MODULE - V

Module 5: Corrosion and New Engineering Materials

Corrosion: Introduction, methods of corrosion, Types of corrosion: Differential metal, differential aeration. Corrosion control- design and selection of material. Numerical on CPR.

Polymers: Introduction, Polymer composites-synthesis, properties and applications of Kevlar Fibre.
Biodegradable and biocompatible polymers. Conducting polymers: Introduction, Synthesis, properties and applications of polyacetylene.
Nanomaterials: Introduction, synthesis of nanoparticles by precipitation method. Graphene - Introduction, properties and engineering applications.
Ceramics: Introduction, classification based on chemical composition, properties and applications of perovskites ($CaTiO_3$).

CORROSION

Definition: *Corrosion is defined as the destruction and consequent loss of metals through chemical or electrochemical attack by the environment.*

Corrosion is classified as

1. **Dry corrosion (Chemical corrosion):** Corrosion of the metals occur by direct attack of atmospheric gases such as oxygen, hydrogen sulphide, halogens and sulphur dioxide in the absence of moisture to form metal oxide layer.
2. **Wet corrosion (Electrochemical corrosion)**: Wet corrosion occurs in the presence of an aqueous solution of electrolyte and atmospheric oxygen by setting up of tiny galvanic cells on the metal surface.

Electrochemical Corrosion:

According to electrochemical theory, corrosion of the metal take place due to the formation of anodic and cathodic regions on the same metal surface in the presence of a conducting medium. At the anodic region oxidation reaction takes place and the metal gets corroded into ions liberating the electrons. Consequently metals undergo corrosion at the anodic region. At the cathodic region reduction reaction takes place. Metal ions in the cathodic region are unaffected by the cathodic reaction.

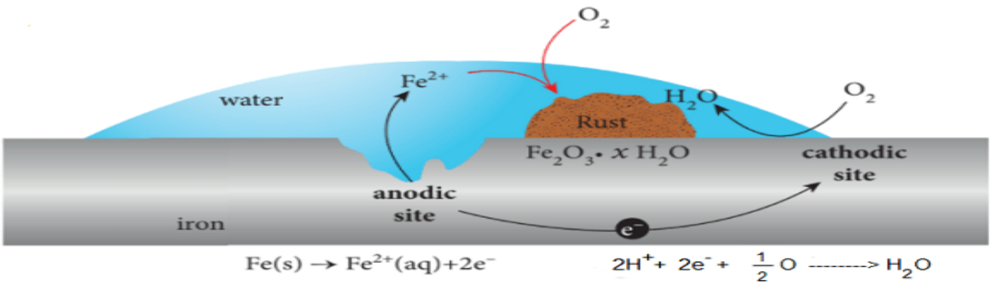


Fig: Rusting of Iron

The electrons liberated at the anodic region migrate towards the cathodic region constituting corrosion current. The metal ions liberated at the anode and some anions formed at the cathode region diffuse towards each other through the conducting medium and form a corrosion product somewhere between the anode and the cathode. Corrosion of metal continues as long as both the anodic and cathodic reactions take place simultaneously.

Types of Corrosion:

(1) Differential metal corrosion (Galvanic corrosion)
(2) Differential Aeration corrosion

(1) Differential metal Corrosion:

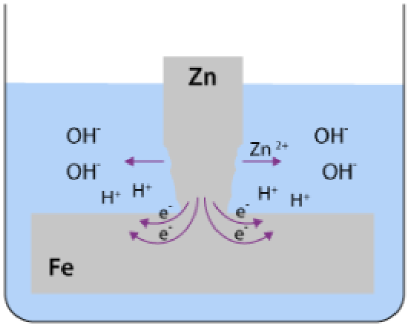
When two dissimilar metals are in contact with each other a potential difference is set up resulting in a galvanic current. The two metals differ in their tendencies to undergo oxidation, the one with lower electrode potential or the more active metal acts as anode and the one with higher electrode potential acts as cathode. The anodic metal undergoes corrosion and the cathodic metal is generally unattacked.

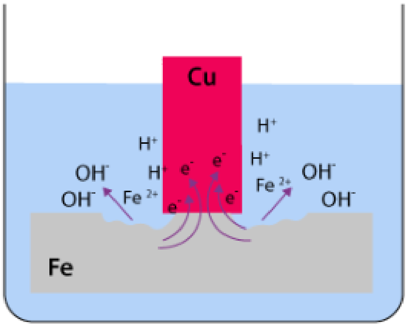
At the anode (less O_2 concentration), $Fe \longrightarrow Fe^{2+} + ne^-$

At the cathode (more O_2 concentration), $H_2O + ½\, O_2 + 2e^- \rightarrow 2OH^-$

$Fe^{2+} + 2OH^- \longrightarrow Fe(OH)_2$

$2Fe(OH)_2 + 1/2O_2 + H_2O \longrightarrow [Fe_2O_3.\ 3H_2O]$ (rust)





(1) Steel pipes joined to Copper plumbing, undergo galvanic corrosion, since Steel acts as the anode.

$E^0_{Fe^{+2}/Fe} = -0.44$ V $\qquad$ $E^0_{Cu^{+2}/Cu} = +0.34$ V

(2) Steel screws or rivets used on Copper sheet, or screws and washers of unlike metals.

In all the above cases steel corrodes due to differential metal corrosion.

(2) Differential Aeration Corrosion:

Differential aeration corrosion occurs when a metal surface is exposed to differential air concentrations of Oxygen concentrations. The part of the metal exposed to higher oxygen concentration acts as a cathodic region and the part of the metal exposed to lower oxygen concentration acts as anodic region.

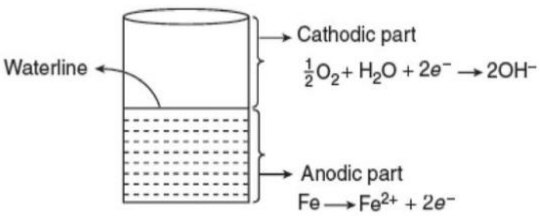
Corrosion of metal arising as a result of the formation of an oxygen concentration cell due to uneven supply of air on the metal surface is known as differential aeration corrosion.

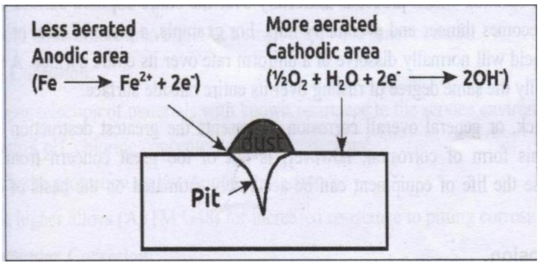
At the anode (less O_2 concentration), $Fe \rightarrow Fe^{2+} + ne^-$

At the cathode (more O_2 concentration), $H_2O + \frac{1}{2} O_2 + 2e^- \rightarrow 2OH^-$

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$

$2Fe(OH)_2 + 1/2O_2 + H_2O \rightarrow [Fe_2O_3 \cdot 3H_2O]$ (rust)





Eg.:- 1. Steel water tanks in which water is stored for a long period.

2. Metal under dirt, dust, scale or water undergoes corrosion.

3. Part of the nail inside the wall, being exposed to lower oxygen concentration than the exposed part, under goes corrosion.

DESIGN AND SELECTION OF MATERIALS:

Corrosion can be controlled by selecting proper materials which resist the corrosive environment and designing them suitably during fabrication. Some practical considerations are given below:

(i) Differential metal corrosion can be reduced by avoiding the use of two dissimilar metals. If their use is unavoidable, the positions of the metals chosen shall be as close as possible in the galvanic series.

(ii) To reduce the rate of corrosion, the anode material must be as large as possible while the cathode should be small. For example, bolt and nut, washer and rivets of a cathodic metal may be used in contact with an anodic sheet of large area. The anode metals should not be painted when in contact with a cathode as this decreases the anodic area

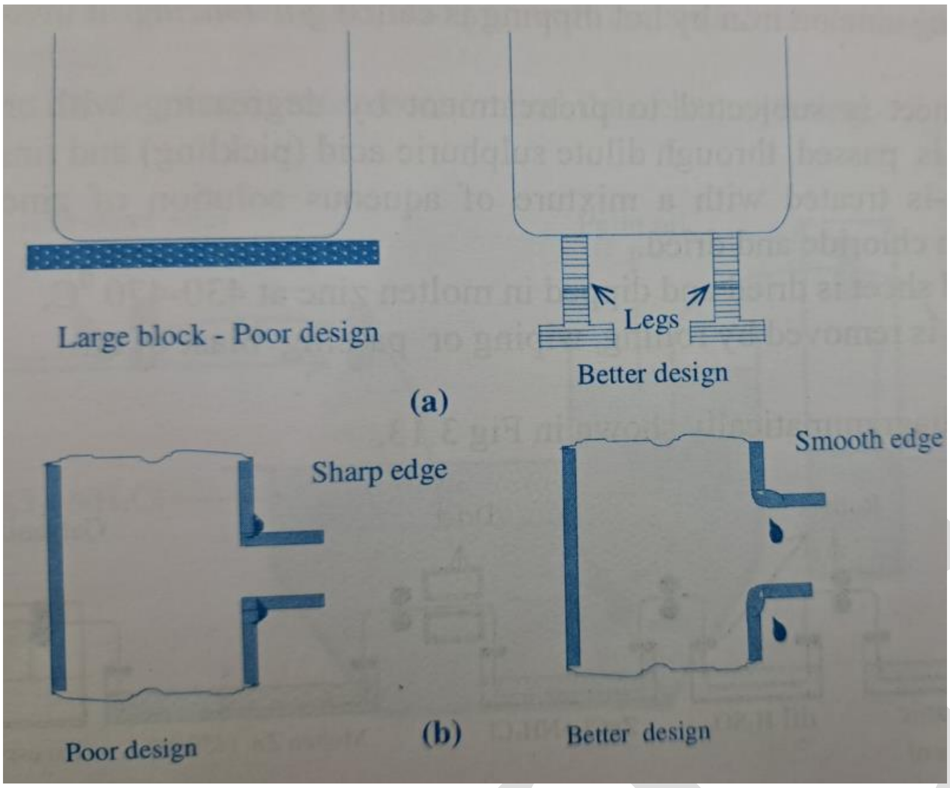
(iii) An insulator should preferably be used at the contact point of two dissimilar metals. However, porous insulators such as asbestos, magnesia and wood should not be used since they absorb and hold liquids which act as electrolytic conductors

(iv) While joining metals, care should be taken not to leave gaps between them, where some liquid or air can be trapped resulting in differential aeration corrosion. The gaps can be avoided by proper designing. For example, welded joints are preferred to rivetted or bolted joints in low pressure boilers and chemical plants.

(v) Stress corrosion may be avoided by annealing the equipment.

(vi) Proper designing of the equipment reduces the rate of corrosion. The equipment should be supported on legs instead of on large blocks as shown in below figure to facilitate free circulation of air and prevention of the formation of stagnant pool or damp areas. Similarly, the equipments should have smooth edges and recesses shown in figure. It should be designed in such a way that it can be easily kept free from dust to reduce the corrosion due to pitting and differential aeration effect.

Corrosion rate may be reduced by considering the above factors during design.



Corrosion Penetration Rate (CPR):

The Corrosion penetration rate is the speed at which any metal or alloy deteriorates in a specific corrosive environment through chemical or electrochemical reactions. It is also defined as the amount of weight loss per year in the thickness of metal or alloy due to corrosion. The Corrosion penetration rate also referred as corrosion rate.

Corrosion penetration rate depends on following factors;

1. Nature of metal.
2. Nature of corrosive environment/medium.
3. Nature corrosion product.
4. Speed at which corrosion spreads in the inner portion of metal.

The Corrosion penetration rate is calculated using the following formula;

$$\text{CPR} = \frac{k\ X\ W}{D\ X\ A\ X\ T}$$

Where,

W is weight loss after exposure time.

T is exposure time in corrosive medium.

D is the density of metal or alloy.

A is surface area of exposed specimen.

K is constant.

Numerical Problem on CPR:

1. A thick steel sheet of area 400 cm^2 is exposed to air near the ocean. After one-year period it was found to experience a weight loss 375 g due to corrosion. If the density of the brass is 7.9 g/cm^2 calculate the corrosion penetrating rate in mpy and mmpy (given K= 534 in mpy and 87.6 in mmpy).

To calculate CPR in mmpy:

	Given	CPR in mmpy
K	534	87.6
W (wt loss)	375 g	375 x 1000 mg
ρ	7.9 g/ cm3	7.9 g/ cm3
A	400 cm^2	400 cm^2
t	1 year	1 x 365 x 24 hrs

$$\text{CPR} = \frac{k \text{ x } W}{D(\rho) \text{ x } A \text{ x } T}$$

$$\text{CPR} = \frac{87.6\ X\ 375\ X\ 1000}{7.9\ X\ 400\ X\ 365\ X\ 24}$$

CPR =1.186 mmpy

To calculate CPR in mpy :

	Given	CPR in mmpy
K		534
W (wt loss)	375 g	375 x 1000 mg
ρ	7.9 g/ cm3	7.9 g/ cm3
A	400 cm^2	400 X 0.155 $inch^2$
t	1 year	1 x 365 x 24 hrs

1 cm^2 = 0.155 $inch^2$)

$$\text{CPR} = \frac{k \text{ x } W}{D(\rho) \text{ x } A \text{ x } T}$$

$$\textbf{CPR} = \frac{\mathbf{534\ X\ 375\ X\ 1000}}{\mathbf{7.9\ X\ 400\ X\ 0.155\ X\ 365\ X\ 24}}$$

CPR = 46.67 mpy

2. Calculate the CPR in both mpy and mmpy for a thick steel sheet of area 100 inch^2 which experiences a weight loss of 485g after one year. (Density of steel=7.9g/cm3).

To calculate CPR in mmpy :

	Given	**CPR in mmpy**
K	534	87.6
W (wt loss)	485 g	485 x 1000 mg
ρ	7.9 g/ cm3	7.9 g/ cm3
A	100 inch ^{2}	100 X 6.45 cm ^{2}
t	1 year	1 x 365 x 24 hrs

1inch^2=6.45cm^2

$$\mathrm{CPR} = \frac{k \times W}{D(\rho) \times A \times T}$$

$$= \frac{87.6 \text{ X } 485 \text{ X } 1000}{7.9 \times 100 \times 6.45 \times 365 \times 24}$$

= 0.9518 mmpy

To calculate CPR in mpy :

	Given	**CPR in mpy**
K	534	534
W (wt loss)	485 g	485 x 1000 mg
ρ	7.9 g/ cm3	7.9 g/ cm3
A	100 inch ^{2}	100 inch ^{2}
t	1 year	1 x 365 x 24 hrs

$$\mathrm{CPR} = \frac{k \times W}{D(\rho) \times A \times T}$$

$$= \frac{534 \text{ X } 485 \text{ X } 1000}{7.9 \times 100 \times 365 \times 24}$$

= 37.424 mpy

3. Estimate the corrosion period (in years) of metal tin bar with surface area of 20 inch^2 shows CPR of 0.8 mpy with a loss of 730 mg of tin. The density of tin is 7.31 g/ cm^3.

$$\boldsymbol{CPR = \frac{k \times W}{D(\rho) \times A \times T}}$$

$$T = \frac{k \times W}{D(\rho) \times A \times CPR}$$

$$T = \frac{534 \times 730}{7.31 \times 20 \times 0.8}$$

T=3335.93 hrs

$$T = \frac{3332.93}{365 \times 24}$$

T=0.38 years

Polymers

Polymer is a giant or macromolecule formed by the repeated union of several simple molecules called monomers.

Mainly there are two types of polymers:

1) Natural polymers: Rubber, resins, cellulose etc.
2) Synthetic polymers: Nylon, PVC, Bakelite etc.

A monomer is a simple molecule having two or more bonding site through which each can link to the other monomer to form a polymer chain. Hence monomers are often called as the **building blocks** of a polymer chain. The properties of polymers are different from that of the monomers from which they are formed. Polymers have high molecular weight (Ranging from 10,000 to 1,00,000)

Polymerization:

- The chemical process by which monomers are converted into polymers is known as polymerization. To convert monomer into polymer, small quantity of chemicals known as initiators are needed. Temperature and pressure should be maintained.

$$\text{Monomer} + \text{Initiator} \xrightarrow[\text{Pressure}]{\text{Temp}} \text{Polymer}$$

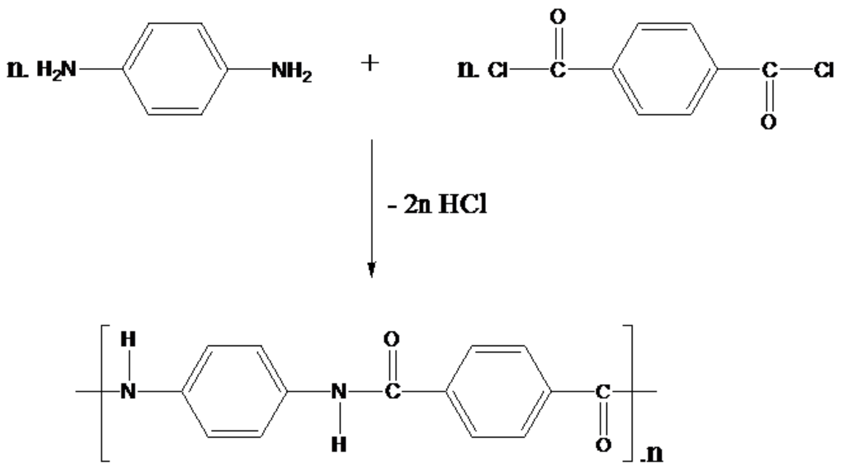
$$n\,CH_2 = CH_2 + \text{peroxide initiator} \xrightarrow[\text{Pressure}]{\text{Temp}} -\!\!\left[CH_2 - CH_2\right]_n\!\!-$$

Ethylene monomer

Polyethylene

Synthesis properties and Applications of Kevlar $[-NH-C_6H_4-NH-CO-C_6H_4-CO-]_n$

- Kevlar is an aromatic polyamide or aramid.
- It was the first organic fiber with sufficient tensile strength and structural rigidity to be used in advanced composites.
- Kevlar is synthesized in solution of N-methyl-pyrrolidone and calcium chloride from the monomers 1,4-phenylene-diamine (para-phenylenediamine) and terephthaloyl chloride through a condensation reaction with the liberation of HCl



Properties:

- ✓ High tensile strength (five times stronger per unit weight than steel)
- ✓ High modulus of elasticity
- ✓ Very low elongation up to breaking point
- ✓ Low weight
- ✓ High chemical inertness
- ✓ Very low coefficient of thermal expansion
- ✓ High fracture toughness (impact resistance)
- ✓ High cut resistance
- ✓ Flame resistance

Uses:

- Used as reinforcement in tyre and rubber mechanical goods.
- Industrial applications are as cables, in asbestos replacements, break linings, and body armor.
- Used in plastic reinforcements for boat hulls, airplanes, and bicycles.
- Kevlar is well known component of personal armor such as combat helmets, ballistic face masks, ec.
- Used as inner lining for some tyres to prevent punctures.
- The Kevlar fiber is used in woven rope and in cables.
- Aramid fibers are widely used for reinforcing composite materials, often in combination with carbon fiber and glass fiber. The matrix for high performance composite is usually epoxy resin. Typical applications include bodies for F1 racing cars, helicopter rotor blades, tennis, table tennis, badminton and squash rackets, cricket bats, and hockey sticks.

Conducting polymers:

An organic polymer with highly delocalized pi- electron system, having electrical conductance of the order of a conductor is called a conducting polymer.

Synthesis:

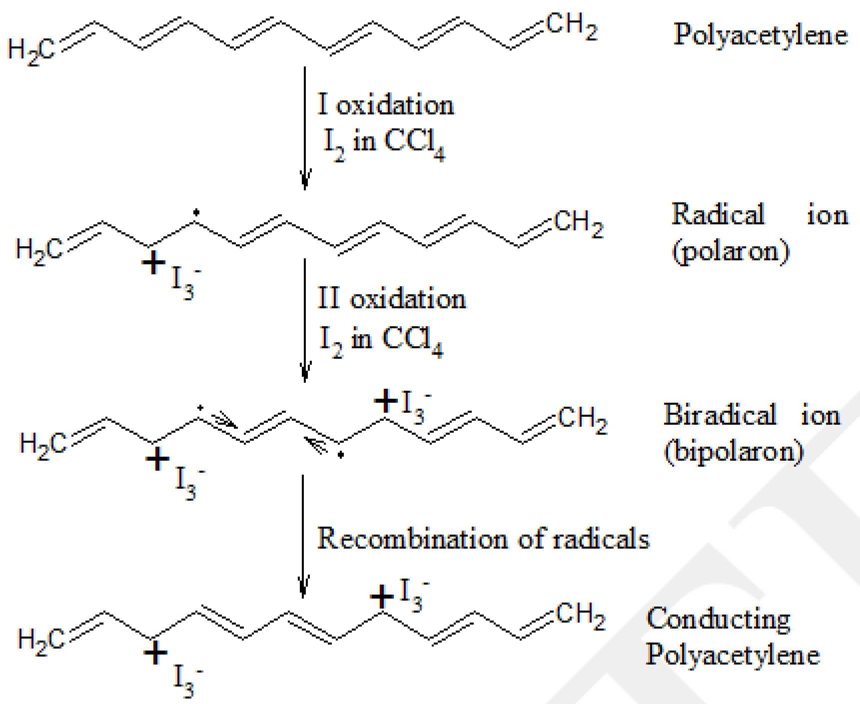
The conducting polymers are synthesized by doping in which charged species are introduced in organic polymers having pi- back bone. The important doping reactions are

1. Oxidative doping (p-doping)
2. Reductive doping(n- doping)
3. Protonic acid doping (p- doping)

Oxidative doping (p- doping): In this process pi- back bone of a polymer is partially oxidized using a suitable oxidizing agent. This creates positively charged site on polymer backbone, which are current carriers for conduction.

The oxidising agents used in p- doping are iodine vapour, iodine in CCl_4, HBF_4, perchloric acid and benzoquine.

Mechanism of conduction in polyacetylene by Oxidative doping:



The removal of an electron from the polymer pi- back bone using a suitable oxidising agent leads to the formation of delocalized radical ion called polaron. The second oxidation of the chain containing polaron followed by radical recombination yields two charge carriers on each chain. The positively charged sites on the polymer chains are compensated by anions I_3^- formed by the oxidising agent during doping.

The delocalized positive charges on the polymer chain are mobile, not the dopant anions. Thus these delocalized positive charges are current carriers for conduction. These charges must move from chain to chain as well as along the chain for bulk conduction.

Applications

- As electrode material for commercial rechargeable batteries(coin type batteries).
- As conductive tracks on printed circuit boards.
- As sensors-humidity sensor, gas sensor, radiation sensor, biosensor for glucose, galactose etc.
- In electrochromic display windows.
- In information storage devices.
- As film membranes for gas separations.
- In light emitting diodes.
- In fuel cells as the electro catalytic materials.

MODULE - V

Biodegradable and Biocompatible polymers

Biopolymers:

Biopolymers are polymers that are produced by or derived from living organisms, such as plants and microbes, rather than from petroleum, the traditional source of polymers. The primary sources of biopolymers are renewable. Many, but not all, biopolymers are biodegradable, which means they ‘are capable of decomposing into carbon dioxide, methane, water, inorganic compounds or biomass by the enzymatic action of microorganisms’.

Choice of biopolymer to be used in construction often depends on mechanical behaviour, moisture absorption, photodegradation stability, availability, compatibility and cost. Polylactic acid (PLA) and Polyhydroxyalkoanate (PHA) are the most common biopolymers in terms of production and use

Properties

- PLA polymers range from amorphous glassy polymer to semi-crystalline and highly crystalline polymer with a
- Glass transition temperature of PLA is 60-65 °C and melting point is 130-180°C
- PLA has high heat stability and mechanical strength
- PLA has degradation properties

Application

- PLA is widely used in 3D printing
- PLA is used in a large variety of consumer products such as disposable plastics housings for kitchen appliances and electronics such as laptops and handheld devices

- It is used for compost bags, food packaging, injection-molded and packaging materials
- PLA has applications in engineering plastics, where the stereocomplex is blended with a rubber-like polymer such as ABS (Acrylonitrile butadiene styrene)
- It is used as medical implants in the form of anchors, screws, plates, pins, rods, and mesh
- PLA is used for automotive parts such as floor mats, panels, and covers

NANO CHEMISTRY

Nanotechnology is an interdisciplinary science involving chemistry, physics, material science, biology, and medicine. Today, everyone uses the term ‘nano’ for anything which is small. But in chemistry, a nano material refers to a material with at least one of its dimensions in nano scale. Typically, size of a nanomaterial varies from a nanometer to hundred nano meters. 1 nano meter = 10-9 meter. Nanomaterials are of interest because at this scale unique optical, magnetic, electrical, and other properties emerge. These emergent properties have the potential for great impacts in electronics, medicine, and other fields. They may be in the form of particles, tubes, rods, or fibers.

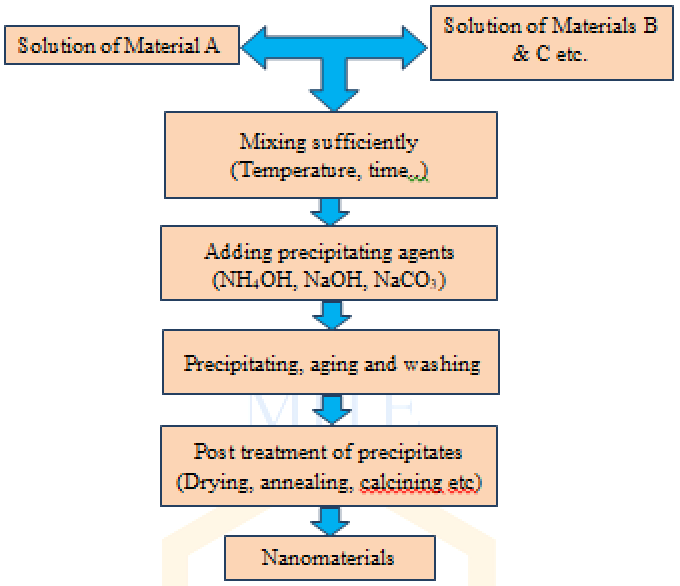
Synthesis of Nanoparticles:

Precipitation process

This method relies on the precipitation of nanometer sized particles within a continuous fluid solvent.

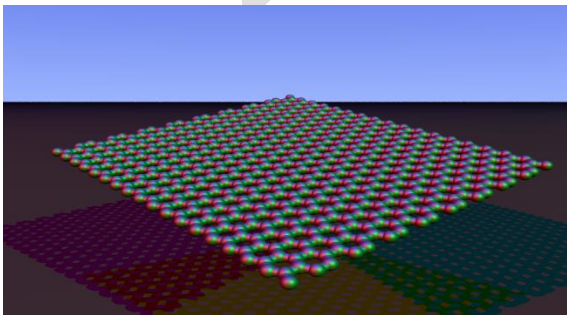
An inorganic metal salt, such as chloride, nitrate, sulphate, etc., is dissolved in water. Metal cations exist in the solution in the form of metal hydrate species, for example, $Al(H_2O)^{3+}$ or $Fe(H_2O)_6^{3+.}$ A precipitating agent like NaOH, NH_4OH or Na_2CO_3 is added to precursor solutions it changes the pH and causes condensation of precursors. It also introduces additional ions into the system. Thus, concentration of solution increases and reaches a critical level called as super saturation. At this concentration, nucleus formation is initiated, and nucleus further grows into particles, which gets precipitated. Particle size of the product depends upon the rate of attainment of super saturation and rate of nucleation. If a solution attains super saturation level slowly and nucleation occurs longer period, then the precipitated with wide particle size is formed. On the other hand, if solution reaches super saturation rapidly nucleation occurs suddenly then nucleus burst into small size of particles.

The precipitated hydrolyzed species like of metal oxides or metal sulphides are filtered, washed, dried and calcined in order to obtain a final nanomaterial product.



Graphene :

Graphene is a two dimensional crystalline allotrope of carbon consisting of a single layer of carbon atoms arranged in hexagonal lattice. It has high electrical conductivity and act like a semi metal with a small overlap between the valence and conduction bands. The carbon atoms are densely packed in a regular hexagonal pattern. The atoms are about 1.42^0 apart. Each carbon atom is sp^2 hybridised and each carbon atom is bonded to three other carbon atoms.



Properties:

- Graphene has excellent electronic conductivity because its conduction and valence bands meet at Dirac point.(Zero gap semiconductor)
- Graphene has excellent optical properties, produces an unexpectedly high opacity for an atomic monolayer in vacuum.
- Grapheme melts into an agglomeration of loosely occupied double bonded chains before becoming a gas.
- Graphene is a strongest material ,with high intrinsic tensile strength.

Applications

- As a conductor for various device applications like solar cells, light emitting diodes, touch panels smart windows and phones.
- In fundamental electronic devices such as capacitors and field effect transistors
- Grapheme super capacitors serve as energy storage alternatives to traditional batteries
- Functionalised graphene for biological and chemical sensors

CERAMICS

A **ceramic** is any of the various hard, brittle, heat-resistant, and corrosion-resistant materials made by shaping and then firing an inorganic, nonmetallic material, such as clay, at a high temperature. Common examples are earthenware, porcelain, and brick. The word ceramic comes from the Ancient Greek word keramikos, meaning "'potter's clay."

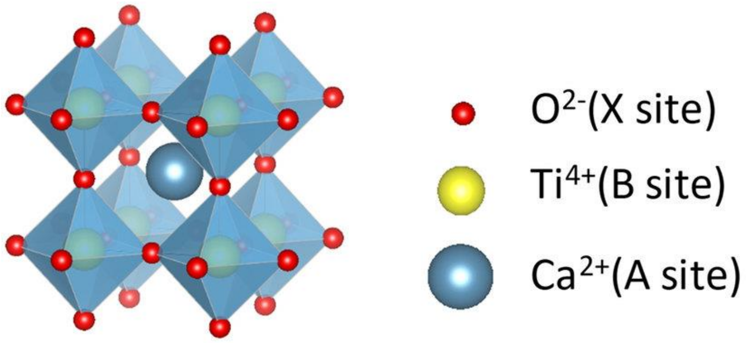
Classification:

Ceramics can also be classified into three distinct material categories:

1. Oxides: alumina, beryllia, ceria, zirconia
2. Non-oxides: carbide, boride, nitride, silicide
3. Composite materials: particulate reinforced, fiber reinforced, combinations of oxides and nonoxides.

Perovskite is a yellow, brown, or black minerals, have $CaTiO_3$ as chemical formula, it obtains its name from mineral named as a calcium titanium oxide. Perovskite materials have emerged as the most promising and efficient low-cost energy materials for various optoelectronic and photonic device applications. The discovery of calcium titanate ($CaTiO_3$)

in 1839 by a Russian mineralogist. Perovski was considered to be the origin of perovskite, and materials with the same type of crystal structure as that of $CaTiO_3$ were known as the perovskite materials (structure). The general chemical formula used to describe the perovskite materials is **ABX_3**, where A and B are cations with A larger than that of B and X is the anion usually oxides or halogens.



Structure of $CaTiO_3$ perovskite

Properties

The unique physical properties of perovskite materials such as-

i. Can change their electrical resistance in the presence of a magnetic field
ii. high-absorption coefficient,
iii. long-range ambipolar charge transport,
iv. low exciton-binding energy,
v. high dielectric constant,
vi. high catalytic activity,
vii. excellent optical and photoluminescence properties,
viii. Ferroelectric properties, etc. have gained a huge interest in these materials for optoelectronic and photovoltaic applications.
ix. Perovskite materials have different phases depending on their temperature. If temperature is lesser than 100 K, stable orthorhombic phase; when temperature increased to 160 K the tetragonal phase; when temperature increases 330 K, stable cubic phase is obtained.

Applications:

- Perovskite materials are also widely used in LEDs ,photodetectors, nano lasers, and waveguides.
- In perovskite thin film based optoelectronic and photovoltaic devices, the quality of the perovskite film (morphology, grain size, uniformity, coverage, etc.) plays a significant role in determining the device performance.
- Recently increased interest has been grown in the development of the low-dimensional (LD) perovskite materials and in exploring their properties for the photonic and optoelectronic device applications.
- Unique features of the LD perovskite materials mainly their tuneable optical and electrical properties due to the quantum-sized effects and their mechanical flexibility are attaining increased attention in the semiconductor materials and optoelectronic devices.
- Different morphologies of LD perovskites developed are perovskite quantum dots (QDs; zero-dimensional). perovskite nanorods or nanowires (NWs; one dimensional), and perovskite nanoplatelets and nanosheets (two dimensional).
- The advantages of reducing the dimensionality of the bulk perovskite materials are prominent on the optoelectronic properties of LD perovskites.
- These properties of LD perovskites have already been used widely in LEDs, photovoltaics, photodetectors, and lasing applications.