

CHAPTER II

PREPARATION METHODS FOR NANOSTRUCTURED MATERIALS

2.1 INTRODUCTION

The preparation of nanoscale structures can be accomplished through “bottom-up” or “top-down” methods. In the bottom-up approach, small building blocks are assembled into larger structures; chemical synthesis is a good example of bottom-up approach used in the synthesis of nanoparticles. In the top-down approach, large objects are modified to give smaller features; attrition or milling is a good example of top-down approach. Both approaches play very important role in modern industry and most significantly in nanotechnology.

Methods to produce nanoparticles from atoms are chemical processes based on transformations in solution e.g. sol-gel processing, chemical vapour deposition (CVD), plasma or flame spraying synthesis, and laser pyrolysis, atomic or molecular condensation. These chemical processes rely on the availability of appropriate “metal-organic” molecules as precursors. Among these methods, sol-gel, chemical bath deposition, successive ionic layer adsorption and reaction, and chemical precipitation methods are simple and cost-effective techniques which have been adopted for the synthesis of nanocrystalline thin films and nanoparticles.

Nanomaterials have been prepared by different researchers using various techniques such as vapor-liquid-solid (VLS) growth, hydrothermal routes, hard template directing technique, surfactant assisted approach, thermal decomposition, metal salt reduction method, microwave heating, radiation methods, micro emulsion techniques, super critical techniques, laser ablation, polyol method, solvothermal method, DC arc discharge method, thermal and sonochemical reduction, chemical vapor deposition, refluxing processes and cellulose-directed growth.

2.1.1 Sol-Gel process

Sol-gel process may be considered the most widely used and developed one among the various synthetic powder preparation methods. Sol-gel method offers specific advantages when used to prepare multi-component oxide ceramics. The early formation of a gel provides a high degree of homogeneity and reduces the need of atomic diffusion during solid-state calcinations. Moreover, the processing often starts with metal alkoxides, many of which are liquids or volatile solids that can easily be purified, providing extremely pure oxide precursors. This factor is important for electro-ceramics synthesis. However, the relatively high costs of metal alkoxides may be prohibitive for certain applications, and release of large amounts of alcohol during the calcination step requires special safety considerations.

The sol-gel process is a wet-chemical technique (also known as chemical solution deposition) recently used widely in the fields of materials science and ceramic engineering. The sol-gel formation steps include formation of stable sol solution and gelation via a polycondensation or polyesterification reaction. Gel aging into a solid mass causes contraction of the gel network, phase transformation and Ostwald ripening (small crystals or sol particles dissolve, and redeposit onto larger crystals or sol). Drying of the gel to remove liquid phase can lead to fundamental changes in the structure of the gel. Dehydration at higher temperatures is used to remove M-OH groups for stabilizing the gel, i.e., to protect it from rehydration. Densification and decomposition of the gel at high temperatures collapses the pores in the gel network and drives out the remaining organic contaminants.

The ultimate microstructure of the final component will clearly be strongly influenced by changes implemented during this phase of processing. The precursor sol can either be deposited on a substrate to form a film (e.g. by spin-coating or dip-coating), cast into a suitable container with the desired shape (e.g. to obtain glasses, membranes, aerogels), or used to synthesize powders (e.g. microspheres, nanospheres). One unique property of sol-gel process is the ability to go all the way from molecular precursor level to product level, allowing a better control of the

whole process and synthesis of tailor made materials for different applications.

2.1.2 Hydrothermal Synthesis

Hydrothermal methods are becoming popular methods to precipitate mixed metal oxides directly from either homogeneous or heterogeneous solutions. Hydrothermal method utilizes water under pressure and at temperatures above its normal boiling point as a means of speeding up the reaction between solids (**Rabenau (1985)**). Water is an excellent solvent because of its high dielectric constant. The dielectric property of water decreases with rise in temperature but increases with increase of pressure with temperature effect. This predominating decreases with rising temperature and increases with rising pressure, with temperature effect predominating. In addition, the high dielectric constant of water is confined to a region of low temperature and high densities (pressure). This property is mainly responsible for increasing the solubility of many sparingly soluble compounds under hydrothermal conditions leading to many useful chemical reactions such as, hydrolysis, precipitation, co-precipitation, and crystal growth. Hydrothermal reactions are usually performed in closed vessels. The reactants are either dissolved or suspended in a known amount of water and are transferred to acid digestion reactors or autoclaves. Under hydrothermal conditions, reactants otherwise, difficult to dissolve, can go into the solution and reprecipitate.

Hydrothermal reaction is a single-step process of preparation of several metal oxides and phosphates (**Rabenau (1985)**, **Clearfield (1991)**, **Haushalter and Mundi (1992)**, **Oguri et al., (1988)**) have obtained narrow size distribution of spherical submicron titanium hydrous oxide, which could be readily transformed into polycrystalline anhydrous anatase with spherical morphology. Fine particles of ferroelectric lead titanate with high Curie temperature have been prepared via hydrothermal technique (**Cheng et al., (1996)**). This technique was further used for the synthesis of nano crystalline metal oxides. This method has also been employed for the synthesis of several other metal oxides, e.g., ZnO, TiO₂, and ZrO₂, with nano size particles (**Sharma et al., (1998)**, **Yang et al., (2000)**).

2.1.3 Chemical Vapour Deposition

Chemical vapour deposition (CVD) can be defined as the deposition of a solid on a heated surface from a chemical reaction in the vapor phase. It is a versatile process suitable for the manufacturing of coatings, powders, fibers, and monolithic components. It is possible to produce most metals, metal oxides, and nonmetallic elements such as, carbon and silicon as a large number of compounds including carbides, nitrides, oxides, intermetallics and many others. The main advantage of CVD is that the deposition rate is high and thick coatings or nanoparticles can be readily obtained. The process is generally competitive and in some cases, more economical than the physical vapor deposition (PVD). Additionally, it is not restricted to a line of sight deposition, which is a general characteristic of sputtering, evaporation, and other PVD processes. However, two major applications of CVD have rapidly been developed in the last 20 years in which includes cutting tool fabrication, and they are the semiconductor industry and the metallurgical coating industry. Very recently, CVD process has been given enormous attention owing to the possibility of mass production of monodisperse nanoscale powders; however, the mechanism of powder synthesis kinetics is still not clear (**Cheng et al., (1994), Kear and Skandan (1997), Kim et al., (1999)**).

2.1.4 Microwave Synthesis

The interest in the use of microwave processing spans a number of fields from food processing to medical applications and chemical applications. A major area of research in microwave processing of ceramics includes microwave material interaction, dielectric measurement, microwave equipment design, new material development, sintering, joining, and modeling. Therefore, the microwave processing of ceramics has emerged as a successful alternative to the conventional processing (**Krage (1981), Roy et al., (1985)**). Nevertheless, microwave method not only offers the advantages of a uniform heating at lower temperature and less time than the conventional method, but also provides an economic method of processing. The microwave energy has been already successively utilized in the fabrication of ceramics as well as carbon fibers at a low temperature and time. **Sharma et al., (2001)** have synthesized various

electroceramics such as, barium strontium titanate (BST) and lead zirconate titanate (PZT) by microwave. These materials are observed to have improved mechanical, electrical and electronic properties. Until recently, microcoiled carbon fibers with large surface area have also been fabricated by using microwave aid (Xie et al., (2002)).

Compared to other techniques, the chemical precipitation technique uses an environmental friendly reaction medium and it has many advantages like mild reaction conditions, less energy consumption, simple equipment and there are large numbers of variable factors in the preparation process. The chemical precipitation method is a simple and cost-effective technique that has been adopted for the synthesis of nanoparticles.

In the present study, chemical precipitation technique has been adopted to prepare Iron, and Silver nanoparticles.

2.2 CHEMICAL PRECIPITATION METHOD

The chemical precipitation method is called as a gravimetric analysis. The gravimetric analysis measures the mass of a material formed in the reaction of the analyte with the reagent. A chemical reaction for the gravimetric analysis is,



where, 'a' moles of the analyte 'A' contained in the sample reacts with 'r' moles of the reagent 'R' to form the precipitate A_aR_r , noted as solid phase (s) in the reaction.

Gravimetric analyses are based on the measurement of weights. This involves weighing of the required constituent either in its elemental form or in the form of a compound of known composition. Typically, a gravimetric estimation involves two weight determinations, first being the original sample, weight and the second being the final weight of the pure precipitate which contains the sample constituent under study.

The precipitate for weighing could be obtained by any one of the following methods:

- (i) Volatilization
- (ii) Electrodeposition
- (iii) Reacting two solutions and filtering the precipitate.

Of these three, the last is commonly adopted. Understanding the nature of the reaction between the dissolved species (which produces a precipitate) the subsequent interaction between the precipitate and the solution phase are important in gravimetric analysis.

The following are the conditions for precipitation:

- (i) The desired constituent must be precipitated quantitatively. This means that the concentration of the constituent left in the solution must be a negligible fraction of the original total amount of that constituent. In other words, the precipitation should yield a precipitate which is sparingly soluble that the constituent left in the solution at a concentration level that would not be easily detectable within the weighing limits of the analytical balance (0.0001g or less).
- (ii) The precipitate must be pure at the time of final measurement of weight and it must be of known purity. At the time of its formation, the precipitate must not include significant quantities of any other substance as impurity. If some substances are associated with the precipitate, they must be removable by washing and drying.
- (iii) The precipitate must be in a physical form, suitable for subsequent handling. It should consist of particles which are large enough to be filtered.
- (iv) The weighing form of the precipitate, after drying, ignition, etc., should be of a definite and known composition.

2.2.1 Types of precipitants

1. Inorganic precipitants
2. Organic precipitants

The advantages of using organic precipitants over inorganic precipitants are:

1. The precipitates formed with organic precipitants are often insoluble in water, so that the degree of separation is highly quantitative.
2. The precipitate has a high formula weight relative to the metal ion being separated, so that a small weight of the metal being estimated gives a large precipitate weight. This allows high sensitivity in the detection of the metal involved with less error in weighing.
3. The organic precipitates have large particle size and therefore can be filtered and washed easily.
4. Organic precipitates can be more easily dried than inorganic precipitates because of their reduced tendency to hold water.

The disadvantages of using organic precipitants are:

1. Drying of organic precipitates sometimes, results in a dried product of uncertain composition. This may be due to partial decomposition or volatilization during drying.
2. The organic precipitants are generally less soluble in water when compared to the inorganic precipitants. This creates a problem in preparing the organic precipitant solution.
3. Organic precipitants are more expensive than inorganic precipitants. Therefore, selection of a precipitant for estimating a particular constituent should be done after carefully considering all these aspects.

2.2.2 Solubility product and precipitation

When a substance is said to be insoluble in water, it actually means that its solubility is negligible. The solubility product is the ultimate value which is attained by the ionic concentration when equilibrium has been established between the solid phase of a difficult soluble salt and the solution. When the product of the concentration of the ions in solution is made to exceed the solubility product, by the addition of a reagent, precipitation of the salt will be the result. Thus, the solubility product concept has an important bearing upon precipitation for solution. The factors which affect solubility of precipitates are:

Temperature: Heat is absorbed as most solids dissolve and hence solubility of the precipitate increases with increase in temperature. Solubility products for most sparing solution compounds increase as temperature increases.

Solvent composition: The nature of solvent influences the solubility of most inorganic substances. It is markedly less in mixtures of water and organic solvents than in pure water.

Rate of precipitate formation: Precipitation reactions are often slow, several minutes or even several hours required for the attainment of equilibrium. This fact can be used to accomplish separations that would not be possible if equilibrium is approached rapidly.

Common ion effect and diverse ion effect: The solubility of a slightly soluble salt is decreased by the presence of an ion which is its common with one of the ions of the slightly soluble salts. The benefit of the common ion effect in suppressing the solubility of a precipitate is lost in the need to wash the precipitate thoroughly to remove the common ion.

Many slightly soluble salts show an increased solubility in the presence of increased concentrations of certain salts having no ion common with those of the

slightly soluble salt. This effect is in addition to the common ion effect. Therefore, very large excess of the precipitating ion is avoided in gravimetric analysis.

2.2.3 Types of precipitates

Precipitates are of two types (i) colloidal (ii) crystalline.

(i) Colloidal precipitates: individual colloidal particles are so small that they cannot be filtered by an ordinary filtering media. Furthermore, Brownian motion prevents their settling from the solution under the influence of gravity. But, the individual particles of most colloids can be coagulated to give a filterable, non crystalline mess that rapidly settles down from the solution. Heating, stirring and adding an electrolyte to the medium hastens the coagulation process.

(ii) Crystalline precipitates: Crystalline precipitates are more easily manipulated than coagulated colloids. The size of individual crystalline particles can be varied to a degree.

2.2.4 Types of precipitation

Co-precipitation:

The process of precipitation of impurity along with the precipitate being separated is called as co-precipitation. It may occur in one or more of the following ways. Inclusion is the process by which impurities are being randomly distributed in the form of individual ions or molecules throughout the crystal. Occlusion is nonhomogeneous distribution of impurities, numerous ionic or molecular impurities within the imperfect crystal lattice of the precipitate. An ion in a crystal of a precipitate may be replaced by an impurity ion of similar size and shape. This phenomenon is isomorphous replacement and owing to this the impurity is permanently incorporated onto the crystal lattice. It cannot be removed by washing.

Post-precipitation:

This is another type of precipitate contamination. Post-precipitation is the precipitation of an impurity from its supersaturated solution onto the surface of an already present precipitate.

2.2.5 Theory of precipitation**Nucleation and crystal growth:**

The formation of a precipitate is both a physical as well as a chemical processes. The physical process consists of two steps: nucleation and crystal growth. Nucleation is formation of smallest particles of the precipitate capable of spontaneous growth. Crystal growth is deposition of ions from the solution on the surface of the solid particles, formed in nucleation and it precedes crystal growth. The number of particles and size of a given mass of precipitate is determined by the number of nuclei formed in the nucleation step.

Supersaturation is a condition in which a solution phase contains more of the dissolved precipitate than that present and can be in equilibrium with the solid phase. It is a temporary condition. This is lost when precipitation starts. The rate of precipitation is given by the equation,

$$Rate = \frac{Q - S}{S} \quad (2.2)$$

in which, Q is actual concentration of the solute as the instant precipitation begins and S is the equilibrium concentration of the solute in the saturated solution. The number of nuclei formed is directly proportional to the extent of supersaturation, (Q-S)/S, existing at the time of nucleation. In general, larger the extent of supersaturation, smaller will be the size of individual particles of the precipitate. Therefore, it is important to have the solutions diluted before precipitation to promote the formation of larger crystals. Larger the crystal size, the easier will be its handling.

Spontaneous and induced nucleation:

Large cluster of ions can join in a supersaturated solution to form a nucleus and this process is called spontaneous nucleation. In solution, some sites can attract and hold ions. These sites will act as centers at which nucleation and crystal growth are promoted and it is called induced nucleation. Nucleation does not occur readily with some solution and in such a case few particles of the precipitate are deliberately added, which can attract and hold ions and it is initial precipitation. Insoluble impurities in the reagents and in the solvent also provide nucleation sites. Mostly, electrostatic forces of attraction hold ions together on nucleation sites. Sometimes, adsorption may also play the same role.

2.2.6 Process of Crystal Growth

Nucleation is the first step in the growth of the crystal. This is followed by two more steps: the diffusion of ions to the surface of the growing crystal and deposition of these ions on the surface. The diffusion rate is influenced by the nature of ions and their concentrations and also by the rate of stirring and temperature of the solution. The rate of deposition of ions is dependent upon the concentration, impurities on the surface and growth characteristics of a particular crystal.

Generally, crystal growth does not occur uniformly on all phases of the crystal and therefore perfect geometrical shapes are rarely formed in precipitation process. Preferential growth on corner may result in irregular, branched crystals called dendrites. The shape of the precipitated particles is markedly influenced by the presence of impurity ions, probably, because they inhibit or aid growth and are related to satisfactory requirement of precipitation and quantitatively separation of chemical species. Physical form, purity and solubility of a precipitated phase are influenced by nucleation and crystal growth.

2.2.7 Precipitation from Homogeneous Medium

In this technique, the precipitant is not added as such, but is slowly generated by a homogeneous reaction within the solution. Therefore, concentration of the reagent remains low at any time and the relative super saturation is always low. This

situation avoids undesirable concentration effect which leads to contamination of the precipitate. The precipitate obtained from this technique is dense and easily filterable. It is possible to alter the time of appearance of the precipitate. The slower the reaction, the larger the crystal is formed. Thus, precipitation from a homogeneous solution is an excellent way of enhancing the purity of a precipitate.

2.2.8 Washing the Precipitate

The digested precipitate contains some other substances as impurity on its surface. They are removed by washing the precipitate with wash liquids or solutions in which the impurities are soluble. Washing removes surface impurities only. Usually, pure water is not used for washing as it would peptize the precipitate, i.e., some precipitate would go into the solution thus, leading to loss of some precipitate resulting in negative error.

A solution, containing an electrolyte having a common ion with the precipitate and which volatilizes when the precipitate gets dried is used for washing the precipitate. This reduces errors due to peptization. Some commonly employed wash solutions are dilute acids, ammonium salt solutions and ammonia solution.

Hot wash solutions are used if the precipitate is insoluble in hot solution. These speeds up the washing process as impurities are more soluble in hot solution thereby, decreasing the time taken for filtration.

Types of wash solution:

There are three types of washing solution which are used; they are:

- i) Solution that prevents the precipitate from passing into the colloidal state and thereby passing through the filter. e.g., ammonium salt solution.
- ii) Solution that reduces solubility of the precipitate. e.g., calcium oxalate precipitate is washed with ammonium oxalate solution.

This is because calcium oxalate is less soluble and some impurities are soluble in ethanol or ether, they are used as wash liquids.

iii) Solution that prevents hydrolysis of the precipitate. e.g., aqueous ammonia is used to wash MgNH_4PO_4 , because the latter hydrolyses to HPO_4^{2-} and OH^- ions.

2.2.9 Drying of Precipitate

The precipitate is to be dried at a suitable temperature. It should be dried at a temperature which is sufficiently high to volatilize water, wash liquid and other volatile impurities, burn out the filter paper completely but, must be well below the decomposition temperature of the precipitate. This is ascertained from the study of the thermogram of the precipitate. Drying is done in a sintered crucible using an air oven. It is dried, cooled and weighed till a constant weight achieved.

Precipitation is a process in which a solid is separated from a suspension, sol or solution. In a sol, the particles are precipitated by coagulation. Separation or precipitation from a dispersed state of suspension particles resulting from their growth may result from prolonged heating, addition of an electrolyte, or from a condensation reaction between solute and solvent. It can also be called as the collecting together of tiny suspended particles into a mass of larger size, one which will settle more rapidly.

Chemical precipitation can be accomplished by using simple apparatus and the precipitation mechanism is shown in Figure 2.1. The positively charged metal ions combine with the negative colloid particles and neutralize their charge. The particles then repel each other less strongly and tend to coagulate or collect into larger particles. The formation of a separable solid substance from a solution either by converting the substance into an insoluble form or by changing the composition of the solvent to diminish the solubility of the substance in it is called precipitation.

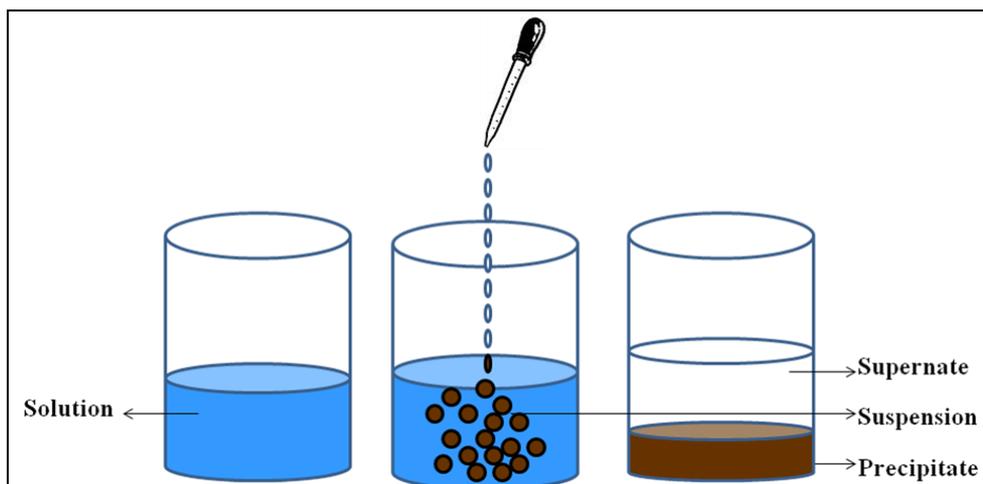


Figure 2.1 Schematic Diagram of Precipitation Process

Precipitation can occur when an insoluble substance is formed in the solution due to a chemical reaction or when a compound has supersaturated the solution. The formation of a precipitate is a sign of a chemical change. In most situations, the solid forms "fall" out of the solute phase and sinks to the bottom of the solution (though it will float if it is less dense than the solvent, or form a suspension). Precipitation of chalcogenide from a solution of chemical composition has been an attractive proposition for researchers, primarily because of the simplicity with which experiments can be conducted in a laboratory.

2.3 PREPARATION PROCESS FOR IRON AND SILVER NANOPARTICLES

2.3.1 Preparation of Iron Nanoparticles

An aqueous solution of 50 mg of ferric nitrate is added to 25 mL of water along with 25 mL of ascorbic acid and the mixer is stirred for about 30 minutes at room temperature, a reddish brown coloured solution is obtained. Then, a freshly prepared sodium borohydride (75mg) solution is added drop-wise to the above mixer (ferric nitrate and ascorbic acid). Now, the brown coloured solution turns into a yellow coloured solution indicating the formation of iron particles in the solution. The stirring is continued until the yellow colour changes into black. The change in colour indicates the formation of iron particles in solution and then, it is stirred for 6 hours at room temperature. The precipitate is allowed to settle down in the beaker.

After 6 hours, the suspensions are centrifuged and washed with water and ethanol several times. The samples are then suspended in ethanol and allowed to age for 2 hours without stirring. After centrifugation, the samples are dried at room temperature and the iron nanoparticles are collected for further use.

The ferric nitrate $\text{Fe}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ reacts with sodium borohydride (NaBH_4) in the presence of stabilizing agent, ascorbic acid. A reduction reaction takes place and it gives Fe^{2+} (unstable ions) under slow reduction. When the reduction is completed, Fe^{2+} ions are converted to stable Fe particles. Then, the soluble compound NaNO_3 (sodium nitrate) is dissolved in water and can be easily eliminated by the centrifugation process. The above preparation process is depicted in the flow chart given below in Figure 2.2.

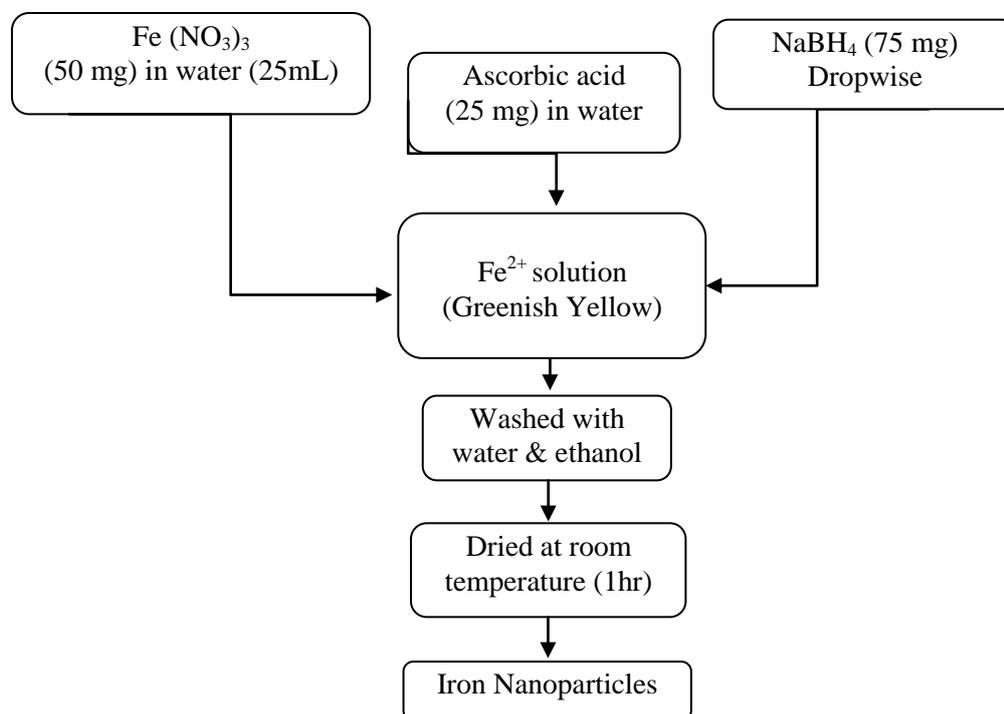


Figure 2.2 Flow-chart depicting the preparation of iron nanoparticles

Ascorbic acid, ferric nitrate and sodium borohydride were used as starting materials to synthesize iron nanoparticles. When ferric nitrate is dissolved in an aqueous medium with the reducing agent, sodium borohydride, it splits up into a positive ferrous ion (Fe^{2+}) and a negative nitrate ion (NO_3^-). In order to turn ferrous

ions into a solid state, the ions have to be reduced by receiving two electrons from the donor.

2.3.2 Preparation of Silver Nanoparticles

An aqueous solution of 0.05M AgNO_3 (50 mg) and starch (10 mg) were dissolved in water and stirred for about one hour at room temperature. Then, 50g of sodium carbonate (0.025 M) was added dropwise to the above mentioned solution. The colour of the solution was changed into yellow, indicating the formation of silver particles. The solution was stirred for 5 hours at room temperature and the colour changed to grey. Then the precipitate was allowed to settle down. After 5 hours, the suspension was centrifuged and washed with water and ethanol several times. The sample was then suspended in ethanol. After centrifugation, the sample was dried at room temperature. The dried sample was displayed in the Petri dish for further use.

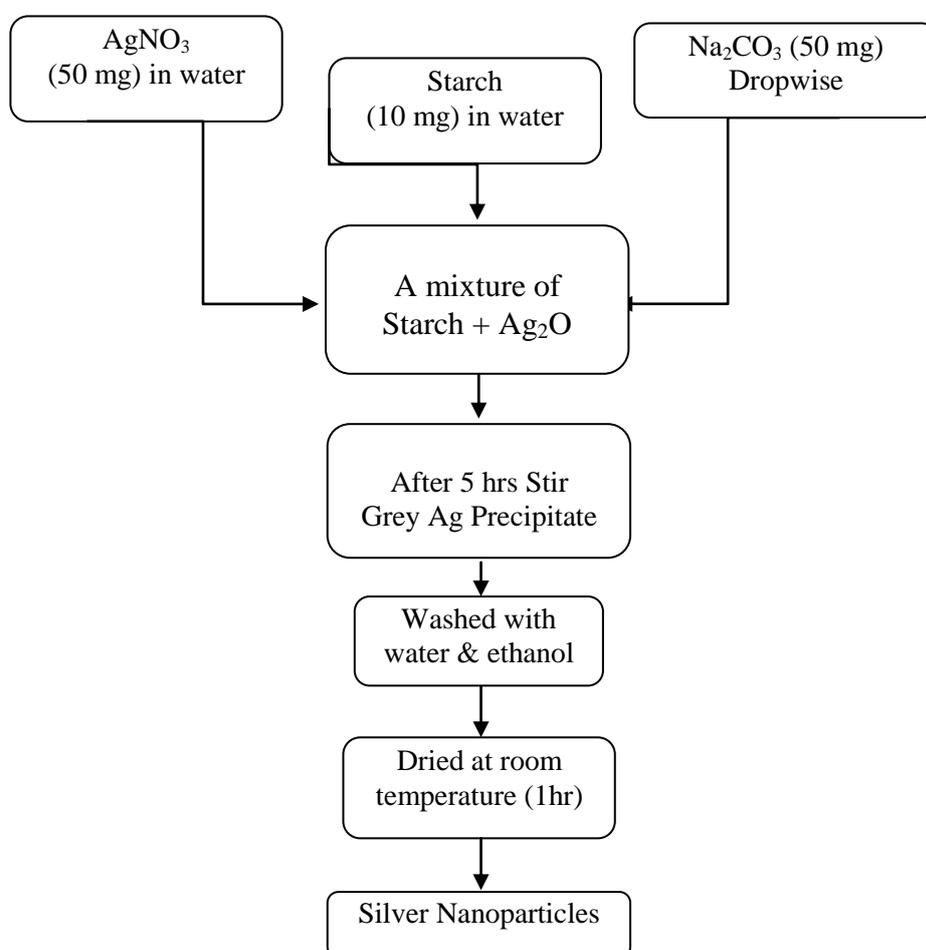


Figure 2.3 Flow-chart depicting the preparation of Silver nanoparticles

When the silver nitrate reacts with starch in the presence of a basic medium, a double decomposition reaction takes place leaving Ag^+ ions in solution. In order to turn Ag^+ ions into solid state, the ions have to be reduced by receiving an electron from a donor. When the reaction is completed, Ag^+ ions are converted to stable Ag particles. Then, the soluble compound is dissolved in water and eliminated by centrifugation process. The above preparation process is depicted in the flow chart given in Figure 2.3.