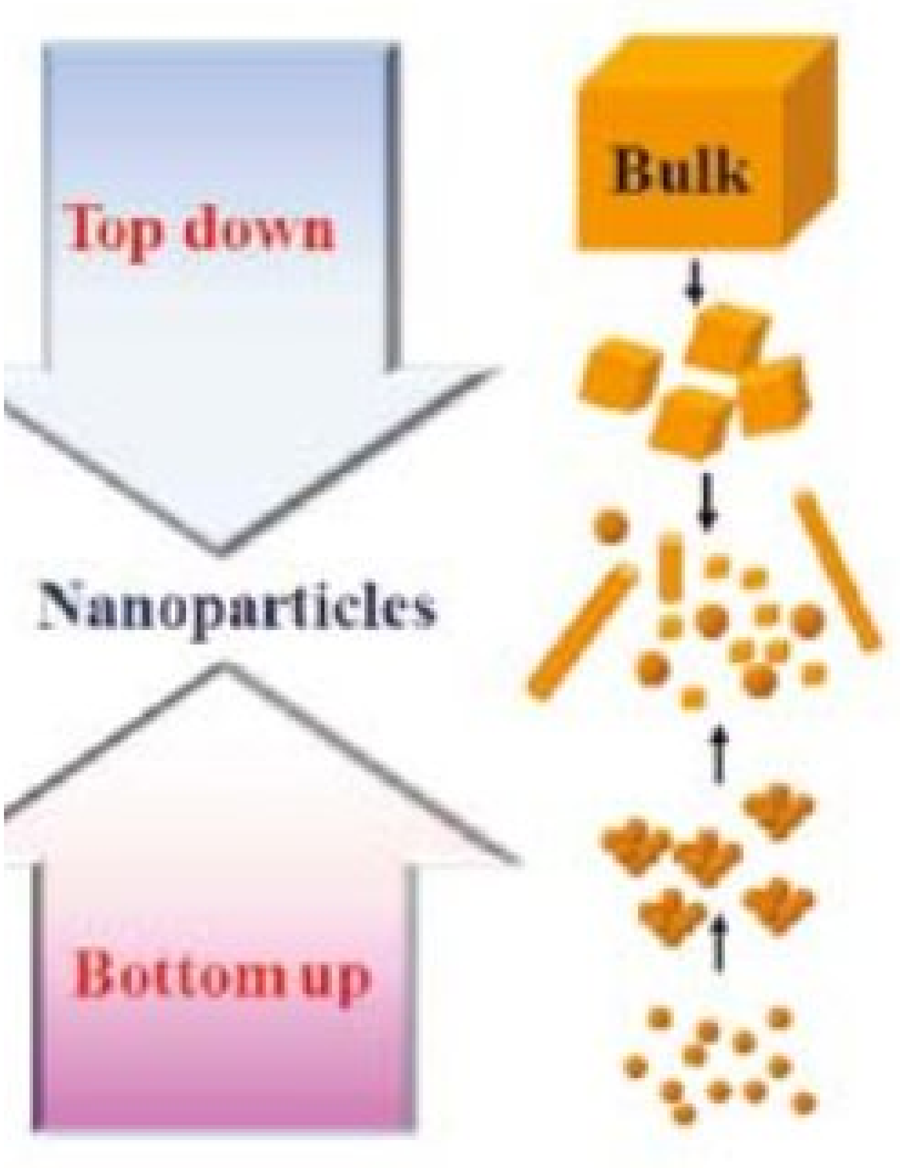
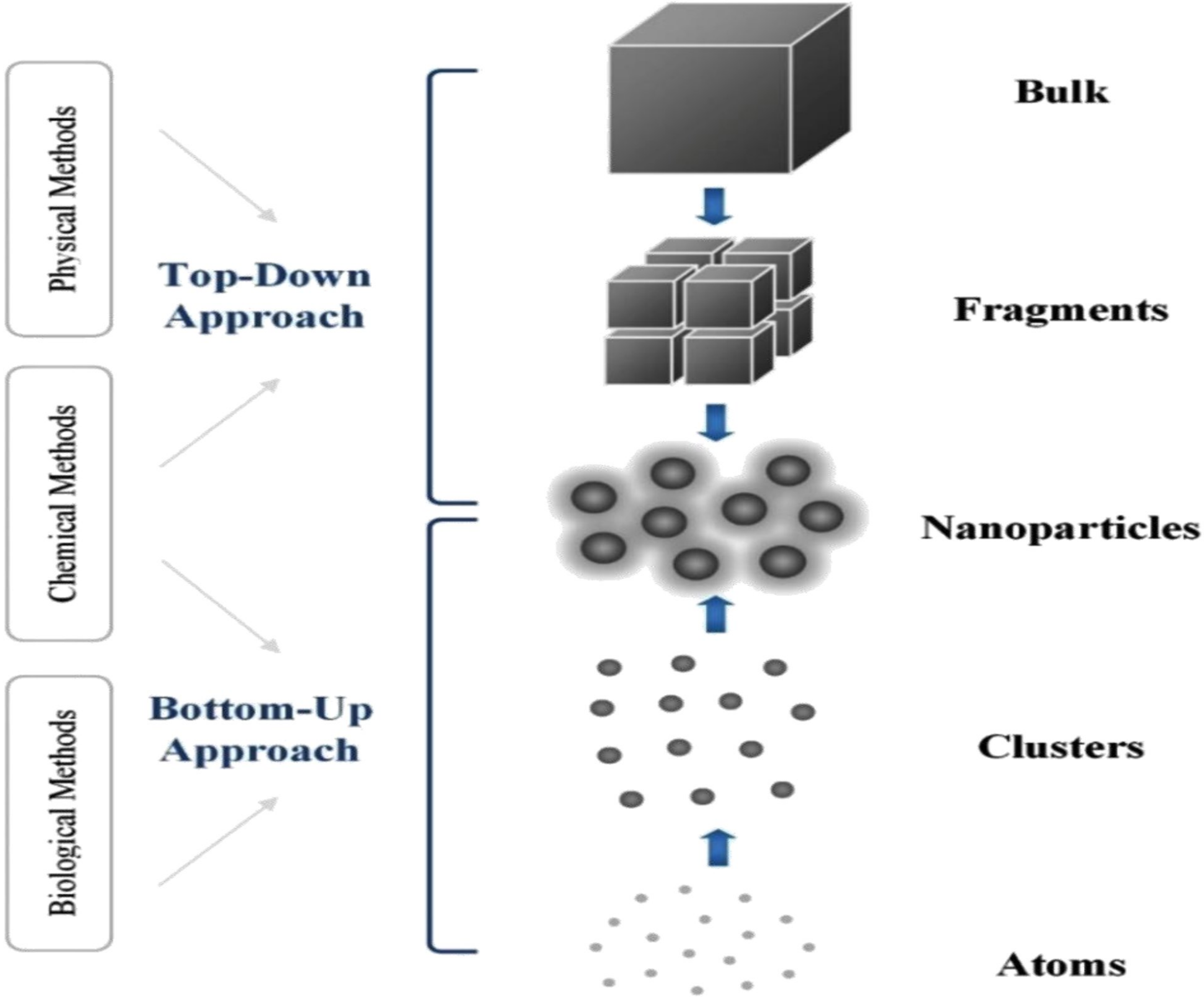
UNIT II
PREPARATION OF NANOMATERIALS

FABRICATION OF NANOMATERIALS

Top-down Approach :
Breaking down matter into more basic building blocks.

Bottoms-up Approach :
Building complex systems by combining simple atomic-level components.





Physical Methods
Chemical Methods
Biological Methods
Top-Down Approach
Bottom-Up Approach
Bulk
Fragments
Nanoparticles
Clusters
Atoms

DIFFERENCE BETWEEN TOP-DOWN AND BOTTOM-UP APPROACH

Aspect	Top-Down Approach	Bottom-Up Approach
Advantages	✓ Well-established and industry-compatible ✓ Scalable for mass production ✓ Enables patterning (e.g., lithography) ✓ Suitable for rigid substrates	✓ Atomic level precision in structure and composition ✓ Fewer defects and better crystallinity ✓ Economical use of raw materials ✓ Greater control over surface chemistry and morphology
Disadvantages	X High energy consumption X Introduces surface defects and dislocations X Limited precision at atomic scale X Material wastage	X Difficult to scale up uniformly X Integration with existing technologies can be challenging X Requires tight control over reaction conditions X Sometimes slower and less predictable
Surface Quality	Often rough and damaged due to mechanical or chemical processing	Smooth and defect-free due to atomically controlled growth

Aspect	Top-Down Approach	Bottom-Up Approach
Cost	Higher due to equipment and energy demands	Lower for chemical synthesis routes, but may require costly precursors
Examples of Techniques	Mechanical methods: ✓ Cutting, Etching, Grinding ✓ Ball milling ✓ Lithographic techniques: ✓ Photolithography ✓ Electron beam lithography	**Physical techniques:** ✓ Evaporation (thermal and electron beam), ✓ Sputtering, ✓ Plasma arching, ✓ Laser ablation **Chemical techniques:** ✓ Chemical vapour deposition, ✓ Electrolytic deposition, ✓ Sol-gel method, ✓ Pyrolysis ✓ Self-assembly, ✓ Hydrothermal synthesis
Application Domains	✓ Microelectronics, ✓ structured surfaces ✓	✓ Nanoparticles, ✓ Quantum dots, ✓ Catalysts, ✓ Nanowires, ✓ Nanocoatings

Top-down and Bottom up approach

synthesis of Nanomaterials : Two approaches

a) Top- down approach b) Bottom–up approach.

Top-down approach:

✓Top-down approach involves the breaking down of the bulk material into nanosized structures or particles.

✓Top-down synthesis techniques are extension of those that have been used for producing micron sized particles.

✓Top-down approaches are inherently simpler and depend either on removal or division of bulk material or on miniaturization of bulk fabrication processes to produce the desired structure with appropriate properties.

✓The biggest problem with the top-down approach is the imperfection of surface structure. Such imperfection would have a significant impact on physical properties and surface chemistry of nanostructures and nanomaterials.

✓It is well known that the conventional top-down technique can cause significant crystallographic damage to the processed patterns.

Top-down and Bottom up approach

Bottom-up approach:

✓ The alternative approach, which has the potential of creating less waste and hence the more economical, is the
'bottom- up'.

✓ Bottom-up approach refers to the build up of a material from the bottom: atom-by-atom, molecule-by-molecule, or
cluster-by cluster.

✓ This route is more often used for preparing most of the nano-scale materials with the ability to generate a uniform size, shape and distribution.

✓ It effectively covers chemical synthesis and precisely controlled the reaction to inhibit further particle growth.

Although the bottom-up approach is nothing new, it plays an important role in the fabrication and processing of nanostructures and nanomaterials.

Ball milling/Mechanical crushing/Pebble mill/ Tumbling mill

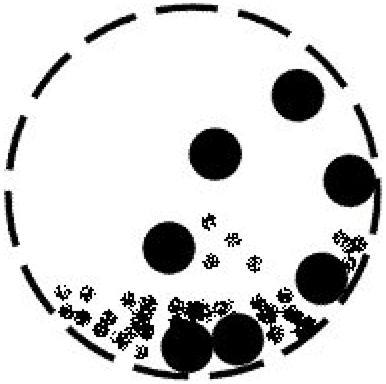


Fig. Ball milling

✓The ball milling method is a typical example of top-down method of fabrication of nano materials.

✓A **ball mill** is a type of grinder used to grind materials into extremely fine powder in order of nm.

✓In this method, small balls of the material are allowed to rotate around the inside of a drum and then fall on a solid with gravity force.

✓The balls are broken in to nano crystallites. This is also known as mechanical crushing.

✓This method is used to prepare a wide range of elemental powders. For example iron nano particles of sizes 13 to 30 nm can be formed.

✓This method is used for produce metal oxide nano crystals (cerium oxide CeO_2 and Zinc oxide ZnO_2).

Ball milling/Mechanical crushing

Major parameters for ball milling:

- ✓ **Temperature**
- ✓ **Size and number of the balls**
- ✓ **Nature of the balls**
- ✓ **Rotation speed**

Advantages:

- ✓ It produces very fine powder (particle size less than or equal to 10 microns).
- ✓ It is suitable for milling toxic materials since it can be used in a completely enclosed form.
- ✓ Has a wide application.
- ✓ Easy maintenance and operation & Low operating cost
- ✓ It can be used for continuous operation.
- ✓ It is used in milling highly abrasive materials.

Ball milling/Mechanical crushing

Disadvantages:

- ✓ Contamination of product may occur as a result of wear and tear which occurs principally from the balls and partially from the casing.
- ✓ High machine noise level especially if the hollow cylinder is made of metal, but much less if rubber is used.
- ✓ Relatively long milling time.
- ✓ It is difficult to clean the machine after use.

Applications:

- ✓ It is widely used in the manufacture industries, such as cement, feldspar, silicate ore, new building material, refractory material, fertilizer, ferrous metal, nonferrous metal and glass ceramics.

- ✓ The small and average capacity ball mills are used for the final grinding of drugs or for grinding suspensions.

- ✓ The maximum capacity ball mills are used for milling ores prior to manufacture of pharmaceutical chemicals.

Sol-gel process

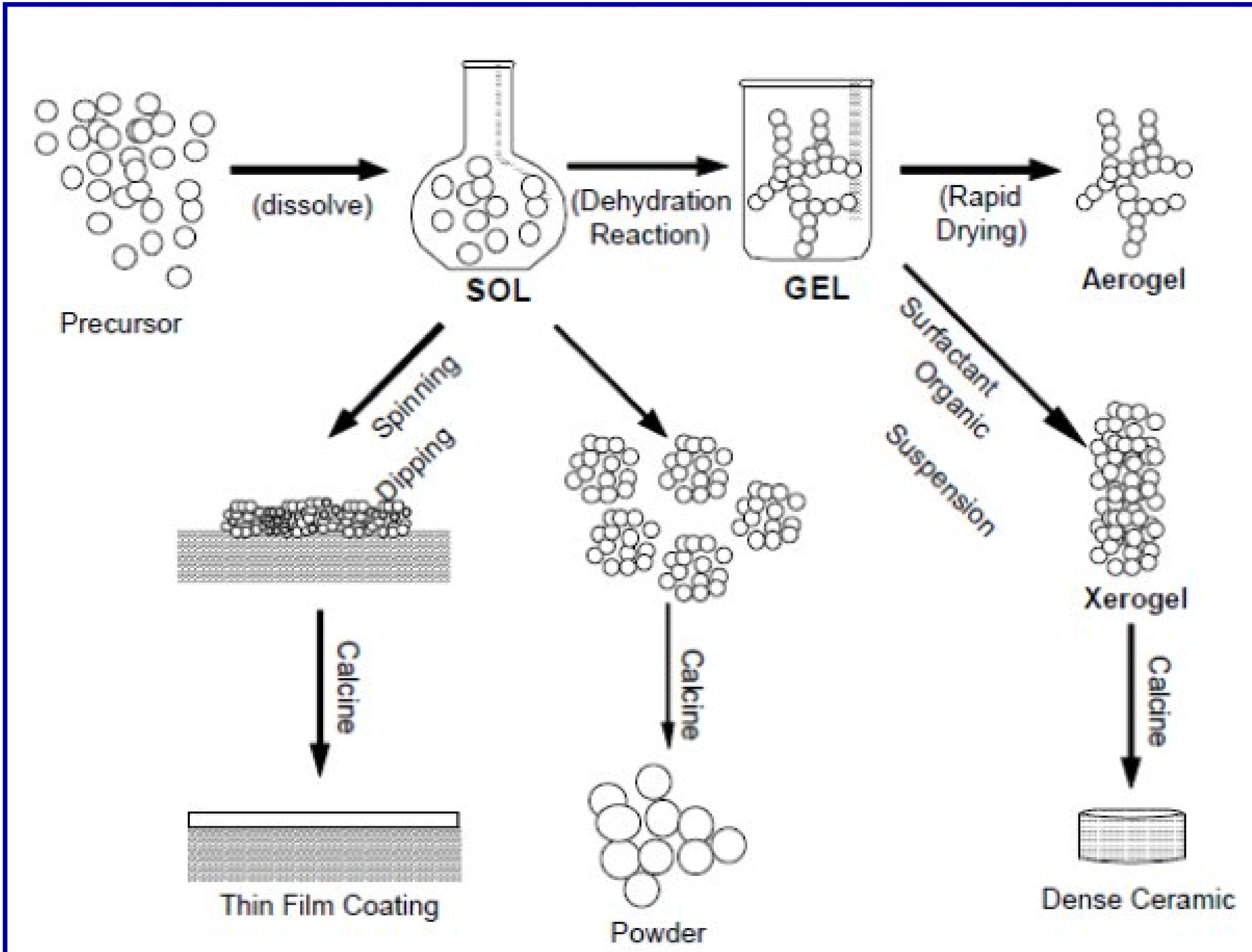
The sol-gel method is a wet-chemical technique used for the production of high purity and homogenous nanomaterials, particularly metal oxide nanoparticles.

The starting materials from a chemical solution leads to the formation of colloidal suspensions known as sol. Then, the sol evolves the formation of an inorganic network containing a liquid phase called the gel.

The removal of the liquid phase from the sol yields the gel.

The particle size and shape are controlled by the sol/gel transitions.

The thermal treatment (firing/calcination) of the gel leads to further polycondensation and enhances the mechanical properties of the products, i.e. oxide nanoparticles.


Precursor
(dissolve)
SOL
(Dehydration Reaction)
GEL
(Rapid Drying)
Aerogel
Spinning
Dipping
Surfactant
Organic
Suspension
Xerogel
Calcine
Calcine
Calcine
Thin Film Coating
Powder
Dense Ceramic

Xerogel : A gel that contains minimum possible amount of liquid

Aerogel: A gel formed by dispersion of air in a solidified matrix

Hydrolysis:
Decomposition of a chemical compound by reaction with water

Condensation: Change of physical state of any matter.
Dehydration process in which two or more things are brought by loss of water/HCL/Alcohol etc.

Surfactant:
A chemical reagent capable of reducing surface tension of a liquid.
It also stabilizes two mixtures.

The sol can be further processed to obtain the substrate in a film, either by dip coating or spin coating, or cast into a container with desired shape or powders by calcinations.

The chemical reaction which takes place in the sol-gel metal alkoxides $M(OR)_2$ during the hydrolysis process and condensation is given below

$$\text{M-O-R} + H_2O \longrightarrow \text{M-OH} + \text{R-OH} \quad \text{(Hydrolysis)}$$

$$\text{M-O-H} + \text{R-O-M} \longrightarrow \text{M-O-M} + \text{R-OH} \quad \text{(Condensation)}$$

Advantages and disadvantages of Sol-gel method

Advantages:

✓Versatile: better control of the structure

✓ Extended composition ranges: it allows the fabrication of any oxide composition

✓Better homogeneity: due to mixing at the molecular level; high purity high purity

✓Less energy consumption: Coatings and thin films, monoliths, composites, porous membranes, powders and fibers; É

✓No need for special or expensive equipment

Disadvantages:

✓Cost of precursors

✓Shrinkage of a wet gel upon drying, which often leads to fracture due to the generation of large capillary stresses.

✓ Preferential precipitation of a particular oxide during sol formation (in multicomponent glasses) due to the different reactivity of the alkoxide precursors

Applications dvantages and disadvantages of Sol-gel method

Applications:

- ✓Protective and decorative coatings
- ✓Thin films and fibers
- ✓Bio sensors
- ✓Ceramic membranes for microfiltration, ultrafiltration, reverse osmosis
- ✓Large area hot mirrors, Cold mirrors, beam splitters
- ✓Sustained delivery of drugs

Chemical Vapour Deposition (CVD)

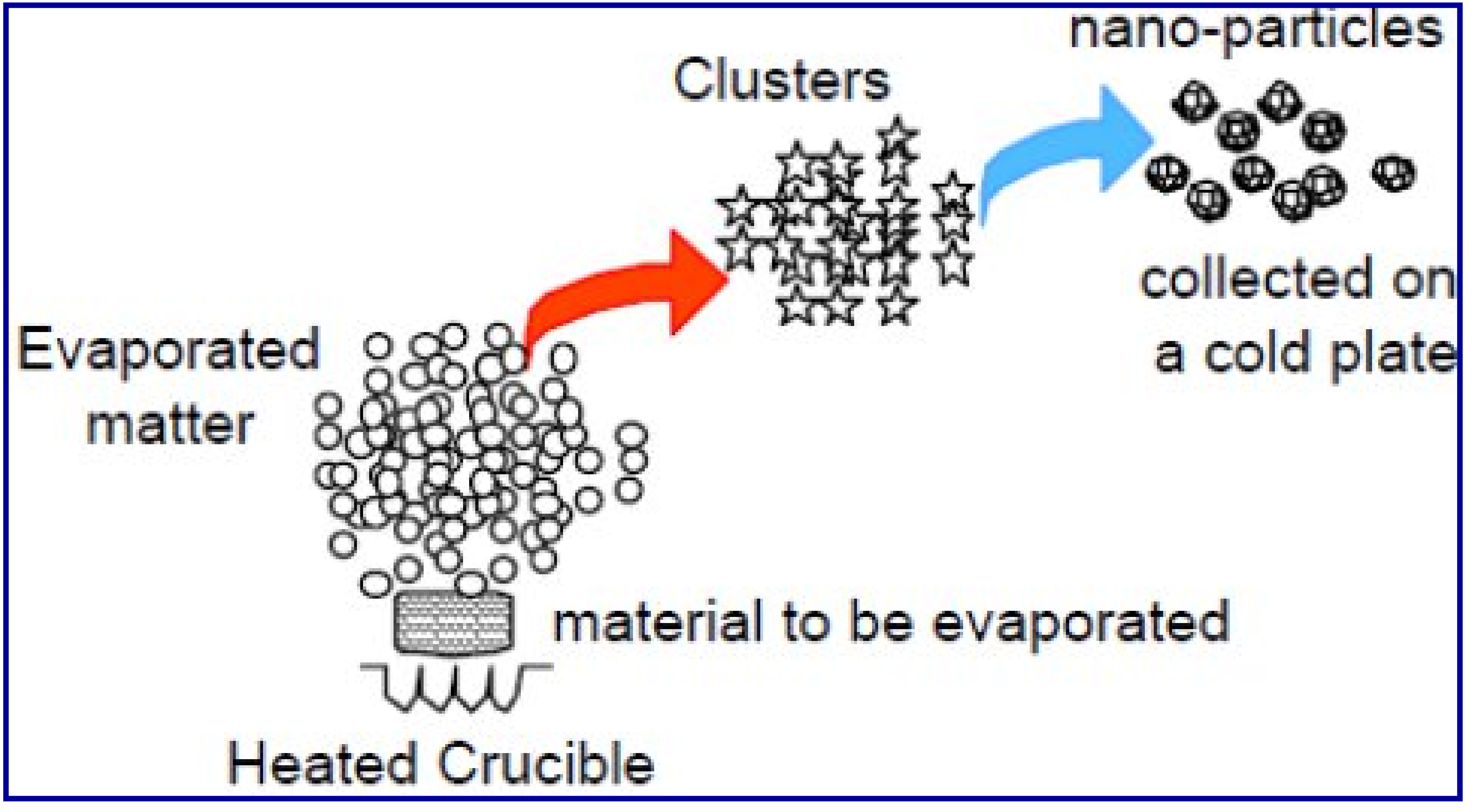
In chemical vapour deposition (CVD), the atoms or molecules which are in the gaseous state are either allowed to react homogenously or heterogeneously depending on the applications.

In the case of homogenous CVD, the particles or atoms/molecules in the gas phase are diffused towards the cold surface due to the thermosphere forces.

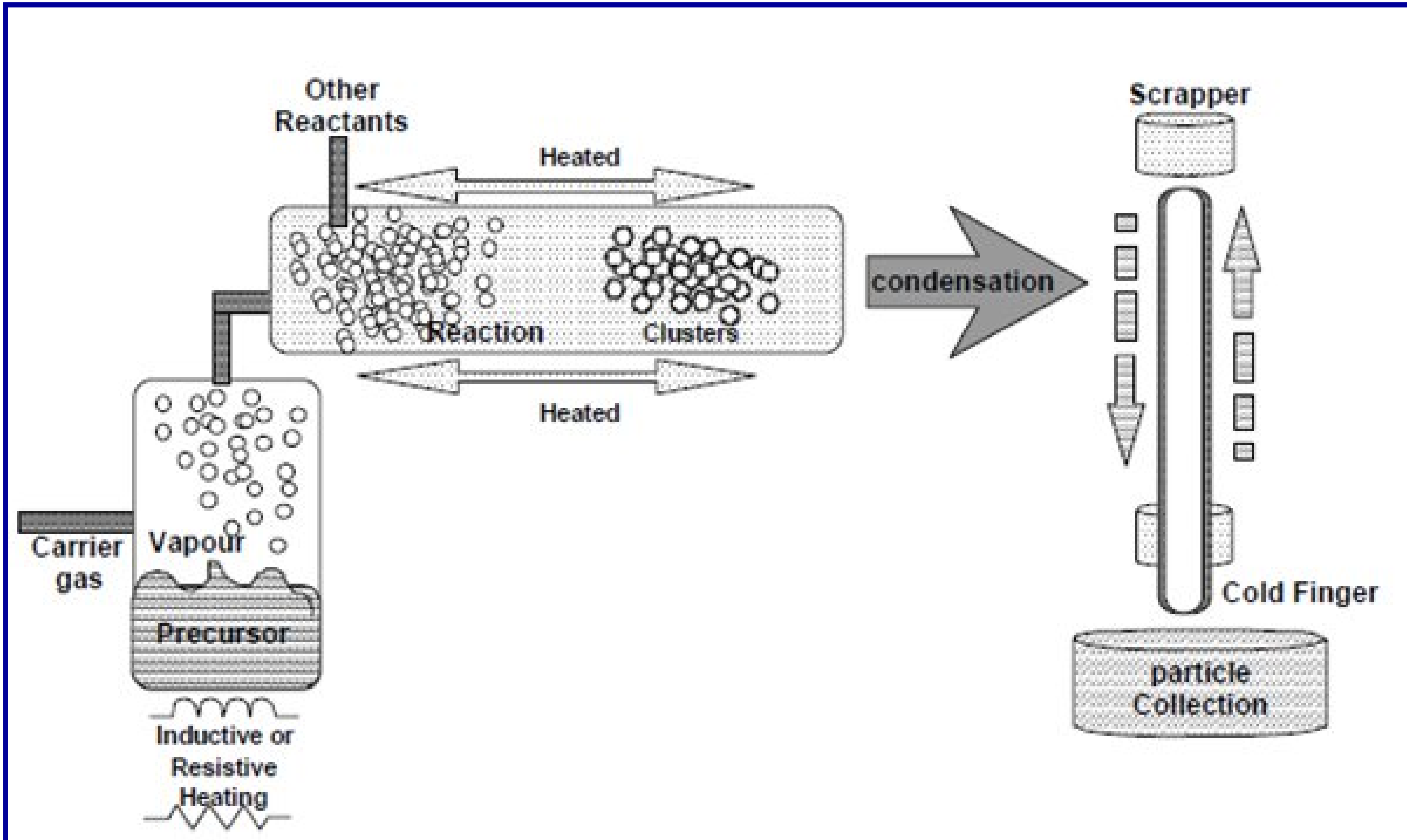
In case of heterogeneous CVD, a dense film of nanoparticles is obtained on the substrate surface.

The diffused particles can be scrapped from the cold surface to give nanopowder (or) deposited onto a substrate to form a film known as *Particulate film*.

Chemical Vapour Deposition Method



Chemical Vapour Deposition Method



1. The metal-organic precursor is introduced into the hot zone of the reactor employing flow controller.

(CVD)

2. The precursor is vaporized employing the inductive or resistive heating method.
3. An inert gas like Ar or Ne is used as carrier gas.
4. The evaporated matter consists of hot atoms which undergoes collision with the atoms in the cold gas and hence, loses its energy.
5. Thus, the colloidal atoms undergo condensation into small clusters through a homogenous nucleation.
6. The clusters continue to grow in a supersaturated region.
7. Other reactants are added to the clusters to control the chemical reactions.
8. The cluster size is controlled by controlling the parameters, namely, rate of evaporation (energy input), and rate of concentration (energy removal) and rate of gas flow (cluster removal).
9. The condensed clusters are allowed to pass through the cold finger. The nanoparticles are collected using a scrapper

Chemical Vapour Deposition (CVD)

Advantages: CVD is an excellent method which is used to control the particle size, shape, crystallinity and chemical compositions.

- **One can use this method to obtain high purity nanomaterials and multicomponent systems as well as controlling the chemical reactions. In addition to the formation of single-phase nanoparticles, two-phase (or) doped nanoparticles can also be synthesized using the CVD method. This can be achieved by supplying two precursors at the first end of the reactor.**
- **The CVD method is used to produce defect-free nanoparticles.**
- **Due to the simplicity of the experiment, the scaling up of the unit for mass production in industry is achieved without any major difficulties.**
- **Disadvantages**

    High Temperatures are required

    Toxic and Corrosive gases should be dealt properly

    Precursors are volatile in nature

Chemical Vapour Deposition (CVD) - Applications

- CVD processes are used by many industries such as the aircraft and automotive industries.
- They are used to modify surfaces to promote adhesion.
- Through the CVD process, coatings increase the longevity of materials, such as making metals resistant to rust and corrosion.
- CVD is used in the semiconductor industry to make materials that are used to produce solar panels, light-emitting diodes, and integrated circuits found in devices like phones and televisions.
- CVD also helps prepare single crystal metal oxides, such as sapphire and ferrites.
- Lastly, it is through the CVD process that net shape products such as tubes and crucibles are produced.
- The substrate is removed and leaves a free-standing thin material.

PLASMA ARCHING / ARC METHOD

✓The arc discharge method is a well-known method for the formation of CNTs.

✓A schematic of an arc discharge chamber as shown.

✓The chamber consists of two electrodes which are mounted horizontally or vertically; one of which (anode) is filled with powdered carbon precursor along with the catalyst and the other electrode (cathode) is usually a pure graphite rod.

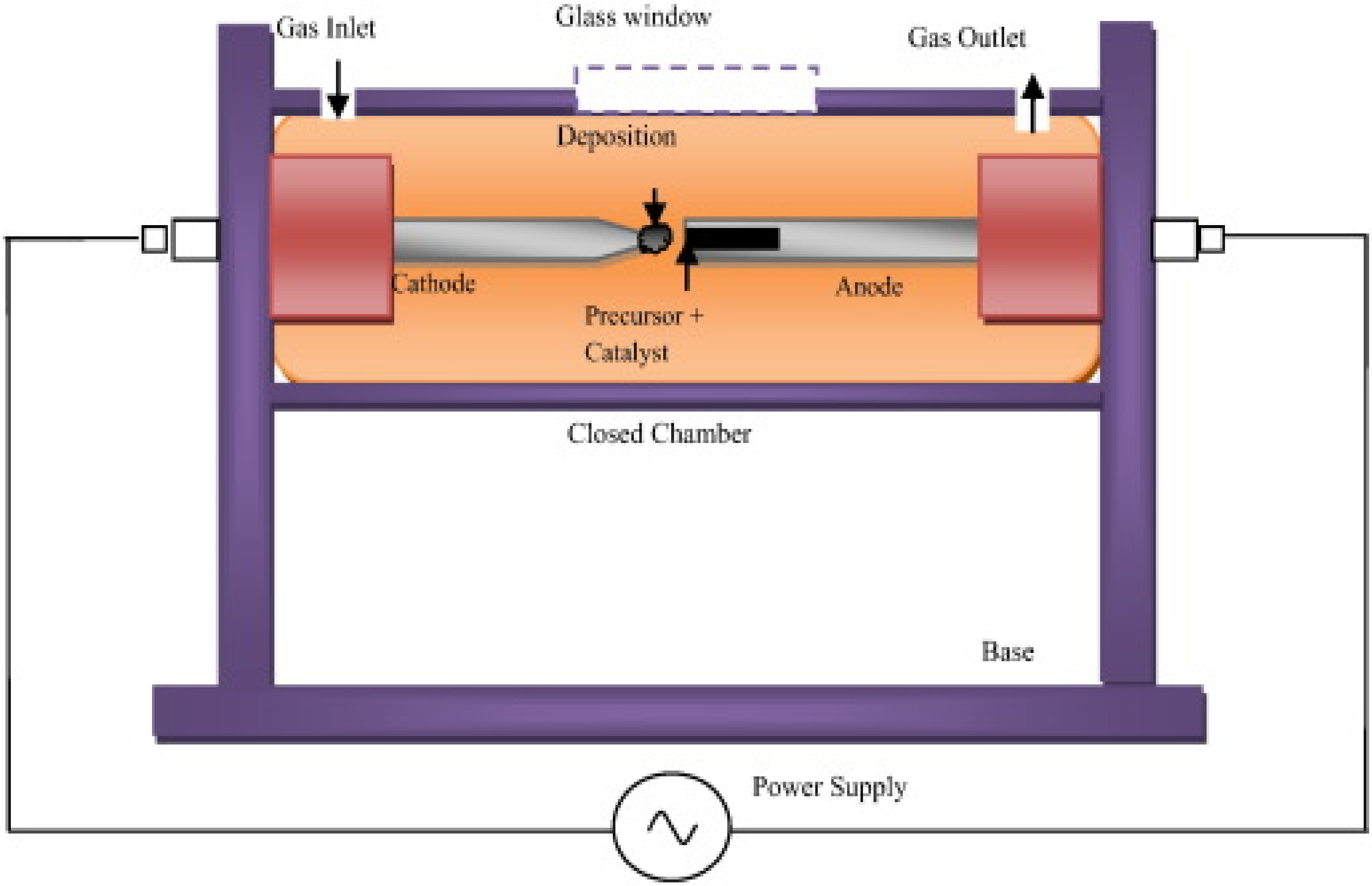
✓The chamber is filled with a gas or submerged inside a liquid environment.

✓After switching on the power supply (AC or DC), the electrodes are brought in contact to generate an arc and are kept at an intermittent gap of 1–2 mm to attain a steady discharge.

✓A constant current is maintained through the electrodes to obtain a non-fluctuating arc for which closed loop automation is employed to adjust the gap automatically.

✓A fluctuating arc results in unstable plasma and the quality of the synthesized product is affected.

PLASMA ARCHING / ARC METHOD



PLASMA ARCHING / ARC METHOD

✓The arc current generates plasma of very high temperature ~ 4000–6000 K, which sublimes the carbon precursor filled inside the anode.

✓The carbon vapours aggregate in the gas phase and drift towards the cathode where it cools down due to the temperature gradient.

✓After an arc application time of few minutes the discharge is stopped and cathodic deposit which contains CNTs along with the soot is collected from the walls of chamber

The quantity and quality such as lengths, diameters, purity and etc. of the nanotubes obtained depend on various parameters such as the

- ✓ Metal concentration,
- ✓ Inert gas pressure,
- ✓ Type of gas,
- ✓ Plasma arc,
- ✓ Temperature,
- ✓ Current and
- ✓ System geometry.

PLASMA ARCHING / ARC METHOD

Advantages:

✓It is a simple process and it is the true method to obtain structurally excellent high quality CNTs.

✓Large scale and high purity of SWCNTs can be obtained (by controlling over the orientation of the nanotubes etc)

✓Arc-discharge method is the cost-efficient technique for the synthesis of carbon nanotubes and the time required for CNT synthesis is also less as compared to other methods.

✓CNTs produced by this method are highly crystalline and have fewer defects than nanotubes produced by other methods

Disadvantages:

✓CNTs by arc discharge in a reduced inert-gas atmosphere (e.g., Ar, He, etc.). Using low pressure and noble gasses can be the disadvantages of this method.

PLASMA ARCHING / ARC METHOD- APPLICATIONS

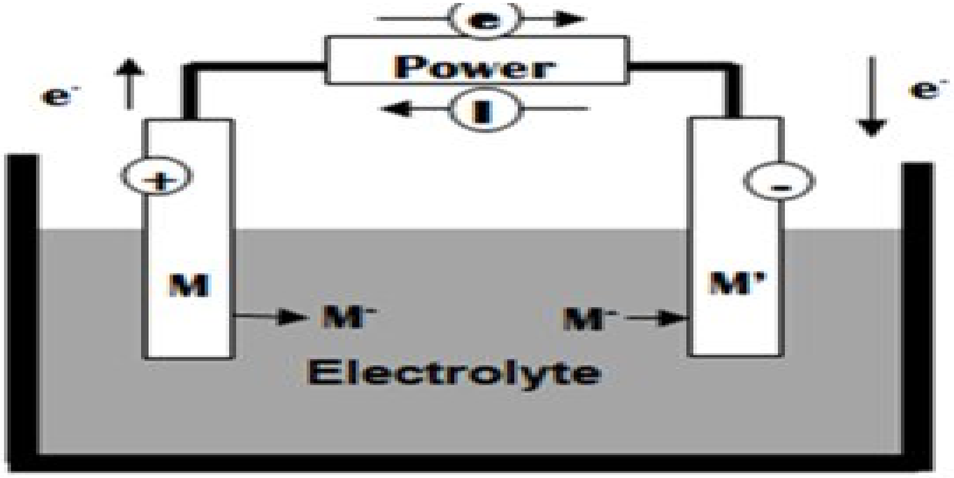
- ✓ Plasma arc methods, including welding and machining, are widely used across various industries due to their precision and ability to handle a range of materials.
- ✓ Plasma arc welding (PAW) is popular for joining materials like stainless steel and titanium, especially in aerospace, marine, and electronics industries.
- ✓ Plasma arc machining (PAM) is used for cutting, turning, and milling hard-to-machine materials, as well as for applying coatings.

Electrochemical Deposition

Electrochemical deposition is a process used to deposit a layer of material onto a substrate through the reduction of metal ions in an electrolyte solution using an electric current.

The ECD Process involves

- ✓ 1.Mass transport in the electrolyte (diffusion, migration, convection),
- ✓ 2. Interfacial charge transfer governed by electrochemical kinetics,
- ✓ 3. Nucleation and growth processes at the electrode surface,
- ✓ 4. Morphological evolution of the deposit.



The electrolyte solution possesses the positively charged nickel ions (or cations) along with the negatively charged chloride ions (or the anions).

When an external field is applied to system, cations migrate to the cathode and deposit as metallic nickel after reduction.

$Ni^{2+} + 2e- \leftrightarrow$ Ni (metal)

Simultaneously, to maintain the neutrality of electrolyte, Ni from anode gets dissolved in the solution.

$Ni \leftrightarrow Ni^{2+} + + 2e-$

This phenomenon is termed as electrolysis.

Usually, Pt mesh acts as anode.

Oxidation of water occurs at the anode: $2H_2O \leftrightarrow 4H^+ + O_2 + 4e-$

The quantity of chloride ions is unchanged during electrolysis but the content of Ni^{2+} ions will decrease while concentration of H^+ions increases with time.

Due to the effect of applied voltage, reorganization of ions takes place near the surface of electrode and it leads to deposition of an Helmholtz double layer (an electrical double layer), succeeded by the creation of diffusion layer.

Applications:

Thickness of electroplated layer at substrate can be controlled by plating time duration. By some modification in electrode and electrolyte solution, this method can be successfully used for

- ✓ fabrication of nanomaterials,
- ✓ nanorods an
- ✓ nanoporos structures.
- ✓ Decorations: Where an expensive metal is coated over the surface of a base metal to enhance its appearance E.g., jewelry, furniture fittings, tableware, etc.
- ✓ Protection: Corrosion resistance coatings including chromium plating of automobile parts as well as appliances for domestic use, nuts, screws, as well as electrical components
- ✓ Electroforming: Producing molds, sieves, screens, dry shaver heads, record stamps, dies, etc.
- ✓ Enhancement: Improving the electrical and thermal conductivities, solderability, reflectivity, printed circuitry and electrical contacts, production of micro parts for MEMS, etc.

Factors that influence the electrodeposition process are:

- ✓ Current density
- ✓ The nature of the anions and cations present in the solution
- ✓ Composition
- ✓ Temperature of the bath
- ✓ Concentration of the solution
- ✓ current
- ✓ The presence of impurities
- ✓ Physical as well as chemical nature of the surface of the substrate