Journal of Ovonic Research Vol. 9, No. 4, July - August 2013, p. 89 - 94

MICROWAVE-ASSISTED SOLVOTHERMAL SYNTHESIS OF POROUS ZINC OXIDE NANOSTRUCTURES

MARÍA DE LA GARZA[a], ISRAEL LÓPEZ[a], FÉLIX AVIÑA[a], IDALIA GÓMEZ[a*]
[a]*Universidad Autónoma de Nuevo León, UANL, Facultad de Ciencias Químicas, Laboratorio de Materiales I, Av. Universidad, Cd. Universitaria 66451, San Nicolás de los Garza, Nuevo León, Mexico*

Porous ZnO nanostructures were synthesized by reaction of zinc acetate dihydrate with water in 2-propanol solution via a facile microwave-assisted solvothermal method. The synthesis was carried out in a conventional microwave oven, using a closed container as solvothermal reactor. Controlled parameters were water concentration and microwave irradiation time. The obtained products were characterized by means of X-ray powder diffraction (XRD), UV-Vis spectrophotometry, Fourier transform infrared spectroscopy (FT-IR) and field emission scanning electron microscopy (FE-SEM). These nanoparticles have a minimum average diameter of 37 nm, which are agglomerated into irregular and spheroidal nanostructures with dimensions larger than 1 μm and high porosity. Mesopores and macropores with hexagonal geometry were found in the nanostructures.

(Received May 17, 2013; Accepted July 15, 2013)

Keywords: Zinc oxide, Microwave-assisted synthesis, Porous structure

1. Introduction

Zinc oxide (ZnO) is a II-VI semiconductor that crystallizes almost exclusively in wurtzite phase [1], which is due to its polar surfaces and lack of symmetry center [2]. This semiconductor shows a wide band gap of 3.37 eV, at 300 K [1]; and has been widely used in light-emitting diodes [3], solar cells [4], photocatalysts [5] and piezoelectric materials [6].

On the other hand, chemical methods provide the possibility to produce nanostructures at low temperature, however, the control of size and morphology is less. Among these methods, the most widely used are electrodeposition [7], sol-gel technique [8], solvothermal [9], hydrothermal [10] and microwave synthesis [11]. Microwave syntheses have the advantage of employing lower reaction times with respect to the other chemical methods. This synthesis method is based on the rapid and uniform heating of materials because of a direct molecular interaction between these ones and the electromagnetic energy of the microwave waves [12].

Zhu et al. [13] reported the microwave-assisted preparation of diverse ZnO nanostructures, however, they used relatively long times (1 h) of synthesis. Nevertheless, it is possible to use lower irradiation times for the synthesis of nanostructured materials. For example, Vázquez et al. [14] synthesized ZnS nanoparticles via microwaves, using a conventional microwave oven and irradiating the precursors for only 60 s.

In general, the liquid-phase syntheses of metal oxide nanoparticles involve the reaction of a metal salt with hydroxide ions, however, Hu et al. [15] reported the synthesis of ZnO nanoparticles from $Zn(CH_3COO)_2 \cdot 2H_2O$ in 2-propanol at different water concentrations.

In this study, ZnO nanostructures were synthesized by combining solvothermal technique and microwave synthesis. Simultaneously, water concentration and microwave irradiation time were varied to determine its effect on ZnO nanostructures. Morphological and optical properties of the synthesized nanostructures were investigated by means of UV-Vis spectrophotometry, Fourier

*Corresponding author: idaliagomezmx@yahoo.com.mx

transform infrared spectroscopy (FT-IR), field emission scanning electron microscopy (FE-SEM) and X-ray powder diffraction (XRD).

2. Materials and methods

2.1 Materials

Zinc acetate dihydrate, $Zn(CH_3COO)_2 \cdot 2H_2O$ (J. T. Baker, 99.0%) and deionized water were used as precursors, and 2-propanol (Fisher Scientific, 99.9%) as solvent. All the reagents were used without any further purification.

2.2 Synthesis of ZnO nanostructures

Synthesis of the ZnO nanostructured was based on the methodology reported by Hu et al. [15], but with some modifications. Porous ZnO nanostructures have been synthesized by reaction of $Zn(CH_3COO)_2 \cdot 2H_2O$ with water, in 2-propanol as solvent, via a facile microwave-assisted solvothermal method. In a typical reaction, a solution of 20 mM $Zn(CH_3COO)_2 \cdot 2H_2O$ in 2-propanol was prepared. Deionized water was incorporated, in the same solution, in order to obtain a final added water concentration of 2, 3 and 4 M. The synthesis was carried out in a conventional microwave oven (1450 W), using a closed-vessel as solvothermal reactor. The prepared solutions were heated by microwave irradiation for 1, 2 and 3 min. The synthesized ZnO nanoparticles were separated by centrifuging, washed with deionized water, and dried at room temperature for their characterization.

2.3 Characterization of ZnO nanostructures

UV-Vis spectrophotometry was performed on a Shimadzu UV-1800 spectrophotometer. For FT-IR spectroscopic analysis was used a Perkin Elmer Paragon 1000 PC spectroscope. The morphology of the nanostructures was observed on a JEOL JSM-6701F microscope. XRD pattern was recorded on a Siemens D5000 diffractometer, with Cu Kα radiation ($\lambda = 1.5418$ Å), at 1.5° per minute of scanning speed.

3. Results and discussion

3.1 Field emission scanning electron microscopy

Fig. 1 shows the FE-SEM images of the ZnO nanostructures synthesized at the different conditions. Mixtures of irregular and spheroidal nanostructures were obtained. At all the experimental conditions, the nanostructures show high porosity. These -nanostructures present mesopores and macropores, whose formation is attributable to the high pressures reached inside the reactor. An average particle size for the ZnO nanostructures, obtained at each different condition, is shown in Table 1. By analyzing the images, we can see that there is not a significant effect of the studied variables over the particle size of the nanostructures. ZnO nanoparticles obtained in the experiment C show the most uniform and well defined porosity.

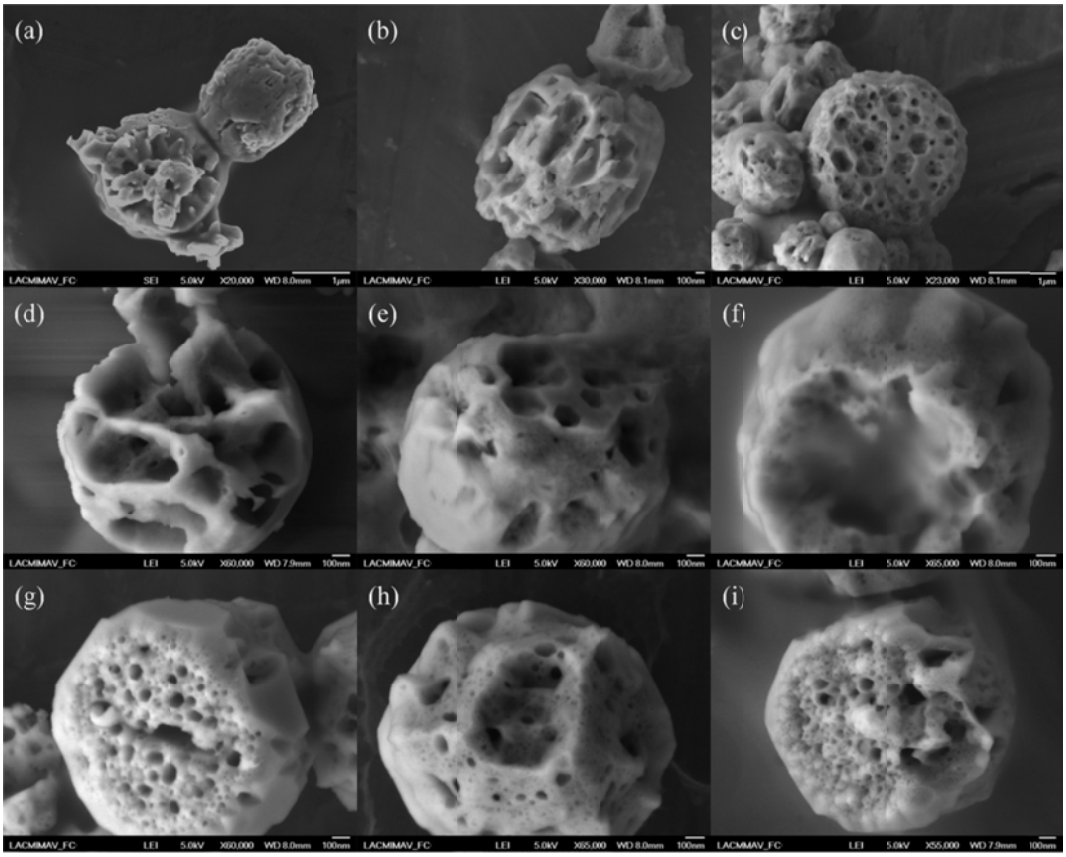

Fig. 1. FE-SEM images of the ZnO nanostructures obtained at added water concentration of 2, 3 and 4 M (up to down), and 1, 2 and 3 min of microwave irradiation time (left to right).

3.2 UV-Vis spectrophotometry

Fig. 2 shows the absorption spectrum of ZnO nanostructures obtained at an added water concentration of 2 M and a microwave irradiation time of 3 min. This spectrum shows a significant blue-shift with respect to the bulk absorption edge. This blue-shift can be attributed to scattering light effects and chemical environment [16], but not to the quantum confinement effect [17], which will be explained in section 3.4 (XRD analysis).

Table 1. Experimental parameters for ZnO synthesis and their average particle size.

Experiment	Added water concentration (M)	Microwave irradiation time (min)	Average particle size (nm)
A	2	1	38
B	2	2	57
C	2	3	47
D	3	1	45
E	3	2	39
F	3	3	35
G	4	1	40
H	4	2	37
I	4	3	54

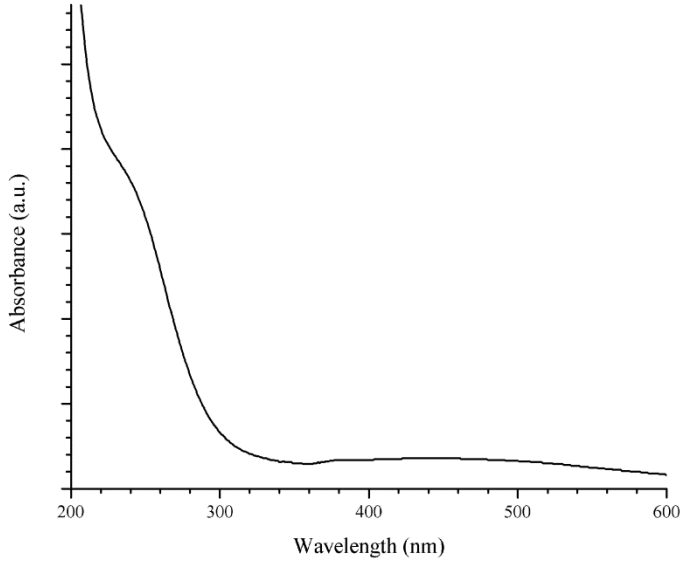

Fig. 2. UV-Vis spectrum of ZnO obtained at an added water concentration of 2 M and 3 min of microwave irradiation time.

3.3 FT-IR spectroscopy

FT-IR spectrum of the ZnO nanoparticles synthesized at the last mentioned conditions is shown in Fig. 3. The peak at 450 cm^{-1} corresponds to the stretching mode of ZnO [18,19]. The bands at 3400, 1554 and 1393 cm^{-1} correspond to water molecules adsorbed on the ZnO surface.

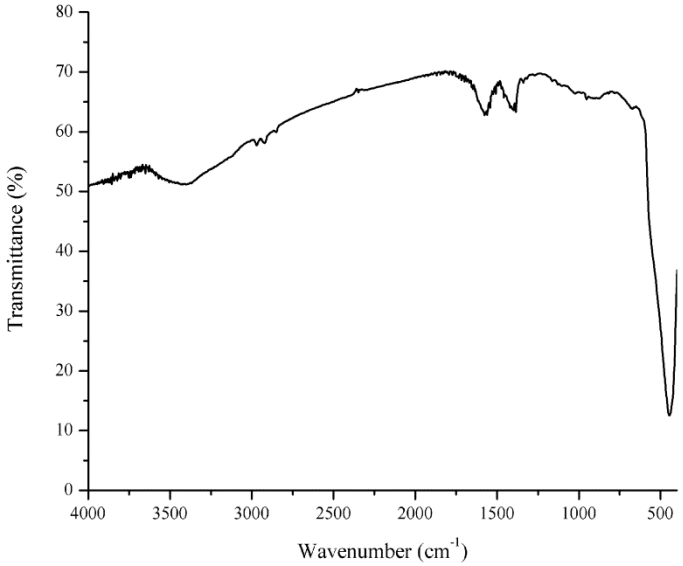

Fig. 3. FT-IR spectrum of ZnO obtained at an added water concentration of 2 M and 3 min of microwave irradiation time.

3.4 X-ray diffraction

Fig. 4 shows the XRD pattern of ZnO nanostructures obtained at the last mentioned conditions. The peaks in the XRD pattern are indexed according to the JCPDS data of the wurtzite structure of ZnO (36-1451). XRD peaks in the pattern at 31.8°, 34.5° and 36.4° correspond to the (100), (002) and (101) crystal planes, respectively. These peaks were used in the Scherrer equation in order to determine the crystal size of the obtained product. Result of this equation shows a crystal size of about 24 nm, which is larger than the exciton Bohr radius (2.34 nm) of bulk ZnO [17]. Therefore, there is no quantum confinement effect, and the blue-shift observed in the UV-Vis spectrum can be attributed to others reasons as surface chemical environment [16].

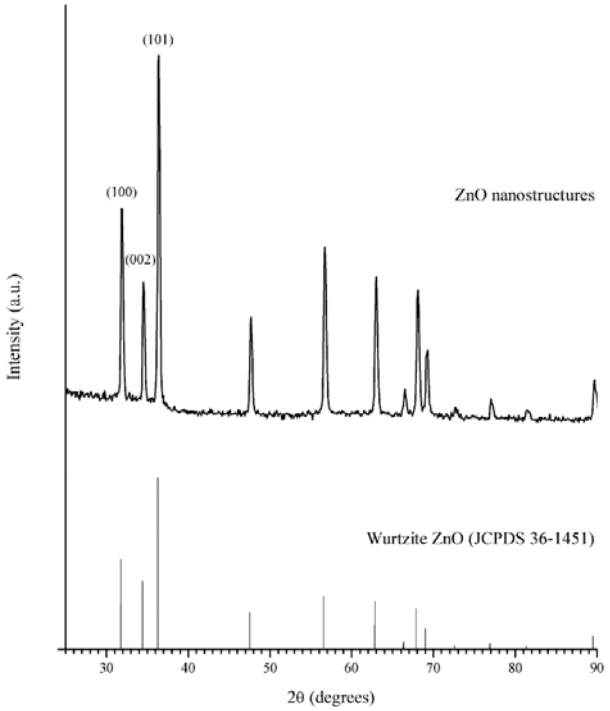

Fig. 4. DRX pattern of ZnO obtained at an added water concentration of 2 M and 3 min of microwave irradiation time, and its comparison with the standard pattern of ZnO in wurtzite phase (JCPDS 36-1451).

4. Conclusions

ZnO nanoparticles were obtained with hexagonal crystalline structure using a microwave-assisted solvothermal method. These nanoparticles have a minimum average diameter of 37 nm, which are agglomerated into irregular and spheroidal nanostructures with dimensions larger than 1 μm and high porosity. Mesopores and macropores with hexagonal geometry were found. It was determined that the size of the ZnO nanostructures is not a function of microwave irradiation time and water concentration. We suggest that the effect of other parameters such as pH, pressure, solvent dielectric constant and cooling rate, over the size and morphology of the ZnO nanostructures, should be studied.

References

[1] C. Klingshirn, J. Fallert, H. Zhou, J. Sartor C. Thiele, F. Maier-Flaig, D. Schneider, H. Kalt, Phys. Status Solidi B **247**, 1424 (2010).
[2] L. Li, T. Zhai, Y. Bando, D. Golberg, Nano Energy **1**, 91 (2012).
[3] A. Wadeasa, S. L. Beegum, S. Raja, O. Nur, M. Willander, Appl. Phys. A **95**, 807 (2009).
[4] J. Katayama, K. Ito, M. Matsuoka J. Tamaki, J. Appl. Electrochem. **34**, 687 (2004).
[5] J. Becker, K. R. Raghupathi, J.S. Pierre, D. Zhao, R. T. Koodali, J. Phys. Chem. C **115**, 13844 (2011).
[6] J. Zhou, P. Fei, Y. Gu, W. Mai, Y. Gao, R. Yang, G. Bao C. Chang, Nano Lett. **8**, 3973 (2008).
[7] Z. Shao, W. Zhu, Z. Li, Q. Yang G. Wang, J. Phys. Chem. C **116**, 2438 (2012).
[8] J. D. Mackenzie, E. P. Bescher, Acc. Chem. Res. **40**, 810 (2007).
[9] S. K. N. Ayudhya, P. Tonto, O. Mekasuwandumrong, V. Pavarajarn, P. Praserthdam, Cryst. Growth Des. **6**, 2446 (2006).
[10] C. L. Kuo, T. J. Kuo, M. H. Huang, J. Phys. Chem. B **109**, 20115 (2005).
[11] S. Cho, S. H. Jung, K. H. Lee, J. Phys. Chem. C **112**, 12769 (2008).
[12] S. Das, A. K. Mukhopadhyay, S. Datta, D. Basu, Bull. Mater. Sci. **32**, 1 (2009).
[13] P. Zhu, J. Zhang, Z. Wu, Z. Zhang, Cryst. Growth Des. **8**, 3148 (2008).
[14] A. Vázquez, J. Aguilar-Garib, I. López, O. Cavazos, I. Gómez, Rev. Mex. Fis. **S55**, 57 (2009).
[15] Z. Hu, D. J. Escamilla, B. E. Heredia, G. Oskam, P. C. Searson, J. Phys. Chem. B **109**, 11209 (2005).
[16] Y. Q. Wang, W. D. Chen, X. B. Liao, Z. X. Cao, Nanotechnol. **14**, 1235 (2003).
[17] C. Li, G. Fang, F. Su, G. Li, X. Wu, X. Zhao, Nanotechnol. **17**, 3740 (2006).
[18] C. H. Lu, C. H. Yeh, Mater. Lett. **33**, 129 (1997).
[19] T. Krishnakumar, R. Jayaprakash, D. S. Raj, N. Pinna, V. N. Singh, A. R. Phani, G. Neri, J. Nanopart. Res. **13**, 3327 (2011).