MODULE - V

Nanotechnology

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Nanotechnology

Nanotechnology: Nanoscale, Quantum confinement, Surface to volume ratio,

Bottom-up fabrication: Sol-gel, precipitation, Combustion methods,

Top-down fabrication: Ball milling, Physical Vapor Deposition (PVD), Chemical Vapor Deposition (CVD)

Characterization techniques: X-ray diffraction (XRD), and Transmission Emission Microscopy (TEM), Applications of Nanomaterials.

Nano-Scale

The word "nano" is derived from a Greek word meaning dwarf or extremely small and means a billionth (10^{-9}) part of a unit. A *nanometer* or *nm is one thousand millionth of a metre*, *i.e.*,

1 nm = 10^{-9} **m =** $\mathbf{10^{-6}}$ **mm = 10 Å.**

One nanometer spans 3 to 5 atoms lined up in a row.

For comparison, a single human hair is about 80,000 nm wide and a red blood cell is approximately 7,000 nm wide. Scientists and Engineers are nowadays interested in the **nanoscale**, which may be taken as **100 nm to 0.2 nm** approximately.

Below this lies the atomic scale 0.1nm.Therefore, the nano-world is a borderland between the quantum world and the macro world.

Nanotechnology

- Nanotechnology is the day-to-day developing subject, with large number of applications.

- Nanotechnology has the potential to create many new materials and devices with wide-ranging applications, such as in medicine, electronics, and energy production.

- Nanotechnology is the design and development of techniques, instruments and devices for fabrication, characterization and application of the nanoparticles.

Nanotechnology

- Many diagnostic instruments like Transmission Electron Microscope (TEM), Scanning Tunneling Microscope (STM), Atomic Force Microscopy (AFM) and Magnetic Resonance Imaging (MRI) have been invented in the Nanotechnology.

- **Nanoscience** is the basic of nanotechnology. The nanoscience relies more on quantum theory.

- **Nanoscience** can be defined as the study of phenomenon and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at larger scale.

Origin of Nanotechnology

The word nanotechnology is relatively new, the existence of nanostructure is not new.

In fourth century, **AD Roman glass makers** fabricated glasses containing nanosized materials. Similarly gold nanoparticles are made long ago.

The concept of nanotechnology was first given by **Richard Feynman**. In eighteenth century British scientists **Thomas Wedgewood and Sir Humphrey Davy** were able to provide images using nitrate and chloride, but their images were not permanent.

Origin of Nanotechnology

In 1960, **Richard Feynman** presented a visionary and prophetic lecture at a meeting of American Physical society entitled ***"there is plenty of room at the bottom"*** where he speculated on the possibility and potent of nanosized materials.

The term nanotechnology was defined by Tokyo Science University **Professor Norio Taniguchi** in a 1974 paper as follows: Nano technology mainly consists of the processing of, separation, consolidation, and deformation of materials by one atom or by one molecule.

Nanomaterials

Nanomaterial means a material whose size is in Nano range, this is an answer which may be generally thought, but there is an implicit meaning.

Suppose, consider a **gold** biscuit of 100 cm^3 cut into two pieces, no properties are changed except its size. Divide it into further small pieces, then also there would not be any change in properties.

Thus, the macroscopic solid pieces of the materials possess size independent properties.

It was found that when gold is divided into fine grains of **nearly 50 nm**, the properties like density, color, hardness, melting point, resistivity etc are changing.

So, the microscopic pieces possess size dependent properties

Nanomaterials

Thus, the size dependency is an essential property of Nanomaterials.

So, Nanomaterial is defined as material having one of its dimensions in nano range and it possesses size dependent properties. Or

Nanomaterials could be defined as those materials which have structured components with size less than 100 nm at least in one dimension.

Generally if one dimension is in nano range, it is called thin films and quantum well.

If two dimensions are in nano range it is called quantum wire & Q-tube.

If three dimensions are in nano range it is called quantum dot.

Application of Nanotechnology

Medicine: Drug delivery systems, Active agents, Contrast medium, Medical rapid tests, Prostheses and implants, Antimicrobial agents and coatings, Agents in cancer therapy.

Chemical industry: Fillers for paint systems, Coating systems based on nanocomposites, Impregnation of papers, Switchable adhesives, Magnetic fluids.

Engineering: Wear protection for tools and machines (anti blocking coatings, scratch resistant coatings on plastic parts, etc), Lubricant-free bearings.

Application of Nanotechnology

Electronic Industry: Data memory (MRAM, GMRHD), Displays (OLED, FED), Laser diodes, Glass fibers, Optical switches, Filters (IR blocking),Conductive antistatic coatings.

Construction: Construction materials, thermal insulation, Flame retardants, Surface-functionalised building materials for wood, floors, stone, facades, tiles, roof tiles, etc., Façade coatings, Groove mortar.

Automotive Industry: Light weight construction, Painting (fillers, base coat, clear coat), Catalysts, Tires (fillers), Sensors, Coatings for windscreen and car bodies.

Textile/ fabrics/ non-wovens: Surface processed textiles, Smart clothes.

Application of Nanotechnology

Energy: Fuel cells, Solar cells, Batteries, Capacitors.

Cosmetics: Sun protection, Lipsticks, Skin creams, Tooth paste.

Food and drinks: Package materials, Storage life sensors, Additives Clarification of fruit juices.

Household: Ceramic coatings for iron, Odors catalyst, Cleaner for glass, ceramic, floor, windows

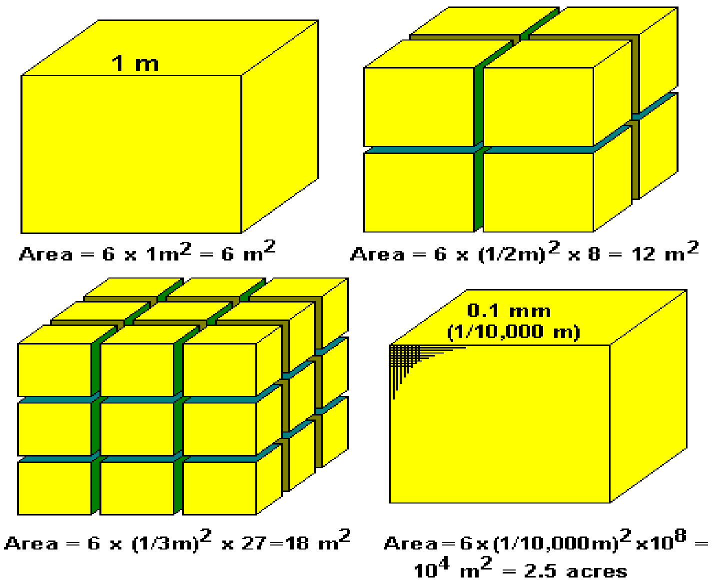
Sports/outdoor: Ski wax, Antifogging of glasses/goggles, Antifouling coatings for ships/boats, Ring forced

Why the properties of Nanoparticles are different

The phenomena due to which properties of nanoparticles are different are:

(i) Surface area to volume ratio

(ii) Quantum confinement effect



<u>Increase in Surface area to volume ratio:</u>

Nanomaterials have relatively larger surface
When compared to the same volume or mass of the

Material produced in larger form. Consider a sphere of radius 'r' .

Its surface area = $4\pi r^2$ & Its volume = $(4/3)\ \pi r^3$

So, surface area to its volume ratio= (3/r).

Surface to volume ratio

As ‘r’ decreases surface area to volume ratio increases. So, the properties of materials will be changing. The material has high surface energy, if it is small in size or vice versa.

As the surface area to volume ratio increases, the materials possess good catalytic properties.
Thus, nanoparticles show enhanced stability and broader scope of applications.

In some cases materials that are inert in their larger form are reactive when produced in their nano scale form. This affects their strength or electrical properties.

For example, a particle of size 30 nm has 5% of its atoms on its surface, at 10 nm 20% of its atoms and at 3 nm 50% of its atoms.

Quantum confinement

When atoms are isolated the energy levels are discrete (Fig. I).

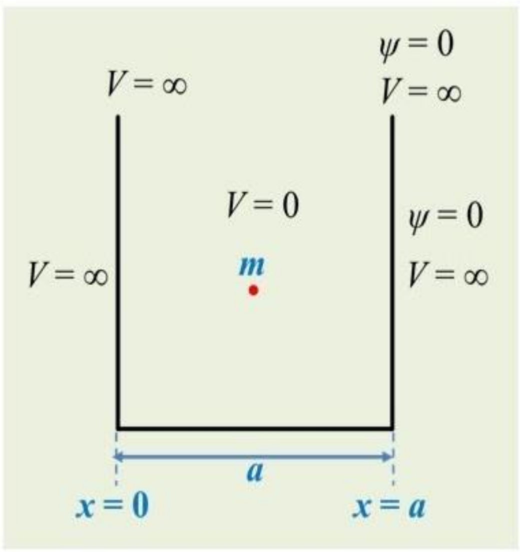
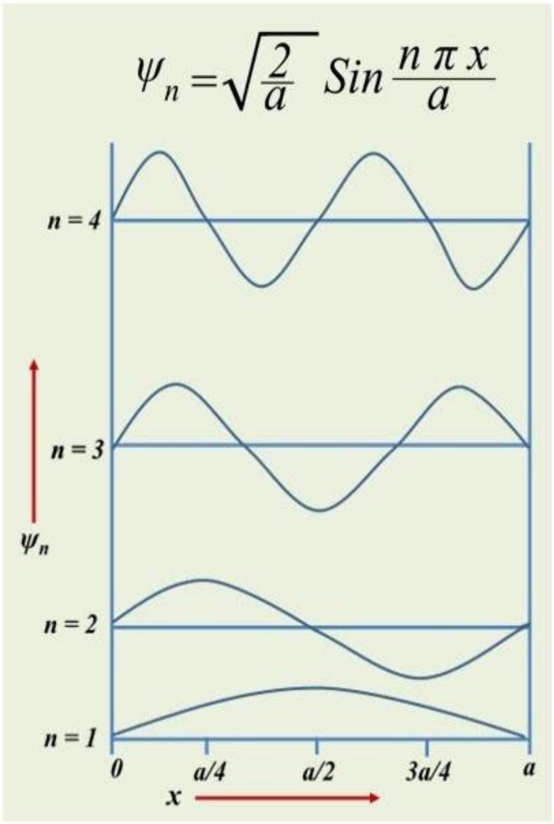
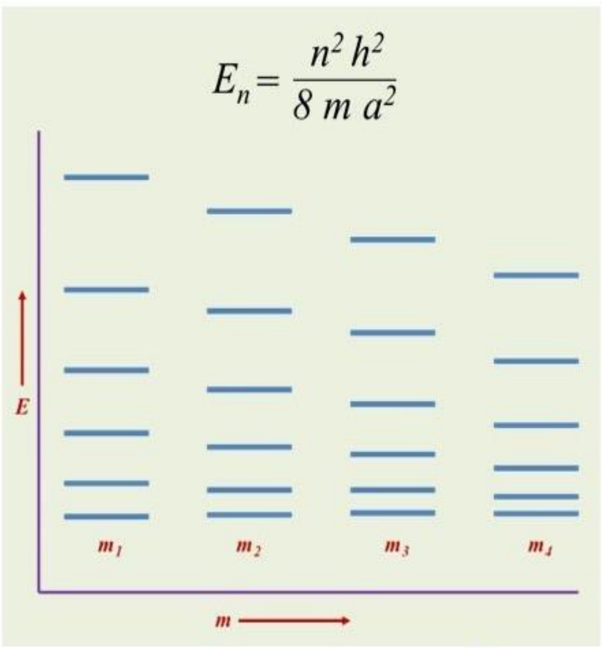


Fig.I





Nanomaterials represent intermediate stage.

When the dimensions of box or wells in which a particle is represented are of the order of De-Broglie wavelength of electrons, energy levels of electrons change.

This effect is called quantum confinement effect.

Quantum confinement

When the material is sufficiently small in size typically 10 nm or less, organization of energy levels into which electrons can climb or fall change.

When very large numbers of atoms are closely packed, to form a solid, the energy levels split and form bands (Fig. II).

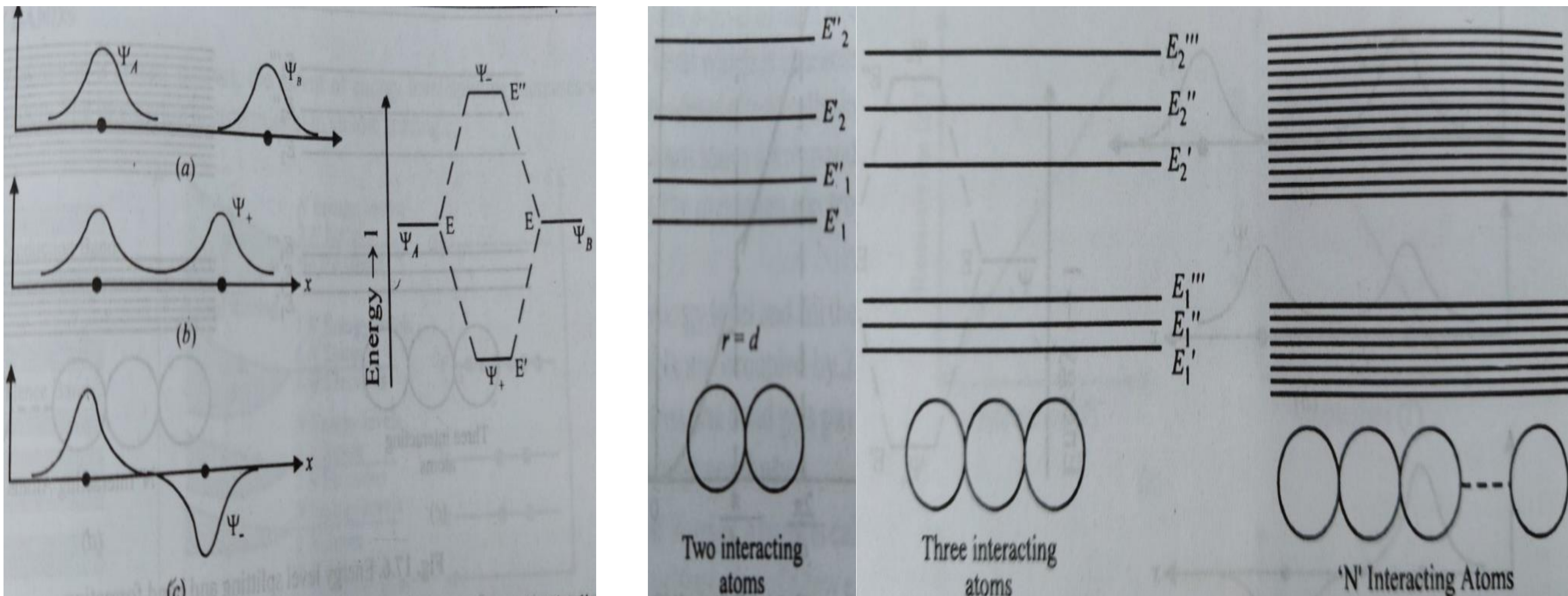


Fig. II

Quantum confinement

Specifically, the phenomenon results from electrons and holes being squeezed into dimension that approaches a critical quantum measurement, called the ‘excited Bohr radius ’.

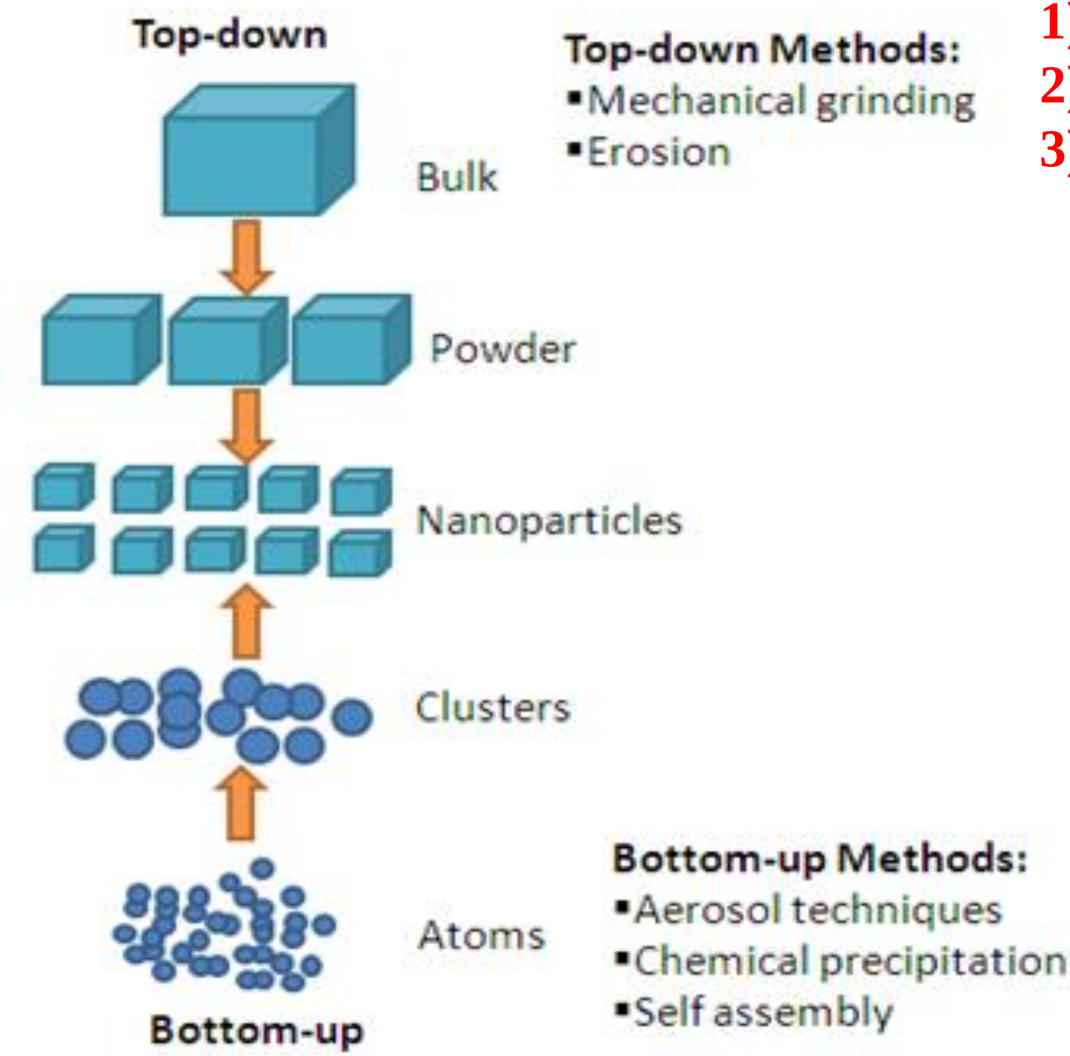
These can affect the optical, electrical and magnetic behavior of materials, particularly as the structure or particle size approaches the smaller end of the nano scale.

In small nano crystals or clusters or grains the electronic energy levels are not continuous as in the bulk and are discrete, because of the confinement of the electronic wave function to the physical dimensions of the particles.

Fabrication of Nano-materials/Nano-particles:

Top-down & Bottom-up approaches

How to prepare the Nano-particle or Nanostructure



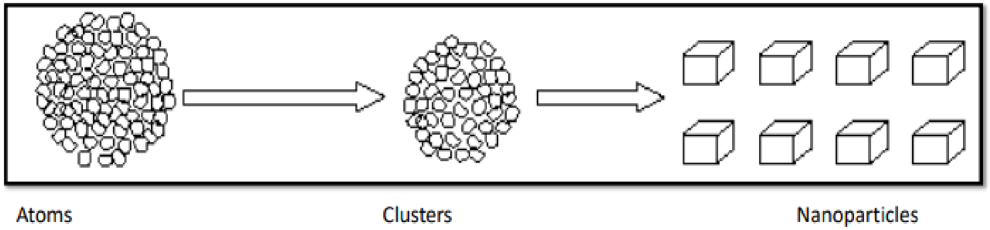
1) Ball milling
2) Physical Vapor Deposition
3) Chemical Vapor Deposition

1) Sol-gel
2) Precipitation
3) Combustion methods

Fabrication of Nano-materials

The two basic approaches used in the fabrication of nanomaterials are:

(i) Bottom-up approach.
(ii) Top-down approach



Bottom-up approach:

In this approach, atoms or molecules or nanoparticles are used as building blocks for the creation of **complex nanostructures**.

These processes are highly controlled, complex chemical synthesis techniques.

In this approach, materials and devices are built from molecular components which assemble themselves chemically by principles of molecular recognition.

These seek to arrange smaller components into more complex assemblies.

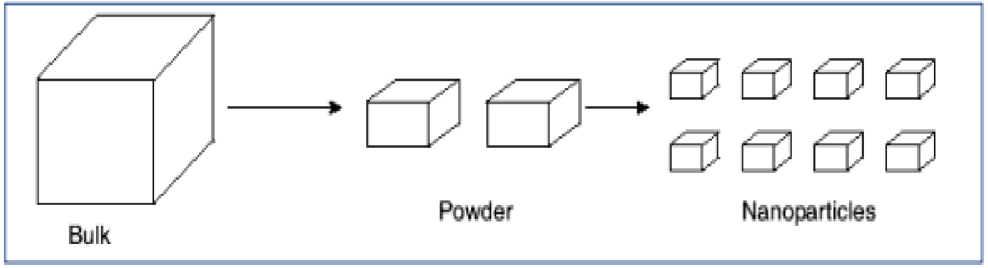
Nanoscale structures are normally achieved by chemical synthesis of materials in liquid or gaseous state.

Fabrication of Nano-materials

Top-down approach:

In this approach, one rely on either division or removal of a bulk material to produce the desired nanostructure or nanoparticles with the desired properties.

These are inherently **much simpler process** when compared with bottom-up approach.



In this approach, nano-objects are constructed from larger entities without atomic level control.

These seek to create smaller devices by using larger ones to direct their assembly. The top-down processes of **preparing nanoparticles** are effectively examples of solid state processing of materials.

Top-down Fabrication methods

In this approach, we discuss three methods that are used for the fabrication:

(i) Ball milling
(ii) Physical vapour deposition; (iii) Chemical vapour deposition

Ball Milling:

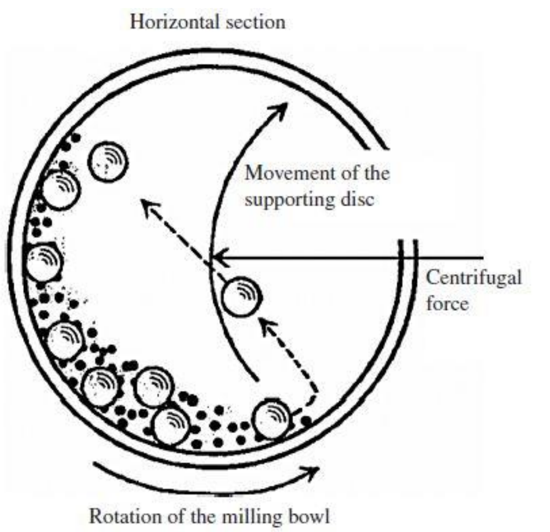
In ball milling, also called **mechanical crushing**, small balls (SiC or tungsten balls) are allowed to rotate around the inside of a drum and then fall on a solid with gravity force and crush the solid into nanocrystallites.

Ball milling can be used to prepare a wide range of elemental and oxide powders.

For example, iron with grain sizes of 10-30 nm can be formed.

Other crystallites, such as iron nitrites, can be made using ammonia gas.

A variety of inter metallic compounds based in nickel and aluminum can be formed. Ball milling is preferred method for preparing metal oxides



Top-down Fabrication methods

Vapor deposition technique:

Vapor deposition refers to any process in which materials in a vapor state are condensed through condensation, chemical reaction or conversion to form a solid material.

These processes are used to form coatings to alter the mechanical, electrical, thermal, optical, corrosion resistance and wear properties of the substrates.

Vapor phase deposition techniques can be classified broadly as:

(i) Physical vapour deposition (PVD); and

(ii) Chemical vapour deposition (CVD).

Top-down Fabrication methods

Physical vapor deposition (PVD) technique:

PVD involves conversion of solid material into gaseous phase by physical process which is then cooled and re-deposited on a substrate as per the requirement.

All the reactive PVD hard processes combined have following steps:
A method for depositing the metal.
Combination with an active gas, such as nitrogen, oxygen or methane.

Plasma bombardment of the substrate to ensure a dense, hard coating.

PVD methods differ in the means for producing the metal vapor and the details of plasma creation.

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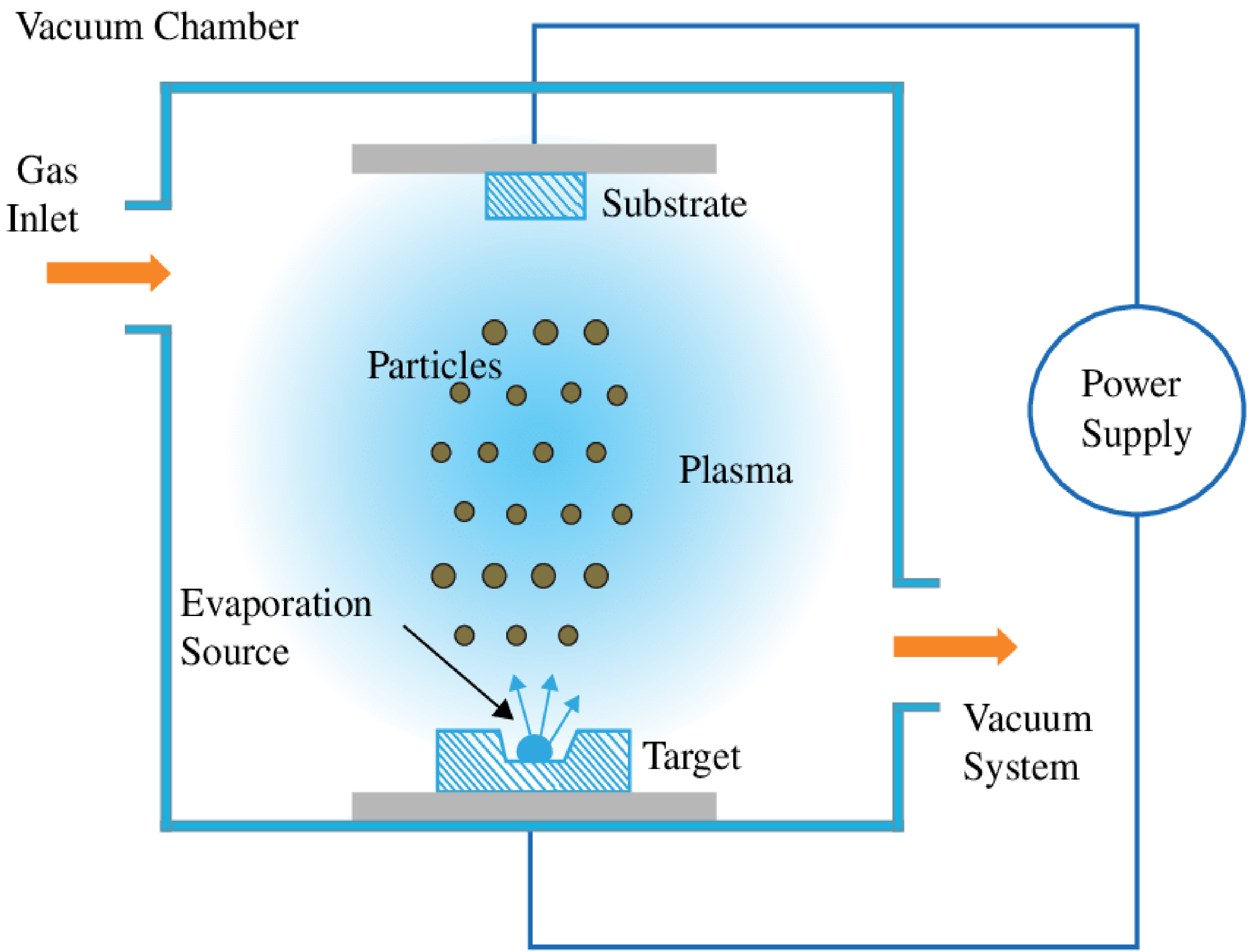
The primary PVD methods are iron plating, ion implantation, spluttering and laser surface alloying.

Top-down Fabrication methods

Physical vapor deposition (PVD) technique:

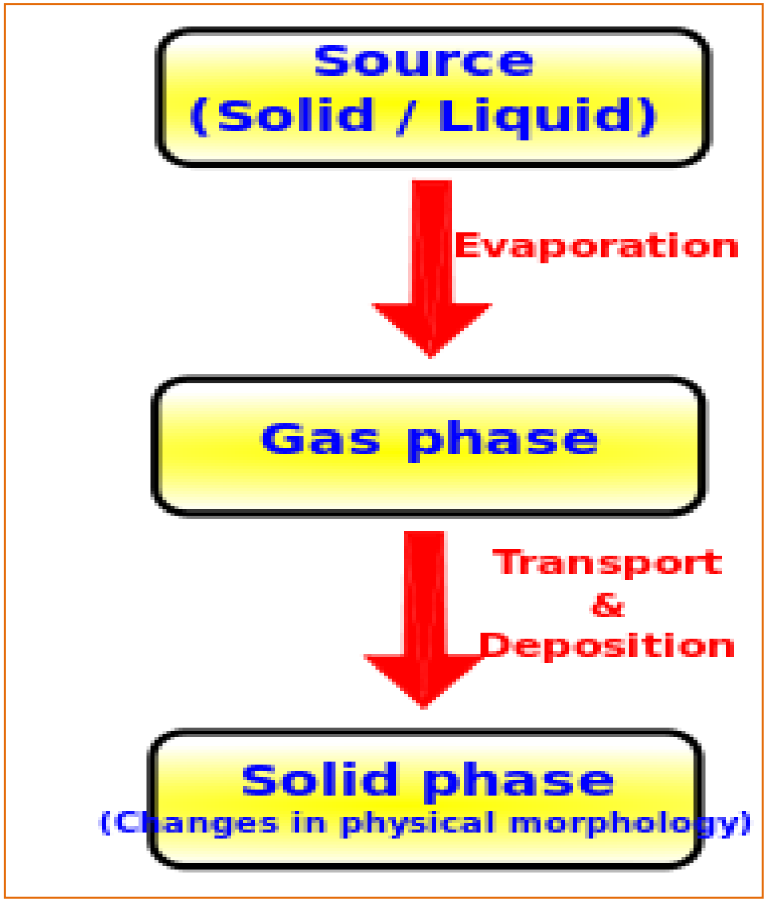


Top-down Fabrication methods

Thermal evaporation is one of the simplest and most popular synthesis methods, and it has been very successful and versatile in fabricating nanobelts and nanowires with various characteristics.

Multi-wall and single-wall carbon nanotubes have been successfully fabricated in this system using hydrogen and methane/acetylene reactants.

Metal catalysts such as Gold, Tin, and Copper etc., have also been used to achieve size control alignment.



Top-down Fabrication methods

Chemical vapor deposition (CVD):

CVD is a widely used method for depositing thin films for a large variety of materials.

Applications of CVD range from the fabrication of microelectronic devices to the deposition of protective coatings.

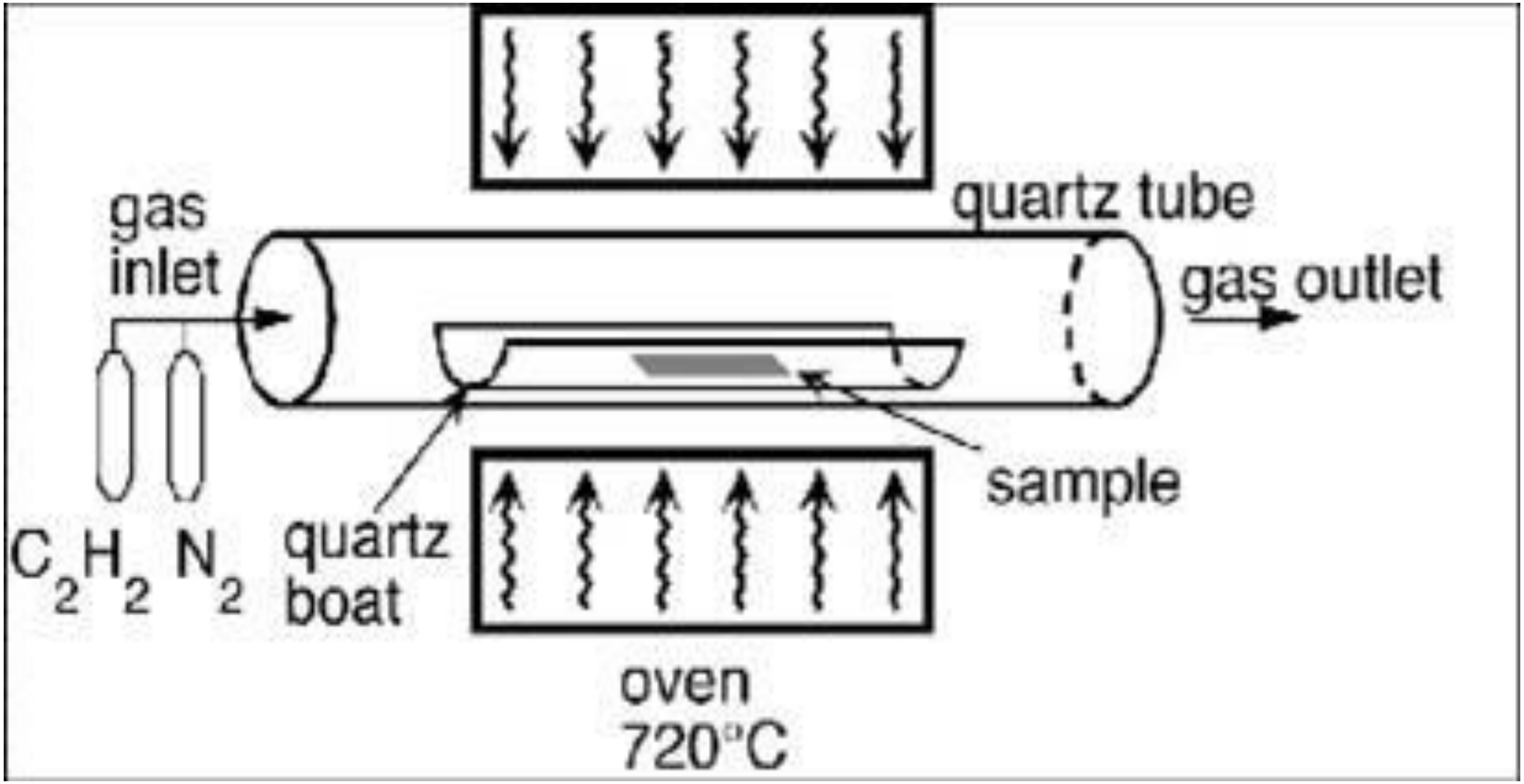
In a typical CVD process, reactant gases at room temperature enter the reaction chamber.

The gas mixture is heated as it approaches the deposition surface, heated radiatively or placed upon a heated substrate.

Depending on the process and operating conditions, the reactant gases may undergo homogenous chemical reactions in the vapor phase before striking the surface.

Top-down Fabrication methods

Chemical vapor deposition (CVD):



Input of acetylene (C_2H_2, purity 99.5 wt%) and electronic grade nitrogen (N_2), purity 99.99 wt% through alumina/quartz tubes was localized in the upper (colder) part of the furnace. Gases were spontaneously premixed at this part, then they flowed through a tubular hot-wall reactor in which the reaction took place.

Top-down Fabrication methods

There are a great variety of CVD processes such as:

(i) Atmospheric pressure chemical vapor deposition (APCVD)
(ii) Plasma Assisted (enhanced) chemical vapor deposition (PACVD,PECVD)
(iii) Low Pressure chemical vapor deposition (LPCVD)
(iv) Photochemical Vapor deposition (PCVD)
(v) Laser Chemical vapor deposition (LCVD)
(vi) Chemical Beam Epitaxy (CBE)
(vii) Chemical vapor Infiltration (CVI)

Chemical vapor deposition (CVD) synthesis is achieved by putting a carbon source in the gas phase and using an energy source, such as Plasma or a resistively heated coil, to transfer energy to a gaseous carbon molecule.

Sol-Gel method:

In solutions, nanosized molecules are dispersed randomly whereas in colloids, the molecules have diameters in the range of 20μm-100μm and are suspended in the solvent. So, the colloid appears cloudy.

A colloid that is suspended in a liquid is called a **Sol**. The gelation of the sol in the liquid to form a network is called **gel**. Gel is the suspension that keeps its shape.

Sol-gel formation occurs in different stages.

- Hydrolysis
- Condensation and polymerization of monomers to form particles.
- Agglomeration of particles.

This is followed by the formation of networks which extends throughout the liquid medium and forms a gel.

Using sol-gel method, silica gels, zirconia and yttrium gels and aluminosilicate gels are formed. Nanostructured surfaces are formed using the sol-gel method

Important steps are used in sol-gel method:

Preparation of sol: The starting materials used in the preparation of the sol are usually inorganic metal salts or metal organic compounds such as metal alkoxides.

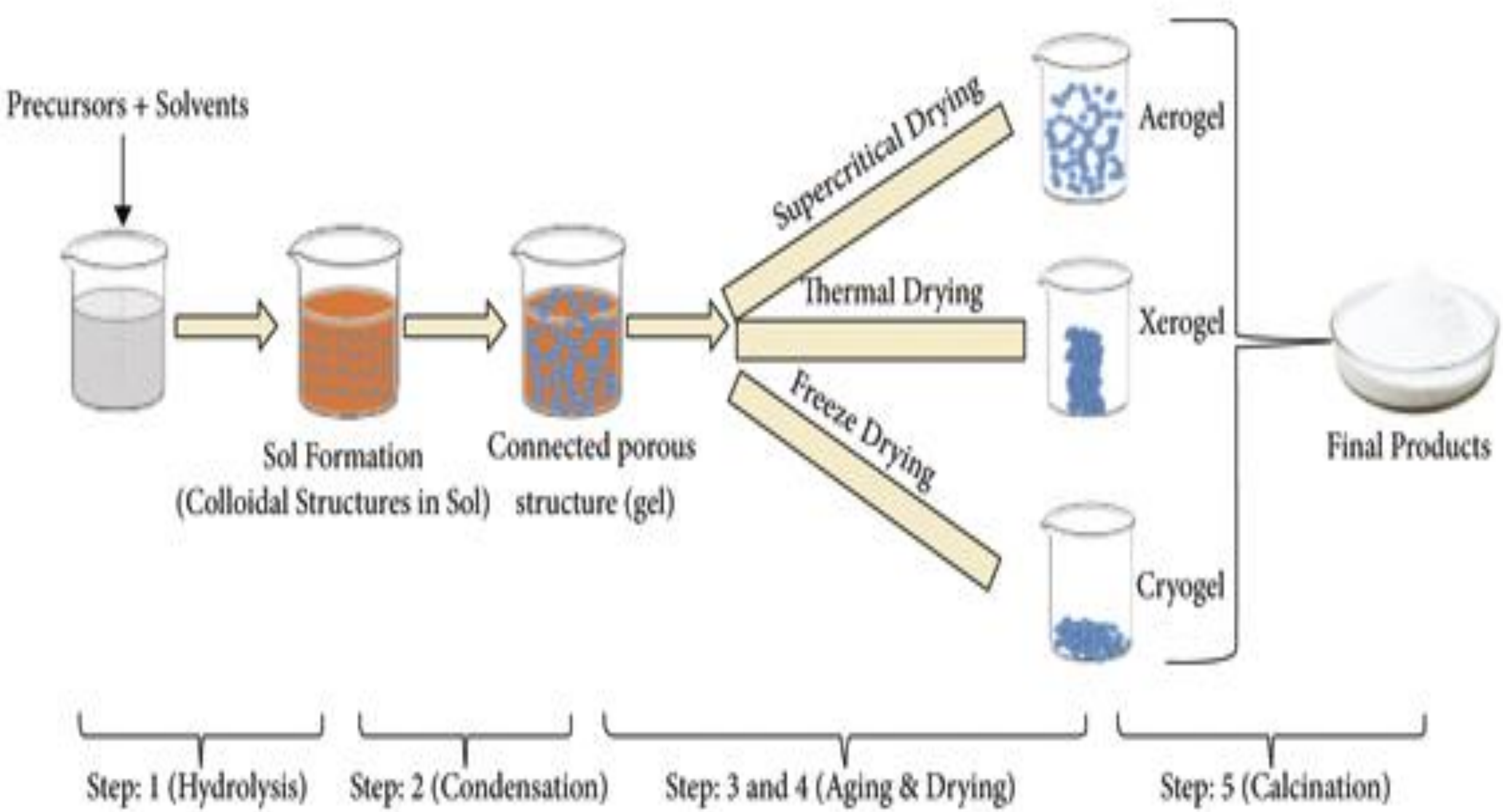
Preparation of gel: a typical sol–gel process, the precursor is subjected to a series of hydrolysis and polymerisation reaction to form a colloidal suspension known as gel.

Drying and purification: In this step, heat treatment is given to the gel emulsion to dry it up to the level necessary for further processing.

Product formation: different techniques, we can fabricate the particles or films of desired shape and size.

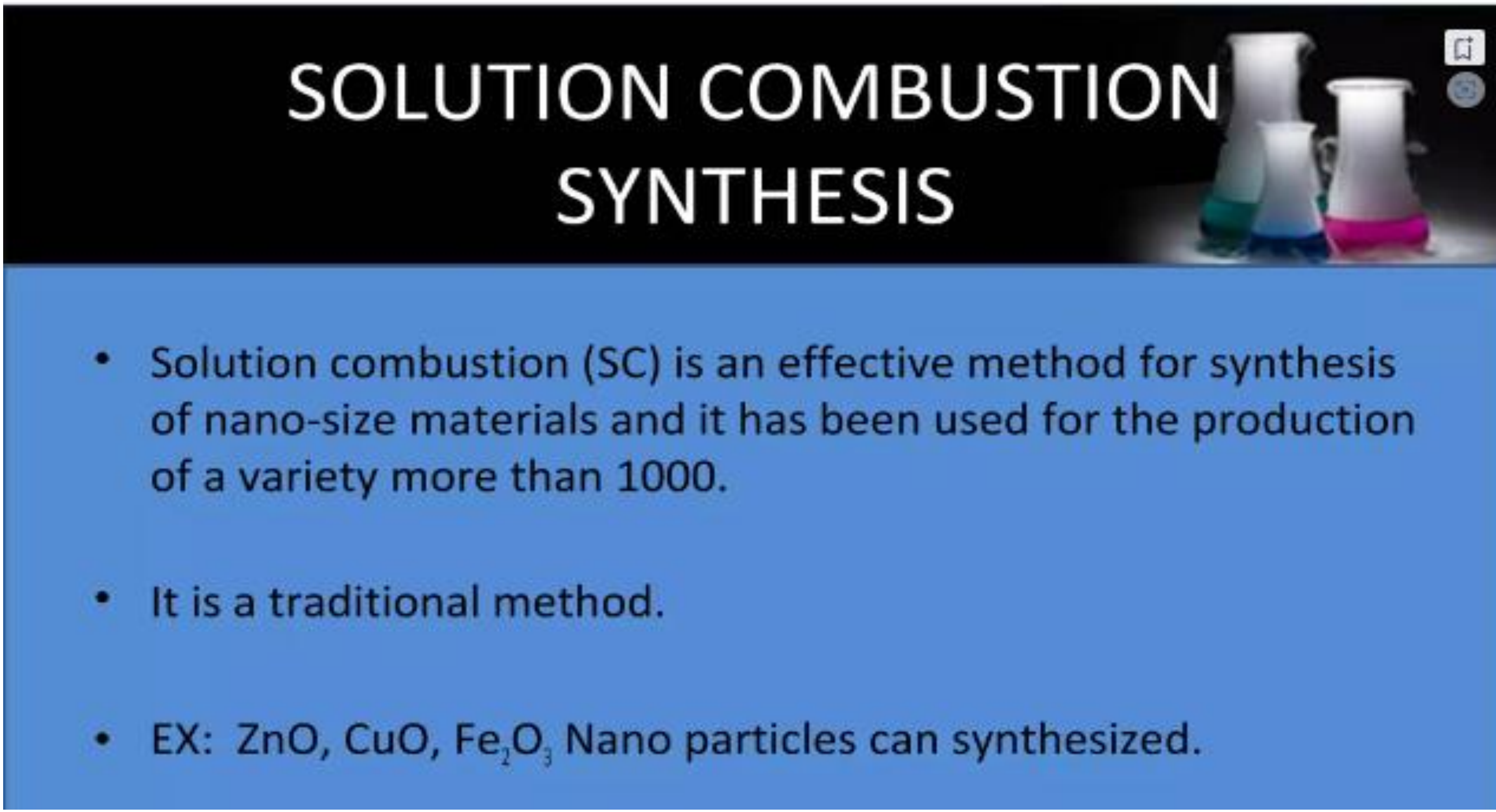
Bottom-up Fabrication methods

Sol-gel Method:



Bottom-up Fabrication methods

Solution Combustion (SC) Method:



Solution Combustion (SC) Method:

This technique is widely used to obtain metal oxide and insulators nanoparticles.

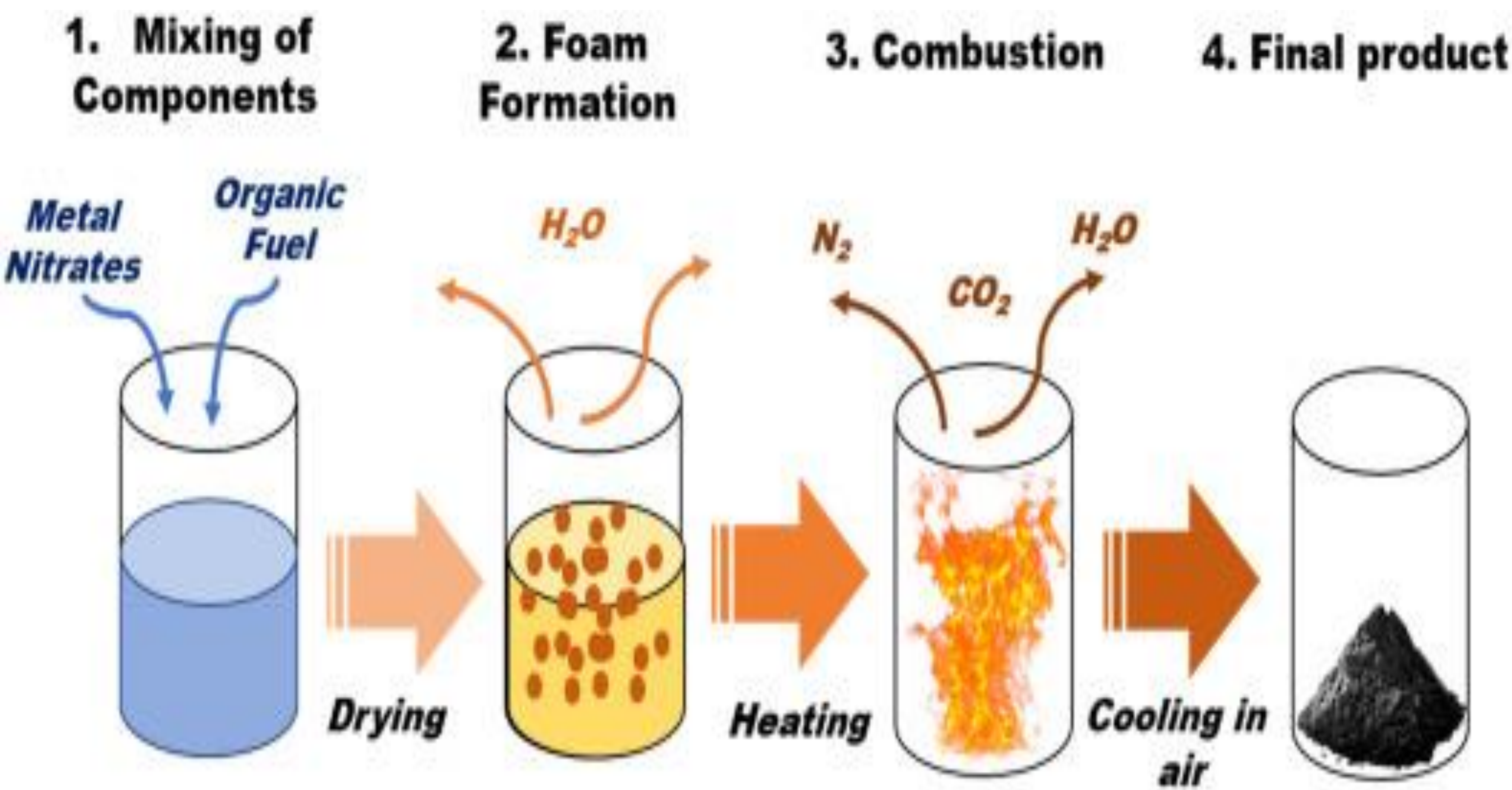
In this technique, first one should make a solution with solutes and solvents. Sometimes making solution may require stirring provision.

Then the solution is heated and once the solution reached auto-ignition temperature, it will start to burn by indication of flames with evolution of some gases.

After completion of burning process, the remaining ash will give us the required nanoparticles.

Bottom-up Fabrication methods

Solution Combustion (SC) Method:



Bottom-up Fabrication methods

Solution Combustion Synthesis (SCS) :

Select the chemicals such that from which we can get the resultant component.

Ex. Oxidizer: For $CuO \rightarrow Cu(NO_3)_2$ **copper nitrate**

For $ZnO \rightarrow Zn(NO_3)_2$ **Zinc nitrate**

Choose the fuel such as containing Carbon and Hydrogen main components.

Ex. Fuel : $C_2H_5NO_2 \rightarrow$ **Glycine**

$C_6H_8O_6 \rightarrow$ **Ascorbic Acid**

Choose the oxidizer and fuel by calculating the (molecular weight * balancing constant)

Take the ratio of fuel /oxidizer

By using the electrical balance take the chemical into butter worth paper

Bottom-up Fabrication methods

Solution Combustion Synthesis (SCS) :

Dissolve the oxidizer into distilled water and mix up with magnetic stirrer.

Add fuel , again stirrer it.

Put the container on electrical heater

After cooling the container, collect the material from the container.

And send for the calcinations

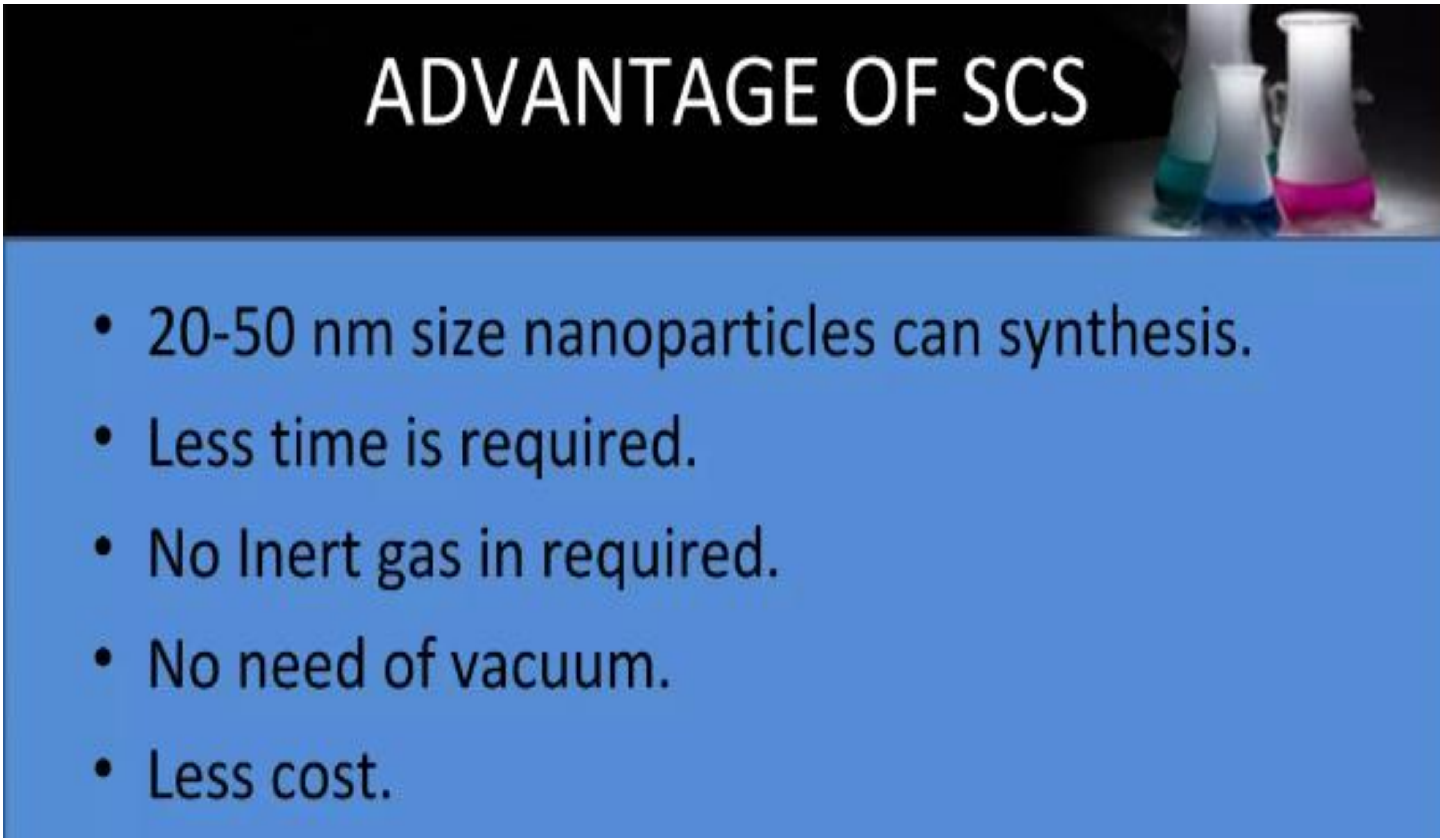
Calcination process normally takes place at temperatures below the melting point of the product materials.

For CuO, the desired melting temperature is 600^{o}C and calcined sample for at least half an hour so that carbon will reduce to carbon-dioxide.

Finally CuO nanoparticles are synthesized.

Bottom-up Fabrication methods

Solution Combustion Synthesis (SCS) :



Chemical Precipitation method/technique :

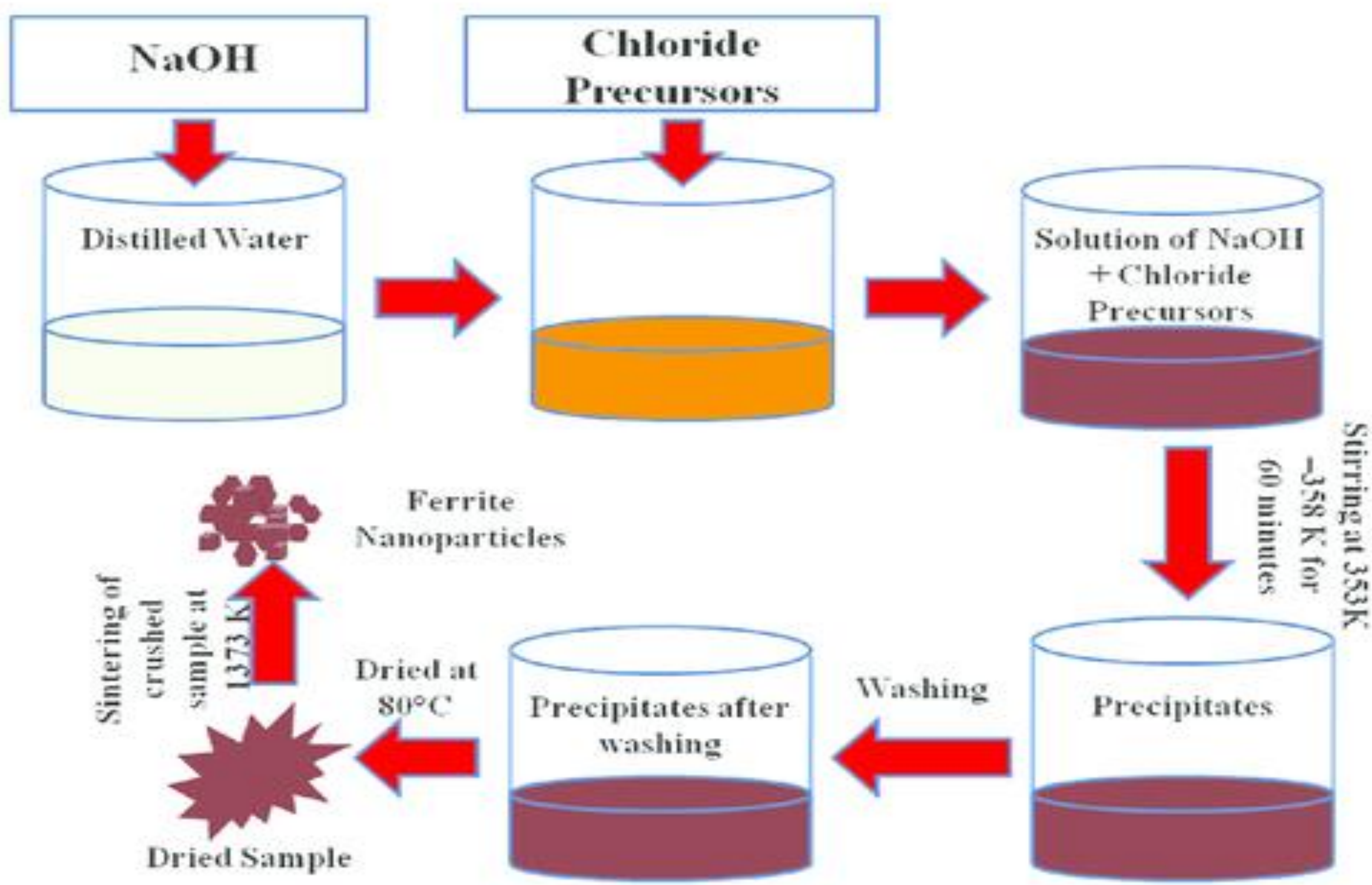
Precipitation is the process of separating the solid particles from the solution by physical and/or chemical changes.

This is one of the simplest chemical technique to obtain the nanoparticles. The principle of this technique is getting the precipitation of our desired materials after reactions occurred by mixing solutes and solvents.

In this case, the precipitation of ions may occur slowly. By washing with some suitable reagents or drying up the precipitation, one can get the required nanoparticles. It is widely used to synthesis metal oxide and insulators with broad band gap along with suitable surface.

Bottom-up Fabrication methods

Chemical Precipitation method/technique :



Characterization Techniques:

X-Ray Diffraction (XRD)

&

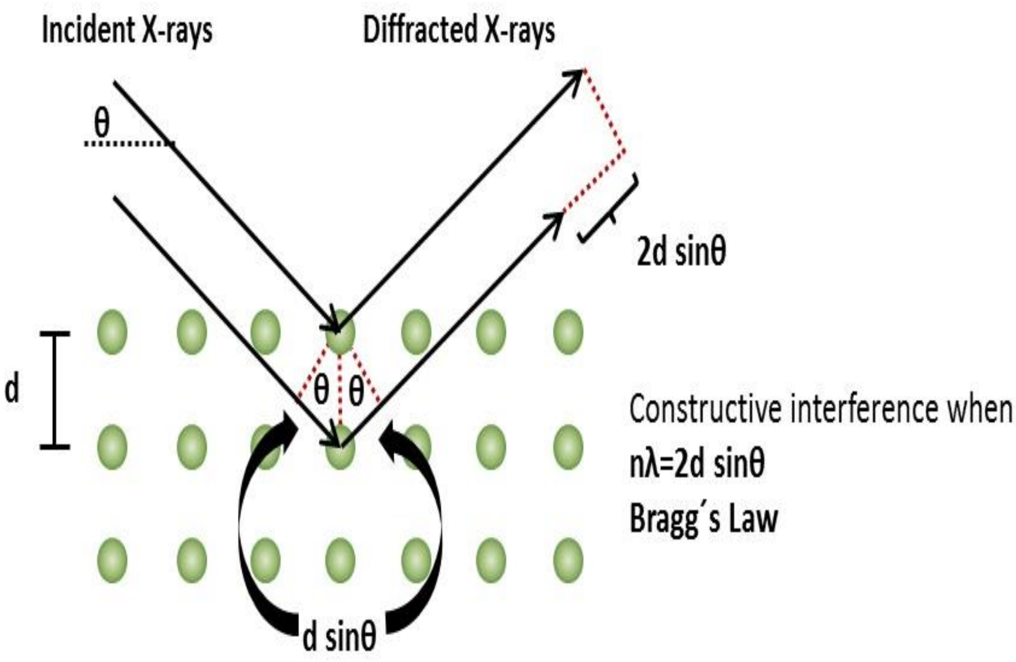
Transmission Electron Microscope (TEM)

X-Ray Diffraction (XRD):

Most of the metals and alloys are crystalline in nature. Hence one of the most useful characterization technique is X-ray diffraction (XRD).

XRD is based on the Bragg's law **$2d \sin\theta = n\lambda$**

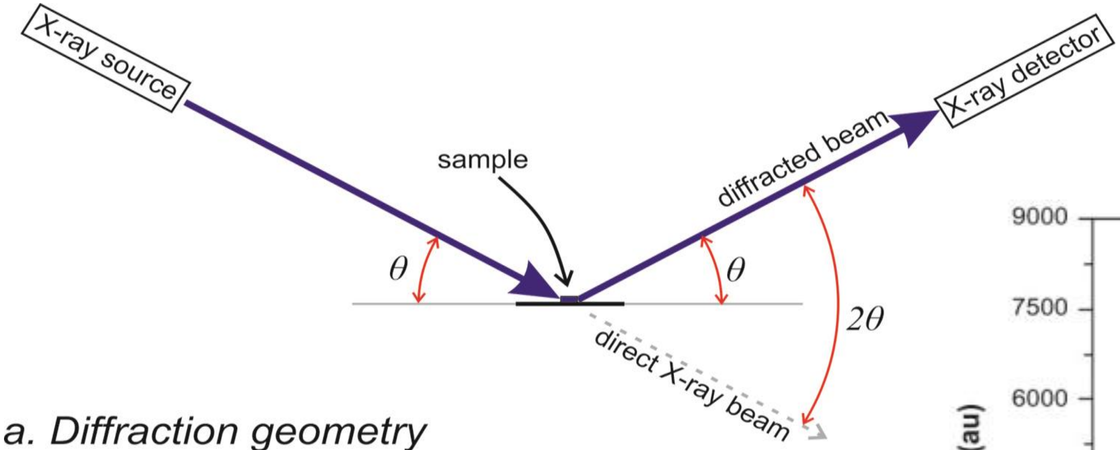
The intensity of diffracted X-Rays is measured as a function of diffracted angle and the specimen orientation.



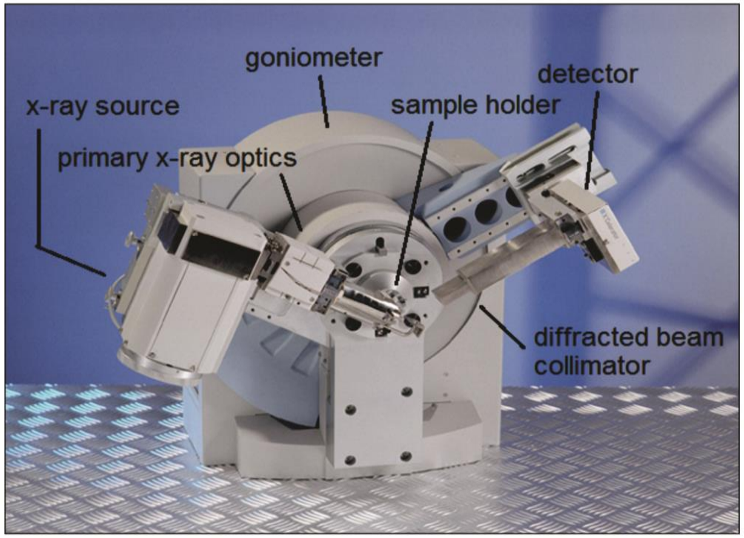
This diffracted pattern is used to identify the specimen's crystalline phases and to measure its structural properties.

The diffraction peaks are accurately measured with XRD which gives information about homogenous and inhomogeneous strains.

X-Ray Diffraction (XRD) Machine:



a. Diffraction geometry



b. An X-ray diffractometer

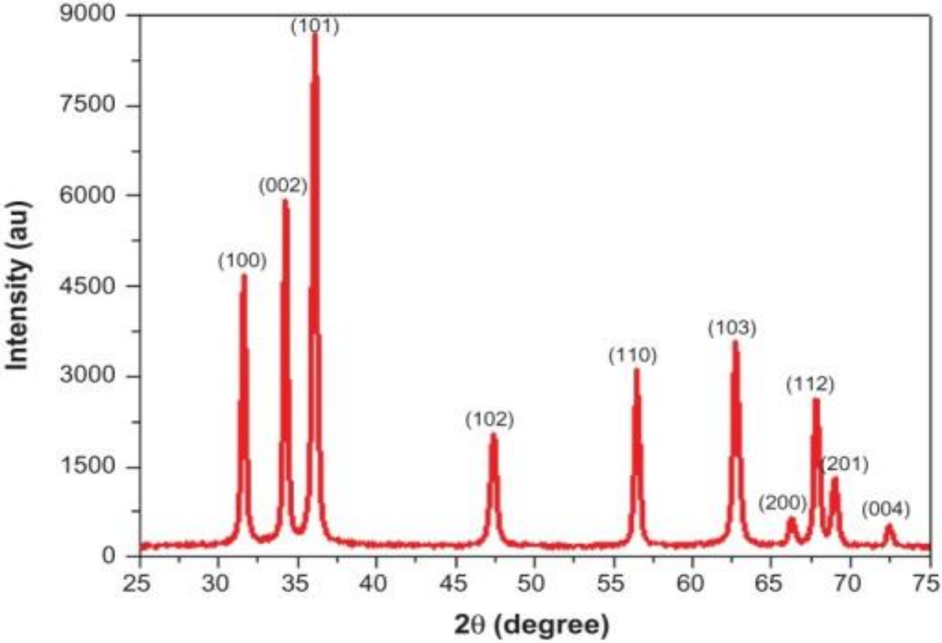


Fig.: XRD pattern of Nano-particles

If there is no inhomogenous strain, the **crystalline size D** can be estimated from the peak width with Scherrer's formula:

$$\mathbf{D = K\lambda / (B \cos \theta_B),}$$

Where λ is wavelength, B is the full width of half maximum of diffraction peaks, θ_B is diffraction angle and K is Scherrer's constant of the order of unity for ordinary crystal.

The XRD is useful for following applications:

Study of d-spacing
Study of mixtures
Study of crystal symmetry
Study of alloys
Stress determination in metals
Determination of particle size

Characterization Techniques

Transmission Electron Microscope (TEM):

In TEM, electrons are accelerated from 10 KeV to 1 MeV projected onto a thin specimen with thickness less than 200 nm. The electron beam is projected on to the specimen by means of condenser lens system and penetrates the sample thickness either deflected or undeflected.

The advantages of TEM are its highest magnification up to the order of **micron** and its ability to provide both image and diffraction information from a single sample.

There are two scattering processes experienced by the electrons during their passage through the specimen. The elastic scattering involves no energy loss and gives rise to diffraction pattern.

Characterization Techniques

Inelastic interactions between primary electrons and secondary electrons at heterogeneities such as grain boundaries, dislocations, defects, density variations in the intensity of transmitted electrons.

The high magnification or resolution of TEM is a result of the small effective electron wavelength which is given by relation $\lambda = \frac{h}{\sqrt{2meV}}$

where *m* and *e* electron mass and charge, h is Planck's constant and *V* is potential difference through which electrons are accelerated.

The higher the operating voltage of a TEM, greater is the lateral spatial resolution.

The disadvantage of TEM is its limited depth resolution.

Characterization Techniques

Selected Area Diffraction (SAD) offers a unique capability to determine the crystal structure of individual nanomaterials such as nanocrystals and nanorods and the crystal structure of different parts of the sample.

SAD patterns are often used to determine the Bravais lattices and lattice parameters of crystalline materials by the same procedure used in XRD.

TEM can be used to determine the melting point of nanocrystals. An electron beam is used to heat up the nanocrystals and the melting points are decided by the disappearance of diffracted pattern.

TEM can be used to measure the mechanical and electrical properties of individual nano-wires and nano-tubes.

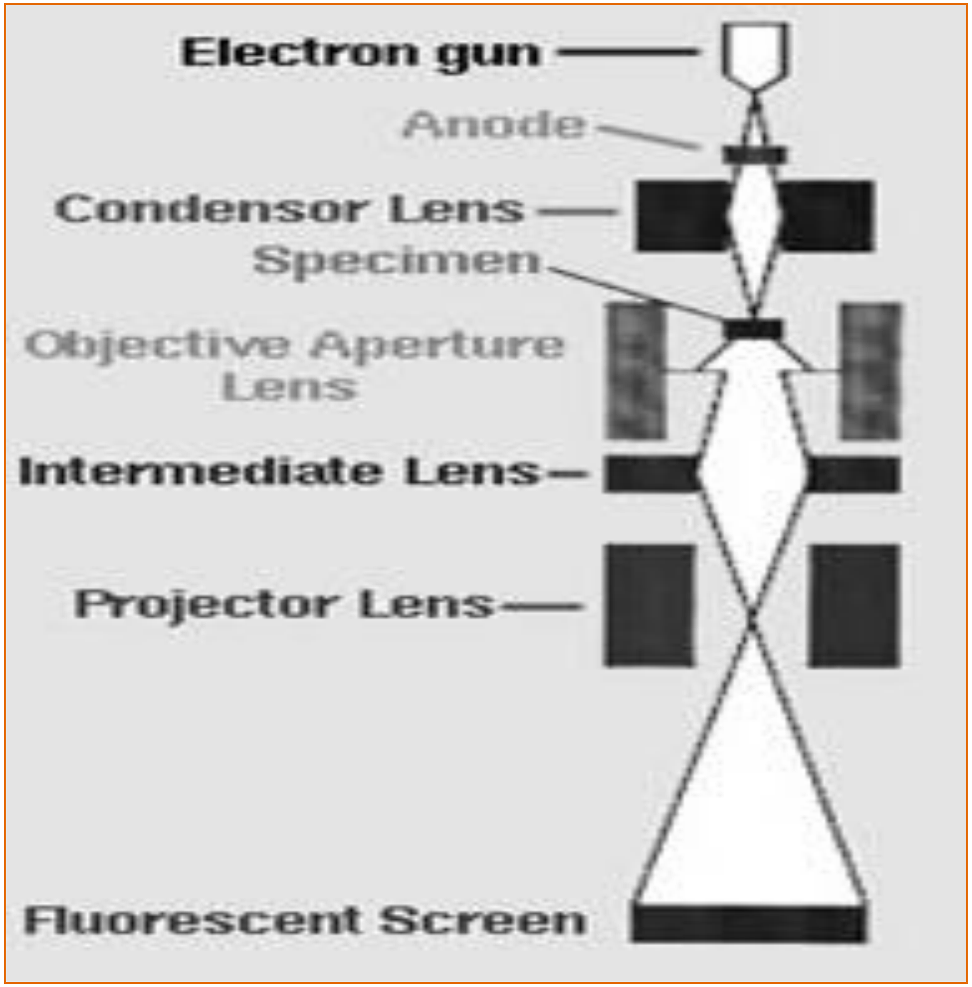
Characterization Techniques

TEM gives the following information:

Morphology: The size, shape and arrangement of particles as well as their relationship to one another on the scale of atomic diameters.

Crystallographic information: The arrangement of atoms in the specimen and their degree of order, detection of atomic-scale defects a few nanometers in diameters.

Compositional information: The elements and compounds the sample is composed of and their relative ratios.




Thank you!

Bottom-up Fabrication methods

Flow Chart for the Solution Combustion Synthesis