Microwave assisted hydrothermal synthesis of ZnO nanorods and their characterization

NADI SHOJAEE

*Ceramic Department, Materials & Energy Research Center,
Tehran, P.O.Box. 14155-4777, Iran
n_shojaee@merc.ac.ir*

TOURADJ EBADZADEH

*Ceramic Department, Materials & Energy Research Center,
Tehran, P.O.Box. 14155-4777, Iran
t-ebadzadeh@merc.ac.ir*

ALIREZA AGHAEI

*Ceramic Department, Materials & Energy Research Center,
Tehran, P.O.Box. 14155-4777, Iran
a-aghaei@merc.ac.ir*

In present study ZnO nanorods were synthesized in an aqueous solution using a domestic microwave oven for irradiation. The nanorods have been grown on substrates immersed in an aqueous solution which contains zinc nitrate and hexamethylenetetramine as precursors. Eventually, effect of some parameters such as precursor's concentration and heating time on growth mechanism was characterized. The product phase was detected using X-ray diffraction (XRD). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) exhibited the resultant structure is uniform and single crystalline. Finally Uv-Vis spectroscopy was used to measure the nanorod's band gap.

Keywords: Zinc oxide; Nanorods; Hydrothermal; Microwave irradiation.

1. Introduction

As semi-conducting nanostructures has special behavior between atomic system and bulk materials, a great attempt is devoted to develop synthesizing methods recently. Zinc oxide is an intelligent material which has key applications in catalysts, piezoelectric transformers, UV light emitters, spin functional devices, gas sensors, transparent electronics and surface acoustic wave devices¹⁻⁴.

ZnO has special characteristics which introduce it as a unique material. These characteristic are: 1) The lack of a centre of symmetry in wurtzite, combined with large electromechanical coupling, results in strong piezoelectric and pyroelectric properties and the consequent use of ZnO in mechanical actuators and piezoelectric sensors⁵. 2) It is a semiconductor with a direct wide band gap near ultra violet (3.37eV) that can be tuned

via divalent substitution on the cation site⁶. 3) Its large excitonic binding energy (60 meV) which could lead to lasing action based on exciton recombination even above room temperature⁷. 4) It is bio-safe and it can be used in medical applications with no further coating⁸.

There are various processes used to synthesize ZnO nanostructures. The most common method to synthesize ZnO nanostructures utilizes a vapor transport process including CVD and carbothermal methods⁹⁻¹⁰. Mechanisms for ZnO nanostructure growth in this approach is vapor/liquid/solid (VLS) and vapor/solid (VS) mechanisms. Although the vapor transport process is the dominant synthesis method for growing semiconducting nanostructures such as ZnO, GaN and Si nanowires, other growth methods such as electrodeposition¹¹, sol-gel¹², catalyst assisted MBE¹³, *etc.* have been developed in parallel. Later many groups reported the growth of ZnO nanowires and other nanostructures from aqueous solution¹⁴. This approach doesn't need high pressure, temperature, vacuum, catalysts or templates. Also contrary to sol-gel method, in ZnO nanostructures synthesized through chemical bath deposition there is no need for further treatment. However, this route has crystallization problems because of low temperature resulted in presentation of a new microwave assisted hydrothermal method. In microwave heating the energy is delivered to the materials through molecular interactions with the electromagnetic field; it has potential advantages of uniform, rapid, and volumetric heating. Although a microwave oven consumes energy more than a simple oven, but when the energy consumption is considered during the necessary time for the process, it is obvious that using microwave is beneficial. Microwave irradiation has several preferences over traditional heating including rapid heating till crystallization point, homogenous nucleation and rapid supersaturation¹⁵. In the present study ZnO nanorods were synthesized via a rapid one-step chemical method, using microwave irradiation.

2. Experimental

In this process, Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and Methenamine (Hexa methylenetetramine; HMT: $(\text{CH}_2)_6\text{N}_4$) were used as Zinc and OH^- sources. Both raw materials were analytical reagents and purchased from MERK chemical Co. Ltd. and used with no further purification. Chemical reactions were done in a microwave oven (Panasonic NN-C2003S, frequency 2.45 GHz, maximum power 1000 W). Glass slides were used as substrates and washed ultrasonically for 5 minutes in alcohol, acetone and distilled water, individually. The molar ratio of Zn^{2+} to HMT was kept 1:1 in prepared solutions. The concentration of Zn^{2+} ions in prepared solutions was 0.1, 0.01 and 0.001 molar. The hydrothermal reaction was carried out in a sealed Teflon bottle heated by Microwave irradiation. The concentration of precursors and heating conditions were changed to characterize their effects on the morphology of nanostructures. After the reaction procedure, the substrates were washed with distilled water to remove any amorphous precipitations and dried in an ambient temperature. X-ray diffraction analysis (XRD) was performed using PHILIPS- PW3710 diffractometer with nickel-filtered Cu-

K_{α} radiation with scanning speed of 0.005 degrees/sec. The morphology of resultant powders was characterized using scanning electron microscopy (SEM) (Stereo Scan360–Leica /Cambridge) and transmission electron microscopy (TEM) (Philios- EM208S). A new statistical software (XY) was used in order to measure nanorods diameter and calculating average of them. The results were confirmed by the ordinary softwares such as Image J or Measurement. UV-vis absorption spectra analysis was recorded on a Sterlarnet spectrophotometer at room temperature.

3. Results and Discussions

The basic rules for microwave-assisted chemical synthesise is the same as what is used for hydrothermal process. In this method zinc nitrate is used as a source of zinc ions and HMT as a source of $(OH)^{-}$ that decomposes gradually. Formation of initial seeds is related to decomposition of zinc salt and HMT as follow:

Zinc oxide nanorods are formed through a two-step process: nucleation and growth. Utilizing microwave irradiation results in a rapid increase of temperature in the first step and formation of fine nuclei. Subsequently, ions in the solution will have contact with these seeds and grow them. This growth is because of the cleavage energy of $\{001\}$ plane which is 60% more than $\{100\}$ and $\{110\}$ non polar planes. As a result of $\{001\}$ plane's polar nature, the surface of ZnO particles is charged negatively or positively; this surface attracts ions with opposite charge (Zn^{+} or OH^{-}) resulting in a one dimensional growth¹⁶. Microwave irradiation in which the energy is transported through molecular interaction with electromagnetic field, has advantages of rapid, volumetric and homogenous heating¹⁷.

Figure 1-(a) illustrates X-ray pattern of resulted ZnO nanorods which were synthesized through irradiation of 0.1 M precursor under a power of 900W for 2 min. During the analysis it was found that because of very fine coating on substrate the characterization of resultant powder was impossible. In order to solve this problem the detection speed was decreased to 0.02 degrees per second. As it is shown in the Figure 1a, nanorods belong to the wurtzite structure ($P6_3mc$ space group, JCPDS^a card No. 36-1451) with lattice parameters of $a=0.32498$ nm and $c=0.52066$ nm. The result is completely in agreement with the reality that ZnO crystals most commonly stabilize with the wurzite structure (hexagonal symmetry), whereas the crystals exhibit the rock salt

^a Joint committee on powder diffraction standards

phase (cubic symmetry) at high pressure¹⁸. Figure 1-b presents TEM image of rod-like ZnO nanostructures which indicates the asymmetrical growth of nanorods. From the image it can be seen that the single rod is typically 100 nm thick and 530 nm long.

Fig. 1. (a) XRD pattern and (b) TEM image of resulted ZnO nanorods.

Figure 2 shows SEM micrographs of ZnO nanorods synthesised in a similar situation in order to compare how initial concentration affects on the final structure. The samples were prepared through irradiation of solutions with different concentrations (0.1, 0.01 and 0.001 M) under 900W for 2 min. Increasing the initial concentration of solution results in the formation of more nuclei in the first stage of precipitation, which has an important role in surface coverage. It seems that microwave irradiation increases the hydrolysis rate of zinc nitrate which is effective in nucleation of zinc oxide nanocrystals¹⁵. When a small portion of initial nuclei would be successful to grow, the rate of precursor consumption is reduced. Eventually, higher concentration leads to more seeds with lower diameters¹⁹. An important role of microwave irradiation is that heating rate is so high that the initial ions in the solution are mostly used to form seeds; the high amount of seeds results to a smaller final sizes and also a narrow size distribution compared to samples produced by a conventional hydrothermal method. As it is shown in Figure 2, since the components are decomposed very quickly in microwave irradiation, they don't have the opportunity to find and join each other. Therefore, in contrast to the traditional hydrothermal method in which low heating rate results in conjunction of initial seeds together increasing of concentration in microwave processing leads to a numerous amount of nuclei and finally the average diameters of nanorods are decreased from 136 to 126 and 117 nm while the concentration was increased from 0.001 to 0.01 and 0.1 respectively.

Figure 3 shows SEM micrographs of ZnO nanorods synthesized through irradiation of 0.1 M precursor in 900W for 2 and 3 minutes. As mentioned previously, at the first stage great amounts of seeds will form in the solution, while after the nucleation step the nanocrystals will grow up. In other words, at the early stage of the process, the growth is in the radius direction; afterwards the nanorods will grow longitudinal. As it is shown in

Figure 3, increasing irradiation time from 2 to 3 minutes leads to a intangible growth in particle size. The average diameters of resultant nanorods are nearly in the same order (112 and 117 nm) while the heating time is increased from 2 min to 3 min. However, it can be seen to some extent that the nanorods grown during 3 min irradiation are longer than the other sample irradiated for 2 min which is similar to particles rather than rods.

Fig. 2. SEM micrographs and grain size distributions of nanorods synthesized with initial concentrations of (a) 0.001 (b) 0.01 and (c) 0.1 M.

Fig. 3. SEM micrographs and grain size distributions of nanorods synthesized during (a) 2 min and (b) 3 min irradiation.

Fig. 4. Uv-Vis absorbance spectroscopy of ZnO nanorods.

The preliminary study on the band gap of samples was carried out and the result is shown in Figure 4. From this figure it can be observed that the nanorods have a band edge at 375nm which has a small blue shift regarding excitonic absorption in bulk ZnO (380nm).

Conclusion

One-dimensional hexagonal wurtzite structured ZnO nanorods were successfully produced using zinc nitrate and methenamine aqueous solutions with a microwave-hydrothermal process. The resultant products were characterized through SEM and TEM microscopy, XRD and UV-Vis spectroscopy analysis. It was found that the concentration of precursors and heating conditions had significant influences on the density and dimensions of the grown nanorods.

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References

1. K. Nomura, H. Ohta, K. Ueda, T. Kamiya, M. Hirano, and H. Hosono, *Science* **300**, 1269 (2003).
2. S. Y. Lee, E. S. Shim, H. S. Kang, S. S. Pang, and J. S. Kang, *Thin Solid Films* **437**, 31 (2005).
3. R. Könenkamp, R. C. Word, and C. Schlegel, *Appl. Phys. Lett.* **85**, 6004 (2004).
4. E. Comini, G. Faglia, G. Sberveglieri, Z.W. Pan, Z.L. Wang, *Appl. Phys. Lett.* **10**, 81 (2002).
5. Z. L. Wang, *Condens. Matter* **16**, R829 (2004).
6. S.J. Pearton, D.P. Norton, K. Ip, Y.W. Heo, T. Steiner, *Prog. Mater. Sci.* **50**, 293 (2005).
7. Ü. Özgür, Ya. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Doğan, V. Avrutin, S.-J. Cho, and H. Morkoç, *J. Appl. Phys.* **98**, 041301 (2005).
8. Z. L. Wang, *Mater. Today*, **7**, 26 (2004).
9. X. Y. Kong, Z. L. Wang, *Nano. Lett.* **3**, 1625 (2003).
10. P. Yang, H. Yan, S. Mao, R. Russo, J. Johnson, R. Saykally, N. Morris, J. Pham, R. He, H.-J. Choi, *Adv. Mater.* **12**, 323 (2002).
11. Y. Li, G. S. Cheng, and L. D. Zhang, *J. Mater. Res.* **15**, 2305 (2000).
12. B. B. Lakshmi, P. K. Dorhout, and C. R. Martin, *Chem. Mater.* **9**, 857 (1997).
13. C. Liu, J.A. Zapien and Y. Yao, *Adv. Materials.* **10**, 838 (2003).
14. L. Vayssieres, K. Keis, S.-E. Lindquist and A. Hagfeldt, *J. Phys. Chem. B.* **105**, 3350 (2001).
15. J. Huang, C. Xia, L. Cao, X. Zeng, *Mater. Sci. Eng., B.* **150** 187 (2008).
16. Z. Chen, L. Gao, *J. Cryst. Growth* **293**, 522 (2006).
17. S. Cho, D. S. Shim, S. H. Jung, E. Oh, B. R. Lee, K. H. Lee, *Mater. Lett.* **63** 739 (2009).
18. Todd Steiner, *Semiconductor Nanostructures for Optoelectronic Applications* (Artech house, Boston, 2004)
19. M. Guo, P. Diao, S. Cai, *J. Solid State Chem.* **178**, 1864 (2005).