Chapter-2

Synthesis and characterizations
This chapter focuses on the synthesis and characterizations of nanostructures (nanosheets, flower-like structures and the nanoparticles) by facile solution method at room temperature. The goal of this chapter is to better understand the synthesis parameters used for the synthesis of ZnO nanostructures, and improve the precision and control. Many of the results attained in this research work may be indicative of the synthesis parameters. This chapter begins with a section that deals with the synthesis parameters related to the synthesis of ZnO nanosheets which is followed by their characterizations. Similarly, the two next sections discuss the synthesis and characterizations of ZnO flower-like structures and nanoparticles, respectively.

2.1. Synthesis of ZnO Nanosheets

**Materials:** Zinc acetate (ZnAc$_2$ or Zn(CH$_3$COO)$_2$) (purity 99.99%) and potassium hydroxide (KOH) (purity 98%) were procured from Sigma-Aldrich (USA) and Merck, respectively. The reagents were used as received without further purification. All reactions were carried out in glassware dried in an oven under ambient conditions.

**Method:** A zinc acetate (ZnAc$_2$) solution (0.5 M) and potassium hydroxide (KOH) solution (0.5M) were formed in ethanol (C$_2$H$_5$OH), separately. In KOH solution, ZnAc$_2$ solution was added drop wise under the vigorous stirring condition at room temperature. In order to monitor growth mechanism of ZnO nanostructures, small quantity of the samples was collected at 0.25, 1, 2 and 4 hours of time intervals from the reaction mixture. Collected precipitate was filtered, washed with deionized water and ethanol to remove undesirable ions such as CH$_3$COO$^{-}$ and K$^{+}$, and dried for 1 hour.

2.1.1. Morphology Control

2.1.1.1. Effect of precursor and alkali concentration

The solubility of ZnO in an alkali solution increases with the concentration of alkali solution and temperature. Commonly, NaOH and KOH are used as alkali solutions. Since divalent metal ions do not hydrolyze in acidic environments therefore, an alkaline solution plays a crucial role for the formation of ZnO nanostructures [121-123]. The reactions involved in the formation of ZnO are [124, 125]:

\[
\text{Zn}^{2+} + 2\text{OH}^{-} \leftrightarrow \text{Zn(OH)}_2
\]  

(2.1)
For the equation (2.2), the product could be different from Zn(OH)$_4^{2-}$, product may be in the form of Zn(OH)$^+$, Zn(OH)$_2$, or Zn(OH)$^{3-}$, depending on the parameters such as the concentration of Zn$^{2+}$ and the pH value as shown in Fig. 2.1. Under different reactions conditions, all the intermediate forms are in equilibrium with the major forms being different [126]. According to the above reactions, the O$^{2-}$ used in the formation of ZnO does not originate from the solvent H$_2$O or C$_2$H$_5$OH rather it comes from the base. Therefore, the formation of ZnO does not require water as the solvent [127], but it could be organic solvents, such as methanol [128], ethanol [129], and butanol [130], or even ionic liquids [131, 132]. The synthesis was done at room temperature by adjusting the ratio of Zn$^{2+}$ and OH$^-$, and ZnO nanostructures under alkali conditions were formed [130]. The phase stability diagram for ZnO (s) and water at room temperature as a function of precursor concentration and pH of the solution is shown in the Fig. 2.1.

![Phase stability diagram](image_url)

**Figure 2.1:** Phase stability diagrams for the ZnO(s) and H$_2$O system at room temperature (dashed lines denote the thermodynamic equilibrium between the Zn$^{2+}$ soluble species and the corresponding solid phases) [126, 133].
In the present work, the results show that the concentration of KOH plays a crucial role for the formation of ZnO nanostructures. Figure 2.2 shows ZnO morphologies formed with different ratios of precursor (ZnAc2) solution and alkali (KOH) solution when ethanol as solvent was used. In Fig. 2.2(a), when the molar ratio of OH−:Zn2+ is 1:4 (conc. of ZnAc2 and KOH is 0.5 M and 0.125 M, respectively), the products are nanoparticles with size 25 nm. Increasing the KOH concentration (0.25 M) in 1:2 ratios in the precursor solution, the nanoparticles aggregated in sheet-like structure as shown in Fig. 2.2(b). A further increase in the KOH concentration (0.5 M) such as 1:1 resulted in the formation of nanosheets (Fig. 2.2(c)). As we know that ZnO is an amphoteric compound, which dissolves in acid or alkali solutions. Therefore, when the molar ratio reached 2:1 (conc. of ZnAc2 and KOH is 0.25 M and 0.5 M) and 4:1 (conc. of ZnAc2 and KOH is 0.125 M and 0.5 M), the ZnO started to dissolve which resulted in the formation of hierarchical structure associated with nanoparticles on their surface (Figs. 2.2(d) and 2.2(e)). In this study, we observed that molar ratio 1:1 of ZnAc2 and KOH is optimum for the formation of uniform ZnO nanosheets.

Along with the molar ratio of 1:1 of OH− to Zn2+, the concentration of precursor and alkali solution also plays an important role in the formation of nanostructure. Initially, we used 0.1 M concentration for both of the solutions, the obtained structure was rough as shown in Fig. 2.3(a). For increased concentration to 0.2 M while keeping the molar ratio 1:1, a small change in the structure was obtained, some sheets-like structure appeared to form (Fig. 2.3(b)). With further increasing the concentration of ZnAc2 and KOH solutions to 0.4 M, the sheets-like structures become clearer as shown in Figs. 2.3(c)-2.3(f), and at 0.5 M of both the solutions, uniform nanosheets appeared as shown inset of Fig. 2.3(g). The concentration 0.6 M of both the solutions gave rise to irregular structure with disappearance of the sheets in the product as shown in Fig. 2.3(h). All the experiments were performed in similar conditions merely the molarities of ZnAc2 and KOH solutions were adjusted. In our study, we found that that in addition to the Zn2+ concentration a certain pH range (pH=9 to 12) is suitable for the formation of ZnO nuclei in solution, which influences the crystal growth rate and the morphologies.
Figure 2.2: FESEM images show changes in morphology by variation of \( \text{OH}^- : \text{Zn}^{2+} \) ratio as (a) 1: 4, (b) 1: 2, (c) 1: 1, (d) 2: 1, and (e) 4: 1.
Figure 2.3: FESEM images show variation in morphology by varying precursor and alkali solution concentration as (a) 0.1 M, (b) 0.2 M, (c) 0.25 M, (d) 0.3 M, (e) 0.4 M, (f) 0.45 M, (g) 0.5 M, and (h) 0.6 M keeping OH⁻: Zn²⁺ ratio = 1: 1.
2.1.1.2. Effect of reaction time

We used ZnAc$_2$ solution (0.5 M) and KOH solution (0.5 M) in ratio 1:1. To explain the effect of reaction time of ZnO nanosheets, the samples were collected at different time intervals (we selected 0.25, 1, 2 and 4 hours) from the reaction mixture. We took same molarity (0.5 M) of both solutions keeping OH$^{-}$: Zn$^{2+}$ ratio = 1: 1. The samples collected at different time intervals are shown in FESEM images (Fig. 2.4). Fig. 2.4 also shows a schematic (left side) of the growth of nanosheets. A uniform reaction temperature 40 °C was maintained till the last sample (at 4 hours) was collected from the reaction chamber. All the samples collected from the reaction chamber were filtered, washed several times with deionised water, and finally dried at 100 °C for 1 hour.

From the FESEM images (Fig. 2.4) of the samples which were formed in C$_2$H$_5$OH medium at successive stages of reaction, it can be concluded that the ZnO nanosheets are resulted from the growth of ZnO nanoparticles. Initially, when the reaction proceeded for 0.25 hour, nanoparticles (around 25 nm in size) were formed as shown in Fig. 2.4(a). For 1 hour reaction time, the nanoparticles starts to aggregate in the sheet-like structure as shown in Fig. 2.4(b). From the Fig. 2.4(b), we can be seen that there are two different types of structures: nanoparticles with a diameter about 25 nm and nanosheets with a thickness about 25 nm. For 2 hours of reaction time, sheet-like structure becomes prominent as shown in Fig. 2.4(c). There sheet-like structure has thickness of 25 nm. Since both the nanoparticles and sheets-like structures have same thickness, it is inferred that initially the nanoparticles are formed which due course of time assemble in the form of sheet to reduce the surface energy. The growth of the nanosheet network continues until whole of the precursor is consumed, and for the prolonged reaction time of 4 hours, larger size nanosheets with a thickness of 25 nm are formed (Fig. 2.4(d)).

The whole process of formation of ZnO nanostructures i.e. nanosheets in brief may be described to proceed via the nucleation of ZnO nanocrystals, then subsequent directional growth to form nanosheet structures. The nucleation takes place in a condition when the concentration of precursors (i.e. nanocrystals or monomers) exceeds the critical super saturation level. In such a condition, smaller nanocrystals grow rapidly until their concentration falls below the critical level for nucleation [134]. According to Ostwald ripening process [126, 135], the large
nanocrystals grow at the cost of smaller nanocrystals. The growth of large nanocrystals proceeds by the capturing of Zn\(^+\) ion formed from the dissolution of smaller nanocrystals and brought near to the surface of larger nanocrystals by the process of diffusion. The whole mechanism for the formation of ZnO nanosheets is described in detail in chapter 3.

**Figure 2.4:** Morphological evolution of the ZnO products with respect to different reaction times: (a) 0.25 hour, (b) 1 hour, (c) 2 hours, and (d) 4 hours. The left of FESEM images corresponds to the schematic diagram of the proposed growth process of ZnO nanosheets.
2.1.1.3. Effect of surfactant

The growth mechanism of ZnO nanostructures is influenced by the existence of surfactant as cetyltrimethylammonium bromide (CTAB) in the solution. In the presence of surfactant, the surface tension of solution is decreased which minimizes the surface energy to form a ZnO nanocrystals. Being an ionic compound, the CTAB completely ionizes in water and forms a positively charged tetrahedron with a long hydrophobic tail, while the Zn(OH)$_4^{2-}$ is considered to be grown for ZnO crystal which has a negatively charged tetrahedron geometry.

The chemical reaction between the surface of ZnO nuclei and the ions produced by the ionization of capping material gives rise to the formation of different morphology. The ZnO nanoparticles with smaller size are obtained if the CTAB is present in the solution because the positively charged CTAB ions surround the surface of ZnO nuclei thereby suppressing the growth of ZnO crystal [136]. In our case too, we obtained ZnO nanoparticles (Fig. 2.5(a)) in the presence of CTAB in precursor solution, while in absence of CTAB, ZnO nanosheets were obtained (Fig. 2.5(b)) for prolonged time.

![FESEM images](image)

**Figure 2.5:** FESEM images show variation in morphology (a) & (b) when 0.005 M surfactant was used while synthesis and (c) & (d) shows surfactant free growth of nanosheets.
2.1.2. Characterizations

2.1.2.1. X-Ray Diffraction (XRD)

Figure 2.6 shows X-ray diffraction pattern of nanosheets synthesized in C₂H₅OH medium for 4 hours of reaction at 40 °C. The diffraction peaks at 2θ = 32.7°, 34.5°, and 36.42° in XRD pattern corresponds to (100), (002) and (101) planes of ZnO. The diffraction peaks match well with the single crystalline hexagonal structure of ZnO (JCPDS file no. 36–1451). The calculated lattice constants (a= 3.253Å and c= 5.211Å) also indicate the hexagonal structure of ZnO. The absence of impurity peaks in the XRD pattern indicates the formation of pure ZnO.

![X-Ray Diffraction Pattern](image)

**Figure 2.6:** X-ray diffraction pattern of ZnO nanosheets synthesized at room temperature for 4 hours of reaction time.

2.1.2.2. Transmission Electron Microscope (TEM)

To explore the structure and elemental composition of nanosheets, we performed TEM and Energy Dispersive X-ray spectroscopy (EDAX) (installed in JEM-2100). The TEM study was carried out at an acceleration voltage of 200 Kilo-Volt and probe current of 1 Nano Ampere. For TEM sampling, powder of ZnO nanosheets was taken in small amount and dissolved in ethanol.
which was dispersed by sonication. Then with the help of a syringe, a drop of ethanol dispersed nanosheets was placed on the carbon coated TEM grid.

Figure 2.7 shows TEM image of ZnO nanosheets. The TEM study was done in order to obtain growth of nanosheet. The TEM in Fig. 2.7(a) shows that nanosheets are interwoven to each other. Fig. 2.7(b) is HRTEM image, in this image the nanosheet has a lattice spacing of 0.26 nm. This lattice spacing is corresponding to the growth direction (002) of the wurtzite structure of ZnO. The elemental characterization was done by EDAX installed in TEM which is shown in Fig. 2.7(c). The EDAX shows that the sample contains only Zn and O elements forming ZnO.

![HRTEM images of ZnO nanosheets grown after 4 hours of reaction](image)

Figure 2.7: HRTEM images of ZnO nanosheets grown after 4 hours of reaction: (a) bunch of ZnO nanosheets, (b) high resolution lattice image of nanosheet shows perfect crystalline structure and (c) EDAX of nanosheets.

### 2.1.2.3. UV-Vis Spectroscopy

UV-visible absorption spectroscopy is widely being used technique to examine the optical properties of nanosized particles. The UV–Vis spectrum of the ZnO nanosheets is shown in Fig. 2.8. The absorption spectrum of ZnO nanosheets presents a sharp absorption peak around 355 nm which is the characteristic single peak of hexagonal ZnO nanosheets. The nature of the optical band gap can be determined using the fundamental absorption, which corresponds to electron excitation from valence band to conduction band. Direct absorption band gaps of the ZnO nanosheets can be obtained by confirming the absorption data to the following equation [137];

\[
\alpha h\nu = B(h\nu-E_g)^n
\]

(2.6)
where $\alpha$ is the absorption coefficient, $h\nu$ is the photon energy, $E_g$ is the optical band gap of the material, $B$ is the material constant and $n$ is either 2 for direct transition or $\frac{1}{2}$ for an indirect transition. Therefore, the optical band gaps of ZnO nanosheets for the absorption edge can be determined by extrapolating the straight portion of the curve $(\alpha h\nu)^2$ versus $h\nu$ when $\alpha = 0$. Another way to estimate band gap is by using following equation;

$$E_g = \frac{1.24}{\lambda} \text{ (\mu m)}$$

(2.7)

where $\lambda$ is absorption or cutoff wavelength in microns. We have used second approach to calculate approximate band gap. Here cutoff wavelength at 355 nm (Fig. 2.8) and calculated $E_g$ value was approx. 3.49 eV for ZnO nanosheets.

**Figure 2.8:** Optical absorption spectrum for ZnO nanosheets prepared by chemical route at room temperature for 4 hours of reaction time.

### 2.1.2.4. Fourier Transform Infrared Spectroscopy (FTIR)

The ZnO nanostructure sample was also investigated by FTIR. Figure 2.9 shows FTIR spectrum of ZnO nanosheets. The FTIR spectrum contains broad peaks at around 3392 and 1635 cm$^{-1}$. These peaks may be assigned to the stretching and bending modes, respectively, of hydroxyl groups (chemisorbed and/or physisorbed H$_2$O molecules) on the surface of ZnO nanocrystals. A
band at 1403 cm\(^{-1}\) related to the symmetrical/asymmetrical stretching modes of the carboxylate group of acetate coordinated to the surface of ZnO nanocrystals is also observed. Also, a high intensity broad band around 884 cm\(^{-1}\) due to the typical bending mode of hydroxyl group is observed in the spectra of the structure. Other unsigned peaks are attributed to remnant organic species in the samples.

![FTIR spectrum](image)

**Figure 2.9:** FTIR spectrum of ZnO nanosheets show IR absorption frequencies of organic functional groups.

### 2.1.2.5. Photoluminescence Spectroscopy (PL)

In order to investigate the defects in as synthesized ZnO nanosheets photoluminescence was performed. The PL spectrum of ZnO nanosheets investigated at an excitation wavelength 340 nm is shown in Fig. 2.10. The PL spectra is fitted with a five Gaussian function at the center wavelengths of 390 nm (UV), 420 nm (violet), 466 nm (blue), 485 nm (blue-green) and 520 nm (green) using origin software, which reproduces the PL spectrum more reasonably. The UV emission around 390 nm (3.17 eV) corresponds to near band edge (NBE) emission [138]. The band edge emission is mainly due to radiative recombination of excitons. The emission at 420
nm (2.95 eV) is attributed to the transition between shallow donors (oxygen vacancy) to the valence band VB [139-141]. The peak at 465 nm (2.66 eV) is related to zinc vacancy and interstitial defects [142]. The emission at 485 nm (2.55 eV) wavelength is assigned to recombination between the oxygen vacancy and interstitial oxygen, and lattice defects related to oxygen and zinc vacancies [140, 143]. A broad peak around 520 nm (2.38 eV) is due to radiative recombination of a photogenerated hole with an electron occupying the oxygen vacancy, which is attributed to the single ionized oxygen vacancy [144]. These transitions confirm the existence of the oxygen and zinc vacancies in nanosheets.

![Visible PL spectrum of ZnO nanosheets grown in ethanol.](image)

**Figure 2.10:** Visible PL spectrum of ZnO nanosheets grown in ethanol. The black solid curves are the experimental data and the green curves are individual peaks from the fittings. Spectrum was recorded at 340 nm excitation wavelength.

### 2.2. Synthesis of ZnO flower-like structures

To synthesize flower-like structure, solutions of 0.5 M ZnAc$_2$ (purity 99.99%, Sigma Aldrich) and 0.5 M KOH (purity 98%, Merck) were prepared in distilled (DI) water. Prepared ZnAc$_2$ solution was added dropwise to the KOH solution at 40 °C under continuous stirring for 4 hours,
and a white precipitate was obtained. After the reaction, the precipitate was filtered and washed several times with DI water and ethyl alcohol. To evaporate the water, the precipitate was dried for 1 hour at 100 °C in a horizontal tube furnace. After drying of the above precipitate, nanosheets were obtained in bunches (which we call flower-like structure).

2.2.1. Morphology Control
2.2.1.1. Effect of precursor and alkali concentration

The experiment showed that the existence of hydroxide ion played an important role in the formation of ZnO structures in water as solvent. It is found that the morphologies of the ZnO structures are sensitive to the amount of KOH. Figure 2.11 shows ZnO morphologies formed with different concentration of precursor solution (ZnAc$_2$) and alkali solution (KOH). Figures 2.11(a)-2.11(d) shows the change in the morphologies of the product with different concentrations of KOH. Figure 2.11(a) shows the FESEM image of the obtained ZnO structure formed for the molar ratio of OH$^-$/Zn$^{2+}$ equal to 2: 1 (conc. of ZnAc$_2$ and KOH is 0.5 M and 1 M, respectively), the octahedral-like structure of micrometer range can be observed. This is inferred due to the more basic nature of the solution due to which recrystallization occurs which give rise to microstructure. The size of the particles goes on increasing with increasing pH of the solution [145]. The decrease in the KOH concentration (0.5 M) for molar ratio 1: 1 results in the formation of flower-like structures (Fig. 2.11(b)). Therefore, it is speculated that the amount of KOH in solution can adjust the ZnO crystal growth. Further, by decreasing the KOH concentration (0.25 M) in 1: 2 ratios in the solution resulted in the formation of nanoparticles as shown in Fig. 2.11(c). A further decrease in the KOH concentration (0.125 M) in ratio 1: 4 resulted in the layered small sheet-like structure network (Fig. 2.11(d)).

Similar to above, Figs 2.11(e)-2.11 (h) shows the morphological change of the product with varying concentration of precursor solution (ZnAc$_2$). In Fig. 2.11(e), when the molar ratio of OH$^-$/Zn$^{2+}$ was chosen as 4: 1 (conc. of ZnAc$_2$ and KOH was set as 0.125 M and 0.5 M, respectively), the obtained products were microstructures having some sheets like structures. An increment in the precursor solution concentration (0.25 M) for 2: 1 ratio of OH$^-$/Zn$^{2+}$ in the solution, a non-uniform aggregation of sheet-like structures was obtained as shown in Fig. 2.11(f). A further increase in the ZnAc$_2$ solution concentration (0.5 M) such as 1: 1 resulted in the formation of flower-like structures (aggregation of sheets) (Fig. 2.11(g)). Further, increase in
precursor solution concentration to 1 M (OH\(^-\): Zn\(^{2+}\) = 1: 2) resulted in the coagulation of sheet-like structure (nest-like structure) (Fig. 2.11(h)). In this study, we observed that molar ratio 1: 1 of ZnAc\(_2\) and KOH is optimum for the formation of uniform ZnO flower-like structures.

**Figure 2.11:** FESEM images show change in the morphology by varying alkali to precursor solution ratio (OH\(^-\): Zn\(^{2+}\)) (varying concentration from 0.125 to 1 M) as (a) 2: 1, (b) 1: 1, (c) 1: 2, (d) 1: 4, and (e) 4: 1, (f) 2: 1 (g) 1: 1 (h) 1: 2, respectively, in H\(_2\)O medium.
In this case too, when water was used as solvent, along with the molar ratio of 1:1 of \( \text{OH}^- \) to \( \text{Zn}^{2+} \), the concentration of precursor and alkali solution also plays an important role in the formation of nanostructure. Initially, we used 0.1 M concentration for both of the solutions, the obtained structure was irregular structure as shown in Fig. 2.1(a). When we increased the concentration to 0.2 M while keeping the molar ratio of precursors as 1:1, a small change in the structure was obtained but still it was irregular microstructures as shown in Fig. 2.1(b). With a further increase in the concentration of \( \text{ZnAc}_2 \) and KOH solutions to 0.4 M, the flower-like structure in large amount as compared with microstructures was obtained as shown in Figs. 2.1(c)-2.1(f). And at 0.5 M of both the solutions, only flower-like structure appeared as shown in Fig. 2.1(g). The concentration 0.6 M of both the solutions gave rise to disappearance of flower-like structure with nanoparticles on their surface in the product as shown in Fig. 2.1(h). All the experiments were performed in similar conditions merely the molarities of \( \text{ZnAc}_2 \) and KOH solutions were adjusted. Similar to the ethanol as a solvent, from these observations we observed that in addition to the \( \text{Zn}^{2+} \) concentration only a certain pH range (pH= 9 to 12) is suitable for the formation of ZnO nuclei in solution in water as solvent, influencing the crystal growth rate and the resulting morphologies.
Figure 2.12: FESEM images show small change in morphology with variation of concentration of precursor and alkali solution concentration simultaneously as (a) 0.1 M, (b) 0.2 M, (c) 0.25 M, (d) 0.3 M, (e) 0.4 M, (f) 0.45 M, (g) 0.5 M, (h) 0.6 M, by keeping OH⁻: Zn²⁺=1: 1.
2.2.1.2. Effect of reaction time

In case of nanoflowers, two possibilities exist for the growth of the flower-like structures in aqueous medium. The first is the growth of monodispersed nanosheets in aqueous solution which aggregate together in the form of flower-like structure (almost spherical) to attain the minimum surface energy. The second is the formation of aggregates of nanoparticles in the solution which by consuming the precursor from the solution grows further and forms a flower-like structure with the passage of time. Each nanoparticle in an aggregate which grows with the passage of time in 2D (sheet like structure), consuming the precursor present in the solution along the (002) direction. A random orientation of the nanosheets (as in Fig. 2.13) may be attributed due to the random orientation of the growth direction in an aggregate. Since the nanoparticles in an aggregate arranged in a random manner their growth direction (002) is also oriented randomly, therefore the nanosheets are randomly oriented.

![FESEM image of a single flower-like structure indicating random orientation of the nanosheets.](image)

**Figure 2.13:** FESEM image of a single flower-like structure indicating random orientation of the nanosheets.

The first possible growth mechanism is unlikely for the reasons. If the nanosheets are grown initially inside the solution they cannot interwoven in a compact manner as indicated in Fig. 2.13. Also, in this image many of the nanosheets can be seen to be grown normally to each
other (nanosheets A is normal to B and C is normal to D in the FESEM image Fig. 2.13). Therefore, the second possibility is more plausible. In this case, flower-like structure is formed as the growth of the ZnO nanoparticles aggregate.

The FESEM images in Fig. 2.14 show the growth of flower-like structure at successive reaction time. A schematic in Fig. 2.14 (left of the FESEM images) represents the growth mechanism of a flower-like structure composed of nanosheets. In the aqueous medium, when the reaction elapsed for 0.25 hour, nanoparticles (size about 25 nm) aggregate in a bunch like structure (Figs. 2.14(a) and 2.14(b)). As the reaction proceeds further each nanoparticle aggregate grows to form a sheet-like structure as indicated in Figs. 2.14(c)-2.14(h). The growth mechanism of nanosheets composing the flower-like in aqueous medium is similar to the growth mechanism of nanosheets in alcohol medium. The mechanism can also be correlated to the adsorption phenomenon of the acetate and hydroxyl ions which is explained in detail in chapter 3. Initially in 0.25 hour time although there is an absence of the sufficient adsorbed ions over the ZnO centers (Fig. 3.3) but due to the strong hydrogen bonding network facilitated by the highly polar water molecules, the adhesion can be seen among ZnO nanoparticles. Further with time the adsorption of the ions increases and more interwoven structures appear and finally in the form of flower-like structures.
Figure 2.14: FESEM images of the products prepared in (a, b) 0.25 hour, (c, d) 1 hour, (e, f) 2 hours and (g, h) 4 hours at a 40 °C reaction temperature. Schematic illustration of the formation stages of different shapes of the ZnO nanostructures (in the left of FESEM image).
2.2.1.3. Effect of surfactant

The growth mechanism of ZnO is different in the existence of surfactant i.e. CTAB in solution. Similar to the case of C₂H₅OH solvent in H₂O too, the capping material CTAB caps the surface of nanoparticles and hinders their further growth. Therefore, we got nanoparticles of ZnO as shown in Figs. 2.15(a) and 2.15(b) in the presence of CTAB in solution while in the absence of surfactant in solution results ZnO flower-like structure (Figs. 2.15(c) and 2.15(d)).

![FESEM images showing variation in morphology](image)

**Figure 2.15**: FESEM images show variation in morphology (a) & (b) when 0.005 M surfactant was used while synthesis and (c) & (d) shows surfactant free growth of flower-like structure.

2.2.2. Characterizations

2.2.2.1. X-Ray Diffraction (XRD)

Figure 2.16 shows the XRD patterns of flower-like. The sharp intense peaks of ZnO confirm good crystalline nature of the product. The peaks originated at (100), (002), (101), (102), and (110) reflections show formation of hexagonal ZnO similar to the case of nanosheets.
Figure 2.16: X-ray diffraction pattern (λ=1.54056 Å) of the flower-like structure grown at 40 °C for 4 hours of reaction time. The diffraction peaks for ZnO are indicated according to the JCPDS file (36-1451).

2.2.2.2. Transmission Electron Microscope (TEM)

To explore the structure and elemental composition of flower-like structures, we performed TEM and Energy Dispersive X-ray spectroscopy (EDAX) (installed in JEM-2100). For TEM sampling, powder of ZnO was taken in small amount and dissolved in ethanol which was dispersed by sonication. Then with the help of a syringe, a drop of ethanol dispersed powder was placed on the carbon-coated TEM grid.

Figure 2.17(a) represents TEM image of flower-like structures. Here each of the flowers is composed of very thin sheets-like structure. Figure 2.17(b) is HRTEM image, which indicates the lattice fringe spacing equal to 0.26 nm. From HRTEM image, ZnO nanostructures i.e. flower-like structure has the crystallographic orientation along (002) direction. The EDAX result obtained for the flower-like is shown in Fig. 2.17(c). The obtained ‘O’ (by 52.43 at. %) and ‘Zn’ (by 47.57 at. %) peaks in EDAX shows that the flower-like structure is composed of ZnO.
Figure 2.17: HRTEM images of ZnO flower-like structure grown after 4 hours of reaction: (a) bunch of ZnO nanoflowers, (b) high resolution lattice image of flower-like structure showing perfect crystalline structure with (c) corresponding EDAX spectrum shows the different elements component.

2.2.2.3. UV-Vis Spectroscopy

The absorption spectrum of ZnO flower-like structures sample is shown in Fig. 2.18. It exhibits a strong absorption peak at about 365 nm wavelength. The band gap calculated from the UV cut-off is 3.39 eV.

Figure 2.18: Optical absorption spectrum of ZnO flower-like structures shows absorbance peak of powder at 365nm wavelength.
2.2.2.4. Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR analysis was carried out to investigate organic functional groups in ZnO flower-like structure. Figure 2.19 shows FTIR spectrum of ZnO flower-like structures. As seen in Fig. 2.19, the ZnO exhibits characteristic peaks around 3392 cm\(^{-1}\) which is attributed to O–H stretching mode. The bending mode of hydroxyl group occurs at 1635 cm\(^{-1}\). The band at 1403 cm\(^{-1}\) is assigned to the symmetrical/asymmetrical stretching modes of the carboxylate group of acetate coordinated to the surface of ZnO nanocrystals. And the band at 884 cm\(^{-1}\) is due to the typical bending mode of hydroxyl group. Other unsigned peaks in FTIR spectrum are attributed to remnant organic species in the samples.

![FTIR Spectrum](image)

**Figure 2.19:** FTIR spectrum of ZnO flower-like structures show IR absorption frequencies of organic functional groups.

2.2.2.5. Photoluminescence Spectroscopy (PL)

The room temperature PL spectrum of ZnO flower-like structures is shown in Fig. 2.20. Bands are observed around 390 nm (UV), 420 nm (violet), 466 nm (blue), 485 nm (blue-green) and 520
nm (green). The UV emission corresponds to the near band edge emission of the wide band gap of ZnO, which is caused by annihilation of the excitons by recombination [146-148]. The observed violet emission is caused by electron transitions from the shallow donor levels of oxygen vacancies to the valence band [139-141]. The blue emission is due to the zinc vacancy and interstitial defects [142], and blue-green emission is related to recombination between the oxygen vacancy and interstitial oxygen, and lattice defects related to oxygen and zinc vacancies [140, 143]. The presence of these peaks indicates UV as well as visible emissions due to surface defects states present in synthesized ZnO structure. The broad green emissions results from the radiative recombination of photogenerated holes with singularly ionized oxygen vacancies [144]. The sharp, intense UV emission indicates that the ZnO structure is highly crystalline with excellent optical properties.

![Figure 2.20: PL spectrum of ZnO flower-like structure grown in water as solvent. The black solid curves are the experimental data and the green curves are individual peaks from the fittings. Spectrum was recorded at 340 nm excitation wavelength.](image-url)
2.3. Synthesis of ZnO Nanoparticles

**Materials:** Zinc acetate (ZnAc₂) (purity 99.99%, Sigma Aldrich), cetyltrimethylammonium bromide (CTAB) (purity 99%, Sigma Aldrich) and potassium hydroxide (KOH) (purity 85%, Merck) were used as the precursor and alkali solutions. Commercially available reagents were used as received without further purification. All reactions were carried out in glassware dried in an oven under ambient conditions.

**Method:** For the synthesis of ZnO nanoparticles, a 0.2 M solution of KOH was added dropwise to 0.1 M ZnAc₂ solution at vigorous stirring. A 0.05 M solution of CTAB was added abruptly to the solution. Thus obtained solution was stirred at 40 °C for 4 hours. After 4 hours, a precipitate was obtained which was filtered, washed with DI water and ethyl alcohol, and finally dried for 2 hours at 60 °C to obtain nanoparticles.

2.3.1. Field Emission Scanning Electron Microscope (FESEM)

Figures 2.21(a) and 2.21(b) are low and high magnification FESEM images of the nanoparticles, respectively. Figure 2.21(b) shows the formation of spherical nanoparticles with a size 20–30 nm. Since during the formation of the nanoparticles, a capping material CTAB, was used to control the growth, therefore small-sized nanoparticles have been obtained.

![FESEM images of ZnO nanoparticles](image)

**Figure 2.21:** FESEM images of ZnO nanoparticles synthesized using CTAB as surfactant, which controls the size of the nanoparticles. (a & b) FESEM images at low magnification and high magnification, respectively. FESEM image in (b) shows the uniform size distribution of the nanoparticles.
2.3.2. X-Ray Diffraction (XRD)

The XRD pattern of nanoparticles is shown in Fig. 2.22. The diffraction peaks at 2θ = 32.7°, 34.5°, and 36.42° correspond to the (100), (002), and (101) planes of the ZnO structure. All the diffraction peaks in this pattern can be perfectly indexed as a wurtzite-structured ZnO with lattice constants a = 0.325 nm and c = 0.521 nm. In addition to these commonly observed orientations, the weak orientations at 47.44° and 56.58° corresponding to (102) and (110), respectively are also observed in the XRD pattern. The recorded XRD pattern well matched with the reference card JCPDS 89-1397 confirming the nanoparticles to be composed of ZnO. No characteristic peaks of impurities are detected in the XRD, which shows the high purity of the product. In addition, the strong and sharp diffraction peaks reveal that the as synthesized ZnO nanoparticles are well crystalline.

![XRD Pattern](image.png)

**Figure 2.22:** XRD pattern from ZnO nanoparticles prepared in the presence of surfactant after 4 hours of reaction time at room temperature.

The size of the particles is calculated by Debye Scherrer’s formula:

\[ D = \frac{k\lambda}{\beta \cos \theta} \]  

(2.8)
where \( k \) is a constant equal to 0.89, \( \lambda \) the X-ray wavelength (0.154095 nm), \( \beta \) the full wavelength at half maximum and \( \theta \) the half diffraction angle. The crystal size of ZnO nanoparticles calculated from FWHM (Full Wave Half Width) is tabulated in Table 2.1.

**Table 2.1:** Particle size estimated from the diffraction spectrum by using half maximum widths.

<table>
<thead>
<tr>
<th>Pos. [°2θ.]</th>
<th>(hkl)</th>
<th>FWHM Left [°2θ.]</th>
<th>d-spacing [Å]</th>
<th>Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>31.724</td>
<td>100</td>
<td>0.315</td>
<td>2.81827</td>
<td>25.94</td>
</tr>
<tr>
<td>34.387</td>
<td>002</td>
<td>0.213</td>
<td>2.60591</td>
<td>38.63</td>
</tr>
<tr>
<td>36.211</td>
<td>101</td>
<td>0.313</td>
<td>2.47872</td>
<td>26.42</td>
</tr>
<tr>
<td>47.488</td>
<td>102</td>
<td>0.36</td>
<td>1.91308</td>
<td>23.85</td>
</tr>
<tr>
<td>56.530</td>
<td>110</td>
<td>0.36</td>
<td>1.62665</td>
<td>24.79</td>
</tr>
</tbody>
</table>

**2.3.3. UV-Vis Spectroscopy**

Figure 2.23 shows optical absorption spectrum of CTAB capped ZnO nanoparticles. Excitonic absorption peaks are blue shifted with respect to the absorption edge which appears at 400 nm at room temperature [149, 150] in the case of bulk ZnO. The excitonic absorption feature for nanosized particles can be seen at about 315 nm which gives approx. 3.93 eV of band gap.

![Figure 2.23](image-url)  

**Figure 2.23:** Optical absorption spectrum of ZnO nanoparticles showing absorption at 315 nm.
2.3.4. Photoluminescence Spectroscopy (PL)

The room temperature PL spectrum of nanoparticles is shown in Fig. 2.24. Characteristic peaks are observed at 390 nm (UV), 420 nm (violet), 466 nm (blue), 485 nm (blue-green) and 520 nm (green). The explanation of these peaks is similar to the nanosheets and flower-like structure. The sharp, intense UV emission indicates that the nanoparticles are highly crystalline with excellent optical properties. Similar to nanosheets and flower-like structure, the presence of these peaks indicates UV as well as visible emissions due to the surface defects states in nanoparticles also.

![Image of PL spectrum]

**Figure 2.24:** PL spectrum of ZnO nanoparticles prepared in presence of surfactant. The black solid curves are the experimental data and the green curves are individual peaks from the fittings. Spectrum was recorded at 340 nm excitation wavelength.