

Preparation of ZnO Rod-like Nanostructures with Different Precursors

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In this work, the precursors zinc nitrate hexahydrate and zinc chloride were used to synthesize zinc oxide (ZnO) nanocrystals, applying a simple solochemical technique. ZnO rod-like nanostructures were successfully obtained by chemical reaction between NaOH and zinc nitrate hexahydrate at 90 °C. The sample formed by chemical reaction between NaOH and zinc chloride at 90 °C showed the ZnO phase mixed with the $Zn_5(OH)_8Cl_2 \cdot H_2O$ phase. Only after thermal treatment at 500 °C for 3 hours, the conversion of $Zn_5(OH)_8Cl_2 \cdot H_2O$ in ZnO was achieved. The samples prepared with different precursors were characterized by X-ray diffraction, Raman spectroscopy and transmission electron microscopy. Rietveld analysis to the X-ray diffraction data indicated that ZnO nanocrystals obtained have hexagonal wurtzite structure and nanometric-sized crystallites.

1. Introduction

ZnO nanostructures receive growing attention due to their extraordinary mechanical, electrical, magnetic, optical and chemical properties. The dimensionality plays a crucial role in determining the properties and performance of nanostructures (Rohani and El-Ruby, 2009). ZnO has hexagonal wurtzite structure and belongs to space group $P6_3mc$ (Özgür et al., 2005). The two important characteristics of the wurtzite structure are the noncentral symmetry and polar surfaces (Wang, 2004). The ZnO crystal lattice can be described as alternating planes composed of Zn^{2+} and O^{2-} which are stacked alternatively along the crystallographic *c*-axis (Wang et al., 2004). The oppositely charged ions form positively charged (0001)-Zn and negatively charged (0001)-O polar surfaces on the top and on the bottom surface of the primary nanoparticles (Li et al., 2009). The nonpolar low symmetry surfaces are more stable than the polar face, leading to faster growth along the polar surface (Asif et al., 2010). As a result, a variety of one-dimensional ZnO nanostructures including nanorods, nanowires, nanobelts, nanorings and nanoflowers can be readily synthesized (Singh et al., 2007; Özgür et al., 2005).

There are several synthesis procedures for the preparation of oxide nanoparticles such as hydrothermal, electrochemical, precipitation and solochemical (Chen et al., 2007; Inguanta et al., 2009; Cai et al., 2008; Vaezi and Sadrnezhad, 2007). Among the routes

for chemical synthesis of ZnO, the solochemical method stands out due to its rapidity, simplicity, mild experimental conditions, low cost and applicability to industrial scale. This technique consists basically in the reaction between a heated alkaline solution and a zinc containing complex (precursor solution), under controlled temperature (Vaezi and Sadrnezhad, 2007; Gusatti et al., 2009; Gusatti et al., 2010).

In this work, different precursors were used to synthesize ZnO nanostructures via the solochemical method. 0.7 M solutions of zinc chloride (ZnCl_2) and zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were adopted as the precursor solutions of the syntheses. The reactions with both precursors were performed at 90 °C. The samples were characterized by X-ray diffraction (XRD), Rietveld method, Raman spectroscopy and transmission electron microscopy (TEM).

2. Experimental Procedure

In this work, the samples were prepared with different precursors ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and ZnCl_2) at concentration of 0.7 M and 1.0 M NaOH. The alkaline and precursor solutions were prepared at room temperature by dissolving the reagents in 100 mL of deionized water. The alkaline solution was heated until 90 °C in a reactor under stirring. At this temperature, a precursor solution ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or ZnCl_2) was slowly added into the reactor for 1 h under vigorous stirring. After complete addition of precursor solution, the suspension formed in the reactor was kept for over 2 h under the same conditions of stirring and temperature. Following the reaction, the materials produced were filtered, washed several times with deionized water and dried in a vacuum oven at 65 °C.

The crystal structure of the samples was determined by XRD using a PanAnalytical X'pert PRO Multi-Purpose diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The sample that has not exhibited only the ZnO phase was annealed at 500 °C for 3 h in a Jung oven model 4213. To estimate the average crystallite size, the XRD patterns were refined with a modified pseudo-Voigt profile function by the Rietveld method using the GSAS program package (Larson and Von Dreele, 2000; Toby, 2001). Refinements were carried out with a starting model based on structural information provided in the ICSD (2007) databases and on instrumental dispersion determined using an Y_2O_3 standard. TEM micrographs were taken on a JEM-1011, employing an accelerating voltage of 100 kV. The Raman spectra were measured in a Renishaw Invia micro-Raman system with a 514 nm excitation wavelength.

3. Results and Discussion

Figure 1 shows the XRD pattern of the sample obtained by the chemical reaction between NaOH and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. This diffractogram reveals that all peaks detected correspond to the characteristic peaks of hexagonal wurtzite structure of ZnO with space group $P6_3mc$, as can be seen comparing it with the dummy pattern of ZnO (ICSD card No. 57 450). The absence of additional peaks confirms that the solochemical technique is suitable for production of ZnO using $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ precursor.

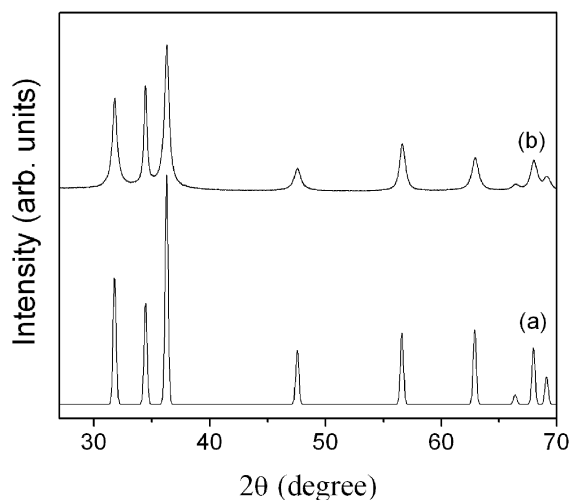


Figure 1: XRD patterns of (a) ZnO (ICSD card No. 57 450) and (b) ZnO sample prepared by the sol-chemical technique with $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ precursor.

The diffractogram of the sample synthesized by the chemical reaction between NaOH and ZnCl_2 (Fig. 2) exhibits characteristic diffraction peaks of ZnO (identified in the diffractogram) and other peaks that can be attributed to the $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ phase (space group $R\text{-}3mH$, lattice parameters $a = 6.34 \text{ \AA}$ and $c = 23.64 \text{ \AA}$, see dummy pattern (Fig. 2(b)) created from ICSD card No. 16 973). After thermal treatment at $500 \text{ }^\circ\text{C}$ for 3 h the $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ phase was completely decomposed into ZnO as shown in Figure 2(d), attesting the instability/metastability of $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ phase.

The XRD pattern of the sample obtained with the $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ precursor were refined by Rietveld method. The anisotropic average crystallite sizes for this sample were 20 nm (perpendicular) and 29 nm (transversal).

TEM images (Fig. 3) of the products obtained at $90 \text{ }^\circ\text{C}$ with (a) $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and (b) ZnCl_2 (after thermal treatment) show that both samples have hexagonal rod-like particles with an average diameter of about 12 nm and 24 nm, respectively.

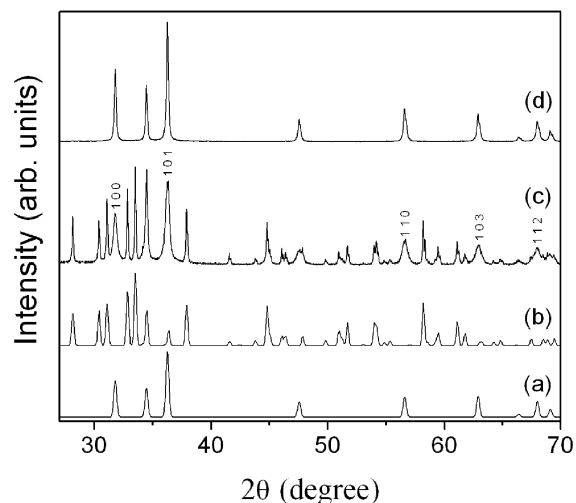


Figure 2: XRD patterns of (a) ZnO (ICSD card No. 57 450), (b) $Zn_5(OH)_8Cl_2 \cdot H_2O$ (ICSD card No. 16 973), ZnO samples prepared with $ZnCl_2$ by the solochemical processing (c) before and (d) after thermal treatment.

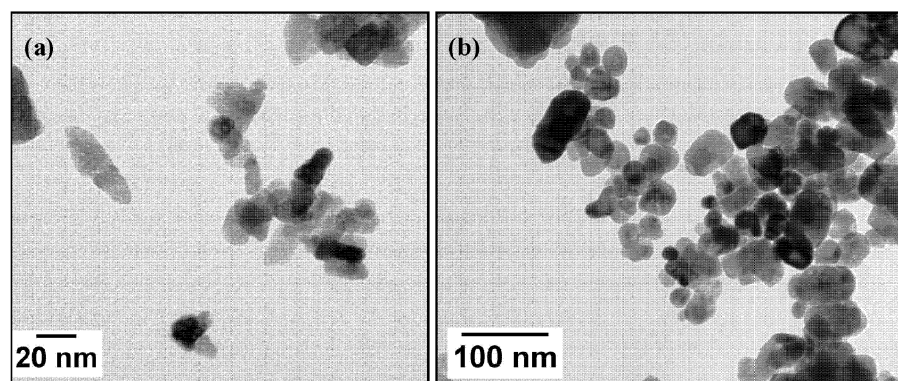


Figure 3: TEM images of the products obtained with (a) $Zn(NO_3)_2 \cdot 6H_2O$ and (b) $ZnCl_2$ after thermal treatment.

Figure 4 shows the Raman spectra of the samples produced in this work and of the ZnO bulk (Fig. 4(a)) for comparison. The spectrum of sample obtained with $Zn(NO_3)_2 \cdot 6H_2O$ (Fig. 4(b)) shows a remarkable peak around 438 cm^{-1} which is the nonpolar optical phonon E_2^{high} mode, corresponding to band characteristic of wurtzite phase, a peak at about 583 cm^{-1} that can be attributed to the longitudinal optical E_1LO mode and another peak around 379 cm^{-1} which can be associated to the polar optical A_1TO mode. The Raman spectrum of the sample obtained with $ZnCl_2$ without thermal treatment (Fig.

(4c)) shows a peak at about 395 cm^{-1} which can be attributed to the transverse optical $E_{1\text{TO}}$ mode and another around 436 cm^{-1} which can be associated with the E_2^{high} mode of wurtzite phase. The other peaks are probably explained by optical modes of $\text{Zn}_5(\text{OH})_8\text{Cl}_2\cdot\text{H}_2\text{O}$ phase.

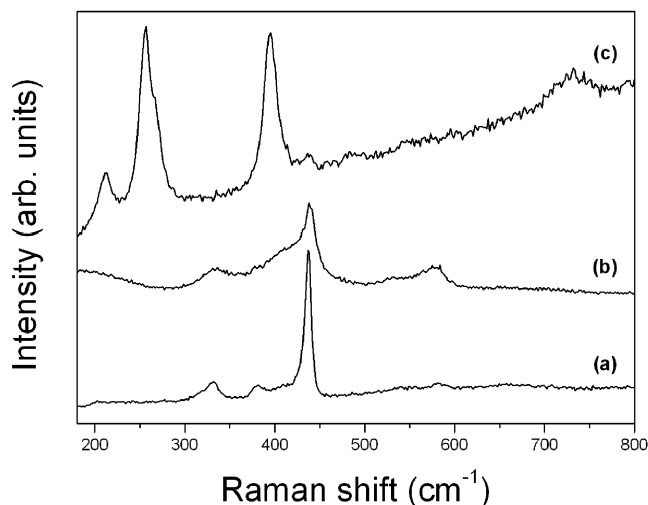


Figure 4: Raman spectra of (a) ZnO bulk and of the samples obtained with (b) $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ and (c) ZnCl_2 before thermal treatment.

4. Conclusions

The present synthesis method is a fast and inexpensive approach, capable of producing ZnO nanocrystals at relatively low temperature using $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ as precursor. The XRD results confirm the formation of well crystallized ZnO particles with hexagonal wurtzite structure. However, XRD results indicate the low efficiency of the proposed solothermal method in the synthesis of pure ZnO nanocrystals using the ZnCl_2 precursor. The sample synthesized with ZnCl_2 is completely converted into ZnO after thermal treatment at $500\text{ }^\circ\text{C}$ for 3 h. TEM images of the samples synthesized with both precursors (after thermal treatment) show that the products have similar morphology.

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