Crystal Structures and Properties of ZnO Nanopowders Prepared by Ultrasonic Method

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Ultra-fine zinc oxide powders were prepared using ultrasonic method at 60°C with zinc acetate, zinc nitrate and potassium hydroxide solution as precursors. The obtained powders were characterized by means of scanning electron microscope, thermogravimetric analysis, X-ray diffraction and infrared spectroscopy. The crystal structures were investigated based on Rietveld method. The results showed that, zinc oxide powders have hexagonal structure (P6₃mc) with particle size in the range of 100-300 nm. The mechanism for the ZnO formation was discussed. The properties of synthesized materials were examined by UV-Vis spectrum and cyclic voltammetry measurement.

Keywords: Zinc oxide; Nanopowders; Ultrasonic method; Crystal structure; Cyclic voltammetry

I. INTRODUCTION

Zinc oxide (ZnO) has been a focus of research in material science because of their physical and electrochemical properties. It can be used for different purposes, such as catalysts, gas sensors, optical waveguides, optoelectronic devices, and anodic active materials for Ni/Zn secondary batteries [1-3]. Therefore, many methods, including precipitation [4, 5], hydrothermal synthesis [6-8], polymerized complex method [9], electrodeposition method [10], microwave synthesis [2, 11], sonochemical process [12-16] and so on, have been developed to prepare ZnO nanopowder. It was confirmed that prepared condition influences strongly on ZnO structure (cubic and/or hexagonal crystal structure) and morphology (nanobelts, nanowires, nanorods, tubes, disks and flower-like), so it also directly affects the properties of ZnO.

Among the different ZnO synthesized methods, sonochemical process was attracted of attention from many material scientists and chemists. ZnO nanorods (ultra-fine trigonal-shaped particles) were prepared by Zhang et al. [12] while decomposition of zinc acetate dihydrate in paraffin oil at temperature higher than 220°C. Recently, Yadav et al. [13], Alammara et al. [14], Li et al. [15], and Azzizian-Kalandaragh et al. [16] reported the preparation of ZnO nanopowders using zinc acetate and/or zinc nitrate, sodium hydroxide, with and without surfactants in a water-alcoholic/ alcoholic solution.

This paper presents our results of ZnO nanopowder synthesis from zinc acetate and zinc nitrate using ultrasonic method. The crystalline structure, physical and electrochemical properties of the obtained ZnO nanopowders were also discussed.

II. EXPERIMENTAL

All chemicals used in this study were purchased from Merck and directly employed without any further purification. Zinc acetate dihydrate (Zn(C₂H₃O₂)₂·2H₂O), zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O), potassium hydroxide (KOH, >85%), and absolute alcohol were used as raw materials. First, stoichiometry of zinc salt solution was added slowly into 2M KOH solution under magnetic stirring. The mixture, in form of white suspension, was then irradiated by ultrasonic waves with different length of time (from 15 minutes to 2 hours) in ultrasonic bath (42 kHz, Col-Parmer Instrument Company) at 60°C. Finally, the product was filtered, washed several times with distilled water, ethanol, and then dried in air oven at 80°C for 5 hours.

Phase identify was determined using Bruker D8 Advance diffractometer with CuKα radiation (λ = 1.5418 Å), the crystal structure of ZnO powder was then refined by Rietveld method from XRD patterns using WinPlotr/ FullProf Suite 2009 software [17]. The morphology of the powder was examined by scanning electron microscopy (SEM, HITACHI S4800). FT-IR spectra of ZnO powders were recorded using Perkin Elmer GX spectrophotometer. Thermogravimetric and differential thermal analysis (TG-DTA) using a SETARAM TG-DTA 92 (rate 10°C/min, under a dry air) were also employed to characterize the obtained ZnO powders. The optical absorption of the ZnO nanoparticles was investigated by UV-Vis spectrophotometer 2800 (Col-Parmer Instrument Company).

Electrochemical measurement was performed in three electrodes with a conventional cell used for electrochemical technique (Autolab 30 instrumentation). The Ag/AgCl was served as a reference electrode (RE), and platinum was used as a counter electrode (CE). The ZnO pressed electrode, which was fabricated from the mixture of 80 wt.% ZnO powder and 20 wt.% Teflon (submicron powder, as an additive) over the Ni plated steel net, was used as a working electrode. The electrolyte was saturated ZnO in 2 M KOH solution.
FIG. 1: Observed (+ symbols), calculated (full curve) and difference (bottom) diffraction patterns for ZnO nanopowder prepared from (a) zinc acetate salt and (b) zinc nitrate salt, reaction time 2 hours.

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns and Rietveld refinement for the product prepared from zinc acetate (Fig. 1(a)) and nitrate salt sources (Fig. 1(b)) under 2 hours of irradiation. All the peaks can be indexed to wurtzite ZnO in comparison with the collected data from Inorganic Crystal Structure Database (ICSD, collection code: 67849, hexagonal structure, space group: P\textsubscript{6}3\textsubscript{mc} (186), a = 3.2539 Å, c = 5.2098 Å), and no other impurity phases are observed. The obtained structure parameters from refinement are represented in Table 1. The refined cell parameters of both ZnO cases are nearly the same with those of the bulk ZnO wurtzite, the free parameter for O, which we obtain as 0.382\,(8) (for product prepared from zinc acetate source) and 0.386\,(5) (for product prepared from zinc nitrate source) compare to 0.389\,(0) for bulk ZnO. On the other hand, it can be seen clearly from refinement results of XRD patterns that the observed intensity (+ symbols) of diffraction peak of the (0002) plane are higher than calculated intensity (full curve). This difference represents the abundance of oriented and grain growth favors in a given \langle 0001 \rangle direction [2, 4, 7, 10].

The morphology of the ZnO synthesized from zinc acetate (ZnO-Act) and zinc nitrate (ZnO-Nit) are shown in Figs. 2(a) and (b) respectively. It can be seen from the SEM images that the shape of ZnO-Act sample is more uniform than the ZnO-Nit. The grain size varies from 100 to 200 nm in diameter and the particles are grown preferential in c-direction. Therefore, the obtained product from nitrate salt can be observed in irregular plate-like morphology with the dimension of plate-like ZnO in the range of 150-300 nm.

Figures 3 (a) and (b) show TGA curves of ZnO-Act and ZnO-Nit powders respectively. As a function of temperature, two regions of weight loss can be seen clearly in both cases. The higher weight loss of 2.55 wt.% was observed in the case of ZnO-Act powder. The first loss weight (maximum ∼ 1%) was assigned for the physical adsorbed degradation of water and/or ethanol onto ZnO surface at lower temperature (50-150°C). Since the degradation step between 150°C to 500°C indicates the decomposition of Zn(OH)\textsubscript{2} [18], or Zn\textsubscript{x}O\textsubscript{y}(OH)\textsubscript{z} compound, as a non-crystalline phase, and we cannot identify them from XRD patterns. On the other hand, it is probability concerning to the degradation of acetate and/or nitrate ions remained as a chemically adsorbed onto surface of ZnO nanopowder (loss weight maximum ∼ 1.55%).

The FT-IR spectra results improve hypothesis above. The absorption bands near 3400 cm\textsuperscript{-1} represent O–H group, and bands at (465 cm\textsuperscript{-1}, 475 cm\textsuperscript{-1}) are clearly represented for Zn–O bonding [9]. Peaks around 1399 cm\textsuperscript{-1}, 1563 cm\textsuperscript{-1} correspond to the stretching vibration of C=O and C–O–H groups in acetate species and/or persist even after washing with ethanol (Fig. 4(a)). In Fig. 4(b), the peak at 1632 cm\textsuperscript{-1} is assigned to the stretching vibration of O-N=O group in nitrate species, which suggests the presence of adsorbed nitrate on the surface of ZnO nanopowders.

The mechanism of ZnO formation under the ultrasonic process was investigated. The irradiations of ultrasonic waves were applied onto white suspension (a mixture of zinc salt and potassium hydroxide obtained at first stage)
at different times from 15 minutes to 2 hours. The result from XRD patterns (not present here) shows that only ZnO phase was identified after 15 minutes of irradiation. This indicates that the formation and growth of ZnO nanocrystal was so rapid. The mechanism of ZnO formation can be proposed as follows:

\[ \text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2 \quad (1) \]

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

\[ \text{Zn}^{2+} + 4\text{OH}^- \rightarrow [\text{Zn(OH)}_4]^2^- \quad (3) \]

\[ [\text{Zn(OH)}_4]^2^- + \cdots + [\text{Zn(OH)}_4]^2^- \rightarrow \text{Zn}_x\text{O}_y(\text{OH})_z \quad (4) \]

\[ \text{Zn}_x\text{O}_y(\text{OH})_z \rightarrow \text{ZnO} + \text{H}_2\text{O} \quad (5) \]

\[ [\text{Zn(OH)}_4]^2^- \rightarrow \text{ZnO} + 2\text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \quad (6) \]

\[ \text{Zn(OH)}_2 \rightarrow \text{ZnO} + \text{H}_2\text{O} \quad (7) \]

Eqs. (4) and (5) are similar to the research of Lin et al. [5]. In the first stage, Zn\(^{2+}\) added into KOH solution, the reactions take place as Eqs. (1)-(3). The product was found in white suspension form. In the second stage, the mixture was irradiated by ultrasonic waves at temperature 60°C; Eqs. (4)-(7) occurred, and rapidly white precipitate of ZnO was formed by the dehydration of Zn\(_x\)O\(_y\)(OH)\(_z\), [Zn(OH)\(_4\)]\(^2-\) and/or Zn(OH)\(_2\).

Figure 5 shows UV-vis absorption spectrum of ZnO nanoparticles prepared at different sonochemical reaction times: 15, 30, 45, 60, 90 and 120 min. For all samples, well defined exciton absorption peaks at 372 nm to 377 nm were observed. These observations are in good agreement with research of Yadav et al. [13].

UV-Vis spectra of ZnO-Act, ZnO-Nit and commercial submicron ZnO powder (purchased from Merck) were recorded. Band gap energy of ZnO samples was calculated from UV-Vis by plot \((\alpha \cdot h \cdot \nu)^{2}\) versus photon energy \((h \cdot \nu)\) as shown in Fig. 6, where \(\alpha\) is an absorption coefficient [8, 10]. Energy band gap \((E_g)\) was obtained by the extrapolation of the linear part until it intersects the energy \((h \cdot \nu)\) - axis. The band gap of both synthesizes ZnO samples (ZnO-Act, ZnO-Nit) was found to be \(E_g \sim 3.29\) eV. These observed values are higher than the value \(E_g\) for commercial ZnO powder \((E_g \sim 3.15\) eV).

The electrochemical property of synthesized materials was investigated using a cyclic voltammetry measurement (CVs). The CVs were recorded with voltage in range of \(-1.5\) to \(-0.75\) V (versus Ag/AgCl) and scan rate was set at \(1\) mV \(\cdot\) s\(^{-1}\) in the solution of saturated ZnO in 2M KOH. Figure 7 presents the cyclic voltammograms of dif-
FIG. 6: Band gaps calculated from UV-Vis data of (a) ZnO-Act, (b) ZnO-Nit, and (c) commercial submicron ZnO powder.

FIG. 7: Cyclic voltammograms of ZnO powder electrodes from (a) ZnO-Act, (b) ZnO-Nit, and (c) commercial submicron ZnO powder.

Therein, the commercial ZnO powder was used as comparison sample.

It can be seen that the anodic current response lies between $-1.37$ and $1.20$ V. The anodic process corresponds to the discharge process of zinc oxide electrode; hence the increase of the anode peak is in accord with the higher discharge voltage of the ZnO materials [3]. The anodic peak has potential value ($E_{p,a}$) of $-1.276$, $-1.276$, and $-1.265$ V and the current density ($I_{p,a}$) = $23.2$, $17.9$, $10.1$ mA·cm$^{-2}$ for ZnO-Act, ZnO-Nit and submicron commercial ZnO electrodes respectively. Hence, both syntheses of ZnO powder have electrochemical activity higher than submicron commercial ZnO powder.

IV. CONCLUSION

ZnO nanopowders were successfully synthesized from zinc acetate and zinc nitrate salts sources in KOH medium using ultrasonic process. The obtained products were characterized to have hexagonal structure, $P6_3mc$. The nanocrystal of ZnO was rapidly growth in the $\langle 0001 \rangle$ direction. Grains size of prepared ZnO materials were in the range of $100 \div 200$ nm and $150 \div 300$ nm for ZnO-Act and ZnO-Nit respectively. Energy band gap was found to be $3.29$ eV in both materials. The obtained results were confirmed that ZnO products have good physical, electrochemical properties so they can be very useful for further applications.

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