UNIT –V
NANO MATERIALS

5.1. INTRODUCTION

The world of materials is rapidly progressing with new and trendiest technologies, and obviously novel applications. Nano technology is among these modern and sophisticated technologies, which is creating waves in the modern times. Actually, nano technology includes the concept of physics and chemistry of materials. It beckons a new field coming to the limelight. So, nano technology is an interesting but emerging field of study, which is under constant evolution offering a very wide scope of research activity.

Nanoscience

Nanoscience is the study of the phenomena and manipulations of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at larger scales.

Nano chemistry

Nano chemistry is a relatively new branch of chemistry concerned with the unique properties associated with assemblies of atoms or molecules in nano dimension (approximately 1 to 100 nm). It also deals with the synthesis, characterization, properties and applications of these nanomaterials.

Nano-technology

Nano-technology is the design, fabrication, characterization and applications of materials at nano-level (1-100 nm) and converting them into useful devices.

Why Nano Technology?

In the materials world, particularly in ceramics, the trend is always to prepare finer powder for the ultimate processing and better sintering to achieve dense materials with dense fine-grained microstructure of the particulates with better and useful properties for various applications. The fineness can reach up to a molecular level (1 nm – 100 nm), by special processing techniques. More is the fineness, more is the surface area, which increases the ‘reactivity’ of the material. So, the densification or consolidation occurs very well at lower temperature than that of conventional ceramic systems, which is finally ‘cost-effective’ and also improves the properties of materials like abrasion resistance, corrosion resistance, mechanical properties, electrical properties, optical properties, magnetic properties, and a host of other properties for various useful applications in diverse fields.

5.2. TYPES OF NANOMATERIALS

Nanoparticles

Nanoparticles are the simplest form of structures with the sizes in nm range. In principle, any collection of atoms bonded together with a structural radius of <100nm can be considered as a nanoparticle.

Nanomaterials

Nanometre is one billionth of a metre. $1\text{nm} = 1\text{x}10^{-9}\text{ m}$

The properties of a bulk material will be different from its nanosized particle.

The unique properties of nanosized particles is mainly due to

i) The smaller particles having a relatively larger surface area compared with their volume, making them chemically more reactive.

ii) When this size is below 100nm, quantum effects can change the optical, electronic or magnetic qualities of materials.

Nanocrystal

Nanocrystal is a material particle having one dimension lesser than 100nm and composed of atoms in either a single or polycrystalline arrangement.

Quantum dot

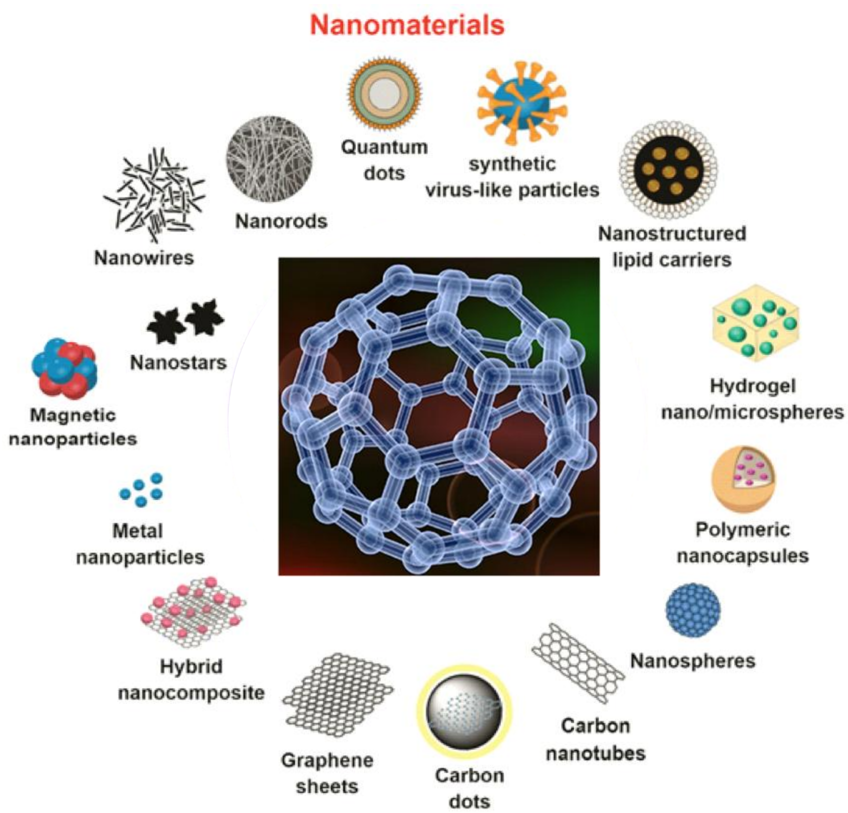
Quantum dot is a nanocrystal made of semiconductor materials.

Polymeric Nanoparticles

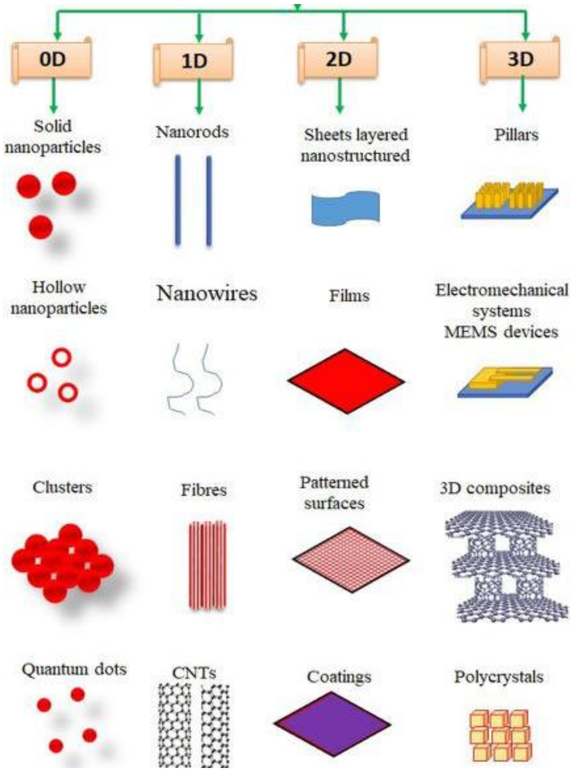
Polymeric nanoparticles are prepared from polymers. They are considered as potential drug delivery devices due to applications in drug targeting to particular organs and tissues.

Dendrimers

Dendrimers is one kind of polymeric nanoparticles constructed by the successive addition of layers of branching groups. The properties of dendrimers are dominated by the functional groups on the molecular surface. It finds its applications as solubilizing agents imaging agents, sensors, drug delivery, Gene therapy, detecting agents such as a dye molecule.



5.3. CLASSIFICATION OF NANOMATERIALS



The main classification of nanomaterials is based on the dimensions of their structural elements.

(i) **Zero-dimensional (0D) nanomaterials:** Nanomaterials having diameter less than 100nm. Example: Nanoparticles, nanoclusters and nanocrystals.

(ii) **One-dimensional (1D) nanomaterials:** One-dimensional (1D) nanostructures are those with a dimension within the range between 1 and 100 nm. It includes nanofibers, nanorods and nanotubes, nanowires.

(iii) **Two-dimensional (2D) nanomaterials:** Two-dimensional (2D) nanomaterials are composed of thin layers that may have a thickness of at least one atomic layer. It includes nanofilms, nanolayers, nanosheets, graphene-based materials, transition metal oxides/dichalcogenides and nano coatings.

(iv) **Three-dimensional (3D) nanomaterials:** All dimensions of a 3D material are outside the nanometer range or greater than 100 nm, but the bulk material is made up of individual blocks that are in the nanometer scale (1–100 nm). It includes powders, fibrous, multilayer and polycrystalline materials.

Table:-1 Distinction between molecules,nano particles and bulk material

Property	**Atoms /Molecules**	**Nanomaterials**	**Bulk Materials**
Size	Few amstrongs (10^{-10}m)	Nanometres(10^{-9}m)	Microns to higher(10^{-6}m)
No. of constituent particles	One atom to few/many atoms	Few atoms to several thousand of atoms	Infinite/ of the order of Avogadro number
Electronic structure	Confined	Confined	Not confined (continous)
Mechanical properties	NA	Properties depend on particle size	Properties independent of particle size
Wave nature	Applicable	Applicable	Applicable to limited extend
Random motion	Present	Present (Brownian)	Not Present
Stability	Stable	Can be stable or unstable depending on surface energy	Stable
Examples	NaCl , CO_2	Carbon nanotube	Gold bar, silver bar

Table:2 Bulk gold materials Vs nanosized gold

Gold bulk	Nanosized gold
Shiny (metallic)	Insulator
Yellow	Red (~10 nm particles absorb green light)
Noble metal	Excellent catalysts (2–3 nm nanoparticles)
FCC structure	Icosahedral symmetry
Non-magnetic	Magnetic
Melts at 1064°C	Much lower melting temperature (sizes depending)
Constant physical Properties. Regardless of its size	Size-dependent properties

5.4. SIZE DEPENDENT PROPERTIES OF NANO MATERIALS

The nano materials have different properties when compared to bulk due to the following reasons

- Large surface area can make nano materials more chemically reactive and affect their strength or electrical properties.
- Quantum effects can begin to dominate the behavior of matter at nanoscale, which affects several properties such as melting point, boiling point, band gap,optical properties, mechanical properties and magnetic properties.

Nanomaterials are composed of grains resulting in a significant increase in the volume fraction of grain boundaries or interfaces, resulting in defect configurations. Hence the mechanical and chemical properties of nanomaterials are significantly altered due to defect dynamics.

The elastic properties of nanomaterials are different from that of bulk alloys due to the presence of increased fraction of defects

Example

1. Nanocrystalline ceramics are tougher and stronger than those with coarse grains

2. Nano-sized metals exhibit significant decreases in toughness and yield strength increases

1. Thermal properties (Melting points)

Nano-materials have a significantly lower melting point or phase transition temperature than bulk materials. This is due to

i. reduced lattice spacing between atoms.

ii. due to huge fraction of surface atoms in the total amount of atoms.

- Nano crystal size decreases → surface energy increases → Melting point decreases
- Example:- Melting point of 3nm CdSe – 700K, Bulk CdSe --1678 K.

2. Optical properties (absorption and scattering of light)

- Nanomaterials exhibit different optical properties due to quantum confinement of electrons within the nanoparticles which increases the energy level spacing.
- Optical properties depend on size, shape, surface characteristics, interaction with the surrounding environment etc.

Example: Bulk gold –yellow in colour. Nano gold can be orange (80 nm) red (20 nm) or purple depending on particle size.

The optical absorption peak of a semiconductor nanoparticles shifts to a short, wavelength, due to an increased band gap

The colour of metallic nanoparticles may change with their sizes due to surface plasma resonance

3. Magnetic properties

Magnetic properties of nanoparticles are different from that of the bulk materials. Ferro-magnetic behavior of bulk materials disappear, when the particle size is reduced and transfer to super- paramagnetic. This is due to the huge surface area.

Example:

Material	**Bulk**	**Nano scale**
Fe,Co and Ni	Ferromagnetic	Super paramagnetism
Na,K	Paramagnetic	Ferromagnetic

4. Mechanical properties

The nano materials have less defects compared to bulk materials, which increases the mechanical strength. As nano-materials are stronger, harder and more wear resistant and corrosion resistant, they are used in spark plugs

Example:

Nano-crystalline carbides are much stronger, harder and wear resistant, which are used in micro drills.

5. Electrical properties

Electrical conductivity decreases with a reduced dimension due to increased surface scattering. However, it can be increased, due to better ordering in micro-structure

Nano-crystalline materials are used as very good separator plates in batteries, because they can hold more energy than the bulk materials.

Example:

Nickel-metal hydride batteries made of nanocrystalline nickel and metal hydride, require far less frequent recharging and last much longer.

6. Chemical Properties

Based on the surface area to volume effect, nanoscale materials have:

a) Increased total surface area.

b) Increased number of atoms accessible on the surface.

c) Increased catalytic activity of those large number surface atoms.

d) Different/tunable surface catalytic properties by the change in shape, size and composition.

Hence, nanoscale catalysts can increase the rate, selectivity and efficiency of various chemical reactions.

5.5. NANOMATERIALS

5.5.1. NANO PARTICLES

- Nanoparticles are the simplest form of structures with sizes in the nm range. In principle any collection of atoms bonded together with a structural radius of <100nm can be considered as a nanoparticle.
- Nanoparticles are very similar to nanoclusters but it contains larger aggregates containing 10^3 or more atoms.
- Nanoparticles may exhibit size-related properties that differ significantly from those observed in fine particles or bulk materials. These are made of metals, semiconductors, or oxides and they show good mechanical, electrical, magnetic, optical , chemical, thermal, diffusion properties.
- The properties of materials change as their size approaches the nanoscale and as the percentage of atoms at the surface of a material becomes significant.

5.5.2. NANOCLUSTERS

- Nano clusters constitute an intermediate state of matter between molecules and bulk materials.
- These are fine aggregates of atoms or molecules.
- A nanocluster is a nanometer sized particle made up of equal subunits. These subunits can be atoms of a single element, molecules or even combinations of atoms of several elements in subunits with equal stoichiometries

Example: Na_n, $(SF_6)_n$,$(H_2O)_n$, $(Cu_3Au)_n$, $(TiO_2)_n$ etc.

- The size of nanoclusters ranges from sub-nanometer to 10 nm in diameter.
- It has been found that clusters of certain critical size (clusters with a certain number of atoms in the group) are more stable than others. Nanoclusters consist of upto a couple of hundred atoms, but larger aggregates containing 103 or more atoms are called nanoparticles.
- Nanoclusters can be classified based on the nature of bonding present between the atoms of the aggregate.

They are (a) vanderwaals cluster (b) ionic cluster (c) metallic cluster (d) network cluster.

(a) **Vander Waals cluster**: Here the interaction between the constituents of the cluster is weak vanderwaals forces (strength of bond is 0.3eV per atom or less). Weak binding leads to weak melting and boiling points.

Example: Molecular clusters like $(SF_6)_n$,$(I_2)_n$

(b) Ionic cluster: Here the force of attraction between the species is electrostatic force

(strength of the bond is 2-4 eV per atom).

Example: $(NaCl)_n$

(c) Metallic cluster: Atoms are held together by metallic bonds. The force of attraction in metal clusters can range from moderate to strong (0.3 – 3 eV per atom).

Example: $(Na)_n$,$(Cu_2\ Au)_n$

(d) Network cluster: Covalent bonding can result in the formation of an atomic network. Bonds in clusters are usually strong(1-4eV per atom).

Example: C_{60}-fullerene

- Atomic clusters are formed by the nucleation of atoms.
- Molecular clusters are formed by the nucleation of molecules.

Properties of nano clusters:

- **Magic number:** Number of atoms present in the clusters of critical sizes with higher stability.
- Clusters containing transition metal atoms have unique electronic, chemical and magnetic properties.
- These properties vary with

(a) The number of constituent atoms.

(b) The type of element

(c) The net charge on the cluster.

- The reactivity of nanoclusters are decreased due to their decrease in size.
- The melting point of nanoclusters is lower than the bulk materials due to the high surface to volume ratio.
- The electronic structure of the nanocluster is more confined than the bulk materials.

Applications of nanocluster

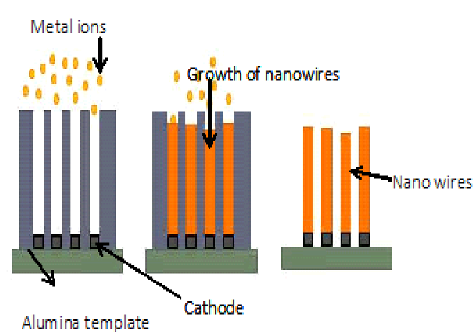
1. It is used as catalysts in many reactions.
2. It is used in nano based chemical sensors.
3. It is also used as a light emitting diode in quantum computers.

5.5.3. NANO WIRES

Nanowire is a one dimensional cylindrical solid material having an aspect ratio i.e, length to width ratio greater than 20. Diameter of the nanowire ranges from 10-100 nm.

Different types of nanowires are

S.No	Types of nanowires	Examples
1.	Metallic nanowires	Au, Ni, Pt
2.	Nanowires of semiconductors	InP, Si, GaN
3.	Nanowires of insulators	SiO_2, TiO_2
4.	Molecular nanowires	DNA



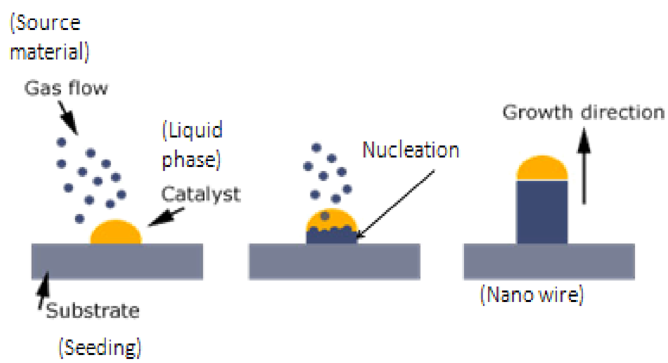
Synthesis of nanowires

1. **Template-assisted synthesis**

Template assisted synthesis of nanowires is a simple way to fabricate nanostructures. These templates contain very small cylindrical pores or voids within the host material and the empty spaces are filled with the chosen material to form nanowires.

2. **VLS (Vapour-Liquid-Solid)method**

- Source material (Gas phase) is absorbed by the catalyst (liquid phase).
- Upon supersaturation of the liquid alloy, a nucleation event generates a solid precipitate (Solid phase).
- This seed serves as a preferred site for further deposition of material at the interface of the liquid droplet.
- And promotes the elongation of the seed into a nanowire.



Reactant + Catalyst Nanoparticles

Properties of nanowires

- Nanowires are one-dimensional material.
- Conductivity is less than that of bulk materials.
- Due to its large surface area it exhibits different optical, chemical, thermal and Electric properties.
- Silicon nanowires show strong photoluminescence characteristics.

Applications of nanowires

- Used to enhance mechanical properties of composites.
- Used to prepare active electronic components like *p-n* junction and logic gates.
- Semiconductor nanowire crossings are used in digital computing.
- It is used in high-density data storage either as magnetic heads or as patterned storage media.
- It replaces conventional coppers in computers, televisions etc.,
- Used to link tiny components into very small circuits.

5.5.4. NANO RODS:

Nanorods are one dimensional nanostructures, shaped like long sticks rods. One dimension is in nanometre, which produces quantum confinement and alters the properties of the material. Usually, diameter is in the nanoscale. If the ratio of length to width is 1-20, it is called a nanorod.

Eg: Zinc oxide, cadmium sulfide, Gallium nitride nano rods.

- It is a two-dimensional cylindrical solid material.
- Length to width ratio < 20.

- **Examples:** ZnO, CdS nanorods etc.,

Synthesis of nanorods:

- It is produced by direct chemical synthesis.
- Combination of ligands is required to control the shape of the nanorods.
- Ligands bond to different facets of the nanorod with varying strengths.
- Thereby, elongated Nanorods grow with desired shape.

Properties:

- Two dimensional materials.
- It exhibits optical and electrical properties.

Applications of nanorods

- Nanorods find application in display technologies.
- It is also used in the manufacturing of micro mechanical switches.
- Nanorods are used in an applied electric field, micro electro mechanical systems etc.,
- Nanorods along with noble metal nanoparticles function as theranostic agents.
- They are used in energy harvesting and light emitting devices.
- Used as cancer therapeutics.

5.5.5. NANO TUBES:

- Nano-tubes are one of the most widespread studied and used materials, consisting of tiny cylinders of carbon and other materials like boron nitride.
- Nano-tubes of carbon and inorganic compounds with structures comparable to the layered structure of graphite have been prepared. Studies on carbon nano-tubes are quite extensive.

Carbon Nanotubes (CNT)

- Carbon nanotubes are allotropes of carbon with a nanostructure having a length-to-diameter ratio greater than 1,000,000.
- When graphite sheets are rolled into a cylinder, their edges joined and form carbon nanotubes
- Nanotubes naturally align themselves into “ropes” and are held together by vanderwaals forces. But each carbon atoms in the carbon nanotubes are linked by the covalent bond.
- Their unique molecular structure results in extraordinary macroscopic properties, including high tensile strength, high electrical conductivity, high ductility, high heat conductivity and relative chemical inactivity.
- It has potential applications in the electronic industry.

Types of carbon nanotubes

Carbon nanotubes are lattice of carbon atoms, in which each carbon is covalently bonded to three other carbon atoms. Depending upon the way in which graphite sheets are rolled, two types of CNTs are formed.

1. Single - walled nanotubes (SWNTs).
2. Multi – Walled nanotubes (MWNTs)

1. Single - walled nanotubes (SWNTs)

- SWNTs consist of one tube of graphite. It is one-atom thick having a diameter of 2 nm and a length of 100
- SWNTs are very important, because they exhibit important electrical properties.
- It is an excellent conductor.

Three kinds of nanotubes are resulted, based on the orientation of the hexagon lattice.

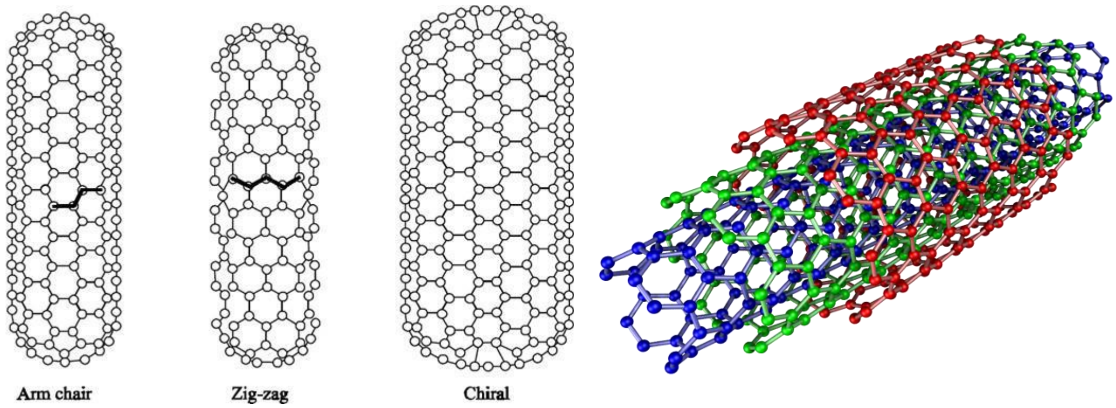


Fig :- Structure of Single walled & multi walled carbon nanotubes

(a) Arm-chair structures: The lines of hexagons are parallel to the axis of the nanotube.

(b) Zig-zag structures: The lines of carbon bonds are down the center.

(c) Chiral nanotubes: It exhibits a twist or spiral around the nanotubes.

It has been confirmed that arm-chair carbon nanotubes are metallic while zig-zag and chiral nanotubes are semiconducting.

2. Multi - walled nanotubes (MWNTs)

MWNTs (nested nanotubes) consist of multiple layers of graphite rolled in on themselves to form a tube shape. It exhibits both metallic and semiconducting properties. It is used for storing fuels such as hydrogen and methane.

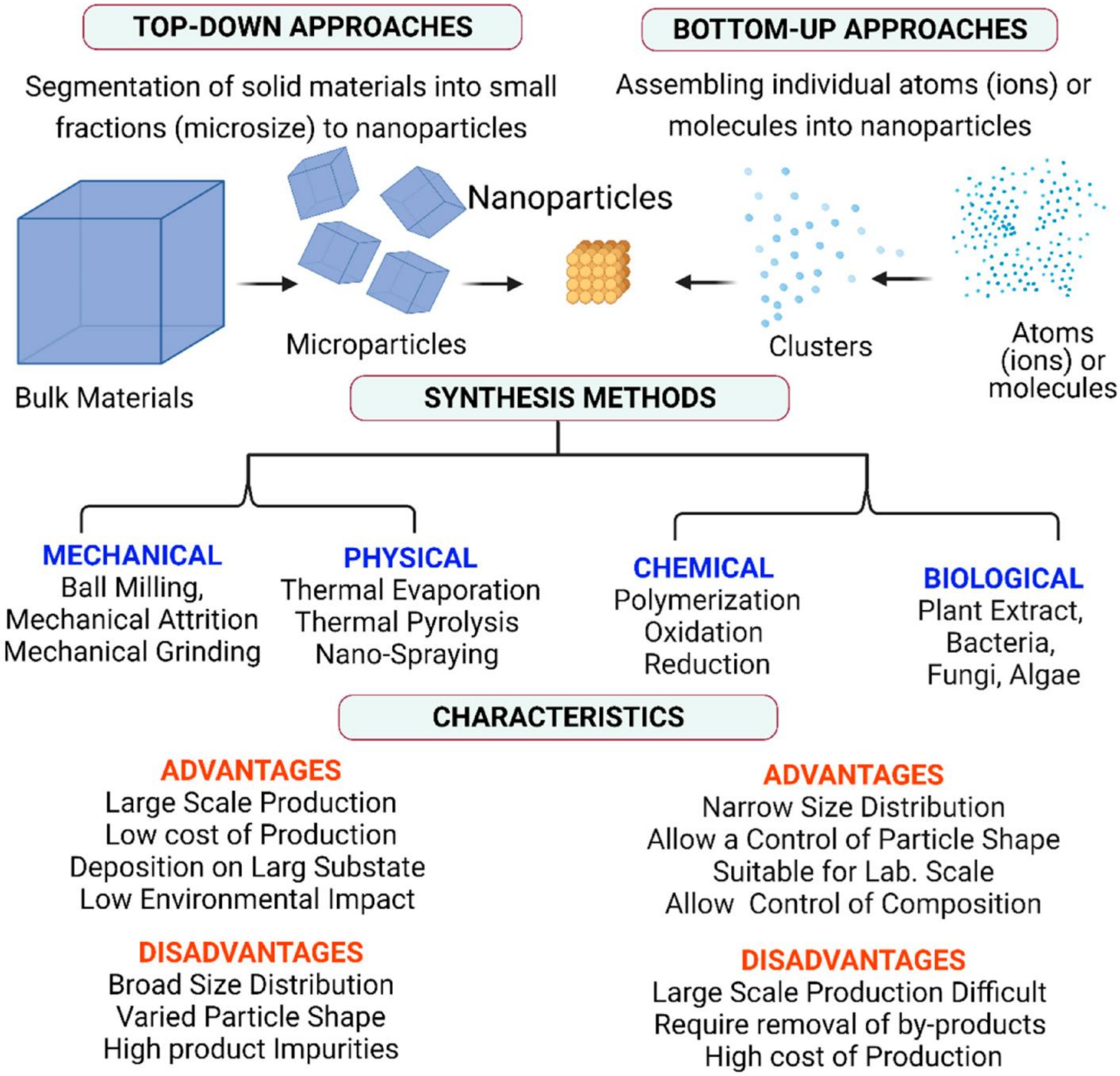
Properties of CNTs

- CNTs are very strong, withstand extreme strain in tension and posses elastic flexibility.
- The atoms in a nano-tube are continuously vibrating back and forth.
- It is highly conducting and behaves like metallic or semiconducting materials.
- It has very high thermal conductivity and kinetic properties.

Applications of CNTs

- It is used in battery technology and in industries as a catalyst.
- It is also used as light weight shielding materials for protecting electronic equipments.
- CNTs are used effectively inside the body for drug delivery.
- It is used in composites, ICs.

5.6. SYNTHESIS OF NANOPARTICLES



5.6.1. CHEMICAL METHODS

I). METAL NANOCRYSTALS BY REDUCTION

(a) Precipitation

$$\textbf{Reactant} \xrightarrow[\text{stabilizing agent}]{\text{Water soluble inorganic}} \underset{\text{(Precipitate)}}{\textbf{Nanoparticles}}$$

Examples: Precipitation of $BaSO_4$ Nanoparticles

Procedure:

10 gm of Sodium hexameta-phosphate (stabilizing agent)

+ 80 mL distilled water/250ml beaker

↓ i.Dissolve it

ii.Add 10 mL of 1M Sodium sulphate solution

+ 10 mL of 1M Barium nitrate solution

↓ Stir it for 1 hour

Precipitate is obtained

↓

Centrifuge, wash with distilled water and dry it in vacuum drier

Reaction:

$$Ba(NO_3)_2 + Na_2SO_4 \xrightarrow{\text{Stabilizing agent}} BaSO_4\downarrow + NaNO_3$$

In the absence of stabilizing agent, Bulk $BaSO_4$ is obtained.

(b) Precipitation by reduction: This method involves reduction of metal salts in appropriate solvents with a variety of ***reducing agents***.

$$\text{Metal salt} \xrightarrow[\text{Reduction}]{} \underset{\text{(Nucleation centre)}}{\text{Metal atom}} \xrightarrow{\text{Stabilizing agent}} \underset{\text{(Atomic clusters)}}{\text{Nanoparticles}}$$

Clusters are surrounded by stabilizing molecule to prevent agglomeration.

Example-1: Reduction of chloroaurate ions in aqueous solution by citric acid or sodium borohyd ride gives gold hydro sol (particle size in the range of 10-640 °A).

Reduction

$$\textbf{Chloro aurite ions + Sodium boro hydride} \xrightarrow{\text{Reduction}} \textbf{Gold hydrosol}$$

- Alcohol, glycol, metal borohydride, Phosphonium chloride are some of the reducing agents involved in this method.
- Sols of metals and semiconductor nano particles are stabilized by the presence of ligand or stabilizing agent(Long chain amines, thiol or polymers)
- Ex: PVA-PVP which prevent the aggregation of the particle
- Nano crystal of CdS, CdSe, Zno, Zns, HgTe, Pbs, Cus, Cu_2 S, AgI and TiO_2 were prepared by this method.

Example-2:

$$\underset{\text{(Dissolved in Toluene)}}{3MoCl_2} + \underset{\text{(Reducing agent)}}{6\,NaBH(C_2H_5)_3} \xrightarrow[\text{Room temperature}]{\text{Stabilizing agent}} 3\,Mo + 6NaCl + 3H_2 + 6B(C_2H_5)_3$$

II. THERMOLYSIS

It is the process of making nanoparticles by the decomposition of solids at high temperature having metal cations and molecular anions (or) metal organic compounds.

(eg)- Lithium nanoparticles are produced by the decomposition of Lithium azide(LiN_3) at 400 °C.

Decomposition

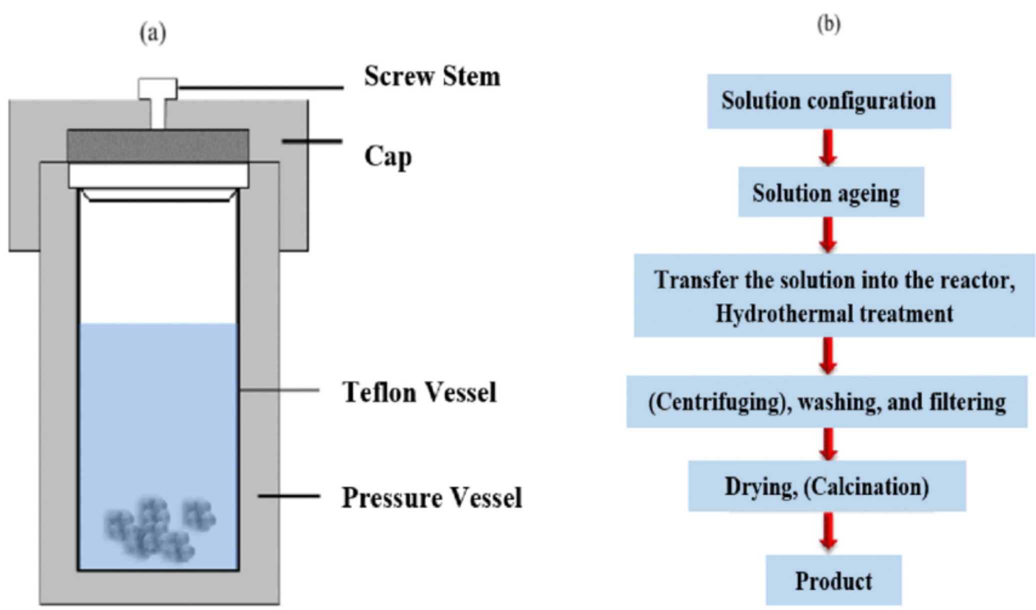
$$\mathbf{LiN_3} \xrightarrow[\mathbf{400\ ^\circ C}]{\text{Decomposition}} \textbf{Li-nano particle}$$

This method is of two types

a. Hydrothermal process and b. Solvo thermal process

(a) Hydrothermal synthesis

- Hydrothermal synthesis is carried out in an autoclave under autogenous (high) pressure and below the supercritical temperature of water (374 °C).
- These conditions are favorable for the crystallization of products.
- pH of the medium to be maintained, pH is generally made alkaline to increase the solubility of the reactants.



Example-Synthesis of ZnO nanoparticles

- This process is carried out in teflon lined sealed stainless steel autoclave at the temperature range of 100 – 200 °C for 6 – 12 hrs under autogenous pressure.
- The stock solution of $Zn(CH_3COO)_2.H_2O$ (0.1M) was prepared in 50 ml methanol under stirring.

- 25 ml of NaOH(0.2 – 0.5M) solution prepared in methanol was added to maintain pH (8-11),Finally at the end of the reaction white ZnO nano particles are formed.

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

$$Zn^{2+} + 2OH^- \longrightarrow ZnO + H_2O$$

- Metal oxides, Carbon nanotubes etc. can be prepared this way.

Advantages

- Solvent used is water.
- Rate of the reaction is much faster at high temperature and pressure.
- Ability to synthesize large crystals of high quality.
- Reagents and solvents can be regenerated.
- Used to prepare nanomaterials of different morphology (powder, rod, wire, tube, single crystals and nanocrystals).

Disadvantages:

- High cost of equipment.
- Sometimes, it is difficult to predict the morphology of the product.

(b) Solvothermal synthesis

- A "solvothermal reaction can be defined as a chemical reaction (or a transformation) between precursor(s) in a solvent (in a close system) at a temperature higher than the boiling temperature of this solvent and under high pressure".
- The Solvothermal method is identical to the hydrothermal method except that a variety of solvents other than water can be used for this process. This method has been found to be a versatile route for the synthesis of a wide variety of nanoparticles with narrow size distributions, particularly when organic solvents with high boiling points are chosen
- It is a method for preparing a variety of materials such as metals, semiconductors, ceramics, and polymers.
- Solvothermal are usually thick walled steel cylinders with hermetic seal which must withstand high temperature and pressure for prolonged periods of times.
- The autoclave material must be inert with respect to the solovent. The closure is the most important element of the autoclave.
- To prevent corroding of the internal cavity of the autoclave, protective inserts are generally used. These may have the same shape of the autoclave and fit in the internal cavity.
- Inserts may be made up of carbon free iron, glass or quartz, copper or Teflon depending on the temperature and material used.
- The process involves the use of a non-aqueous solvent under moderate to high pressure (typically between 1 atm and 10,000 atm) and temperature (typically between 100 °C and 1000 °C) that facilitates the interaction between reactants during synthesis

- High temperature and pressure facilitates the dissolution of the reactants and products are generally obtained in the nanocrystalline form. It is then washed and then dried.

Example-1:- Nano crystals of CdSe have been prepared by reacting cadmium stereate with selenium powder using toluene as solvent, tetrahydro phenolphthalein as reducing agent.

$$\textbf{Cadmium stereate + Selenium} \xrightarrow{\text{Toluene}} \textbf{CdSe}$$

Example-2(eg-2):- Cadmium oxalate and chalcogens undergo reaction in presence of pyridine as solvent to produce cadmium nanoparticle**.**

$$CdC_2O_4 + E \xrightarrow{\text{Pyridine}} CdE$$

E = Chalcogenide(S, Se,Te)

Advantages:

- Relatively easy and cheap method.
- Products obtained are in crystalline form. So no purification required.
- Can be used for preparing nanomaterials of different morphology (powder, rod, wire, tube, single crystals and nanocrystals).
- Precise control over the size, shape distribution and crystallinity of nanoparticles by varying experimental conditions.
- Variety of organic solvents can be used as it helps the dispersion nanocrystallites and may stabilize some metastable phases.

Disadvantages:

- Inability to monitor crystals in the process of their growth.
- The need for an expensive autoclave.
- Safety issues during the reaction process.

Applications

- Various kind of nanostructures can be center size of through solvothermal approaches including metal oxides carbonaceous Nano structures and etc.,
- This method can also be used produce zeolite ,nano wires, carbon nanotubes

III. SOL-GEL PRECIPITATION

Sol-Gel Process: "Formation of an oxide network through polycondensation reactions of a molecular precursor in a liquid"**.**

Precursors

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

Examples

- Tetra methoxy silane [$Si(O_3CH_4)$]

- Tetra ethoxy silane [Si($O_2C_5H_4$)]
- Tetra butoxy titanate [Ti(O4C_9H_4)]

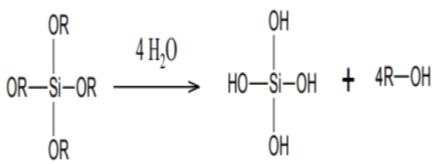
Process (Synthesis of silica aerogel

This process consists of four main steps.

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

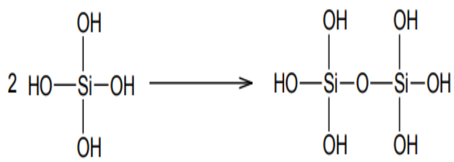
1. Hydrolysis

It occurs by the addition of water to any one of the precursor material to form silanol (SiOH) particles.



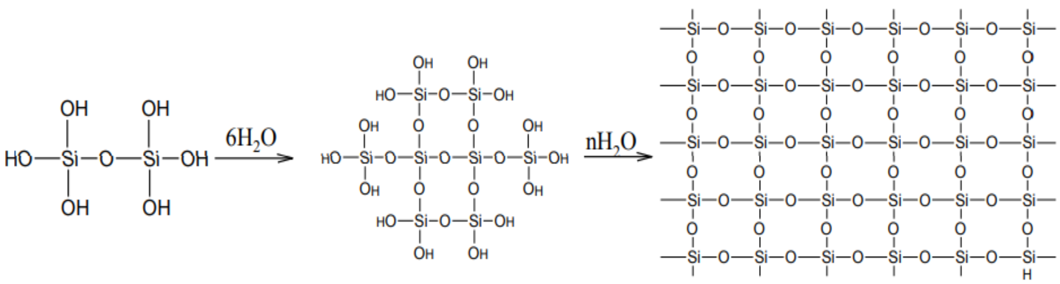
2. Condensation

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



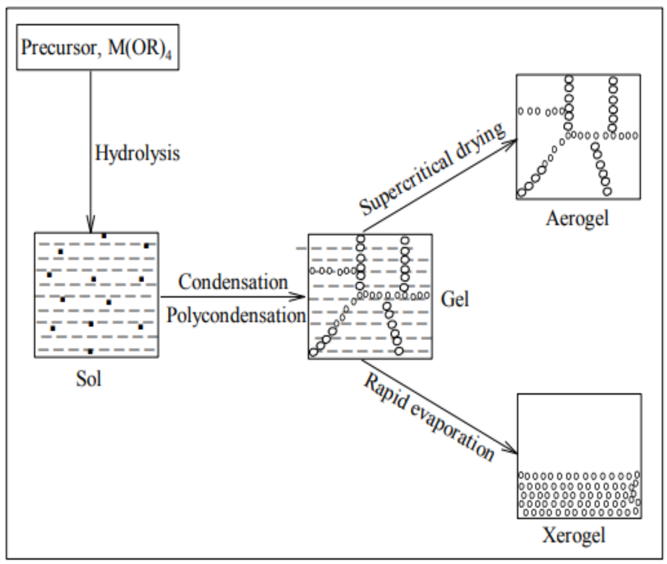
3. Polycondensation

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



4. Drying

The gels are subjected to super critical drying in an autoclave. The critical pressure and critical temperature used are 78 bars and 294°C respectively in order to remove liquid from silica gel to form the network structure of silica aerogel.



Advantages of Sol-gel process

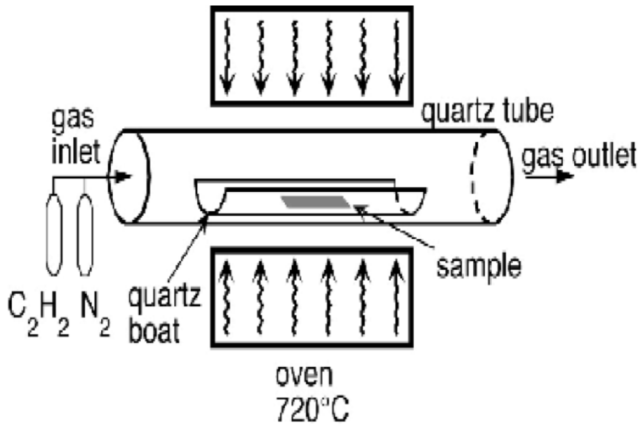
- It produces thin bond-coating to provide excellent adhesion between the metallic substrate and the top coat.
- It produces a thick coating to provide corrosion protection performance.
- It easily shapes materials into complex geometries in a gel state.
- It has low temperature sintering capability,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

Applications of Sol-gel process

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

IV. CHEMICAL VAPOR DEPOSITION (CVD)

- Chemical Vapor Deposition is the formation of a non-volatile solid film on a substrate by the reaction of vapor phase chemicals (reactants) that contain the required constituents.
- The reactant gases are introduced into a reaction chamber and are decomposed and reacted at a heated surface to form the thin film.



- CVD involves the formation of nanomaterials from the gas phase at elevated temperatures usually onto a solid substrate or catalyst.
- The process involves passing a hydrocarbon vapor through a tubular reactor containing catalyst
- At temperature (600–1200^{o}C) hydro- carbon decomposes to carbon vapours, which condense on the cooler surface.
- The formed nanotubes diffuse to the growth sites.
- Desorption of products from the reacting surface.
- The CVD method produces both single-wall and multi-wall nanotubes

Mechanism

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

a) Transport of precursors into the reactors.

b) Absorption and diffusion of precursors on the substrate.

c) Chemical reactions at the substrate.

d) Deposition and growth of film.

e) Transport of unreacted precursors and by-products.

Advantages:-

- Extremely high purity nanomaterials are produced.
- CVD produces high dense films.
- It can produce 1D nanomaterials.
- Economical in production since many products can be coated at a time.
- Controllable thickness and morphology.
- Conforms homogeneously to contours of substrate surface.
- Forms alloys.

Disadvantages:-

- Expensive.
- Use of toxic gases causes a number of environmental problems.

Applications

- CVD can be used for the synthesis of nanotubes and nanowires.
- CVD can be used for hard coatings and metal films which are used in microelectronics.
- CVD can also be used for preparing semiconducting devices, dielectrics, energy conversion devices etc.
- BioMEMS and biosensor coating to reduce "drift" in device performance.
- Promote biocompatibility between natural and synthetic materials Copper capping Anticorrosive coating.

V. MICROWAVE IRRADIATION

- Microwave synthesis has been employed in the synthesis of nanoparticles as it combines the advantage of speed and homogeneous heating of the precursor materials. Microwave irradiation has a penetration characteristic, which makes it possible to homogeneously heat up the reaction solution.
- This method uses a high-frequency wave to heat the starting materials.
- Microwave synthesizers work by exposing chemical reactions to electric fields under high pressure; this rapidly heats the molecules through motion generated either through dipolar polarization or ionic conduction. Because of the high pressure, solvents can be heated beyond their standard boiling points.

Microwave-Assisted Synthesis of CuO Nanoparticles Using Leaf Extract

Materials

- Cupric acetate ($Cu(CH_3COO)_2 . H_2O$)
- Sodium hydroxide (NaOH)
- Plant Extract

Extract Preparation

- The plant leaves were washed thoroughly several times with tap water and distilled water sequentially to remove dust particles attached to the surface of the plant and then allowed to air dry. Then, the dried leaves were powdered using a grinder. 20 g leaf powder and 200 mL distilled water were mixed in a 1000 mL conical flask and stirred for 20 min.

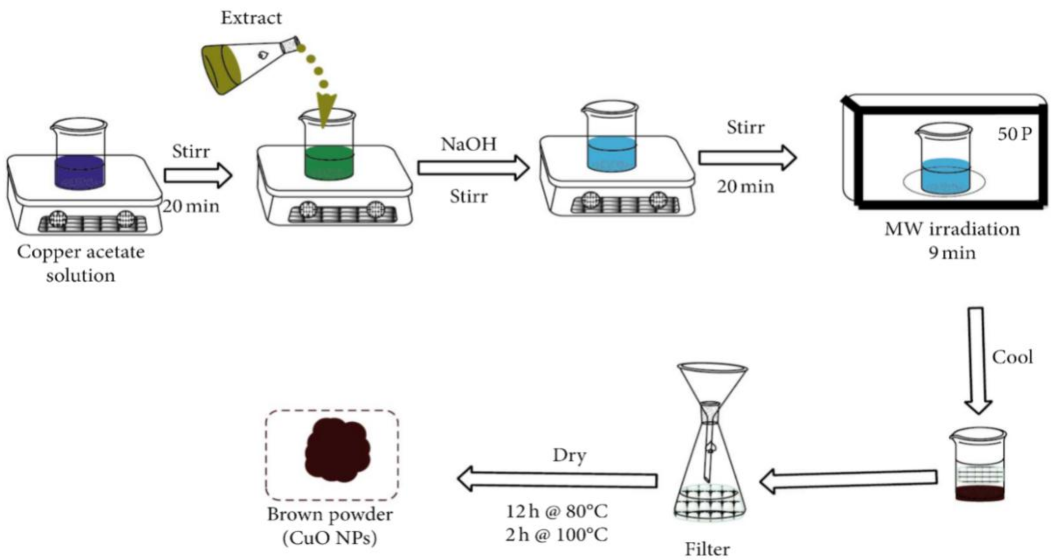
- Then, the mixture was heated up to the boiling point and allowed to boil for 10 min under stirring. After cooling to room temperature, it was stirring continued for 20 min and then filtered to obtain an extract using Whatman filter paper. The resulting extract was stored at about 4°C for further use.

CuO Synthesis

- CuO NPs were prepared by the MW-assisted modified method using $Cu(CH_3COO)_2.H_2O$ and plant extract. In a typical procedure, 6.2 g $Cu(CH_3COO)_2.H_2O$ was added to a 1000 mL beaker containing 100 mL DW and then stirred for 20 min.

- Then, 10 mL of the extract was added to the $Cu(CH_3COO)_2.H_2O$ solution under stirring. To adjust the pH, NaOH aqueous solution was added drop wise while stirring.

- After 20 min of stirring, the mixture was placed into a domestic microwave (MW) oven with a maximum power of 1000 W, and only 50% power output was used for 9 min.
- The brown precipitates were collected and washed with DW and ethanol sequentially. Finally, the residue was dried at 80°C for 12 h and then at 100°C for 2 h.
- The dried powder was powdered using a mortar and pestle. The flow chart of the synthesis of the CuO NPs is shown in Scheme.



Advantages

- MW irradiation can freely pass through the walls of the reaction vessel, coupling directly with molecules and ions of the reaction mixture. Thus, the tendency for the reaction mixture to boil is reduced.
- In fact, superheating above the boiling point of the solvent is known to occur under MW conditions.

VI. ELECTRO DEPOSITION

Electrodeposition is an electrochemical method in which ions from the solution are deposited at the surface of the cathode. Template-assisted electrodeposition is an important technique for synthesizing metallic nanomaterials with controlled shape and size.

Array of nano-structured materials with specific arrangements can be prepared by this method using an active template as a cathode.

Process of Electro-deposition

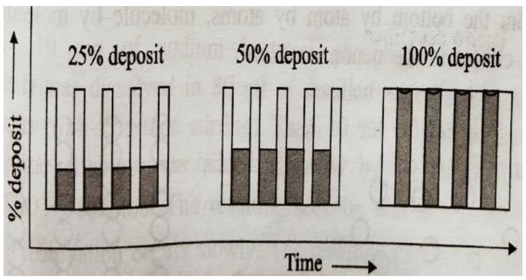
The cell consists of a reference electrode, specially designed cathode and anode. All these electrodes are connected with the battery through a voltmeter and dipped in an electrolyte solution of a soluble metal.

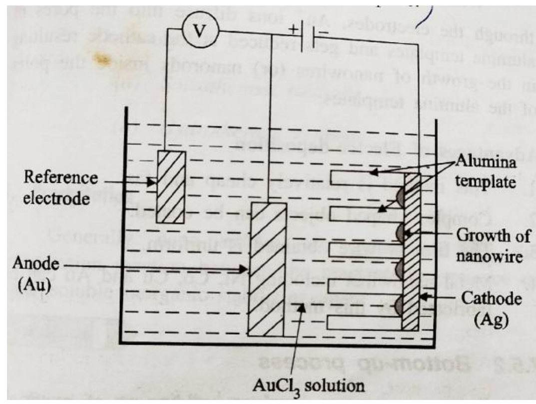
When the current is passed through the electrodes of template, the metal ion from the solution enter into the pores and gets reduced at the cathode, resulting in the growth of nanowire inside the pores of the template.

Example: Electrodeposition of gold on silver

Nanostructured gold can be prepared by the Electrodeposition technique using gold sheets as an anode and silver plate as a cathode and $AuCl_3$ is used as an electrolyte.

When the current of required strength is applied through the electrodes, an Au^+ ion diffuse into the pores of alumina templates and gets reduced at the cathode resulting in the growth of nanowires (or) nanorods inside the pores of the alumina templates.





Advantages of Electro-deposition

- This method relatively cheap and fast.
- Complex shaped objects can be coated.
- The film or wire obtained is uniform.
- Metal nanowires including Ni, Co, Cu and Au can be fabricated by this method.

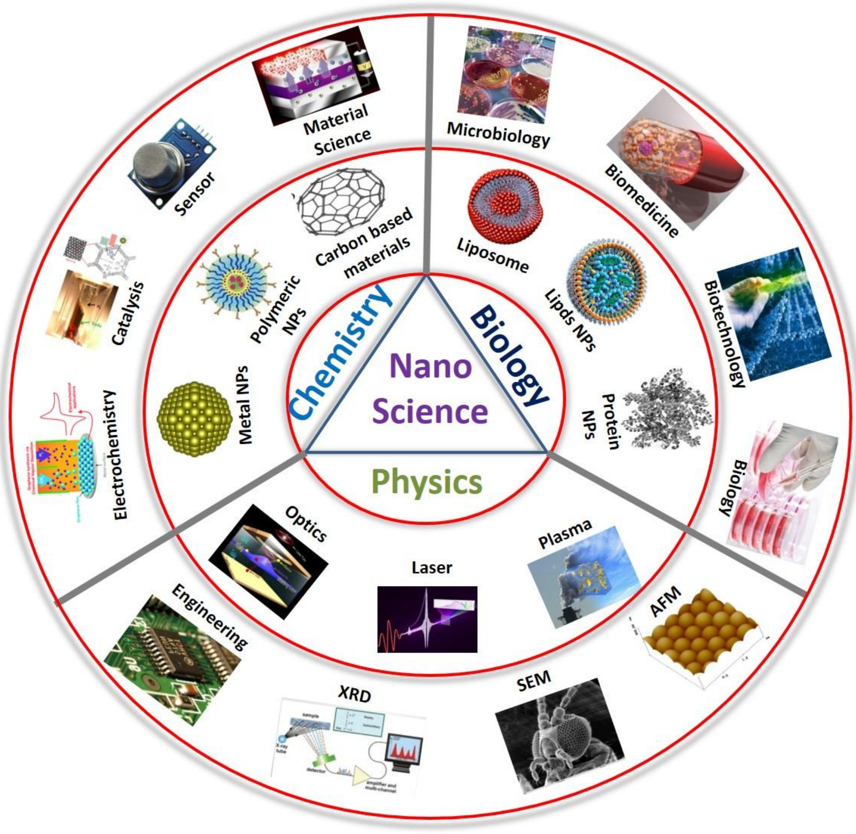
APPLICATIONS OF NANOMATERIALS

Applications in Electronics

- Nanomagnets are used as switches, transistors, in electrical circuits which lower power consumption.
- Silver nanoparticle ink was used to form the conductive lines needed in circuit boards.
- Combining gold nanoparticles with organic molecules to create a transistor known as NOMFET (Nanoparticle Organic Memory Filed –Effect Transistor).
- Nano wires are used to build transistors without p-n junctions.
- MOSFET (Metal Oxide Semi conductor Field Effect Transistor), performs both as switches and as amplifiers.
- Nanomaterials with less than 100nm in size are used in micropocesors in the electronic industry because smaller sizes allow faster processing times and also more processing power.
- The density of memory chips can be increased by nanomaterials.
- Integrated nanosensors are used for collecting, processing and communicating massive amounts of data with minimal size, weight and power consumption.

APPLICATIONS IN MEDICINE

- Nanotechnology has its applications in field of health and medicine called nanomedicine.
- Nanoparticles to deliver drugs, are engineered so that they are attracted to diseased cells, which allows direct treatment of those cells.
- Nanomedicine has the potential to enable early detection and prevention, and to essentially improve diagnosis, treatment and follow-up of diseases.
- Nanoparticles used to deliver vaccine and trigger a stronger immune response.
- Nanocapsules containing an enzyme, release insulin. When the glucose level rises the nanocapsules release hydrogen ions.
- Nanoparticle is used to defeat viruses. It delivers an enzyme that prevents the reproduction of viruses molecules in the patient's bloodstream.
- Gold nanorods are used for early detection of kidney damage.
- A sensor using nanotubes can detect a very low level of cancer cells, as low as 3-5 cancer cells in a one millilitre in 1ml of a blood sample.
- Gold coated nanoshells converts light into heat, enabling the destruction of tumours.
- Protein analysis can be done using nanomaterials.
- Nanotechnology is used to partially repair neurological damage.
- Nanotechnology can help to reproduce or to repair damaged tissue. This so called tissue engineering makes use of artificially stimulated cell. It might replace today's conventional treatments eg., transplantation of organs or artificial implants.
- The technology is also being used to develop sensors for cancer diagnostics.



ADVANTAGES OF NANOTECHNOLOGY

1. It Resulted in a Significant Change in Electronic Goods

Most of the electronic goods that we use today are produced using nanotechnology. Nobody could have predicted that a device with thousands of memory cells would only be a few millimeters in size. The intricate circuitry has finished the chip's function and made it portable so that users may transport any electronic device from one location to another. Nowadays, we do even sophisticated calculations on a little smartphone rather than using supercomputers for basic calculations.

2. Nanotechnology has Greatly Enhanced Medical Fieldwork

Enhanced medical fieldwork, which is a blessing for the medical industry. Utilizing nanotechnology to its fullest potential, the medical field has created several medications to treat previously incurable illnesses like cancer. The condition may now be easily identified, and the methods for treating it are likewise readily available. Therefore, nanotechnology is beneficial to the medical industry. Drugs made using nanotechnology can be made to connect only to certain biological targets. These specially formulated drugs wouldn't affect healthy tissue; they would only affect the targeted, particular sick tissue. These medications would also be individualized and created for a particular person with a particular ailment. Not only would this eliminate the trial-and-error process of using prescription drugs, but it would also decrease the amount of real medication, giving out fewer side effects and a faster physiological reaction.

3. Benefits for Manufacturing

Modern manufacturing concerns need nanoproducts like nanotubes, nanoparticles, etc., that are resilient, powerful, and lighter than equivalent products made without nanotechnology. As a result, the production environment has transformed and become considerably more favorable to them thanks to nanotechnology.

4. Energy Production

The field of energy production has benefited greatly from nanotechnology. Batteries, cells, and other energy-efficient storage technologies have been widely used. These have proven to be energy-saving technologies that have improved human lives. The methods through which humans produce and consume energy may change due to nanotechnology. New ways of producing and storing energy will become possible thanks to nanotechnology. Nanotechnology is particularly likely to increase the affordability of solar energy by lowering the cost of producing solar panels and accompanying machinery. As a consequence, energy storage devices will operate more effectively.

5. It is Feasible to Cure Illnesses to a Large Extent

Now nanotechnology has made significant contributions to this sector. The treatment of several incurable diseases and illnesses has involved the use of various tools and equipment. With the use of nanotechnology, the condition may be quickly diagnosed. After a diagnosis, it is much simpler to treat the illness and aid in the patient's quick recovery.

6. Nanotechnology in Computing and Electronics

Nanotechnology has the potential to transform the electronics industry. For instance, quantum dots are extremely small light-producing cells that may be utilized for display screens or lighting.

Millions of components can already be found on silicon chips. Still, as technology advances, circuits are so tiny that if a molecule is out of position, the circuit won't function as intended. Nanotechnology will make it possible to build circuits precisely at the atomic level.

7. Coatings Made of Nanoparticles

Traditional prostheses can increase their lifespan with nanoparticle coatings. It is often carbon-based for this coating to remain neutral to the body. Such a coating would shield a prosthesis from the body's rejection and eventual destruction. Long-term costs to amputee patients would be lower since the prosthesis would last longer.

8. Easily Accessible Large and Impractical Diagnostic Tools

Many formerly large and impractical diagnostic tools are now easily accessible to critically ill individuals and may be used to diagnose their condition. Nanotechnology is frequently used in the diagnosis and treatment of hidden diseases.