Chapter 2: Synthesis
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Synthesis

2.1 Introduction

The synthesis of nanoparticles had started centuries ago. Gold nanoparticles and colloidal gold were used extensively 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 red color to the ceramic porcelains. Colloidal gold had its major application 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 War II [2].

The research in the field of nanometer scale world accelerated after the advent of the technologies which could see and manipulate the matter in this dimension. Modern quantum dot (nanoparticle) technology traces its origin back to the mid 1970s.

2.2 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.

2.2.1 Top-down approach

This approach produces the nanoparticles by breaking the bulk material into small pieces of nanometer dimension. It can be done by following four methods,
(a) Milling: This method is mainly used to produce nanoparticles for use in nanocomposites and nanograined bulk materials. This method suffers from the following drawbacks,

(i) The nanoparticles fabricated by milling have a broad size, shape and geometry 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 nanograined 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 also 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. But, this method is difficult to control.

(d) Lithography: It is the process of transferring a pattern into a reactive polymer film, termed as resist, which will subsequently be 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.

2.2.2 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, 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 the 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 dissolved in anhydrate 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 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 etching e.g., nanowires made by lithography is not smooth and may have impurities and imperfections at the surface. These may 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 excessive heat and thus impose extra challenge to the device design 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 closer to the equilibrium state. In top-down approach, there is internal stress in addition to defects and contamination.

2.2.3 Chemical and physical methods

The methods are also grouped broadly into chemical and physical techniques. All the above methods are mainly chemical methods except lithography. 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) Focused 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) Microcontact printing

(ii) Molding

(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
The main advantage of chemical method is that it is simple and less expensive. In the chemical techniques, there is a possibility of manipulation at the molecular level. Because of mixing at the molecular level, good chemical homogeneity can be achieved. 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 tailor designed to prepare novel starting components. Better control of the particle size, shape and size distribution can be achieved in particle synthesis. To get benefit from the advantages of chemical processing, an understanding of the principles of crystal chemistry, thermodynamics, and phase equilibrium and reaction kinetics is required. Chemical method is also having some 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 desired properties. For some of the systems, it may become 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.

2.3 Properties aimed to be achieved in the nanoparticles prepared

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

(1) Identical size of all the particles (mono sized 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 same crystal structure).

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

2.4 Methods adopted by other workers

Various methods have been adopted for the preparation of nanostructures. Among them, chemical route is very popular and is followed by various workers for the synthesis of nanoparticles. Karar et al. [100], prepared Mn doped ZnS nanocrystallites by following chemical method. Li et al. [57] adopted aqueous one-step method to prepare non-heavy-metal ZnS quantum dots. Mn doped nanocrystals of ZnS were prepared by following chemical process by Bhargava et al. [24]. Shang et al. [76] controlled the morphologies of nanostructured ZnO by following a simple solution method. Mn doped ZnS nanoparticles were prepared by co-precipitation reaction by Warad et al. [21]. Rathore et al. [58] followed chemical method to prepare ZnS nanoparticles of different sizes. Kumbhojkar et al. [18] followed wet chemical routes to prepare ZnS nanoclusters. Other than chemical methods, other methods like vapor phase transport, molecular beam epitaxy etc. are also popular. ZnO nanowire and nanonail arrays have been synthesized by oxygen assisted thermal evaporation of metallic zinc on quartz substrate by Kar et al. [73]. Phase controlled synthesis of ZnS nanobelts was carried out by following vapor-liquid-solid process by Ding et al. [56]. Hamedani et al. [75] followed microwave irradiation technique to prepare ZnO nanocrystals. Lu et al. [19] prepared ZnO quantum dots by vapor phase transport growth process. Zhang et al. [68] controllably fabricated nanostructures of ZnO having different shapes by citric acid assisted hydrothermal process.
2.5 Present Work

In the present investigation, chemical and quenching methods are followed to prepare samples of ZnS and ZnO, respectively. In both the cases, poly-vinyl alcohol (PVOH) is used as the matrix. The samples prepared are: ZnS, ZnS:Cu, ZnS:Fe, ZnO, ZnO:Cu and ZnO:Fe.

(a) Undoped ZnS samples

Chemical method is followed to prepare ZnS nanocrystals embedded in polymer matrix (PVOH). 5wt% solution of poly-vinyl alcohol is taken as the matrix (capping agent). It is prepared by stirring 5gm of PVOH powder in 100ml of distilled water at 70°C and 300rpm for 3hrs. Aqueous solutions of ZnCl₂ and Na₂S are used to prepare ZnS nanocrystals. These solutions are prepared in such a way that the molecular weight ratio of the chemicals in the solutions becomes 1:1 (for sample S₇, it is 2:1). PVOH and ZnCl₂ solutions are then mixed in 2:1 volume ratio in magnetic stirrer at controlled temperature and rotations per minute (table 2.1). Few drops of HNO₃ are added to control the pH of the samples (table 2.1). To the above solution, Na₂S solution is added drop by drop, to make the solution completely milky. The solution is then kept overnight at room temperature for stabilization. A good number of samples are prepared, by keeping pH constant and varying temperature, stirring rate and duration of stirring. This is repeated for each of the pH value given in table 2.1. The samples, thus prepared, are characterized. The samples with suitable characterization results are selected (table 2.1) for further detailed investigation.

The reaction followed in the synthesis of ZnS nanocrystals is as follows:

\[
PVOH + ZnCl₂ + Na₂S \rightarrow PVOH + ZnS + 2NaCl
\]
Table 2.1 Conditions maintained for preparing undoped ZnS samples

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>pH</th>
<th>Conditions of mixing PVOH and ZnCl₂</th>
<th>RPM</th>
<th>Temp (°C)</th>
<th>Time(min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S₁</td>
<td>1.6</td>
<td></td>
<td>200</td>
<td>Room Temp</td>
<td>10</td>
</tr>
<tr>
<td>S₂</td>
<td>2.9</td>
<td></td>
<td>200</td>
<td>Room Temp</td>
<td>10</td>
</tr>
<tr>
<td>S₃</td>
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<td>200</td>
<td>60</td>
<td>10</td>
</tr>
<tr>
<td>S₄</td>
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<td>60</td>
<td>10</td>
</tr>
<tr>
<td>S₅</td>
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<td></td>
<td>500</td>
<td>40</td>
<td>15</td>
</tr>
<tr>
<td>S₆</td>
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<td></td>
<td>500</td>
<td>Room Temp</td>
<td>15</td>
</tr>
<tr>
<td>S₇</td>
<td>2.2</td>
<td></td>
<td>500</td>
<td>Room Temp</td>
<td>15</td>
</tr>
</tbody>
</table>

(b) Cu doped samples (ZnS:Cu)

Cu doping is done in the samples using CuCl₂. Aqueous solution of CuCl₂ is prepared by dissolving variable weight (table 2.2) of CuCl₂ in 100ml of distilled water. This is done in magnetic stirrer at 40°C and 600rpm for half an hour. This solution (25% by volume) is then simply added to the ZnCl₂ solution, and the steps given in 2.2.1-(i) are followed. Two samples have been doped with copper (table 2.2).

(c) Iron doped ZnS samples (ZnS:Fe)

Fe doping is done by FeCl₃. Aqueous solution of FeCl₃ is prepared by dissolving variable weight of FeCl₃ (table 2.2) in 100ml of distilled water. The procedure to make the solution is similar to the one used to prepare CuCl₂ solution. This solution (25% by volume) is then simply added to the ZnCl₂ solution, and the steps given in 2.2.1-(i) are followed. Three samples have been doped by iron (table 2.2).

(d) Undoped ZnO samples
Table 2.2 Conditions maintained for preparing doped ZnS samples

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>pH</th>
<th>Weight (gm)</th>
<th>Conditions of mixing PVOH and dopant</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CuCl₂</td>
<td>FeCl₃</td>
</tr>
<tr>
<td>S₅:Cu</td>
<td>4.7</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>S₆:Cu</td>
<td>3.8</td>
<td>1.345</td>
<td></td>
</tr>
<tr>
<td>S₅:Fe</td>
<td>0.8</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>S₆:Fe</td>
<td>0.2</td>
<td>1.62</td>
<td></td>
</tr>
<tr>
<td>S₇:Fe</td>
<td>0.1</td>
<td>1.62</td>
<td></td>
</tr>
</tbody>
</table>

ZnO nanocrystals are grown by adopting quenching method with poly-vinyl alcohol (PVOH) as the matrix. The nanoparticles are incorporated into the polymer matrix by sintering ZnO powder at very high temperature (~ 800°C) for 5hrs followed by its sudden cooling in ice-cold matrix. The weight of PVOH and ZnO is changed to get samples of different weight ratio of PVOH to ZnO (table 2.3). The solution is then stirred at room temperature for half an hour at 200 rpm and is then kept overnight for stabilization. The sample is then casted over glass substrate for further experimentation.

(e) Copper doped ZnO sample (ZnO:Cu)

ZnO is doped by adding few drops of 1wt% solution of CuCl₂ (prepared in a similar way as in case of Cu doped ZnS samples) in the solution in which ZnO is quenched. The solution is then stirred for half an hour at room temperature.

(f) Iron doped ZnO sample (ZnO:Fe)

ZnO is doped by adding few drops of 1wt% solution of FeCl₃ (prepared in a similar way as in case of Fe doped ZnS samples) in the solution in which ZnO is quenched. The solution is then stirred for half an hour at room temperature.
Table 2.3 PVOH/ZnO weight ratios for the undoped and doped ZnO samples

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Weight Ratio (PVOH/ZnO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₁</td>
<td>15</td>
</tr>
<tr>
<td>O₂</td>
<td>4</td>
</tr>
<tr>
<td>O₃</td>
<td>3</td>
</tr>
<tr>
<td>O₄</td>
<td>3.33</td>
</tr>
<tr>
<td>O₅</td>
<td>10</td>
</tr>
<tr>
<td>O₆</td>
<td>5</td>
</tr>
<tr>
<td>O₇:Cu</td>
<td>3.33</td>
</tr>
<tr>
<td>O₇:Fe</td>
<td>3.33</td>
</tr>
</tbody>
</table>

Figure 2.1 Undoped ZnS and ZnO samples in liquid form

Figure 2.2 Undoped ZnS and ZnO samples in thin film form

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