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Synthesis of Nanomaterials—Physical Methods

5.1. INTRODUCTION

There are various techniques for the synthesis of nanostructure materials (and/or nanoparticles). Methods of synthesis may be broadly classified into two categories- top-down methods or bottom-up methods. Synthesis methods are further divided into three classes :

1. Physical Methods : Nanoparticles may be synthesized using a number of physical methods which are listed in Fig. 5.1. These methods are of two types viz mechanical type and vapour deposition type. These methods work at high temperatures. The highest working temperatures are usually greater than 350°C.

2. Chemical Methods : These are simple and inexpensive methods for synthesizing nanoparticles. The highest working temperatures are usually below 350°C. Large quantities of materials can be produced with variety of sizes and shapes of particles. A number of chemical methods are possible as shown in Fig. 5.1.

3. Biological Methods : Biological methods are based on the use of micro-organisms (fungi, yeast, bacteria etc.) or plant extracts (and enzymes) or use of templates such as DNA, viruses and membranes etc. This type of synthesis is environment friendly and least toxic and therefore called green synthesis. Various green methods for synthesis of nanoparticles are shown in Fig. 5.1.

5.2. FACTORS AFFECTING SYNTHESIS OF NANOPARTICLES

There are various factors which must be taken into consideration while synthesizing and characterizing nanoparticles. A brief discussion of these factors is as follows :

1. Temperature : It is an important parameter that affects the synthesis of nanoparticles using physical, chemical or biological methods. In physical methods highest working temperatures are required which are usually above 350°C. Chemical methods require a temperature less than 350°C. However in biological methods, synthesis of nanoparticles requires either ambient temperature or a temperature of less than 100°C. Temperature of the reaction medium determines the nature of the nanoparticle formed.

2. Pressure : The pressure is another important parameter for the synthesis of nanoparticles. Pressure applied to the reaction medium affects the shape and size of the nanoparticles being synthesized.

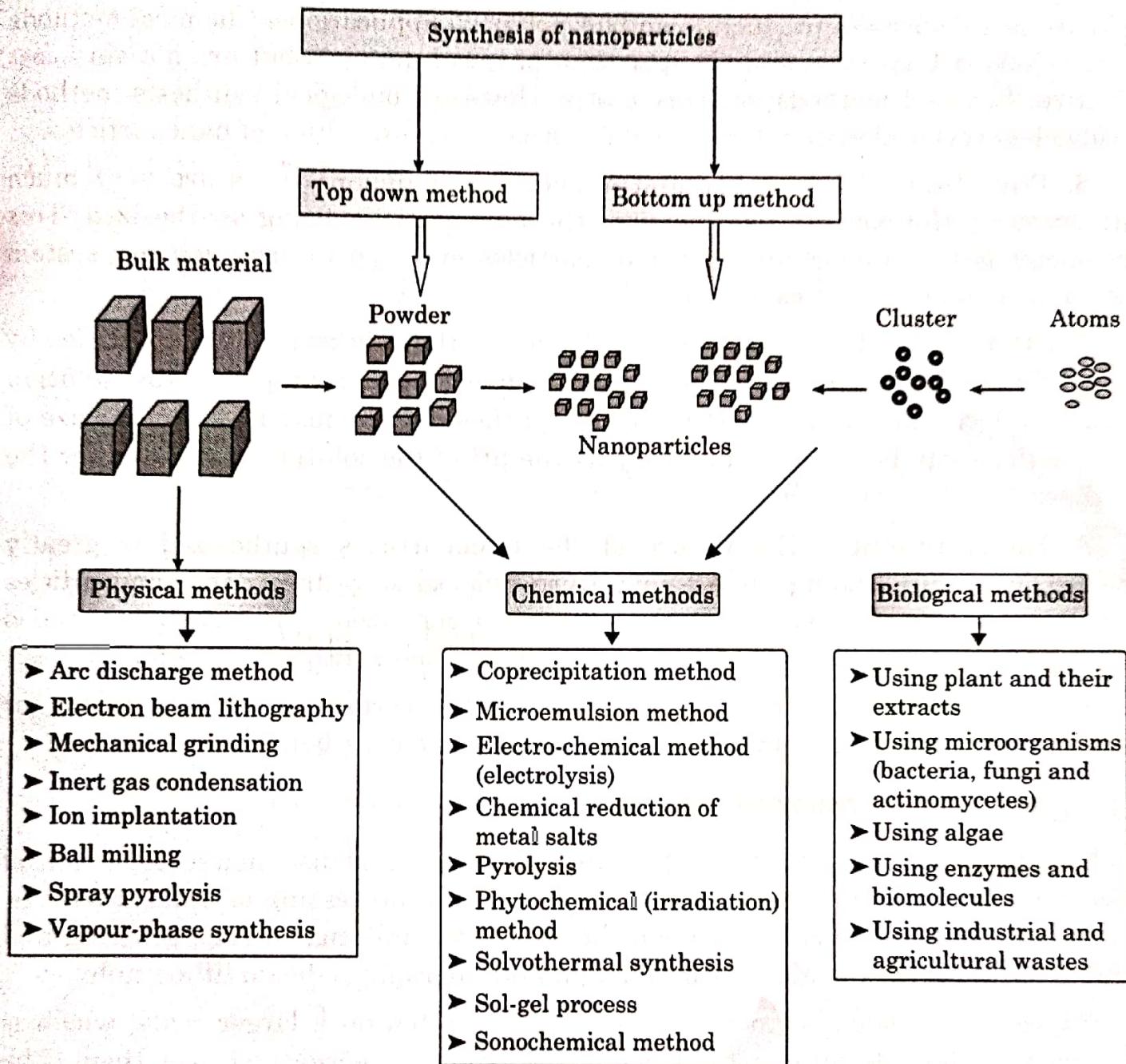


Fig. 5.1. Methods for synthesis of nanoparticles

3. Time : The quality and type of nanoparticle being synthesized depends upon the length of time during which reaction medium is incubated.

4. Particle Size and Shape : Particle size is a key factor in determining the properties of nanoparticles. For example the melting point of nanoparticles decreases with decrease in size of particles. The colour of emitted light also changes with nanoparticle size. The shape of the nanoparticles influence the chemical properties. Capping agents (e.g. polyvinylpyrrolidone) are used to stop the overgrowth of nanoparticles in colloidal synthesis of particles.

5. Cost of Preparation : The cost of synthesis of nanomaterials is a key issue which decides the potential applications of these materials. The cost of synthesis needs to be regulated and controlled. Method of synthesis should be cost effective so as to be useful for mass production and for potential applications. Chemical methods though have a high yield and cheaper than physical methods but are not very cost effective. Physical methods are very costly. However, biological synthesis methods involve less cost and is therefore useful for large scale production of nanoparticles.

6. Pore Size : The quality and application of nanoparticles are very much influenced by the porosity parameter of the nanoparticles being synthesized. This parameter is very important when nanoparticles are used in drug delivery system e.g., in the treatment of cancerous cells.

7. pH Value : This is an important factor for the synthesis of nanoparticles by chemical and biological methods. It has been observed that pH of the solution medium affects the size and texture of the synthesized nanoparticles. So the size of nanoparticles can be controlled by varying the pH of the solution being used for the synthesis.

8. Environment : The nature of the nanoparticles synthesized is greatly affected by the surrounding environment. During biological synthesis, the nanoparticles form a coating that makes them thicker and larger sized. The environment also influences the physical structure and chemistry of the synthesized nanoparticles.

Besides the above discussed factors, there are certain other parameters (or factors) that greatly influence the nature of nanoparticles being synthesized.

5.3. TOP-DOWN APPROACHES

Top-down approaches of synthesizing nanomaterials use macroscopic initial structures, which can be externally controlled in the processing of nanostructures. Typical examples are etching through the mask, ball milling, cutting, grinding and application of severe plastic deformation, photolithography, e-beam lithography etc.

Top-down methods begin with a pattern generated on a larger scale, which is reduced to nanoscale after a sequence of operations is performed over them. The **major drawback** of these methods is that they require large installations and huge capital is required for building their set-up. Therefore these methods are **quite expensive**. Moreover the **growth process is slow** and hence these methods are not suitable for large scale production. However top-down methods are very suitable for laboratory experimentation.

Top-down approaches are based on grinding of material. Thus these processes are subtractive in nature. The parts of mechanical devices used to shape objects are stiff and hard, so these methods are **not suitable for soft samples**. The top-down approach anticipates nanodevices that must be built piece by piece in a number of stages, much like manufactured items are made. Scanning probe microscopy (SPM)

is an important technique used both for synthesis and characterization of nanomaterials by top-down approach. Atomic force microscope (AFM) tips can be used as a nanoscale "write head" to deposit a resist, which is then followed by an etching process to remove material in a top-down method. **Very high quality thin films can be deposited** with nanometer control perpendicular to the plane of a substratum and this method is called **physical vapour deposition (PVD)**. In this method the material to be deposited is evaporated from the reservoir or sputtered from the target.

Chemical vapour deposition (CVD) is another technique for the synthesis of nanostructures using top-down approach. In this method, the precursor (which is a compound that participates in a chemical reaction that produces another compound) of the thin layer is a reactive gas or mixture of gases and the substratum is typically heated to accelerate chemical reaction to form a solid product deposited as a film. The decomposition can be enhanced with a plasma. In MOCVD, the growth of crystals is by chemical reactions instead of physical deposition (as in MBE).

Metal-Organic Chemical Vapour Deposition (MOCVD) also known as Vapour Phase Epitaxy (MOVPE) takes place not in a vacuum, but from the gas phase at moderate pressures (2 to 100 kPa). This is a suitable technique for **growing compound semiconductors** from the surface reaction of organic compounds and metal hydrides containing the required chemical elements.

Ion implantation is used to modify existing surfaces of materials. In this method, electrostatically charged high energy (10-100 Kev) ions are directed towards the surface, where they arrive with kinetic energies several orders of magnitude higher than the binding energy of the host material, and become implanted in a surface layer that may be tens of nanometers thick.

In the top-down approach nano-objects are obtained from larger entities without atomic level control. Many technologies that emerged out of conventional solid state silicon methods for fabricating microprocessors are now capable of creating features smaller than 100 nm, which lie in the domain of nano-technology. Giant magneto resistance (GMR) based hard drives which have been already commercialized use top-down approach. Top-down methods can also be used to create nano-electromechanical systems (NEMS). Top-down methods use lithography in which a bulk material is reduced in size to nanoscale pattern. In top-down approach cutting, milling and shaping of materials into the desired shape and order takes place.

Electron beam lithography and **X-ray lithography** have been developed as an alternative to photolithography technique used in top-down methods. However electron beam technique is very expensive and also very slow. In top-down methods the starting material is generally solid. In these methods the material suffers an **increase in surface defects** since the material is subjected to internal stress.

5.4. BOTTOM-UP APPROACHES

Bottom-up approaches of synthesis of nanomaterials include the miniaturization of materials components to atomic level with further self assembly process leading to the formation of nanostructures. During self assembly the physical forces operating at nanoscale combine basic units into larger stable structures. Typical examples are quantum dot formation during epitaxial growth and formation of nanoparticles from colloidal dispersion, physical vapour deposition, chemical vapour deposition etc.

In the bottom-up methods we start with atoms or molecules and build nanostructures by the direct manipulation of atoms or molecules. *Bottom-up methods involve atom-by atom, molecule-by-molecule or cluster-by-cluster manipulation for synthesis of nanostructures.* In these methods the starting material is either in liquid state or gaseous state. These techniques include chemical synthesis, self-assembly and positional assembly. Dual polarisation interferometry is one tool suitable for characterization of self assembled thin films.

Bottom-up approach is based on the principle of molecular recognition (*i.e.*, self assembly). Self assembly means growing more and more things of one's kind from themselves. The idea of self assembly (shake and bake) is to gather precursors in random positions and orientations and supply energy (shaking) to allow them to sample configuration space. The hugeness of this space suggests that a convergent pathway is inherent in the process in order to allow it to be completed in a reasonable time. Once the precursors are in position, "baking" may be required to strengthen the bonds connecting them and fix the final object permanently.

Many biological systems exhibit remarkable capabilities of assembling themselves starting from a randomly arranged mixture of components. The examples are bacteriophage virus, and proteins and ribonucleic acids (RNA) which can be spontaneously transformed from a random coil of the linear polymer to a compact, ordered 3D structure. In this approach the starting precursors of the final structures have to be very carefully designed.

The highly specialized chemistry of living systems, the fragility of many of its products and its inherent variability at many levels have made self assembly unsuitable for mimicking directly and incorporating into our present industrial system.

Bottom-up approaches are capable of producing devices in parallel and much cheaper than top-down methods but becomes difficult as the size and complexity of the desired assembly increases. Most useful structures require complex and thermodynamically unlikely arrangements of atoms. Watson-Crick base pairing and enzyme substrate interactions are notable examples of self assembly based on molecular recognition in biology. Approaches from the field of "Classical Chemical" synthesis also aim at designing molecules with well defined shape. AFM tips can be used as a nanoscale "write head" to deposit a chemical upon a surface in a desired pattern in a process called **dip pen nano-lithography**.

In the bottom-up methods high precision actuators (devices that convert electrical energy to mechanical energy and vice-versa) move atoms from place to place. Micro tips such as AFM tips emboss or imprint materials. Electron or ion beams are directed onto the surface at which device is to be grown.

Nature uses self-assembly in ultra-fine ways. The natural world is self assembled. In nature, spontaneous organization of molecules into stable, structurally well defined aggregates of nanometer dimensions takes place. Molecules can be transported to surfaces through liquids to form self-assembled monolayers (i.e. single atom thick layers). Atomic layer deposition (ALD) is one of the bottom-up methods which is very useful in depositing thin atomic layers on a substrate. Bottom-up methods provide improved nanostructures with less or defect free, homogeneous and long and short range orders.

5.5. BALL MILLING

A ball mill is a device used to grind and blend materials for use in mineral dressing processes, paints, pyrotechnics, ceramics and selective laser sintering. It is a **physical method of synthesis of nanoparticles** and is an example of **top down approach** of producing nanomaterials.

The ball mill consists of a hollow cylindrical shell which rotates about its axis. The axis of the shell may be either horizontal or inclined at a small angle to the horizontal. It is partially filled with the balls which may be made of chrome steel, stainless steel, ceramic or rubber. These balls form the grinding media of the ball mill. The inner surface of the cylindrical shell is generally lined (i.e., coated) with an abrasion resistant material e.g., rubber or manganese steel. Rubber is preferred for this purpose due to less wear in mills lined with rubber. The length and diameter of the ball mill are nearly equal.

Principle : A ball mill works on the **principle of impact and attrition** (i.e. friction). The size reduction is carried out by impact as the balls drop from near the top of the shell. In a continuously operated ball mill, the material to be ground is fed from the left through a 60° cone and the resulting material (product) is discharged through a 30° cone to the right both not shown in the figure 5.2. With the rotation of the shell, the balls are lifted up on the rising side of the shell and then they drop down on to

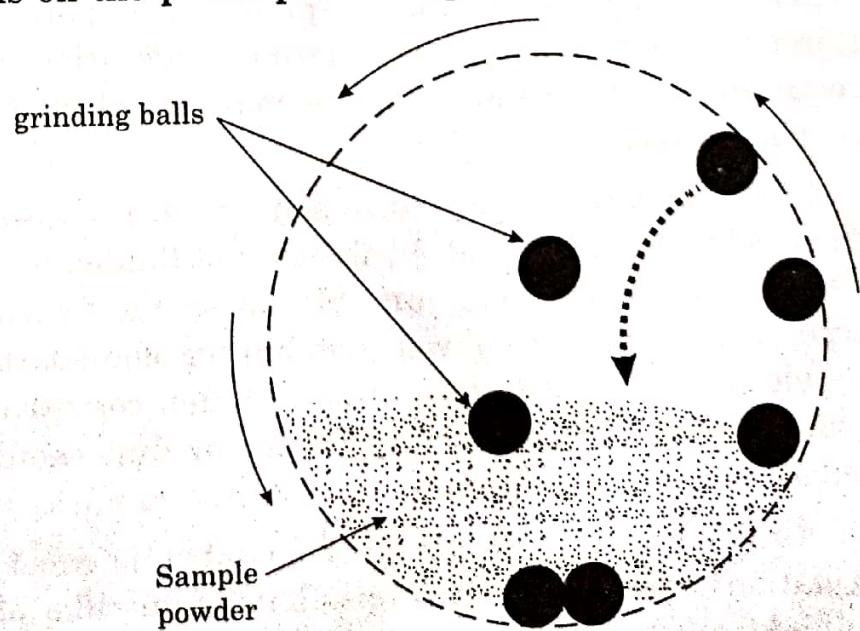


Fig. 5.2. Ball Mill

the feed, from near the top of the shell. In this process, the solid particles in between the balls and ground are reduced in size by impact. A number of materials can be used as grinding media in a ball mill e.g., ceramic balls, flint pebbles and stainless steel balls.

The grinding works on the principle of critical speed which is the speed after which the steel balls start rotating along the direction of the cylindrical device, thus causing no further grinding. Industrial ball mills can operate continuously, fed at one end and discharge at the other end.

High quality ball mills are potentially expensive and can grind mixture particles to as small as 5 nm which enormously increases the surface area and the reaction rates.

Grinding Media

Many types of grinding media are suitable for use in a ball mill, each material having its own specific properties and advantages. The key properties of grinding media which should be taken into consideration at the time of their selection are its size, density, hardness and composition. Let us discuss the effect of these parameters one by one :

1. Size : The smaller the media particles, the smaller the size of the particles of the final product. However, the grinding media particles should be substantially larger than the largest pieces of the material which is to be ground by the mill.

2. Density : The density of the grinding media should be more than the density of the material being ground. The grinding media should not float at all on top of the material to be ground.

3. Hardness : The grinding media should be hard enough to grind the material but its toughness should not wear down the tumbler at a fast pace.

4. Composition : Various grinding applications have special requirements. Where the colour of the finished product is important, the colour and material of the grinding media must be taken into consideration. In the case of low contamination requirement, the grinding media may be selected for ease of separation from the finished product.

An alternative approach to separation is to use media of the same material as the product being ground. In the case of flammable products, steel media cannot be used as steel can become an ignition source for such products. Therefore for such type of products, either wet grinding or non-sparking media like ceramic or lead should be chosen for this purpose. When corrosive substances are present during grinding then stainless steel, ceramic or flint should be used as grinding media to reduce or discourage corrosion.

In some cases, the grinding chamber is filled with an inert gas. It prevents oxidation or explosive reactions that might take place in its absence between the ambient air inside the mill and the material to be ground.

Types of Ball Mill

There are two kinds of ball mill (i) grate type, and (ii) overfall type, according to different ways of discharging material. Large to medium sized ball mills are mechanically rotated on their axis, but small ones normally consists of a cylindrical capped container that sits on two drive shafts. Some of the common ball mills are as follows :

1. Vibrating ball mill
2. Low energy tumbling ball mill
3. High energy ball mill

Besides common ball mills as discussed above, there is also a planetary ball mill. A **planetary ball mill** is smaller than a common ball mill and is generally used in laboratories for research purpose. It consists of at least one grinding jar which is arranged eccentrically on a sun wheel. The sun wheel moves in a direction opposite to that of the grinding jars. The grinding balls in the grinding jars are subjected to superimposed rotational movements. The difference in speeds between the balls and grinding jars produces an interaction between frictional and impact forces due to which high energies are released. The interplay between frictional or impact forces results in very effective size reduction of the particles of the material to be ground in a planetary ball mill. Planetary Ball mill is a most frequently used system for mechanical alloying since only a very small amount of powder is required. It can be used for high speed ball milling.

Advantages of a Ball Mill : Ball mills have several advantages over other systems used for making material in the powder form. These are :

1. The cost of installation and grinding medium is low hence inexpensive process.
2. Ball milling is suitable for both batch and continuous operation
3. Ball milling is suitable for both open and closed circuit grinding
4. Material of any hardness can be grounded
5. Small particles with narrow size distribution (2 to 20 nm) can be produced.

Drawbacks of high Energy Ball Milling : Low surface, highly polydisperse size distribution and partially amorphous state of the powder. Shape of the nanomaterial is irregular. Contamination of product may occur as a result of wear and tear.

Applications

A ball mill can be used for the synthesis of nanostructured metaloxides for gas detection. It can also be used for grinding materials such as ores, chemicals, ceramic raw materials and paints etc. Grinding can be carried out either wet or dry but wet grinding is performed at low speed. Ball mills are used in pyrotechnics and the manufacture of black powder. However, it cannot be used in the preparation of some

6.5. SOL-GEL PROCESS

It is a **bottom-up approach** of synthesis which is in use since late 1800s. The modern sol-gel technique started around 1970s. It is an example of liquid phase synthesis. A sol is a colloidal or molecular suspension of solid particles or ions in a solvent. A gel is a semi-rigid mass that forms when the solvent from the sol begins to evaporate and the particles or ions left behind begin to join together in a continuous network. Sol-gel is a **multi-step chemical solution process** (i.e. a wet chemical technique) widely used recently in the fields of materials science and ceramic engineering to make ceramic and glass materials in the form of thin films, fibers, or powders.

The process of sol-gel generally starts with the mixing of metal alkoxides or salts in water or in a suitable solvent (in most cases alcohol) at ambient or slightly elevated temperatures. Thus metal alkoxides and metal chlorides are typical precursors in this process which undergo hydrolysis and polycondensation reactions. The most widely used are tetramethoxysilane (TMOS), and tetraethoxysilanes (TEOS) which form silica gels. Alkoxides are immiscible in water. They are organometallic precursors for silica, aluminum, titanium, zirconium and many others. In the process metal-oxo or metal-hydroxo polymers are formed.

In sol-gel process it is **very important to control the pH of the starting solution** to avoid the precipitation as well as to form the homogeneous gel, which can be achieved by the addition of base or acidic solutions. Organic compounds with hydrophilic functional groups in small molecules such as citric acid, succinic acid, oxalic acid, tartaric acid etc. and polymers (e.g. polyacrylic acid and polyvinyl pyridine) can be used with metal ion sources to form the sol as well as control the particle size and uniformity of the products. **A catalyst is used to start the reaction and control pH of the solution.**

Sol-gel formation occurs in four stages:

1. Hydrolysis
2. Condensation
3. Growth of particles
4. Agglomeration of particles.

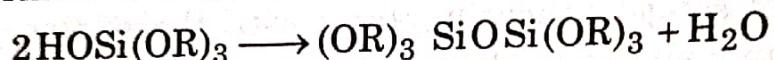
These processing steps are discussed below :

Hydrolysis : In hydrolysis, addition of water replaces alkoxy groups [OR] with hydroxyl groups [OH]. Hydrolysis occurs by attack of oxygen on silicon atoms in silica gel. A catalyst such as HCl and NH₃ accelerates the hydrolysis. Hydrolysis

continues until all [OR] groups are replaced by [OH-] groups. Subsequent condensation involving silanol group (Si-OH) produced siloxane bonds (Si-O-Si), alcohol and water.

Condensation : Polymerization to form siloxane bond occurs by either a water producing or alcohol producing condensation reaction. Condensation reaction finally results in the formation of monomer, dimer, cyclic tetramer, and high order rings. Hydrolysis rate is influenced by pH, reagent concentration and H₂O/Si molar ratio. Ageing and drying are also important steps. By controlling these factors the structure and properties of sol-gel derived inorganic networks can be varied.

Growth and Agglomeration : With increase in the number of siloxane bonds, the molecules aggregate in the solution, where they form a network and then a gel is formed upon drying. The water and alcohol are driven off and the network shrinks. For pH values greater than 7 and H₂O/Si value ranging from 7 to 5, spherical nanoparticles are formed. The reactions involved are as follows:



For pH > 7, silica is more soluble and silica particles grow in size. The growth of particles stops when the difference in solubility between the smallest and largest particles becomes indistinguishable. Higher temperatures result in the formation of larger particles.

Advantages of Sol-Gel Technique

- Sol-gel method of thin film deposition is a cheap and low temperature technique with fine control on the chemical composition of the product.
- It is able to produce high purity products because the organo-metallic precursor of the desired ceramic oxides can be mixed, dissolved in a specified solvent and hydrolyzed into a sol, and subsequently a gel.
- By this process we can get at low temperature, high density glass without high temperature re-crystallization.
- Smaller particle size and morphological control in powder synthesis.
- It can produce thin bond coating to provide excellent adhesion between the metallic substrate and the top coat.
- This process is able to coat onto large or complex shape objects.
- Sol-gel process can produce thick coating to provide corrosion protection performance.
- This process can have low temperature sintering capability, usually in the range 200-600°C
- Sol-gel is a versatile process as it can produce aerogels, xerogels, ceramic materials, nanopowders, nanorods and nanostructured thin films etc.

Disadvantages of Sol-Gel Technique

- The cost of the raw materials (i.e. chemicals) may be high as compared to mineral based metal ion sources .
- Products would contain high carbon content when organic reagents are used in preparative steps and this would inhibit densification during sintering
- There is often a large volume shrinkage and cracking during drying due to the generation of large capillary stresses .
- It is difficult to avoid residual porosity and OH-groups
- Being a multi-step process, close monitoring is required
- The process is not very clean. It contains undesired atoms, molecules, ions etc. This deteriorates electrical and optical properties of deposited material.

Applications

- Sol-gel process has been extensively used for forming coatings on window glass
- It can be used to produce powders and fibers
- Sol-gel technique can be used to deposit films and coatings on a range of different surfaces, enabling a flexibility which is not available in many vapour phase methods
- It is used in drug delivery systems
- In making ultraviolet (UV) protection gels
- For producing lubricants and scratch free paints
- In developing new fire retardant materials.

6.6. ELECTRODEPOSITION

Electrodeposition is a liquid phase chemical method of synthesis of nanostructured materials. It belongs to the category of **bottom-up approach** of synthesizing nanomaterials. Thin films have been extensively used in microelectronics. There are numerous and growing applications in communications, optical electronics, coatings of all kinds and in energy generation. Electrodeposition is a long established method to deposit metal layers on a conducting substrate. Ions in the solution are deposited onto the negatively charged cathode, carrying charge at the rate which is measured in the form of a current in the external circuit. The layer thickness is a function of current density and the time for which the current flows. The deposit can be detached if the substrate is chosen to be soluble by dissolving it away (Fig. 6.3).

Electrodeposition is the most suitable technique for depositing nanostructured thin films from aqueous solution served as samples under investigation. It is particularly suited to the fabrication of heterojunctions simply through a change in the deposition electrolyte. Electrodeposition of metallic layers

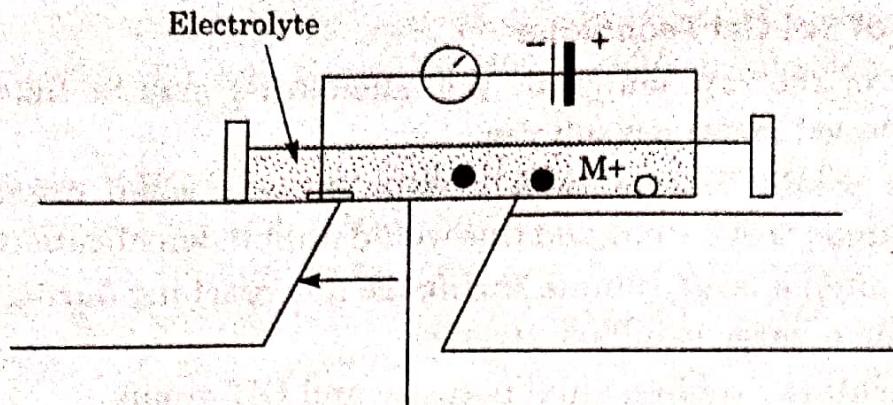


Fig. 6.3. Electrodeposition

from aqueous solution is based on the discharge of metal ions present in the electrolyte at a cathode surface (the substrate or component). The metal ions accept an electron from the electrically conducting material at the solid-electrolyte interface and then deposit as metal atoms onto the surface. The electrons required for this purpose are either supplied from an externally applied potential source or are surrounded by a reducing agent present in solution (electroless reduction). The metal ions are derived either from metal salts added to solution, or by the anodic dissolution of the so-called **sacrificial anode** which is made of the same metal that is to be deposited at the cathode.

Electrodeposited thin films are mechanically strong and uniform. It has been observed that certain properties of nanostructured deposits such as hardness, wear resistance and electrical resistivity are strongly affected by the grain size. A combination of increased hardness and wear resistance gives superior coating performance. Nanocomponents fabricated using electrodeposition include wires consisting of alternating magnetic and non-magnetic layers each only a few nanometers thick and single-electron transistors (SETs) using niobium. A slow electrodeposition process will produce a better finished product.

Advantages

- Electrodeposition is relatively cheap and fast process and allows complex shapes
- It has high utilization rate of the raw materials
- Low energy consumption process
- Low material waste
- Ease of implementation and room temperature operation
- An exceptionally versatile process
- Precise control of film thickness, morphology, stoichiometry, doping etc. is possible
- Isothermal technique which avoids the negative effects of inter-diffusion, contamination, and dopant redistribution.

Applications

- Electrodeposition has three main characteristics that make it so well suited for nano-, bio- and microtechnologies. These characteristics are-
- Electrodeposition can be used to grow functional material through complex 3D masks.
- It can be performed near room temperature from water-based electrolytes.
- This process can be scaled down to the deposition of a few atoms or up to large dimensions.

Besides continuing traditional applications, new applications of electrodeposition will emerge rapidly, especially in the fields of nanoelectronics, biotechnology, and energy engineering. Some specific applications of electrodeposition are as follows:

- Polymers and biomaterials are electrodeposited for biomedical applications
- Metal oxides and compound semiconductors are grown electrochemically for electronic or optoelectronic applications.