UNIT-2

NANOCHEMISTRY

1. **With a neat sketch explain sol-gel synthesis of Nanomaterials**.

Definitation:

The sol-gel process is the conversion of colloidal solution (sol) to “gel” like structure.

Principles of Sol-gel process

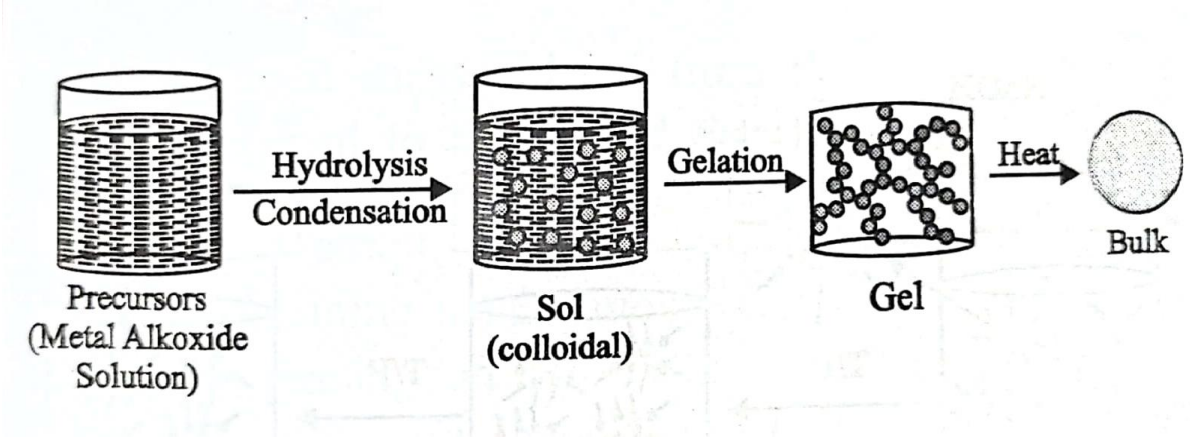
It is a method of producing solid materials from small molecules. In this method, the precursor is dissolved in water (or) alcohol to form "sol" and then converted to gel like structure by heating.

Sol-gel process is a wet chemical technique. Generally, it is used to produce metal oxides.

Preparation:

Preparation of metal oxide sol-gel

Preparation of sol-gel involves the following steps.



Step 1: Preparation of monomers (precursor)

Metal alkoxide is dissolved in alcohol and then diluted with water. Metal alkoxide gets hydrolysed to form reactive monomers

$$\underset{\text{(metal alkoxide)}}{\text{M-OR}} + \underset{\text{(catalyst)}}{H_2O} \longrightarrow \underset{\text{(monomer)}}{\text{M-OH + ROH}}$$

Step II: Formation of "Sol"

Condensation of these monomers to form colloid like solution (sol).

$$\text{M-OH} + \text{ROM} \longrightarrow \text{M-O-M + ROH}$$

$$\text{M-OH} + \text{HO-M} \longrightarrow \text{M-O-M} + H_2O$$

Step III: Formation of "Gel"

"Sol" gets converted to "gel" via polycondensation.

Step IV: Aging process

It is the process, where condensation occurs with the gel network that can cause expulsion of solvent.

Step V: Drying

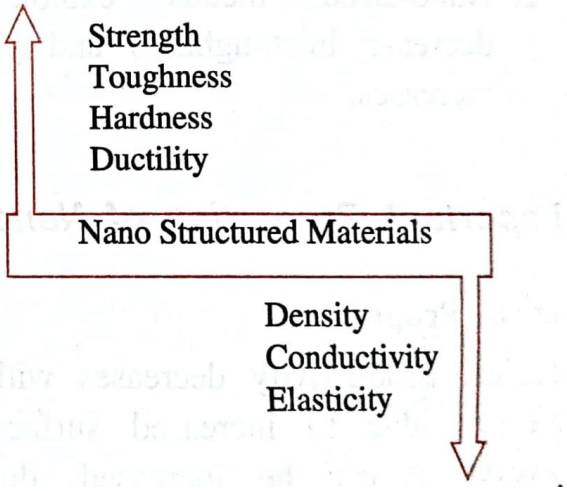
It removes liquid phases and M-OH groups

Step VI: Tempering

It is the process of densification of the gel to remove the pores of the gel network.

2. Discuss the size dependent properties of Nanomaterials

Nearly all the properties as shown in figure like hardness, strength, ductility, melting point and density, change for nanomaterials. These behaviors vary so significantly by a mere reduction in grain size.



Nanomaterials are composed of grains and grain boundaries. Nanometre sized grains contains only a few thousands of atoms with in each grain.

A large number of atoms reside at the grain boundaries. As the grain size decreases, there is a significant increase in the volume fraction of grain boundaries (or) interfaces.

The properties of the materials are bound to be governed to a large extent by defect configurations. Hence the mechanical and chemical properties of nanomaterials are significantly altered due to defect dynamics. The elastic property of nanomaterials are different from that of bulk alloys due to the presence of increased fraction of defects.

Examples:

1. Nanocrystalline ceramics are tougher and stronger than those with coarse grains.
2. Nano-sized metals exhibit significant decrease in toughness and yield strength increases.

3. **Discuss the applications of Nanomaterials in energy, medicine, sensor and catalysis.**

Nano-technology finds significant impact on all most all the industries and all areas of society. Since nano-materials possess unique beneficial chemical, physical and mechanical properties, they can be used for a wide variety of applications.

(i) In Energy

Nanomaterials are used in several applications to improve the efficiency of energy generation (or) develop new methods to generate energy.

- **Power generation**

Sun light, concentrated on nanoparticles, can produce steam with high energy efficiency, which can even be used in running power plants.

- **Generating hydrogen sea water**

The use of a nanostructured thin film of nickel selenide as a catalyst for the electrolysis of hydrogen from sea water.

- **Producing high efficiency light bulbs**

Nano-engineered polymer matrix is used for the production of high efficiency light bulbs.

- **Increasing the electricity generated by wind mills**

Stronger and lower weight blades, made from nanotubes-filled epoxy, in wind mills increases the amount electricity.

- **Generating electricity from waste heat**

Sheets of nanotubes have been used to build thermocells that generates electricity, when the sides of the are at different temperature

- **Storing hydrogen for fuel cell powered cars**

Graphene layers are used in fuel tank, resulting higher amount of hydrogen storage and therefore lighter weight fuel tank.

- **Reducing power loss in electric transmission wires**
  The wires containing carbon nanotubes lowers resistance than the wires currently used in the electric transmission grid.

- **Reducing the cost of solar cell**
  Nanotech solar cells are manufactured at significantly lower cost than the conventional solar cells.
- **Nano battery and fuel cell**
  Nanomaterials, used in batteries and fuel cell, increases their efficiency.

(ii) Medicine

- **Nano drugs**

Nano materials are used as nano drugs for the cancer and TB therapy,

- **Laboratories on a chip**

Nano technology is used in the production of laboratories on a chip.

- **Nano-medibots**

Nano particles function as nano-medibots that release anti-cancer drug and treat cancer.

- **Gold-coated nanoshells**

It converts light into heat, enabling the destruction of tumours. Gold nano particles as sensors Gold nano particles undergo colour change during the transition of nano particles.

- **Protein analysis**

Protein analysis can also be done using nanomaterials.

- **Gold nanoshells for blood immuno assay**

Gold nano shells are used for blood immuno assay.

- **Gold nano shells in imaging**

Optical properties of the gold nano shells are utilized for both imaging and therapy.

- **Targeted drug delivery using gold nano particles**

It involves slow and selective release of drugs to the targeted organs.

- **Repairing work**

Nano technology is used to partially repair neurological damage.

(iii) Electronics

- Quantum wires are found to have high electrical conductivity. 2. The integrated memory circuits have been found to be effective devices.

- A called NOMFET, (Nanoparticle Organic Memory Field Effect Transistor) is created by combining gold nanoparticles with organic molecules.
- Nano wires are used to build transistors without p-n junctions.
- Nano radios are the other important devices, using carbon nanotubes.
- MOSFET (Metal Oxide Semi-conductor Field Effect Transistor), performs both as switches and as amplifiers.

(iv) In Catalysis.

Nanoparticle catalysts are highly effective because of the following two reasons

  - huge surface area
  - enhanced reactivity

- **Water purification**

Nano silver catalyst is highly efficient in controlling microbes in water.

- **Bio-diesel production**

Solid base nano catalyst KF/CaO can be used for biodiesel production with yield more than 96%.

- **Fuel cell application.**

Carbon supported electro-catalysts play an important role in fuel cell.

- **In drug delivery Lives**

Carbon nanomaterials find more applications in biological fields.

CNTS may be suitable for bio-applications in bio recognition and drug delivery systems.

- **Gold nanoparticles**

It is an important catalyst in co-oxidation, epoxidation of propylene, hydrogenation of unsaturated hydrocarbons.

- Nanopowder silica catalyst (or) platinum nanoparticles exhibit very strong catalytic activity for hydrolysation reactions.
- Titania-based nanocatalysts are being increasingly used in photocatalysis.
- Nanocrystalline MgO particles act as an effective catalyst for dehydrogeneration.

In Agriculture

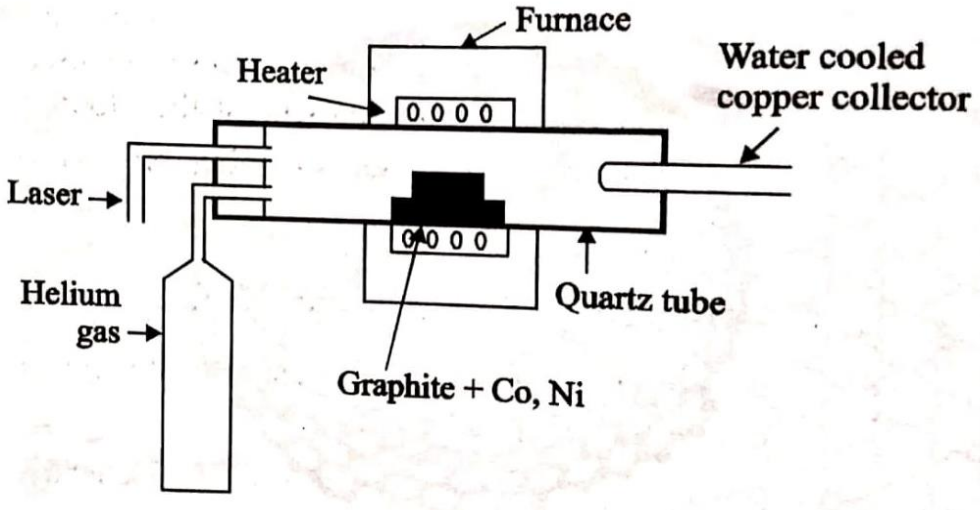
- Nanomaterials prepared by eco-friendly and green method with plant extracts (Nano formulations) could increase agriculture potential for improving fertilization process, plant growth regulators.
- They also minimize the amount of harmful chemicals that pollute the environment.
- Nano sensors are used in crop protection for the identification of diseases and residues of agrochemicals

- Nanodevices are used for the genetic engineering of plants.
- Nanomaterials are used in plant disease diagnostics. It is also used in postharvest management.
- Precision farming techniques might be used to further improve the crop yields but not damage soil and water.
- Some nanomaterials are used as antimicrobial agents infood packing especially silver nanoparticles are in great interest.
- Nano particle-based pesticides and herbicides are being explored for the application of antimicrobial agents to protect crops from various diseases.

4. Explain laser ablation process for producing nanomaterials with a neat diagram.

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 to as the ablation rate.

This method involves vaporization of target material containing small amount of catalyst (nickel or cobalt) by passing an intense pulsed laser beam at a higher temperature to about 120°C 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 20 nm and 100 nm 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.

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

5. Explain the synthesis, properties and uses of Carbon Nanotubes.

Synthesis of Carbon Nanotubes:

Carbon nanotubes can be synthesized by the following methods.

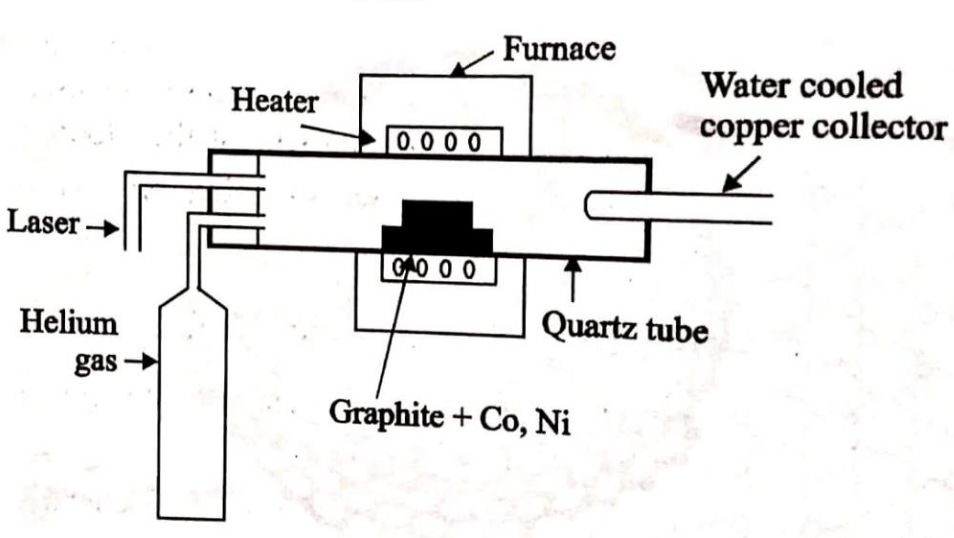
1. Pyrolysis of hydrocarbons.
2. Laser evaporation.

1. Pyrolysis

Carbon nanotubes are synthesized by the pyrolysis of hydrocarbons such as acetylene at about 700°C in the presence of Fe-silica or Fe-graphite catalyst under inert conditions.

2. Laser evaporation Technique

It involves vapourization of graphite target, containing small amount of cobalt and nickel, by exposing it to an intense pulsed laser beam at higher temperature (1200°C) in a quartz tube reactor. An inert gas such as argon (or) helium is simultaneously allowed to pass into the reactor to sweep the evaporated carbon atoms from the furnace to the colder copper collector, on which they condense as carbon nanotubes.



Properties of CNTs

1. CNTs are very strong, withstand extreme strain in tension and posses elastic flexibility.

2. The atoms in a nano-tube are continuously vibrating back and forth.

3. It is highly conducting and behaves like metallic or semiconducting materials.

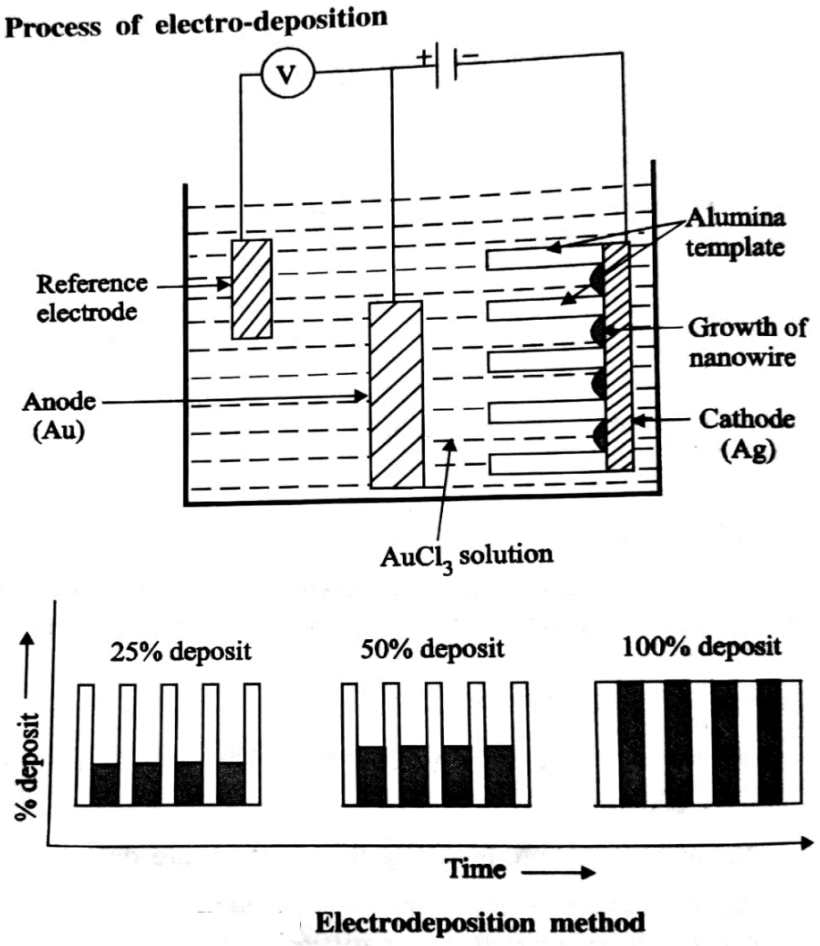
4. It has very high thermal conductivity and kinetic properties

Uses of CNTs:

- It is used in battery technology and in industries as catalyst.
- It is also used as light weight shielding materials for protecting electronic equipment.
- CNTs are used effectively inside the body for drug delivery.
- It is used in composites, ICs.
- It also acts as an efficient catalysts for some chemical reactions.
- It acts as a very good biosensor. Due to its chemical inertness carbon nanotubes are used to detect many molecules present in the blood.
- It is also used in water softening process as a filter.

6. Write a short note on Electrodeposition.

- Electro-deposition is an electrochemical method in which ions from 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.



The cell consists of a reference electrode, specially designed cathode and anode. All these electrodes are connected with the battery through an 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.

Example

Electrodeposition of Gold on Silver

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

When the current of required strength is applied through the electrodes, Au ions 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 is 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.