

METHODS OF PREPARATION OF NANOPARTICLES – A REVIEW

Namita Rajput
Govt. Polytechnic College Balaghat (M.P.) India

ABSTRACT

Nanomaterials and Nanotechnologies attract tremendous attention in recent researches. New physical properties and new technologies both in sample preparation and device fabrication evoke on account of the development of nanoscience. Various research fields including physics, chemists, material scientists, and engineers of mechanical and electrical are involved in this research. Synthesis of nanomaterials that are synonyms to quantum confined atom is an important milestone in the pursuit. Materials scientists and engineers have made significant developments in the improvement of methods of synthesis of nanomaterial solids. In this review various methods of preparing nanomaterials including Gas Condensation, Vacuum Deposition and Vaporization, Chemical Vapor Deposition (CVD) and Chemical Vapor Condensation (CVC), Mechanical Attrition, Chemical Precipitation, Sol-Gel Techniques, Electrodeposition are discussed.

KEYWORDS: *Nanoparticles, Surfactant, Hydrolysis, electrodeposition.*

I. INTRODUCTION

The man in his quest for knowledge has been conceiving and developing physical world and its components in bigger than the biggest and smaller than the smallest dimensions of mass, length and time. Though the smallest entity with individual characteristic features that was established happened to be an atom of an element but realization of the single atom in physical form and serving mankind remained a dream till recently. It is achieved through the development of nanocrystalline materials, discovery of concept of quantum confined atom and synthesis of doped nanocrystalline materials. Investigation of growth mechanism of nanoparticles is present large scientific and practical interest. As, nanoparticles with given size and characteristics are required in nanotechnology. Nanoparticles growth mechanism determines distribution function of nanoparticles on size, physical-chemical properties of nanoparticles medium and etc. Because of, known of growth mechanism give possibility control of preparation of nanoparticles and to obtain nanoparticles with given parameters (mean diameter, standard deviation, coefficient polydispersity and other) and characteristics (magnetic moment). Nanoparticles growth mechanism is enough complex process and depended from many conditions (temperature, viscosity, concentration of medium and etc.). Conditions determinant of nanoparticle growth are changed in the dependence on method preparation of nanoparticles. Materials scientists and engineers have made significant developments in the improvement of methods of synthesis of nanomaterial solids [1-3]. A brief review is given in this article.

II. SYNTHESIS OF NANOMATERIAL

It is classified as bottom-up manufacturing which involves building up of the atom or molecular constituents as against the top method which involves making smaller and smaller structures through etching from the bulk material as exemplified by the semiconductor industry.

2.1 Gas Condensation

Gas condensation was the first technique used to synthesize nanocrystalline metals and alloys. In this technique, a metallic or inorganic material is vaporized using thermal evaporation sources such as a

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 [2]. 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.

2.2 Vacuum Deposition and Vaporization

Before proceeding to the other methods, it is important to understand the terms vacuum deposition and vaporization or vacuum evaporation. 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 [5-7]. 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.

2.3 Chemical Vapor Deposition (CVD) and Chemical Vapor Condensation (CVC)

CVD is a well known process in which a solid is deposited on a heated surface via a chemical reaction from the vapor or gas phase. CVC reaction requires activation energy to proceed. This energy can be provided by several methods. In thermal CVD the reaction is activated by a high temperature above 900°C. A typical apparatus comprises of gas supply system, deposition chamber and an exhaust system. In plasma CVD, the reaction is activated by plasma at temperatures between 300 and 700°C. In laser CVD, pyrolysis occurs when laser thermal energy heats an absorbing substrate. In photo-laser CVD, the chemical reaction is induced by ultra violet radiation which has sufficient photon energy, to break the chemical bond in the reactant molecules. In this process, the reaction is photon activated and deposition occurs at room temperature. Nano composite powders have been prepared by CVD. SiC/Si₃N composite powder was prepared using SiH₄, CH₄, WF₆ and H₂ as a source of gas at 1400°C. Another process called chemical vapor condensation (CVC) was developed in Germany in 1994. It

involves pyrolysis of vapors of metal organic precursors in a reduced pressure atmosphere. Particles of ZrO_2 , Y_2O_3 and nanowhiskers have been produced by CVC method [5-8]. A metalorganic precursor is introduced in the hot zone of the reactor using mass flow controller. For instance, hexamethyldisilazane $(CH_3)_3SiNHSi(CH_3)_3$ was used to produce SiC_xNyO_z powder by CVC technique. The reactor allows synthesis of mixtures of nanoparticles of two phases or doped nanoparticles by supplying two precursors at the front end of reactor and coated nanoparticles, n- ZrO_2 , coated with n- Al_2O_3 by supplying a second precursor in a second stage of reactor. The process yields quantities in excess of 20 g/hr. The yield can be further improved by enlarging the diameter of hot wall reactor and mass of fluid through the reactor. Typical nanocrystalline materials which have been synthesized are shown in Table 1.

Table 1. Typical nanocrystalline materials synthesized by the CVC method

| Precursor | Product Powder | Phase as prepared | Average Particle size (nm) | Surface (m^2/g) | Area |
|--------------------------|----------------|-------------------|----------------------------|---------------------|------|
| $(CH_3)_3SiNHSi(CH_3)_3$ | SiC_xNyO_z | Amorphous | 4 | 377 | |
| $Si(CH_3)_4$ | SiC | β -phase | 9 | 201 | |
| $Al[2-OC_4H_9]_3$ | Al_2O_3 | Amorphous | 3.5 | 449 | |
| $Ti[I-OC_3H_7]_4$ | TiO_2 | Anatase | 8 | 193 | |
| $Si[OC_2H_5]_4$ | SiO_2 | Amorphous | 6 | 432 | |
| $Zr[3-OC_4H_9]_4$ | ZrO_2 | Monoclinic | 7 | 134 | |

2.4 Mechanical Attrition

Unlike many of the methods mentioned above, mechanical attrition produces its nanostructures not by cluster assembly but 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. 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 [8-10].

High energy mills include:

- Attrition Ball Mill
- Planetary Ball Mill
- Vibrating Ball Mill
- Low Energy Tumbling Mill
- High Energy Ball Mill

2.4.1 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.

2.4.2 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).

2.4.3 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).

2.4.4 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 $Al_{30}Ta_{70}$ 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.

2.4.5 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.

2.5 Chemical Precipitation

In this strategy the size is control by arrested precipitation technique. The basic trick has been to synthesis and studies the nanomaterial in situ i.e. in the same liquid medium avoiding the physical changes and aggregation of tiny crystallites. Thermal coagulation and Oswald ripening were controlled by double layer repulsion of crystallites using non-aqueous solvents at lower temperatures for synthesis. The synthesis involved reaction between constituent material in suitable solvent . The dopant is added to the parent solution before precipitation reaction. Surfactant is used to maintain separation between the particles formed . Thus formed nanocrystal are separated by centrifugation, washed and vacuum dried. The dried material was further subjected to UV curing for possible polymerization of surfactant capping film on the surface of nano cluster for imparting true quantum confinement [8-10].

2.6 Sol-Gel Techniques

In addition to techniques mentioned above, the sol-gel processing techniques have also been extensively used. Colloidal particles are much larger than normal molecules or nanoparticles. However, upon mixing with a liquid colloids appear bulky whereas the nanosized molecules always look clear. It involves the evolution of networks through the formation of colloidal suspension (sol) and gelatin to form a network in continuous liquid phase (gel). The precursor for synthesizing these colloids consists of ions of metal alkoxides and aloxysilanes. The most widely used are tetramethoxysilane (TMOS), and tetraethoxysilanes (TEOS) which form silica gels. Alkoxides are immiscible in water. They are organo metallic precursors for silica, aluminum, titanium, zirconium and many others. Mutual solvent alcohol is used. The sol gel process involves initially a homogeneous solution of one or more selected alkoxides. These are organic precursors for silica, alumina, titania, zirconia, among others. Mortia et al [11-14] A catalyst is used to start reaction and control pH. Sol-gel formation occurs in four stages.

- Hydrolysis
- Condensation
- Growth of particles
- Agglomeration of particles

2.6.1 Hydrolysis

During hydrolysis, addition of water results in the replacement of [OR] group with [OH-]group. Hydrolysis occurs by attack of oxygen on silicon atoms in silica gel. Hydrolysis can be accelerated by adding a catalyst such as HCl and NH₃. Hydrolysis continues until all alkoxy groups are replaced by hydroxyl groups. Subsequent condensation involving silanol group (Si-OH) produced siloxane bonds (Si-O-Si) and alcohol and water. Hydrolysis occurs by attack of oxygen contained in the water on the silicon atom.

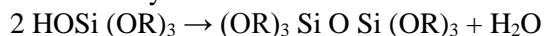
2.6.2 Condensation

Polymerization to form siloxane bond occurs by either a water producing or alcohol producing condensation reaction. The end result of condensation products is the formation of monomer, dimer, cyclic tetramer, and high order rings. The rate of hydrolysis is affected by pH, reagent concentration and H₂O/Si molar ratio (in case of silica gels). Also ageing and drying are important. By control of these factors, it is possible to vary the structure and properties of sol-gel derived inorganic networks.

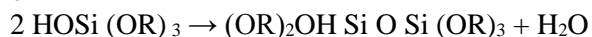
2.6.3 Growth and Agglomeration

As the number of siloxane bonds increase, the molecules aggregate in the solution, where they form a network, a gel is formed upon drying. The water and alcohol are driven off and the network shrinks.

At values of pH of greater than 7, and H₂O/Si value ranging from 7 to 5. Spherical nano-particles are formed. Polymerization to form siloxane bonds by either an alcohol producing or water producing



or



Above pH of 7, Silica is more soluble and silica particles grow in size. Growth stops when the difference in solubility between the smallest and largest particles becomes indistinguishable. Larger particles are formed at higher temperatures. Zirconium and Yttrium gels can be similarly produced.

Despite improvements in both chemical and physical methods of synthesis, there remain some problems and limitations. Laser vaporization technique has offered several advantages over other heating techniques. A high energy pulsed laser with an intensity flux of 10⁶ - 10⁷ W/cm² is forced on target material. The plasma causes high vaporization and high temperature (10,000°C). Typical yields are 10¹⁴-10¹⁵ atoms from the surface area of 0.01 cm² in a 10⁻⁸ s pulse. Thus a high density of vapor is produced in a very short time (10⁻⁸ s), which is useful for direct deposition of particles.

2.7 Electrodeposition

Nanostructured materials can also be produced by electrodeposition. These films are mechanically strong, uniform and strong. Substantial progress has been made in nanostructured coatings applied either by DVD or CVD. Many other non-conventional processes such as hypersonic plasma particle deposition (HPPD) have been used to synthesize and deposit nanoparticles. The significant potential of nanomaterial synthesis and their applications is virtually unexplored. They offer numerous challenges to overcome. Understanding more of synthesis would help in designing better materials. It has been shown that certain properties of nanostructured deposits such as hardness, wear resistance and electrical resistivity are strongly affected by grain size. A combination of increased hardness and wear resistance results in a superior coating performance [15-16].

III. SUMMARY

Nanomaterials have been extensively investigated during the last decade due to their wide variety of applications. It is observed that field of nanomaterial synthesis is very dynamic. Many processes such as gas condensation, chemical vapor synthesis, mechanical attrition, chemical precipitation, Sol-Gel technique, electrodeposition, some other methods widely used are molecular beam epitaxy, ionised cluster beam, liquid metal ion source, consolidation, sputtering and gas aggregation of monomers. Chemical precipitation in presence of capping agents, reaction in microemulsions and autocombustion are commonly used techniques for synthesis of nanophosphors. Nanomaterials prepared using the processes include a wide variety.

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AUTHORS

Namita Rajput received her Ph. D. of Condensed Matter Physics in 2007 from Rani Durgavati University Jabalpur (M.P) India. She has more than 10 years of work experience in R&D. She also has 10 years of work experience in different post graduate degree colleges. Currently she is Lecturer in Govt. Polytechnic College Balaghat (M.P.) India. Her general expertise falls in the areas of Mechanoluminescence, electroluminescence and nanomaterials.

