

Methods of Synthesis of Nanoparticles

Divya Sanganabhatla, Shyam Sunder.R

Abstract: Nanoparticles are particles between 1 to 100nm in size. Nanotechnology is an interdisciplinary and crossing-over technology. The most important thing is observing and characterizing the phenomena showing in the nanotechnology, but also the practical use of new and unusual properties of nanoparticles. In this present work a comparative study on the different preparation methods of nano materials including Chemical Vapor Deposition, Chemical Vapor Condensation, Mechanical Attrition, Chemical Precipitation, Gas Condensation, Sol-Gel Techniques, Electrodeposition, are studied.

Keywords: Nanoparticles, Preparation, Chemical Vapor Condensation, Mechanical Attrition, Sol Gel Method.

I. INTRODUCTION

The concept of nanotechnology was introduced by physics Nobel laureate Richard P Feynman in his famous lecture entitled 'There's plenty of room at the bottom' at the December 1959 meeting of the American Physical Society. Nanotechnologies are now widely considered to have the potential to bring benefits in areas as diverse as drug development, information and communication technologies, and the production of stronger and lighter materials. The development of nanotechnologies is a modern multidisciplinary science involving the fields of physics, chemistry, biology and engineering, the production of nanoparticles. Nanocrystalline materials can be prepared by combining small clusters or breaking-up of larger material to smaller and smaller particles. There is a variety of methods for preparation of nanostructural materials from the gaseous, liquid or solid phase. In recent years, nanostructured materials have been prepared mainly using the following methods.

II. PREPARATION OF NANOPARTICLES

Nanocrystalline materials can be prepared by combining small clusters or breaking-up of larger material into smaller particles. There is a variety of methods for preparation of nanostructural materials from the gaseous, liquid or solid phase.

A. Physical Methods:

- a. Mechanical Attrition
- b. Vapourization

a. Mechanical attrition: It produces its nanostructures by the structural decomposition of coarser grained structures as a result of plastic deformation. Elemental powders of Al and β -SiC were prepared in a high energy ball mill. More recently, Ceramic/ceramic nanocomposite WC-14% MgO material has been fabricated.

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Divya Sanganabhatla, Research Scholar, University College of Technology, Osmania University, Hyderabad -500007, India. E-mail: divya.dharba@gmail.com

Shyam Sunder R, Professor, University College of Technology, Hyderabad -500007, India

The ball milling and rod milling techniques belong to the mechanical alloying process which has received much attention as a powerful tool for the fabrication of several advanced materials. Mechanical alloying is a unique process, which can be carried out at room temperature. The process can be performed on both high energy mills, centrifugal type mill and vibratory type mill, and low energy tumbling mill [1-3]. High energy mills include: Attrition Ball Mill Planetary Ball Mill Vibrating Ball Mill Low Energy Tumbling Mill High Energy Ball Mill

Attrition Ball Mill: The milling procedure takes place by a stirring action of a agitator which has a vertical rotator central shaft with horizontal arms (impellers). The rotation speed was later increased to 500 rpm. Also, the milling temperature was in greater control.

Planetary Ball Mill: Centrifugal forces are caused by rotation of the supporting disc and autonomous turning of the vial. The milling media and charge powder alternatively roll on the inner wall of the vial and are thrown off across the bowl at high speed (360 rpm).

Vibrating Ball Mill: It is used mainly for production of amorphous alloys. The changes of powder and milling tools are agitated in the perpendicular direction at very high speed (1200 rpm).

Low Energy Tumbling Mill: They have been used for successful preparation of mechanically alloyed powder. They are simple to operate with low operation costs. A laboratory scale rod mill was used to prepare homogenous amorphous Al₃₀Ta₇₀ powder by using S.S. cylinder rods. Single-phase amorphous powder of Al_xTm_{100-x} with low iron concentration can be formed by this technique.

High Energy Ball Mill high-energy ball milling is an already established technology, however, it has been considered dirty because of contamination problems with iron. However, the use of tungsten carbide component and inert atmosphere and/or high vacuum processes has reduced impurity levels to within acceptable limits. Common drawbacks include low surface, highly poly disperse size distribution, and partially amorphous state of the powder. These powders are highly reactive with oxygen, hydrogen and nitrogen. Mechanical alloying leads to the fabrication of alloys, which cannot be produced by conventional techniques. It would not be possible to produce an alloy of Al-Ta, because of the difference in melting points of Al (933 K) and Ta (3293 K) by any conventional process. However, it can be fabricated by mechanical alloying using ball milling process.

III. VAPOURIZATION METHOD

Gas Condensation: Gas condensation was the first technique used to synthesize nanocrystalline metals and alloys. In this technique,



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a metallic or inorganic material is vaporized using thermal evaporation sources such as Joule heated refractory crucibles, electron beam evaporation devices, in an atmosphere of 1-50 m bar. In gas evaporation, a high residual gas pressure causes the formation of ultra fine particles (100 nm) by gas phase collision. The ultrafine particles are formed by collision of evaporated atoms with residual gas molecules. Gas pressures greater than 3 mPa (10 torr) are required. Vaporization sources may be resistive heating, high energy electron beams, low energy electron beam and inducting heating. Clusters form in the vicinity of the source by homogenous nucleation in the gas phase grew by incorporation by atoms in the gas phase. It comprises of a ultra high vacuum (UHV) system fitted evaporation source, a cluster collection device of liquid nitrogen filled cold finger scrapper assembly and compaction device. During heating, atoms condense in the supersaturation zone close to Joule heating device. The nanoparticles are removed by scrapper in the form of a metallic plate. Evaporation is to be done from W, Ta or Mo refractory metal crucibles [4]. If the metals react with crucibles, electron beam evaporation technique is to be used. The method is extremely slow. The method suffers from limitations such as a source-precursor incompatibility, temperature ranges and dissimilar evaporation rates in an alloy. Alternative sources have been developed over the years. For instance, Fe is evaporated into an inert gas atmosphere (He). Through collision with the atoms the evaporated Fe atoms loose kinetic energy and condense in the form of small crystallite crystals, which accumulate as a loose powder. Sputtering or laser evaporation may be used instead of thermal evaporation [5]. Sputtering is a non-thermal process in which surface atoms are physically ejected from the surface by momentum transfer from an energetic bombarding species of atomic/molecular size. Typical sputtering uses a glow discharge or ion beam. Interaction events which occur at and near the target surface during the sputtering process in magnetron sputtering has advantage over diode and triode sputtering. In magnetron sputtering, most of the plasma is confined to the near target region. Other alternate energy sources which have been successfully used to produce clusters or ultra fine particles are sputtering electron beam heating and plasma methods. Sputtering has been used in low pressure environment to produce a variety of clusters including Ag, Fe and Si.

Vacuum Deposition and Vaporization: In vacuum deposition process, elements, alloys or compounds are vaporized and deposited in a vacuum. The vaporization source is the one that vaporizes materials by thermal processes. The process is carried out at pressure of less than 0.1 Pa (1 m Torr) and in vacuum levels of 10 to 0.1 MPa. The substrate temperature ranges from ambient to 500°C. The saturation or equilibrium vapor pressure of a material is defined as the vapor pressure of the material in equilibrium with the solid or liquid surface. For vacuum deposition, a reasonable deposition rate can be obtained if the vaporization rate is fairly high. A useful deposition rate is obtained at a vapor pressure of 1.3 Pa (0.01 Torr). Vapor phase nucleation can occur in dense vapor cloud by multibody collisions, The atoms are passed through a gas to provide necessary collision and cooling for nucleation.

These particles are in the range of 1 to 100 nm and are called ultra fine particles or clusters [6-9]. The advantages associated with vacuum deposition process are high deposition rates and economy. However, the deposition of many compounds is difficult. Nanoparticles produced from a supersaturated vapor are usually longer than the cluster

IV. CHEMICAL METHODS

a. Chemical Vapor Deposition: This method is designated as chemical due to the fact that a layer on the surface of the coated substrate forms as a result of a chemical reaction of precursors, in contrast to the physical deposition, where physical principles are applied for the formation of a layer. In the first phase the precursors are gasified at high temperatures and individual molecules are lead to the cvd reactor, where they are adsorbed on the substrate surface. the coated substrate is during the deposition subjected to effects of one or more volatile precursors, which interact between each other on its surface or they decompose, while the demanded product is originating.

Chemical deposition from vapors consists of three basic steps: transport of atoms, molecules or ions of the precursor to the substrate surface at high temperature. chemical reactions on the substrate surface involving formation of the new material (chemical reactions). removing more volatile side products from the substrate surface using a gas stream or vacuum. het first and the third step are generally dependent on each other, because the diffusion rate of reactants affects the diffusion rate of side products. The second step is usually the most complicated and involves the following reactions: simultaneous adsorption and desorption (chemisorption and physical absorption) and nucleation processes. It is necessary to prevent the particle homogenous growth in the gaseous phase (in contrast to the chemical condensation from vapors), since it affects considerably the very deposition and results in an uneven layer thickness and deposition of undesirable particles. If the temperature is maintained on a value substantially higher than the temperature of pyrolysis of the reactants, their faster decomposition on the substrate surface is ensured, whereas the growth rate is limited by the reactant mass transport onto the substrate surface through the border layers, particularly by its kinetics and a change in the free energy[10].

b. Chemical Vapor Condensation Chemical vapor condensation (cvc) is a method for the manufacture of nanoparticles through a modified cvd process. the cvc principle is also based on nucleation in the gaseous phase, however, in contrast to cvd this is the homogenous nucleation and thin films do not form, but particularly fine powders. In the first step, the carrier gas is bubbled through the precursor reservoir at room temperature, as in the case of the chemical deposition. Follow-up, this vapor stream (of a controlled speed) containing precursor molecules is fed via a needle valve through a heated tubing into the vacuum (reaction) chamber. In the heated tube the induction of chemical reactions among the gas molecules occurs,



Namely by means of the energy supplied in the form of laser or plasma heating. During a short moment and under specific conditions molecules begin to decompose thermally and coagulate to small clusters and particles [11].

The outlet from the heated tube the beam of clusters or particles extends and by this their growth moderates. In the final phase the particles condensate on a rotating liquid nitrogen cooled substrate, from which the final powder product is scraped off and collected.

c. Electrodeposition This is a simple and well-established process and can be easily adapted to produce nanocrystalline materials. Electrodeposition of multilayered (1-D) metals[12] can be achieved using either two separate electrolytes or, much more conveniently, from one electrolyte by appropriate control of agitation and the electrical conditions (particularly voltage). Also, 3-D nanostructured crystallites can be prepared using this method by utilizing the interference of one ion with the deposition of the other ion. This technique was originally used to synthesize small quantities of nanostructured pure metals. 1) The systems using the principle of evaporation and condensation differ in: a) the method of input of evaporated material b) the method of supplying energy for evaporation c) the working medium d) setup of the condensation process e) the system for collecting the produced powder. A method of the condensation of metal vapours in a gas atmosphere is the process of dispersion of a metal by means of an electric arc in a liquid with subsequent condensation of metallic vapours in liquid vapours.

d. Salting Out Method Salting out based on the separation of a water-miscible solvent from aqueous solution via a salting-out effect, Salting-out is based on the separation of a water miscible solvent from aqueous solution via a salting-out effect. Polymer and drug are initially dissolved in a solvent which is subsequently emulsified into an aqueous gel containing the salting out agent (electrolytes, such as magnesium chloride and calcium chloride, or non-electrolytes such as sucrose) and a colloidal stabilizer[13]

e. Solvent Displacement: Precipitation method Solvent displacement: It involves the precipitation of a preformed polymer from an organic solution and the diffusion of the organic solvent in the aqueous medium in the presence or absence of surfactant. Polymers, drug, and or lipophilic surfactant are dissolved in a semipolar water miscible solvent such as acetone or ethanol[14,15]. The solution is then poured or injected into an aqueous solution containing stabilizer under magnetic stirring. Nanoparticles are formed instantaneously by the rapid solvent diffusion. The solvent is then removed from the suspensions under reduced pressure. The rates of addition of the organic phase into the aqueous phase affect the particles size. It was observed that a decrease in both particles size and drug entrapment occurs as the rate of mixing of the two phase increases.

f. Sol-gel Method: In this chemical procedure, the solution gradually converts into a gel like diphasic system, which contains both liquid phase and solid phase. The morphologies of these two phases range from discrete particles to continuous polymer networks. Initially a significant amount of fluid may have to be removed from solution to recognize the gel like properties. Sol-gel method is a low temperature technique and moreover it is cheap. In

this method the chemical composition of the product can be controlled. In this method the solution can be doped with organic dyes and rare earth metals[16]. The dopants are uniformly dispersed in the final product. This technique can be used in ceramics processing and producing thin films of metal oxides. Nano materials derived by this method have wide applications in electronics, medicine, separation technology, and optics.

V. BIO-BASED METHODS

A number of reports prevailed in the literatures indicate that synthesis of nanoparticles by chemical approaches are eco-unfriendly and expensive. Thus, there is a growing need to develop environmentally and economically friendly processes, which do not use toxic chemicals in the synthesis protocols.

A. Fungi

Silver NPs (5-50 nm) could be synthesized extracellularly using *Fusarium oxysporum*, with no evidence of flocculation of the particles even a month after the reaction [17]. The long-term stability of the nanoparticle solution might be due to the stabilization of the silver particles by proteins. Silver NPs have been reported to interact strongly with proteins including cytochrome *c* (Cc). This protein could be self-assembled on citrate-reduced silver colloid surface [18]. The NPs produced within 15-20 min and were spherical with a broad size distribution in the range of 5-40 nm with the average diameter of 13 nm. A nitrate-dependent reductase enzyme might act as the reducing agent. The white rot fungus, *Phanerochaete chrysosporium*, also reduced silver ions to form nano-silver particles [19].

The extracellular filtrate of *Cladosporium cladosporioides* biomass was used to synthesize silver NPs [20]. It was suggested that proteins, organic acids and polysaccharides released by *C. cladosporioides* were responsible for formation of spherical crystalline silver NPs. Sanghi and colleagues [21] have investigated the ability of *Coriulus versicolor* in formation of monodisperse spherical silver NPs. The time taken for production of silver NPs was reduced from 72 h to 1 h under alkaline conditions (pH 10). It was indicated that alkaline conditions might be involved in bioreduction of silver ions, water hydrolysis and interaction with protein functionalities

B. Algae

A few reports are available regarding gold accumulation using algal genera including cyanobacteria as biological reagent. Cyanobacteria and eukaryotic alga genera such as *Lyngbya majuscula*, *Spirulina subsalsa*, *Rhizoclonium heiroglyphicum*, *Chlorella vulgaris*, *Cladophora prolifera*, *Padina pavonica*, *Spirulina platensis*, and *Sargassum fluitans* can be used as cost effective means for biorecovery of gold out of the aqueous solutions, as well as the formation of gold NPs [22-25]. Marine algae like *Chaetoceros calcitrans*, *Chlorella salina*, *Isochrysis galbana* and *Tetraselmis gracilis* can also be used for reduction of silver ions,



And thereby synthesis of Ag NPs [26]. Marine cyanobacterium, *Oscillatoria willei* NTDM01 has been used for synthesis of silver NPs (100-200 nm). Silver nitrate solution incubated with washed marine cyanobacteria changed to a yellow color from 72 h onwards, indicating the formation of silver NPs.

C. Plants

Synthesis of NPs using plants is very cost effective, and thus can be used as an economic and valuable alternative for the large-scale production of NPs [27]. *Camellia sinensis* (green tea) extract has been used as a reducing and stabilizing agent for the biosynthesis of silver NPs [28]. Phenolic acid-type biomolecules (e.g., caffeine and theophylline) present in the *C. sinensis* extract seemed to be responsible for the formation and stabilization of silver NPs. Black tea leaf extracts were also used in the production of silver NPs [29]. The NPs were stable and had different shapes, such as spheres, trapezoids, prisms, and rods. Polyphenols and flavonoids seemed to be responsible for the biosynthesis of these NPs.

Plant extracts from alfalfa (*Medicago sativa*), lemongrass (*Cymbopogon flexuosus*), and geranium (*Pelargonium graveolens*) have served as green reactants in silver nanoparticle synthesis. Moreover, a high density of extremely stable silver NPs (16-40 nm) was rapidly synthesized by challenging silver ions with *Datura metel* leaf extract [30]. The leaf extracts of this plant contains biomolecules, including alkaloids, proteins/enzymes, amino acids, alcoholic compounds, and poly-saccharides which could be used as reductant to react with silver ions, and therefore used as scaffolds to direct the formation of silver NPs in the solution.

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