Chapter 5
Chapter 5

5.1 Introduction

Crystalline flower-like ZnO was synthesized by an aminolytic reaction in the aqueous media at an alkaline pH, at low temperature (4 °C) using zinc acetate dihydrate (ZA) and ethanolamine (EA). Effect of various factors such as ageing time, temperature, type of Ligand, type of precursor, and effect of amount of water as a solvent on the crystallinity, morphology, photocatalytic activity and optical properties of flower-like ZnO have been studied. It is observed that on ageing; thin visible film forms at the air-liquid interface by self assembly of flower-like ZnO. Diffraction studies show rearrangement of the single crystalline units at the air-liquid interface leading to the formation of nanobelts. These nanobelts overlap systematically to form petal of flower-like structure.

The morphology and direction of growth are vectorially governed by the type of ligand used. It is seen that, when a monodentate ligand like EA is used then flower-like hierarchical structure is obtained with (001) as the preferred direction of growth. Whereas, when ethylenediamine (ED) is used as a ligand then well separated hexagonal nanoplates (~25 nm) are obtained. When ethylene glycol is used as the ligand no precipitation occurs as it is a weak chelating and precipitating agent and hence product is not formed even after refluxing at the boiling point temperature for several hours. The synthesis of flower-like or hexagonal plates is a kinetically controlled process. Temperature at which the reaction is carried out is an important parameter to decide the crystallinity and morphology of ZnO. ZnO synthesized using ZA and EA at higher temperature gives spindle-like morphology. The amount of water which is used as a solvent also plays a crucial role in the synthesis of crystalline ZnO. The type of precursor also affects building of the final morphology. A clear relationship between the surface defects, photocatalytic and photoluminescent properties of ZnO are observed. More the higher energy defects higher is the photocatalytic activity. ZnO synthesized exhibits blue shift (3.56 eV) in the band emission as compared to bulk ZnO (3.37 eV). The photodegradation of MB over ZnO catalyst synthesized under different conditions shows enhanced photocatalytic activity. The sub-bands formed due to surface defects facilitate separation of charge
carriers increasing their lifetime leading to enhanced photocatalytic activity of flower-like ZnO.

For the ease of understanding influence of various factors on the structure, crystallinity, morphology, photocatalytic and optical properties, this chapter has been divided in two sections:

**Section I: Photocatalytic and Optical Properties of Single Crystalline ZnO at the Air-Liquid Interface:**

This section includes the influence of ageing time on the structure, crystallinity, optical and photocatalytic properties.

And

**Section II: Influence of Various Factors on the Structure, Crystallinity, Optical and Photocatalytic Properties of Flower-Like ZnO:**

This section includes the influence of various factors on the structure, crystallinity, optical and photocatalytic properties of ZnO.
5.2 Section I. Photocatalytic and Optical Properties of Single Crystalline ZnO at the Air-Liquid Interface.

Effect of ageing time on the structure and morphology of ZnO samples synthesized at low temperature has been explained in the present chapter. Optical and photocatalytic properties of the ZnO samples has been studied and correlated.
5.2.1 Introduction

In continuation with the synthesis of ZnO at low temperature in an aqueous system at alkaline pH as described in chapter 4, study of ageing time effect on the crystallinity, morphology, optical and photocatalytic properties of flower-like ZnO was carried out. The crystalline flower-like ZnO at the air-liquid interface and in the sediments have been obtained along with Zn(OH)₂ only in the sediments.

The aqueous solution of Zinc acetate dihydrate (ZA) became cloudy after addition of Ethanolamine (EA) and flower-like ZnO precipitate was formed. Once the EA was added to the aqueous solution of ZA, Zn-EA chelate was formed initially as given in equation 5.1.

\[
Zn^{2+} + 3 [H_2N-(CH_2)_2OH] \rightleftharpoons (Zn(H_2N-(CH_2)_2OH)) \text{P}^{1+} \quad (5.1)
\]

The equilibrium of equation 1 shifts to left when excess of EA reacts with water to release OH⁻ ions and H₃N⁺-(CH₂)₂-OH (EAH⁺) ions as given in equation 5.2 along with lattice energy from the hexagonal lattices of water formed at 4°C due to dissociation of water.

\[
H_2N-(CH_2)_2OH \rightleftharpoons OH^- + H_3N^+(CH_2)_2-OH \quad (5.2)
\]

The Zn²⁺(aq), CH₃COO⁻(aq) and OH⁻(aq) react to form zinc hydroxyacetate nanobelts \{Zn(OH)ₓ(CH₃COO)ᵧ·zH₂O\} according to equation 5.3.

\[
Zn^{2+} + CH₃COO^- + OH^- \rightleftharpoons Zn(OH)ₓ(CH₃COO)ᵧ·zH₂O \quad (5.3)
\]

At 4°C water possesses highest density with tiny hexagonal lattices formed in liquid water. The reaction of amine with water is an exothermic reaction and releases OH⁻ ions and also the lattice energy from the hexagonal lattices of water. This released energy favors the conversion of zinc hydroxyl acetate Zn(OH)ₓ(CH₃COO)ᵧ·zH₂O nanobelts to ZnO according to equation 5.4 as reported earlier [345].
The EAH$^+$ ions (equation 5.2) bind to the negative polar plane of ZnO formed and covers the side surfaces to give flower-like structure. This is confirmed from the fact that when the sample is washed with an organic solvent, the flower-like structure is not retained because of the simple reason that the ligand gets washed away in the organic solvent (Figure 5.2.1).

![Figure 5.2.1](image.png)

**Figure 5.2.1.** SEM images of as-prepared ZnO (ZM4) washed with (a) ethanol and (b) an organic solvent.

The ligand not only provides organized surface for structure formation but also induces a vector growth on the surface, the direction of which differs from characteristically preferred direction of the unit cell.

### 5.2.2 X-ray Diffraction Analysis

ZnO precipitate formed settles down with time and a thin film appears at the air-liquid interface and sediments with crystalline wurtzite ZnO structure. Zn(OH)$_2$ exists along with ZnO in the sediments. The sample code for samples with different ageing period and the corresponding pH of the solution is given in Table 5.2.1
Table 5.2.1 Sample code for the ZnO samples at air-liquid interface and in the sediments with different ageing period and corresponding pH of the solution.

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Sample code</th>
<th>Ageing time (Days)</th>
<th>pH of the solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ZM4 (as prepared flower-like ZnO)</td>
<td>0</td>
<td>9.25</td>
</tr>
<tr>
<td></td>
<td>ZnO film at air-liquid interface</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>ZnO in the sediments</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Liquid between the two layers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>AL1 S1 F1</td>
<td>7</td>
<td>9.24</td>
</tr>
<tr>
<td>3</td>
<td>AL2 S2 F2</td>
<td>14</td>
<td>9.21</td>
</tr>
<tr>
<td>4</td>
<td>AL3 S3 F3</td>
<td>28</td>
<td>9.19</td>
</tr>
<tr>
<td>5</td>
<td>AL4 S4 F4</td>
<td>28</td>
<td>9.08</td>
</tr>
</tbody>
</table>

The XRD profile in Figure 5.2.2 clearly shows formation of ZnO at the air-liquid interface and in the sediments.

Figure 5.2.2 a) XRD of flower-like ZnO along with Zn(OH)$_2$ and Zn(OH)$_x$(CH$_3$COO)$_y$·zH$_2$O in the sediment samples (**indicates Zinc hydroxyl acetate and *indicates zinc hydroxide peaks).
Figure 5.2.2 b) XRD of ZM4 and ZnO samples at air-liquid interface (# indicates the direction of growth).

The sediment samples show formation of orthorhombic zinc hydroxide (Zn(OH)$_2$ (JCPDS 76-1778), along with ZnO (JCPDS file No. 36-1451). Under alkaline conditions, ZnO solubilizes as Zn(OH)$_2$ and Zn(OH)$_4^{2-}$ as given in the equation 5.5. Concentration of Zn(OH)$_2$ in the sediments increases till 7$^{th}$ day (S1) and later on again decreases as can be seen in Figure 5.2.2-a.

$$\text{ZnO}_{(s)} + \text{H}_2\text{O}_{(l)} + \text{OH}^-_{(aq)} \leftrightarrow \text{Zn(OH)}_{2\text{aq}}^+ + [\text{Zn(OH)}_{4}^{2-}]_{(aq)} \hspace{1cm} (5.5)$$

The solution between the two layers becomes intensely colored with time as can be seen in the photograph (Figure 5.2.3). According to Goux A, et al. [346] at room temperature the pK$_s$ of ZnO and Zn(OH)$_2$ are 16.8 and 16.5, respectively. Hence it should be possible theoretically to prepare ZnO at room temperature but experimentally due to kinetic aspects, Zn(OH)$_2$ is the dominant species formed at room temperature [347]. Thus in the present case though we get hexagonal wurtzite at 4°C; Zn(OH)$_2$ species dominates as the system attains room temperature. Figure 5.2.2-a shows the formation of Zn(OH)$_2$ as the dominant species but later on with
ageing its intensity decreases drastically due to the formation of Zn(OH)$_4^{2-}$. \(\text{Zn(OH)}_4^{2-}\) formed is soluble in water which in turn may interact with the free acetate and EAH$^+$ ions in the solution to form soluble complex structures giving (colorless $\rightarrow$ yellow $\rightarrow$ orange) an intense orange color to the solution as shown in the photograph in Figure 5.2.3.

Figure 5.2.3 Photograph presents ageing effect on as-prepared flower-like ZnO (ZM4).

Concentration of Zn(OH)$_4^{2-}$ increases with time as the color of the solution becomes more and more intense. The decrease in the pH of solution as given in Table 5.2.1 supports the above statement. Due to close pKa values there is competition between formation of Zn(OH)$_2$ and ZnO and hence dissolution-reprecipitation mechanism is favored.

XRD study of ZnO at air-liquid interface suggests that the growth of ZnO is dominated in (001) direction for the AL2 and AL3 samples (peak marked with # in Figure 5.2.2-b). However, with time growth along (001) direction is suppressed in AL3 while the intensity of (100) and (101) peak increases as compared to AL2. As per equation 5, ZnO solubilizes as Zn(OH)$_2$ and Zn(OH)$_4^{2-}$ may get adsorbed on the surface of ZnO suppressing the growth in the (001) direction for the AL3 sample. The broad amorphous peak observed in Figure 5.2.2-a between $20^\circ – 30^\circ$ (2\(\theta\)) is due to the glass sample holder.
Film of ZnO at the air-liquid interface is formed by rearrangement of flower-like ZnO by the amide formed in the aminolytic reaction (equation 5.6). Formation of ZnO goes through an aminolytic reaction [345] as given in equation 5.6,

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{O} \\
\text{C} & \quad \text{Zn} \\
\text{O} & \quad \text{NH}_2 \\
\text{CH}_2 & \quad \text{CH}_3 \\
\text{CH}_2 & \quad \text{OH} \\
\end{align*}
\xrightarrow{\Delta} \begin{align*}
\text{ZnO} & \quad \text{O} \\
\text{H}_3\text{C} & \quad \text{C} \\
\text{NH} & \quad \text{CH}_2 \\
\text{CH}_2 & \quad \text{OH} \quad + \quad \text{H}_2\text{O}
\end{align*}
\]

Wherein the amide formed facilitates formation of thin layer of ZnO at the air-liquid interface. Initially the amide formed brings along with it flower-like ZnO to the surface of liquid and forms a layer and with time it grows towards the liquid side. The molecules are also held together by the intermolecular and intramolecular hydrogen bonding. This fact is confirmed from the FTIR spectra.
5.2.3 FT-IR Spectroscopy

Figure 5.2.4 shows comparative FTIR spectra of as-prepared ZnO (ZM4), ZnO at the air-liquid interface and in the sediments.

![FTIR spectra](image)

**Figure 5.2.4** FTIR spectra showing the functionality changes in the layer at air-liquid interface and in the sediments as compared to as prepared flower-like ZnO.

The broad band observed at 3370 cm\(^{-1}\) is due to the hydrogen bonded O-H and N-H stretching frequencies. This broad band also includes the C-H stretching frequencies. This band is common in all FTIR spectra. This broad spectrum is sharper for the layer at air-liquid interface indicating decrease in the hydrogen bonded O-H functionality. The FTIR of the layer at air-liquid interface and in the sediment shows major differences. The band at 2935 cm\(^{-1}\) corresponds to the methylene (\(-\text{CH}_2\)) C-H asym/sym stretch and the band at 2850 cm\(^{-1}\) is attributed to the methyl (\(-\text{CH}_3\)) C-H asymmetric/symmetric stretch, the intensity of these two bands is significant in the layer at air-liquid interface and is insignificant in the sediments. The weak band at
1640 cm\(^{-1}\) in the sediment and ZM4 may be assigned to the N-H bending in the primary amine. This band disappears in the layer formed at air-liquid interface and a distinct band appears at 1750 cm\(^{-1}\). This frequency is attributed to the amide group (-CO-NH, equation 5.6). The band at about 1555 cm\(^{-1}\) and 1400 cm\(^{-1}\) are attributed to COO\(^-\) stretching modes in the acetate group indicating the presence of acetate group attached to ZnO [345]. Band at 1388 cm\(^{-1}\) is due to H\(_3\)N\(^+\)- ion in H\(_3\)N\(^+\)--CH\(_2\)--CH\(_2\)--OH (equation 2), and the 1340 cm\(^{-1}\) frequency is due to C-N stretching. The weak bands in the region 800-1200 cm\(^{-1}\) are attributed to C-O, C-C single bond and N-O aliphatic amine oxide stretching, and from N-H bending in primary amine indicating the role of amine in the formation of flower-like structure. The broad band at 895 cm\(^{-1}\) is clearly visible in case of sediments whereas for the layer at air-liquid interface single peak disappears and multiplet appears. Formation of broad band suggests intermolecular and intramolecular hydrogen bonding due to the presence of amine and hydroxyl group. The presence of the N-H and O-H stretching frequencies for the ZnO samples in the FTIR spectra prove the role of EA in the formation of flower-like structure of zinc oxide and supports the formation of ZnO layer at air-liquid interface by rearrangement through amide (equation 6). The band at ~480 cm\(^{-1}\) is attributed to ZnO.

Thus we propose formation of ZnO at the air-liquid interface through two processes: 1) aggregation of flower-like ZnO due to the presence of amide formed in the aminolytic reaction in aqueous medium directing ZnO formation at the air-liquid interface and 2) further growth of flower-like ZnO towards the liquid side by dissolution-reprecipitation mechanism.
5.2.4 SEM Analysis

Figure 5.2.5 shows SEM images of ZnO at the air-liquid interface and of the sediments.

![SEM images of samples at air-liquid interface and in the sediments collected at different time intervals.](image)

**Figure 5.2.5** SEM images of samples at air-liquid interface and in the sediments collected at different time intervals.

The SEM images of ZnO at the air-liquid interface clearly show the aggregation of flower-like structure. It can be seen that the flowerlike structures aggregate by stacking of one layer over the other. With time these layers get attached to one another by the intermolecular and intramolecular hydrogen bonding. Each petal is of ~1μm in length with tapering tip. The SEM images of ZnO in the sediments show formation of sheet-like structures along with the flower-like structures. This is probably due to the dissolution-reprecipitation at alkaline pH.
5.2.5 TEM Analysis

Figure 5.2.6 shows the TEM images of flower-like ZnO formed at the air-liquid interface.

![TEM images and SAED pattern of samples at air-liquid interface and in the sediments collected at different time intervals.](image)

**Figure 5.2.6** TEM images and SAED pattern of samples at air-liquid interface and in the sediments collected at different time intervals.

Each individual flower-like structure is formed by overlapping of nanobelts. The selected area electron diffraction (SAED) pattern for the nanobelt indicates that the nanobelt is single crystalline and can be indexed as the hexagonal ZnO phase. This is in accordance with the XRD results implying that the flower-like ZnO film consists of nanobelts with single crystal hexagonal phase. The SAED pattern also shows diffraction from zinc hydroxy acetate group as well its presence along with ZnO in the layer at air-liquid interface. This is also supported by the FTIR results. With time the surfaces of the nanobelts get curved due to the fact that once the layer is
formed at air-liquid interface; further growth of ZnO layer takes place from the solution side and hence surface of the nanobelt goes on getting a curvature. The TEM images for the S1 and S4 samples clearly indicate that the individual flower-like structure merge to form sheet-like structure in an alkaline medium by dissolution-reprecipitation mechanism.

5.2.6 RT-PL Spectroscopic Studies

Figure 5.2.7 shows the RT-PL spectra of ZM4, ZnO at air-liquid interface and in the sediments. Figure 5.2.7 (a, b) shows the solid state RT-PL spectra of ZnO with an excitation wavelength of 325 nm.

![RT-PL spectra of the samples at air liquid interface with λ<sub>exc</sub> of 325 nm.](image)

**Figure 5.2.7(a)** RT-PL spectra of the samples at air liquid interface with λ<sub>exc</sub> of 325 nm.
The sharp peak at 349 nm corresponds to the band emission. There is no shift in the emission peak position with time in the layer at air-liquid interface as well as in the sediments. The band gap of ZnO is calculated to be 3.56 eV. Thus we assign a blue shift in the band emission from 3.37 eV in bulk ZnO to 3.56 eV in the flower-like ZnO. The confinement effect observed may be attributed to the typical flower-like morphology, wherein each flower-like structure is formed from crystalline nanobelts. Thus, it supports synthesis of flower-like ZnO with modified electronic properties as compared to bulk ZnO. Figure 5.2.7-c shows solid state RT-PL spectra of the flower-like ZnO at air-liquid interface and Figure 5.2.7-d shows RT-PL spectra of flower-like ZnO at air-liquid interface dispersed in ethanol with an excitation wavelength of 370 nm.

**Figure 5.2.7(b)** RT-PL spectra of the samples in the sediments with $\lambda_{\text{exc.}}$ of 325 nm.
Figure 5.2.7(c) solid state RT-PL spectra for the ZnO samples at air-liquid interface with $\lambda_{\text{exc.}}$ of 370 nm.

Figure 5.2.7-c shows defect related peaks at 405 nm (3.07 eV) and 425 nm (2.92 eV). The intensity of the peak at 405nm is seen to increase for the AL2 and AL3 samples. There is no significant change in the intensity of the peaks in the AL1 and AL4 samples. The defect related peaks are clear and intense as compared to ZM4. The other defect related peaks at 448 nm (2.77 eV), 473 nm (2.63 eV) [283] and 522 nm (2.38 eV) [348] disappear in the layer at the air-liquid interface.
Figure 5.2.7(d) RT-PL spectra of ZnO samples at air-liquid interface dispersed in ethanol in comparison with as prepared flower-like ZnO (ZM4) with $\lambda_{\text{exc.}}$ of 370 nm.

Figure 5.2.7-d shows single broad peak at 420 nm (2.96 eV) for all the samples obtained from air-liquid interface (AL1-AL4) thus showing a blue shift in the emission peak from 440 nm (2.82 eV) for the as-prepared sample to 420 nm in ZnO at the air-liquid interface. Also other defect related peaks in the visible region disappear in the ZnO samples at air-liquid interface.
Figure 5.2.7(e) solid state RT-PL spectra of sediment sample.

Figure 5.2.7(f) RT-PL spectra of sediment sample dispersed in ethanol in comparison with as prepared flower-like ZnO (ZM4) with $\lambda_{\text{exc.}}$ of 370 nm.

Figure 5.2.7-e shows solid state RT-PL spectra of the flower-like ZnO in the sediments and Figure 5.2.7-f shows the RT-PL spectra of the same dispersed in ethanol.
5.2.7 Photocatalytic activity and its Correlation with photoluminescence properties

As we reported earlier [345] photocatalytic activity follows a pathway through the formation of hydroxyl radical as an oxidizing intermediate. UV irradiation of ZnO catalyst leads to the formation of electron ($e_{(CB)}^-$) and hole ($h_{(VB)}^+$) pair. Some of the electron-hole pairs recombine while other lead to the formation of hydroxyl radical which is a strong oxidizing agent for the dye. Figure 5.2.8 shows the degradation of MB over ZnO catalyst.

![Figure 5.2.8](image)

**Figure 5.2.8** A comparative photocatalytic activity of degradation of MB over as-prepared flower-like ZnO, ZnO samples in the layer at air-liquid interface and in the sediments.

The photocatalytic activity of the samples at the air-liquid interface shows higher catalytic activity than as-prepared ZnO (ZM4) sample, this may be attributed to the defects corresponding to 3.07 eV and 2.92 eV energy. These high energy defects promote charge separation in the sample which increases the catalytic activity through hydroxyl radical formation. Also significant interaction of adsorbates on the surface may probably lead to high photocatalytic activity. The general behavior of the photocatalytic activity of ZM4, AL1 and AL4 is same during the initial time, more
precisely there is a steady decrease followed by a plateau. However AL4 catalyst shows highest photocatalytic activity; more than 80% of the dye gets oxidized within 10 min. After 10 min slow degradation occurs and requires nearly 50 min to get nearly complete degradation. In comparison the sedimented samples steadily degrade the dye and require nearly 50 min for complete degradation of the dye. Thus, the increase in the photocatalytic activity of the layer at air-liquid interface with respect to ZM4 can be attributed to the increased intensity and blue shift of the defect related peak in the visible region. S1 and S4 have comparable photocatalytic activity. If we consider the surface area of ZM4 (31 m²/g), S1 (14 m²/g) and S4 (12 m²/g), the increase in the catalytic activity is not dependent on the surface area in the present case. Thus increase in catalytic activity is attributed to the defects present on the surface of ZnO synthesized.

The visible emission observed in the RT-PL spectra of ZnO (Figure 5.2.7) in addition to the UV excited emission peaks are due to the intrinsic or extrinsic defects. The emission is dependent on the type of defect. According to the earlier reported work, the defects can greatly affect the optical, electronic, magnetic and photocatalytic, properties of ZnO. [349-352] Thus we have correlated photoluminescence and photocatalytic activity. Understanding this relationship will provide insight into the origin of defect emission and chemistry behind photocatalysis. And hence this will advance our ability to utilize ZnO.

Figure 5.2.7-c shows the RT-PL spectra of solid state ZnO at the air-liquid interface. The emissions corresponding to ~3.07 eV (405 nm), 3.03 eV (410 nm) are mainly due to the zinc vacancy (VZn) and the emission at 2.92 eV (425 nm) is due to zinc interstitial. [351, 353-355] Zinc Vacancies create hole in the valence band (VZn + hVB) which facilitate the photocatalytic degradation according to the mechanism studied by us previously. [345]. One of the strongly adsorbed species on ZnO surface is oxygen [356]. These adsorbed oxygen molecule can easily trap the photoexcited electrons to form superoxide anion radical (•O2̇) [357]. The overall catalytic reaction is determined by oxygen reduction to •O2̇:[358]. The oxygen molecules present in solution may replace the desorbed once. The overall photocatalytic mechanism may be thus given as depicted schematically in Figure 5.2.9.
Figure 5.2.9 Schematic representation of photocatalytic degradation of MB over ZnO in the presence of surface defect states.

If we compare the RT-PL spectra of AL1 and AL4, the intensity of the emission peak at ~405 is higher for the AL4 sample. This contributes to the high catalytic activity of the ZnO samples at the air-liquid interface. The as-prepared ZnO and the sediment samples show a very weak emission at ~410 nm (~3.03 eV) which indicates decrease in the emission related to the zinc vacancy. The low energy emissions are also attributed to the presence of Zn(OH)$_2$ in ZnO. Figure 5.1.2-a clearly indicates the presence of the Zn(OH)$_2$ along with ZnO in the sediment samples. FTIR of the samples (Figure 5.1.4) indicates the presence of hydrogen bonded –OH groups on the surface of the ZnO samples. The broad band due to hydrogen bonded –OH groups for the as-prepared ZnO and the sediment samples become sharp for the ZnO layer at the air-liquid interface. Due to the presence of Zn(OH)$_2$ in the sediment samples and the surface adsorbed OH on as-prepared ZnO the luminescence at 410 nm is quenched [359] compared to the samples at the air-liquid interface. The other low energy defect related emission peaks (~473 nm and
~522 nm) present in the sediment layer are absent in the ZnO samples at air-liquid interface. Moreover, in nanocrystalline ZnO the sub-bands formed due to surface defects facilitate separation of charge carriers increasing its lifetime leading to enhanced photocatalytic activity.

### 5.2.8 Growth Mechanism

The growth rate of a crystal face is usually related to its surface energy, if the same growth mechanism acts on each face. The fast growing faces have high surface energies disappear in the final morphology, and vice versa. This treatment assumes that the equilibrium morphology of a crystal is defined by the minimum energy resulting from the sum of the products of the surface energy and the surface area of all exposed faces (Wulff rule). [360] The driving force for this spontaneously oriented attachment is that the elimination of the pairs with a high surface energy leading to the substantial reduction in the free energy of the surface from the thermodynamic viewpoint. [343, 361, 362]

Wurtzite ZnO being a polar crystal, Zn forms a positive polar plane (0001) and O forms a negative polar plane (000̅1). Zn$^{2+}$ and O$^{2-}$ ions are tetrahedrally coordinated and stack alternatively along the c-axis thus, ZnO grows along the c-axis. When EA is added in the aqueous solution, it gets hydrolyzed according to the equation 2 and forms EAH$^+$ molecule. Thus, by coulomb interaction EAH$^+$ molecule gets adsorbed on the negative polar plane retarding the growth of ZnO along the negative polar plane. Therefore, when optimum amount of EA is used which covers the side surfaces of ZnO crystal, enhancing growth along the (001) direction. When EA concentration is low, i.e. inadequate to cover the whole surface, the Oswald ripening takes place and thereby role of EAH$^+$ in the growth of ZnO crystal results in the formation of flower-like structure where individual petal is formed by the overlay of nanobelts as seen in the Figure 4.

Initially ZnO thin layer is formed by the diffusion of ZnO particles at the air–liquid interface via amide (Equation 6). This is supported by FTIR results. Further the growth units could diffuse only onto the ZnO contacted with water and grow freely. Growth does not occur on the ZnO crystal facing towards air. Due to the alkaline conditions dissolution-reprecipitation occurs; favoring growth of ZnO on the surface in contact with the aqueous solution. Thus the petals are curved laterally on the side in contact with the aqueous solution (Figure 5.2.6). Dissolution-reprecipitation
mechanism can be confirmed from the RT-PL spectra of the samples in the sediments and the layer at air-liquid interface. The enhanced color intensity of the aqueous solution with time seen in the photograph (Figure 5.2.3) and the increase in the intensity of the absorption peak in the UV-Vis spectra of the Liquid between the two layers as shown in Figure 5.2.8 supports the dissolution-reprecipitation mechanism.

![UV-VIS spectra of the liquid between the layer at air-liquid interface and in the sediments collected at different time interval.](image)

**Figure 5.2.9** UV-VIS spectra of the liquid between the layer at air-liquid interface and in the sediments collected at different time interval.

The liquid collected at different time intervals [F1 (7 days), F2 (14 days), F3 (21 days), F4 (28 days)] after separating the layer at the air-liquid interface and in the sediments exhibits increasing intensity and width of the absorption peak in the visible region and color of the solution with time which is due to the dissolution of ZnO with time at high pH (equation 5). This confirms the dissolution-reprecipitation mechanism for the formation of ZnO layer at the air-liquid interface with time. The liquid between the two layers shows a broad absorption band in violet and blue region, accordingly the liquid emits the complementary yellow and orange color as the absorption intensity and width of the spectra increases with time.

The growth of ZnO units is favored in the (001) direction as can be clearly observed from the XRD of AL2 and AL3 samples. The growth of ZnO at air-solution interface takes place in the (001) direction to minimize the total surface energy [363]
of the polar planes. After 21 days (AL3) though the growth in the (001) direction is favored the (100) and (101) peak intensity is also seen to be increased as compared to the XRD after 14 days (AL2). After 28 days (AL4) the growth is seen to take place along all the crystallographic direction.

5.2.9 Conclusions

The facile low temperature (4°C) synthesis using ZA and EA produces flower-like ZnO. Flower-like ZnO synthesized in this study self-assemble at the air-liquid interface via the amide formed in the aminolytic reaction and by dissolution reprecipitation mechanism. TEM characterization shows that each petal of flower-like structure is formed from single crystalline nanobelts with hexagonal ZnO and zinc hydroxyl acetate phase. Simultaneous evolution of Zn(OH)₂ and ZnO in the sediments is evidenced from the XRD and FTIR studies. The RT-PL of as-prepared flower-like ZnO, ZnO at air-liquid interface and in the sediments shows blue shift in the band emission from 3.37 eV (bulk ZnO) to 3.56 eV. Flower-like ZnO at air-liquid interface and in the sediments show blue shift from 440 nm to 420 nm with respect to as prepared flower-like ZnO. The photodegradation of MB over the flower-like ZnO catalyst formed at the air-water interface and in the sediments show enhanced photocatalytic activity as compared with as-prepared flower-like ZnO. Almost 80% of the dye is degraded by AL4 sample in 10 min. The high catalytic activity of AL4 is attributed to the increase in zinc vacancy (3.06 eV) defects.
Chapter 5

5.3 Section II: Influence of Various Factors on the Structure, Crystallinity, Optical and Photocatalytic Properties of Flower-Like ZnO.

Effect of pH, ageing time, Temperature, type of ligand, amount of water and precursor has been discussed in detail in the present chapter. Effect of these factors on the optical and photocatalytic property of ZnO has been correlated.
5.3.1 Introduction

The kinetics of growth of a solid from a solution, which is the most popular chemical method to produce wide variety of systems with dimensions in the nanometer region, has been interest of investigation. Solution chemistry is the most versatile and highly flexible technique to tune the size and size distribution of nanocrystals. From a fundamental point of view, the growth kinetics of a solid in solution constitutes a very important field of study. There are relatively very few such investigations. Thus on the basis of the experimental results obtained, this section presents the effect of various parameters on the growth of technologically important ZnO nanostructures using solution method. Various factors include: 1) Effect of pH. 2) Effect of ageing time. 3) Effect of temperature. 4) Effect of type of ligand. 5) Effect of dilution. 6) Effect of precursor.

5.3.2 Effect of pH

Concentration of OH\(^{-}\) plays a significant role in the synthesis of ZnO. pH of the solution depends on the concentration of the OH\(^{-}\) ions produced by reaction of ethanolamine with the aqueous solvent. The effect of pH (concentration of ethanolamine) on the structure, crystallinity, optical and photocatalytic properties of ZnO has been described in detail [345] in chapter 4. Briefly; increase in pH of the solution decreases the size of the nanobelts, which than systematically overlap to form flower-like structure. According to classical theory of nucleation the increase of supersaturation produces a decrease of nucleation activation energy and consequently an increase in nucleation rate may occur. At high pH values there can be burst of large number of nuclei and formation of nanobelts with smaller size. Along with decrease in nanobelt size the surface defect states in the visible region increases. Increase in the defect states leads to increase in the photocatalytic activity of the ZnO samples.

5.3.3 Effect of ageing time

As mentioned in Section I of this chapter, the effect of ageing time results in the formation of single crystalline flower-like ZnO at the air-liquid interface and in the sediments. The samples at air-liquid interface and in the sediments show enhanced
photocatalytic activity which has been correlated with the type of defects formed on the ZnO surface.

5.3.4 Effect of type of ligands

To study the effect of type of ligand on the structure, morphology, optical and photocatalytic properties of ZnO, three different ligands were selected. Keeping the same carbon skeleton the end groups were varied. The three different ligands used were Ethanolamine [EA], ethylenediamine [ED] and ethylene glycol [EG]. These three ligands are also assumed to act as a capping agent and also a source of OH- ions. Zinc acetate dihydrate (ZA) is used as the zinc precursor. The effect of capping agent depends on the type of capping agent used. Capping agents inhibit the growth of nanocrystals by effectively passivating their surfaces. Concentration and the type of capping agent are important in deciding the size and morphology of the nanocrystals.

Typically ZnO nanostructures were synthesized by adding EA or ED or EG to the 0.1 M aqueous zinc acetate solution at 4 °C. As studied previously in chapter 4, to synthesize flower-like ZnO, ZA: EA optimum molar ratio was 1:4. Keeping this molar ratio constant the ligand is changed to study its effect on structure, morphology, optical and photocatalytic properties of ZnO synthesized. Effect of EA as a ligand has been discussed in detail in chapter 4. It was observed that when ED is used as the ligand, no product was obtained. Initially dropwise addition of ED to ZA solution gives ZnO precipitate but further addition of ED interacts with ZnO precipitate forming Zn(OH)$_4^{2-}$. ED is strong binding agent and excess ligand concentration used forms a soluble complex under the given conditions of temperature and concentration. Whereas, use of EG as a ligand, no product is precipitated out under the given conditions and even after refluxing the solution at boiling temperature for several hours. So the concentration of ED and EG ligand was decreased with corresponding ZA:ligand molar ratio of 1:1. The details of the synthesis with the sample codes are given in Table 5.3.1.
Table 5.3.1 Sample code and preparation parameters with different ligands used for ZnO synthesis.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Type of ligands used</th>
<th>ZA:Ligand molar ratio</th>
<th>Temperature of reaction (°C)</th>
<th>Shape of ZnO Nanostructures obtained</th>
<th>Sample code</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>EA</td>
<td>1:4</td>
<td>4</td>
<td>Flower-like ZnO</td>
<td>ZM4</td>
</tr>
<tr>
<td>2a</td>
<td>ED</td>
<td>1:1</td>
<td>4</td>
<td>Hexagonal ZnO nanoplates</td>
<td>ZL1</td>
</tr>
<tr>
<td>2b</td>
<td>ED</td>
<td>1:4</td>
<td>4</td>
<td>Product formed dissolves completely</td>
<td>-</td>
</tr>
<tr>
<td>3a</td>
<td>EG</td>
<td>1:1</td>
<td>4, 100</td>
<td>No product</td>
<td>-</td>
</tr>
<tr>
<td>3b</td>
<td>EG</td>
<td>1:4</td>
<td>4, 100</td>
<td>No product</td>
<td>-</td>
</tr>
</tbody>
</table>
5.3.4.1 XRD analysis

Figure 5.3.1 shows XRD of ZnO nanostructures obtained using EA and ED as the ligand and the capping agent.

![XRD Profile of ZnO Nanostructures](image)

**Figure 5.3.1** XRD of ZnO obtained with EA (ZM4) and ED (ZL1) as the ligand and capping agent.

XRD profile of ZM4 shows wurtzite hexagonal ZnO phase with (001) as the direction of growth. (Chapter 4). Whereas XRD of ZL1 reveals that ED suppresses the growth of ZnO along (001) direction and the direction of growth is (101). The difference in the direction of growth is mainly due to the concentration of OH⁻ ions produced by each ligand. According to equation 5.7 and 5.8 given below

\[
\text{HO-}(\text{CH}_3)_2\text{NH}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{HO-}(\text{CH}_3)_2\text{NH}_2\text{O}^{-} + \text{HO}^- \quad \ldots\ldots (5.7)
\]

\[
\text{H}_3\text{N-}(\text{CH}_3)_2\text{NH}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{H}^+\text{NH}_3\text{O}^- + \text{H}_2\text{O}^- + 2\text{HO}^- \quad \ldots\ldots (5.8)
\]

the excess of OH⁻(aq) ions produced by ED reacts with Zn²⁺(aq) ions to give Zn(OH)₄²⁻(aq) in water as per equation 5.9.
It is well known that in hexagonal wurtzite ZnO structure each Zn and O are tetrahedrally coordinated. ZnO being a polar crystal, Zn forms the positive plane and O forms the negative polar plane along the c-axis [84]. The zincate ions (Zn(OH)$_4^{2-}$) being negatively charged arrest the growth of ZnO in (001) direction by getting adsorbed on the positive Zn polar plane. Ethylene glycol does not react with zinc acetate at 4°C and even after refluxing the solution at higher temperature (~100 °C) for several hours. This may be due to a weak ligand and requirement of higher energy and heating at a molecular level for ZnO formation.

5.3.4.2 FT-IR analysis

Figure 5.3.2 shows the changes in the functionality of ZnO with EA and ED ligands used as the source of OH$^-$ ions and capping agent.

![FT-IR spectra of ZnO obtained with EA (ZM4) and ED (ZL1) as the ligand and capping agent.](image)

**Figure 5.3.2** FT-IR spectra of ZnO obtained with EA (ZM4) and ED (ZL1) as the ligand and capping agent.
Figure 5.3.2 indicates that when EA is used as the ligand it is involved in the structure formation [345], where bands at 3400 cm\(^{-1}\) correspond to the hydrogen bonded O-H and N-H stretching frequencies; it also includes the C-H stretching frequencies. Band at 1640 cm\(^{-1}\) is attributed to the N-H stretching in primary amine, band at 1489 cm\(^{-1}\), 1388 cm\(^{-1}\) are due to the acetate ion and the \(^{\prime}\)NH\(_3\) ions, respectively. The broad band centered at 895 cm\(^{-1}\) includes C-O, C-C single bond and N-O aliphatic amine oxide stretching. Band at 530 cm\(^{-1}\) is attributed to ZnO. Thus EA plays a significant role in the formation of flower-like structure. Whereas, when ED is used as the ligand broad band at 3400 cm\(^{-1}\) suggests presence of hydrogen bonded OH stretching on ZnO surface. Band at 530 cm\(^{-1}\) represents Zn-O bond formation. Absence of any other frequencies for C-C, C-N, and C-O suggests that ED is not attached to the hexagonal ZnO nanoplates.

5.3.4.3 SEM analysis

Figure 5.2.3 shows the SEM images of ZnO synthesized using the two ligands.

![SEM images](image)

**Figure 5.3.3** (a, b) Flower-like ZnO obtained using EA and (c, d) rod shaped and hexagonal dumbbell shape structures of ZnO obtained with ED.
When EA is used as the ligand, flower-like ZnO (ZM4) is obtained where individual flower possesses well defined petals with pointed tips. Petals grow centrosymmetrically. The flower-like ZnO size varies from ~ 700 nm to 1 μm. The flower-like structure forms clusters due to hydrogen bonding in the surface hydroxyl groups as proved from the FT-IR spectra of the sample (Figure 5.3.2). ED gives rod-shaped and dumbbell-shaped ZnO (Figure 5.3.3-c, d). The difference in the morphology may be attributed to the type of ligand used.

**5.3.4.4 TEM, HRTEM and SAED analysis**

To characterize the material at higher magnification TEM, SAED and HRTEM analysis was done. Figure 5.3.4 shows the TEM, SAED and HRTEM images.

**Figure 5.3.4** (a, b) flower-like structure and petal of flower-like structure respectively obtained using EA as the ligand. (c-e) cage-like structure and well separated hexagonal particles of ZnO obtained using ED as ligand followed by its (f) diffraction pattern and (g) HRTEM (arrow shows the direction of growth).
EA gives flower-like structure formed by systematic overlapping of the nanobelts (Figure 5.3.4-a,b) whereas ED gives well separated hexagonal particles (Figure 5.3.4-d,e) of average size ~25 nm and cage-like (Figure 5.2.4-c) structure. Figure 5.3.4-f gives the diffraction pattern of hexagonal ZnO nanoparticles which matches well with the wurtzite ZnO phase. Thus pure nanocrystalline ZnO has been synthesized with surface hydroxyl group at 4 °C without involving any other functionality into the ZnO matrix. The nanoparticles are separated with well defined hexagonal shape. The direction of growth of the hexagonal nanoparticles is (101) (Figure 5.2.4-g), the growth in the (001) direction is suppressed in comparison with flower-like structure which has (001) (chapter 4, section 4.2.4), as the direction of growth. Change in the morphology is attributed to reaction of excess of OH⁻ ions produced by ED form zincate ions (equations 5.7, 5.8, 5.9). The zincate ions being negatively charged gets adsorbed on the positive plane of ZnO polar crystal and hence suppresses the growth along c-axis, which gives rise to the hexagonal plate-like morphology with (101) as the direction of growth. When EA is used as the ligand, growth is seen to be one dimensional i.e. along the c-axis, and hence nanobelts are formed which overlap systematically to give three dimensional flower-like structure. HRTEM in Figure 5.3.4-g clearly shows that the interplanar distance d matches well with that of (101) plane as calculated from the XRD profile of ZL1 shown in Figure 5.3.1. The defects formed are also clearly visible (Figure 5.3.4-g, particle in a square bracket) from the HRTEM images.

5.3.5 Effect of Temperature

The classical route for ZnO formation in solution is based on the oxide precipitation by reacting zinc salts with hydroxide ions. In the Zn system, the most stable solid phase in contact with the media will be in general precipitate first. To understand the reaction kinetics and the growth mechanism of a flower-like ZnO structure, synthesis procedure of flower-like ZnO was repeated at 4, 25, 60, and 100 °C. Typically 200 ml 0.1 M ZA solution was taken in a beaker and ethanolamine used as the source of OH⁻ ions and chelating agent was added at different temperature. Molar ratio of ZA and EA used was 1:4. Temperature is one of the most important parameter responsible for the structure, crystallinity, and morphology of ZnO synthesized.
Table 5.3.2 Sample code and preparation parameters with for ZnO synthesized at different temperatures.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Temperature of reaction (°C)</th>
<th>Zinc acetate:Ligand molar ratio</th>
<th>Shape of ZnO Nanostructures obtained</th>
<th>Sample code</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4</td>
<td>1:4</td>
<td>Flower-like ZnO</td>
<td>ZM4</td>
</tr>
<tr>
<td>2</td>
<td>25</td>
<td>1:4</td>
<td>No product</td>
<td>T1</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>1:4</td>
<td>Spindle-like ZnO</td>
<td>T2</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>1:4</td>
<td>No product</td>
<td>-</td>
</tr>
</tbody>
</table>

5.3.5.1 X-ray diffraction

The dissociation constant of water is an important factor for the synthesis of ZnO in aqueous media. Since OH⁻ ions are produced by reaction of amine with water. Increase in reaction temperature will enhance the hydrolysis of amine thus producing large number of OH⁻ ions which in turn increase the rate of reaction drastically. Figure 5.3.5 shows formation of crystalline ZnO phase at 4 °C (ZM4) and higher at 60 °C (T2).

Figure 5.3.5 XRD of samples synthesized at 4 °C (ZM4), 25 °C (T1) and 60 °C (T2).
At 25 °C zinc hydroxy acetate and Zinc hydroxide phase is formed. At room temperature the pKs of ZnO and Zn(OH)₂ are 16.8 and 16.5 respectively [346]. Hence ZnO is more stable thermodynamically than Zn(OH)₂ and it should be theoretically possible to prepare ZnO at room temperature. However, the two pKₙ values are close and a competition occurs for the formation of these two compounds due to kinetic aspects. But experimentally (Figure 5.3.5) Zn(OH)₂ is clearly the dominant species formed at the room temperature. This can be attributed to the fact that at 4 °C water is in the most dense state with tiny hexagonal lattices formed in liquid water. The reaction of amine with water being exothermic it releases energy with formation of OH⁻ ions along with the release of lattice energy from the hexagonal lattices of water. This released energy favors the reaction of Zn²⁺ and the OH⁻ to form ZnO through zinc hydroxyacetate intermediate phase [345]. Whereas at room temperature (25 °C) energy is not enough to convert the zinc hydroxyacetate intermediate into ZnO however it is possible at higher temperature (60 °C) because of availability of supply of energy from outside in terms of heat.

A first approach to overcome the difficulty of ZnO synthesis at room temperature consists of substituting the aqueous solvent by an organic one which favors the formation of the dehydrated product at low temperature. The second solution consists of raising the preparation temperature above 50 °C in order to accelerate the oxide formation reaction. In both cases, ZnO powders are obtained by homogeneous nucleation in the liquid [347]. Thus in the present case instead of replacing aqueous solvent by organic one ZnO was synthesized at low temperature (4 °C) in aqueous media also the synthesis was repeated at 25 °C, 60 °C and 100 °C. At low temperature flower-like and at 60 °C spindle shaped ZnO nanostructures were obtained with wurtzite phase. The change in the morphology is clearly due to the reaction kinetics. At 100 °C as soon as EA is added to zinc acetate solution, the solution turns green in color. The color of the solution may be due to the formation of complex of zinc with ethanolamine.
5.3.5.2 FT-IR analysis

Figure 5.3.6 shows the FT-IR spectra of the ZnO samples obtained at 4 °C and 60 °C.

![FT-IR spectra](image)

**Figure 5.3.6** FT-IR of flower-like ZnO (ZM4) and Spindle-like ZnO (T2) synthesized at 4 °C and 60 °C.

As discussed in section 5.3.4.2 FT-IR analysis of ZM4 and ZL1, ethanolamine plays important role in the structure formation of flower-like and also spindle-like ZnO at 4 °C and 60 °C respectively. For spindle shaped ZnO the band due to acetate ions at 1489 cm⁻¹ disappears. At elevated temperature due to the higher rate of decomposition of the [Zn(EA₃)]⁺³ and hydrolysis of EA , the concentration of Zn⁺² and OH⁻ increases and ZnO nuclei start to form. At 60 °C the reaction is faster as compared to the same at 4 °C. At low temperature, reaction is slow enough to form the superlattice by overlapping of nanobelts to give flower-like three dimensional structures.
5.3.5.3 SEM Analysis

**Figure 5.3.7** SEM images of ZM4, T1 and T2 synthesized at 4 °C, 25 °C, and 60 °C, respectively.

SEM images of ZM4 shows formation of flower-like morphology whereas T1 shows formation of plate-like structure arising from bulk structure. The T2 shows scattered morphology. To understand the growth mechanism the samples were characterized at higher magnification by TEM and SAED techniques.
5.3.5.4 TEM and SAED Analysis

Figure 5.3.8 shows TEM images and SAED patterns of flower-like and spindle-like structures at prepared at 4 °C and 60 °C.

![TEM images and SAED patterns of (a-c) ZM4 synthesized at 4 °C and (d-i) T2 synthesized at 60 °C.](image)

**Figure 5.3.8** TEM images and Diffraction patterns of (a-c) ZM4 synthesized at 4 °C and (d-i) T2 synthesized at 60 °C.

Figure 5.3.8 (a,b) shows formation of flower-like ZnO at 4 °C, where each petal is formed by systematic overlapping of nanobelts of ~20 nm size. The SAED pattern shows formation of wurtzite ZnO. When the same reaction is carried out at 60 °C spindle-like structures are formed. The spindle shaped structures formed are of different types. Figure 5.3.8 (d-g) shows the difference in the spindle structure formed. Spindle may have a single (Figure 5.3.8-d) budding or double budding (Figure 5.3.8-e). Petal-like structures along with spindle-like structures also exist (Figure 5.3.8-f). Spindle may exist as single spindle structure or may exist with a middle interface (Figure 5.3.8-g). The spindle structure has a tapering tip which is seen to be formed from the overlapping of well aligned belt-like structures. The
buddings are seen to arise from the interface. Figure 5.3.8-h shows the spindle structures grow from the interface of a twin spindle; it also shows the formation of spherical particles. Thus when the reaction is carried out at 60 °C the rate of the reaction is increased i.e. formation of ZnO by the decomposition of Zn-EA complex increases and hence spindle shaped morphology is arrested from the formation of flower-like structures. Thus the flower-like structure is formed by the growth of spindle shaped structures at the interface of twin spindle structure.

5.3.5.5 Growth mechanism

As mentioned in Section I formation of flower-like ZnO systematically goes through the formation of [Zn(EA)₃]⁺² complex, followed by the formation of zinc hydroxyacetate nanobelts which leads to formation of flower-like ZnO at 4 °C by an aminolytic reaction (equation 5.1.-5.5 in section I). Thus on the basis of above discussion and experimental evidences one can outline the formation of flower-like and spindle shaped ZnO structures as follows. At 4 °C the rate decomposition of [Zn(EA)₃]⁺² complex is low thus Zn⁺² and OH⁻ concentration is low. Thus initially spindle shaped ZnO nuclei are formed with an interface. The interface has high surface energy, thus [Zn(EA)₃]⁺² gets adsorbed on the interface and minimizes the surface energy. This triggers the growth of ZnO at the interface. Thus [Zn(EA)₃]⁺² adsorbed at the interface eventually leads to the formation of flower-like structure at 4 °C. At 60 °C The decomposition rate of [Zn(EA)₃]⁺² is higher and hence the concentration of Zn⁺² ions and OH⁻ ions is higher. This increases the rate of the overall aminolytic reaction. Increased rate of the reaction arrests the spindle shaped structure from growing as flower-like structure.

5.3.6 Effect of the type of precursor

To study the effect of Zn⁺² precursor on the crystallinity, morphology, optical and photocatalytic properties of ZnO synthesis of ZnO was carried out by using zinc acetate dihydrate (ZA) as well as zinc nitrate hexahydrate (ZN) precursors. EA was used as the source of OH⁻ ions and as a capping or chelating agent. In a typical procedure the 0.1 M Zn⁺² solution was prepared in aqueous solvent. The solution was maintained at 4 °C. Once the solution attains the temperature, EA was added drop-wise to the solution with constant magnetic stirring and maintaining the solution at 4 °C. The ZnO precipitate was collected by centrifugation followed by washing with
water and ethanol. Its morphology, crystallinity, optical and photocatalytic properties were examined. Table 5.3.3 gives the details of the synthesis parameters and the sample code.

**Table 5.3.3** Sample code and preparation parameters for ZnO synthesized with different precursor.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Temperature of reaction (°C)</th>
<th>Zinc acetate or Zinc nitrate: Ligand molar ratio</th>
<th>Shape of ZnO Nanostructures obtained</th>
<th>Sample code</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4</td>
<td>1:4</td>
<td>Flower-like ZnO</td>
<td>ZM4</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>1:4</td>
<td>Flower-like ZnO</td>
<td>ZN</td>
</tr>
</tbody>
</table>

5.3.6.1 XRD analysis.

Figure 5.3.9 shows the XRD profile of ZM4 and ZN

![XRD profile](image)

**Figure 5.3.9** XRD profile of ZnO obtained from ZA as the precursor (ZM4) and ZN as the precursor (ZN).

XRD profile of ZM4 and ZN shows formation crystalline hexagonal wurtzite ZnO structure.
5.3.6.2 FT-IR analysis

![FT-IR spectra](image)

**Figure 5.3.10** FT-IR spectra of ZnO obtained from ZA as the precursor (ZM4) and ZN as the precursor (ZN).

FTIR spectra shows similar spectra as that of ZM4 except the band at 1489 cm\(^{-1}\) due to acetate ions almost merges into the broad band due to H\(_3\)N\(^+\)-(CH\(_2\))\(_2\)-OH ions. This indicates the amine plays a vital role in the formation of ZnO with a particular morphology.
5.3.6.3 SEM Analysis

Figure 5.3.11 SEM images of ZnO obtained from (a,b) ZA as the precursor (ZM4) and (c,d) ZN as the precursor (ZN).

Figure 5.3.11 shows SEM images of ZM4 and ZN. Though flowerlike structures are obtained in both the cases, Flower-like structures are more well defined when ZA is used as the zinc precursor. Each petal of the flowerlike structure is clearly visible. Whereas, when ZN is used as the precursor ZnO is formed with flowerlike structure with certain irregularities. Flower and petal structures are not well defined as compared to ZM4. To determine the structure more precisely TEM analysis was carried out.
5.3.6.4 TEM and SAED Analysis

Figure 5.3.12 shows the TEM images and SAED pattern of ZM4 (a-b, c) and ZN (d-e, f).

![TEM images and SAED pattern of ZnO](image)

**Figure 5.3.12** TEM images and SAED pattern of ZnO obtained from (a, b, c) ZA as the precursor (ZM4) and (d, e, f) ZN as the precursor (ZN).

TEM analysis shows clearly the differences in the flower-like structures when ZA and ZN are used as the precursors. When ZA is used as the precursor flower-like structure with well defined petals is formed. Where each petal is formed by systematic overlapping of the nanobelts. Whereas, when ZN is used as a precursor flower-like structures are also formed along with some spindle shaped structure having budding at the center. The flower-like structures are not well defined. The petals of each flower-like or spindle structure are formed by some irregular one dimensional structures. Diffraction pattern of ZM4 and ZN shows formation of ZnO with hexagonal wurtzite phase.

5.3.7 Effect of amount of water

In a typical experiment synthesis of ZnO was carried out in an aqueous media at 4 °C. Zinc acetate and ethanolamine reagents were used in a molar ratio of 1:4. The
amount of aqueous solvent used was varied from 100 ml, 175 ml, 200 ml, 225 ml and 1000 ml keeping all the other parameters constant.

Water plays an important role in controlling the growth kinetics and finally determines the particle morphology. Synthesis of ZnO in aqueous solvent depends on the dissociation of water, since hydroxyl ions are produced from the dissociation of water by ethanolamine. The ZnO nanocrystal is formed from the tetrahedral coordination of Zn and O atoms. The surface of ZnO is terminated with a hydroxyl ion instead of O ion (proved from the FTIR spectra). Thus the cluster growth takes place through dehydration of surface hydroxyl (terminated) with the freely available dissociated OH⁻ ions in the solution. This is followed by capturing Zn⁺² ions available in the solution to the surface by diffusion process. These Zn⁺² ions further capture the OH⁻ ions from the solution and the growth of the ZnO cluster continues. In the present study the availability of OH⁻ ions is governed by the reaction of the ligand (amine) with water to produce OH⁻ ions. The concentration of OH⁻ ions is thus governed by the concentration and the type of ligand and the amount of aqueous solvent. Thus amount of aqueous solvent and the type of ligand are the important factors governing the ZnO synthesis. The amount of solvent will also affect the diffusion of the Zn⁺² ions on to the surface of seed ZnO and thus the rate of reaction or influence the growth process. At lower temperature and lower quantity of aqueous solvent, nucleation is not separated from the growth of ZnO nanocrystals.

Water can induce hydrolysis and condensation reactions of zinc precursor. ZnO is nucleated via successive hydrolysis and condensation reactions. Once the nucleation is accomplished, the particles can grow by addition of the intermediate species. The particle morphology also depends on hydration ratio (h) defined as the ratio of molar concentration of total water (as a solvent + water of hydration) to zinc acetate. Paul et al. reported that various morphologies can be controlled by the hydration ratio, and the particle sizes tend to become smaller with decreasing hydration ratio [364].

Table 5.3.4 gives the reaction parameters and sample codes for the study of effect of amount of water as a solvent.
Table 5.3.4 Sample code with reaction parameters to study the effect of amount of solvent on the synthesis of ZnO at 4 °C.

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Amount of aqueous solvent used (ml)</th>
<th>Zinc acetate:Ligand molar ratio</th>
<th>Sample code</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>1:4</td>
<td>d1</td>
</tr>
<tr>
<td>2</td>
<td>175</td>
<td>1:4</td>
<td>d2</td>
</tr>
<tr>
<td>3</td>
<td>200</td>
<td>1:4</td>
<td>ZM4</td>
</tr>
<tr>
<td>4</td>
<td>225</td>
<td>1:4</td>
<td>d3</td>
</tr>
<tr>
<td>5</td>
<td>1000</td>
<td>1:4</td>
<td>d4</td>
</tr>
</tbody>
</table>

5.3.7.1 XRD analysis

Figure 5.3.13 XRD profile of showing effect of solvent on the crystallinity of ZnO (ZM4).

Zinc oxide synthesized with ZA and EA at 4°C with ZA:EA molar ratio of 1:4 in 200 ml of aqueous media may be represented as given in equations 5.1-5.5 in section I. From the XRD pattern it is clear that when amount of solvent is little less (175ml, d1) or little more (225 ml, d2) than the optimum quantity required (200 ml)
for the precipitation of zinc oxide with wurtzite hexagonal phase at 4 °C, the equilibrium of reaction 5.7 shifts to left giving zinc hydroxyl acetate. Zinc hydroxide phase is formed along with ZnO and zinc hydroxyl acetate phase. When the quantity of water is half then that of optimum (200 ml) the concentration of zinc hydroxyl acetate and zinc hydroxide phases are seen along with negligible amount of ZnO phase. Zinc hydroxide phase is seen to be dominant phase. But as the amount of the aqueous solvent increases to 175 ml, the intensity of the peak due to zinc hydroxy acetate and zinc oxide increases and that of zinc hydroxide decreases. Thus zinc hydroxide phase is formed first with increase in OH$^{-1}$ concentration. With increase in the amount of water zinc hydroxide reacts with acetate ions in the solution to form zinc hydroxy acetate. With further increase in the amount of water to an optimum value of 200 ml ZnO phase appears with disappearance of zinc hydroxide and zinc hydroxy acetate. With further increase in the amount of water to 225 ml the zinc hydroxy phase appears again showing a shift of equilibrium of reaction to left as per the equation 4 in section I. With further increase in the quantity of the aqueous solvent to 5 fold (1000 ml) then that of optimum value, Zinc oxide is seen to be the dominant phase which can be attributed to the diffusion kinetics of the ions in the solution ZnO phase formed dominantly with negligible amounts of zinc hydroxyl acetate phase.
5.3.7.2 FT-IR analysis

The XRD results are supported by the FT-IR spectra of the samples. Figure 5.2.14 gives the FT-IR spectra of d1, d2, d3 and ZM4.

![FT-IR spectra](image)

**Figure 5.3.14** FT-IR spectra of showing effect of solvent on the chemical composition of ZnO (ZM4).

The appearance of the bands due to acetate group at 1555 cm\(^{-1}\), 1510 cm\(^{-1}\), 1396 cm\(^{-1}\) for the d1, d2, d3 and d4 samples clearly supports the fact that, equilibrium of equation 4, (5.2 section I), shifts to left with a small change in the amount of the aqueous solvent used for synthesis. The broad band at 3400 cm\(^{-1}\) is due to the hydrogen bonded hydroxy groups on the ZnO surface. The width of the band increases for the d1 sample this may be due to the presence of the dominant zinc hydroxide along with zinc hydroxyl acetate as confirmed from XRD. Thus increase in the hydroxy group increases the intermolecular hydrogen bonding and hence the width of the band increases. The band at 1488 cm\(^{-1}\) due to the H\(_3\)N\(^-\)-(CH2)\(_2\)-OH ions and that at 1340 is due to C-N stretching. The weak bands in the region 800 – 1000 cm\(^{-1}\) are attributed to C-O, C-C, single bond and N-O aliphatic amine oxide stretching and from N-H bending in primary amine, indicating the role of amine in the structure formation. The band at 530 cm\(^{-1}\) is attributed to ZnO.
5.3.7.3 SEM Analysis

Figure 5.3.15 SEM images of (a, b) d1 (c) d2 (d) ZM4, (e, f) d3 (g-i) d3 showing morphological changes with the amount of solvent.

Figure 5.2.15 shows the SEM images of d1, d2, and d3 samples in comparison with as-prepared flower-like ZnO (ZM4). (a, b) shows the SEM images of d1. Stacking of nanostructures with petal-like structure with pointed tip as shown in the inset of (a) and also formation of flower-like structures connected to each other through plate-like structures is seen. This cross linking occurs due to the hydrogen bonding in the presence of zinc hydroxide and zinchydroxyacetate phase having OH⁻ ions as confirmed from XRD and FT-IR analysis. With increase in amount of water to 175 ml flower-like structures are formed. With further increase in the amount of water to 200 ml flower-like structures with well defined shapes are seen. Clusters of flowers are formed due to the hydrogen bonding through hydroxy groups present on the surface of flower-like ZnO. With further increase in the amount of water to 225 again an increase in the formation of plate like structures interconnecting flowerlike structures is seen which is due to increase in the zinc hydroxyacetate phase as observed from the XRD and FT-IR profile. When the amount of water is increased to five fold (1000 ml) than the optimum amount (200 ml) required to form ZnO phase. The reduced size flower-like structures with less number of petals as compared to
ZM4 are obtained. This may be because of the fact that with large quantity of solvents the diffusion of Zn$^{2+}$ ions slows down leading to separated small sized petals.

**5.3.7.4 TEM and SAED Analysis**

![TEM images and SAED pattern of d4.](image)

**Figure 5.3.16** TEM images and SAED pattern of d4.

Figure 5.3.16 shows the TEM images of d4 having flowerlike morphology with ZnO wurtzite phase. Each petal seems to be formed by the systematic overlapping of smaller units. As compared to the flowerlike structure formed by the optimum amount of solvent (ZM4) the size of the flower for the higher (1000 ml) amount of the solvent. The size of the flower reduces along with the variation in the structure.
5.3.8 RT-PL spectroscopic analysis of ZnO samples.

Figure 5.3.17- shows the RT-PL spectra of ZnO samples with an excitation wavelength of 325 nm.

![RT-PL spectra of ZnO samples with λ_{exc.} = 325 nm](image)

Photoluminescence spectra of all the ZnO samples show a blue shift in the band emission from 3.37 eV for that of bulk ZnO as reported in the literature to 3.56 eV for the ZnO samples synthesized in the present case.

Figure 5.3.17-b shows the RT-PL spectra of the ZnO sample with an excitation wavelength of 370 nm.
The intensity of the defects formed in the visible region for ZM4 and d3 are comparable whereas the intensities of the defects for T2 and ZN are comparable. ZL1 shows formation of defects related to zinc vacancies at ~395 nm (3.14 eV) and ~410 nm (3.03 eV) along with other defects in the visible region. Formation of zinc vacancy defects in ZL1 may be traced back to the XRD and HRTEM analysis of ZL1. Zn vacancies are formed due to the fact that the growth along the (001) direction is suppressed as shown in the XRD profile (Figure 5.2.1). HRTEM also shows the growth direction of ZL1 along (101). As explained earlier in the related text, ED (5.3.4) used as the ligand produces large number of OH⁻ ions leading to the formation of the zincate ions (Zn(OH)₄²⁻). These ions are negatively charged. These negatively charged zincate ions get adsorbed on the positive Zn plane of the ZnO polar crystal. Thus suppressing the growth in the (001) direction leading to the formation of the zinc vacancies.

According to the literature, green emission in the visible region is attributed to the emission caused by the intrinsic defects in ZnO such as oxygen vacancy, zinc vacancy, interstitial zinc, oxygen antisite, oxygen interstitial. Thus the source of green emission is not clear, and is controversial. A detailed description on green emission with literature survey has been given in chapter 6 (6.2.5).
5.3.9 Photocatalytic activity of ZnO samples

Figure 5.3.18 shows degradation of MB over the ZnO samples synthesized under different experimental conditions.

![Figure 5.3.18](image)

Figure 5.3.18 comparative photocatalytic activity of ZnO samples.

ZL1 shows the highest photocatalytic activity. T2 has comparative photocatalytic activity to that of ZL1. The highest photocatalytic activity of ZL1 may be attributed to the defects formed due to zinc vacancy [~395 nm (3.14 eV), ~410 nm (3.03 eV)] and well separated hexagonal nanoplates of size ~25 nm. Due to smaller particle size surface/volume ratio increases which in turn increases the photocatalytic activity. Photocatalytic activity of spindle shaped ZnO (T2) is higher than flower-like (ZM4, ZN) ZnO. Higher photocatalytic activity of T2 is attributed to smaller size leading to higher surface to volume ratio. ZM4 and d3 have low photocatalytic activity due to lower surface defects and due to the flowerlike structure which reduces the surface/volume ratio as compared to ZL1 and T2 samples. Higher photocatalytic activity of d3 is due to smaller size of the flower-like structure as compared to ZM4. Thus the photocatalytic activity is seen to depend on the size, and defects formed in the crystalline structure.

The defect related mechanism for the photocatalytic process with a schematic representation may be refered to chapter5 (section I: 5.2.7)
5.3.10 Conclusions

Effect and correlation of the ligand used as the source of OH⁻ ions and the capping agent, temperature of synthesis, zinc precursor and the amount of aqueous solvent has been studied in detail. ED and EA used as the two ligands give hexagonal plate-like and flower-like morphologies respectively. The two ZnO samples vary in the crystalline structure. Flower-like structure shows growth in the (001) direction while hexagonal nanoplates show growth in (101) direction leading to the formation of zinc defects in the crystal lattice. Due to kinetic aspects at room temperature Zn(OH)₂ is precipitated out in competition with ZnO though ZnO has higher pKₐ value (16.8) than Zn(OH)₂ (16.5). At high temperature (60 °C) spindle shaped ZnO is obtained whereas at 4 °C flower-like ZnO is formed. The difference in the morphology is attributed to the rate of the reaction. The two zinc precursors used though give flower-like morphology the major difference is in the nanostructures which built flower-like structure. When ZA is used as precursor nanobelts with regular shape and width of ~20 nm overlap systematically and give rise to the flower-like structure. Whereas when ZN is used as a precursor, flower-like structure is built with the overlapping of one dimensional structures of irregular shape. Along with flower-like structures spindle shaped structures are also formed with budding at the center of the structure. Crystallinity and morphology of the samples vary with the amount of aqueous solvent. This is attributed to the number of OH⁻ ions produced and effect of dilution on the diffusion of Zn²⁺ ions on to the surface of ZnO nuclei.