CHAPTER II

EFFECT OF pH, VARIATION IN IONIC STRENGTH AND DIFFERENT ZINC ION SOURCES ON THE GROWTH OF ZnO NANOSTRUCTURES

2.1 Introduction

In hydrothermal synthesis of nanocrystalline zinc oxide, the experimental conditions play an important role in determining the growth kinetics, formation of nuclei and further the growth of different nanostructures onto the nuclei. In order to study the effect of the experimental parameters, the key parameters like pH of the mother cursor, temperature of the hydrothermal experiment, and time duration of the hydrothermal treatment are considered. Their effect on the hydrothermal conditions is studied. Usually for synthesizing zinc oxide nanostructure, a zinc salt solution and an alkaline solution is needed. This alkaline solution which is known as the mineralizer helps separating the Zn metal atom from the solution and forms different intermediate complexes whose population decides the rate of formation of nucleation sites and subsequent growth onto the nuclei. Here, concentration of mineralizer can influence the speed of formation of the intermediate complexes. Increase in pH value is an indication of the increase in the mineralizer concentration. But, for producing the complexes, hydroxyl (OH⁻) ions are to be separated from the solvent water. For doing so only we need hydrothermal conditions in which we can heat water above its boiling point. Therefore, heating the aqueous solution to higher temperatures above the boiling point can quickly produce hydroxyl ions. Further, higher temperature combined with higher pH can even speed-up the process. The differences can be seen in the results of the different experimental conditions. When the time duration of the hydrothermal treatment is extended, dramatic
changes could be created in the system under investigation. In the first section (Section A) the effect of the foresaid experimental conditions on the hydrothermal synthesis of zinc oxide nanostructures are presented.

In the second section (Section B), it is intended to study the variation in the ionic strength of the metal source and the mineralizer strength. The modifications which could be created by varying the ionic strength in the growth kinetics were the interests. Ten different varied combinations of anions (OH\(^-\)) and cations, in an otherwise similar experimental conditions are tested and the formation of the resultant nanostructures are explained on the basis of the nucleation kinetics, growth kinetics etc.,

In materials it is always coveted to have larger surface to volume ratio for an efficient usage of matter. Larger surface area means, more effectively the material is used. In order to prepare different morphologies with variable surface areas, certain modifications in chemical routes are tested for which the composition of the starting material is changed. Different zinc ion sources are chosen as the starting materials along with the various mineralisers (separately or in combination) as required for the formation of ZnO nanoparticles. The selections of these combinations are made from previous trial runs.

Since the solubility of different Zn ion sources in water is different, they play a different physical chemistry in the hydrothermal reaction. Therefore, the growth kinetics is also dissimilar. Solubility is inversely proportional to interfacial tension and stability. Hence a higher solubility will have a comparatively lower stability. Lower stability favours faster precipitation. Since the chosen Zn sources are having dissimilar solubility, their precipitating time will also be different. By using this principle and also by the
addition of different composition of mineralisers the nucleation and growth kinetics have been exploited to get a variety of nanoarchitectures such as hexagonal hollow nano-tube bunches, nanorods bunches, nanosheet bunches, spherical nanogranules and submicro-dumb-bell shapes etc., have been formed.

2.2 Brief outline of the present work

Among the transparent conducting oxides, ZnO is a direct wide band gap (3.3 eV) material with a large exciton binding energy of 60 meV [1-3]. It is widely studied for its unique properties which have large potentials for electronic, optoelectronic and optical applications. A variety of ZnO nanostructures are recently studied and their properties are discussed [4-10]. In this report for the first time, the formation of nanorod bunches are reported along with the nanoflakes-like, and nano-flower petal- like structures. In spite of elaborate research in the growth mechanism, relationship of growth conditions to the morphology, and the properties dependent on the morphology of the nanostructures, there are still some details remain unexplored. In this study we have made an attempt to find out the influence of the experimental conditions on size and shape of Zinc Oxide Nanostructures (ZNS) which can give nanocrystals with lattice parameters nearest to the standard JCPDS value. SECTION A holds the record of the above experimental work in this chapter.

Diverse shaped and differently sized controllable structures of ZnO such as nanowires [11], nanotubes [12], nanotetrapods[13], nanocombs and a few more [14-16], are reported recently. These kinds of structures can be selectively administered by altering the precursor chemicals and altering their concentrations and by tuning the growth temperatures. The growth of the ZnO crystal is determined by the internal structure of the crystal, but is also sensitive to a number of external conditions such as
pH, in the precursors zinc source and mineralizer producing its counter ion, the presence of complexing agents if any added and the nucleation conditions etc. In this report we intend to study the different possible ways of forming engineered nanostructures by altering their chemical environments. The growth phenomena, reaction mechanisms, reasons for the selective emergence of particular structures of the formed morphologies are discussed. Especially their microstructural deviations are predicted by the results derived from their x-ray reflection line broadenings. The above concepts are experimented and presented in **SECTION B**.

In **SECTION C**, the investigations on the feasibility of achieving control over the growth of nanoarchitectures of ZnO in different tailor-made morphologies such as nano-flower, nano-twigs and solid hexagonal nanorods etc., by simply altering the cationic and anionic strength are presented. Since the growth parameters are directly influenced by the anionic and cationic strength, it enables us to gain control over the growth phenomenon such as energy of formation of nuclei, the concentration of the nucleating unit, growth unit etc., and consequently on the shape and size of the nano architectures. In our experimental attempt ten different possible combinations of varying cationic and anionic strengths using the same metal ion source (zinc acetate dihydrate) and the mineralizer (NaOH) are under consideration.
2.3 SECTION A: EFFECT OF pH, REACTION TEMPERATURE AND TIME DURATION OF THE REACTION

2.3.1 Experimental Preparation

In a typical hydrothermal experiment, 0.6g of LR grade zinc acetate dihydrate was dissolved in 100 ml of de-ionized water. Adding 15 ml of 2 molar sodium hydroxide solution with the zinc acetate solution turns the mixture slightly turbid which when stirred vigorously for 10 minutes gives a homogeneous mixture. This mixture reads a pH of 12 in the pH meter. This mother liquor was transferred to a Teflon-lined stainless-steel autoclave (Berghof BAR 945) of 250 ml capacity and then sealed properly. The solutions for different experiments were prepared separately and were treated for different time durations from 5 hour – 20 hour. The chosen temperatures were 120°C, 160°C and 180°C. The pH values selected for different experiments were 13.5, 9.5, and 10.5. Solutions with the above said desired pH are achieved by using 32 ml of 2 M NaOH, 3 ml, 5 ml of ammonia solutions respectively. Ten different experiments are done with at least one variation from the other in the experimental parameters. The experimental conditions of all the ten attempts are detailed in Table 2.1. In our experiments the pressure generated within the autoclave was measured to be ~ 4.8 kg/m². This pressure will change for experiments with different temperatures. After the hydrothermal treatment for stipulated predetermined time, the autoclave was allowed to cool down to ambient naturally. The produced suspension containing nanoparticles was centrifuged and washed with de-mineralized water and ethanol respectively for a few times. The centrifugate was dried in a laboratory oven to completely evaporate the alcohol.
2.4 CHARACTERIZATION

2.4.1 Structural Analysis

The dry white powder was characterized by X-ray diffraction (Panalytical - X'pertPro) and confirmed as hexagonal Zinc Oxide (mineral name: zincite) from the JCPDS Card No. 36-1451. **Figure 2.1** shows the XRD pattern of the resultant ZnO powder. In **Table 2.2**, a comparison between the measured XRD parameters with that of the standard pattern is given and they are comparable. The average particle size (‘D’) of all the samples is calculated from Debye Scherer’s formula [17-18]. The lattice parameter values of all the ZNS are calculated by using the interplanar spacing (d). The average particle size ranges from 23 to 64 nm for different ZNS. The ratio of the lattice parameters ‘c/a’ is used to compare the nearness of the standard value with that of all the ZNS.
**Table. 2.1.** Details of mineralizer used, pH of the mother solution, experimental conditions such as temperature and time duration applied for different hydrothermal experiments.

<table>
<thead>
<tr>
<th>Sample identity</th>
<th>Mineralizer</th>
<th>pH</th>
<th>Temperature °C</th>
<th>Time duration/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZNS #1</td>
<td>NaOH</td>
<td>12</td>
<td>180</td>
<td>5</td>
</tr>
<tr>
<td>ZNS #2</td>
<td>NaOH</td>
<td>12</td>
<td>180</td>
<td>12</td>
</tr>
<tr>
<td>ZNS #3</td>
<td>NaOH</td>
<td>12</td>
<td>180</td>
<td>16</td>
</tr>
<tr>
<td>ZNS #4</td>
<td>NaOH</td>
<td>12</td>
<td>120</td>
<td>18</td>
</tr>
<tr>
<td>ZNS #5</td>
<td>NaOH</td>
<td>12</td>
<td>150</td>
<td>18</td>
</tr>
<tr>
<td>ZNS #6</td>
<td>NaOH</td>
<td>13.5</td>
<td>180</td>
<td>18</td>
</tr>
<tr>
<td>ZNS #7</td>
<td>NH₃</td>
<td>9.5</td>
<td>120</td>
<td>18</td>
</tr>
<tr>
<td>ZNS #8</td>
<td>NH₃</td>
<td>9.5</td>
<td>180</td>
<td>18</td>
</tr>
<tr>
<td>ZNS #9</td>
<td>NH₃</td>
<td>10.5</td>
<td>150</td>
<td>4</td>
</tr>
<tr>
<td>ZNS #10</td>
<td>NH₃</td>
<td>10.5</td>
<td>180</td>
<td>18</td>
</tr>
</tbody>
</table>
2.4.2 Morphological Analysis

When sodium hydroxide was used as the mineralizer and when the pH was 12, only due to the difference in time duration of the hydrothermal treatment, various morphologies have resulted. The nanoflakes-like, nanorods bunch-like, nanoflower petal-like and discrete nanorods could be produced in 5 hr, 12 hr, 16 hr and 18 hr respectively. Various morphologies of the prepared ZnO nanostructures as observed in scanning electron microscopy are shown in Figure 2.2

![X-ray diffraction pattern of ZnO nanostructure](image)

**Figure 2.1** X-ray diffraction pattern of ZnO nanostructure which exactly matches with the standard JCPDS Card. No.34-1451 with all characteristic peaks and high intensity exhibiting good crystallinity. (All the nanostructures posses identical x-ray diffractograms).
Figure 2.2 Shapes of different ZnO nanostructures as seen from scanning electron microscopy. Number inscribed on the top right corner of the figures represents their appropriate growth conditions as depicted in Table 2.1. (#1 - #4)
Figure 2.3 Shapes of ZnO nanostructures prepared under the conditions as given detailed in table 2.1 (#5 - #10).
Table 2.2. X-RD result showing the measured ‘2 θ’ and ‘d’ values in comparison
with the standard JCPDS value

<table>
<thead>
<tr>
<th>Sl.No</th>
<th>Position 2θ degree from XRD result</th>
<th>JCPDS#</th>
<th>Measured d-spacing (Å)</th>
<th>Calculated values</th>
<th>(hkl)</th>
<th>Relative intensity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>32.034</td>
<td>31.770</td>
<td>2.794</td>
<td>2.799</td>
<td>(100)</td>
<td>58.87</td>
</tr>
<tr>
<td>2</td>
<td>34.678</td>
<td>34.422</td>
<td>2.586</td>
<td>2.586</td>
<td>(002)</td>
<td>47.02</td>
</tr>
<tr>
<td>3</td>
<td>36.496</td>
<td>36.253</td>
<td>2.461</td>
<td>2.462</td>
<td>(101)</td>
<td>100.0</td>
</tr>
<tr>
<td>4</td>
<td>47.726</td>
<td>47.539</td>
<td>1.905</td>
<td>1.899</td>
<td>(102)</td>
<td>18.37</td>
</tr>
<tr>
<td>5</td>
<td>56.843</td>
<td>56.603</td>
<td>1.619</td>
<td>1.615</td>
<td>(110)</td>
<td>28.80</td>
</tr>
<tr>
<td>6</td>
<td>63.108</td>
<td>62.864</td>
<td>1.473</td>
<td>1.468</td>
<td>(103)</td>
<td>23.18</td>
</tr>
<tr>
<td>7</td>
<td>68.111</td>
<td>67.963</td>
<td>1.376</td>
<td>1.370</td>
<td>(200)</td>
<td>18.06</td>
</tr>
<tr>
<td>8</td>
<td>69.375</td>
<td>69.100</td>
<td>1.354</td>
<td>1.351</td>
<td>(112)</td>
<td>9.59</td>
</tr>
<tr>
<td>9</td>
<td>72.562</td>
<td>72.562</td>
<td>1.299</td>
<td>1.293</td>
<td>(004)</td>
<td>1.80</td>
</tr>
</tbody>
</table>

*JCPDS Card No.: 36-1451*
The lattice parameter ratio of all the nanostructures are shown in Figure 2.5 in the form of a bar diagram. This figure illustrates, the well defined hexagonal nanorod is the best matching perfect lattice parameters as that of standard characteristic ZnO unit cell. The c/a ratio of non-geometrical morphologies such as flakes and petals fall largely apart from the standard c/a value of ZnO. Nanorods and nanorod bundles produced from NaOH mineralizer at pH 12, 13.5 (ZNS #5 & #6) respectively show nearness to the standard ZnO next to well defined hexagonal nanorods produced from pH 12, time 12 hr. In the case of ammonia as mineralizer rods and particles produced at lower pH range of 9.5 show nearness.

2.5 Results and Discussion

2.5.1. Growth mechanism

For the growth of nanocrystals, nuclei and growth units are the key. In this hydrothermal synthesis Zn(OH)₂ is responsible for nuclei and [Zn(OH)₄]²⁻ is for growth. Mineralizer is the source of producing hydroxyl ions. So, the concentration of the mineralizer has a great influence on the growth and morphology of the ZnO due to its anisotropic growth. The equations (2.1) (2.2) and (2.3) represent the reaction for the growth mechanism. The anionic co-ordination [Zn(OH)₄]²⁻ is easily attracted by the positive [0001] zinc phase [19]. So, the zinc phase grows faster than the negatively charged oxygen [0001̅] phase. This causes the c-axis of ZnO to grow faster and it leads to the formation of hexagonal rods. In the presence of high temperature and pressure many active sites are formed around the ZnO nuclei and it grows further. Even after the formation of active sites, if the anionic co-ordination formed is not sufficiently enough in number, it cannot afford to grow normally as a rod. In this case the petal-like
nanostructures are more likely to form. All the other ZNS formed are in the intermediate state of the nano petal or flower to hexagonal nanorods or a mixture of both. Due to the production of larger number of nuclei and lesser number of growth units, the growth of the most of the nuclei are incomplete to produce a well defined characteristic hexagonal morphology in the case of ZnO.

\[
\text{ZnO (nutrient)} + 2 \text{OH}^- + \text{H}_2\text{O} \rightarrow \text{Zn(OH)}_4^{2-} \quad (2.1)
\]

\[
\text{Zn (OH)}_4^{2-} \rightarrow \text{ZnO}_2^{2-} + 2 \text{H}_2\text{O} \quad (2.2)
\]

\[
\text{ZnO}_2^{2-} + 2 \text{H}_2\text{O} \rightarrow \text{ZnO (crystal)} + 2 \text{OH}^- \quad (2.3)
\]

**Figure 2.4** The plot showing the formation of intermediate complexes at different pH values.

2.5.2. **Comparison of Lattice parameters**

The calculated 'd' values, found to vary according to the time duration and temperature of the experiments. The particle size increases with the increase in
temperature [20]. For ZNS #7 to #10 in which ammonia is used as a mineralizer, the ‘D’ values are 26 nm, 43 nm, 26 nm, 26 nm respectively. These values are found to depend on the experimental conditions i.e., ‘D’ value is higher when either the temperature or the time duration of the experiment are higher. For similar morphologies of ZNS #9 & #10 they are the same. But, when NaOH is used as the mineralizer, these values are not found to have dependence on the experimental conditions. The different morphologies of the nanostructures may be the reason for this independence. Electron micrographs of all the resultant morphologies exhibited by ten different ZNS are shown in Figures 2.2. The standard c/a ratio in the JCPDS card is 1.6023. Figure 2.5 (a), shows the variation of c/a of the ZNS prepared at different time duration of the hydrothermal treatment, while the other hydrothermal conditions are same. A decrease of the c/a value for 4 to 16 hr is seen and thereafter it again increases from 16 to 18 hr. The horizontal straight line marks the standard c/a value. It is noteworthy that the ZNS produced in 16 hr and 18 hr possessing nearest value to the standard are well defined nanorods, while the other two at 4 hr and 16 hour are nanoflakes and nanopetals respectively. Out of the four pH of the mother solutions experimented, the ZNS formed from the lowest and the highest pH (9.5 and 13.5) are found to exhibit nearness to the standard c/a where pH 10.5 and 12 show a slight deviation as shown in figure 2.5.
Figure 2.5 (a) plot showing c/a ratio of different structures formed during different time durations; (b) comparison of different c/a values of all the formed structures and (c) variation of c/a with time duration of the experiment.
2.6 SECTION B: EFFECT OF VARIATION IN IONIC STRENGTHS (Zn\textsuperscript{2+} AND OH\textsuperscript{-}) ON THE GROWTH OF ZnO NANOSTRUCTURES.

2.6.1 EXPERIMENTAL DETAILS

Two different strengths of NaOH (1.5M and 2.5M) are reacted with five different concentrations of zinc acetate dihydrate varying from 0.02 to 0.1M with an increment of 0.02 M from the previous one. Thereby, ten different combinations of cationic and anionic strengths were achieved. 0.02 M, 0.04 M, 0.06 M, 0.08 M and 0.1 molar solutions of zinc acetate dihydrate are made in separate containers in two numbers each. One of them in all five concentrations is reacted with 15 ml of 1.5M NaOH solution each. In another set, 2.5 M NaOH solution was added, 15 ml each in all the containers. For easy identification, the experiment with 1.5 M NaOH, and 0.02M Zn\textsuperscript{2+} is denoted as Z11, in which the left digit stands for concentration of the mineralizer (#1) and the right digit stands for the cationic strength (#1 – 0.02M of Zn\textsuperscript{2+}). Consecutively ‘Z12’ stands for 1.5M NaOH and 0.04 M of Zn\textsuperscript{2+} and so on. The combination of 2.5M of NaOH and 0.02M Zn\textsuperscript{2+} is denoted as ‘Z21’ and so on. The clear details of the combinations experimented along with their morphologies obtained from SEM images are shown in Table 2.3. In a typical experiment for the concentration of 0.02 M Zn salt, 1.5 M of NaOH solution, the mixture was stirred well until a homogeneous solution is obtained. The thoroughly stirred mother liquor was transferred to Teflon-lined stainless-steel autoclave. The autoclave was filled with solution up to a filling ratio of 80% was tightly sealed, then the mixture inside was treated hydrothermally at a set temperature of 180\textdegree C for 4 hour. Similarly all the other combinations are mixed and filled into the autoclave. The reaction conditions were maintained the same for all the experiments. After the
reaction was over, the autoclave was allowed to cool naturally to the ambient. Then, the particles separated by repeated centrifugation were washed several times with de-mineralised water and ethanol to remove the ionic impurities if any. For the higher concentration cases, where Zn salt concentration is 0.8, the yield will obviously be more, they need to be washed few more times, than the lower concentration cases. The white powders were then dried in hot air oven at 120°C, for a few hour to get free from the solvents. Then, the dried white powder was preserved and utilised for further analysis.

**2.7 CHARACTERISATION ANALYSIS**

The prepared ZnO powders were characterized by powder X-ray diffraction (XRD) technique to identify the product. The XRD reflection lines match well with JCPDS card no.36-1451 of wurtzite zinc oxide. Two representative diffractograms of the as prepared ZnO nanopowders are displayed in Figure 2.6. The scanning electron microscope images show a variety of nanostructures ranging from nano-flower, nanorod-bunches, discrete nanotwigs of various diameters, aspect ratio etc., and some cauliflower-like agglomerations. Figure 2.7 (a-g) shows the SEM images that resulted in the experiments Z11 – Z15 for which the NaOH concentration is the same (1.5 M). When the zinc salt concentration is lower, the shape of the ZnO nano-architecture obtained was flower shaped. On the increase of Zn salt concentration, the flower petals-like shape has shrunk in, to become nano-needles bunch-like structure. On further increasing the cationic concentration, the poorly defined shapes are produced and they all are exhibited in Figure 2.8 (a-h). This pattern has recurred the same when the concentration of NaOH is increased by a value of 1M (from 1.5M to 2.5M). Histograms were drawn based on the SEM images, for different shapes of the nano-architectures. They clearly illustrate the
diameter variation among the nano-architectures. TEM pictures taken for the twig-like nanoarchitecture, are portrayed in Figure 2.9 which clearly shows a uniaxially predominant growth. This shape is obtained for the combination ‘Z22’ which is as given in detail in Table 2.3. At the growing end of the nanotwigs, an angular tip pointed at the centre are formed which is usually due to the faster growth rate of the particular polar plane, than the other non-polar planes [21].

Figure 2.6 XRD patterns of ZnO nanoparticles grown from two different ionic concentrations.
Figure 2.7. Scanning Electron Microscopy images clearly depicting nanoflowers-like, nanorod bunch-like, cauli-flower like nanostructures.
Figure 2.8 Scanning Electron micrographs of ZnO nanoparticles revealing the sharp nano-twig like morphology, and nanorods-bunch like morphologies.
Table 2.3 Experimental details showing the precursor concentration and resultant morphologies.

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Sample identity</th>
<th>Zinc ion concentration (M)</th>
<th>Mineralizer concentration</th>
<th>Shape of the resultant nanostructure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Z11</td>
<td>0.02</td>
<td>1.5</td>
<td>Nanoflower-consisting of petals</td>
</tr>
<tr>
<td>2</td>
<td>Z12</td>
<td>0.04</td>
<td>1.5</td>
<td>Nanoflower-like consisting of rods</td>
</tr>
<tr>
<td>3</td>
<td>Z13</td>
<td>0.06</td>
<td>1.5</td>
<td>Fibrous nanorods bunch-like</td>
</tr>
<tr>
<td>4</td>
<td>Z14</td>
<td>0.08</td>
<td>1.5</td>
<td>Cauliflower or mushroom like</td>
</tr>
<tr>
<td>5</td>
<td>Z15</td>
<td>0.1</td>
<td>1.5</td>
<td>Poorly shaped Agglomeration – (Not shown)</td>
</tr>
<tr>
<td>6</td>
<td>Z21</td>
<td>0.02</td>
<td>2.5</td>
<td>Twig-like discrete nanorods</td>
</tr>
<tr>
<td>7</td>
<td>Z22</td>
<td>0.04</td>
<td>2.5</td>
<td>Shorter nanorods</td>
</tr>
<tr>
<td>8</td>
<td>Z23</td>
<td>0.06</td>
<td>2.5</td>
<td>Fibrous rod bunches</td>
</tr>
<tr>
<td>9</td>
<td>Z24</td>
<td>0.08</td>
<td>2.5</td>
<td>Rods and mushroom-like</td>
</tr>
<tr>
<td>10</td>
<td>Z25</td>
<td>0.1</td>
<td>2.5</td>
<td>Poorly shaped Agglomeration – (Not shown)</td>
</tr>
</tbody>
</table>
Figure 2.9 Transmission Electron Micrographs of nanotwigs-like structure in different magnifications.
2.8 RESULTS AND DISCUSSION

At high ionic strength, the surface charge density in the system may reach a maximum. When the charge density is maximum, the interfacial tension of the system will reach a minimum. A reduced interfacial tension eventually will lead to a reduced particle size because of the lowering of the nucleation energy barrier [22].

In the growth of crystals from solution, at first a population of unstable nuclei is produced. These intrinsically unstable nuclei are known as embryos. These embryos have equal probabilities either to get redissolved in the solution, or to grow further into stable particles. For a particle to be stable it should attain a minimum radius which is known as critical radius \( (R_c) \). The growth of the embryos or the thermodynamically induced redissolution of the embryo are determined by the resultant competition between the surface energy required to form the embryo, i.e.,

\[
E_s = 4\pi R^2 \sigma
\]

\( (2.4) \)

and the energy released when a spherical particle is formed,

\[
E_v = 4\pi R^3 \rho L/3
\]

\( (2.5) \)

where ‘\( \sigma \)’ is the surface energy per unit area

‘\( \rho \)’ is the density of solid and \( L \) is the heat of solution.

As very smaller embryos have high surface energies and they get dissolved easily. If the embryo (unstable nucleus) has a volume which possesses the energy \( E_v \) mentioned above, they can withstand in the solution and will afford to grow into bigger nucleus. The
above mentioned process where in the anions and cations are in the exceeding limit of the solubility product, is called homogeneous nucleation.

Wurtzite structured ZnO could be described as a number of alternating planes composed of tetrahedrally coordinated $\text{O}^{2-}$ and $\text{Zn}^{2+}$ ions that are stacked alternatively along the c-axis. The oppositely charged ions produce positively charged Zinc (0001) and the negatively charged Oxygen (000-1) polar surfaces. This results in a normal dipole moment and spontaneous polarization also along the c-axis [23]. In the solution, before the formation of precipitation, there needs to be an induction period, before the nucleation. The duration of the induction period is influenced by the precursor concentration. Higher the precursor concentration, longer will be the induction period [24]. At higher precursor concentration many more nuclei are produced. They eventually can aggregate into closely packed structures.

In all these hydrothermal experiments the temperature of system was maintained at the same level and hence the variation in size and morphology reported herein are solely due to the variations made in the anionic and cationic concentrations in the precursors.

Based on the energy minimization concept, ZnO crystallizes in zinc hydroxyl nuclei and favourably grow along the c-axis. At higher precursor concentration, the nuclei produced are rapid [25]. Wenqin Peng et.al., have observed that ZnO nanostructures obtained at low pH are smaller and shorter. In the reported results, the lower concentration of $\text{Zn}^{2+}$ (0.02M) along with 1.5 M concentration of NaOH has produced flower like ZnO morphology (Figure 2.7 a). In the subsequent experiments
denoted by ZnO nanostructure number Z12-Z15, the cationic strength is gradually increased in a step of 0.02M. So, the case Z11 is having the lowest Zn\(^{2+}\) population when compared to other experiments followed on. In the chosen NaOH concentration of 1.5 M, the first experiment Z11 has a lowest cationic concentration against the anions (OH\(^{-}\)). The ZnO nano-flower consists of petals which are short. When the cationic strength is increased by a step 0.02M in the experiment ‘Z12’, the morphology is slightly modified. Here the structures look like bunches consisting of fibrous nanorods. As seen from the SEM image Figure 2.7, the aspect ratios of the constituent nanorods are improved. The diameter looks reduced when compared to their length. This is different from the morphology of previous case Z11. On further increase of the cationic concentration, thin fibrous nano-needles bunches are found to form Figure 2.7 (e, f). In the maximum Zn\(^{2+}\), cases, these produced bunches are found to coalesce to form a mushroom or cauli-flower like structure Figure 2.7 (g).

In another set of experiments, keeping the NaOH concentration constant at 2.5M, the same cationic strengths in the solution were repeated in order to find the effect of improved pH. These experiments are numbered as Z21 – Z25 for easy identification. In these five experiments, the cationic strength is kept on increasing in a step of 0.02M starting from 0.02M as before in the Z11-Z15 experiments. From the SEM images shown in Figure 2.8, it is seen that for a lower cationic concentration thin discrete nanorods are formed. For the further increase of cationic concentration, the resultant rods seem to have reduced length, and bunching of them is found to be more pronounced.
The variations in shape and aspect ratio of the formed nanostructures are due to the difference in the physical entities such as surface charge density, interfacial tension etc., inside the system.

When interfacial tension is increased in a system, small unstable embryos would not survive any more. They sacrifice to the solution by re-dissolution and hence homogeneous nucleations of discrete nucleations might have been reduced to a considerable extent. But, in heterogeneous nucleations the subcritical nuclei will tend to adhere to bigger particles; thereby they reduce the surface energy and become supercritical. So, they could overcome the minimum interfacial tension, which prevents them from dissolution. In cases, where nuclei are not rapidly produced, and nucleation and growth occur simultaneously will result in different sizes. The variation is sizes are seen when the initially formed stable nuclei have developed to a particular size and the newly formed nuclei at any instant would not have grown to that size and therefore they will be smaller. From our observations, even for the change of 0.02M, there is a slight variation which is clearly seen from the SEM images. A clear illustration of the same is made by drawing a histogram showing the size variations which are evident from the Figure 2.10 (a) and (b). When nucleations and growth are proceeding simultaneously, many such instances occur which are the key reason for more size distribution.
2.9 Optical analysis (UV-VIS-NIR – absorption spectroscopy)

The representative shapes of the prepared nanostructured ZnO powders were investigated by UV-VIS-NIR absorption spectroscopy. The resultant optical absorption edges are denoted by the extrapolation of the peaks as depicted in the Figure 2.11. From the calculations by using the value of intersection of the extrapolated line on x-axis [26], they show that the absorption edges are centred in the region near about 400 nm which possess the band energy gap of $\approx 3.03$ eV which is slightly lower than the bulk energy gap 3.34 eV of ZnO. The reduction in energy gap can be attributed to the nanometric dimension of the produced crystalline ZnO architectures.
Figure 2.11 Optical Absorption spectrum of four of the representative nanostructures (a - Z11, b – Z14, c – Z15, d – Z25).

2.10 SECTION C: INVESTIGATIONS ON THE SHAPE ENGINEERED NANOCRYSTALLINE ZnO BY HYDROTHERMAL METHOD BY USING DIFFERENT Zn ION SOURCES AND MINERALIZERS

2.10.1 Experimental

Three different sources of zinc metal salts separately and in selected combination are treated with Hexamine, Trioctlyamine and with NaOH separately and chosen combinations are utilized for the demonstration of the shape engineering of a variety of morphology of zinc oxide nanostructures. The details of the reactants used in various experiments are detailed in Table 2.4. The results reported here are only the selective outcomes of various combinations of a few number of attempts for the formation of nanocrystalline ZnO. In all the cases, 0.5 g of zinc salt was dissolved to prepare aqueous
solutions and the mineralisers were added in appropriate quantity to reach optimum level of pH, pre-determined by various trial attempts. Due to the addition of amine or alkali to the aqueous solution of zinc salt, a variation in pH is produced which creates a major difference in the production of nuclei and subsequent growth during the hydrothermal treatment. The as prepared solution was then stirred well to obtain a homogeneously turbid liquid which when treated hydrothermally for 3 to 4 hours at 115°C has produced curdy white precipitates. The powders sediment is separated by centrifuging several times and washing with water and ethanol to remove the ionic impurities if any followed by drying in hot air oven. The dried white powders were analysed by various tools to characterize their properties.

2.11 RESULTS AND DISCUSSION

2.11.1 XRD analysis

The prepared powders are confirmed to be nanocrystalline zinc oxide with hexagonal wurtzite structure which very well identify with standard JCPDS card no.36-1451 of space group P6₃.mc [27]. The well defined crystalline peaks as shown in Figure 2.12 contain no more additional peaks other than ZnO. For all the cases the diffraction peaks obtained are at the same 2θ position with slight variations in the FWHM and intensity. These details are exploited for the calculations of all possible microstructural analysis by calculations which are discussed in subsequent sections.
Table 2.4. Details of the reactants in the mother cursor in all experiments, their pH values and the resultant shapes as observed by SEM and the aspect ratio as inferred from the SEM images.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Chemicals</th>
<th>pH</th>
<th>Shape</th>
<th>Aspect ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO # 1</td>
<td>(ZnNO$_3$)$_2$ + HMTA</td>
<td>7</td>
<td>Nanotube bunches</td>
<td>7</td>
</tr>
<tr>
<td>ZnO # 2</td>
<td>(ZnNO$_3$)$_2$ + Zn(Ac)$_2$ + HMTA</td>
<td>7</td>
<td>Dumb Bell</td>
<td>2.5</td>
</tr>
<tr>
<td>ZnO # 3</td>
<td>(ZnNO$_3$)$_2$ + TEOA + HCl</td>
<td>8</td>
<td>Sphere</td>
<td>-</td>
</tr>
<tr>
<td>ZnO # 4</td>
<td>(ZnNO$_3$)$_2$ + HMTA + NaOH</td>
<td>12</td>
<td>Coral reef like</td>
<td>3.5</td>
</tr>
<tr>
<td>ZnO # 5</td>
<td>(ZnNO$_3$)$_2$ + NaOH</td>
<td>12</td>
<td>Taper tipped nanorod bunches</td>
<td>6.6</td>
</tr>
<tr>
<td>ZnO # 6</td>
<td>Zn(Ac) + HMTA + NaOH</td>
<td>12.5</td>
<td>Flakes array</td>
<td></td>
</tr>
<tr>
<td>ZnO # 7</td>
<td>ZnSO$_4$ + NaOH</td>
<td>12</td>
<td>Poorly formed morphology</td>
<td>-</td>
</tr>
<tr>
<td>ZnO # 8</td>
<td>ZnSO$_4$ + HMTA</td>
<td>7</td>
<td>Nano flakes</td>
<td>14</td>
</tr>
</tbody>
</table>
2.11.2 SEM analysis

The morphologies as seen through Scanning Electron Microscope are shown in Figure 2.13. The corresponding nanostructures originated from the hydrothermal process of various precursors are detailed in Table 2.4. The nanotube bunch like structures consisting of hollow hexagonal nanorods and hexagonal rods with cavities.

![Figure 2.12 X-ray diffraction patterns of all the 8 different nanostructures.](image)

Figure 2.12 X-ray diffraction patterns of all the 8 different nanostructures.
Figure 2.13. SEM images of all the eight different nanostructures produced from different zinc ion sources and mineralizer combinations.
posses an average aspect (length /diameter) ratio of 7. In this the smaller rods are solid and as they scale up to higher dimension the core of the rod becomes hollow due to the faster growth rate of outer surface. The emergence of cavities in medium sized nanorods confirms the hollowing up of solid rods in subsequent growth. The peculiar nanocrystalline **dumb-bell like** ZnO having an interface at the middle has two hexagonal rods attached to each other whose faster growing ends are in the opposite directions. These exhibit hexagonal cross section with flat upper and lower surface including interface at the middle. This is also termed as spindle crystal [28, 29]. In particular this dumb-bell shaped morphology when coated on fabric is reported to have a higher UV blocking property than any other shapes [30].

**Nanospheres** are the most stable structure since they represent a smallest surface energy. Coral reef like or nanorods bundles like morphology is having hexagonal cross section on the upper surface. This growth of nanorod bundles does not follow the simple Lamer theory [28], as appears that there are several nucleation events.

Even monodisperse populations can form though the nucleation extends over a period of time, if the particle growth is low relative to nucleation. After the first nucleation, the particles begin to grow by diffusion of the reactants through the solution to the surface of growing particles. While this is taking place, further nucleation also occurs. This coral reef like structure may be explained by the coalescence of several nuclei to grow. [31].

The **taper tipped nanorod bunches** in the characteristic hexagonal morphology are consistent with the idealized growth habit of ZnO crystal along (0001) direction. The
crystal facet with faster growth velocity tends to disappear and the facet with slower velocity is prone to remain. Hence sharp tips are formed during the growth. In particular these results are found in the synthesis of nanorods with hexagonal phase [32].

**Nanoflakes array** is due to the formation of geometrical aggregates of nanosheets and rods. These different morphologies are obtained due to various chemical concentrations. Influence of OH⁻ concentration in precursor, leads to the formation of nanosheets and nanorods as shown in **figure 2.13 (f)**. When zinc complex is prepared at pH 12, uniform nanosheets are obtained which tend to link together to form bundles of nanosheets. In real, it is necessary to reduce in nanotechnology to bunch nano objects for easy handling. In this present work a considerable effort has been paid to form nanosheet bunches. The well defined nanosheet structure bunches reported are a novel shape reported here. Wrinkled ZnO nanosheets are of fundamental interest as this is a special geometrical shape and probably with potential applications. On the other hand formation of such strong bunches of nano object is of applied interest. **Poorly shaped aggregates** are formed when the moderately soluble ZnSO₄ reacts with sodium hydroxide **Figure 2.13 (g)**.

### 2.11.3 Transmission Electron Microscopy Analysis

Transmission Electron microscopy (TEM) of one of the structure (nanoflakes – ZnO # 8) is taken and the same is displayed in **Figure 2.14**. A continuous thin flakes of area in micrometers and thickness less than 50 nm is clearly seen from the picture. The continuous growth depicts the successful growth of high aspect ratio structure (thickness/surface area – here). The electron diffraction pattern for the nanoflake is also taken using
High Resolution TEM (HRTEM) analysis. HRTEM result portrays a pattern of bright spots, which confirm the single crystallinity [33-35] of the prepared nanostructures.

Figure 2.14 TEM images of nanoflakes-like morphology. (a- c) Selected Area Electron Diffraction pattern of the nanoflakes (d).

Diffraction pattern of the nanoflakes (d).
2.11.4 Solubility and Interfacial tension on nucleation:

In all the process of formation of phase transition from Zn(OH) to ZnO occurs through a dissolution and recrystallisation process in such a way to comply with the surface energy minimization of the system. In a dissolution (or) recrystallisation process, the highest soluble one has got the lowest stability i.e., in the crystallographically metastable phase favours precipitation first. In our experimental study the three different zinc divalent cation sources are ZnNO$_3$.9 H$_2$O, ZnSO$_4$, H$_2$O and ZnCH$_3$COO.6H$_2$O and a selected combination of these three along with different variety of mineralisers in a chosen volume. Among these the solubility is in the order zinc acetate < zinc sulphate < zinc nitrate. The solubility is inversely proportional to interfacial tension and to stability. In other words higher solubility leads to lower stability and leads to faster precipitation. Eventually there is shorter induction period, faster and more will be the nucleations. So, the nucleation rates will be highest in zinc nitrate solution and least in the case of zinc acetate.

So, from this experimental measurement, there is a possibility that the highest soluble zinc nitrate has the lowest stability and favours precipitation earlier than the other cases when different zinc divalent cation sources such as sulphate or acetate is used. Spherical shape possesses a smallest surface area for a given volume. In reality nanoparticles intend to minimize their energy by forming a spherical morphology. A maximum is found for the first derivative of the free enthalpy of nucleation. Such a maximum depends on the interfacial tension at the cubic power [36].

$$\Delta G^* = \frac{16 \pi v^2 \gamma^3}{3 \left( RT LnS \right)^2}$$

2.6
It is noteworthy that lowering the interfacial tension eventually lowers the nucleation energy barrier, which as a result favours the decrease of nanoparticles size. According to the relation between free enthalpy of nucleation and interfacial tension also it is true that zinc nitrate can favour a higher free enthalpy of nucleation and causes larger number of nucleations than the other two considered zinc cation sources.

Reaction mechanism for the formation of various shapes or nanostructures of zinc oxide is as evident in Figure 2.15 and Figure 2.16. The formation of ZnO in different architectured shapes is also due to the population or availability of OH\(^-\) ions for the intermediate complex formation. The different mineralisers are Sodium hydroxide, Hexamethylene Tetra amine, and Triethanolamine.

The commonly used precursors for hydrothermal growth process are zinc nitrate (source of Zn\(^{2+}\) ions) and hexamethylenetetramine (HMTA), commonly called hexamine. HMTA is a highly water soluble tetra dentate cyclic tertiary amine. For controlling the nucleation it is used separately or combined along with NaOH. It acts as a pH buffer by a slow release of OH\(^-\) ions through thermal decomposition as in the following reaction [37, 38].
Figure 2.15 The schematic illustration of formation of rod bunches and coral-reef like structures
Figure 2.16 The schematic illustration showing the formation of dumb bell-like morphology and flower petal-like formation.

\[
\text{Zn} \ (\text{NO}_3)_2 + \text{H}_2\text{O} \quad \Rightarrow \quad \text{Zn}^{2+} + 2\text{HNO}_3 \quad (2.7)
\]

\[
(\text{CH}_2)_6\text{N}_4^+ + 6 \text{H}_2\text{O} \quad \Rightarrow \quad 6\text{CHOH} + 4\text{NH}_3 \quad (2.8)
\]

\[
\text{NH}_3 + \text{H}_2\text{O} \quad \Leftrightarrow \quad \text{NH}_4^+ + \text{OH}^- \quad (2.9)
\]

Due to the presence of hexamine in the solution, it ensures the availability of hydroxyl ions throughout the reaction by slowly producing ammonia which forms
Zn(NH₃)₄²⁺. It is capable of bridging two zinc (II) ions in solution. So, on the whole, it keeps the divalent zinc cation concentration at the low level allowing growth of the nucleated structures [39, 40].

In a phenomenological perspective, ZnO crystal exhibits partial polar characteristics, and in a typical wurzite structure the (001) plane is the basal polar plane. It is believed that, in the chemical bath, hexamine being a non-polar chelating agent would preferentially attach to non-polar facets of the nano structures (Figure 2.17).

![Figure 2.17](image_url)  
Figure 2.17 (a) Polar and non polar faces of hexagonal zinc oxide (b) attachment of hexamine on to non-polar faces in the hexagon.
2.11.5 Zn – O polarity and termination:

In the wurtzite structured ZnO, Zn and O are tetrahedrally co-ordinated. So, the Zn$^{2+}$ and O$^{2-}$ are alternately arranged. Due to this the growing end can be of four types. They are zinc polarity with oxygen atom termination, zinc polarity with zinc atom termination, oxygen polarity with zinc atom termination and oxygen polarity with oxygen atom termination. These kinds of polarity and termination are determined by competition between the zinc cations and hydroxyl ion concentration in the solution. Initially when nucleations are produced one particular type of polarity and termination is favoured by the chemical environment at the vicinity of the growing end of a nanostructure say a nanorod. Further, it has been reported by Ye Sun et al that the zinc polar surface with oxygen atom termination can favour ZnO nanorod with smaller aspect ratio [41]. When it is of zinc atom termination at the zinc polar surface, thinner and tapered nanorods are more likely to form. A decreased Zn$^{2+}$ to OH$^{-}$ ratio at the same surface can produce nanotubes instead of nanorods. Another feasible reason for the tubular growth is the faster growth rate along the (0001) direction. Since the faster growing plane disappears quickly the faster growing end vanishes and turns up into hollow tubular structure. This will also be favoured only when the ratio of Zn$^{2+}$ to OH$^{-}$ are lower. But, this is not the case when there is large population of Zn$^{2+}$ ions are present in the growth ambient. The presence of Hexamine keeps producing Zn$^{2+}$ at a lower rate throughout the growth and hence it ensures a steady ratio of metal to hydroxyl ion population. Since in our experiments we have used various amounts of NaOH and Hexamine, the difference in the population of Zn$^{2+}$ and OH$^{-}$ is the key factor which is controlled for the production of the various kinds of nanostructures with a range of aspect ratio. When hexamine or NaOH is
not used, Triethanolamine an aliphatic tertiary amine is used. Due to the lone pair of electrons on the nitrogen atom it acts like a weak base. Zinc nitrate, zinc sulphate and zinc acetate are the metal cation sources used.

Reaction mechanism of nanostructure ZnO #2 (Sphere) is explained as follows. The formation of ZnO nanostructures is due to the decomposition of amine based zinc complex in basic medium hexamine in this case, the solution pH during the formation and decomposition of the Zinc complex has an important influence on the morphology of ZnO microspheres [42]. During the course of hydrothermal reaction, there occurs decomposition of the precursors, which enables a difference in the initial and the final pH. It may due to the faster rate of nucleation rather than the rate of growth. For higher value of pH (10), just the nucleation rate increases to avoid continuous growth of the particles to achieve larger sizes. HCl was added only to get the final value of pH.

For the preparation of nanostructure ZnO #6, (Flakes Array), zinc acetate is used as the source of Zn2+ ions which has lead to the formation of nanosheet bunches. However, in this case, the number of growth units ([Zn (OH)4]²⁻) is still not enough to make nanorods from the circumference of ZnO particles. From this we can deduce the growth process of the nanosheet bunches or nanoflakes array. There are many separated colloidal Zn(OH)₂ clusters in the performed suspension, some of which act as the nuclei for the growth of ZnO nanosheets. The hybrid colloids might agglomerate through self-assembly and serve as growth centre for the growth of ZnO nanosheets from the clusters.

For the preparation of nanostructure ZnO #7 (flower petal-poorly), the ZnSO₄ could not supply enough number of growth units [Zn(OH)₄]²⁻ in competition with
Zn(OH)$_2$ is still not enough to make ZnO nanorods to grow from the circumference of ZnO nanoparticles. Therefore, the formation of flower-like nanoaggregates may be favoured.

The formation of the micro **dumb-bells** from nanostructure (**ZnO #2**) is understood by the following route of reaction. By the hydrolysis of HMT at elevated temperature, the concentration of Zn$^{2+}$ and OH$^{-}$ increases correspondingly, and Zn(OH)$_2$ and/or ZnO nuclei start to form when the degree of supersaturation exceeds the critical value. In the hydrothermal process, twin crystal ZnO nuclei will be developed under the low precursor concentration and the action of HMT, forming spindle like crystals called micro dumb-bells with a middle interface [28, 43]. The organic additive HMT may be helpful for the formation of micro dumb-bells by providing templates for the nucleation and the orientation growth of ZnO micro dumb-bells. Further specific deeper investigations on the growth kinetics may be required to ascertain this concept. In all the experiments performed here, the effect of mineralizer is clearly associated with its interaction with the solute (or by its modification of the water–solute interaction). The following is the common reaction while NaOH is used as a mineralizer.

The possible reaction mechanism is,

\[
\begin{align*}
\text{Zn}^{2+} + 2\text{OH}^- & \rightleftharpoons \text{Zn(OH)}_2 \quad (2.10) \\
\text{Zn(OH)}_2 + 2\text{OH}^- & \rightleftharpoons [\text{Zn(OH)}_4]^{2-} \quad (2.11) \\
[\text{Zn(OH)}_4]^{2-} & \rightleftharpoons \text{Zn(OH)}_2 + 2\text{OH}^- \text{(dissolution)} \quad (2.12) \\
\text{OH}^- + \text{Zn}^{2+} (\text{aq}) & \rightarrow \text{ZnO}_{(s)} + \text{H}_2\text{O} \text{(nucleation)} \quad (2.13)
\end{align*}
\]
2.11.6 Surface to Volume ratio:

It is always coveted in materials to have a larger surface to volume ratio for an efficient usage of matter since larger surface area means a more efficient usage of matter contained within the shape.

As far as the geometrical shapes are concerned, the variations in surface to volume ratio to different shapes are obvious. Starting from sphere, the hierarchy ascends as $<\text{cylinder}<$ rectangular prism $<\text{cone}<$ hexagonal prism $<\text{square based pyramid}$. In our experiments we have successfully produced hexagonal solid nanorods, tapered nanorods, and hollow hexagonal nanorods. Among them, the hollow nanorod shape is supposed to have the more surface to volume ratio; the next is the solid hexagonal nanorods. The tapered tips have a slight difference with that of the former shape. Spheres have the lowest surface to volume ratio whereas the nanoflakes-like morphology has got the highest.

2.11.7 XRD Analysis:

From the Full Width at Half Maximum of x-ray reflection lines, the following parameters viz (i) $u$ parameter (ii) cell volume (iii) lattice distortion have been calculated. The hexagonally close packed wurtzite structure of ZnO is comparatively more stable than the other two zinc blende and rock salt structures. In ZnO, the Zn and O atoms are tetrahedrally co-ordinated to each other. The lattice parameters of ZnO is such that they hold a ratio $c/a = \sqrt[3]{8} = 1.633$. In nature this structure has two interpenetrating sublattices in which the two constituent atoms are displaced by each other by a value of $‘u’ = 3/8 = 0.375 \text{ Å}$. This ‘$u$’ value is equal to the length of the bond parallel to c-axis in
units of the ‘c’ value. The relation can be given as \( u - \left( \frac{1}{4} \right) = \left( \frac{1}{3} \right) \left( \frac{a^2}{c^2} \right) \). So, naturally there is a mismatch between the perfect wurtzite structure and that of zinc oxide. This is adjusted spontaneously by altering the value of ‘c/a’ and ‘u’ in it [44, 45]. The ‘u’ value for all the nanostructures are calculated from the x-ray reflection spectrum and they are tabulated in Table 2.

**Table 2.5** The lattice parameter values of different nanocrystalline ZnO derived from the line broadening of x-ray reflection lines. The ‘u’ parameter, cell volume and lattice distortion calculated subsequently from the former results.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>a Å</th>
<th>c Å</th>
<th>‘u’ parameter</th>
<th>Cell Volume Å(^3)</th>
<th>Lattice Distortion (Vo-V/Vo)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO # 1</td>
<td>3.291</td>
<td>5.227</td>
<td>0.382139</td>
<td>49.02766</td>
<td>0.03016</td>
</tr>
<tr>
<td>ZnO # 2</td>
<td>3.292</td>
<td>5.227</td>
<td>0.382219</td>
<td>49.05746</td>
<td>0.030786</td>
</tr>
<tr>
<td>ZnO # 3</td>
<td>3.307</td>
<td>5.22</td>
<td>0.383785</td>
<td>49.43924</td>
<td>0.038808</td>
</tr>
<tr>
<td>ZnO # 4</td>
<td>3.285</td>
<td>5.234</td>
<td>0.381305</td>
<td>48.91448</td>
<td>0.027781</td>
</tr>
<tr>
<td>ZnO # 5</td>
<td>3.289</td>
<td>5.227</td>
<td>0.381978</td>
<td>48.96809</td>
<td>0.028908</td>
</tr>
<tr>
<td>ZnO # 6</td>
<td>3.289</td>
<td>5.212</td>
<td>0.382739</td>
<td>48.82757</td>
<td>0.025955</td>
</tr>
<tr>
<td>ZnO # 7</td>
<td>3.287</td>
<td>5.249</td>
<td>0.380715</td>
<td>49.11441</td>
<td>0.031982</td>
</tr>
<tr>
<td>ZnO # 8</td>
<td>3.300</td>
<td>5.241</td>
<td>0.382153</td>
<td>49.42822</td>
<td>0.038576</td>
</tr>
<tr>
<td>STANDA RD</td>
<td>3.249</td>
<td>5.206</td>
<td>0.379828</td>
<td>47.59228</td>
<td>----</td>
</tr>
</tbody>
</table>
As there is always a slight deviation of the lattice parameter values in reality with that of the ideal or standard wurtzite structure, naturally the differences in the lattice parameters alter the volume of the unit cell. The difference is denoted here as lattice distortion \([46]\) and the same is calculated by the following relation.

\[
\text{Lattice distortion} = \frac{V_o - V}{V_o}
\]

Here, ‘\(V_o\)’ – stands for the standard volume of the cell and is equal to 47.59228 Å as per the lattice parameters in the JCPDS standard card. ‘\(V\)’ – stands for the cell volume derived from the x-ray diffraction measurements of the nanostructure of interest. The lattice distortion values i.e., the deviation of cell volumes of the hydrothermally prepared nanostructures from the standard cell volume is tabulated in Table. 2.

2.12 CONCLUSION

The time duration and temperature of the hydrothermal treatment have been found to have significant influence on complete formation of well defined characteristic hexagonal morphology of ZnO. The difference in the population of growth units and nuclei are found to determine the morphology of the nanostructure. Due to the different morphologies produced the calculated particle size, is not found to directly dependent only upon experimental conditions. Well defined characteristic hexagonal ZnO nanorods do show perfect standard lattice parameter values than the non-geometrical morphologies like nanoflakes-like and nanopetals-like. Time duration of 16-18 hours and the mother solution with pH 9.5, 13.5 do result with the lattice parameters nearest to the standard value. (SECTION A)
Hydrothermal experiments, by altering the ionic strengths of the solution, different morphologies and aspect ratios varied nanostructures, of zinc oxide are produced. The role of the ionic strength in altering the interfacial energy of the system, and thereby the particle size are clearly illustrated. Different ambiances wherein homogeneous and heterogeneous nucleations could be produced are discussed. The possible reasons for the formation of agglomeration of laterally produced nuclei onto the previously grown nanocrystals are explained on the basis of energy of formation of nuclei. Finally, a simple method to modify the key physical entities in the hydrothermal growth of ZnO nanostructures are studied and reported elaborately. (SECTION B)

Prolonging or shortening the nucleation time and rate is made feasible by using different sources for zinc cations along with various alkalis and the same is exploited to produce a range of shapes of nanocrystalline ZnO. So, the synthesis of nanostructures with a variety of morphologies showing variations in their surface to volume ratio is demonstrated. The ways reported here may be useful for choosing the desired morphology and it shows that engineering the shapes and aspect ratio are controllable eventhough they are very delicate (SECTION C).
References:


