

Microwave-assisted hydrothermal synthesis of ZnO powders with different reagents

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ABSTRACT

In this work, zinc oxide powders were synthesized by microwave-assisted hydrothermal method in basic medium. These powders were analyzed by X-ray diffraction (XRD), Field-emission scanning electron microscopy (FEG-SEM), Ultraviolet-visible (UV-vis) absorption spectroscopy and photoluminescence (PL) measurements. XRD pattern confirmed that the pure ZnO phases were obtained after MH processing performed at 130 °C/ 1h. FEG-SEM micrographs reveals that these nanostructures are made up of ZnO plates. UV-vis results were employed to determine the optical band gap these materials. Also, it showed existence of photoluminescence (PL) in the different zinc powders. An orange PL emission when excited by 350 nm wavelength at room temperature was observed in the different powders.

Keywords: zinc oxide, microwave-hydrothermal, hexagonal structure, photoluminescence

1 INTRODUCTION

ZnO is a direct wide band gap (3.37 eV) semiconductor with a large excitonic binding energy (60 meV) at room temperature^[1]. ZnO based materials find a wide range of applications in solar cells, transparent conducting films, ultraviolet-protection films, chemical sensors, light emitting diodes, laser diodes, field emission devices, catalysis, gas sensors¹. Well-crystalline ZnO nano and microstructures with different morphologies^[2-6] have been successfully synthesized by different techniques^[7,8]. The hydrothermal method has been recently reported as a simple way to grow one-dimensional nanostructures because of its easy and low cost procedure, low growth temperature, great control over experimental parameters and convenience for synthesis in high quality^[9-13]. In the addition, the variation of this technique, i.e., hydrothermal synthesis using microwave ((microwave hydrothermal), accelerates the crystallization process, increasing the nucleation rate and, hence, leads to the formation of fine particles with homogeneous distribution^[14-16]. Recently, researchers have used this method for the rapid preparation of several materials with different morphologies^[19-21]. The very simple, attractive, and novel procedure concentrates microwave radiation into the solution, thereby enhancing the structural and morphological properties.

The present work reports on the PL properties at room temperature of ZnO powders processed in a domestic microwave-hydrothermal with zinc different reagents at 130 °C for 1 h. The corresponding structural properties and morphology of the powders have been characterized by X-ray diffraction (XRD), Fourier transform Raman spectroscopy (FT-Raman), Ultraviolet-visible (UV-vis) absorption spectroscopy, were analyzed by X-ray diffraction (XRD), field-emission scanning electron microscopy (FEG-SEM), and Photoluminescence measurements.

2 EXPERIMENTAL SECTION

2.1 Synthesis of the Precursors

ZnO powders were processed by the MH method. More details on this equipment have been reported in Ref. ^[23]. The typical experimental procedure is described as follows: 5×10^{-3} mol of zinc nitrate (99% purity, Sigma-Aldrich) were dissolved in 90 mL of deionized water. The solution pH was adjusted up to 12 by the addition of potassium hydroxide [KOH] (2 mol/L) (Merck, 99.5%). Afterwards, this solution was stirred for 15 min at room temperature. In the sequence, the mixture was transferred into a Teflon autoclave, which was sealed and placed into a MH system (2.45 GHz, maximum power of 800W). The MH conditions were performed at 130 °C for 1 h, respectively. The heating rate in this system was fixed at 10 °C/min and the pressure into the autoclave was stabilized at 294 kPa. After the chemical reactions and MH processing, the autoclave was naturally cooled to room temperature. The resultant solution was washed with deionized water several times to neutralize the solution (pH 7). Finally, the white precipitates were collected and dried in a conventional furnace at 75 °C for some hours. The same procedure for the synthesis was performed using zinc acetate and sulphate.

2.2 Characterization

ZnO powders were structurally characterized by X-ray powder diffraction (XRD) using a Rigaku-DMax/2500PC (Japan) with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) in the 2θ range from 20° to 75°. Fourier transform Raman (FT-Raman) spectroscopy measurements were performed using a Bruker-RFS/100. The 1064 nm line of an Nd:YAG ion laser was used as excitation source, the power was kept at

55mW. The morphologies were investigated with a FEG-SEM (Supra 35-VP, Carl Zeiss, Germany) operated at 6 keV. UV-vis spectra were taken using a Cary 5G (Varian, USA) equipment in diffuse reflectance mode. PL measurements were performed using a Monospec 27 monochromator (Thermal Jarrel Ash, USA) coupled to a R446 photo-multiplier (Hamamatsu, Japan). A krypton ion laser (Coherent Innova 90 K, USA) (λ 350 nm) was used as excitation source, keeping its maximum output power at 200 mW. UV-vis and PL spectra were taken three times for each sample in order to ensure the reliability of the measurements. All measurements were performed at room temperature

3 RESULTS AND DISCUSSION

3.1. X-ray diffraction analysis

Figure 1 shows the XRD patterns of ZnO powders processed in MH at 130 °C for 1 h. The diffraction peaks can be used to evaluate the structural order at long-range or periodicity of the material. All peaks can be indexed to the wurtzite phase in a hexagonal structure with space group $P6_3mc$ of ZnO (JCPDS 36-1451). The intensity of the relative peaks indicates the high purity of the ZnO hexagonal phase of the samples and good crystallinity, demonstrating that ZnO. No characteristics peaks for impurities were observed.

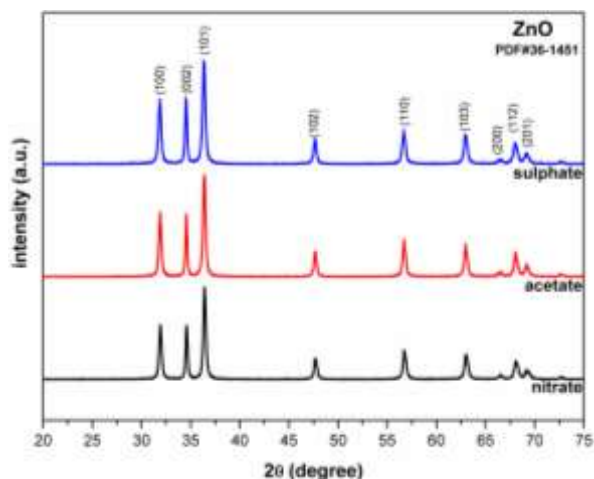


Figure 1: XRD pattern of ZnO powders processed by the microwave hydrothermal method at 130 °C for 1 hour with different reagents.

3.2. Fourier transform raman analysis

Figure 2 illustrates the typically Raman modes of the ZnO phase. The Raman spectra of ZnO powders display four bands which can be observed in the graphs below:

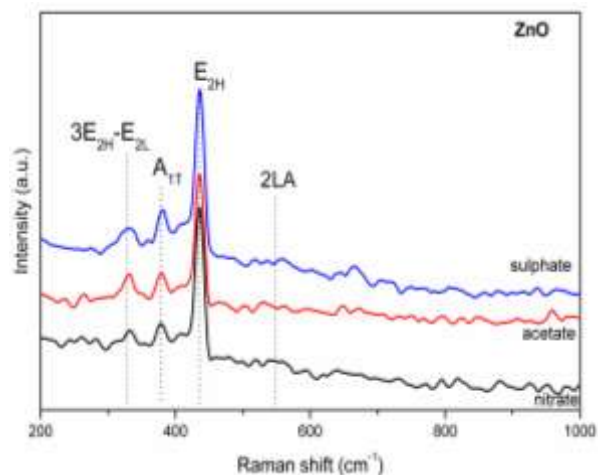


Figure 2: Raman spectra of ZnO powders processed by the microwave hydrothermal method at 130 °C for 1 hour with different reagents.

3.3. Morphology and structure

Figure 3 shows the FEG-SEM micrographs of ZnO powders processed in MH at 130 °C for 1 h. After MH processing performed at 130 °C for 1 h, it was verified that the ZnO powders synthesized with different reagents are constituted by several aggregated plates. The samples of nitrate and acetate forming irregular flowers-like morphologies. It's observed that the zinc sample synthesized with sulphate presents only plates of aleatory form. These results shown that the different zinc reagents can have the same structure, as seen in the results of x-ray, but with different morphologies oriented.

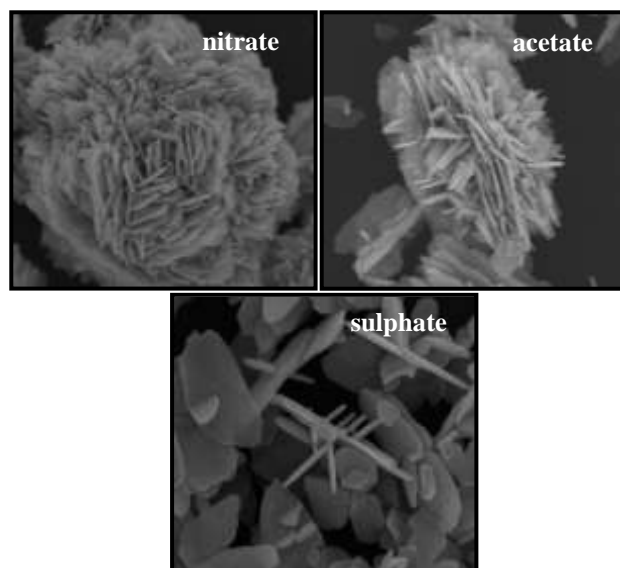


Figure 3: FEG-SEM micrographs of ZnO powders processed by the microwave hydrothermal method at 130 °C for 1 hour with different reagents.

3.4. Ultraviolet-visible absorption spectroscopy analysis

Table 1 shows the results UV-vis of ZnO powders processed in MH at 130 °C for 1 h. The optical band gap energy (E_{gap}) was estimated by the method proposed by Wood and Tauc^[22]. According to these authors, the E_{gap} is associated with absorbance and photon energy by the following equation:

$$h\nu\alpha \propto (h\nu - E_g)^n \quad (1)$$

where α is the absorbance, h is the Planck constant, n is the frequency, E_{gap} is the optical band gap and n is a constant associated to the different electronic transitions ($n = 1/2, 2, 3/2$ or 3 for direct allowed, indirect allowed, direct forbidden and indirect forbidden transitions, respectively). In this work, the UV-vis results suggested an indirect allowed transition and, therefore, the $n = 2$ was used in Eq. (1). The obtained results indicate a small difference in the E_{gap} values with the different reagents, suggesting probably contribution of defects in the energy levels of the optical band gap according to the type of zinc reagent used to obtain in the synthesis of powders.

Zinc reagent	Gap values
nitrate	3.2 eV
acetate	3.24 eV
sulphate	3.27 eV

Table 1: Gap Values of ZnO powders processed by microwave hydrothermal at 130 °C for 1h.

3.5. Photoluminescence emission analysis

The optical property of ZnO powders was investigated by photoluminescence at room temperature. Figure 4 shows the photoluminescence spectrum of ZnO powders prepared with different zinc reagents. An orange PL emission when excited by 350 nm wavelength at room temperature was observed in the different zinc powders. The origin of the orange PL emission of these materials can be probably attributed to the existence of singly ionized oxygen vacancies and/or distortions on the $[\text{ZnO}_4]$ clusters into the lattice. The PL maximum emission intensity is related to the effects of structural order and disorder in the material which result in different electron transfer processes due to different distributions of intermediate levels of energy between the valence band and conduction band.

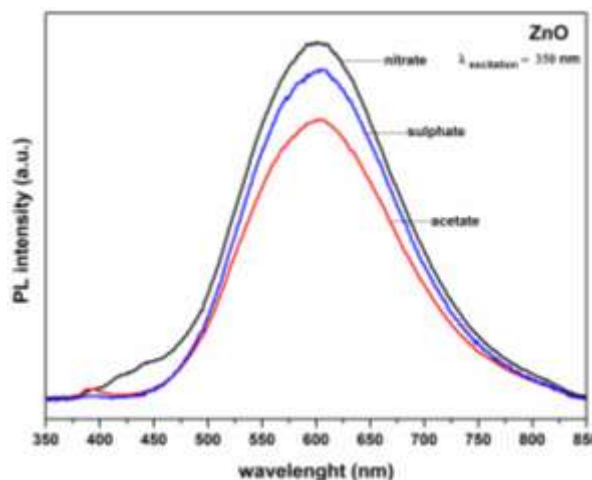


Figure 4: PL spectra at room temperature of ZnO powders processed by the microwave hydrothermal method at 130 °C for 1 hour with different reagents.

4 CONCLUSIONS

In summary, flowers-like ZnO particles were obtained by the MH processing at 130 °C for 1 h with different zinc reagents. XRD patterns confirmed that the pure ZnO phase with hexagonal structure was obtained with the different reagents. UV-vis absorption spectra showed a small difference in the E_{gap} values. This phenomenon was mainly attributed to contribution of defects in the intermediary energy levels of the optical band gap. The origin of the orange PL emission of the materials was attributed to the existence of singly ionized oxygen vacancies and/or distortions on the $[\text{ZnO}_4]$ clusters into the lattice.

5 ACKNOWLEDGEMENTS

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