

2.4 Synthesis of nanomaterials:

Nanostructure materials have attracted a great deal of attention because their physical, chemical, electronic and magnetic properties show dramatic change from higher dimensional counterparts and depends on their shape and size.

Many techniques have been developed to synthesize and fabricate nanostructure materials with controlled shape, size, dimensionality and structure.

The performance of materials depends on their properties. The properties in turn depend on the atomic structure, composition, microstructure, defects and interfaces which are controlled by thermodynamics and kinetics of the synthesis.

Classification of Techniques for synthesis of Nanomaterials

There are two general approaches for the synthesis of nanomaterials.

(a) Top down approach

(b) Bottom up approach

(a) 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.

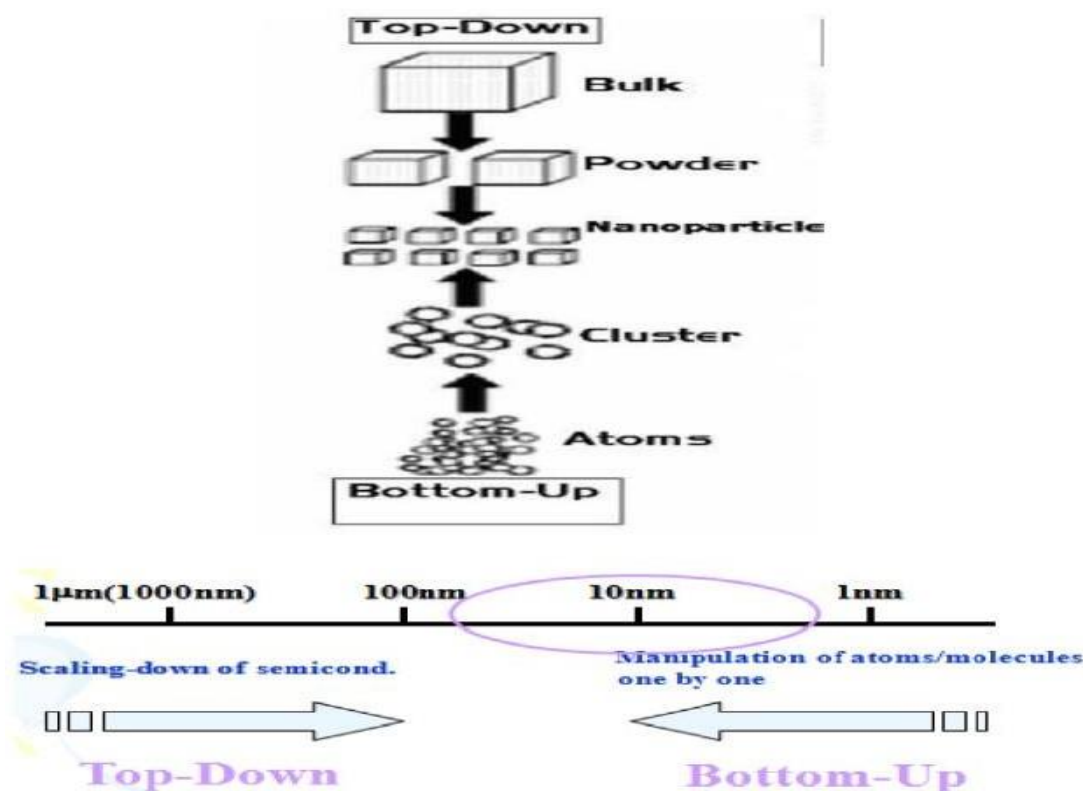
Top-down approaches are inherently simpler and depend either on removal or division of bulk material or on miniaturization of bulk fabrication processes to produce the desired structure with appropriate properties.

The biggest problem with the top-down approach is the imperfection of surface structure.

For example, nanowires made by lithography are not smooth and may contain a lot of impurities and structural defects on its surface. Examples of such techniques are high-energy wet ball milling, electron beam lithography, atomic force manipulation, gas-phase condensation, aerosol spray, etc.

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.
- Many of these techniques are still under development or are just beginning to be used for commercial production of nanopowders.
- Organometallic chemical route, reverse-micelle route, sol-gel synthesis, colloidal precipitation, hydrothermal synthesis, template assisted sol-gel, electrodeposition etc, are some of the well-known bottom-up techniques reported for the preparation of luminescent nanoparticles.



Schematic representation of 'top-down' and 'bottom-up' approaches for synthesis of nanoscale materials

1. Sol-Gel Techniques:

Sol-gel can be defined as the formation of an oxide network through polycondensation reactions of a molecular precursor in a liquid; The sol-gel method was developed in the 1960s mainly due to the need of new synthesis methods in the nuclear industry. A method was needed where dust was reduced (compared to the ceramic method) and which needed a lower sintering temperature. In addition, it should be possible to do the synthesis by remote control. The main benefits of sol-gel processing are the high purity and uniform nanostructure achievable at low temperatures. And many other advantages can be achieved such as; Sol-gel technique - to "dissolve" the compound in a liquid in order to bring it back as a solid in a controlled manner.

- Multi component compounds may be prepared with a controlled stoichiometry by mixing sols of different compounds. - The sol-gel method prevents the problems with co-precipitation, which may be inhomogeneous, be a gelation reaction. to convert everything to SiO_2 . A water ratio of $\text{RW}=1$ leads to complete hydrolysis but no condensation. Increasing the water content (i.e. lower RW) will reduce condensation Reducing the water content increases the condensation c- Type of catalyst used The electron density on Si will influence the reaction rate. $\text{Si-R} > \text{Si-OR} > \text{Si-OH} > \text{Si-O-Si}$ Acid catalyzed reaction demands high electron density Base catalyzed reaction demands low electron density This results in: Acid catalyzed: more straight chains Base catalyzed: more branched network. d- Type of solvent and ratio; the polarity, dipolar moment, viscosity, protolytic/non protolytic properties are important for the reactions taking place. Polar solvents stabilize polar gels by hydrogenbonding. Non-polar solvents are better for systems which are not completely hydrolyzed. e- Temperature f- pH g- Relative and absolute concentrations of the reactants.

Gelation: During reaction, objects will grow. However, a gel may not form As the sol aggregates the viscosity will increase until a gel is formed. The sol-gel transition (gel-point) is reached when a continuous network is formed. The gel- time is determined as the time when it is possible to turn the container upside- down. All fluid is kept in the gel, and the volume is maintained.

Ageing: structure modifications with time depending on temperature, solvent and pH conditions When the gel is formed, a large number of sol particles and clusters will still not have reacted. Ageing of the gel is therefore a very important stage in the process. The gel point is not a thermodynamic event As the viscosity rapidly increase, the solvent

is “trapped” inside the gel. The structure may change considerably with time, depending on pH, temperature and solvent. The gel is still “alive”. The liquid phase still contains sol particles and agglomerates, which will continue to react, and will condense as the gel dries. The gel is originally flexible. Groups on neighboring branches will condense, making the gel even more viscous. This will squeeze out the liquid from the interior of the gel, and shrinkage occur. This process will continue as long as there is flexibility in the gel.

Drying: Removing of the solvent phase Method influenced by the intended use of the dried material : When the liquid is removed from the gel several things may happen. When the liquid in the gel is replaced by air, major changes to the network structure may occur. If the structure is maintained, an aerogel is formed. If the structure collapses, a xerogel is formed. Normal drying of the gel leads to structural collapse due capillary forces drawing the walls of the pores together, and reducing the pore size. Cracking may occur when the tension in the gel is so large that it cannot shrink anymore.

Gas will enter the pores with a thin film of liquid on the walls. This will evaporate and only isolated spaces with liquid are left.

Densification: heating to convert the dried gel to a dense ceramic. For silica gels, the following reactions occur : - desorption of physically adsorbed solvent and water from the walls of micropores (100-200°C) - decomposition of residual organic groups into CO₂ (300- 500°C) - collapse of small pores (400-500°C) - collapse of larger pores (700-900°C) - continued polycondensation (100-700°C)

Sol-gel synthesis may be used to prepare materials with a variety of shapes, such as porous structures, thin fibers, dense powders and thin films.

Solvothermal Synthesis of Nanoparticles:

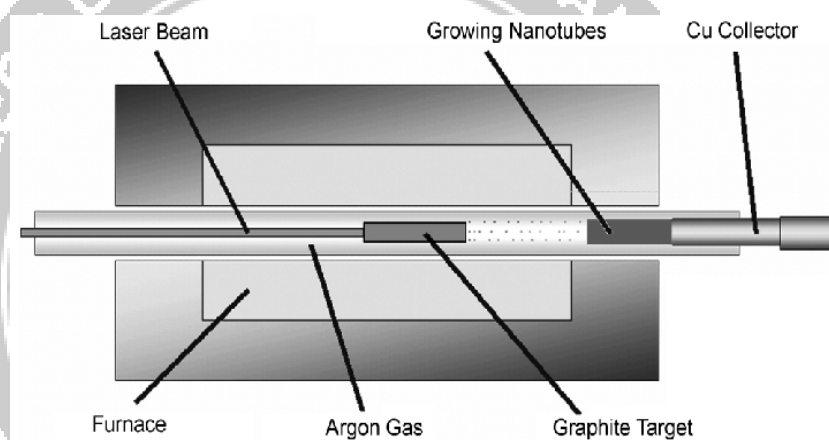
Solvothermal synthesis is a method for preparing a variety of materials such as metals, semiconductors, ceramics, and polymers. The process involves the use of a solvent under moderate to high pressure (typically between 1 atm and 10,000 atm) and temperature (typically between 100 °C and 1000 °C) that facilitates the interaction of precursors during synthesis. If water is used as the solvent, the method is called “hydrothermal synthesis.” The synthesis under hydrothermal conditions is usually performed below the supercritical temperature of water (374 °C). The process can be used to prepare many geometries including thin films, bulk powders, single crystals, and nanocrystals. In addition, the morphology (sphere (3D), rod (2D), or wire (1D)) of the crystals formed is controlled by manipulating the solvent super saturation, chemical of interest concentration, and kinetic control. The method can be used to prepare thermodynamically stable and metastable states including novel materials that cannot be easily formed from other synthetic routes. Over the last decade, a majority (~80%) of the literature concerning solvothermal synthesis has focused on nanocrystals; therefore, this review will highlight some advances in nanocrystalline, solvothermal synthesis.

Example of Zinc oxide compound that can be prepared solvothermally and will exhibit quantum dot effects. In one method, zinc acetate dihydrate was dissolved in 2-propanol at 50 °C. Subsequently, the solution was cooled to 0 °C and NaOH was added to precipitate ZnO. The solution was then heated to 65 °C to allow ZnO growth for a period of time before a capping agent (1-dodecanethiol) was injected into the suspension to arrest the growth.

The rod-shaped ZnO nanocrystals exhibit an absorption spectrum indicative of the quantum effect.

Laser ablation:

This method is applicable for high melting point elements and transition metals.



In this method, a solid metal rod is ablated using a Nd:YAG laser (high Power) in a chamber containing Ar gas. In the plasma that results from the laser ablation, metal atoms are evaporated and condensed on water cooled substrate. Later the substrate is heated to remove the impurities.

NPs of Iron, gold, palladium, and compounds of sulphide are prepared by this method.

Advantage:

capable of High deposition rate of 2-3 g/min

disadvantages:

High temperature method

low quality of material deposited

Chemical vapour deposition:

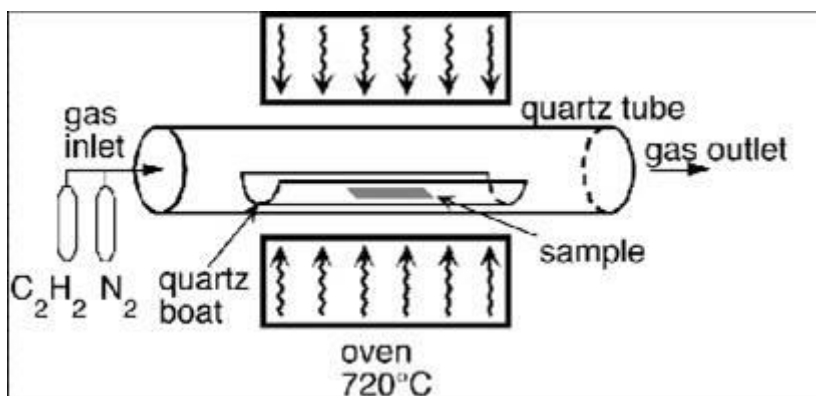
The chemical vapour deposition method (CVD) involves a chemical reaction. CVD procedure is mostly used in semiconductor manufacturing for depositing thin films of different materials. The method involves one or more volatile precursors, the substrate is exposed to those precursors that decompose on it and form the desired deposit. The vaporized precursors are inserted into a CVD reactor and adsorb onto a substance being placed at high temperature. The molecules that get adsorbed react with other molecules or decompose to form crystals. The three steps in CVD method are:

Reactants are transported on the growth surface by a boundary layer.

Chemical reactions occur on the growth surface.

By products produced by the gas-phase reaction has to be removed from the surface. Homogeneous nucleation occurs in gas phase and heterogeneous nucleation happens in a substrate.

The CVD method can synthesize ultrafine particles of less than $1\ \mu\text{m}$ by the chemical reaction taking place in the gaseous phase. The reaction can be controlled to produce nanoparticles of size ranging from 10 to 100 nm



ELECTROSPINNING:

Electrospinning is a fiber production method which uses electric force to draw charged threads of polymer solutions or polymer melts up to fiber diameters in the order of some hundred nanometers.

Electrospinning shares characteristics of both electrospaying and conventional solution dry spinning of fibres.

The process does not require the use of coagulation chemistry or high temperatures to produce solid threads from solution.

This makes the process particularly suited to the production of fibres using large and complex molecules.

Electrospinning from molten precursors is also practiced; this method ensures that no solvent can be carried over into the final product.

STEPS OF PROCESSING

When a sufficiently high voltage is applied to a liquid droplet, the body of the liquid becomes charged, and electrostatic repulsion counteracts the surface tension and the droplet is stretched; at a critical point a stream of liquid erupts from the surface. This point of eruption is known as the Taylor cone.

If the molecular cohesion of the liquid is sufficiently high, stream breakup does not occur (if it does, droplets are electrospayed) and a charged liquid jet is formed.

As the jet dries in flight, the mode of current flow changes from osmic to convective as the charge migrates to the surface of the fiber.

The jet is then elongated by a whipping process caused by electrostatic repulsion initiated at small bends in the fiber, until it is finally deposited on the grounded collector. The elongation and thinning of the fiber resulting from this bending instability leads to the formation of uniform fibres with nanometer-scale diameters.

PARAMETERS OF ELECTROSPINNING

- ✚ Molecular weight, molecular-weight distribution and architecture (branched, linear etc.) of the polymer
- ✚ Solution properties (viscosity, conductivity and surface tension)
- ✚ Electric potential, flow rate and concentration
- ✚ Distance between the capillary and collection screen
- ✚ Ambient parameters (temperature, humidity and air velocity in the chamber)
- ✚ Motion and size of target screen (collector)
- ✚ Needle gauge