CHAPTER – III

SYNTHESIS OF ZnO NANOSTRUCTURES WITH DIFFERENT MORPHOLOGIES

3.1 INTRODUCTION

Zinc oxide nanostructures possess several unique advantages, such as high specific surface area, chemical stability, electrochemical activity and high electron communication features, with the reduction in size, which mainly result from the quantum confinement effect. Such properties indicate a wide range of novel applications in photodetectors, sensors, light emitting diodes and varistors. Different synthesis techniques, such as physical vapor deposition (PVD), chemical vapor deposition (CVD) and solution based chemistry (SBC) are employed to produce ZnO nanostructures of different morphologies. Among the techniques employed, those belonging to the solution based chemistry (hydrothermal, sol-gel and precipitation method) are suitable for the preparation of ZnO nanostructures in industrial scale (Wu et al., 2006) since they are relatively cheap and provide a high uniformity of the final product (Hu and Chen, 2008).

In this study, cauliflower-like, flower like, hexagonal shaped and spherical shaped ZnO nanostructures were synthesized in short reaction time and in relatively low temperature by the solochemical method using different precursors, such as zinc nitrate tetrahydrate and zinc acetate dihydrate without any posterior treatments. Solochemical (SC) processing is a sol-gel technique used for the production of zinc oxide nanopowder. This method involves preparation of a solution containing zinc complex and subsequent decomposition of the complex into the zinc oxide nanopowder. Another name for this
method is two-stage solochemical (TSSC) method. The structural and phase formation of the samples were identified by X-ray diffraction (XRD) technique. The morphology and size of the ZnO nanostructures were evaluated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The optical properties were confirmed by UV-vis diffuse reflectance/absorption spectroscopy.

3.2 EXPERIMENTAL

3.2.1 Materials

The source materials, such as zinc nitrate tetrahydrate [(Zn(NO$_3$)$_2$.4H$_2$O], zinc acetate dihydrate [Zn(CH$_3$COO)$_2$.2H$_2$O], sodium hydroxide (NaOH), potassium hydroxide (KOH) and ammonia solution (25% NH$_4$OH) were of analytical grade and used as purchased. Solutions were prepared by dissolving appropriate amount of the compounds in double distilled water.

3.2.2 Synthesis of Cauliflower-like ZnO Nanostructures (Sample code: A)

In this method, 0.5 M aqueous solution of zinc nitrate tetrahydrate and 1.0 M aqueous solution of sodium hydroxide (NaOH) were prepared in distilled water. The beaker containing NaOH solution was then heated to a temperature of about 60 °C. The zinc nitrate tetrahydrate solution was added dropwise for 45 minutes to the above heated solution under vigorous stirring. The beaker was sealed at this condition for 2 hours. The precipitate obtained was cleaned with deionized water and ethanol several times and then dried in air at 60 °C.
Reaction Mechanism

In the initial stage zinc nitrate may convert into zinc hydroxide \([\text{Zn(OH)}_2]\) colloids under alkali solution, as shown in reaction (1). During the process, part of the \(\text{Zn(OH)}_2\) colloids dissolves into \(\text{Zn}^{2+}\) and \(\text{OH}^-\) according to reaction (2). When the concentration of \(\text{Zn}^{2+}\) and \(\text{OH}^-\) reaches the super saturation degree of \(\text{ZnO}\), \(\text{ZnO}\) nuclei will form according to reaction (3).

\[
\text{Zn(NO}_3\text{)}_2 \cdot 4\text{H}_2\text{O} + 2\text{NaOH} \rightarrow \text{Zn(OH)}_2 + 2\text{NaNO}_3 + 4\text{H}_2\text{O} \tag{3.1}
\]
\[
\text{Zn(OH)}_2 + 2\text{H}_2\text{O} \rightarrow \text{Zn}^{2+} + 2\text{OH}^- + 2\text{H}_2\text{O} \rightarrow \text{Zn(OH)}_4^{2-} + 2\text{H}^+ \tag{3.2}
\]
\[
\text{Zn(OH)}_4^{2-} \rightarrow \text{ZnO} + \text{H}_2\text{O} + 2\text{OH}^- \tag{3.3}
\]

3.2.3 Synthesis of \(\text{ZnO}\) Nanoflowers (Sample code: B)

In this method, 6 mL of \(\text{NH}_4\text{OH}\) was first dissolved in 94 mL of distilled water in a 600 mL conical flask. Simultaneously, 0.2 M zinc acetate dihydrate was dissolved in 100 mL of distilled water and then added dropwise into \(\text{NH}_4\text{OH}\) solution. White precipitate was formed immediately and it was heated to 70 °C and maintained at that temperature for 1 hour. The precipitate was filtered after being cooled and then rinsed with distilled water and absolute ethanol. Finally it was dried in air at 60 °C.

Reaction Mechanism

The overall reactions for the \(\text{ZnO}\) growth may be expressed as follows:

\[
\text{Zn(CH}_3\text{COO)}_2 \cdot 2\text{H}_2\text{O} + 2\text{NH}_4\text{OH} \rightarrow 2\text{CH}_3\text{COONH}_4 + \text{Zn(OH)}_2 \tag{3.4}
\]
\[
\text{Zn(OH)}_2 + 2\text{OH} \rightarrow \text{Zn(OH)}_4^{2-} \tag{3.5}
\]
\[
\text{Zn(OH)}_4^{2-} \rightarrow \text{ZnO} + \text{H}_2\text{O} + 2\text{OH}^- \tag{3.6}
\]
3.2.4 Synthesis of Hexagonal ZnO Nanostructures (Sample code: C)

In this method, 1.0 M aqueous solution of NaOH was added dropwise into 0.3 M aqueous solution of zinc acetate dihydrate under continuous stirring. The solution was then heated for 30 minutes at 80 °C. The resulting white precipitate was washed with methanol several times and dried at room temperature.

**Reaction Mechanism**

The general reactions occurring during the synthesis process can be described by the following equations:

\[
\text{Zn(CH}_3\text{COO)}_2\cdot2\text{H}_2\text{O} + 2\text{NaOH} \rightarrow \text{Zn(OH)}_2 + 2\text{CH}_3\text{COONa} + 2\text{H}_2\text{O} \quad (3.7)
\]

\[
\text{Zn(OH)}_2 + 2\text{H}_2\text{O} \rightarrow \text{Zn(OH)}_4^{2-} + 2\text{H}^+ \quad (3.8)
\]

\[
\text{Zn(OH)}_4^{2-} \rightarrow \text{ZnO} + \text{H}_2\text{O} + 2\text{OH}^- \quad (3.9)
\]

3.2.5 Synthesis of Spherical ZnO Nanostructures (Sample code: D)

In this method, 0.5 M aqueous solution of zinc nitrate tetrahydrate and 1.0 M aqueous solution of potassium hydroxide (KOH) were prepared in distilled water. The reaction solution was heated at 50 °C under continuous stirring for 1 hour. The precipitate formed was collected and washed with ethanol and dried at room temperature.

**Reaction Mechanism**

The overall reactions for the growth of ZnO may be expressed as follows:

\[
\text{Zn(NO}_3)_2\cdot4\text{H}_2\text{O} + 2\text{KOH} \rightarrow \text{Zn(OH)}_2^+ 2\text{KNO}_3 + 4\text{H}_2\text{O} \quad (3.10)
\]

\[
\text{Zn(OH)}_2 + 2\text{H}_2\text{O} \rightarrow \text{Zn}^{2+} + 2\text{OH}^- + 2\text{H}_2\text{O} \rightarrow \text{Zn(OH)}_4^{2-} + 2\text{H}^+ \quad (3.11)
\]

\[
\text{Zn(OH)}_4^{2-} \rightarrow \text{ZnO} + \text{H}_2\text{O} + 2\text{OH}^- \quad (3.12)
\]
3.3 CHARACTERIZATION OF ZnO NANOSTRUCTURES

The structural and phase formation of the synthesized ZnO samples were identified by Reich Seifert XRD 3003 diffractometer using Cu-Kα (λ=1.5406 Å) radiation. The morphology and size of the ZnO nanoparticles were evaluated by scanning electron microscopy (SEM, FEI-Quanta 250) and transmission electronic microscopy (TEM, FEI-Technai Sprit). UV-vis measurements were made by Lamda 650 UV-vis diffuse reflectance spectrometer (PerkinElmer).

3.4 RESULTS AND DISCUSSION

3.4.1 Structural Characterization of ZnO Samples

The XRD patterns of the synthesized ZnO samples are shown in Fig. 3.1. The XRD patterns of the samples reveal that all peaks correspond to the characteristic peaks of the hexagonal wurtzite structure of ZnO with space group P6₃mc and lattice parameters of \( a = b = 0.3250 \) nm and \( c = 0.5207 \) nm according to the JCPDS database 36-1451. The average crystallite size of ZnO samples is determined by Debye-Scherrer’s formula \( D = \frac{K \lambda}{\beta \cos \theta} \), where D is the average crystallite size, \( K \) is a constant equal to 0.89, \( \lambda \) is the wavelength of the X-ray used, \( \beta \) is a line width in radians at half maximum intensity of the observed peaks and \( \theta \) is the Bragg angle. The calculated crystallite size of ZnO samples A, B, C and D are 35 nm, 41 nm, 55 nm and 50 nm respectively. No peaks of any other phase are detected, indicating that the ZnO samples obtained by current synthetic route are highly pure. The sharp peaks indicate that the products are well crystallized.
Fig. 3.1. XRD patterns of ZnO nanostructures
3.4.2 Morphology and Size of ZnO Nanostructures using SEM and TEM

The SEM images of the samples are shown in Fig. 3.2. The SEM image of sample A demonstrates the existence of bulk quantity of flower like bunches. Each bunch is gathered by closely packed nanometer scale rods and forms a cauliflower-like structure.

![SEM images of ZnO samples](image)

**Fig. 3.2.** SEM images of ZnO samples

The SEM image of sample B clearly reveals the flower-shaped structure that is constituted by the accumulation of a number of hexagonal nanorods. All the nanorods are seen originated from a single centre exhibiting flower-like morphologies. The SEM
image of sample C apparently exhibits hexagonal pillars with the holes on their top surface and an empty interior. It also shows agglomeration of nanopillars scatteringly. The SEM image of sample D manifests semi-spherical shaped nanostructures which are agglomerated patchingly.

The TEM images of samples are shown in Fig. 3.3. ZnO nanorods holding the cauliflower shaped structure is observable from the image of sample A. The diameter of the stalk is in the range of 50 nm and that of the individual rods giving the cauliflower
shape are 25 nm. The TEM image of sample B clearly reveals the presence of nanorods which is one of the ZnO typical morphologies. These nanorods have an average diameter of about 45 nm. The TEM image of sample C depicts the top surface of the ZnO hexagonal pillar with an inner diameter 50 nm. The TEM image of sample D exhibits semi-spherical ZnO nanostructures with the diameter ranging from 40-60 nm.

3.4.3 Optical Properties of ZnO Nanostructures

The UV-vis absorption spectra of the samples are shown in Fig. 3.4(a). The absorption peaks of ZnO samples A, B, C, and D are 345 nm, 347 nm, 353 nm and 361 nm respectively. The absorption peaks of the samples are lower than that of bulk ZnO (373 nm). Compared to bulk ZnO the ZnO nanostructured samples exhibit a blue-shift in

Fig. 3.4(a). UV-vis absorption spectra
cut off wavelength which may be ascribed to size effect and their unique morphology (Hou, 2006). The diffuse reflectance spectra of the samples are shown in Fig. 3.4(b). The low reflectance values of the spectra of samples indicate high absorption in the corresponding wavelength region.

![UV-vis diffuse reflectance spectra](image)

**Fig. 3.4(b).** UV-vis diffuse reflectance spectra

For analysis purposes the diffuse reflectance, R, of the samples can be related to the Kubelka_Munk function $F(R)$ by the relation $F(R) = (1-R)^2/2R$, (Kortum, 1969). The band gap energy ($E_g$) for the ZnO nanoparticles was determined by the plot of the square of the modified Kubelka_Munk function vs. the photon energy ($h\nu$), shown in Fig. 3.5, (Cimitan, 2009). The band gap values of ZnO samples A, B, C and D are determined to
be 3.39 eV, 3.38 eV, 3.37 eV and 3.37 eV respectively by the extrapolation of the linear portion of the graph down to $[F(R)\times h\nu]^2 = 0$.

![Graph showing plots of $(F(R)\times h\nu)^2$ vs. $h\nu$](image)

**Fig. 3.5.** Plot of $(F(R)\times h\nu)^2$ vs. $h\nu$

### 3.5 CONCLUSION

ZnO nanostructures were prepared by a cost effective and simple solocatalytic technique using zinc nitrate and zinc acetate precursors. The XRD analysis confirmed that the nanoparticles have the hexagonal *wurtzite*-type structure of ZnO. SEM and TEM images of the samples showed the different morphology and size of the ZnO
nanostructures. The UV-vis absorption spectra of the ZnO samples exhibit a blue-shift in cut off wavelength with respect to the bulk. The shape and size of ZnO nanostructures directly affected the band gap values obtained. A wider band gap value was obtained for the ZnO sample A which has cauliflower-like structure and smaller size.