Available online at www.sciencedirect.com

ScienceDirect

Procedia Materials Science 11 (2015) 320 – 325

Procedia Materials Science

www.elsevier.com/locate/procedia

5th International Biennial Conference on Ultrafine Grained and Nanostructured Materials, UFGNSM15

Microwave-assisted synthesis of zinc oxide nanoparticles

M.Hasanpoor[a], M. Aliofkhazraei[a,*], H. Delavari[a]

[a]*Department of Materials Engineering, Faculty of Engineering, Tarbiat Modares University, P.O. Box: 14115-143, Tehran, Iran*

Abstract

Synthesis of nanoparticles and ultrafine particles of zinc oxide with controlled morphology using microwave irradiation is carried out by various methods. The effect of type of precursor as well as the time and the microwave irradiation power on the structure and size of ZnO nanoparticles have been studied. Particles Studied by SEM, TEM images and XRD analyze. By increasing the time of synthesis from 10 to 15 minutes needle-shaped particles with a diameter of 50-150 nm can be achieved. While increasing the microwave power from 540 to 680 watts, flower-shaped particles are obtained. By replacing zinc nitrate with zinc acetate, at different power and time of irradiation, needle-shaped particles are obtained and diameter of needles is decreased.

Peer-review under responsibility of the organizing committee of UFGNSM15

Keywords: Nanoparticle; Zinc oxide; Microwave; Synthesis; Hydrothermal.

1. Introduction

ZnO is a semiconductor with a wide band gap (3.37 eV) and a large binding energy (E_g=60 meV) that we can expect an exciton emission at room temperature under low excitation energy. Its functional properties such as non-toxic, gas sensors, photocatalytic agent optical devices, serve it as an important oxide in the laboratory applications. ZnO nanostructure is used in catalytic reaction process due to its large surface area and high catalytic activity, Comini et al. , Bayoumy et al. (2013), Fodor et al. (2014), Periyat et al. (2015), Seo et al. (2015). Some of the properties such as physical and chemical properties changed in different morphology, so the physical and chemical properties of synthesized zinc oxide are to be investigated in terms of its morphology, Al-Gaashani et al. (2011), Liang et al. (2014). on the other hand, ZnO nanoparticles have some attractive application in nanolasers and semiconductor material, Wu et al. (2014). In the literature, for micro and nanostructure ZnO productions several

* Corresponding author. Tel.: +98 912 6905626; fax: +98 21 82884969.
E-mail address: khazraei@modares.ac.ir

Peer-review under responsibility of the organizing committee of UFGNSM15
doi:10.1016/j.mspro.2015.11.101

methods have been studied such as metal-organic chemical vapor deposition (MOCVD), vapor phase deposition, sol-gel, laser ablation, hydrothermal methods, electrochemical depositions, thermal deposition and combustion method, Guillén et al. (2015), Fragalà et al. (2011), Sáenz-Trevizo et al. (2015). In this method, hydrothermal reaction conditions control the size and morphology of zinc oxide particles; although, in chemical methods the reaction time is generally too long. In the previous studies of the hydrothermal syntheses of zinc oxide, reaction procedure has been investigated. Briefly, in alkaline solution (i.e. pH 11.5) $Zn(OH)_4^{2-}$ ions make up the majority of the solution species and then, this ion decompose into $Zn(OH)_2$ at moderate temperature after calcination zinc hydroxide decompose into zinc oxide.

Recently, microwave-assisted synthesis methods have been widely used to produce oxide, hydroxide, sulfide nanoparticles, and etc, Zhao et al. (2011). This method is simple, clean, and without thermal gradient effects problems, Pimentel et al. (2014). Some of the advantage of this method in comparison to convenient hydrothermal methods are (a) quick reaction, (b) simple medium, (c) short time to reach the suitable temperature for reaction, and (d)its morphology of particles are in control.

In this paper, zinc oxide nanoparticle synthesized with different morphologies by using a microwave-assisted hydrothermal method. In this process, changing in power and time of microwave irradiation caused different ZnO morphologies.

2. Experimental procedure

2.1. Preparation of ZnO nanostructured materials

Zinc oxide nanostructure were fabricated from aqueous solutions of zinc nitrate-6-hydrate (Zn(NO3)2.6H2O), zinc acetate dehydrate (Zn(CH3COO).2H2O) and hydrazine hydrate (N2H4) and ammonia (NH3). All chemical reagents used were analytical-grade purity. Schematic chart of experimental procedure is illustrated in Fig. 1. At first solution which is called A, 100 ml aqueous solution of zinc ion with 0.06 M concentration have been prepared, then ammonia was added to reach the pH of 11.5. Subsequently, prepared aqueous solutions was irradiated in two different groups,A1 and A2, with a microwave synthesis instrument (LG-MS1040SM) for 15 min at 510 W (A1)and 10 min at 680 W(A2), respectively. At second solution zinc acetate and hydrazine hydrate were mixed in a molar ratio of 1:4 in 100 ml of deionized water under fast stirring for 30 min, then prepared solution irradiated with microwave oven for 15 min at 150 Watts, this solution called B. All preparing nanoparticle procedures for three precursors were done uniformly. Ultrasonic treatment was performed for 30 minutes. Finally, after collecting, the zinc oxide nanoparticles were centrifuged for 10 min. Then, nanoparticles washed with deionized water four times and anhydrous methanol two times; prepared nanoparticles were cooled in dryer oven at 100◦ C for 2 h.

2.2. Characterization

After preparation of nanoparticles, structure of samples was analyzed with a X-ray diffraction (XRD) (X'Pert MPD) using the Co Kα (λ=1.79(Å)) radiation source. Synthesis nanoparticles size was studied using a Transmission Electron Microscopy (Philips CM30). The SEM (Philips xl30) images presented in Fig. 2 showed different particle size in various precursors. Morphology of synthesized nanoparticles were studied with Scanning Electron Microscope.

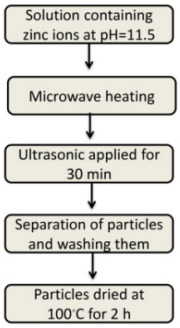

Fig. 1. Experiment procedure flow chart for the fabrication of zinc oxide nanoparticles.

3. Results and discussion

Using two different powers in same precursors (A1 and A2) make separate shape of ZnO nanoparticles. Lower irradiation power (540 W), for precursor A1, yielded needle-shape and higher irradiation power (680 W), for precursor A2, yielded zinc oxide with flower-shape morphology, Cao et al. (2004), Cao et al. (2011), Li et al. (2011), Rai et al. (2012). The addition of ammonia has wide effect on the aqueous solution, depending on the amount of ammonia into the solution, different zinc hydroxide complex like $Zn(OH)^{+}$, $Zn(OH)_2$, $Zn(OH)^{-}_3$, $Zn(OH)^{2-}_4$ will be appeared. Studies on the molar ratio of zinc ion and hydroxide ion showed that, as the amount of ammonia in solution increases, the amount of hydroxide ion (OH^-) increase, when molar ration between these ions was 1:2 (Zn^{2+} **:** OH^-) $Zn(OH)_2$ fabricated, With most adding ammonia in solution for increasing in the amount of hydroxide ions, $Zn(OH)^{-}_3$, $Zn(OH)^{2-}_4$ ions will be fabricated. According to reaction equation, reaction between water and ammonia create hydroxide ions and then these ions reaction with zinc cation ions and make zinc hydroxide complex, Belomestnykh et al. (1987), Wang et al. (2011).

1) $Zn(NO)_3(s) + 2NH_3(l) + 2H_2O(l) \longrightarrow Zn(OH)_2(s) + 2NH_4NO_3(aq)$

2) $NH_3(l) + H_2O(l) \longrightarrow NH_4^+(aq) + OH^-(aq)$

According to studies, exchanging zinc hydroxide to zinc oxide following dissolution-reprecipitation mechanism, Jia et al. (2012), Jia et al. (2013). By increasing the concentration of zinc ions in solution the amount of $Zn(OH)_2$ deposits increases, Jiang et al. (2011). By applying microwave irradiation power at 680 W, Fig. 2c, sufficient energy for reaction initiation is given to the solution so particles growt in flower-shape.

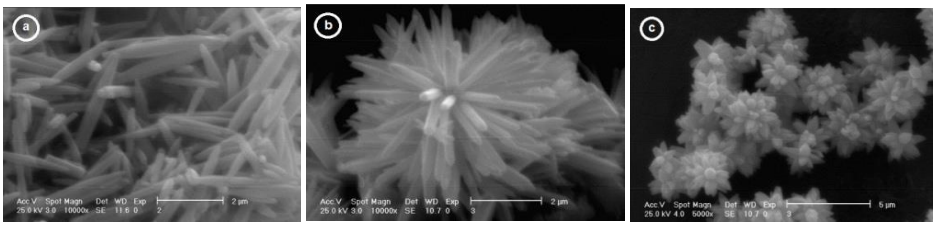

Fig. 2. (a) zinc oxide nanorods produced from B solution; (b) irradiation applied for 15 min at 540 watts microwave power to precursor A1;

(c) irradiation applied for 10 min at 680 watts microwave power to precursor A2.

The XRD analyzed patterns for as-prepared particles presented in Fig. 3(a-c) that show precursor A1, A2 and B, respectively. Conform peaks at 2θ= 37.3, 40.19, 42.31, 55.78, 66.72, 74.5 and 78.85 were observed for zinc oxide nanoparticles. These picks represents diffraction plans respectively in (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), and (1 1 2) of wurzite-type hexagonal ZnO, Köseoğlu (2014), Caglar et al. (2015). Between the recognized peaks, (1 0 1) plane was the prominent one, so growth orientation was on this plane.

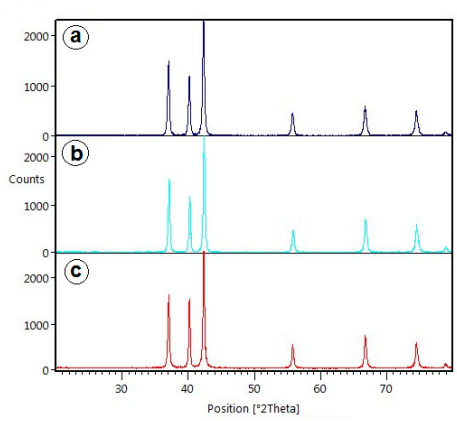

Fig. 3. The XRD analyze patterns for (a) precursor A1; (b) precursor A2; (c) precursor B.

The SEM images of zinc oxide nanoparticles are shown in Fig. 2a and 2c, these images belong to precursors A1, A2 and B, respectively. As can be seen in Fig. 2a ZnO nanoparticles have needle-type, ultrasonic treatment for 30 min separating these needles. It is obvious from Fig. 2b, by increasing the microwave power from 510 to 680 watts, the shape of nanoparticles completely changed into flower-type, Wang et al. (2013). In order to considering the effect of precursors on morphology of ZnO nanoparticles zinc acetate was replaced with zinc nitrate and hydrazine hydrate was added to solvent as reduction agent. As can be seen in Fig. 2a with changing in raw materials, nanoparticles morphology has been changed to needle-type with uniform distribution. Fig. 4 shows TEM image of precursor A1 after calcination for 3 hours at 600◦C. In this magnification, the particles are spherical, while its dimensions are not identical, Ma et al. (2013). In comparison with Fig. 2b, TEM image is entirely different from SEM image, on the other hand, synthesis pattern is different in microwave-assisted hydrothermal procedure and particles with different size are synthesis.

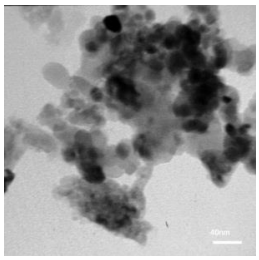

Fig. 4. TEM image of ZnO nanoparticle synthesized in domestic microwave oven, In power of 510 watts for 15 minutes.

4. Conclusion

In summary, zinc oxide nanoparticles with various morphology and particle size successfully synthesis with microwave-assisted hydrothermal procedure. Flower-type, needle-type and spherical type nanoparticles have successfully synthesized with this hydrothermal procedure. XRD analyses and SEM images let us to conclude that formation of zinc oxide nanoparticle, following dissolution-precipitation of $Zn(OH)_4^{2-}$.

Reference

Agocs, E., Fodor, B., Pollakowski, B., Beckhoff , B., Nutsch, A., Jank, M., Petrik, P., 2014. Approaches to calculate the dielectric function of ZnO around the band gap. Thin Solid Films 571(3), 684-688.

Al-Gaashani, R., Radiman, S. Tabet, N., Daud, A.R., 2011. Effect of microwave power on the morphology and optical property of zinc oxide nano-structures prepared via a microwave-assisted aqueous solution method. Materials Chemistry and Physics 125(3), 846-852.

Belomestnykh, I. P., Voikina, N. V., 1987. Phase Composition of Products of The Reaction Of Zinc and Chromium Nitrates with Ammonia and its Effect on the Catalytic Properties of Zinc-Chromium Oxide Systems. Kinetics and Catalysis 28(3 Pt 2), 602-608.

Caglar, Y.Y., Gorgun, K. Aksoy, S., 2015. Effect of deposition parameters on the structural properties of ZnO nanopowders prepared by microwave-assisted hydrothermal synthesis. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 138, 617-622.

Cao, J., Wang, J., 2004. Microwave-assisted synthesis of flower-like ZnO nanosheet aggregates in a room-temperature ionic liquid. Chemistry Letters 33(10), 1332-1333.

Cao, Y., Liu, B., Huang, R., Xia, Z., Ge, S., 2011. Flash synthesis of flower-like ZnO nanostructures by microwave-induced combustion process. Materials Letters 65(2), 160-163.

Fragalà, M. E., Aleeva, Y. Malandrino, G., 2011. Effects of Metal-Organic Chemical Vapour Deposition grown seed layer on the fabrication of well aligned ZnO nanorods by Chemical Bath Deposition. Thin Solid Films 519(22), 7694-7701.

Galstyan, V., Comini, E., Nanostructured ZnO Chemical Gas sensors. Ceramics International.

Guillén, G. G., Palma, M. I. M., Krishnan, B., 2015. Structure and morphologies of ZnO nanoparticles synthesized by pulsed laser ablation in liquid: Effects of temperature and energy fluence. Materials Chemistry and Physics 162, 561–570.

Jia, W., Dang, S., 2012. Evidence of the formation mechanism of ZnO in aqueous solution. Materials Letters 82, 99-101.

Jia, W., Li, T. B., 2013. Formation mechanism of ZnO prepared by chemical bath deposition. Rengong Jingti Xuebao/Journal of Synthetic Crystals 42(10), 2007-2012.

Jiang, Y., Sheng, Y., Lan, X., Wang, C., Li, S., Liu, X., Zhong, H., 2011. Mechanism and growth of flexible ZnO nanostructure arrays in a facile controlled way. Journal of Nanomaterials 2011, No. 4.

Köseoğlu, Y., 2014. A simple microwave-assisted combustion synthesis and structural, optical and magnetic characterization of ZnO nanoplatelets. Ceramics International 40(3), 4673-4679.

Li, H., Liu, E., Chan, F.Y.F., Lu, Z., Chen, R., 2011. Fabrication of ordered flower-like ZnO nanostructures by a microwave and ultrasonic combined technique and their enhanced photocatalytic activity. Materials Letters 65(23–24), 3440-3443.

Liang, S., Zhu, L., 2014. Synthesis of morphology-controlled ZnO microstructures via a microwave-assisted hydrothermal method and their gas-sensing property. Ultrasonics Sonochemistry 21(4), 1335-1342.

Ma, J., Liu, J., Bao, Y., Zhu, Z., Wang, X., Zhang, J., 2013. Synthesis of large-scale uniform mulberry-like ZnO particles with microwave hydrothermal method and its antibacterial property. Ceramics International 39(3), 2803-2810.

Mousa, M. A., Bayoumy, W. A. A., Khairy, M., 2013. Characterization and photo-chemical applications of nano-ZnO prepared by wet chemical and thermal decomposition methods. Materials Research Bulletin 48(11), 4576-4582.

Periyat, P., Ullattil S. G., 2015. Sol–gel derived nanocrystalline ZnO photoanode film for dye sensitized solar cells. Materials Science in Semiconductor Processing 31, 139-146.

Pimentel, A., Nunes, D., Duarte, P., 2014. Synthesis of long ZnO nanorods under microwave irradiation or conventional heating. Journal of Physical Chemistry C 118(26), 14629-14639.

Rai, P., Kim, S. G., Yu, Y.T., 2012. Microwave assisted synthesis of flower-like ZnO and effect of annealing atmosphere on its photoluminescence property. Journal of Materials Science: Materials in Electronics 23(2), 344-348.

Sáenz-Trevizo, A., Amézaga-Madrid, P., 2015. Single and multi-layered core-shell structures based on ZnO nanorods obtained by aerosol assisted chemical vapor deposition. Materials Characterization 105, 64-70.

Seo, H.-K., Shin H.S., 2015. Study on photocatalytic activity of ZnO nanodisks for the degradation of Rhodamine B dye. Materials Letters 159, 265-268.

Wang, H., Li, C., 2013. Preparation of nano-sized flower-like ZnO bunches by a direct precipitation method. Advanced Powder Technology 24(3), 599-604.

Wang, M., Zhou, Y., Zhang, Y., Hahn, S.H., Kim, E.J., 2011. From Zn(OH)2 to ZnO: a study on the mechanism of phase transformation. CrystEngComm 13(20), 6024-6026.

Wu, K.-H., Peng, L.Y., 2014. Fabrication and optimization process of p-type Li: ZnO oxide semiconductor. Thin Solid Films 570, Part B, 417-422.

Zhao, J., Yan W., 2011. Chapter 8 - Microwave-assisted Inorganic Syntheses. Modern Inorganic Synthetic Chemistry. R. Xu, W. Pang and Q. Huo. Amsterdam, Elsevier: 173-195.