

Hydrothermal synthesis of shaped ZnO nanostructures

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Zinc oxide (ZnO) powders were synthesized by a simple hydrothermal process in the temperature range of 50 to 100 °C. Nanocrystallites were formed by a simple hydrothermal route from aqueous solutions of zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and NaOH under controlled process conditions such as precursor concentration (0.07 to 1 mol/L), reaction pH (7 to 11) and temperatures. Single phase ZnO particles can be easily synthesized at low precursor concentration, high reaction pH and high temperature. The synthesized powders prepared at 80 °C exhibited short hexagonal tablet, tapered multipod, or rod-shaped morphologies. The particles, primarily, had a nanometric three-dimensional six-fold symmetry, which was related to the hexagonal wurtzite structure and the particle morphologies were largely influenced by the hydrothermal processing parameters. Rod-shaped ZnO particulates consisting of the elongated crystals of interconnected or separate forms were predominantly developed at high precursor concentration and high pH condition. Consequently, it has been proposed that the morphological features could be tailored by changing the process parameters.

Key words: Hydrothermal synthesis, ZnO, Crystal morphology, Nanostructures, Nano-rod.

Introduction

Zinc oxide (ZnO) has attracted considerable interest owing to its prominent electrochemical or electro-optic properties and its wide range of applications such as photocatalysts, solar cells, chemical sensors, phosphors and other electronic devices [1,2]. In the last few decades, nanostructured materials have gained importance in science and technology, and ZnO nanostructures have also drawn a lot of attention due to its unique or novel properties and high efficacy [3-7].

ZnO nanostructures can be grown either in solution or from gaseous sources. The gas phase synthesis methods are expensive and complicated while the solution process offers advantageous features such as a simple and low-temperature synthesis. Among a large variety of solution techniques for the preparation of ZnO nanoparticles, the aqueous routes provide further advantages of fast and low-cost in addition to an environmentally friendly process. There have been much works on preparing ZnO nanoparticles in aqueous medium [8-11]; however, the preparative techniques may involve hazardous chemicals, complicated process control, post heat-treatment at high temperature or long process time. Therefore, it is still desirable to obtain ZnO nanoparticles in a relatively simple and highly efficient way.

The objective of this study was to develop a simple process synthesizing shape-tuned ZnO nanoparticles

via an aqueous processing route using a hydrothermal technique. Among various wet chemical processes including sol-gel, salt decomposition and spray pyrolysis, alternatively, the hydrothermal process has been proposed to be an effective method for the industrial requirements of various ceramic powders due to its attractive processing features of economic and low-temperature processing without calcination and milling step [12, 13].

Although Zn^{2+} aqueous chemistry has been examined by a number of workers [14, 15], there remain questions about the Zn-complexes stability at different concentration, temperature and pH values. Since the relationship between synthesis parameters and resulting powder properties has not yet been fully elucidated, there is still a need for an understanding the nanoparticle synthesis method in the aqueous medium in which the powder morphology and phase are controllable by the variation of processing parameters. In order to clarify the effect of the processing parameters such as pH, temperature and precursor concentration on the powder properties, this study has been carried out without any capping or surface modifying agents. A systematic study of the effect of processing parameters on the phases and morphologies of nanostructured powders has been done.

Experimental Procedure

A simple hydrothermal treatment has been employed in this study. Zn-nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was used as the Zn precursor and sodium hydroxide (NaOH) was used for adjusting the pH of aqueous solutions. The Zn-precursor aqueous solutions of 0.07 to 1 mol/L (M), and the sodium hydroxide aqueous solution

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of 1.2 M were used. Since the yield of precipitation was too low for the Zn-precursor concentration below 0.07 M and the maximum Zn^{2+} solubility was limited near 1 M, the low and high precursor concentration-limits were determined as 0.07 and 1 M, respectively in this study.

The hydrothermal process involves simple mixing and heating the aqueous solutions containing Zn-nitrate hexahydrate with NaOH to adjust the pH in the range 7 to 11. In the process, the mixture of precursor suspension was sealed into a teflon-lined autoclave with the filling factor of 70%. Subsequently, the autoclave was hydrothermally treated at different temperatures up to 100 °C for 1 hr. The reaction products were filtered and washed with distilled water to remove soluble components and then vacuum dried at room temperature for 12 hrs.

In order to show a controlled-morphology of the ZnO crystallites by the hydrothermal process, a ZnO nano-rod coating on a ZnO-coated glass substrate has been conducted under the nano-rod synthesis condition of pH 11 and 80 °C for 1 hr, with the Zn-precursor concentration of 0.3 M.

The morphologies and particle sizes of synthesized ZnO particles were determined by a scanning electron microscope (SEM). X-ray diffraction (XRD, Cu- K_α) was performed to identify the phases of prepared powders. The particle sizes of the synthesized powders were also calculated by the XRD peak broadening according to the Scherrer's equation (D_{cal} (particle size) = $0.9 \lambda / (B \cos \theta)$: where λ is the wavelength, B is the full width at half maxima (FWHM) in radians and θ is the diffraction angle).

Results and Discussion

Hydrothermal processing parameters may affect the powder properties of morphology and phase formation. The phase formation and shapes of synthesized ZnO powders with different precursor concentration and reaction pH values at 80 °C are depicted in Fig. 1, in which the diagram was defined based on the experimental

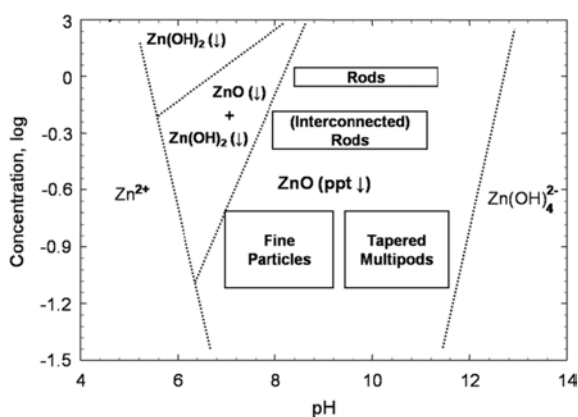


Fig. 1. Phase formation and particulate shapes of hydrothermally prepared powders as a function of Zn-precursor concentration and reaction pH at 80 °C.

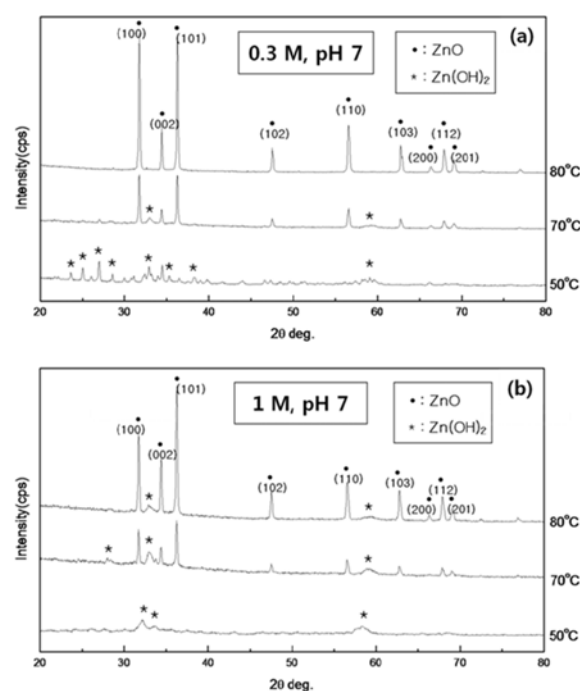


Fig. 2. XRD patterns of ZnO particles hydrothermally prepared at pH 7 and different temperatures, with different Zn-precursor concentrations of (a) 0.3 and (b) 1 M.

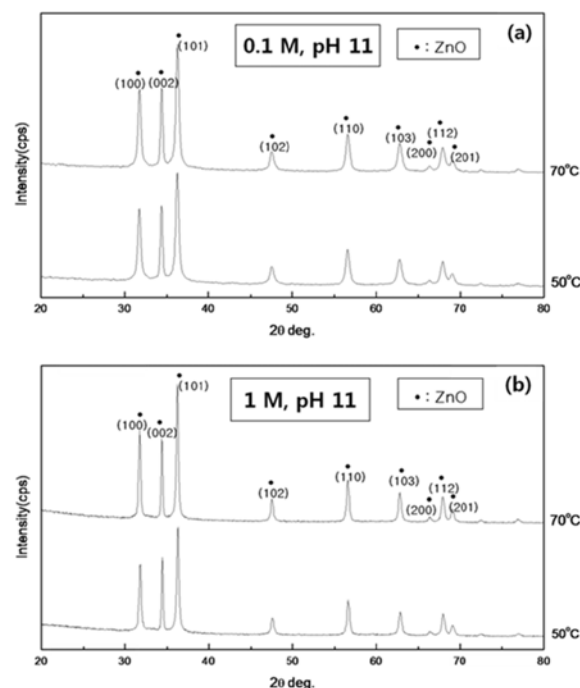


Fig. 3. XRD patterns of ZnO particles hydrothermally prepared at pH 11 and different temperatures, with different Zn-precursor concentrations of (a) 0.1 and (b) 1 M.

results, in addition to the well-established Zn^{+2} chemistry occurred in aqueous solution [14–16]. Although the Zn-ion concentrations affect the ZnO solubility, single phase ZnO powders can be generally synthesized at the wider range of reaction pH of $7 \leq \text{pH} \leq 11$. Under lower pH < 8, the increase in the Zn-precursor concentration led to the

preferential $\text{Zn}(\text{OH})_2$ precipitates formation over the ZnO phase.

Fig. 1 also shows the effect of processing conditions on the morphologies of synthesized powders. The synthesized powders exhibited fine nanometer-size particles, tapered multipods, interconnected or separated rods morphologies depending on the Zn-precursor concentration and reaction pH. In the higher Zn-precursor concentrations of > 0.5 M, separated rods particles were mainly formed. Lower Zn-precursor concentrations (< 0.3 M) at the high reaction of pH 11 led to the tapered multipod-shape crystallites. At the region of lower concentration and pH, < 0.3 M and below pH 9, respectively, the fine particles of short hexagonal tablets were developed. In the middle concentration and pH range, crystallization and growth conditions are optimum then well-developed rod-shaped particulates, sometimes interconnected, were easily formed.

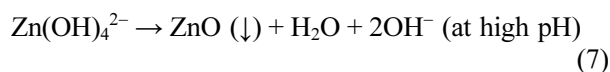
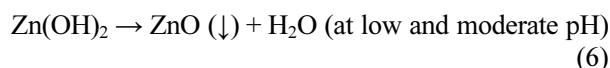
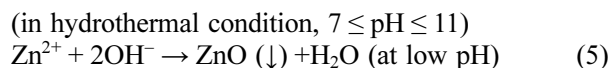
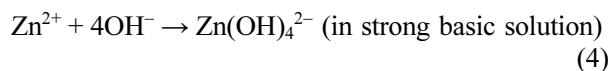
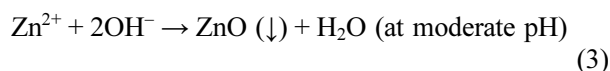
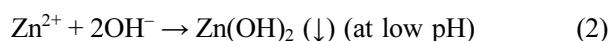
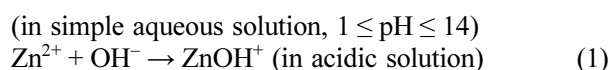
XRD patterns of synthesized powders are shown in Figs. 2 and 3, which illustrates the effect of hydrothermal processing parameters on the phase formation of the prepared powders. The XRD patterns reveal that all ZnO peaks correspond to the characteristic peaks of the hexagonal wurtzite structure (space group P6₃mc, $a = 0.324$ nm and $c = 0.520$ nm) indexed in JCPDS card (No. 36-1451).

In randomly oriented ZnO particles, the peak ratio of (100)/(002) is 1.3 from the JCPDS card. However, the well-developed (100) peak having the ratio ((100)/(002)) of 2.9 shown in Fig. 2(a) at 80 °C indicates the preferred orientation of a-axis, which is aligned perpendicular to the incident X-ray beam with forming the one dimensional rod-shaped crystallites. The XRD patterns also indicate that the powders obtained at the higher Zn-concentration of 1 M and lower pH of 7 have a poor crystalline nature showing ZnO and $\text{Zn}(\text{OH})_2$ coexistence (Fig. 2(b)). At the higher pH condition of 11 as shown in Fig. 3, well developed ZnO peaks were found in all samples regardless of the Zn-concentration and reaction temperature. As the Zn-precursor concentration decreased and the reaction pH

increased, a purer ZnO phase was formed over $\text{Zn}(\text{OH})_2$. It was also shown that an enhanced crystallinity of the synthesized ZnO was obtained under both the higher reaction temperature and pH at the same precursor concentration.

Fig. 4 shows a phase formation result, defined by XRD results, with a variation of the reaction pH and temperatures at the Zn-precursor concentrations of 0.1, 0.5 and 1 M. As the precursor concentration decreased and both the reaction temperature and pH increased, phase pure and well crystallized ZnO particles were easily obtained. At pH 7, single phase ZnO particles were synthesized above 90 °C for 1 M precursor solution, while, for 0.1 M solution, a ZnO single phase could be formed at the reaction temperature as low as 50 °C.

In hydrothermal synthesis, the powder synthesis mechanism through the dissolution of metal-hydroxide and recrystallization to metal-oxide is well established. For the ZnO aqueous chemistry of solution synthesis, the following reactions would most likely be involved.



(↓: precipitation)

Since ZnO is an amphoteric oxide in aqueous solution, it is soluble under acidic and basic conditions. A clear solution containing the ZnOH^+ ion was formed under an acidic condition (Eq. (1)). Although the exact solution chemistry may differ depending on the Zn-ion concentration, $\text{Zn}(\text{OH})_2$ as well as ZnO precipitates can be generally prepared under relatively basic conditions in the pH range of $7 \leq \text{pH} \leq 11$. As increase in OH^- concentration by adding a strong base such as sodium hydroxide ($\text{NaOH} \rightarrow \text{Na}^+ + \text{OH}^-$), $\text{Zn}(\text{OH})_2$ precipitates will be seen (Eq. (2)). When sufficient sodium hydroxide is added, zinc oxide precipitates could be formed (Eq. (3)). Under the high basic condition, over pH 11, of excess sodium hydroxide added, a clear solution of zincate ion, $\text{Zn}(\text{OH})_4^{2-}$, will form again by following Eq. (4).

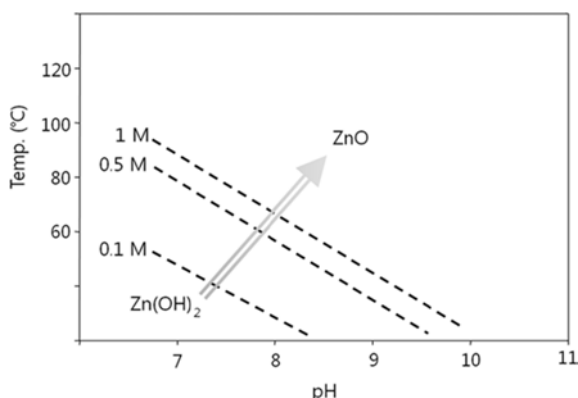


Fig. 4. Phase formation as a function of reaction pH and temperature relevant to the Zn-precursor concentrations.

In hydrothermal synthesis, ZnO precipitates are easily obtained by Eq. (5)~(7) at a wider pH range compared to the precipitation condition for the simple aqueous precipitation system, such as Eq. (3), without pressure. Under moderate hydrothermal conditions (reaction temperature of 50~100 °C and Zn precursor concentration of 0.1 ~ 0.5 M), the following reaction would occur; in lower pH conditions below pH 7, there are few OH⁻ ions and the nucleation and growth rates for the ZnO crystallites according to the Eq. (5) are slow. Since the ZnO crystal formation is difficult, the ZnO phase mixed with Zn(OH)₂ was often found. In the strong basic condition of near pH 11, the abundant OH⁻ leads to the Zn(OH)₄²⁻ formation. Zn(OH)₄²⁻ is a well known complex acting as a growth enhancer of ZnO crystals preferentially along the [0001] direction and the preferential growth normally led to the tapered or rod-shape crystal growth following Eq. (7) [17]. In the moderate pH range of 8~10, the general hydrothermal transformation to ZnO can be easily achieved by following Eq. (6) which normally would lead to the single ZnO phase and well-developed crystallites.

SEM images of ZnO powders synthesized hydrothermally under different precursor concentrations and preparation conditions are shown in Figs. 5-7. The SEM morphologies of ZnO powders synthesized at 80 °C under different basicities of pH 7, 9 and 11 are shown in Figs. 5, 6 and 7, respectively. Fig. 5 shows the particle morphologies obtained from pH 7, which is the lowest pH of the present study to get the crystalline ZnO under the hydrothermal condition. It is observed that the shapes of the obtained ZnO particles changes shortened prismatic (tablet) to interconnected or separated rods, as the precursor solution concentration increases from 0.07 to 1 M. As can be seen, all the synthesized particles display hexagonal prismatic basically.

For the lowest concentration of 0.07 M at pH 7, since there was a lack of Zn ions and OH⁻ species, the low nucleation and growth rates were obtained which results in finer ZnO crystals with short hexagonal tablet crystallites (Fig. 5(a)). Otherwise larger ZnO rods were formed in higher Zn-precursor concentration solutions (Fig. 5(b-d)), while the crystallinity was poor with the ZnO and Zn(OH)₂ coexistence as shown in the XRD results (Fig. 2(b)). The rod samples with the diameter of 300 ~ 500 nm and the length ranging 2 to 4 μm, and the aspect ratio of ~ 5 were formed (Fig. 5(b-d)). Crystallite size (D_{cal}) of the powders synthesized at the condition of 0.07 M and pH 7 was 60 nm and the value was the smallest compared to the other powders obtained at the higher precursor concentration and reaction pH in this study.

In a similar manner, Fig. 6 shows that the ZnO particles synthesized under moderate basicity of pH 9 change from fine particulates (Fig. 6(a): D_{cal} : 95 nm) to large rods as the Zn-precursor concentration increases from 0.1 to 1 M.

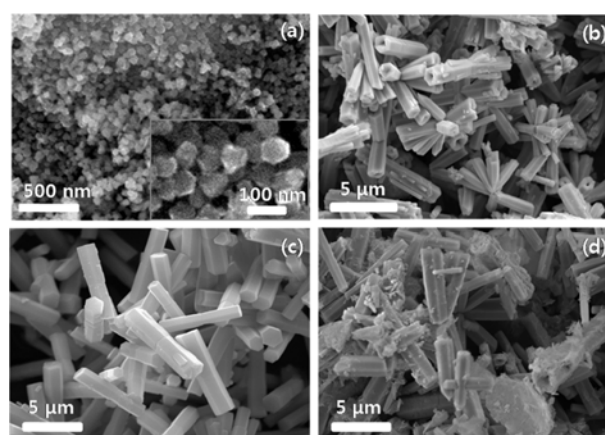


Fig. 5. SEM morphologies of ZnO particles prepared at pH 7 and 80 °C, with different Zn-precursor concentrations; (a) 0.07 M (D_{cal} : 60 nm), (b) 0.3 M, (c) 0.5 M, and (d) 1 M. (Note: (a) inset: close up of the crystallites showing the clear 6-fold symmetry).

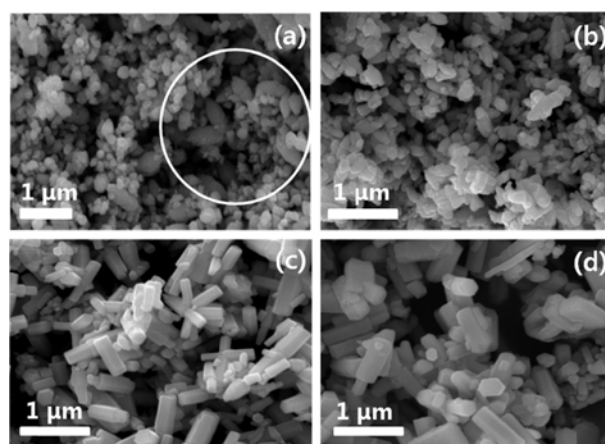


Fig. 6. SEM morphologies of ZnO particles prepared at pH 9 and 80 °C, with different Zn-precursor concentrations; (a) 0.1 M (D_{cal} : 85 nm), (b) 0.3 M (D_{cal} : 125 nm), (c) 0.5 M, and (d) 1 M. (Note: (a) some tapered crystallite in the circle).

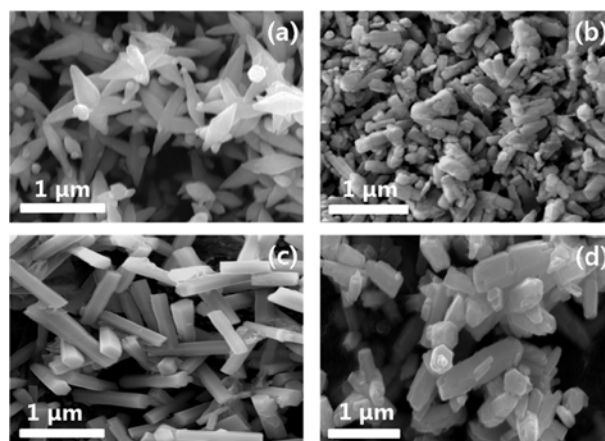


Fig. 7. SEM morphologies of ZnO particles prepared at pH 11 and 80 °C, with different Zn-precursor concentrations; (a) 0.1 M, (b) 0.3 M, (c) 0.5 M, and (d) 1 M.

The ZnO particles synthesized under the higher basicity of pH 11 change from tapered multipods to

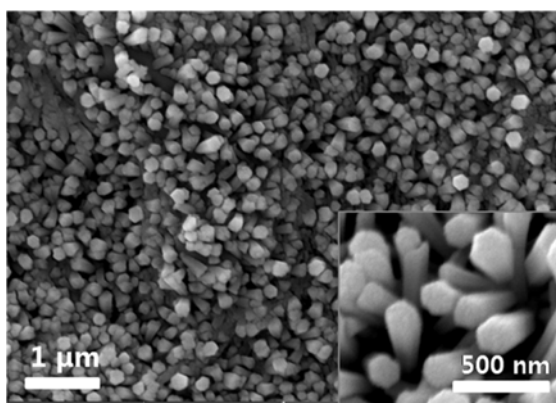


Fig. 8. SEM morphologies of ZnO rods hydrothermally grown on a ZnO-coated slide glass, at pH 11 and 80 °C and the precursor concentration of 0.3 M. (Inset: close-up of the crystallites).

rods, as the precursor solution concentration increases from 0.1 to 1 M (Fig. 7). Both the concentration and basicity will influence the nucleation and growth rates of ZnO particulates. Under the high pH, the optimal growth condition of nucleation and growth rates was achieved and the phase pure and fully developed ZnO crystallites were easily attained.

As the reaction pH increases from pH 7 to 11 under the lower Zn-precursor concentration ≤ 0.1 M, the shapes of prepared powders were changed from fine particles to tapered multipods. Some tapered crystallites can be observed at pH 9, as shown in Fig. 6(a), of an intermediate stage for the shape changing process to the tapered multipods. It can be presumed that, at higher pH condition near 11, the faster (001) plane growth rate from Eq. (7) led to the disappearance of the plane leading to the pointed shape at the end of the c-axis.

Based on the above results, the growth mechanism for the ZnO crystallites can be discussed as follows. All the microstructures are related to the hexagonal six-fold symmetry of the wurtzite structure. As the reaction pH and precursor concentration increased, the enhanced c-axis ([0001]) growth was achieved so that the hexagonal prismatic morphology was mostly obtained. Rods-shaped ZnO was predominantly developed resulting from the enhanced c-axis growth under the higher reaction pH and precursor concentration in this study.

Furthermore, it was possible to tailor the morphology of a ZnO nano-rod coating. Fig. 8 shows the morphology of the ZnO nano-rod coating prepared by the hydrothermal process on a ZnO-coated glass under the nano-rod synthesis condition of pH 11 and 80 °C for 1 hr, with the Zn-precursor concentration of 0.3 M. The coating microstructure was attributed to the small rod-like particle formation, as shown in Fig 6(b) under the hydrothermal condition, which was easily attached on the already ZnO seeded (coated) glass surface.

It has been shown that the hydrothermal synthesis

parameters are key factors in the formation and growth of ZnO nucleus. By controlling hydrothermal parameters, the ZnO morphologies could be easily tailored.

Conclusions

It has been shown that ZnO nanostructures could be produced conveniently by a hydrothermal method in a wider pH range compared to the simple aqueous precipitation process. The route of synthesis employed demonstrated to be promising, allowing the precipitates of ZnO nanostructures at relatively low temperatures and in a simple manner. The X-ray diffraction results confirmed the efficiency of the hydrothermal process under moderate synthesis conditions. The SEM morphologies of all the samples obtained indicated that the particles had, predominantly, a nanometric three-dimensional six-fold symmetry, which was related to the hexagonal wurtzite structure. The ZnO nanocrystallites of hexagonal tablets, tapered multipods, interconnected or separate rods, could be obtained and the shapes would be efficiently controllable by controlling hydrothermal conditions.

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