Unit II

NANOCHEMISTRY.

Part - A (2 mark)

1. **Define the term 'nanochemistry'? (may 2011)**

Nanochemistry is the branch of nano-science which deals with the chemical applications of nanomaterials. It also includes the study of synthesis and characterization of nanomaterials.

2. **Mention some important applications of CNTs.**
   - It is used in storage devices.
   - It is used as catalyst.
   - It is used as protective shields.
   - It is a very good reinforcing element in composites.
   - It is used as sensor for gases like NO_2 and NH_3.

3. **What are the carbon nanotubes?**

Carbon nanotubes are tubular form allotropes of carbon with a nanostructure with 1-3 nm diameter and length few nm to microns. When graphite sheets are rolled into cylinder, their edges joined and form carbon nanotubes.

4. **Define nano-wires.**

Nano-wire is a material having an aspect ratio ie., lenth to width ratio greater than 20. Nano- wires are also referred to as quantum wires.

5. **Distinguish between bulk particles and nano-particles.**

Nano-particles	**Bulk particles**
Size is less than 100 nm.	Size is larger in micron size.
Collection of few molecules.	Collection of thousands of molecules.
Surface area is more.	Surface area is less.
Strength, hardness are more.	Strength, hardness are less.

6. **What is CVD?**

CVD is Chemical Vapour Deposition. It is a process of chemically reacting a volatile compound of a material with other gases, to produce a non-volatile solid that deposits automatically on a suitably placed substrate.

7. **Mention some important application of nano-wires.**
   - Nanowires are used for enhancing mechanical properties of Composites
   - It is also used to prepare active electronic compounds such as p-n junction and logic gates.

8. **What are nanoclusters?**

Nanoclusters are fine aggregates of atoms or molecules. The size of which ranges from 0.1 to 10nm. Ot nano materials, nanoclusres are the smallest sized nano materials because of their close packing arrangement of atoms.

9. List any four nano-materials. (Jan 2010)

- Carbon nanotubes.
- Nanowire.
- Nanorod.
- Nanoclusters.

10. What are nanoclusters? (Dec 2012)

Nanoclusters are fine aggregates of atoms. The size ranges from 0.1 to 10nm. These are smallest sized nano material because of close packing arrangement of atoms.

11. What is Magic number?

It is the number of atoms in the clusters of critical sizes with higher stability.

NANOCHEMISTRY.

Part - B

1. Distinguish molecules, nanoparticles and bulk materials

No	Molecules	Nanoparticles	Bulk materials
1	It consists of mostly two atoms.	It consists of one or two or three dimensional arrangements of few atoms.	It consists of three dimensional arrangement of a large number of atoms.
2	Their properties are size independent.	Size dependent.	Size independent.
3	Their sizes are smaller than nanoparticles and bulk materials	Their sizes are intermediate between molecules and bulk materials.	Their sizes are larger than molecules and nanoparticles.
4.	Their sizes are expressed in Angstrom (A) unit.	Expressed in nanometer (nm) unit.	Expressed millimeter unit.
5.	Their electronics structure in confined.	Confined.	Continuous.
6.	They have well defined structure.	They have well defined structure.	The nature of bulk material decides the geometrical structure.
7	NaCl, HCl	$(NaCl)_n$	Gold bar & Silver bar

2. Explain nano materials with their examples, properties and applications.

Nano particles are the particles the size of which ranges from 1 to 100 nm. These are tiny aggregates of atoms. Example – TiO_2, Gold, Silver, ZnO Etc.,

Applications

- TiO2 is used in cosmetics as they are very good UV absorber
- Nano silver particles are used as a catalyst in industries and used in making bone cement, surgical instruments etc.,
- Nano particles are used as medicine

1. Nanoclusters or nanosperes

- Nanoclusters are the smallest sized nanomaterials because of its close arrangement of atoms.
- It is an example of zero dimensional nanomaterials.
- Their size ranges from 1 nm to 10 nm.
- They are the intermediate state of matter between molecules and bulk materials.
- They are the fine aggregates of atoms or molecules.
- They are bound by forces like-metallic, ionic, covalent, hydrogen bond, and weak van der Wall's forces.

Magic number

It is the number of atoms in the clusters of critical size with higher stability.

Production of Nanoclusters

Nanoclusters can be produced using both bottom-up and top-down methods.

Examples: ZnO; SiO_2; CdS.

Properties

- They have properties and structures which are very sensitive to their composition and size.
- They have more confined electronic structures.
- Their melting point is lower than the bulk material.

Applications

- They are of technological interest in numerous areas of applied science.
- They are used as catalyst in various organic synthesis.

2. Nanowires

- They are also called quantum wires.
- It is the material having an aspect ratio (i.e., length to width ratio) greater than 20.
- They can be used to link tiny components into extremely small circuits.

Types and examples of nanowires

- Metallic nanowires - Ni; Pt; Au

- Molecular nanowires - DNA
- Insulator nanowires - TiO_2; SiO_2
- Semiconducting nanowires - Si; InP; GaN

Production

Nanowires are produces by

- Template assisted synthesis

  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.

- VLS (Vapour - Liquid – Solid) process.

  It involves the adsorption of the source material from the gas phase into a liquid phase of catalyst

Properties

- They are two dimensional materials.
- They show strong photoluminescence property
- Their conductivity is less than the bulk materials
- They exhibit distinct thermal, optical and chemical properties.

Applications

- Semiconducting silicon nanowires are used for sensing proteins and chemicals.
- They can be used to build the next generation computing devices.
- They are used to enhance mechanical properties of composites.
- They are used to prepare active electronic components like p-n junction and logic gates.
- Silicon nanowires are used to fabricate (Field Effect Transistor) FET – based chemo/biosensors.

3. Nanorods

- They are two dimensional cylindrical solid materials.
- It is the material having an aspect ratio (i.e., length to width ratio) less than 20.
- They can be used to link tiny components into extremely small circuits.

Examples of nanorods

Zinc oxide, Cadmium sulphide, Gallium nitride etc.,

Production

- Nanorods are produces by direct chemical synthesis as same as nanowires.

Properties

- They are two dimensional materials.
- They exhibit distinct optical and electrical properties.

Applications

- Nanorods find application in display technologies.
- They can be used in micro mechanical switches.
- They are used to in an applied electric field, micro electric mechanical system etc.,
- Nanorods with noble gases act as theragnostic agents.
- It is used in light emitting devices and they act as cancer therapeutics.

3. Write short notes on carbon nanotubes.

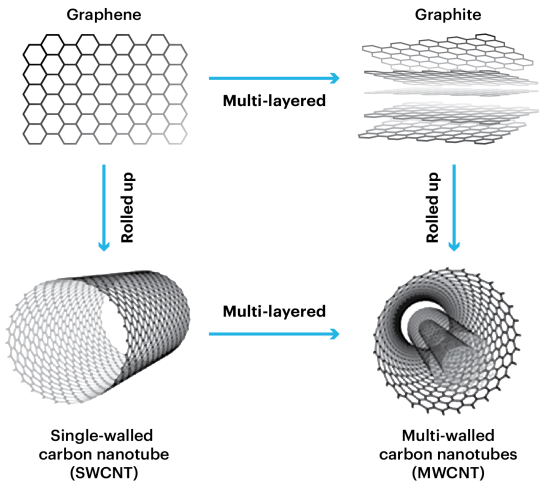
(OR) Explain the properties and advantages of carbon nanotubes.

Carbon in the solid phase exists in different allotropic forms like graphite, diamond, fullerence and nanotubes.

Carbon nanotubes are configurationally equivalent to a two dimensional tube/ cylinder. It is a tubular form of carbon with 1-3 nm diameter and a length of few nm to microns. When graphite sheets are rolled into a cylinder, their edges join to each other form carbon nanotubes. Each carbon atom in the carbon nanotube is linked by the **covalent bond**. But number of nanotubes align into ropes and are held together by weak vander waals forces.

Structures or types of CNTs

There are two types of CNTs: Single and multi-walled carbon nanotubes



1. Single-walled carbon nanotubes (SWCNT)
   - It consists of one tube of graphite
   - Having a diameter of 2nm and a length of 100μm.
   - They are very important because they exhibit important electrical properties.

- It is an excellent conductor.

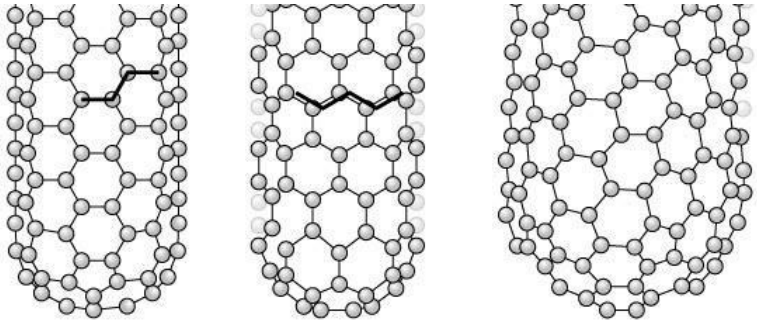
Types of SWCNTs

Based on the orientation of the hexagon lattice, these are classified three types of SWCNTs.

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

b) Zig-Zag structure: lines of hexagons are down the centre of the nanotube.

c) Chiral nanotubes: lines of hexagons are inclined to the axis of the nanotube.



2. Multi-walled carbon nanotubes (MWCNT)

- It consists of multi layers of graphite rolled in on themselves to form a tube shape.
- It exhibits both metallic and semiconducting properties.
- It is used for fuels such as hydrogen and methane.

Preparation of CNTs

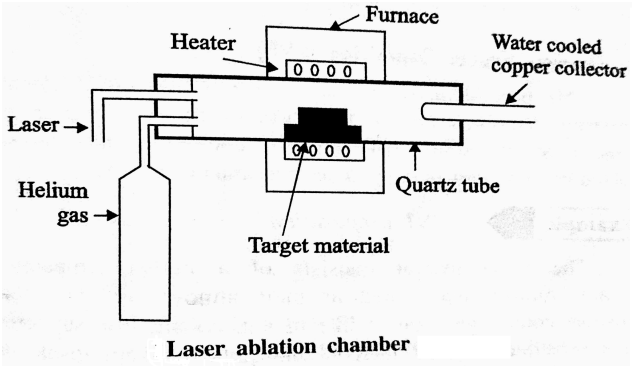
Synthesized by following methods

1. Pyrolysis of hydrocarbon

CNT are prepared by pyrolysis of hydrocarbons such as acetylene at about 700 C in the presence of catalyst (Fe-Silica or Fe-graphite) under inert conditions

2. Laser evaporation

This method involves vapourisation of target material containing small amount of catalyst (nickel or cobalt) by passing an intense pulsed laser beam at a higher temperature to about 120ºC in a quartz tube reactor, Simultaneously, an inert gas such as argon, helium is allowed to pass into the reactor to sweep the evaporated particles from the furnace to the colder collector.



Laser ablation chamber

Properties of CNTs

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

Uses of CNTs:

- ❖ Used in battery technology and in industries as catalyst.
- ❖ Used as light weight shielding materials for protecting electronic equipments.
- ❖ Used effectively for drug delivery.
- ❖ Used in composites, ICs.
- ❖ It act as very good biosensor.
- ❖ It is also used in water in water softening process as a filter.

5. Discuss various types of synthesis involved in the preparation of nanomaterials.

There are two approaches used for the synthesis of nanomaterials

i) **Top-down process**

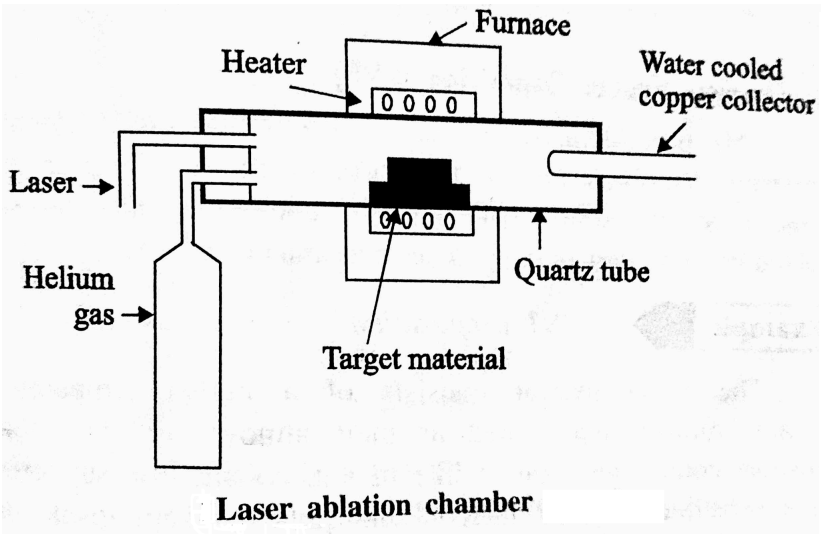
The conversion of bulk materials into nanoscale particals is called ***Top-down process.***

It can be done by Laser ablation (LA), Chemical vapour deposition (CVD) and Electro deposition method

1. **Laser ablation:**

In laser ablation technique, high power laser pulse is used to evaporate the material from the target. The stoichiometry of the material is protected in the interaction.

The total mass ablated from the target per laser pulse is referred as the *ablation rate.*



Laser ablation chamber

This method involves vapourisation of target material containing small amount of catalyst (nickel or cobalt) by passing an intense pulsed laser beam at a higher temperature to about 120ºC in a quartz tube reactor, Simultaneously, an inert gas such as argon, helium is allowed to pass into the reactor to sweep the evaporated particles from the furnace to the colder collector.

Uses

1. Nanotubes having a diameter of 10 to 20nm and 100μm can be produced by this method.
2. Ceramic particles and coating can be produced.
3. Other materials like silicon, carbon can also be converted into nanoparticles by this method.

Advantages of laser ablation

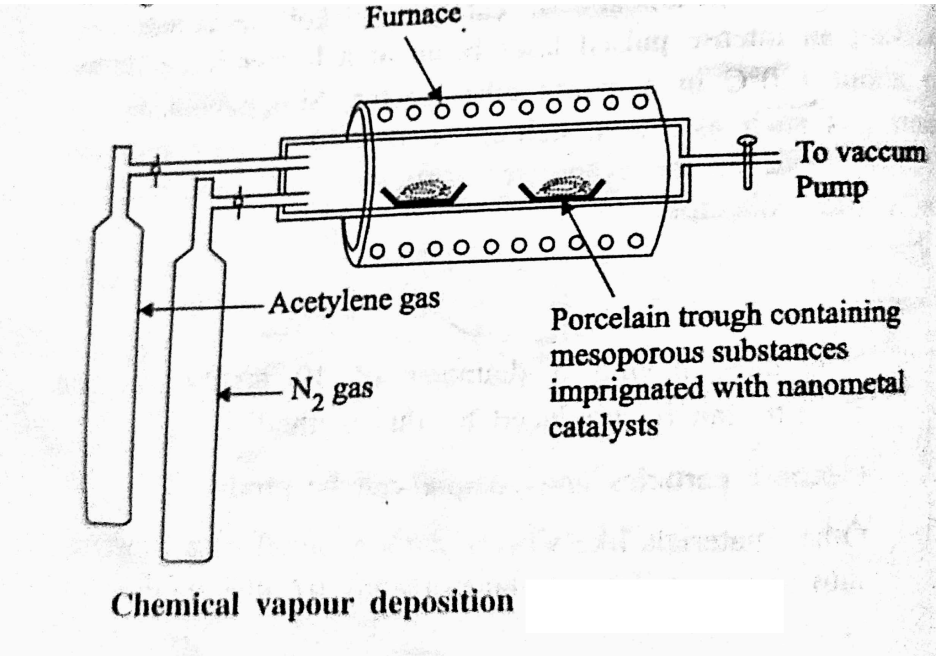
1. It is very easy to operate.
2. The amount of heat required is less.
3. It is eco-friendly method because no solvent is used.
4. The product, obtained by this method, is stable.
5. This process is economical.

2. **Chemical vapour deposition :**

This process involves conversion of gaseous molecules into solid nanomaterials in the form of tubes, wires or thin films. First the solid materials are converted into gaseous molecules and then deposited as nanomaterials.

Example: CNT preparation

The CVD reactor consists of higher temperature vacuum furnace maintained at inert atmosphere. The solid substrate containing catalyst like nickel, cobalt, iron supported on a substrate material like, silica, quarts is kept inside the furnace. The hydrocarbons such as ethylene, acetylene and nitrogen cylinders are connected to the furnace. Carbon atoms, produced by the decomposition at 1000 ºC, condense on the cooler surface of the catalyst.



As this process is continuous, CNT is produced continuously.

Types of CVD Reactor

Generally the CVD reactors are of two types

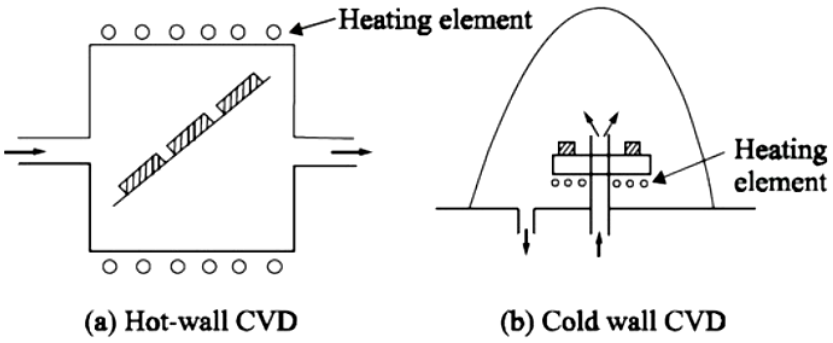


Fig . CVD Reactors

1. Hot-wall CVD

Hot wall CVD reactors are usually tubular in form. Heating is done by surrounding the reactor with resistance elements.

2. **Cold-Wall CVD**

In Cold-wall CVD reactors, substance are directly heated inductively while chamber walls are air (or) water cooled.

Advantages of CVD

1. Nanomaterials, produced by this method, is highly pure.
2. It is economical.

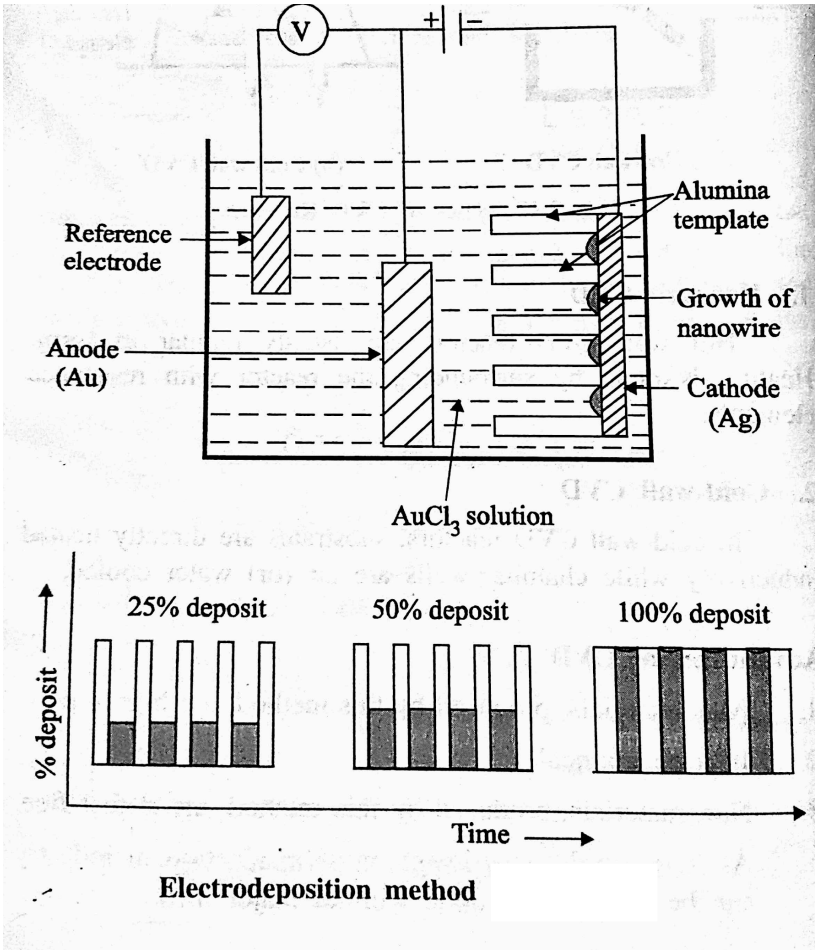
3. Nanomaterials, produced by this method, are defect free.
4. As it is simple experiment, mass production in industry can be done without major difficulties.

3. **Electrodeposition method:**

Electro-deposition is electrochemical method in which ions form the solution are deposited at the surface of cathode. Template assisted electro-deposition 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 electrolytic solution of a soluble metal as shown in figure. When the current is passed through the electrodes of template, the metal ions 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.



Electrodeposition method

Example:

Nanostructured gold can be prepared by the Electrodeposition technique using gold sheets as an anode and silver plate as a cathode. An array of alumina template is kept over the cathode as shown in the figure and $AuCl_3$ is used as an electrolyte.

When the current of required strength is applied through the electrodes, the 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

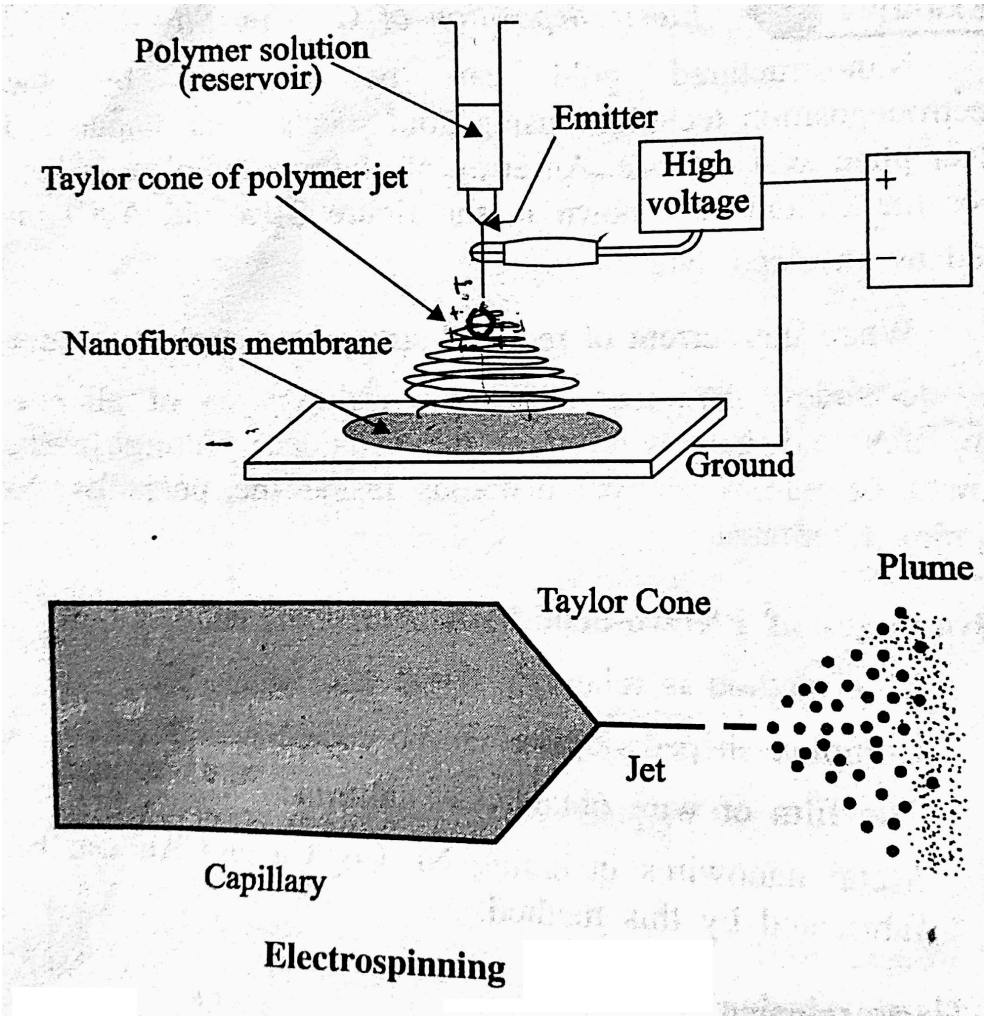
1. This method is relatively cheap and fast.
2. Complex shaped objects can be coated.
3. The film or wire obtained is uniform.
4. Metal nanowires including Ni, Co, Cu and Au can be fabricated by this method.

4. Electro spinning

It is the method of producing nano fibers by charging.

Components

1. A high voltage power supply
2. A polymer reservoir that can maintain constant flow rate of solution
3. A conductive needle connected to the high voltage power supply
4. A conductive collector



Process

- ❖ Polymer is dissolved in suitable solvent and is filled with the capillary reservoir.
- ❖ High voltage is applied to create an electric between needle tip and the collector.
- ❖ Electrostatic repulsion is higher than surface tension the liquid meniscus is deformed into conically structure known as a Taylor cone.
- ❖ Once the cone is formed, the charged liquid jet is ejected towards the collector.
- ❖ Solid fibers will be formed as the solvent evaporates.

Applications

1. It is used in diagnosis and treatment of diabetes
2. Used in energy storage devices such as solar cell, fuel cell super capacitors
3. Used in textile for smart clothing, protecting clothing and fire retardant fiber
4. Used as sensors (gas, chemical and fluorescence)
5. Used in drug delivery, artificial blood vessel and wound dressing.

ii)Bottom-up process

This process involves building-up of materials from the bottom by atom by atoms, molecules by molecules or cluster to the nanomaterials.

It can be done by

a) **Solvothermolysis**

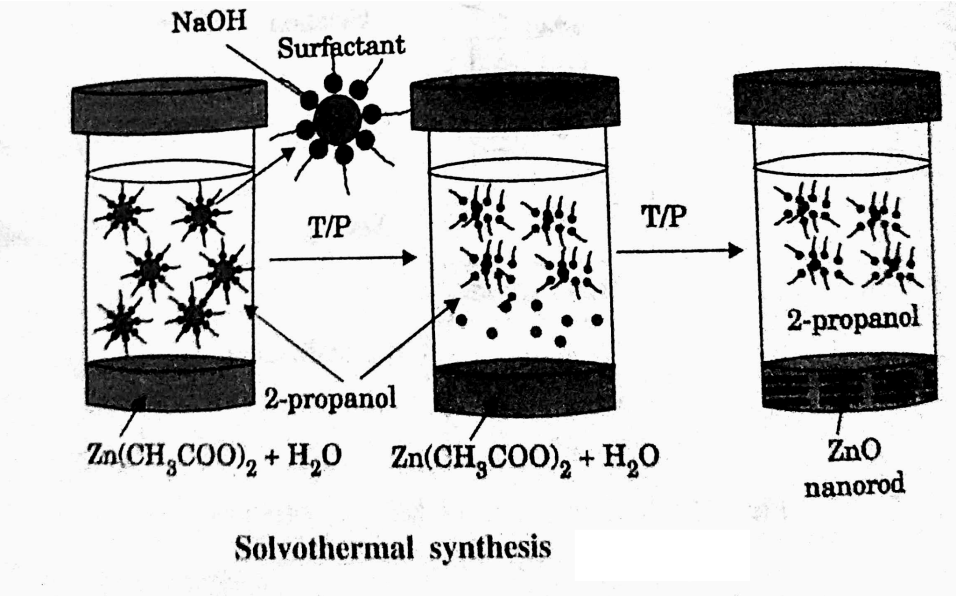
This process involves the use of a solvent under moderate to high pressure (1 to 10^4 atm) and temperature (100 ºC to 1000 ºC).

Method

A solvent like ethanol, methanol, 2-propanol is mixed with certain metal precursors and the solution mixer is placed in an autoclave kept at relatively high temperature and pressure in an oven to carry out the crystal growth.

The pressure generated in the vessel due to the solvent vapour elevates the boiling point of the solvent.

It is the method used to prepare variety of nano-materials such as metals, ceramics, polymers, semi-conductors, metal oxides.



Solvothermal synthesis

Example: Solvothermal synthesis of Zinc oxide

ZnO nanorod is prepared by dissolving Zinc acetate dihydrate in 2-proponol at 50 ºC. It is then cooled to 0 ºC. Sodium hydroxide is added to precipitate ZnO. The solution is then heated to 65 ºC to allow ZnO growth, 1-dodecanethiol is used as decapping agent.

b) Sol-Gel Process

It is wet chemical technique also known as chemical solution deposition. This method is used for the fabrication of metal oxide. It involves conversion of monomers into acolloidal solution (Sol) that acts as precursors. This colloidal solution gradually evolves towards the formation of a gel like system.

It involves the following steps,

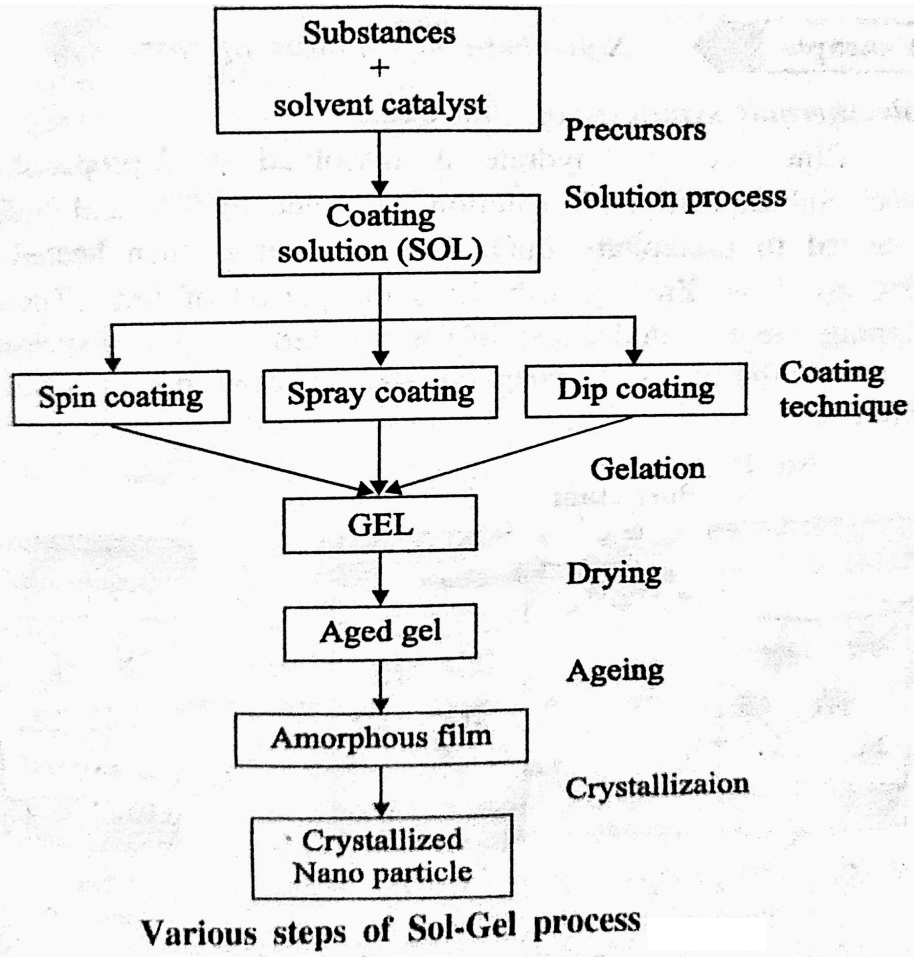
1. Hydrolysis and polycondensation
1. Gelation
2. Aging
3. Drying
4. Densification
5. Crystallization

The volume fraction of particles reduced by two methods

1. Sedimentation: Allowed to keep for some time, for sedimentation to occur and then pour off remaining liquid.
2. Centrifugation: It can also be used to accelerate the process of phase separation.

Drying and densification: Removal of the remaining liquid is done by drying process which accompanied by shrinkage and densification.

Firing or Crystallization: it is necessary to enhance mechanical properties and structural stability.



Various steps of Sol-Gel process

6. Explain the application of nanomaterials.

i. **Medicine**

- Nano drugs
- Laboratories on a chip
- Nano-medibots
- Gold-coated nanoshells
- Gold nanoparticles as sensors
- Protein analysis
- Gold nanoshells for blood immune assay
- Gold nano shells in imaging
- Targeted drug delivery using gold nanoparticles
- Reparing work

ii. **Agriculture**

- Nano formulation could increase agriculture potential
- It minimize the amount of harmful chemicals
- Nanosensors are used in crop protection
- Nanodevices are used for the genetic engineering
- Used in plant disease diagnostics
- Used as antimicrobial agents

iii. **Energy**

- Power generation
- Generating hydrogen from sea water
- Producing high efficiency light bulbs
- Increasing electricity generated by wind mills
- Generating electricity from waste heat
- Nano battery and fuel cell.

iv. **Electronics**

- Quantum wires are found to have high electrical conductivity
- Nanowire used to build transistors without p-n junctions
- Nano radios are the other important devices, using CNT
- NOMFET is created by combining gold nanoparticles with organic molecules
- MOSFET performs both as switches and as amplifiers

v. **Catalysis**

- Water purification
- Bio diesel production
- Fuel cell application
- In drug delivery
- Gold nanoparticles