Chapter 3

Synthesis

The general processes of synthesis of nanoparticles through different techniques are discussed in this chapter. We then present our approach of the synthesis of PbS/PVA quantum dots and Ag nps through chemical method and bio-synthesis of Ag nanoparticles in tea leaf extracts.

3.1 Introduction:

The synthesis of nanoparticles was started centuries ago. Gold nanoparticles and colloidal gold were extensively used in some countries for various purposes. Around thousand years ago gold nanoparticle was used as an inorganic dye in China. They used it for giving colour to the ceramic porcelains. Colloidal gold had its major application in ancient times in medical field, for example, for the treatment of arthritis, which still continues. In 1857, Faraday published his study on the preparation and properties of colloidal dispersion of gold and the samples prepared by him were stable for almost a century before being destroyed during World WarII [1-2].

The research in the nanometer scale world accelerated after the advent of the technologies which could see and manipulate the matter in this dimension. Modern quantum dot technology traces its origin back to the mid 1970s [2,3].

3.2 Methods adopted to prepare nanoparticles;

There are many methods to synthesize nanoparticles and also many ways to group these methods. On the basis of the approaches followed to fabricate the nanoparticles,
they are grouped as [2] top-down and bottom-up approaches, which may again be grouped broadly as chemical and physical methods.

**3.2.1 Top-down approach**

This approach produces the nanoparticles by breaking the bulk material into small pieces of nanometer dimension. It can be done by the following methods:

(a) *Milling*: This method is mainly used to produce nanoparticles for use in nanocomposites and nanograin bulk materials. This method suffers from the following drawbacks:

(i) The nanoparticles fabricated by milling have a broad size, shape and geometrical distribution,

(ii) Lots of impurities from milling medium come.

(iii) Defects are noticed in the nanoparticles produced by milling. But the preparation of nanocomposites and nanograin bulk materials require lower sintering temperature and in these materials the defects can be annealed by sintering.

(b) *Attrition*: nanoparticles produced by this method have sizes ranging from few tens to several hundred nanometers in diameter.

(c) *Repeated Thermal Quenching*: This method produces nanoparticles by breaking a bulk material into small pieces, provided the material has low thermal conductivity and large volume change with increase in temperature.

(d) *Lithography*: It is the process of transferring a pattern into a reactive polymer film, termed as resist, which will be subsequently used to replicate that pattern into an underlying thin film or substrate.
Lithography is sometimes considered as hybrid approach, since the growth of thin films is bottom-up whereas etching is top-down approach, while nanolithography and nanomanipulation are commonly a bottom-up approach.

3.2.2 Bottom-up approach

Bottom-up approach means building up of a material from bottom atom-by-atom, molecule-by-molecule or cluster-by-cluster. In crystal growth, species such as atoms, ions and molecules, after impinging onto the growth surface, assemble into crystal structure one after another, generally called self-assembly. It has two approaches, namely, thermodynamic and kinetic.

(a) Thermodynamic approach: This method follows the following sequence to fabricate nanoparticles,

(i) Generation of super saturation
(ii) Nucleation
(iii) Subsequent growth

The steps followed, specifically for metals, non-oxide and oxide semiconductors are as follows,

(1) Metallic nanoparticles: By reduction of metal complexes in dilute solution, thereby producing metal colloidal dispersions.
(2) Non-oxide semiconductor nanoparticles: Pyrolysis of organometallic precursors are dissolved in anhydride solvents at elevated temperatures in an airless environment in the presence of polymer stabilizer or capping material.
(3) Oxide nanoparticles: By sol-gel processing, forced hydrolysis, controlled release of ions, vapor phase reactions and solid state phase segregation.
The above methods follow homogeneous nucleation. Following are the methods which follow heterogeneous nucleation method:

(1) Thermal oxidation

(2) Sputtering and thermal oxidation

(3) Argon plasma and ulterior thermal oxidation

(b) Kinetic approach: In this method, formation of nanoparticles is achieved by any one of the following techniques:

(i) by limiting the amount of precursors available for the growth, for example in Molecular Beam Epitaxy (MBE)

(ii) by confining the process in a limited space: this is done by the following four ways:

(1) Liquid droplets in gas phase as in aerosol synthesis and spray pyrolysis

(2) Liquid droplets in liquid as in micelle and micro emulsion synthesis

(3) Template based synthesis

(4) Self-terminating synthesis

In top-down approach, some problems are faced like imperfection in surface structure, crystallographic damage to the processed patterns, defects due to the etching eg. nanowires made by lithography is not smooth and may have impurities and imperfections at the surface. These lead to changes in physical properties and surface chemistry, since the surface to volume ratio is very large in nanoparticles. These imperfections may again lead to reduced conductivity due to inelastic surface scattering which leads to the generation of excess heat and thus impose extra challenge to the device fabrication.
Bottom-up approach is comparatively better in case of nanomaterials, because in nanometer scale, all the tools are too big to deal with the dimensions. Bottom-up approach also gives structure with less defects, more homogeneous composition and better short and long range ordering. In bottom-up approach, the synthesis is mainly driven by the reduction of Gibbs free energy, so the nanomaterials produced are close to the equilibrium state. In top-down approach, there is internal stress in addition to defects and contamination.

3.2.3 Chemical and physical methods

The methods are also grouped broadly into chemical and physical techniques. Following are the physical techniques used to synthesize the nanoparticles,

(a) Lithographic techniques
   (i) Photolithography
   (ii) Phase shifting optical lithography
   (iii) Electron beam lithography
   (iv) X-ray lithography
   (v) Focussed ion beam lithography
   (vi) Neutral atomic beam lithography

(b) Nanomanipulation and nanolithography
   (i) Scanning Tunneling Microscopy(STM)
   (ii) Atomic Force Microscopy(AFM)
   (iii) Near-field scanning optical microscopy(NSOM)
   (iv) Nanomanipulation
   (v) Nanolithography
(c) Soft lithography

(i) Microcontract printing
(ii) Moulding
(iii) Nanoimprint
(iv) Dip-pen lithography

(d) Self-assembly of nanoparticles or nanowires

(i) Capillary force induced assembly
(ii) Dispersion interaction assisted assembly
(iii) Shear force assisted assembly
(iv) Electric-field assisted assembly
(v) Covalently linked assembly
(vi) Gravitational field assisted assembly
(vii) Template assisted assembly

The main advantage of chemical method is that it is simple and less expensive. In the chemical method, there is possibility of manipulation in the molecular level. Because of mixing in the molecular level, good chemical homogeneity can be obtained. Also by understanding the relationship between how matter is assembled on an atomic and molecular level, and the material macroscopic properties, molecular synthetic chemistry can be tailored to prepare novel starting components. Better control of the particle size and shape distribution can be achieved in particle synthesis. To get benefit from the advantages of chemical processing, an understanding of the principles of the crystal chemistry, thermodynamics, phase equilibrium and reaction kinetics are required. Chemical method is also having problems like, in some preparations, the chemistry is complex and hazardous. Entrapment of impurities in the final product are found, which
needs to be avoided or minimized to obtain the desired properties. For some of the systems it may be difficult to scale up for economical production of a large quantity of material. Agglomeration is also a problem and must be avoided at any stage of the synthesis process.

3.2.4 Biosynthesis

The nanoparticles synthesised through chemical route cannot be considered as environment friendly because a lot of chemicals are used which are hazardous for health. But recently, the fabrication of nanoparticles through green route has gained interest because the methods are considered safe as they utilise non-toxic chemicals and solvents. Moreover, it does not require the use of any kind of stabilizers. Various environmental friendly materials like plant extracts, bacteria, actinomycetes, fungi and enzymes come under ‘green synthesis’ arena. The process of using microorganisms for the synthesis of nanoparticles also involves the culture of the microorganisms which is tedious and hence the use of plant or plant extracts is an advantage over the use of microorganisms. These processes can be easily scaled up for the synthesis of nanoparticles without involving any high pressure, energy and temperature conditions.

3.3. Properties aimed to be achieved in the nanoparticles prepared

The following ideal properties in the nanoparticles prepared by any method are essential [2]

(1) Identical size of all the particles (monosized or with uniform size distribution)

(2) Identical shape or morphology
(3) Identical chemical composition

(4) Identical crystal structure among different particles and within individual particle (the core and the surface of the particle must have the same crystal structure)

(5) Individually dispersed or monodispersed. No agglomeration should be there. If it is there then it must be re-dispersible.

3.4 Methods adopted for synthesis of PbS QDs & Ag nps by other workers

Various methods have been adopted for the preparation of nanostructures by workers all over the globe. Among them, the chemical route is the most popular to prepare the semiconductor nanoparticles. Wang et al. in the year 1987 synthesised PbS quantum dots on the polymer matrix by exchanging Pb⁺⁺ into polymer film and then reacting with H₂S[4]. Borrelli et al. in the year 1994 developed PbS quantum dots on silicate glass matrix [5]. Chang et al. in the year 2000 demonstrated that superlattices of nanometer sized PbS quantum dots can be generated in solutions by ‘Crystallisation’ of monodisperse colloids[6]. Successful preparation of colloidal PbS nanocrystal was reported using a solution based organometallic route and lead oleate (PbO) and bis(trimethylsilyl) sulphide (TMS)[7]. Silva et al. in the year 2006 reported synthesis of PbS quantum dots embedded in sulphur doped oxide glass matrix (S-doped glass matrix) by means of fusion method [8]. Egorov et al. in the year 2007 used photochemical technique and synthesized PbS nanoparticles in photolysis of aqueous solution of lead thiosulphate complex (LTC) [9]. By using ionic exchange process in alkaline aqueous solution, PbS quantum dots were synthesised in Zeolite Na-X matrix[10]. Acosta et al. in the year 2007 [10], Nenadovic et al in the year 1990 reported synthesis of high quality, monodisperse PbS quantum dots in Polyvinyl
alcohol(PVA)[11]. Lu et al. in the year 2002 reported PbS nanocrystals with a particles size of 3.3 nm synthesised in PVA coating on fused silica glass substrate [12]. Hines et al. in the year 2003 synthesized PbS nanocrystals via the solution phase organometallic approach [13].

A variety of preparation route by various workers for preparation of Ag nanoparticles have been reported by Poonam Benjwal [14]. S. Navaladian et al. [15] in the year 2010 reported synthesis of Ag nanoparticles by thermal decomposition of silver oxalate in water and in ethylene glycol. Javed Ijaj Hussain et al. in the year 2011 [16] reported chemical reduction process to synthesize stable and various shapes of silver nanoparticles in water by the use of reducing agents. Jie et al. [17] in the year 2008 reported the thermal reduction method for synthesis of Ag nanoparticles. Poonam Pal Singh et al. [18] in the year 2012 reported the green synthesis of Ag nanoparticles from leaves and barks. The biosynthesis of nanoparticles as an emerging highlight of the intersection of nanotechnology and biotechnology has increased the attention due to a growing need to develop environmentally benign technologies in material synthesis (Kalishwaralal et al.2008). The first evidence of synthesizing silver nanoparticles by green route was established in 1984 using Pseudomonas stutzeri (Haefeli et al. 1984, Zhang et al. 2005; Nair and Pradeep 2002). Huang et al. in the year 2008 suggested the use of Cinnamomum camphora leaves to synthesise the Ag nanoparticles. Various works have been reported where Ag nanoparticles are synthesized by the use of templates like DNA, membrane, viruses and diatoms [19].
3.5 Present Work

In the present work, chemical route is followed for the synthesis of PbS/PVA & Ag/PVA nanocomposites for fabricating electronic devices and green route is followed for synthesis of Ag nps in tea leaf extract for application in bio-medical science.

3.5.1 Synthesis of PbS/PVA nanoparticles

3.5.1.1 Materials:

Polyvinyl Alcohol PVA(), Pb(NO3)2 (assay ≥99% ),Na2S(assay 55-58%) were purchased from Merck Specialities Private Limited and used as received. Distilled water is used in the process of synthesis.

3.5.1.2 Experimental Section:

The experiment is done in the following steps:

(i) Preparation of the matrix: A beaker is taken and is washed with detergent and distilled water several times. It is lastly cleaned by acetone and then placed inside the oven to dry. After it is properly dried, it is filled with four hundred ml of distilled water. The digital weight machine is turned on. A small piece of clean, dry paper is placed over the balance and the weight machine is adjusted to zero. The PVA powder is then poured very gently by a spoon over the paper such that exactly sixteen grams of the powder is weighed. During weighing, care is taken that the balance is not disturbed and the window is remain closed. The PVA powder is then poured in the beaker.
The small piece of magnet is also placed inside the beaker. The magnetic stirrer is switched on. The temperature is maintained between 60-70°C. The rpm (revolution per minute) is adjusted to a higher value. The beaker is then placed over the magnetic stirrer. The solution is stirred for atleast three hours. Thus 4% of PVA solution is obtained. The solution is kept overnight for stabilization.

(ii) Preparation of Lead Nitrate\([\text{Pb(NO}_3\text{)}_2]\) solution: One gram of \(\text{Pb(NO}_3\text{)}_2\) powder is weighed in the digital weighing machine and is added to 50ml of distilled water and is stirred in the magnetic stirrer at the same temperature and rpm [step (i)] for about half an hour and kept separately.

(iii) Preparation of \(\text{Na}_2\text{S}\) solution: One gram of \(\text{Na}_2\text{S}\) flakes is weighed in the digital weighing machine and is added to 50ml of distilled water and is stirred in the magnetic stirrer at the same temperature and rpm (as in i) for about five minutes and kept separately.

(iv) Preparation of \(\text{PbS}\) nanoparticles: 20ml of PVA solution [(step(i)] is added in a cleaned beaker. To it, 10ml of \(\text{Pb(NO}_3\text{)}_2\) solution is added and stirred in the magnetic stirrer at a temperature of 60°C. After stirring for about 15 mins, \(\text{Na}_2\text{S}\) solution [step(iii)] is added drop by drop till the colour of the solution changes to light brown. The solution is then stirred for about another 15 mins. The colour is observed to change to deep brown. One of the sample is thus prepared.

Different samples are prepared adopting the above steps by changing the following parameters:

(a) ph value
(b) temperature

c) time of stirring

By adopting the above procedure, samples are prepared as shown in table 3.1. The samples are kept overnight for stabilisation.

Table 3.1: Physical parameters for the PbS/PVA samples

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Stirring Time of PVA(hr)</th>
<th>Stirring rate for PVA(RPM)</th>
<th>Temperature in °C for the PVA while stirring</th>
<th>Stirring rate for PVA and PbS(RPM)</th>
<th>Temperature in °C for PVA while stirring with PbS</th>
<th>Time in (hr) while stirring PVA and PbS</th>
<th>pH value of the mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>S_1</td>
<td>2 ½</td>
<td>900</td>
<td>50-60</td>
<td>900</td>
<td>60-70</td>
<td>1</td>
<td>7.1</td>
</tr>
<tr>
<td>S_2</td>
<td>3</td>
<td>600</td>
<td>60-70</td>
<td>600</td>
<td>70-80</td>
<td>1</td>
<td>7.2</td>
</tr>
<tr>
<td>S_3</td>
<td>3 ½</td>
<td>400</td>
<td>70-80</td>
<td>400</td>
<td>80-90</td>
<td>1</td>
<td>6.9</td>
</tr>
<tr>
<td>S_4</td>
<td>2 ½</td>
<td>900</td>
<td>50-60</td>
<td>900</td>
<td>80-90</td>
<td>1 ½</td>
<td>7</td>
</tr>
<tr>
<td>S_5</td>
<td>3</td>
<td>600</td>
<td>60-70</td>
<td>600</td>
<td>80-90</td>
<td>2</td>
<td>6.8</td>
</tr>
<tr>
<td>S_6</td>
<td>3 ½</td>
<td>400</td>
<td>70-80</td>
<td>400</td>
<td>80-90</td>
<td>2 ½</td>
<td>6.9</td>
</tr>
<tr>
<td>S_7</td>
<td>2 ½</td>
<td>900</td>
<td>50-60</td>
<td>900</td>
<td>70-80</td>
<td>1</td>
<td>4.5</td>
</tr>
<tr>
<td>S_8</td>
<td>3</td>
<td>600</td>
<td>60-70</td>
<td>600</td>
<td>70-80</td>
<td>1</td>
<td>4.8</td>
</tr>
<tr>
<td>S_9</td>
<td>3 ½</td>
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<td>70-80</td>
<td>400</td>
<td>70-80</td>
<td>1</td>
<td>5.5</td>
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<tr>
<td>S_10</td>
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<td>4.8</td>
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<tr>
<td>S_11</td>
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<td>60-70</td>
<td>600</td>
<td>60-70</td>
<td>2 ½</td>
<td>5.5</td>
</tr>
<tr>
<td>S_12</td>
<td>4</td>
<td>400</td>
<td>70-80</td>
<td>400</td>
<td>80-90</td>
<td>1 ½</td>
<td>4.5</td>
</tr>
</tbody>
</table>
3.5.2 Synthesis of Ag/PVA nanocomposites

3.5.2.1 Materials: Silver nitrate (AgNO₃) (assay ≥99%) was purchased from Merck Specialities Private Limited, Polyvinyl Alcohol PVA(), distilled water.

3.5.2.2 Experimental Section:

AgNO₃ solution is prepared by dissolving AgNO₃ powder in distilled water. The mixture is stirred at room temperature. PVA solution is prepared as discussed in the section 3.5.2.1. AgNO₃ solution and PVA solution is mixed in the ratio of 1:1 and then the reaction mixture is heated to 900°C. Different samples (table 3.2) are prepared by keeping them in the oven for different time intervals.

Table 3.2: Physical parameters for Ag/PVA samples

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Temp. of stirring of PVA(˚C)</th>
<th>Time of stirring of PVA(hr)</th>
<th>Time of heating (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgP₁</td>
<td>60-70</td>
<td>3</td>
<td>10</td>
</tr>
<tr>
<td>AgP₂</td>
<td>70-80</td>
<td>3½</td>
<td>20</td>
</tr>
<tr>
<td>AgP₃</td>
<td>80-90</td>
<td>4</td>
<td>30</td>
</tr>
<tr>
<td>AgP₄</td>
<td>90-100</td>
<td>4½</td>
<td>40</td>
</tr>
</tbody>
</table>

3.5.3 Synthesis of Ag nanoparticles in tea leaf extracts

3.5.3.1 Materials: Silver nitrate (AgNO₃) (assay ≥99%) was purchased from Merck Specialities Private Limited, fresh tea leaves were collected from tea garden of upper Assam,
3.5.3.2 Experimental Section:

The process of synthesis can be described as follows:

Two grams of tea leaves (fresh green leaves collected from the garden) is weighed and transferred to a beaker containing 20ml of distilled water. The mixture is thoroughly agitated for the whole night by using a magnetic stirrer keeping the rotations at a slow rate. Next day the mixture is filtered to obtain the deep brown liquor. The liquor is centrifuged and then again filtered to remove the impurities.

![Tea leaf extract and the Ag nano sample](image)

Figure 2.1: Tea leaf extract and the Ag nano sample

1 molar of silver nitrate solution is prepared in distilled water. Now different samples are prepared by taking same concentrations of silver nitrate and different concentrations of tea extract and distilled water as given in table 3.3: The sample solutions are kept overnight for stabilization whereas tea leaf extract (figure 2.1) is stored in refrigerator to be used for some days.
Table 3.3: physical parameters for Ag/tea extract samples

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Volume of AgNO$_3$ (ml)</th>
<th>Volume of Tea extract (ml)</th>
<th>Volume of water (ml)</th>
<th>Total Volume (ml)</th>
<th>Concentration of tea</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_gG_1$</td>
<td>0.2</td>
<td>0.002</td>
<td>3.798</td>
<td>4</td>
<td>0.0005</td>
</tr>
<tr>
<td>$A_gG_2$</td>
<td>0.2</td>
<td>0.01</td>
<td>3.7</td>
<td>4</td>
<td>0.0025</td>
</tr>
<tr>
<td>$A_gG_3$</td>
<td>0.2</td>
<td>0.05</td>
<td>3.75</td>
<td>4</td>
<td>0.0125</td>
</tr>
<tr>
<td>$A_gG_4$</td>
<td>0.2</td>
<td>0.1</td>
<td>3.7</td>
<td>4</td>
<td>0.025</td>
</tr>
</tbody>
</table>

All the as-prepared samples are then subjected to various characterization techniques, which are detailed in the next chapter.

References:


http://dspace.thapar.edu:8080/dspace/bitstream/10266/11613/1161.pdf


