood access
- White-water canoes
- Buffer edging for furniture and joinery panels
- Luggage and protective carrying cases
- Small kitchen appliances
- Keyboard keycaps
- Toys, including Lego and Kre-O bricks
- Golf club heads (because of its good shock absorbance)
- Household and consumer goods



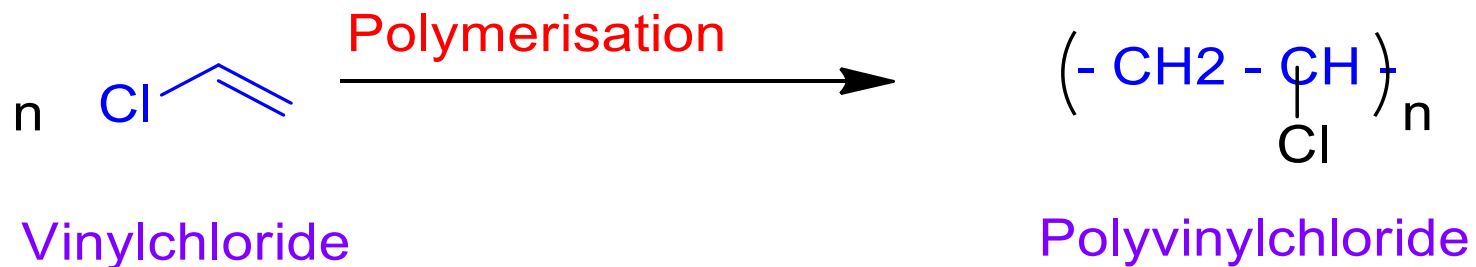
ii. Polyvinyl Chloride (PVC)

Preparation: Preparation of PVC involves the following two steps

1st step: Vinyl chloride is prepared by treating **acetylene with hydrogen chloride at 60-80°C in the presence of metal chloride as catalyst**



2nd step: Polyvinylchloride is obtained by **heating water emulsion of vinyl chloride in presence of benzoyl peroxide (or) hydrogen peroxide under pressure**

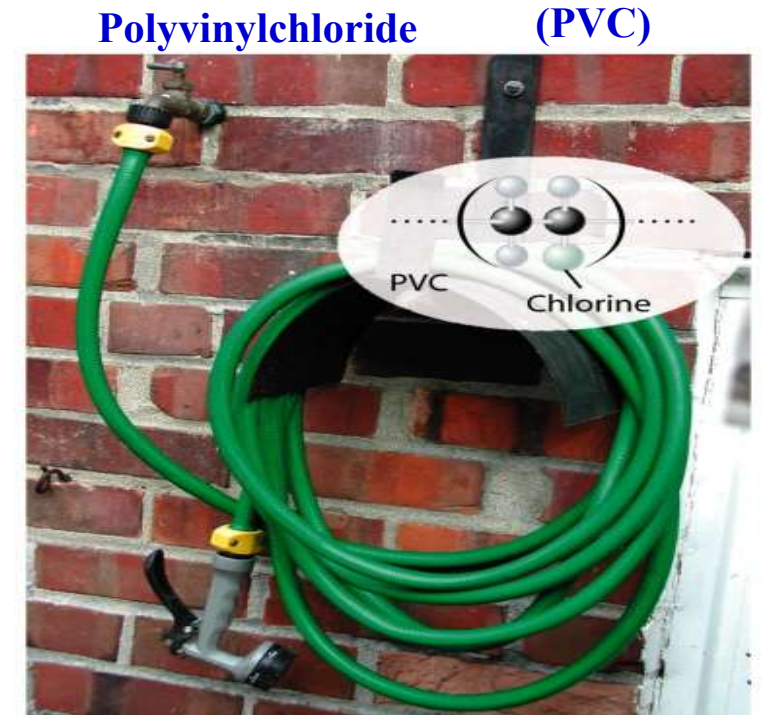


Properties of PVC:

1. PVC is colourless, odourless and chemically inert powder
2. It is insoluble in inorganic acids and alkalis, but soluble in hot chlorinated hydrocarbons such as ethylchloride
3. It undergoes degradation in presence of heat (or) light

Uses of PVC

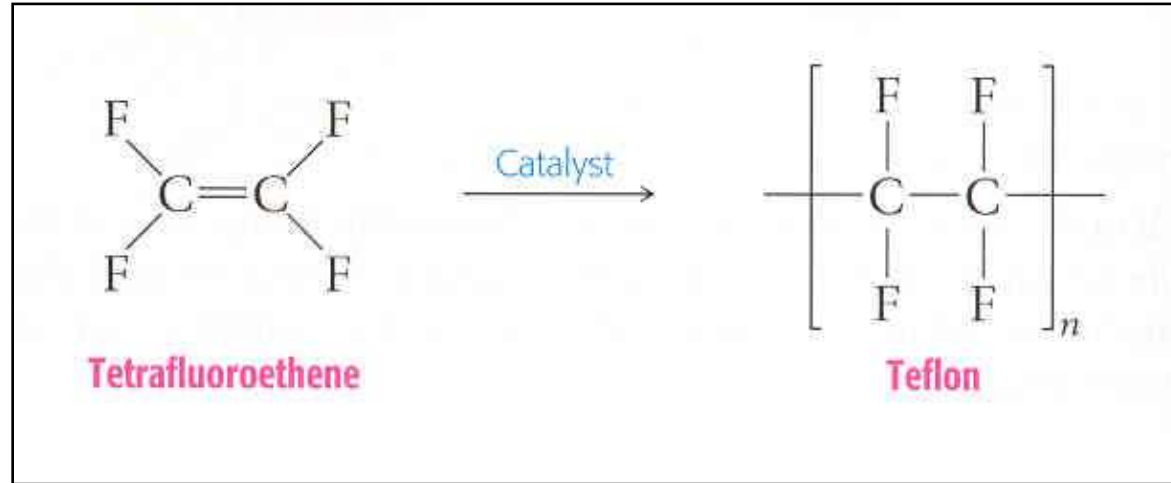
1. It is used in the production of pipes, cable insulations, table covers and rain-coats etc.,
2. It is also used for making sheets, which are employed for tank-linings, light fittings, refrigerator components, etc.,



iii. TEFLON (PTFE):

The trivial name of 'PTFE' (Polytetrafluoroethylene) is TEFLON.

Teflon is made by the polymerization of tetrafluoroethene as shown bellow.



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

iii. TEFLON

Uses of TEFLON

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



iv. Bakelite

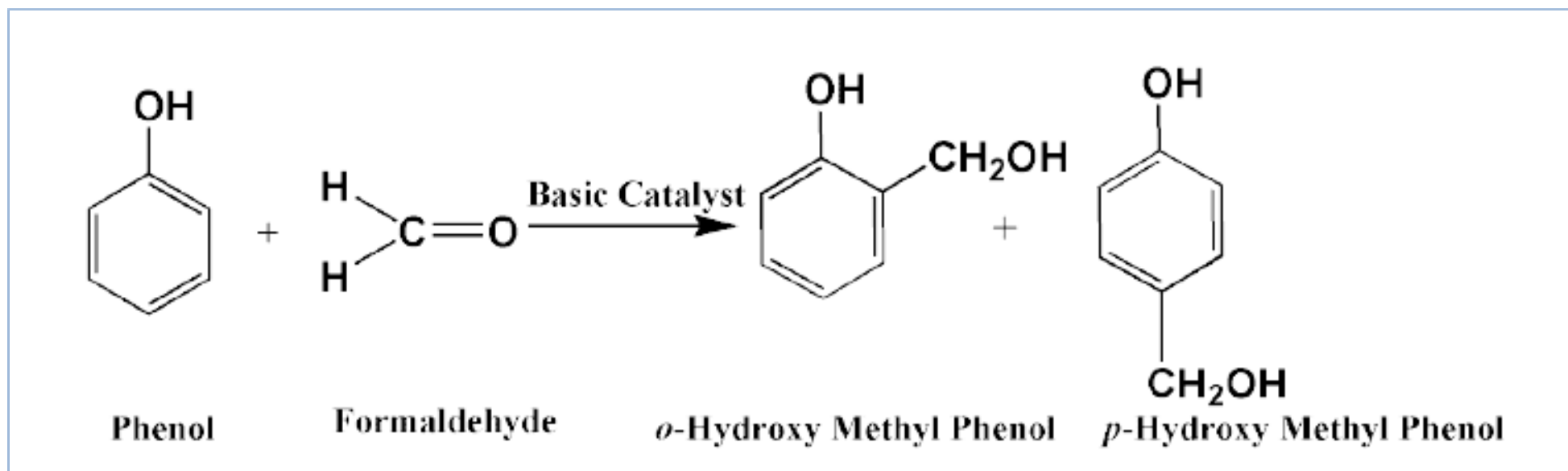
Bakelite is obtained by the condensation polymerisation of phenol and formaldehyde in the presence of acid or alkali catalyst

Preparation

The reaction involves the following **3 steps**

Stage:1

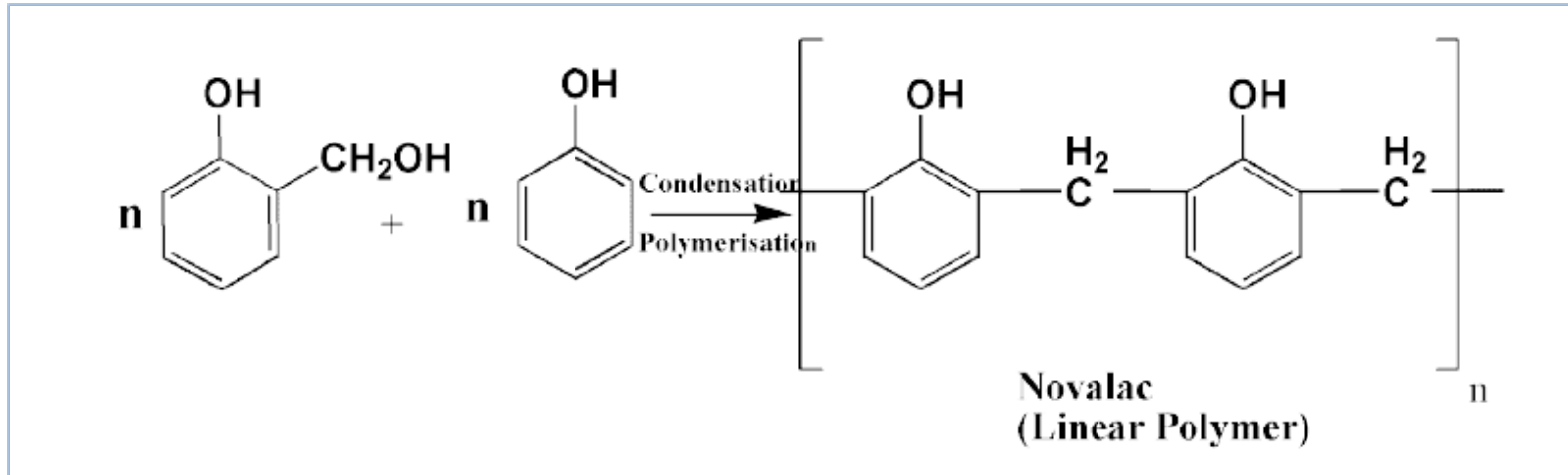
The first step is the reaction between phenol and formaldehyde in presence of acidic / alkaline catalyst to form to produce **methylo phenols** (o- and p- hydroxy methyl phenols)



iv. Bakelite

Stage 2: Synthesis of linear polymer Novolac

- When methylol phenols are heated with excess of formaldehyde in presence of alkaline catalyst, *the methylol phenols condense either through methylene linkages or through ether linkages to form resoles.*
- **Resole** is a **low molecular weight linear polymer**. It is completely **soluble** in **alkaline solution**.



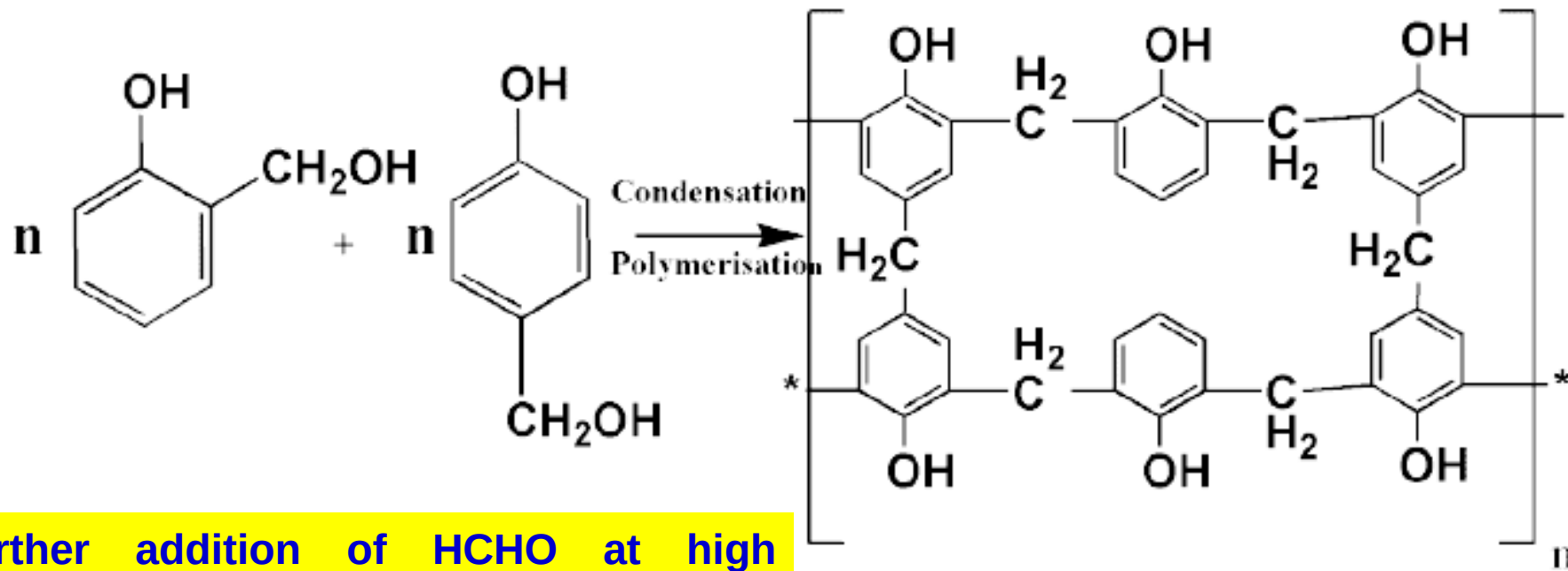
Monomethylol phenol further reacts with Phenol to form a linear polymer "Novolac".

Water is removed as the by-product.

iv. Bakelite

Stage 3: Synthesis of cross linked polymer Bakelite or phenol formaldehyde resin

By reacting the methylol phenols in the presence of a **curing agent** ([*hexamethylene tetramine*](#)) produces hard, rigid, infusible, cross-linked polymer called **bakelite**



Bakelite
(Cross-linked Polymer)

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

Bakelite

Properties of Bakelite

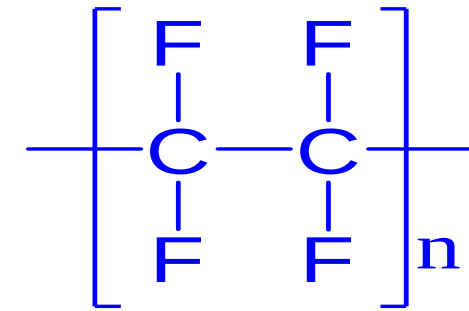
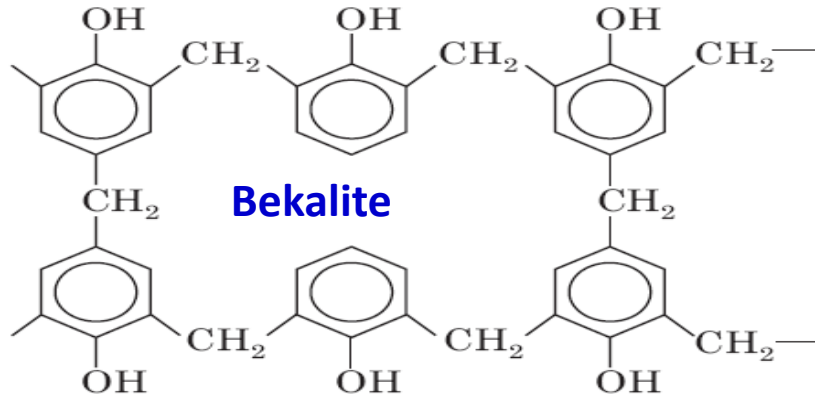
- Bakelite is resistant to acids, salts and most organic solvents, but it is attacked by alkalis because of the presence of -OH groups
- It possesses excellent electrical insulating property

Uses of Bakelite

- Bakelite is used as an adhesive in plywood laminations & grinding wheels etc
- It is also widely used in paints, varnishes
- Cooker with Bakelite Handles
- As *hydrogen exchanger resins* in water softening
- It is used for making electrical insulator parts like plugs, switches, heater handles, etc.,

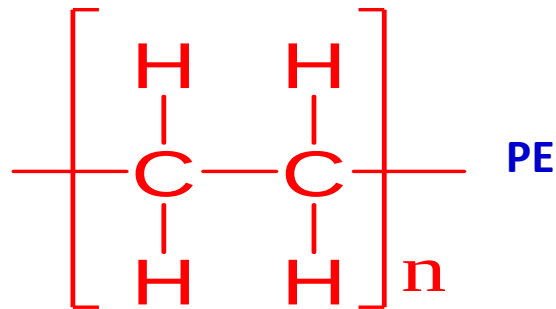


The polymers so far we have studied

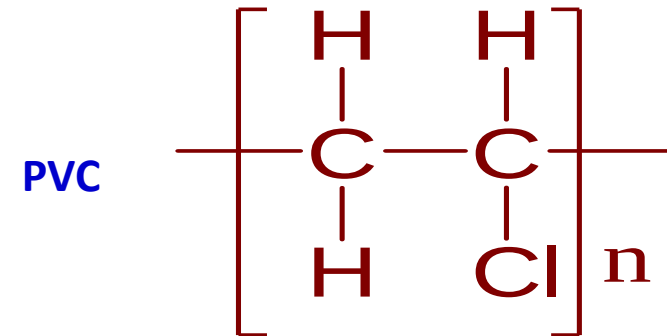


PTFE

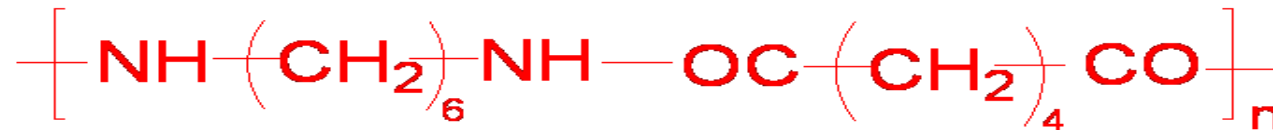
All are Insulators



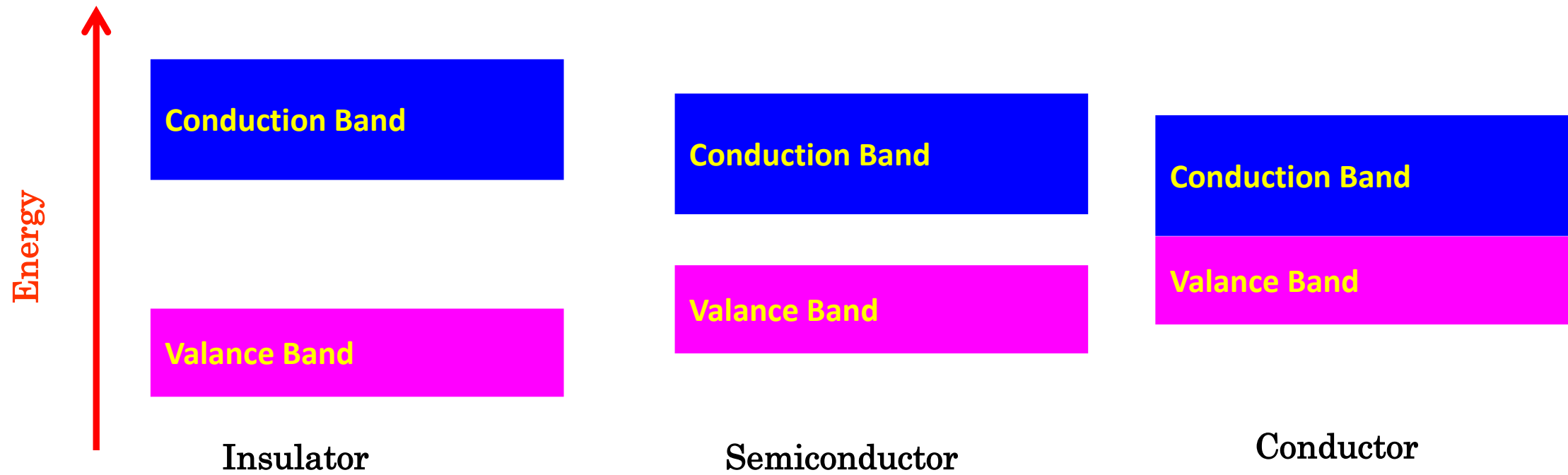
PE



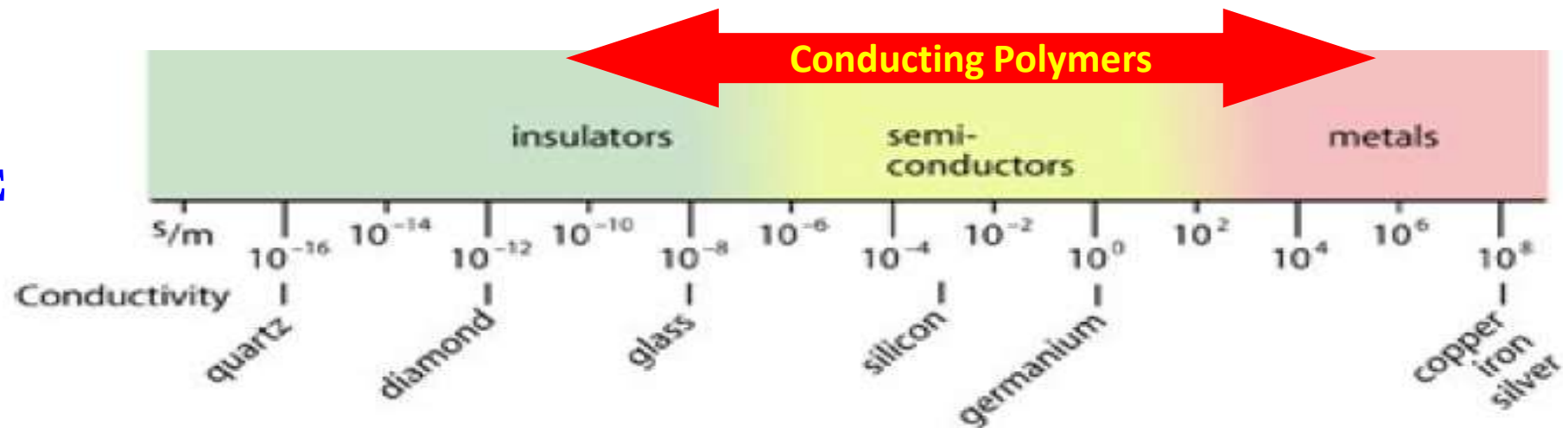
PVC



Nylon 66



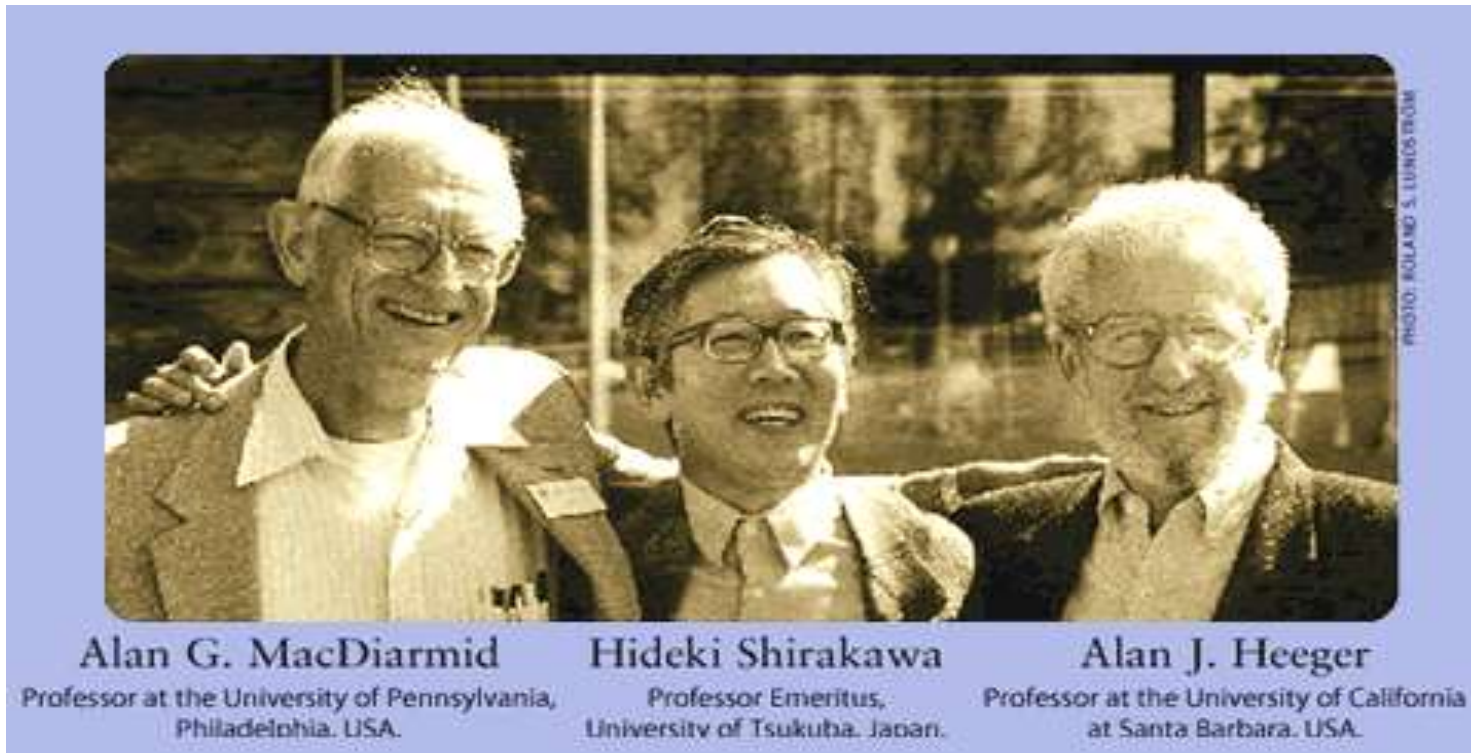
PMMA
Nylon
PS, PE, PTFE



But some Polymers do conduct electricity and are called as Conducting Polymers

Conducting Polymers

- ❑ Polymers are **typically insulators** due to their very high resistivity. Insulators have tightly bound electrons so that nearly no electron flow occurs, and they offer high resistance to charge flow.
- ❑ For conductance free electrons are needed. **Conductivity in polymers can be induced by delocalizing their orbital with conjugated p-electron backbones.**



*Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa discovered that **Polyacetylene** can be made conductive almost like a metal (Nobel Prize for Chemistry in 2000).*

Conductive polymers, which are almost always organic, may have extended *delocalized bonds* (often composed of linear or *aromatic* units) that create a band structure [Fig. 7.11 (a)] similar to silicon [Fig. 7.11 (b)], but with localized states [Fig. 7.11 (c)]. When *charge carriers* (from the addition or removal of electrons) are introduced into the conduction or valence bands the electrical conductivity increases dramatically.

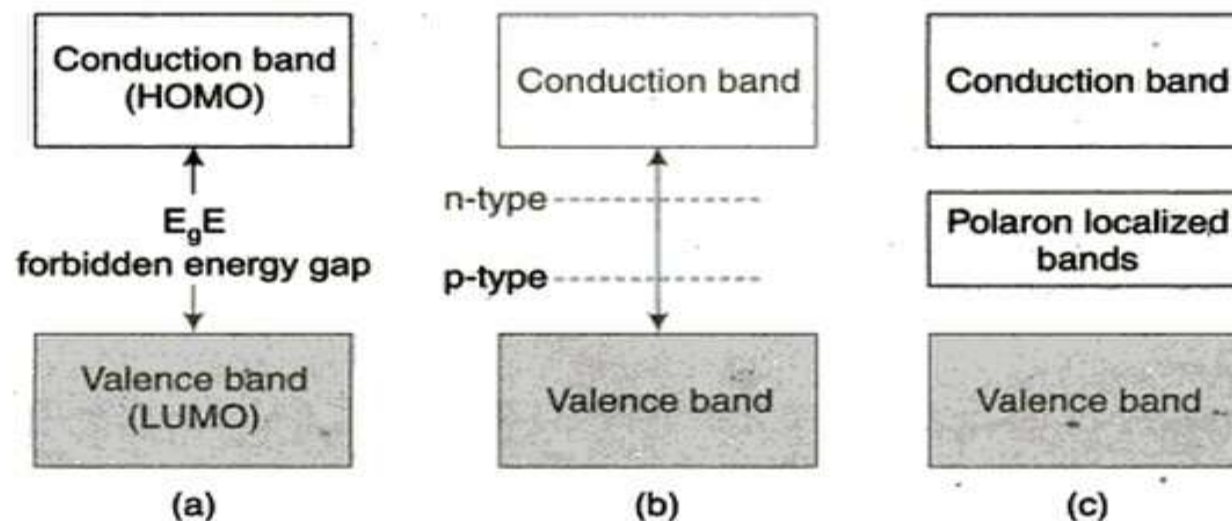


Fig. 7.11 *Energy bands of semiconductors*

Conjugated polymers are organic semiconductors. They have a *band gap*.

- They can emit light, the colour of which is tailorable through the chemical structure. They can generate a current upon absorbing light, and so can be used in photovoltaic devices.
- The conductivity of conjugated polymers can be varied.
- Like silicon, their conductivity depends on the doping level.
- The doping level depends on the oxidation state of the polymer, which can be electrochemically controlled.

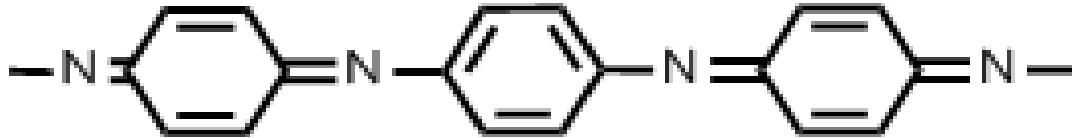
Some Examples of Conductive Polymers



trans-polyacetylene



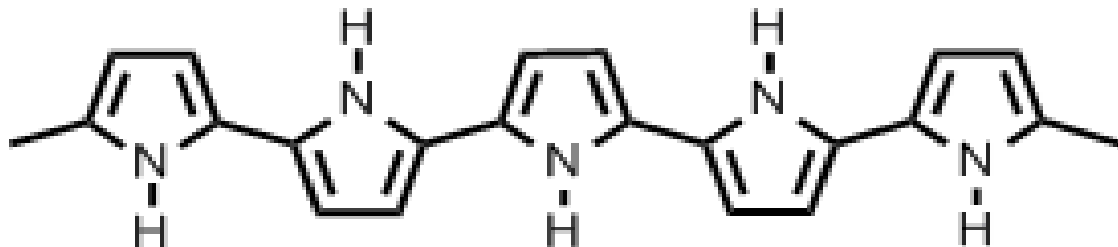
polythiophene



polyaniline



poly(p-phenylene)

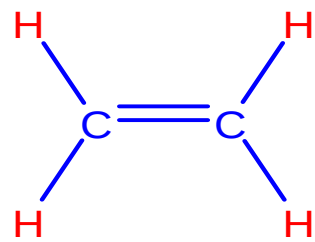


polypyrrole

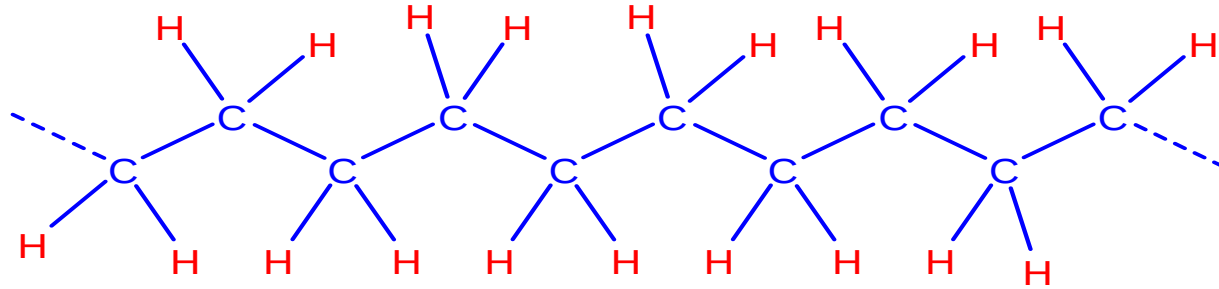
Conducting Polymers

Conjugated polymers having extended π -electron delocalization over the polymer backbone through which electron moves from one end to other end of the polymer chain.

Eg. Polyacetylene, Polyaniline (PANi), Polypyrrole, etc.



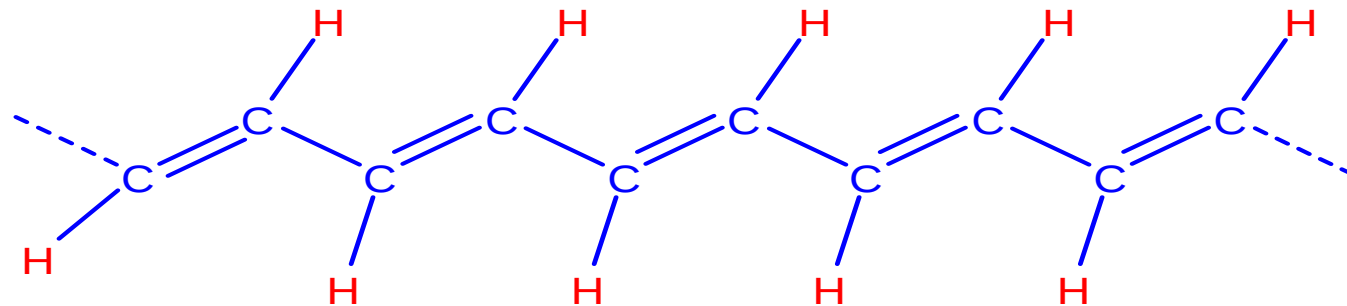
Ethylene



Polyethylene



Acetylene



Polyacetylene

What are the two conditions for a insulating polymer to become a conducting polymer?

1st Condition: The polymer should consist of alternating single and double bonds, called **conjugated double bonds**.

In conjugation, the bonds between the carbon atoms are alternately single and double. Every bond contains a localized “sigma” (σ) bond which forms a strong chemical bond. In addition, every double bond also contains a less strongly localized “pi” (π) bond which is weaker.

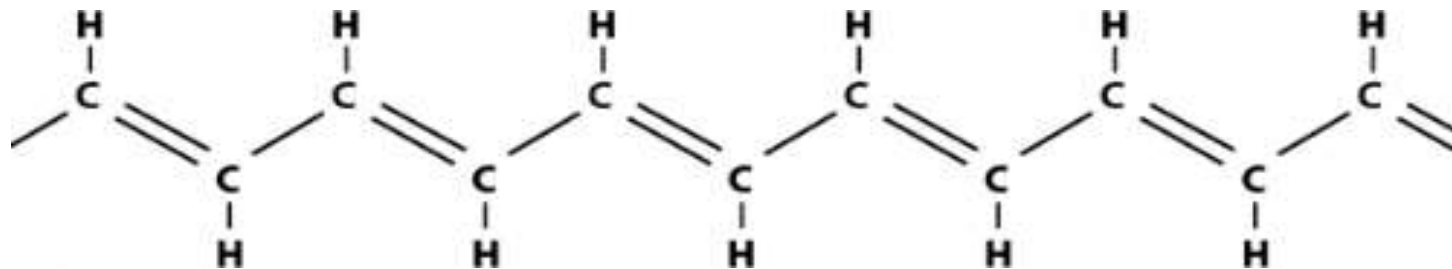
2nd Condition: The polymer structure has to be disturbed - either by removing electrons from (oxidation), or inserting them into (reduction), the material. The process is known as **Doping**.

Different Types of Conducting Polymers

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

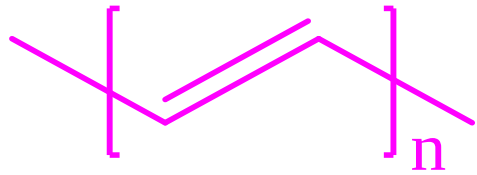


Polyacetylene

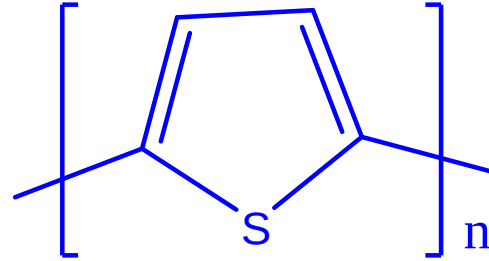
1. Intrinsically Conducting Polymers (ICP) (or) Conjugated π -electrons conducting polymer

Delocalization of π -electron over the entire polymer backbone

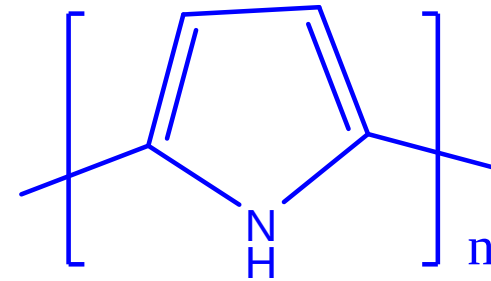
Example:



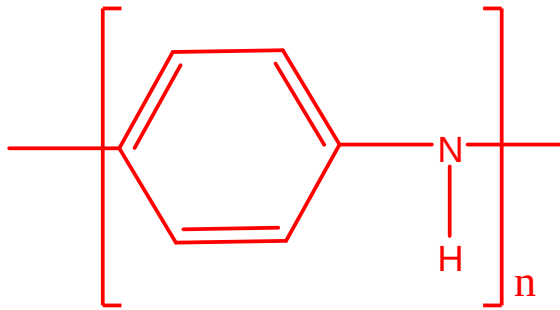
Trans- polyacetylene



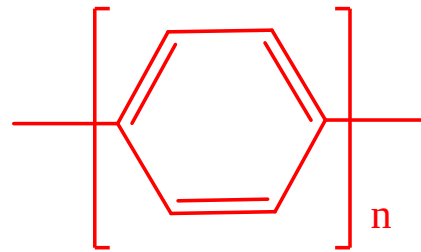
Polythiophene



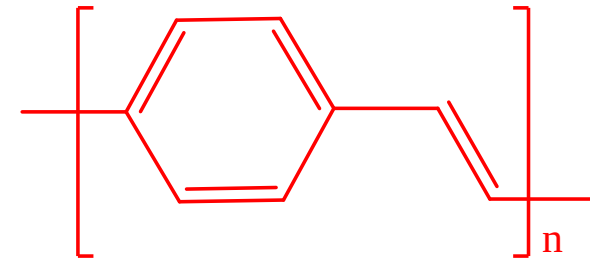
Polypyrrole



Polyaniline



Pol(p-phenylene)



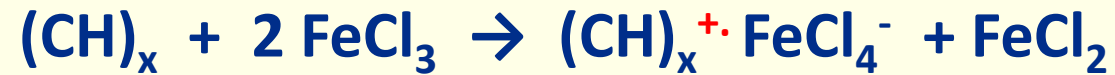
Pol(p-phenylenevinylene)

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

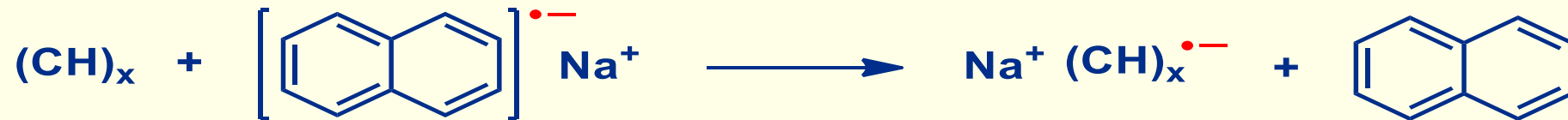
- p-doping is achieved by oxidation process. It is also known as the **oxidative doping**.
- It involves treatment of an polyacetylene with a **Lewis acid or iodine** which leads to oxidation process and positive charges on the polymer backbone are created.
- Some of the p-dopants are I_2 , Br_2 , AsF_5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

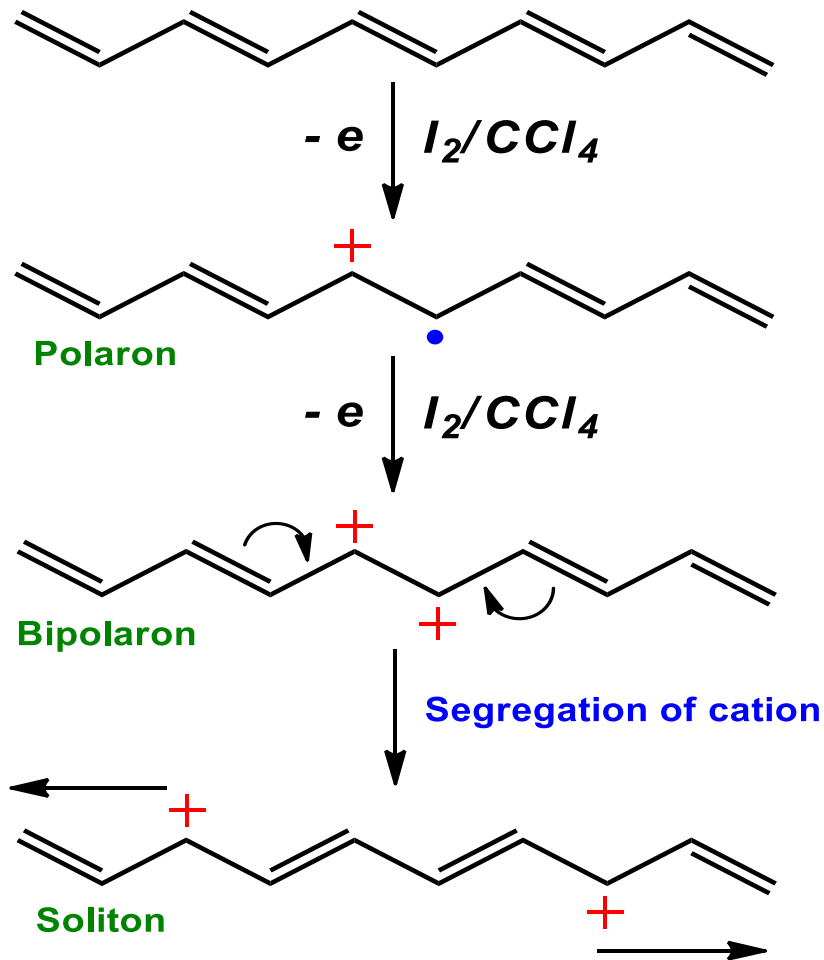
- n-doping is achieved by reduction process. It is also known as the **reductive doping**.
- It involves treatment of an polyacetylene with a **Lewis base** which leads to reduction process and negative charges on the polymer backbone are created.
- Some commonly available p-dopants are **Li, Na, Ca,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



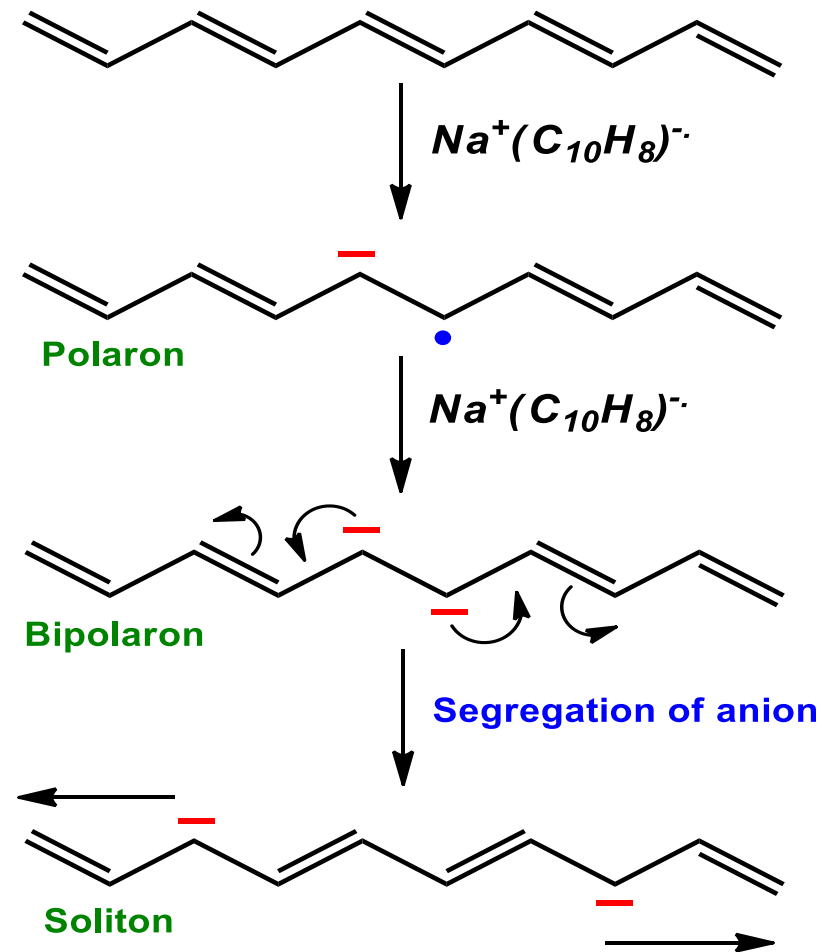
- This reduction process or the donation of one electron leads to the formation of **delocalized radical anion, an anionic polaron**
- Second reduction, followed by radical recombination generates negatively charged **soliton**

Doping in ICP

p-doping

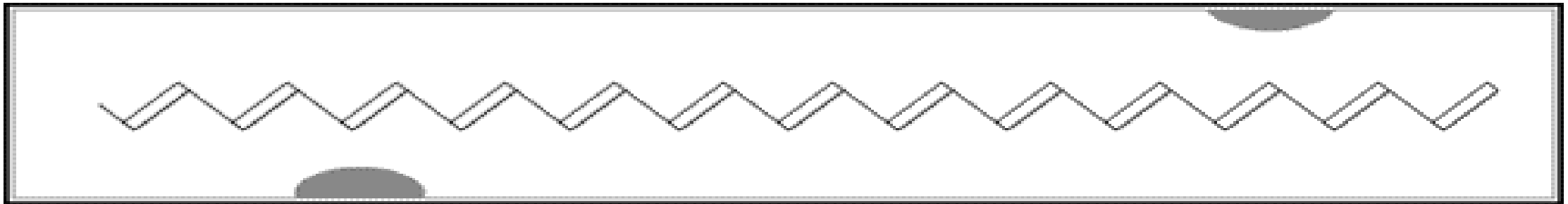


n-doping

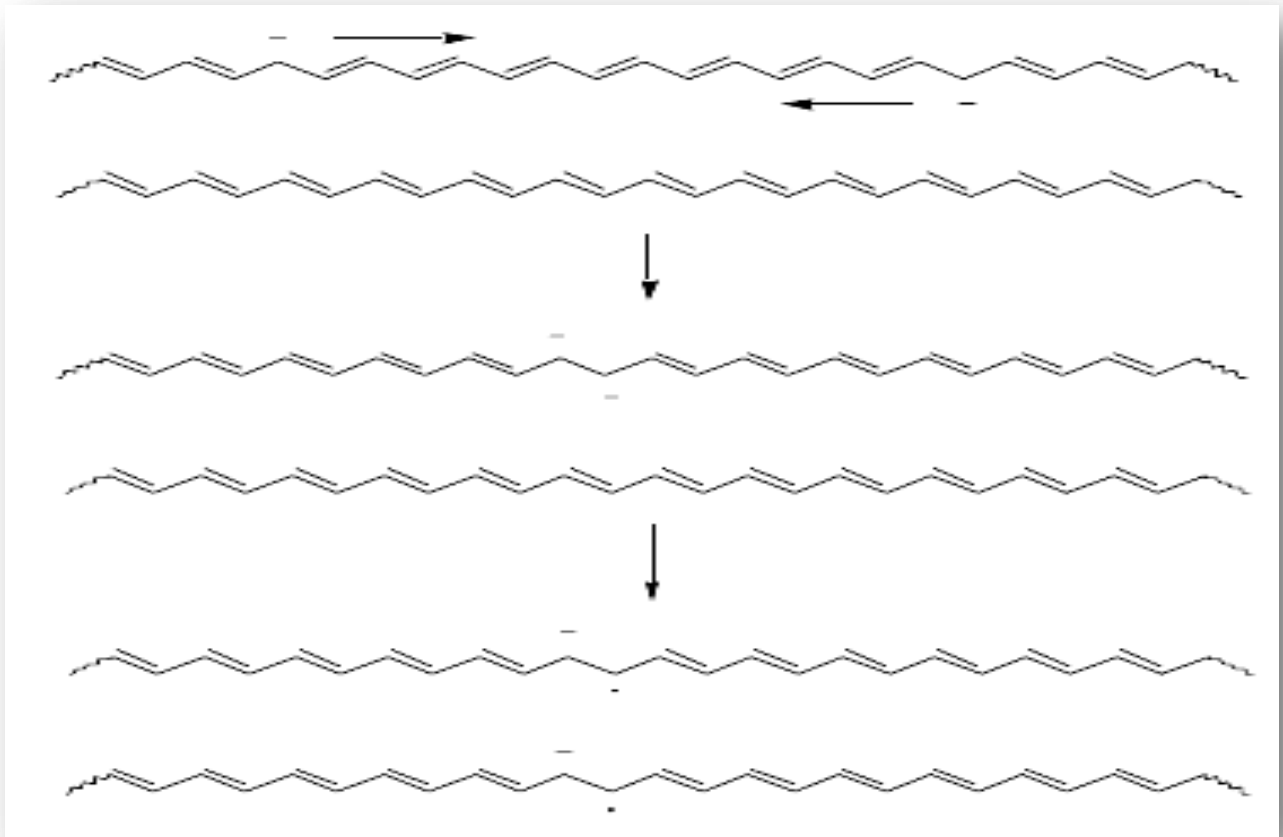


- What is a soliton? The soliton is a charged or a neutral defect in the polyacetylene chain that propagates down the chain, thereby reducing the barrier for interconversion.

- 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 lone 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.



- ✱ 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.



Applications of Conducting Polymers

- ❖ Constituents in solar cells and semiconductor devices.
- ❖ As sensors.
- ❖ As light weight rechargeable batteries.
- ❖ In LEDs.
- ❖ Conducting polymer textiles as a camouflage for defense machinery. Since the textiles has no sharp edges they absorb more than 50% of the incident microwave radiation.
- ❖ In electrochemical actuators, the anode and cathode strip changes its size at different rates during charging and discharging.
- ❖ Biocompatible conducting polymers may be used to transport small electrical signals through the body. i.e., act as artificial nerves.
- ❖ By coating aircraft with a conducting polymer the electricity can be directed away from the vulnerable internals of the aircraft.
- ❖ In controlled drug release applications, etc.

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

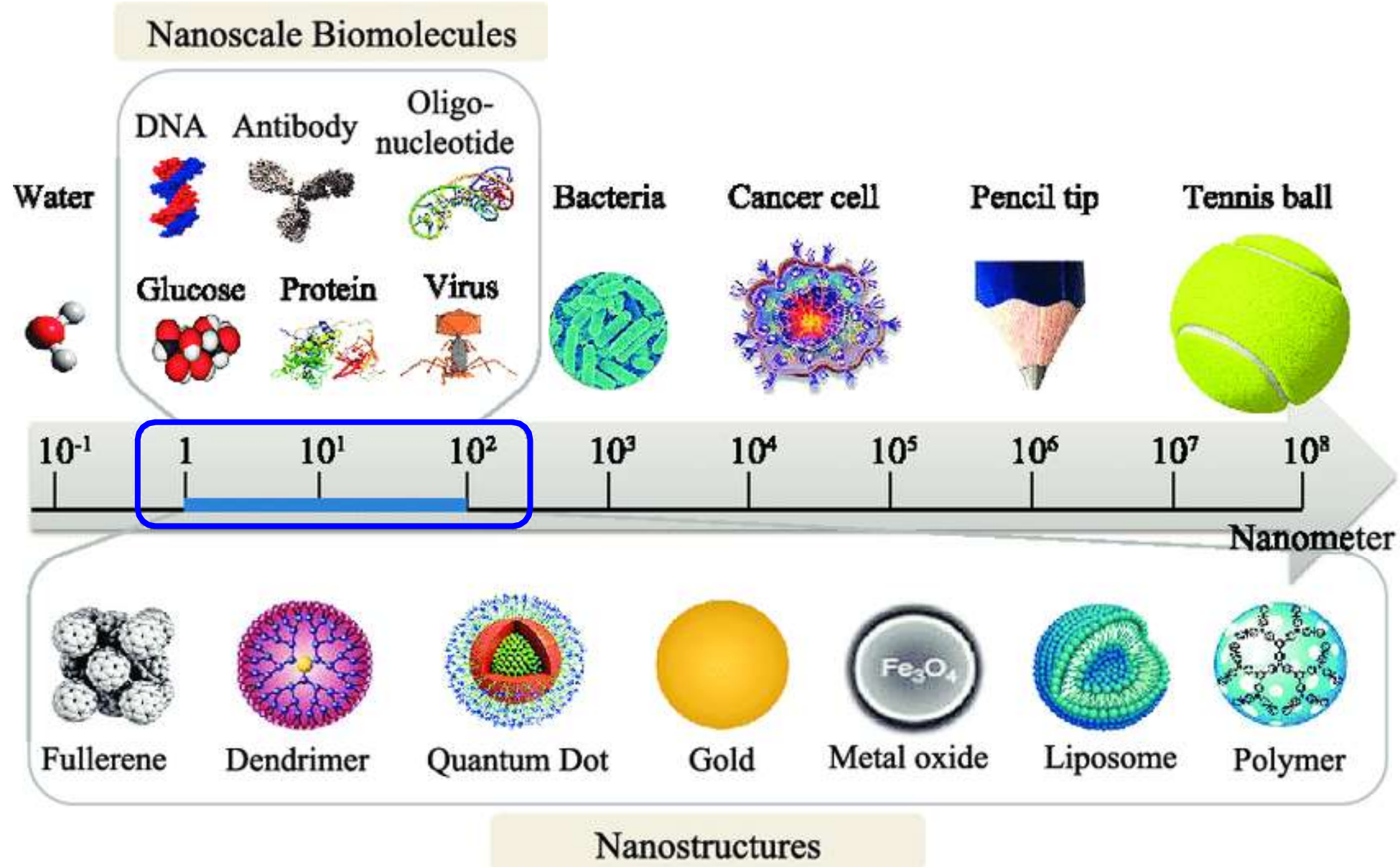
Size (nm)	Examples	Terminology
0.1-0.5	Individual chemical bonds	Molecular/atomic
0.5-1.0	Small molecules, pores in zeolites	Molecular
1-1000	Proteins, DNA, inorganic nanoparticles	Nano
10^3 - 10^4	living cells, human hair	Micro
$>10^4$	Normal bulk matter	Macro



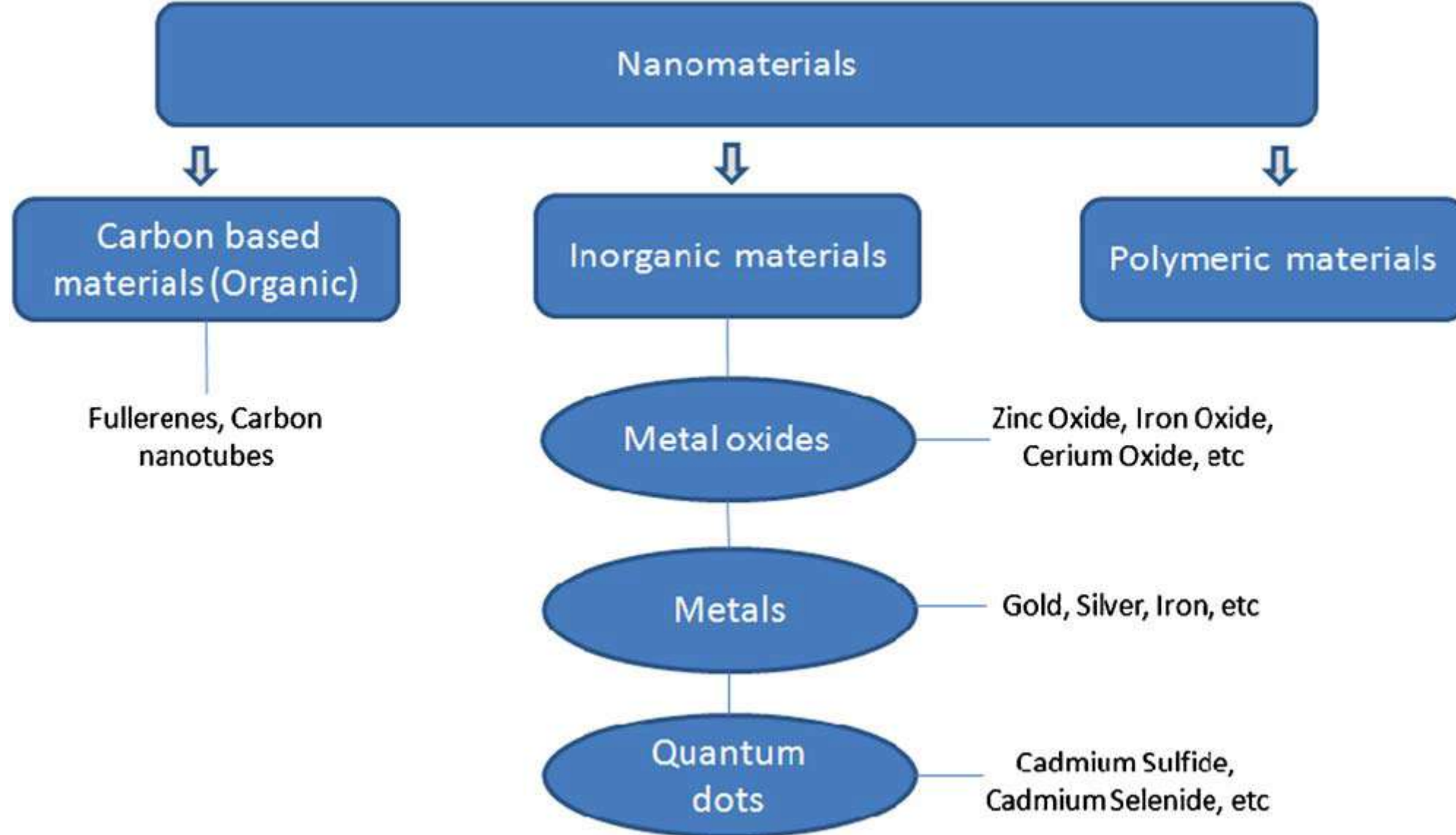
Bulk Gold

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

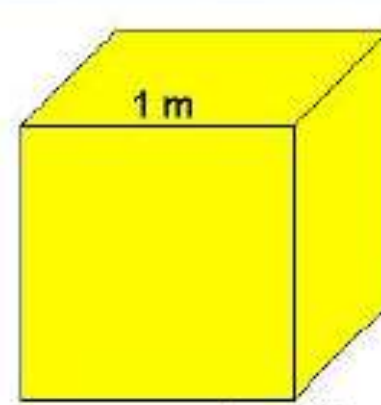
- Surface to volume ratio

2. Quantum effect

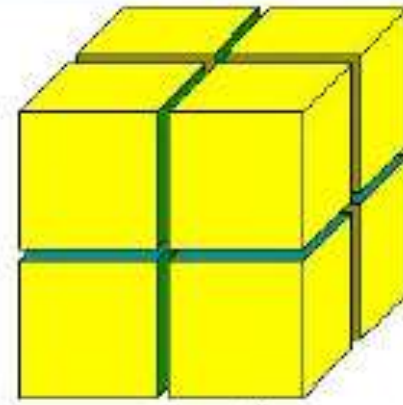
- Quantum confinement

Surface Area to Volume Ratio Increases

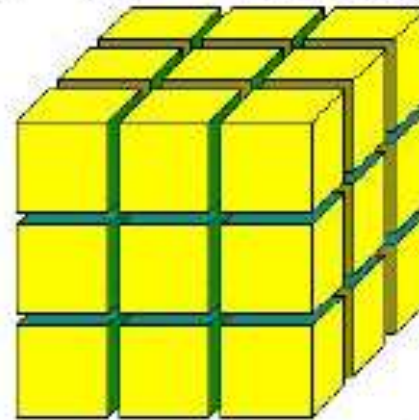
- As surface area to volume ratio increases
 - A greater amount of a substance comes in contact with surrounding material
 - This results in better catalysts, since a greater proportion of the material is exposed for potential reaction



$$\text{Area} = 6 \times 1\text{m}^2 = 6\text{ m}^2$$

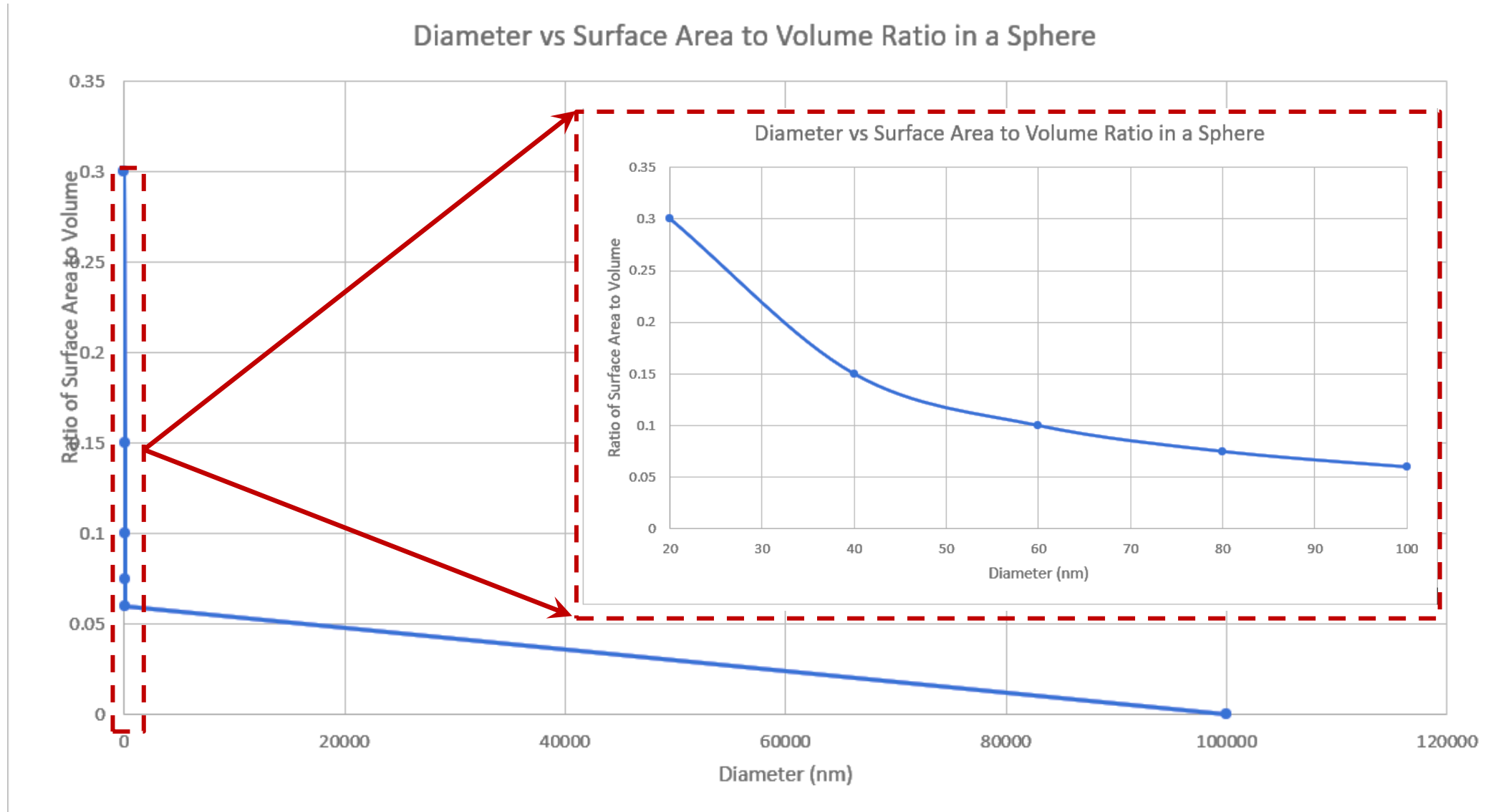


$$\text{Area} = 6 \times (1/2\text{m})^2 \times 8 = 12\text{ m}^2$$



$$\text{Area} = 6 \times (1/3\text{m})^2 \times 27 = 18\text{ m}^2$$

1. Surface area effect

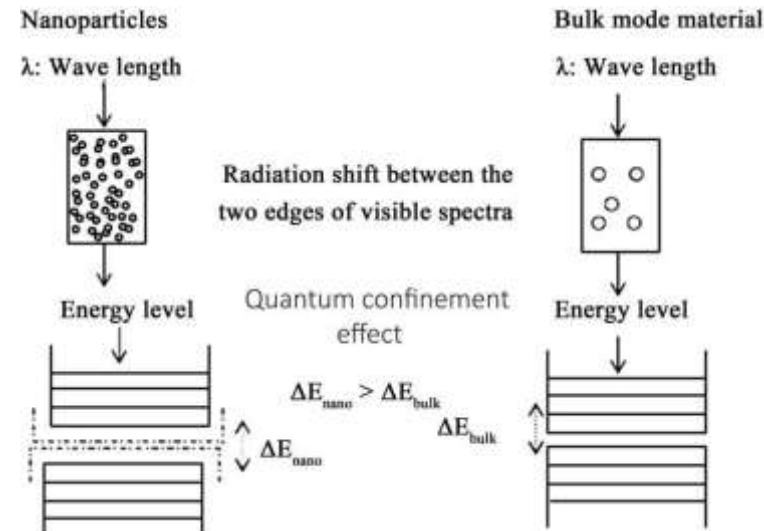


2. Quantum effect

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

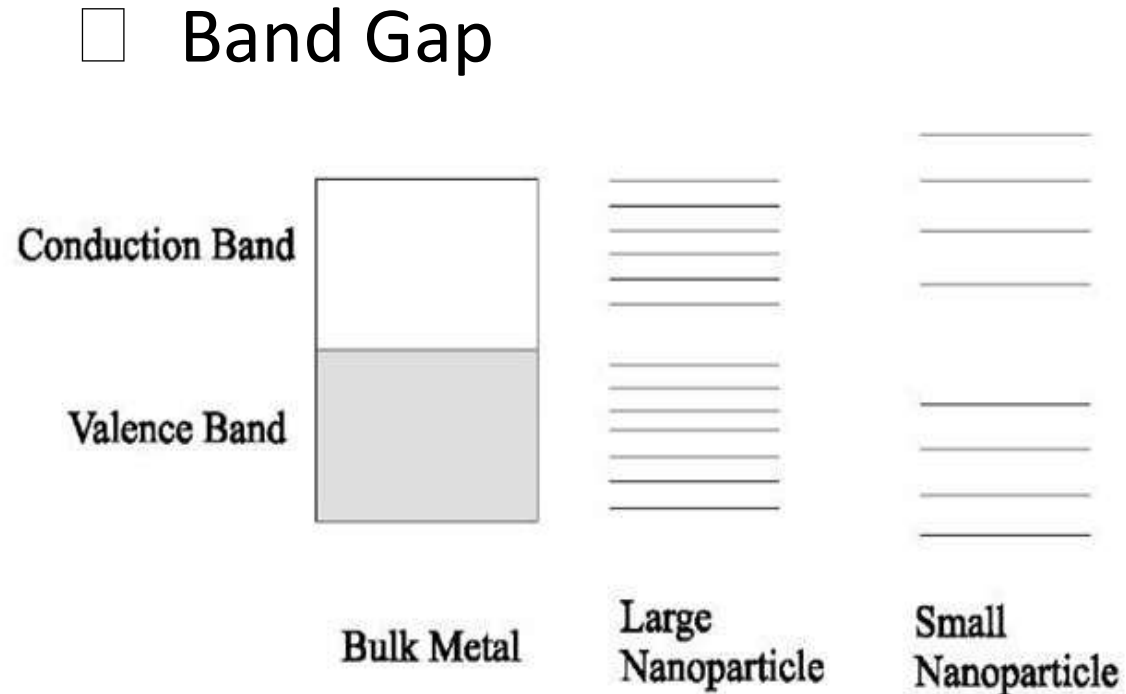
⇒ requires a new set of physics laws (**quantum mechanics**) to explain

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



2. Quantum effect

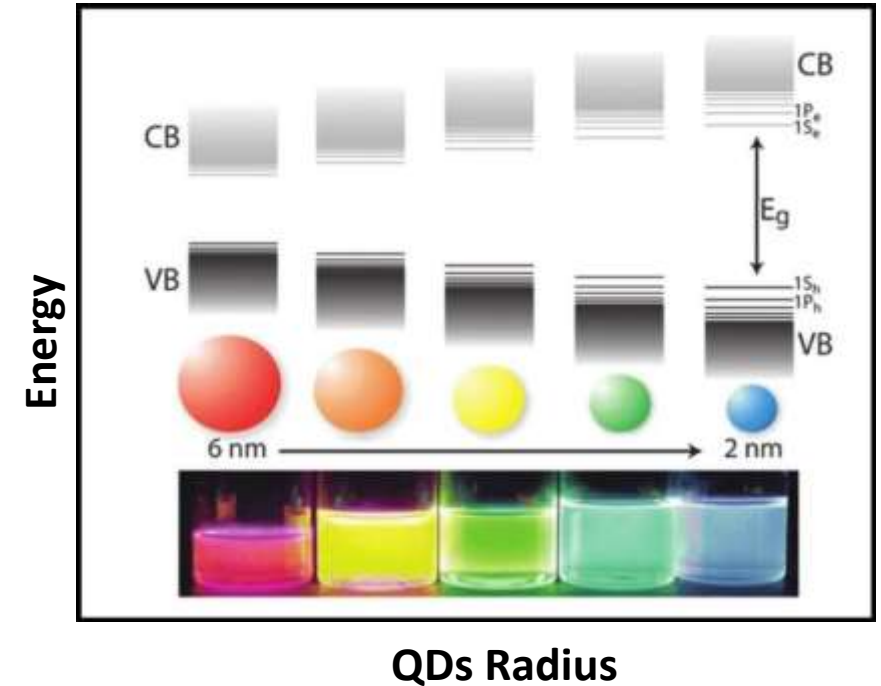
BAND GAP IN NANO AND BULK MATERIALS



Synthetic Methods of Quantum Dots

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

Quantum confinement



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

Properties of Semiconductor Nanomaterials

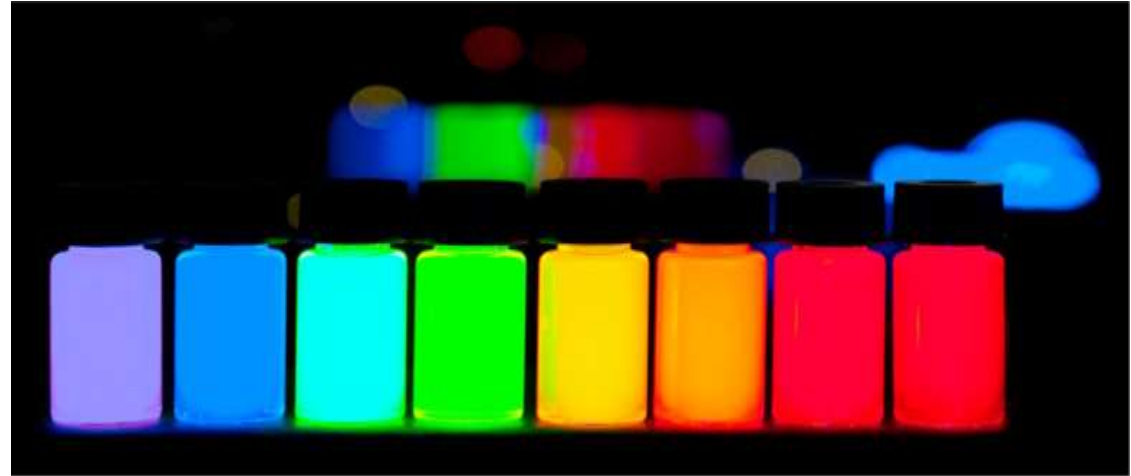
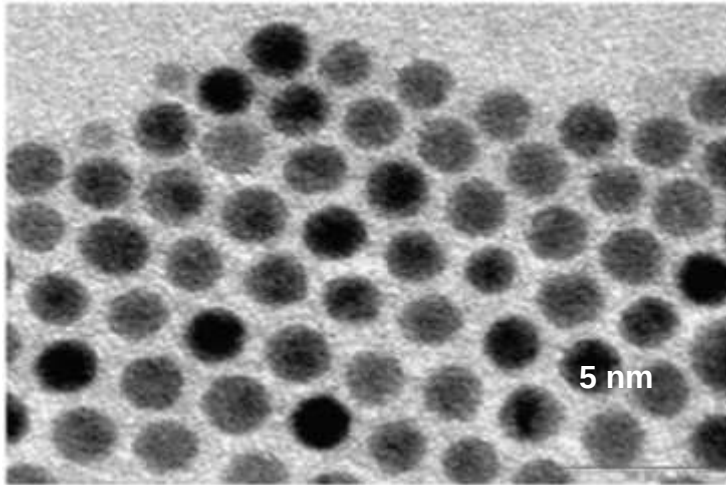
- ❖ The properties of nanosized semiconductor particles depend very sensitively on the particle size .
- ❖ The physical properties of semiconductor nanocrystals are dominated by the **spatial confinement of excitations** (electronic and vibrational).
- ❖ **Quantum confinement** that manifests itself in widening of HOMO-LUMO gap or the bandgap increase with decreasing crystallite size and it's implications on the electronic structure and photophysics of the crystallites has generated considerable interest.

Quantum Confinement

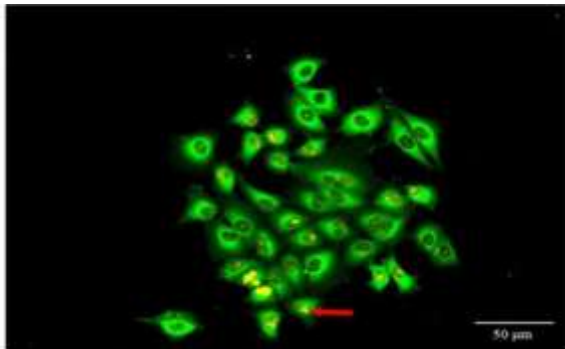
- ❖ In the nanoparticles with **some of its dimensions smaller than 10 nm**, show new effects, since the laws of classical physics no longer valid and we need quantum physics to explain them.
- ❖ For example, the **minimum potential energy** of an electron confined in a nanoparticle is **higher than expected in classical physics** and **energy levels of different electronic states are discrete.**
- ❖ Due to quantum confinement, the particle size has a **drastic effect** on the **density of electronic states** and thus on the **optical response**

Quantum Dots and applications

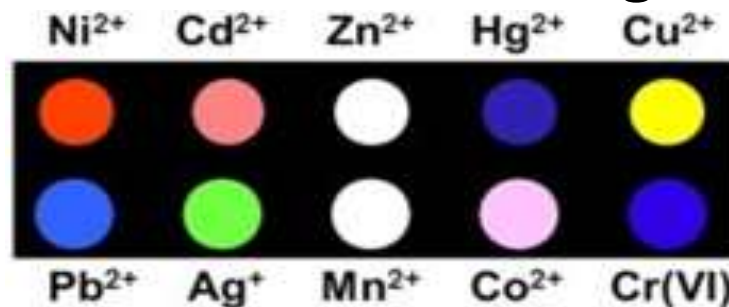
Quantum dots (QDs) are **semiconductor particles of few nanometers (<10 nm) in size**, having optical and electronic properties that differ from larger particles.



Cancer cell imaging



Metal ions sensing



Light emitting diode



Size and shape dependent colors of Au and Ag nanoparticles

Gold NPs in Glass

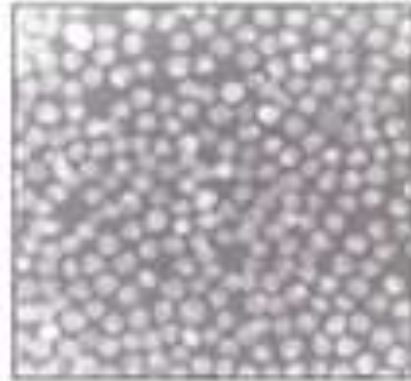
25 nm
Sphere
reflected

Size*: 25 nm
Shape: sphere
Color reflected:



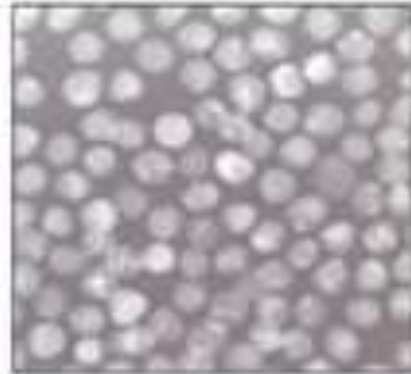
100 nanometers =
0.0001 millimeter

Gold particles in glass



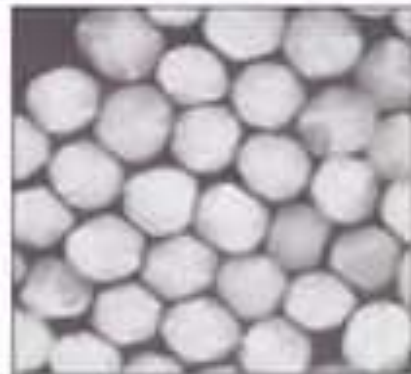
50 nm
Sphere
reflected

Size*: 50 nm
Shape: sphere
Color reflected:

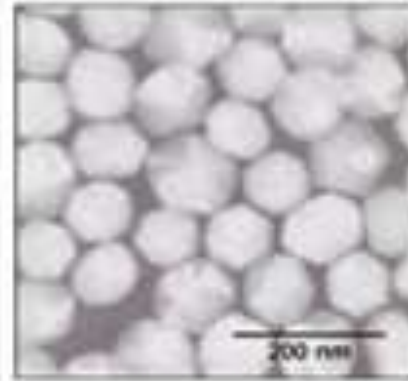


100 nm
Sphere
reflected

Size*: 100 nm
Shape: sphere
Color reflected:



Silver particles in glass



Size*: 100 nm
Shape: sphere
Color reflected:



Silver NPs in Glass

100 nm
Sphere
reflected

Size*: 40 nm
Shape: sphere
Color reflected:



40 nm
Sphere
reflected

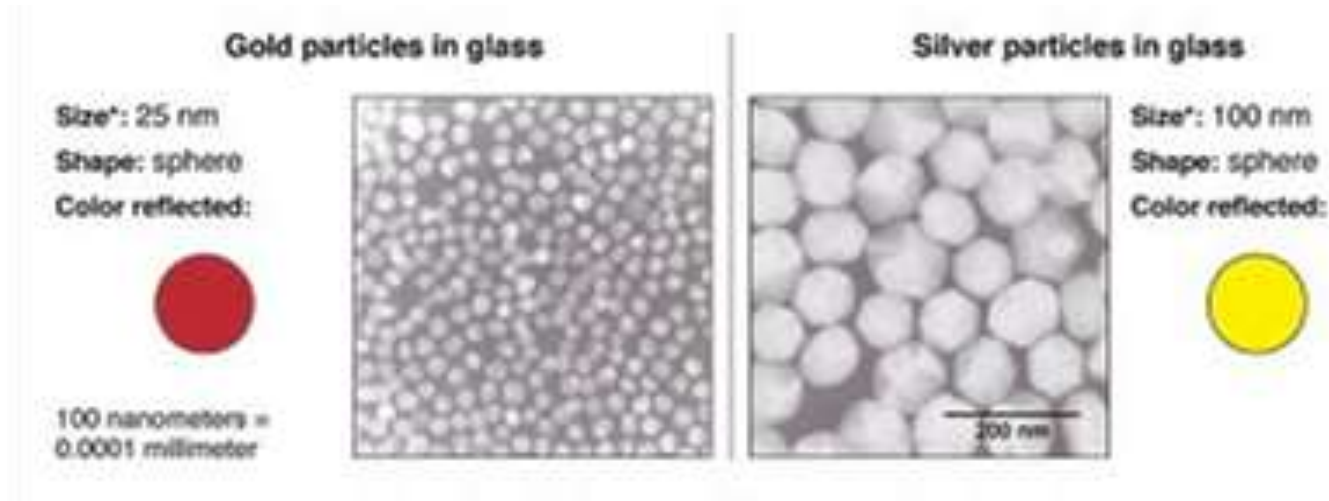
Size*: 100 nm
Shape: prism
Color reflected:



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

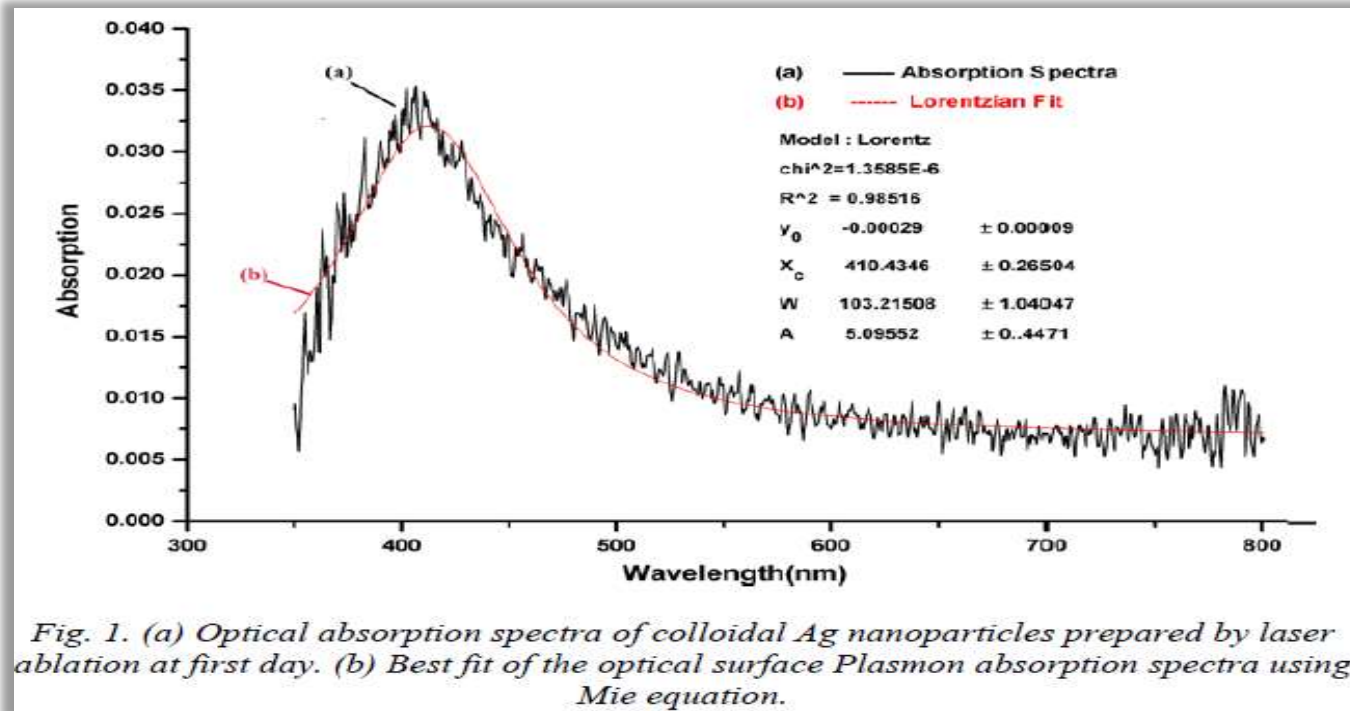
Surface plasmon resonance:

- Excitation of surface plasmons (propagation of surface electromagnetic waves) 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.

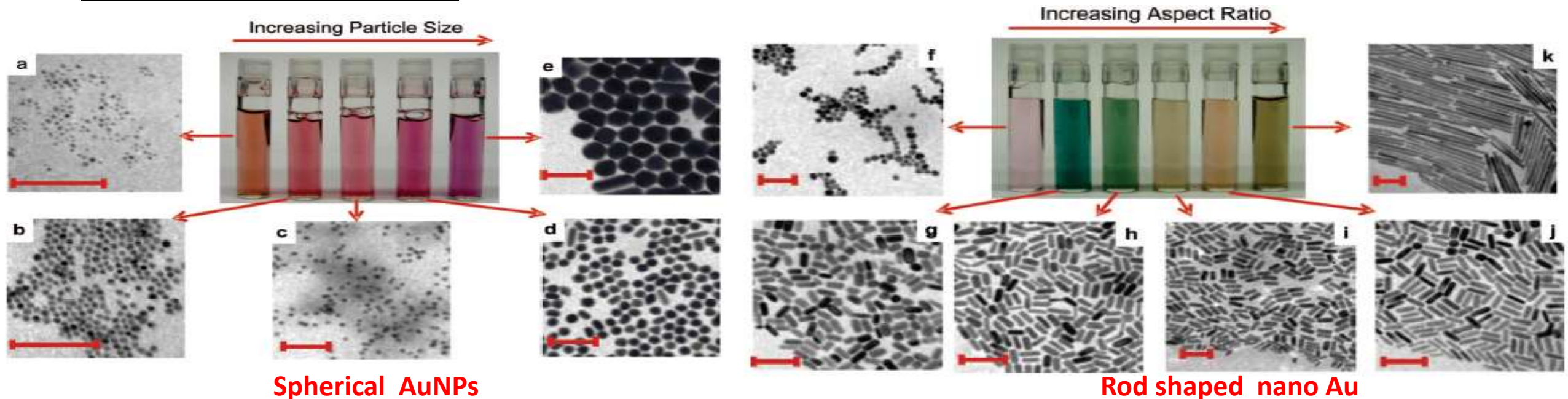
Nanomaterials show unusual

- ☐ Mechanical
- ☐ Electrical
- ☐ Optical
- ☐ Magnetic properties.

Hence it has potential **applications in**

- ☐ Many industries
- ☐ **Biomedical**
- ☐ 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.

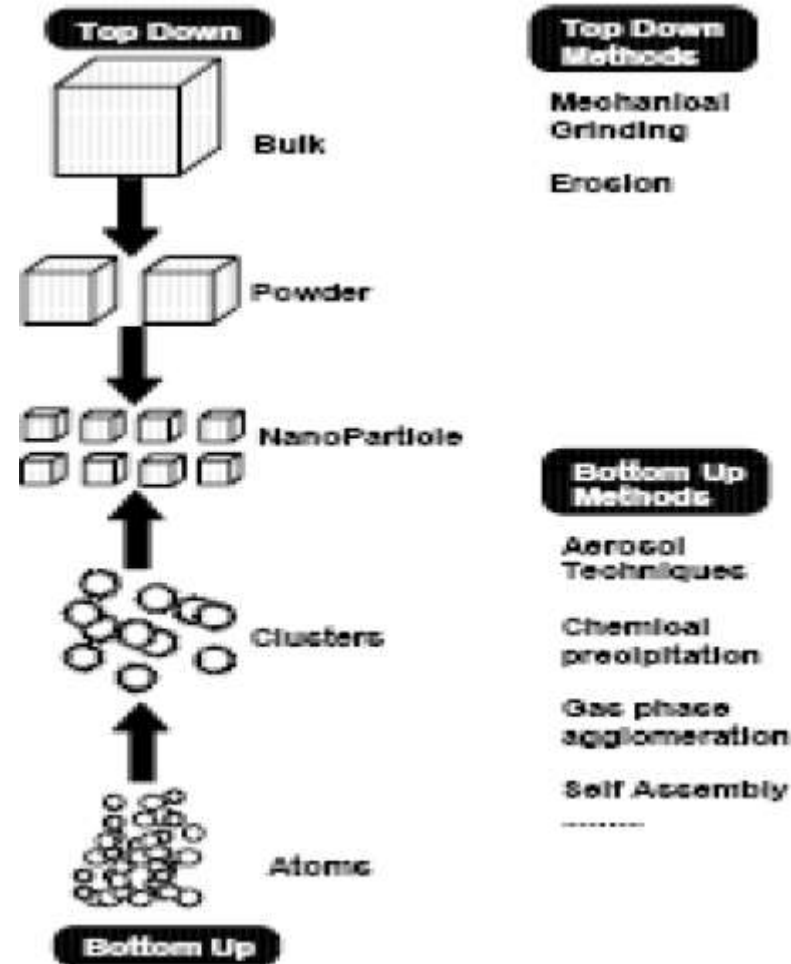


Gold : Bulk vs. Nano

	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	

Schematic representation of the 'bottom up' and top down' synthesis processes of nanomaterials

High-energy
wet ball milling



By
atom-by-atom
molecule-by-molecule
cluster-by-cluster
Less waste
More economical

Nanoparticles preparation:

❖ Top-down approaches

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

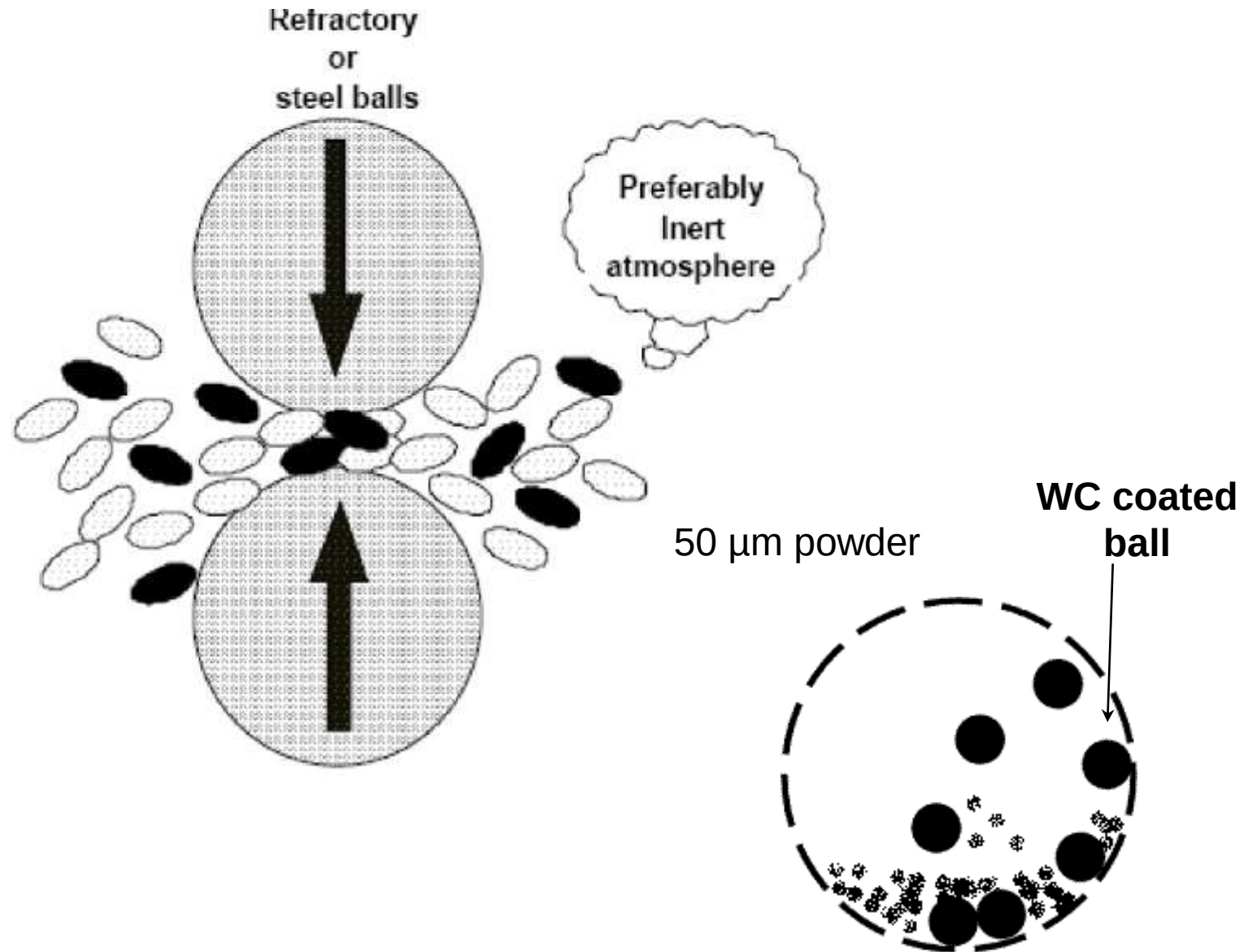
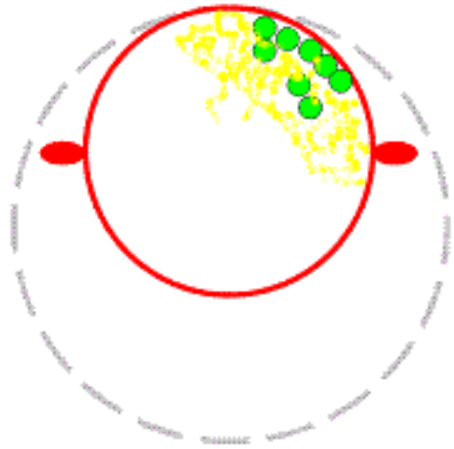
❖ Bottom-up approaches

- ❖ 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.

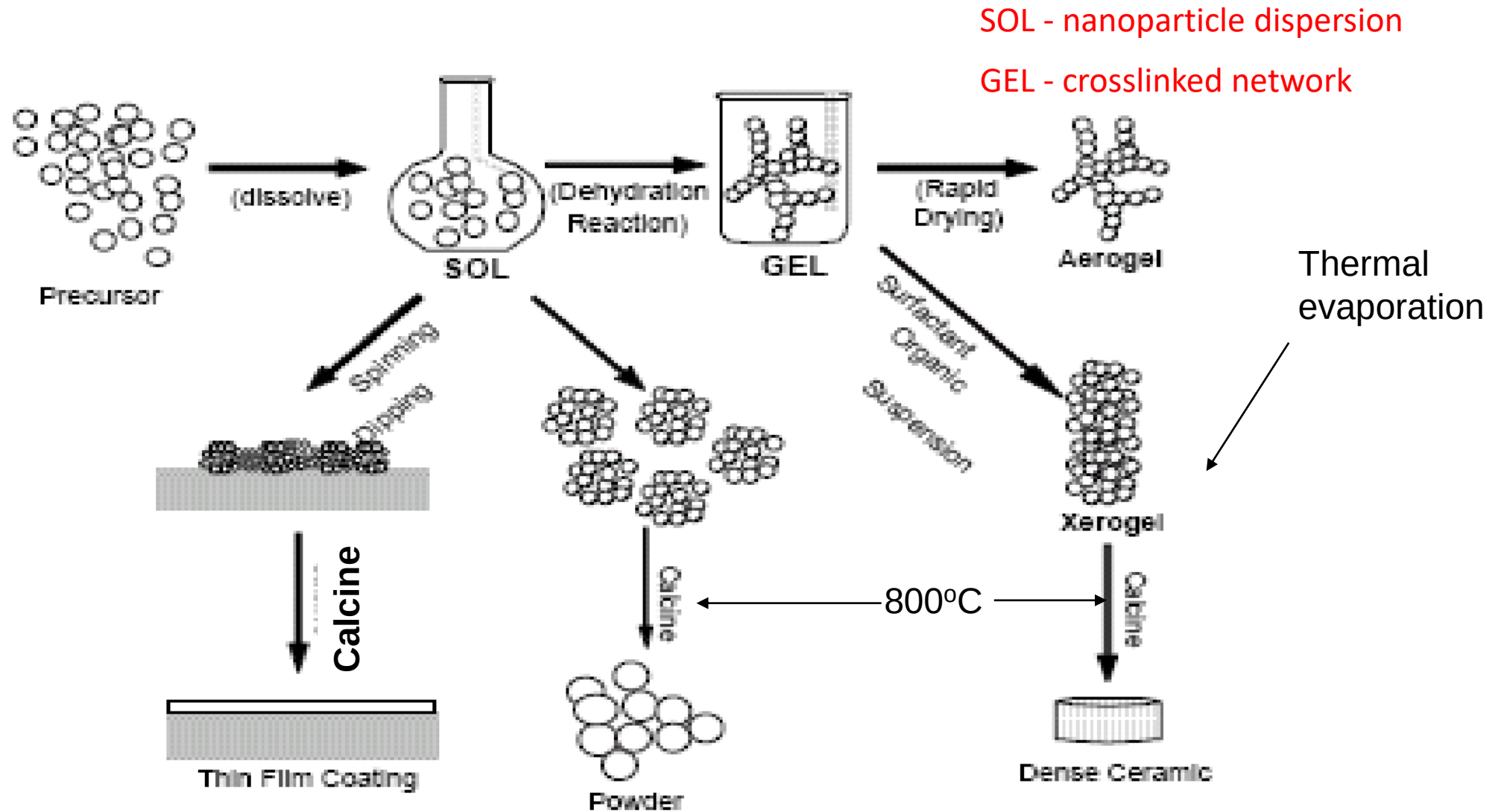
- Shaker mills (e.g. SPEX model 8000) uses small batches of powder (approximately 10 cm³ is sufficient)

❖ 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%)

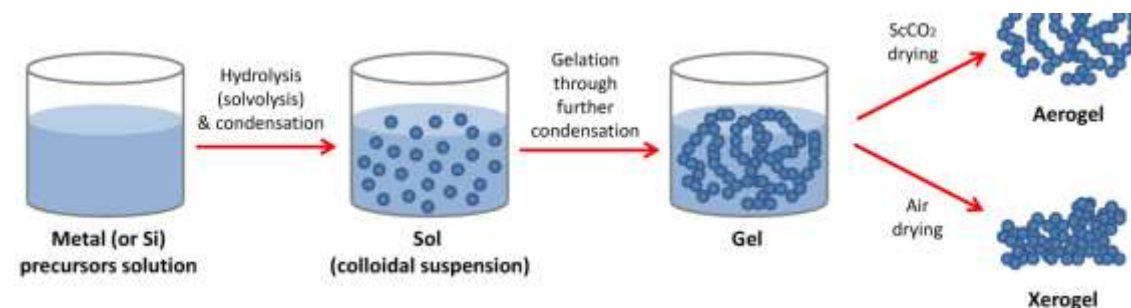
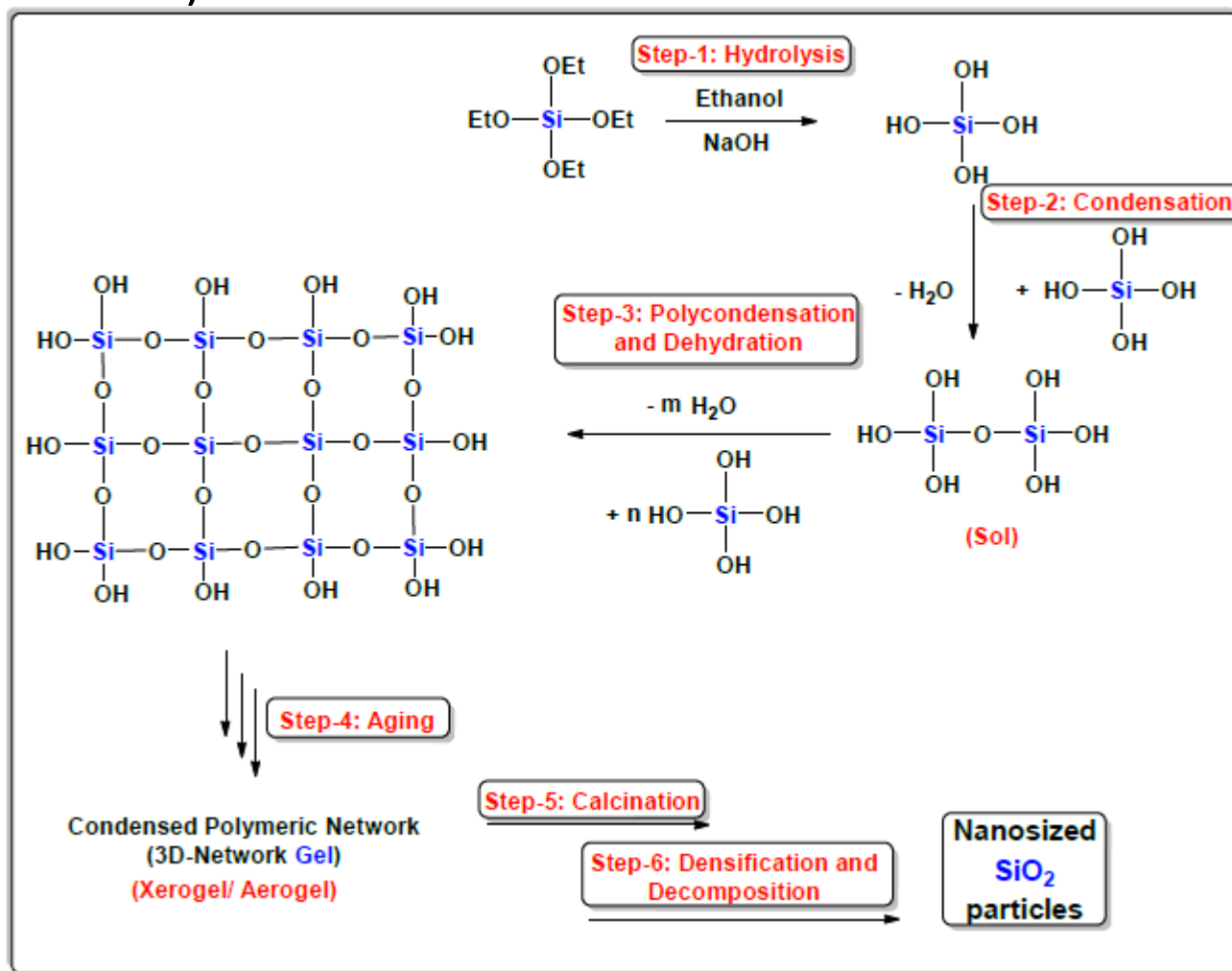
Wet Chemical Synthesis of nanomaterials (Sol-gel process)



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

Sol-Gel Processing

- Creation of Sol (solid particles in solution)
- Followed by 2 generic sol-gel processes
- Sol/gel transition controls the particle size and shape. Calcination of the gel produces the product (eg. Oxide).



Colloidal solution (sol) → Condensed polymeric network (gel) → Dried form (Threedimensional network) (gel)

- 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**

Overall Steps:

- **Step 1:** Formation of different stable solutions of the hydroxide (the sol).
- **Step 2:** Gelation resulting from the formation of an oxide- or alcohol-bridged network (the gel) by a **polycondensation 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.

❖ 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 (form into a mass).
- 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

e-Book for Nanomaterial:

<https://drive.google.com/file/d/18GiueZtfwNd5atOi5V8sijg9oqR-LvjM/view?usp=sharing>