

Influence of the Precursor Solution Addition Time on the Structural Properties of ZnO Nanocrystals

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Abstract. The solochemical method was applied to prepare ZnO nanocrystals at low temperature, using sodium hydroxide and zinc chloride as starting materials. In this work, different addition times of the precursor solution were adopted and their effects on the crystalline domains (or crystallite) size and particle morphology of the obtained samples were investigated. The synthesized products were characterized by X-ray powder diffraction (XRPD) and transmission electron microscopy (TEM) techniques. The XRPD results revealed that all samples produced have a single ZnO hexagonal wurtzite phase (space group $P6_3mc$) under anisotropic strain. The parallel to perpendicular crystallite size ratio was about 1.21 for the sample produced with instantaneous addition of the precursor solution and 1.19 for 1 h longer addition time. The anisotropic strains become about 12% smaller for the sample produced with longer addition time. The TEM results of the samples showed ZnO nanometric particles with nearly rounded and rod-like morphologies.

Introduction

The increasing development of the nanotechnology is a breakthrough in all fields of science, but especially in materials engineering. Bringing materials to the nanoscale enables the development of incredibly innovative compounds, exhibiting properties that are even different from the material itself in a larger scale.

Zinc oxide is one of the most promising materials for nanotechnological applications due to its extraordinary mechanical, electrical, magnetic, optical and chemical properties. ZnO in microscale is a well known material that stands out among other semiconductors for its large band gap (3.37 eV) associated with a high excitation binding energy (60 meV) [1-2]. ZnO has hexagonal wurtzite structure and belongs to space group $P6_3mc$ with lattice parameters $a = b = 3.25 \text{ \AA}$ and $c = 5.21 \text{ \AA}$ [3-4]. The production of nanometric ZnO particles provides not only a great surface area, but also changes significantly its properties, as they are strongly dependent on the size, orientation and morphology of the particles [5]. One of the consequences of the size-reduction is the high density of states at the band edges, caused by radial quantum confinement effect [6]. Such outstanding properties make ZnO suitable for application as optic-electronic devices, catalysts, cosmetics, gas sensors, varistors and pigments [7-10].

The synthesis of nanostructured ZnO was already reported to be achievable by physical and chemical routes. However, for industrial scale production, chemical methods seem to be more suitable approaches [11], due to higher cost-effectiveness and easy production of nanostructures with uniform size and morphology [12]. The solochemical method is a remarkable technique for the production of such particles due to its simplicity, quickness and low cost production of high quality

nanocrystals. Furthermore, on contrary of most chemical approaches described so far, the solochemical technique requires only milder reaction conditions [13]. The method consists of a sol-gel-like reaction between a precursor solution at room temperature and a heated alkaline solution. Decomposition reactions take place, causing the immediate formation of ZnO nanocrystals [14].

In a previous study [15], the effects of temperature in the solochemical synthesis of ZnO nanoparticles were investigated. Such parameter has shown to have great influence in the final product characteristics. In this work, different addition times of the precursor solution were adopted to investigate their effects on the anisotropic crystallite size/strain and particle morphology of the obtained ZnO powder samples by using X-ray powder diffraction, Rietveld method and transmission electron microscopy, respectively.

Experimental Procedure

In this work, the samples were prepared using 0.5 M ZnCl₂ precursor solution and 1.0 M NaOH alkaline solution. Both solutions were prepared at room temperature by dissolving the reagents in 100 mL of deionized water. The alkaline solution was heated to 70 °C in a reactor under stirring. At this temperature, the precursor solution was added into the reactor using different times: instantaneously (0 h) and dripping during 1 h, under vigorous stirring. After complete addition of the precursor solution, the suspension formed in the reactor was kept for over 2 h under the same stirring and temperature conditions. After reaction, the materials produced were filtered, washed several times with deionized water and dried in a vacuum oven at 65 °C.

The crystalline structure of the samples was determined by XRPD using a PanAnalytical X'pert PRO Multi-Purpose diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). In order to estimate the average crystalline domain (crystallite) size and microstrain of ZnO phase, the XRPD patterns were analyzed by the Rietveld method using the GSAS+EXPGUI program package [16-17]. Using a modified pseudo-Voigt peak profile function, which includes anisotropic microstrain broadening following the description defined by P. Stephens [18]. Refinements were carried out with a starting model based on structural information provided in the ICSD databases [19] and on instrumental dispersion determined using an Y₂O₃ standard. TEM micrographs were taken on a JEM-1011, employing an accelerating voltage of 100 kV.

Results and Discussion

Fig. 1(a) and Fig. 1(b) illustrate the XRPD patterns of the samples obtained with instantaneous mixing and with dripping of the precursor solution during 1 h, respectively. The diffraction peaks of the samples are similar to those of ZnO informed in ICSD (card No. 57450), confirming the hexagonal wurtzite structure with space group *P6₃mc*. The results indicate that the products consist of pure ZnO phases, as characteristic peaks of impurities are completely absent.

The XRPD results revealed that all samples produced have a single nanocrystalline ZnO hexagonal phase under anisotropic strain (see Miller index in Fig. 1). The parallel and perpendicular crystallite sizes ($L_{//}$ and L_{\perp} , respectively) as well as the microstrains s obtained from the Rietveld analysis are summarized in Table I. It can be seen that the ZnO samples presented in this paper has almost the same c/a ratio (1.602) reported for ZnO single crystals [20], revealing that the precursor solution method is able to produce nanometric crystallites keeping the ZnO structural characteristic found in almost perfect crystals. However, the anisotropic strain s values reveal that ZnO samples produced by this method contain high levels of structural imperfections. The addition time of the precursor solution did not present significant influence on the crystallite size or microstrain of the ZnO powder samples analyzed.

The morphology of the ZnO samples was investigated by TEM. The TEM images of as-prepared ZnO samples are shown in Fig. 2. Fig. 2(a) shows the predominant formation of nanoparticles with nearly rounded shape having average size of about 20 nm when prepared with instantaneous mixing of the reagents. The circles in Fig. 2(a) emphasize the particles possessing a clear hexagonal geometry. Fig. 2(b) shows the formation of particles with predominant rod-like morphology when

synthesized with 1 h of dripping of the precursor solution. The average diameter (equivalent to perpendicular crystallite size) of the ZnO nanorods was estimated to be 31 nm while the average length (equivalent to parallel crystallite size) was around 35 nm, in agreement with XRPD results.

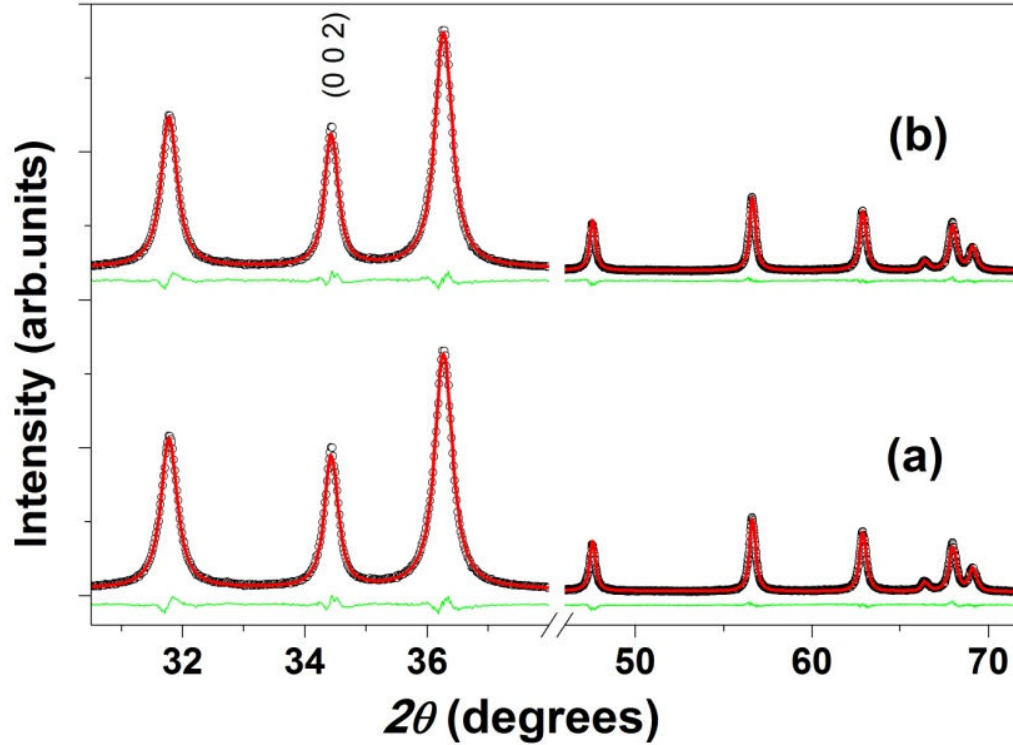


Fig. 1: XRPD patterns of ZnO samples prepared by solochemical technique applying (a) instantaneous mixing (0 h) and (b) 1 h of dripping of the precursor solution. Open circles represent the experimental data and red (green) lines represent the calculated (difference) patterns. The (2 0 0) represent the Miller index corresponding to the Bragg peak that was only fitted by the anisotropic strain model [18].

Table 1: Crystallographic parameter obtained from Rietveld analysis of the XRPD patterns of the ZnO samples prepared by solochemical technique applying instantaneous mixing (0 h) and 1 h of dripping of the precursor solution.

Addition Time	a (Å)	c (Å)	L_{\perp} (nm)	L_{\parallel} (nm)	s (%)		
					(1 0 0)	(1 1 0)	(1 1 1)
0 h	3.2514	5.2096	32.2	38.3	0.15	0.18	0.23
1 h	3.2514	5.2097	32.0	38.7	0.18	0.21	0.26
Ref. [20]	3.2494	5.2054					

Conclusions

The ZnO samples presented in this paper has almost the same c/a ratio reported for ZnO single crystals, revealing that the precursor solution method is able to produce nanometric crystallites keeping the ZnO structural characteristic found in almost perfect crystals. However, the anisotropic strain s values reveal that ZnO samples produced by this method contain high levels of structural imperfections. Furthermore, the addition time of the precursor solution did not present any significant influence on the crystallite size or microstrain.

The nanoparticles morphology changed from rounded to rod-like with the dripping of the precursor solution, indicating that the shape depend on this experimental parameter. This process is well repeatable and easily controlled, which may offer an attractive strategy for the fabrication of other oxide nanoparticles.

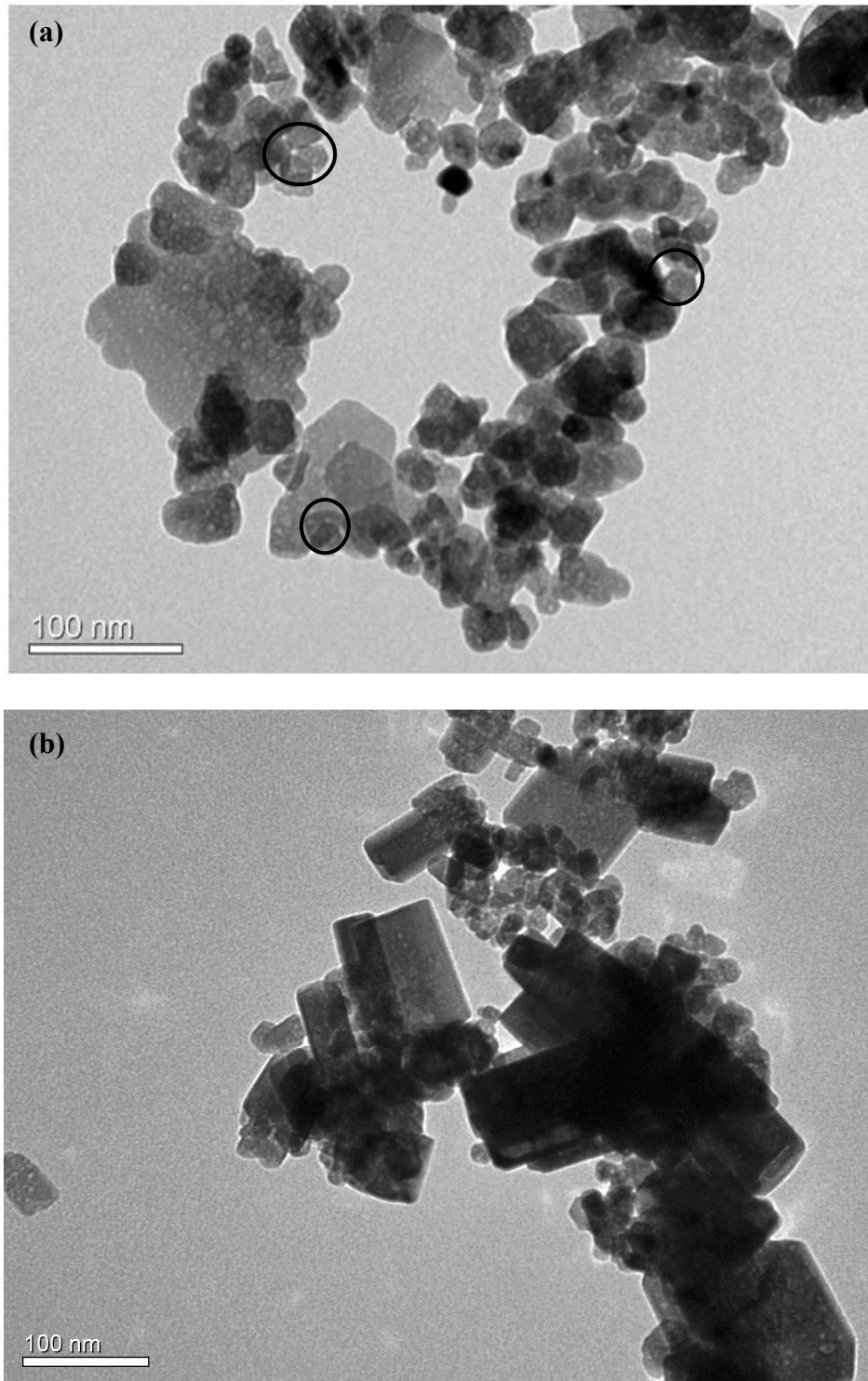


Fig. 2. TEM images of ZnO nanocrystals prepared using (a) instantaneous mixing (0 h) and (b) 1 h of dripping of the precursor solution via solochemical technique. In (a) circles emphasize the hexagonal feature of the particles.

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