CHAPTER 3

Synthesis of Undoped and Mn Doped ZnO Nanostructures by Chemical Route
3.1 Introduction

Synthesis and study of nanostructure materials have become current topic of research worldwide. It is well known that many fundamental properties of nanostructure materials can be expressed as a function of their size, composition and structural order. Meanwhile, nanostructures with different morphologies are nuclear parts of functional nanostructure devices. In the recent years, workers all over the world have used different preparative techniques like chemical vapour deposition (CVD), electrodeposition (ED), hydrothermal route, sol–gel process, vapour–liquid–solid process, pulsed laser deposition, layer-by-layer method and thermal decomposition for the preparation of zinc oxide nanoparticles with varied morphologies [1–8].

For the synthesis of the ZnO nanostructures we adopted the following methods stated below:

(1) Hydrothermal technique (used for preparing ZnO nanorods)

(2) Microwave irradiation technique (used for preparing undoped and Mn doped ZnO nanoparticles)

Why Hydrothermal Technique???

Hydrothermal technique is a promising alternative synthetic method because of the low process temperature and very easy to control the particle size. The hydrothermal process have several advantage over other growth processes such as use of simple equipment, catalyst-free growth, low cost, large production possible, environmental friendliness and less hazardous.

Why Microwave Irradiation Method???

The utilization of microwave irradiation in the preparation of nanoparticles is reported in recent years. Compared to the conventional methods, the microwave synthesis has the advantages of producing small particle size metal oxide with high
purity owing to short reaction time. It is found that this method is fast, mild, energy efficient and environment friendly route to produce ZnO nanoparticles.

**Why Doping of Mn in ZnO Nanostructure??**

Recently, there has been much attention focused on modifying ZnO by doping with transition metals such as Ag, Ni, Mn, Cu, Co, Cr, Ti. Doping of 3d transition metal Mn into the ZnO lattice offers an interesting way to tailor various properties of ZnO. ZnO nanostructures uniformly doped with Mn can have advantages as dilute ferromagnetic semiconductor (DLS) with characteristic luminescence. For exploitation of luminescent and magnetic nanoparticles such as ZnO:Mn in biological systems, nanoparticles have to be functionalized with certain organic compounds. These studies demonstrated that the metals can change $E_g$ of ZnO and that the dopants can control ZnO grain size [9]. ZnO is also considered for spintronics applications with magnetic ions (Co, Ni, V, Fe and Mn) doping. For this reason, Mn doping has valuable spin off in structural, morphological, electrical, optical and magnetic properties of ZnO [10]. Surface area and surface defect play an important role in photocatalyst activities of metal oxides. The reason is that doping of metal oxide and/or transition metals [like Mn] increase the surface defects. In addition it affects the optical and electronic properties and can presumably shift the optical absorption towards the visible region [11]. Among all the magnetic transition ion-doped ZnO systems, Mn doping is usually the single most concerned mainly because of the fact that the thermal solubility of metallic Mn is larger than 10 mol% in ZnO, and the ‘electron effective mass’ is as large as approximately 0.3 $m_e$, where ‘$m_e$’ is the free-electron mass [12]. Therefore, injected spins and carriers in the nanostructures can be large, thus making Mn-doped ZnO ideal for the fabrication of spintronic nanodevices (spin + electronics), a proposed technology that uses the electron spin rather than the electron charge for reading and writing informations [13].
3.2 Chemical Approach for the Synthesis of ZnO Nanostructures

3.2.1 Materials

The Zinc acetate dihydrate \([\text{Zn(CH}_3\text{COO)}_2\cdot 2\text{H}_2\text{O}]\) (99.5%), Sodium hydroxide \([\text{NaOH}]\) (98%), Manganese acetate tetrahydrate \([\text{Mn(CH}_3\text{COO)}_2\cdot 4\text{H}_2\text{O}]\) (99.5%), Potassium hydroxide \([\text{KOH}]\) (85%) and PolyVinylPyrolidone (PVP) were all from AR Grade LOBA CHEMIE PVT. LTD. Mumbai, INDIA.

Methanol (99.8%) and Ethanol (99.8%) were purchased from HiMedia Laboratory PVT. LTD. Mumbai, INDIA.

All chemicals were directly used without special treatment.

3.2.2 Synthesis of ZnO Nanorods by Hydrothermal Method

- To synthesize the ZnO nanorods, stocks solution of 0.1 M zinc acetate dihydrate was prepared in 50 ml methanol under stirring.
- To this stock solution, 15 ml of 0.5 M sodium hydroxide solution prepared in methanol was added under continuous stirring for 30 minutes in order to get the pH value of the reactants 10.6.
- This solution was transferred into steel lined sealed stainless steel autoclave and maintained at temperature 120\(^\circ\)C for 2 hrs under autogenous pressure.
- Then, it was allowed to cool naturally to room temperature.
- After the reaction was completed, the resulting white solid products were washed with methanol, filtered and then dried in an oven at 60\(^\circ\)C for 24 hrs.

Chemical Reaction Mechanism:

\[
\text{Zn(CH}_3\text{COO)}_2 \cdot 2\text{H}_2\text{O} + \text{NaOH} \rightarrow \text{Zn(CH}_3\text{COO)}\text{OH} + \text{Na(CH}_3\text{COO)} + 2\text{H}_2\text{O} \quad \ldots \ldots \ (1)
\]

\[
\text{Zn(CH}_3\text{COO)}\text{OH} + \text{NaOH} + 2\text{H}_2\text{O} \rightarrow \text{ZnO} + \text{Na(CH}_3\text{COO)} + 3\text{H}_2\text{O} \quad \ldots \ldots \ (2)
\]
Figure 3.1 shows the block diagram of hydrothermal synthesis of ZnO nanorods. Figure 3.2 and figure 3.3 shows the pictorial view of as synthesized solution and powder form of ZnO nanorods respectively.

Figure 3.1 The block diagram of hydrothermal synthesis ZnO nanorods
Figure 3.2 The synthesized solution containing ZnO nanorods

Figure 3.3 The dried powder form of ZnO nanorods
3.2.3 Synthesis of ZnO Nanoparticles by Microwave Irradiation Method

(a) Undoped ZnO Nanoparticles

The undoped ZnO nanoparticles, synthesized under the microwave irradiation are stated below:

- 0.2 M zinc acetate dihydrate was dissolved in 50 ml distilled water.
- 0.4 M sodium hydroxide was dissolved in 50 ml distilled water.
- 0.12 gm PolyVinylPyrolidone (PVP) was dissolved in 50 ml distilled water.
- 25 ml of each zinc acetate dihydrate and sodium hydroxide was mixed together and stirred for 30 minutes.
- While continuous stirring, 25 ml of PVP was added dropwise.
- The prepared mixture was placed under microwave irradiation for 20 sec at 720 watt.
- The precipitates which get formed are separated from the solution by filtration, washed several times with deionized water and absolute ethanol, and then dried in oven at 60°C for 24 hours to obtain ZnO nanocrystalline powder.

Chemical Reaction Mechanism:

\[
\text{Zn(CH}_3\text{COO)}_2 \cdot 2\text{H}_2\text{O} + \text{NaOH} + \text{PVP} \rightarrow \text{PVP} - [\text{Zn(CH}_3\text{COO)}\text{OH}]_n + \text{Na(CH}_3\text{COO)} + 2\text{H}_2\text{O} \quad \ldots \quad (3)
\]

\[
\text{PVP} - [\text{Zn(CH}_3\text{COO)}\text{OH}]_n + n(\text{NaOH}) + 2\text{H}_2\text{O} \rightarrow \text{PVP} - (\text{ZnO})_n + \text{Na(CH}_3\text{COO)} + 3\text{H}_2\text{O} \quad \ldots \quad (4)
\]

**Figure 3.4** shows the block diagram of microwave synthesis of undoped ZnO nanoparticles. **Figure 3.5** and **figure 3.6** shows the pictorial view of synthesized solution and powder form of undoped ZnO nanoparticles respectively.
Figure 3.4 The block diagram of microwave irradiation synthesis of undoped ZnO nanoparticles

Figure 3.5 The synthesized solution of undoped ZnO nanoparticles
(b) Mn Doped ZnO Nanoparticles

- For synthesizing Mn doped ZnO nanoparticles (with Mn content of Y = 5 mol%, 10 mol% and 15 mol%), we took 45 mM of zinc acetate dihydrate and X mM (X= 2.4, 4.4 and 6.4) of manganese acetate tetrahydrate in 200 ml of deionized water respectively and then mixed together and stirred at room temperature followed by microwave irradiation for 20 sec at 720 watt.
- After that, 140 mM of potassium hydroxide in 200 ml deionized water was prepared and added drop by drop to the above solution.
- The precipitates which get formed were separated from the solution by filtration, washed several times with distilled water and absolute ethanol, and then dried in oven at 60°C for 24 hours to obtain Y mol% Mn doped ZnO nanoparticles respectively.
Chemical Reaction Mechanism:

\[
\text{Zn(CH}_3\text{COO)}_2 \cdot 2\text{H}_2\text{O} + \text{Mn(CH}_3\text{COO)}_2 \cdot 4\text{H}_2\text{O} + 2\text{KOH} \rightarrow \text{Zn(CH}_3\text{COO)}\text{OH} + \text{Mn(CH}_3\text{COO)}\text{OH} + 2\text{K(}\text{CH}_3\text{COO)} + 6\text{H}_2\text{O} \quad \ldots \quad (5)
\]

\[
\text{Zn(CH}_3\text{COO)}\text{OH} + \text{Mn(CH}_3\text{COO)}\text{OH} + 2\text{KOH} + 6\text{H}_2\text{O} \rightarrow \text{ZnO: Mn}^{2+} + 2\text{K(}\text{CH}_3\text{COO)} + 8\text{H}_2\text{O} \quad \ldots \quad (6)
\]

**Figure 3.7** shows the block diagram of Microwave synthesis of Y mol% (Y = 5, 10 and 15) Mn doped ZnO nanoparticles. **Figure 3.8**, **figure 3.9** and **figure 3.10** shows the pictorial view of powder form of Y mol% (Y = 5, 10 and 15) Mn doped ZnO nanoparticles respectively.
Figure 3.8 The dried powder form of 5 mol% Mn doped ZnO nanoparticles

Figure 3.9 The dried powder form of 10 mol% Mn doped ZnO nanoparticles
Figure 3.10 The dried powder form of 15 mol% Mn doped ZnO nanoparticles
3.3 Conclusion

1. ZnO nanorods are synthesized using zinc acetate dihydrate and sodium hydroxide as a precursor in methanol medium by hydrothermal technique.

2. We have successfully synthesized undoped ZnO nanoparticles using zinc acetate dihydrate and sodium hydroxide as a precursor by microwave irradiation at 720 watt. Mn doped (with Mn content: 5 mol%, 10 mol% and 15 mol%) ZnO nanoparticles are successfully synthesized using zinc acetate dihydrate, manganese acetate tetrahydrate and potassium hydroxide as a precursor by microwave irradiation at 720 watt.

3. The undoped ZnO nanoparticles appear white in color, whereas Mn-doped ZnO nanoparticles for different concentrations become light brown, and the color becomes deep brownish with increasing Mn concentration.
3.4 References


