CHEMICAL ENGINEERING TRANSACTIONS Volume 17, 2009
Editor Sauro Pierucci
 ISBN 978-88-95608-01-3 ISSN 1974-9791
DOI: 10.3303/CET0917170

Synthesis of ZnO Nanostructures in Low Reaction Temperature

Marivone Gusatti[1], Jeane A. Rosário[1], Gilvan S. Barroso[1], Carlos E. M. Campos[2], Humberto G. Riella[1], Nivaldo C. Kunhen[1]
[1] LABMAC, Departamento de Eng. Química, Universidade Federal de Santa Catarina
[2] LSCM, Departamento de Física, Universidade Federal de Santa Catarina
LABMAC, Departamento de Eng. Química, Universidade Federal de Santa Catarina, Campus Trindade, Caixa Postal 476, 88.040-900, Florianópolis, SC, Brasil.

In this work, ZnO nanostructures were synthesized via solochemical method in the reaction temperature of 70°C without any posterior treatments. Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) and sodium hydroxide (NaOH) were adopted as synthesis precursors and the production of ZnO nanostructures occurred in few hours. The ZnO nanostructures obtained were characterized by X-ray diffraction (XRD), transmission electronic microscopy (TEM) and the Rietveld method. The ZnO powders have hexagonal *wurtzite* structure and nanometric-sized crystallites. The TEM image of the sample showed that the powder has, predominantly, a nanometric rod-like morphology.

1. Introduction

The development of new materials on the length scale of approximately 1-100 nm has become the focus of the investigations currently due to progress in all areas of industry and technology (Gleiter, 2000). These nanomaterials have unique properties and functions that are substantially different from those of bulk materials due to their small size and large surface area (Cushing et al., 2004; Alivisatos, 1996). Parameters such as size, distribution of size and morphology may significantly alter the electrical, optical and magnetic properties, which determine the practical applications of nanomaterials (Lisiecki, 2005).

Among the nanomaterials with industrial relevance stands out zinc oxide (ZnO), an *n*-type semiconductor that displays a hexagonal crystalline *wurtzite*-type structure, with space group $P6_3mc$ and lattice parameters of $a = b = 0.3250$ nm and $c = 0.5207$ nm (Liu et al., 2001). The importance of ZnO is due to its unusual physical properties such as high conductance, chemical and thermal stability (Kaur et al., 2006), wide and direct band gap of 3.37 eV (Kubota et al., 2003) and a high excitation binding energy of 60 MeV (Singh et al., 2007). Moreover, it has good radiation resistance (Reynolds et al., 2001) and is harmless to the environment (Wu et al., 2006).

The ZnO nanostructures has great potentiality for being used in preparing solar cell, acoustic, electrical and optical devices, chemical sensors (Hong et al., 2006; Wu et al., 2006), catalysts, pigments, cosmetics, varistors and gas sensors (Park et al., 2004; Vaezi

Please cite this article as: Gusatti M., Rosario J., Barroso G.S., Campos C.E.M., Riella H. and Kunhen N.C., (2009), Sinthesys of zno nanostructures in low reaction temperature, Chemical Engineering Transactions, 17, 1017-1022 DOI: 10.3303/CET0917170

and Sadrnezhaad, 2007). Different techniques are employed to produce these nanostructures, such as molecular beam epitaxy, thermal decomposition, hydrothermal method, synthesis by vapor phase (Hu and Chen, 2008), precipitation (Cai et al., 2008), sol-gel (Moghaddam and Saeidian, 2007) and solochemical method (Vaezi and Sadrnezhaad, 2007). Among the techniques employed, those belonging to the chemical routes are suitable for the preparation of ZnO nanostructures in industrial scale (Wu et al., 2006) since are relatively cheap and provide a high uniformity of the final product (Hu and Chen, 2008).

As a method for preparing high-quality ZnO powders, the solochemical synthetic route has advantage to obtain high crystallized powders and with high purity, without necessity of any posterior treatments. The particle properties such as morphology and size can be altered via this method by adjusting of parameters such as reaction temperature, concentration and reaction time. Compared with other techniques, this synthetic route presents as advantages the production of nanostructures in a short reaction time and in relatively low temperatures. Due the simplicity, versatility and low cost of this route, the solochemical method is a process extremely viable for industrial production of zinc oxide (Vaezi and Sadrnezhaad, 2007). However, the use of this method in the preparation of nanostructures is new and few studies involving this technique have been published.

This study aims the achievement of ZnO nanostructures in the reaction temperature of 70°C by the solochemical method using zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) and sodium hydroxide (NaOH) without any posterior treatments. The product obtained was characterized by X-ray diffraction (XRD) technique and the Rietveld method. The morphology and size of the ZnO particles were evaluated by transmission electronic microscopy (TEM).

2. Experimental Procedure

All the reagents used in this experiment, NaOH and $Zn(NO_3)_2.6H_2O$, were of analytical grade and were used without any further purification.

The production unit of ZnO nanostructures consists basically of a jacketed three-neck glass flask and of a magnetic stirrer with temperature control. In the three-neck glass flask, NaOH was dissolved in deionized water to a concentration of 1.0 M and the resulting solution was heated, under constant stirring, to the temperature of 70°C. After achieving this temperature, a solution of 0.5 M $Zn(NO_3)_2.6H_2O$ was added slowly (dripped for 60 minutes) into the three-neck glass flask containing the NaOH aqueous solution under continual stirring. In this procedure the reaction temperature was constantly maintained in 70°C.

The suspension formed with the dropping of 0.5 M $Zn(NO_3)_2.6H_2O$ solution to the alkaline aqueous solution was kept stirred for two hours in the temperature of 70°C. The material formed was filtered and washed several times with deionized water. The washed sample was dried at 65°C in oven for several hours.

The yield of the ZnO nanostructures by this method is about 95%.

The crystalline structure of the dried powder was assessed by XRD with a Rigaku diffractometer (Mini-Flex model) using Cu Kα (λ = 1.5418 Å) as incident radiation. To obtain the average crystallite size and microstrain, the X-ray diffraction pattern was

fitted with a TCH-pseudo-Voigt profile function by the Rietveld method using the GSAS program package (Larson and Von Dreele, 2000; Toby, 2001). Refinement was carried out from a starting model based on information given in the Inorganic Crystal Structure Database (ICSD). The size and morphology of the ZnO particles synthesized were evaluated by transmission electron microscopy (TEM, JEOL 2100) under maximum acceleration voltage of 200 kV.

3. Results and discussion

The XRD pattern of the ZnO nanostructures synthesized at 70°C by the solochemical method is shown in Figure 1(a). The XRD pattern reveals that all peaks correspond to the characteristic peaks of the hexagonal *wurtzite* structure of ZnO (space group $P6_3mc$) reported in ICSD card (No. 57450). No peaks of any other phase were detected, indicating that the ZnO sample obtained by current synthetic route is high pure. The sharp peaks indicate that the product was well crystallized.

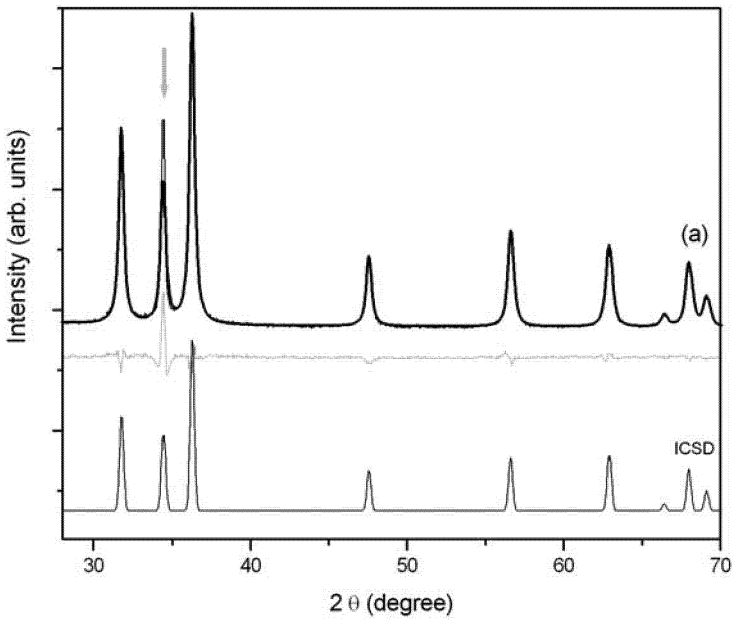

Figure 1. Experimental and fitted XRD patterns of the ZnO sample prepared by the solochemical method at (a) 70°C. The difference between experimental and fitted is shown in light gray. Dummy pattern of the ICSD card no. 57450 is also presented.

Pattern (a) was further analyzed by Rietveld refinement. There is a slight misfit of the (0 0 2) reflection (see arrow in Figure 1) and it is interesting to notice no satisfactory improvements of the fitting was achieved neither considering anisotropic nor preferential orientation terms. Quantitative analysis revealed that the powder consists of single phase ZnO with lattice parameters a = 3.2533 Å and c = 5.2120 Å, (3.2494 and

5.2038 Å for the card no. 57450), average crystallites size of 25.38 nm and microstrain of 0.21%.

The morphology and particle size of ZnO sample synthesized at 70°C were examined by using TEM, as shown in Figure 2. As can be seen, the particles display rod-like form basically, which indicate the growth of the nanostructures along a certain direction. The particle size determined from TEM varies between 25 and 28.5 nm. This value is in reasonable agreement with that calculated from XRD peaks.

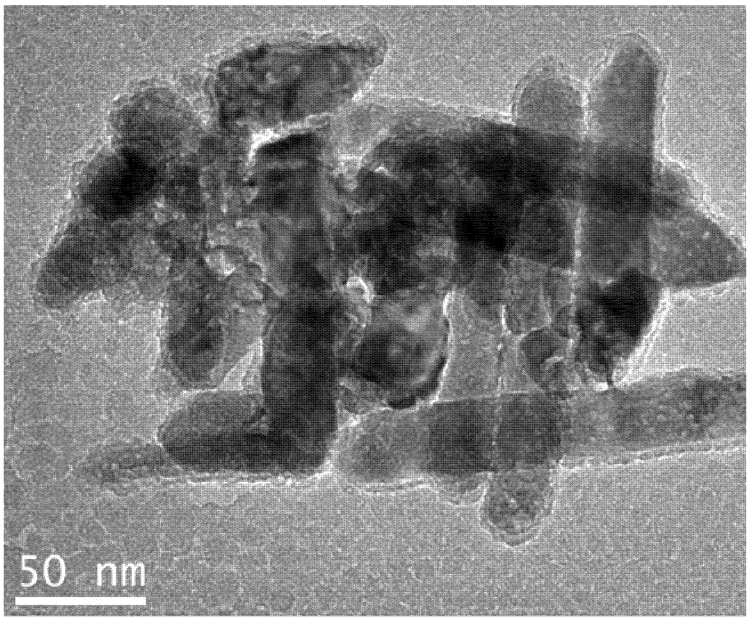

Figure 2. TEM micrograph of ZnO nanostructures obtained by the solochemical method at 70°C.

4. Conclusion

This work shows that ZnO nanostructures can be produced in few hours by solochemical method. The route of synthesis employed showed to be promising, allowing the obtainment of ZnO nanostructures of high quality, effortlessness and at relatively low temperatures. The X-ray diffraction results confirmed the synthesis process efficiency, showing only the hexagonal phase pattern, and the nanometric character of the crystallites produced. The TEM image of the sample obtained showed that the powder has, predominantly, a nanometric rod-like morphology.

References

Alivisatos A.P., 1996, Perspectives on the physical chemistry of semiconductor nanocrystals, J. Phys. Chem. 100, 13226-13239.

Cai K.F., He X.R. and Zhang L.C., 2008, Fabrication, properties and sintering of ZnO nanopowder, Mater. Lett. 62, 1223–1225.

Cushing B.L., Kolesnichenko V.L. and O'Connor C.J., 2004, Recent advances in the liquid-phase syntheses of inorganic nanoparticles, Chem. Rev. 104, 3893-3946.

Gleiter H., 2000, Nanostructured materials: basic concepts and microstructure, Acta mater. 48, 1-29.

Hong R., Pan T., Qian J. and Li H., 2006, Synthesis and surface modification of ZnO nanoparticles, Chem. Eng. J. 119, 71-81.

Hu Y. and Chen H.J., 2008, Preparation and characterization of nanocrystalline ZnO particles from a hydrothermal process, J. Nanopart. Res. 10, 401-407.

Kaur R., Singh A.V., Sehrawat K., Mehra N.C. and Mehra R.M., 2006, Sol–gel derived yttrium doped ZnO nanostructures, J. Non-Cryst. Solids 352, 2565-2568.

Kubota J., Haga K., Kashiwaba Y., Watanabe H., Zhang B.P. and Segawa Y., 2003, Characteristics of ZnO whiskers prepared from organic-zinc, Appl. Surf. Sci. 216, 431-435.

Larson A.C. and Von Dreele R.B., 2000, Generalised Crystal Structure Analysis System (GSAS). Los Alamos National Laboratory Report LAUR, California.

Lisiecki I., 2005, Size, shape, and structural control of metallic nanocrystals, J. Phys. Chem. B 109, 12231-12244.

Liu R., Vertegel A.A., Bohannan E.W., Sorenson T.A. and Switzer J.A., 2001, Epitaxial electrodeposition of zinc oxide nanopillars on single-crystal gold, Chem. Mater. 13, 508-512.

Moghaddam F.M. and Saeidian H., 2007, Controlled microwave-assisted synthesis of ZnO nanopowder and its catalytic activity for O-acylation of alcohol and phenol, Mater. Sci. and Eng. B 139, 265-269.

Park J.-H., Oh S.-G. and Jo B.-W., 2004, Fabrication of silver nanotubes using functionalized silica rod as templates, Mater. Chem. Phys. 87, 301–310.

Reynolds D.C., Look D.C. and Jogai B., 2001, Fine structure on the green band in ZnO, J. Appl. Phys. 89, 6189-6191.

Singh S., Thiyagarajan P., Kant K.M., Anita D., Thirupathiah S., Rama N., Tiwari B., Kottaisamy M. and Rao M.S.R., 2007, Structure, microstructure and physical properties of ZnO based materials in various forms: bulk, thin film and nano, J. Phys. D: Appl. Phys. 40, 6312-6327.

Toby B.H., 2001, EXPGUI, a graphical user interface for GSAS, J. Appl. Cryst. 34, 210-213.

Vaezi M.R. and Sadrnezhaad S.K., 2007, Nanopowder synthesis of zinc oxide via solochemical processing, Mater. Des. 28, 515-519.

Wu C., Qiao X., Chen J., Wang H., Tan F. and Li S., 2006, A novel chemical route to prepare ZnO nanoparticles, Mater. Lett. 60, 1828-1832.