

Effect of Precursor Type on Zinc Oxide Formation and Morphology Development during Hydrothermal Synthesis

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ABSTRACT

Semiconducting metal oxide sensors have been widely studied due to their small dimensions, low cost and low power consumption. ZnO is a potential material for gas sensor applications because of its high piezoelectric coefficient, great stability of its hexagonal phase and its pyroelectric property. Hydrothermal synthesis is one of the most useful methods to produce homogeneous, nanosized ZnO powders with high purity, controlled particle size and morphology. The research objectives of this study were to understand formation and growth process of ZnO particles with various morphologies and to investigate role of starting materials, (i.e., zinc chloride ($ZnCl_2$) and zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) on the particle morphology. ZnO particles with various morphologies were synthesized via an unstirred hydrothermal method. When using $ZnCl_2$ as a precursor, the final morphology was rod like with a tapered tip (length of the rod 0.5-1 μm) after 12 h at 100 °C. On the other hand, final morphology of the produced ZnO particles was branch rod like (5-10 μm) when using $Zn(NO_3)_2 \cdot 6H_2O$ as precursor under the same synthesis conditions. Accordingly, a proposed growth mechanism has been suggested.

Keywords: ZnO; Hydrothermal synthesis; Phase development; Morphology; Growth mechanism

INTRODUCTION

Zinc oxide is an important technological material due to its wide band gap (3.37 eV), high electron mobility and large exciton binding energy at room temperature [1]. Because of these unique characteristics, zinc oxide (ZnO) is a very attractive materials for various applications such as conductive oxide, antistatic coating, sensors, band gap optoelectronic devices, pigments and an UV filters in sunscreens. Depending upon the different synthesis methods, it can be synthesised with various type of morphology such as rod like, sphere like, flower like or urchinlike morphologies [1-3]. The crystal structure, particle size and morphology of ZnO particles are important parameters which affect the properties of the powder and hence determine application areas. For example, ZnO particles with large surface area can be utilised for enhancing gas sensing applications [4] where the amount of absorbed oxygen is strongly depending on morphology, surface area and grain size of the sensing material [5].

The morphology of ZnO crystals strongly depends on the type of precursor and mineralizers in the form of

different zinc salts in alkaline solution such as Zn-nitrate, Zn-acetate and Zn-chloride with alkaline KOH, NaOH or NH_4OH . The solubility of ZnO in these solutions varies with the pH and concentration, and depending on the OH^- concentration and temperature, various Zn^{2+} -hydroxo complexes are formed. From these complexes, the ZnO precipitates through condensation reaction [6]. Particle size and morphology are also dependent on powder synthesis method and parameters (temperature, time, concentration etc.). Zang et al. reported the controlling of ZnO morphology by using different precursor ($Zn(OH)_4^{2-}$ and $Zn(NH_3)_4^{2+}$) and simple solution route. They founded that ZnO particles had a prismlike morphology after reaction process where NH_3 was formed as a by-product from $Zn(NH_3)_4^{2+}$ whereas ZnO particles had a rod like or the flower like morphology depending on the concentration of OH^- in the $Zn(OH)_4^{2-}$ solution [2].

Sing et al. studied the effect of the different precursor solutions (zinc chloride, zinc nitrate and zinc acetate) on the morphology of ZnO and its sensing behaviour by co-precipitation method. They found out that among

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all the precursor solution, zinc acetate yielded most suitable morphology of zinc oxide with small length rods (about 400-800 nm) which exhibited enhanced sensing response towards alcohols [4]. Rai et al. have also studied the synthesis of ZnO nanostructures from different precursors (zinc chloride, zinc nitrate and zinc acetate) via solvothermal method and established the relationship between morphology and gas sensing behaviour by comparing their response. They found that the shape and size of ZnO nanostructures greatly affected the gas sensing property and the response of ZnO nanorods synthesised from zinc nitrate or zinc acetate was higher than ZnO particles synthesised from zinc chloride for NO₂ and CO gases [3].

Hydrothermal synthesis is one of the most useful method among the other solution based synthesis methods such as direct strike and homogeneous precipitation, microemulsion, sol-gel, gel combustion etc. to produce homogeneous, nanosized ZnO powders with high purity, controlled particle size and morphology. An important advantage of this method is that the purity of hydrothermally synthesized powders significantly exceeds the purity of the starting materials.

There are several studies on the effect of precursor and synthesis parameters on morphology of ZnO for different synthesis methods such as co-precipitation, solvothermal and hydrothermal method. However, the effect of precursors which have acidic or basic nature on the particle morphology of ZnO crystals and growth mechanism in the different solution characteristics has not well understood yet for hydrothermal synthesis. Therefore, in the present study, the research objectives were to investigate role of starting materials, (i.e., zinc chloride (ZnCl₂) and zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O)) on the particle morphology by using hydrothermal synthesis and understand formation and growth mechanisms of ZnO particles with various morphologies.

MATERIALS AND METHODS

In this study, zinc chloride (ZnCl₂; Merck) and zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O; Sigma aldrich) were used as zinc sources to produce zinc oxide by hydrothermal method. All of the chemicals were of analytical grade (>99.99 % purity) and were used without further purification. Zinc chloride or zinc nitrate hexahydrate were dissolved into distilled water to form transparent solution (0.25-1 M), and then, 4 M ammonium hydroxide (NH₄OH) solution, used as a mineralizer (pH=8.4), was added dropwise into the salt solution during magnetic stirring. To prevent the effect of anions on the formation mechanisms of ZnO powder, the precipitates were centrifuged at 5000 rpm for 5 min and washed in several times with deionized water to remove residual anions.

The precipitated product with pH 8.9 was charged into an autoclave (600 ml capacity) up to 60 % fill. The hydrothermal reaction was conducted at 100 °C for 1-24 h under autogenous pressure. After the autoclave reached 100°C, 5 minutes soaking time was given to all samples in order to achieve temperature stability. After the hydrothermal reaction was completed, the autoclave was cooled down to room temperature. The product was washed with distilled water and dried in an oven at 90 °C over a period of 24-48 h. The phase development of the ZnO powder was analysed by the x-ray diffraction (XRD) method (Rigaku Co. Ltd., Tokyo, Japan) with a monochromatic CuKα radiation source (λ = 1.542 Å) between 10 ° and 80 ° with 2 °C/min scan rate. The effects of processing parameters such as the precursor type, initial concentrations of materials and reaction time on the morphology and particle size of the ZnO powders were investigated by a scanning electron microscope (SEM; Zeiss Supra 50 V, Carl-Zeiss, Germany) and scanning transmission electron microscopy (STEM; JEOL 2100F, FEI, 200 kV HRTEM, Japan). The transmission electron microscopy (TEM) sample was prepared by sonicating the ZnO crystals in ethanol and drop casting them on carbon coated TEM grids. The average particle size of synthesised powder was measured by using SEM images corresponding Image J programme. Particle size and distribution of each samples was calculated by monitoring of approximately 30 individual particles in the SEM images.

RESULTS AND DISCUSSION

Phase development

To examine the phase formation of ZnO depending on the precursor type, ZnO powders were synthesised under hydrothermal synthesis conditions at 100 °C for 0-3 hours using different precursors (ZnCl₂ and Zn(NO₃)₂·6H₂O). The XRD patterns of these powders synthesised at different time (0-3h) are given in Figures 1 and 2. Starting with ZnCl₂ salt solution, simonkolleite (Zn₅(OH)₈Cl₂·H₂O)

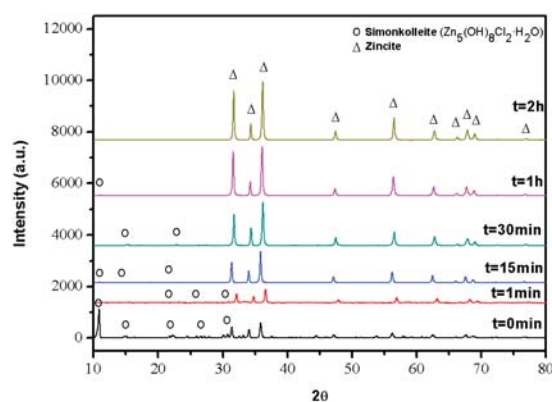


Figure 1. XRD patterns of ZnO powders synthesised using ZnCl₂ precursor at different time (0-2h).

was observed as a major phase with a small amount of zincite (zinc oxide) at $t=0$ min (Fig. 1). After 1h, all of the peaks can be well indexed by the zincite (ZnO ; JCPDS No. 89-1397). Starting with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ precursor, zincite phase and unidentified peaks probably belong to zinc hydroxide complexes as reported earlier in the literature [6] were detected at $t=0$ min. After 3 h, pure zincite was formed as shown in Figure 2.

Effect of the treatment time on particle size and morphology

To investigate the effect of the treatment time on the phase formation and particle characteristics, ZnO powders were hydrothermally synthesized at 100°C for different times from different precursors (ZnCl_2 and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$). Figure 3 shows the SEM images of the ZnO powders prepared by using ZnCl_2 precursor for different times. At $t=0$ min, the zinc containing gel was occurred and a small amount of ZnO precipitated on this zinc containing gel (Fig. 3a). Small amount of ZnO and incomplete phase of $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ dissolved and ZnO particles with ellipsoidal morphology occurred during hydrothermal synthesis for 15 min (Fig.3b). When treatment time reaches the 2 h (Fig.3f), all intermediate phase of $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ dissolve and single phase ZnO particles was formed as evidenced by the XRD results given in Fig.2 and Fig.3. As shown in Figure 3f, ZnO particles exhibit high uniformity with respect to size and morphology after 2 h of hydrothermal treatments. The length of individual ellipsoidal rod like ZnO crystals with a tapered tip was about $0.5\text{-}1\ \mu\text{m}$ with high aspect ratio.

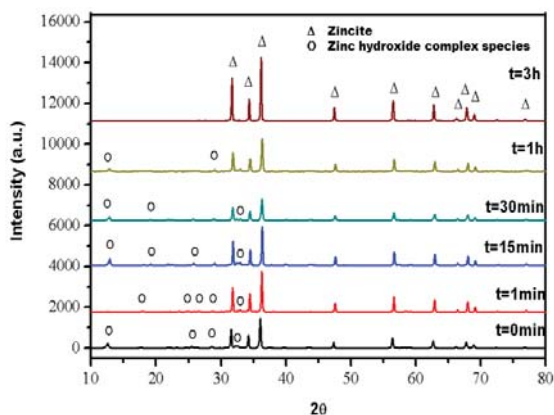


Figure 2. XRD patterns of ZnO powders synthesised using $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ precursor at different time (0-3h)

Figure 4 shows the SEM images of the ZnO powders prepared using $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ precursor. Even at $t=0$ min (Fig. 4a), as confirmed by XRD data, large amount of ZnO particle precipitation was observed. Precipitated ZnO does not dissolve completely and dissolved gel begins to grow on

the existing ZnO particles with branch rod like morphology during hydrothermal synthesis. After 3h (Fig. 4f), all gel phase completely disappeared and branch rod like ZnO particles which looks like flower with an average length of $5\text{-}7\ \mu\text{m}$.

SEM images of ZnO crystals given in Figure 3 and Figure 4 clearly show that crystal morphology of ZnO particles was strongly affected from precursor type. ZnO crystals grew as an individual ellipsoidal rod like with a tapered tip when used ZnCl_2 precursor, but branch rod like ZnO particle with flower shape were formed when used $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ precursor.

In the light of the literature, these differences observed in the crystal morphologies can be explained with nature of ZnO and suspension pH and characteristics. Each crystallographic plane of ZnO exhibits different growth kinetics due to different attachment ratio of the growth unit $[\text{Zn}(\text{OH})_4]^{2-}$ to crystallographic planes [8]. The order of the crystallographic planes according to their growth rate in ZnO is follows; $V(0001) > V(\bar{1}0\bar{1}\bar{1}) > V(\bar{1}01\bar{1}) > V(\bar{1}011) > V(000\bar{1})$. Since the plane with greater growth rate disappears earlier [7], the (0001) plane, the most rapid growing plane, disappears during the hydrothermal process while other planes grow, which leads to the pointed (taped) shape in and of the c axis as observed in Figure 3f.

Different crystal growth rate along certain crystal faces are also affected from various solution basicities. The acidic strength of the zinc oxide precursors affects the crystal growth rate is in the following manner: chloride > nitrate > acetate [2]. Since ZnCl_2 is acidic salt, it induced chemical etching of the polar surface of ZnO and as a result rods with tapered ends were obtained [4]. However $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ precursor which has a basic characteristic yields the branches rod like morphology.

Morphology of the ZnO crystals is controlled by altering pH of solution. At lower pH, smaller petal like or rod like ZnO crystals are formed where the nucleation is less intense and the final crystals obtained an energetically more favourable, elongated morphology. At higher pH, there are larger numbers of strongly nucleophilic OH^- groups, which absorb to the Zn-terminated surfaces and hinder in plane crystallization, while the prismatic planes grow without constrain. Consequently at higher pH values the crystals growth in the [0001] direction is hindered and the resulting crystals are plate-like [6].

Effect of the cation concentration on particle size and morphology

Figure 5 shows the SEM images of ZnO particles synthesised from ZnCl_2 precursor at 100°C for 24 h with diffe-

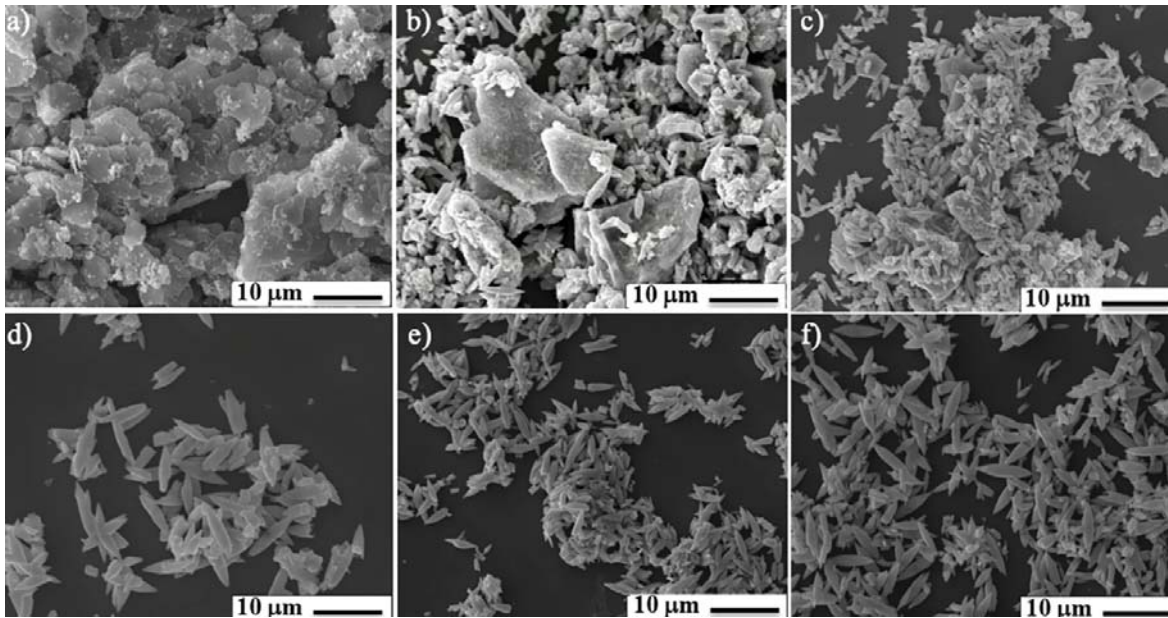


Figure 3. SEM images (10 μm) of ZnO powders synthesised using ZnCl_2 precursor at (a) 0 min (b) 1 min (c) 15 min (d) 30 min (e) 1 h and (f) 2 h treatment times.

rent initial concentration ratios (0.25, 0.50, 0.75 and 1 M).

Individual ellipsoidal rod like ZnO particles with tapered tip were formed at 0.25 and 0.5 M concentration values given in Fig.5a and Fig.5b. With increasing initial concentration to 0.75 and 1 M, ellipsoidal rod like ZnO particles were had a tendency to agglomerate (Fig. 5c and Fig. 5d). Average particle size of crystals determined from SEM images decreased sharply from 12 μm to 3 μm by length as shown in Figure 6.

Figure 7 shows the SEM images of ZnO particles synthesised from $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ precursor at 100°C for 24 h with different initial concentration ratios (0.25, 0.50, 0.75 and 1 M). As shown in Fig. 7a, ZnO particles with branch rod like morphology formed at low cation concentration value (at 0.25 M). With increasing molarity of zinc nitrate solution, flower like morphology was observed (Fig. 7b-d) and average particle size of flower like particles increased from 5 μm to 12 μm by length as shown in Figure 8.

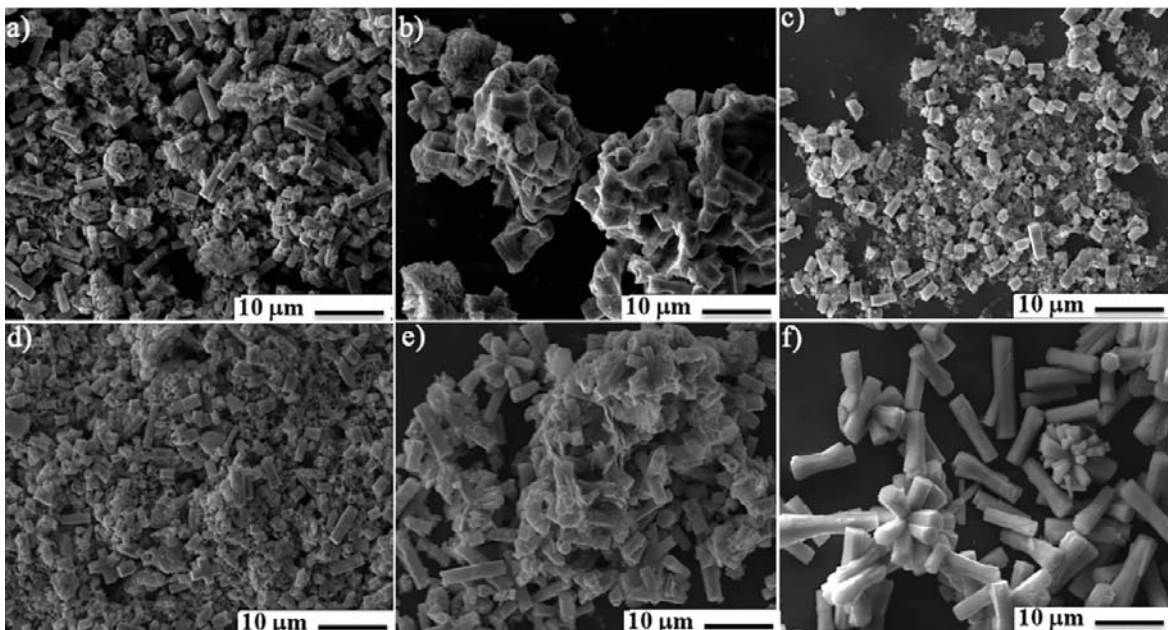


Figure 4. SEM images (10 μm) of ZnO powders synthesised using $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ precursor at (a) 0 min (b) 1 min (c) 15 min (d) 30 min (e) 1 h, and (f) 3 h treatment times.

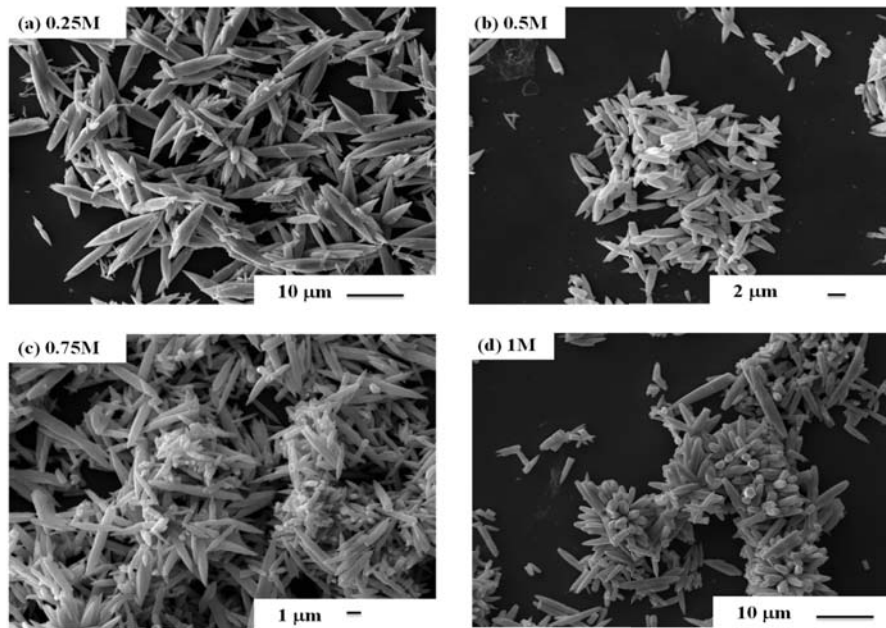


Figure 5. SEM images of ZnO powders synthesised using $ZnCl_2$ precursor with initial concentration of (a) 0.25 M (b) 0.5 M (c) 0.75 M and (d) 1 M.

Flower like branched ZnO particles produced from 0.5 M $Zn(NO_3)_2 \cdot 6H_2O$ precursor were also analyzed by using scanning transmission electron microscope (STEM). STEM image of such a particle is presented in Figure 9. As shown in Figure 9, rods on the flower like particle were grown in different directions from center of the particle and all of the rods were single crystals. Average particle size of a flowerlike particle was determined as 4-6 μm and average rod length and width in this flower like particle were 5.843 μm and 0.549 μm , respectively.

Proposed growth model

The growth habit of ZnO crystal particles and the effect of reaction medium on the growth habit were successfully explained by Li and co-workers [8]. In solution, the growth unit of a crystal is the complex that is formed by the connection of cation with OH^- ions. In the supersaturation solution, zinc hydroxide gel dissolved in the solution complex with OH^- ions forms growth units ($Zn(OH)_2 \cdot 4H_2O$) by the attraction of ions as follows:

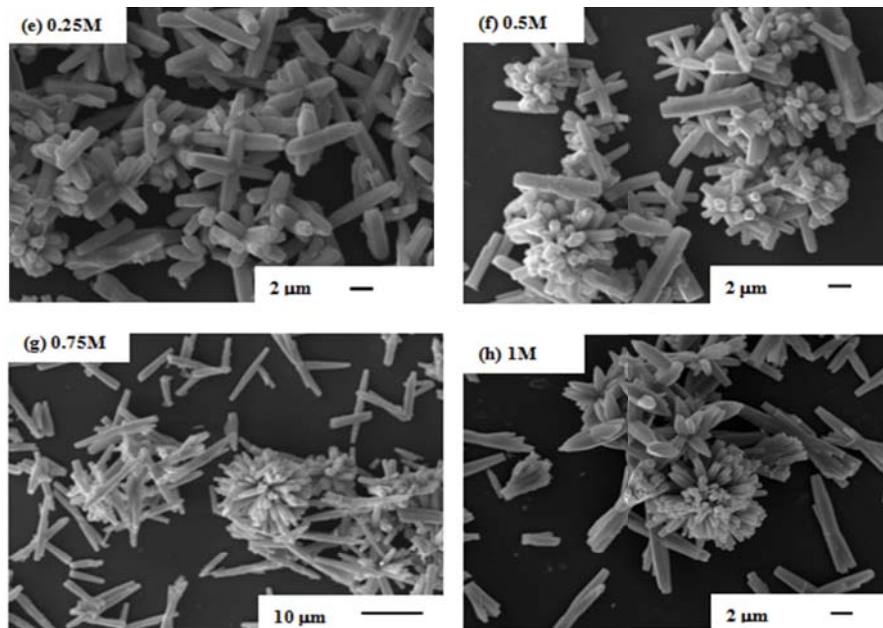
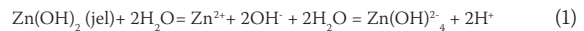


Figure 7. SEM images of powders synthesised using $Zn(NO_3)_2 \cdot 6H_2O$ precursor with initial concentration of (a) 0.25 M (b) 0.5 M (c) 0.75 M and (d) 1 M.

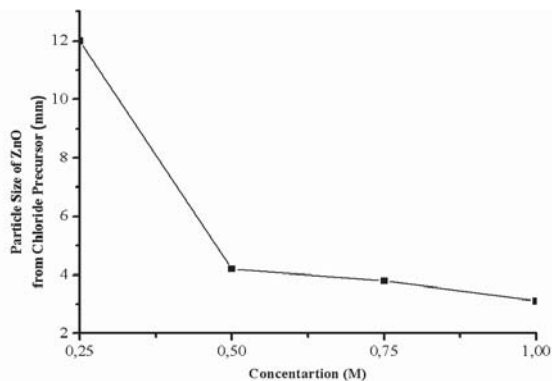


Figure 6. Average particle size of ZnO synthesised using $ZnCl_2$ precursor depending on cation concentration.

Since the growth unit ($Zn(OH)_4^{2-}$) incorporating into the crystal lattice take place by the dehydration reaction between OH^- ligands, the growth habit of the ZnO crystal is related to OH^- ligands at the interface or the reaction medium [8,9].

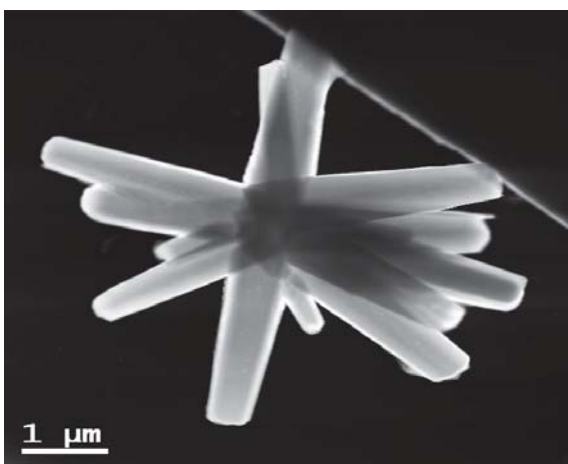


Figure 9. STEM image of flower like ZnO particle produced from 0.5M $Zn(NO_3)_2 \cdot 6H_2O$ precursor.

In our study, different particle size and morphology of ZnO particles were obtained when different $ZnCl_2$ and $Zn(NO_3)_2 \cdot 6H_2O$ precursor were used and this is consistent with the previously reported studies.

It is clear that concentration of OH^- ions and existence of Cl^- and NO_3^- ions in the medium affect the growth mechanism of ZnO particle. However, more works is needed to be done for further understanding.

According to the obtained results in this study and the literature, growth process of ZnO particles synthesized by using different precursor can be simply illustrated as shown in Figure 10. Starting with $ZnCl_2$ precursor, small amount of ZnO phases (Figure 1, at $t=0$) precipitate on the unstable simonkolloite phase in the initial stage of the synthesis and new ZnO nuclei were formed from simonkolloite phase during the chemical reaction. With increasing the reaction

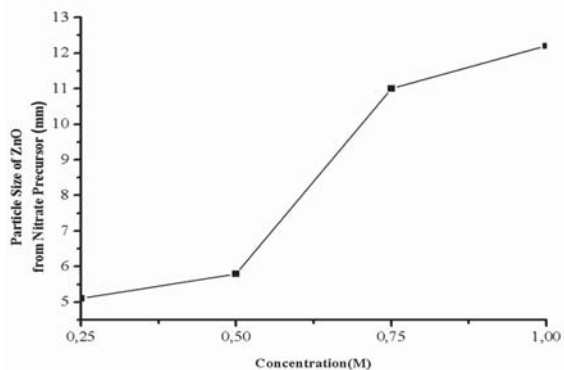


Figure 8. Average particle size of ZnO synthesised using $Zn(NO_3)_2 \cdot 6H_2O$ precursor depending on cation concentration.

time of the hydrothermal synthesis to 30 min, ZnO crystals grow and large ellipsoidal rod like crystals of ZnO start to appear (as shown in Figure 3). With increasing concentration of $ZnCl_2$ precursor, particle size of individual ellipsoidal

rod like ZnO crystals reduced as shown in Figure 5 and Figure 6. Therefore, it can be concluded that zinc oxide powders synthesized from $ZnCl_2$ precursor are grown via classical nucleation and growth theory mechanism. In the classical crystallisation mechanism, the crystal grows from a stable nucleus in a supersaturated solution. Raising the concentrations of reactants makes the reaction happen at a faster rate. Following a very fast nucleation period the material crystallizes with a very narrow size distribution. Since the reaction take place rapidly, particles (kinetically favoured) need no more time to growth as a result smaller particle is formed [8].

In the case of starting with $Zn(NO_3)_2 \cdot 6H_2O$ precursor, the small rod like ZnO crystals and zinc hydroxide complex were coexist in the initial stage (Figure 4a). With increasing the reaction time to 30 min, these phases dissolved and then recrystallized as a branched rod like ZnO crystal. With increasing initial concentration of precursor, average particle size of branched rod like particles increases and the flower like particles are formed as shown in Figure 7b-d. According to these results, it can be concluded that zinc oxide particles grow via Ostwald ripening mechanism under such conditions.

Ostwald ripening process is a spontaneous process that occurs because larger crystals are more energetically favored than smaller crystals. In this case, kinetically favored tiny crystallites nucleate first in supersaturated medium and are followed by the growth of larger particles (thermodynamically favored) due to the energy difference between large and smaller particles of higher solubility based on the Gibbs-Thomson law [10]. The aqueous solution of zinc nitrate can produce $Zn(OH)_2$ in the presence of OH^- ions. During the hydrothermal process, part of the $Zn(OH)_2$ dissolves into Zn^{2+} and OH^- . When the concentration of Zn^{2+} and OH^- re-

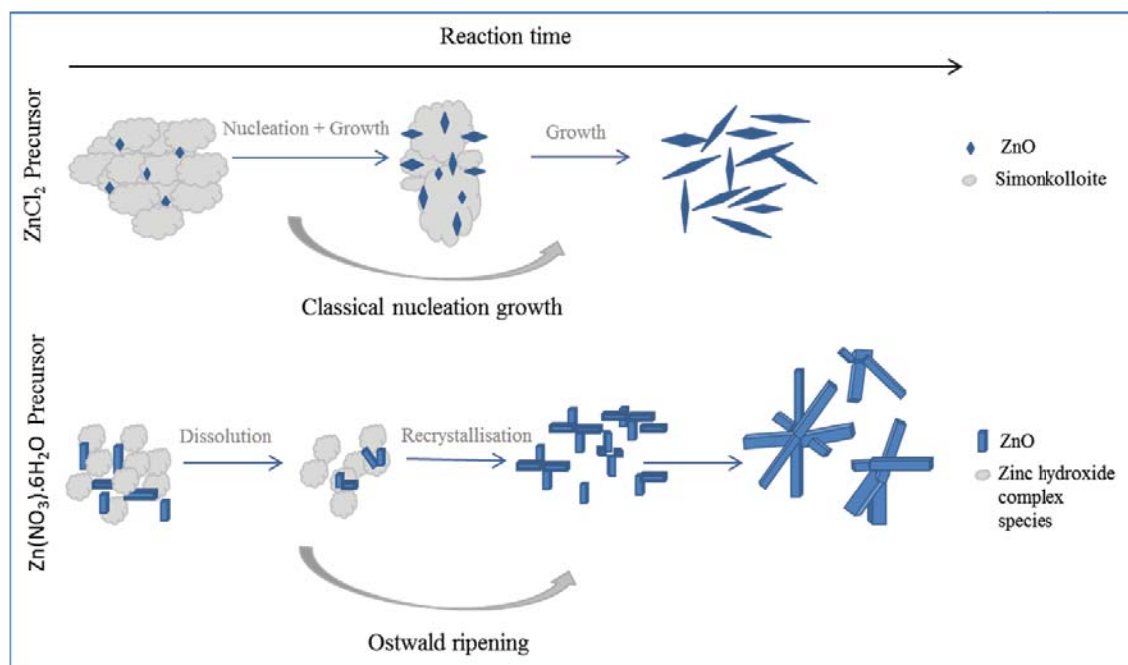


Figure 10. Proposed growth mechanisms of ZnO particles synthesized from different precursor.

aches the supersaturation degree of ZnO, ZnO nuclei will form spontaneously in the aqueous complex solution[7].

CONCLUSIONS

In this study, the dependence of the phase development and particle characteristics of the resulting ZnO powders on the precursors with initial concentration and synthesis time was evaluated during hydrothermal process. Results reveal that morphology and particle size of ZnO powder can be controlled by different precursors. With using ZnCl_2 precursor, agglomerated ellipsoidal rod like morphology was formed whereas flower like morphology was obtained with using $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ precursor. Particle size of ZnO crystals were also affected from precursor type and initial concentration. With increasing concentration of precursors, average particle size of ZnO crystals was decreased from $12 \mu\text{m}$ to $3 \mu\text{m}$ using ZnCl_2 precursor in contrast, it was increased from $5 \mu\text{m}$ to $12 \mu\text{m}$ using $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Accordingly, zinc oxide particles grow via classical nucleation theory by using ZnCl_2 and Ostwald ripening mechanism by using $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The proposed growth mechanism was depicted as shown in Figure 10.

These results are particularly important to demonstrate that ZnO powder can be synthesized in different size and morphology by the hydrothermal method changing precursor type and concentration. These results can be successfully used in different application areas where designing of the specific particle morphology is needed to enhance the particle performance.

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