

# Microwave-assisted synthesis and characterization of microstar shaped zinc oxide

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## Resumen

A microwave-assisted solution-phase approach has been applied for the synthesis of zinc oxide microstructures. The synthesis procedure was carried out by using the reagents: Zinc nitrate and Methenamine, at stoichiometric ratio. Analysis by means of X-ray Diffraction (XRD) shows a crystalline phase in hexagonal wurtzite arrangement for ZnO. The presence of microstar shaped zinc oxide (2-3µm) with nanorods (50nm) arranged has been confirmed from High Resolution Scanning Electron Microscopy (HRSEM). The formation of nanorods was confirmed by Transmission Electron Microscopy. In Raman spectroscopy a red shift was detected in the microstructures compared with ZnO bulk. High crystalline materials without additional post-synthesis treatment were found.

**Palabras clave:** ZnO, microstructures, microwave synthesis.

## 1. Introduction

Zinc oxide is a wide band gap (3.37 eV) semiconductor with large binding energy and possesses unique properties. The zinc oxide material has found numerous applications, such as gas sensors [1]; UV photodiodes [2]; piezoelectric devices [3]; varistors [4]; acoustic wave devices [5]; transparent electrodes [6]; facial powders [7]; etc. Semiconductor nanostructured materials have been prepared by serious methods such as microwave heating [8]; non-aqueous approaches [9]; chemical-precipitation [10]; sol-gel process [11]; gas condensation [12]; hydrothermal process [13]; aerosol spray process [14]; and hydrolysis in polyol medium [15]. Microwave synthesis is a synthesis method which entirely differs from the other synthesis techniques. In the microwave technique, a radiation in the wavelength of microwaves penetrates to the material and it is heated volumetrically. This causes the stabilization of the bulk temperature to be reached during microwave processing. It means that the microwave energy penetrates inside the bulk material, which is heated and the heat energy dissipates to the surface of the material. But in case of conventional heating a reverse of heat flow has occurred. Microwave synthesis is promising due to its unique effects such as energy saving, higher reaction rates, rapid volumetric heating, higher selectivity and higher yields of products. Compared to the conventional heating process, (a) microwaves generate higher power densities, enabling increased production speeds and decreased production costs. (b) Microwave energy is precisely controllable and can be turned on and off instantly, eliminating the need for warm-up and cool-down and (c) microwave energy is selectively absorbed by areas of greater moisture resulting in more uniform temperature and moisture

profiles, improved yields and enhanced product performance. The interaction between the microwave (MW) radiation and the solution containing the precursor salt, produce a fast heating. Basically, two absorption mechanisms are present: dipole rotation and ion migration. In the first mechanism, the electric dipoles will align with the applied external field and oscillate at the microwave frequency, this produces a damped molecular motion that increases the temperature of the solution; therefore changing the electromagnetic field will produce a permanent rotation of the molecules which finally will increase the temperature of the solution. In the second mechanism, ionic migration is produced by migration of charged particles (ions) in the direction of the electromagnetic field. When the microwave radiation penetrates the solution, their power dissipation is fairly uniform throughout the solvent. Water has a very high dipole moment which makes it one of the best solvents for microwave assisted reactions. The microwave technique has become a powerful tool for production of nanoparticles due to the accelerated dynamics processes present during the synthesis.

## 2. Experimental Procedure

The microwave technique used to obtain microstructures of ZnO employs a conventional microwave oven with applied power of 1000 W at a frequency of 2.5 Hz.  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{C}_6\text{H}_{12}\text{N}_4$  mixture at 1:1 concentration in an aqueous solution were used in the processes. Times from 1 to 3 minutes were studied. The samples obtained were washed with deionized water. After, all samples were analyzed by XRD diffraction, RAMAN spectroscopy, HRSEM and TEM.

### 3. Results and Discussion

The spectrum by XRD of the sample obtained at 1 minute is shown in figure 1. In it can be seen a perfectly matching with the hexagonal wurtzite structure. The planes (100), (002), (101), (102), (110), (103), (200), (112) and (201) observed in the sample are according with the reported in JCPDS 36-1451 [16]. The samples obtained at 2 and 3 minutes presented similar spectra. The samples were analyzed by HRSEM, figure 2 presents four images of the sample obtained at 1 minute. All images have shown the morphology of star-like shaped ZnO nanostructures. The formation of star morphology consists of sharp rods which look like stars as can be seen clearly in figure 2C) and 2D). The formation of the star-like shape is probably due to the peculiar property of the methenamine, which acts as a ligand and capping agent. After more, there are some reports that when  $C_6H_{12}N_4$  was added to the solution with the increase of temperature,  $Zn(OH)_2$  precipitated, ZnO nuclei were formed from the precipitate and then ZnO nanorods grew [17]. The sizes of the stars are already of 2-3  $\mu m$ .

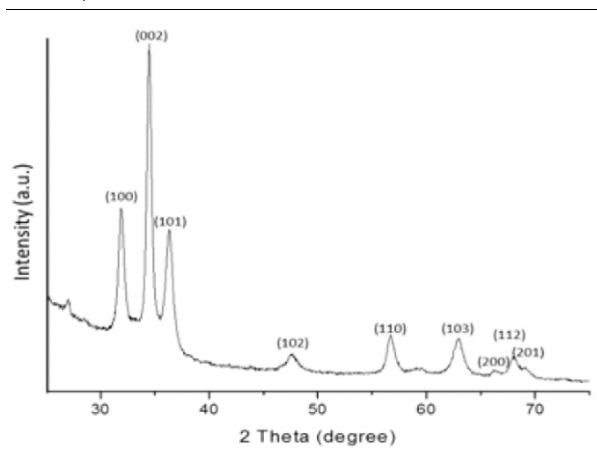


Figure 1. XRD spectrum of zinc oxide sample obtained at 1 minute.

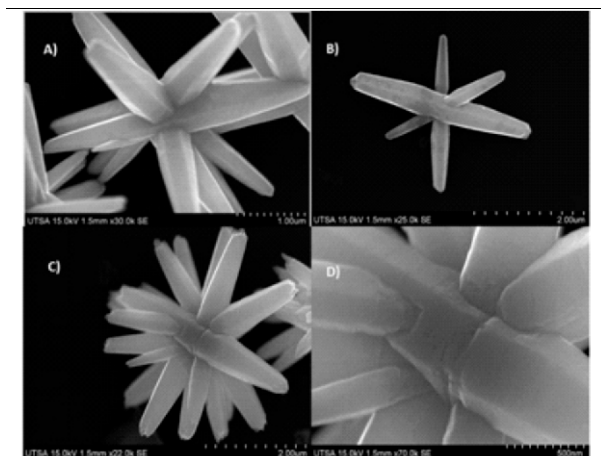


Figure 2. HRSEM images of zinc oxide sample obtained at 1 minute.

In figure 3 is shown an image from TEM. In it can be seen the structural arrangement of one of the nanorods that confirms the star morphology of the ZnO. This has a diameter that starts at 50nm.

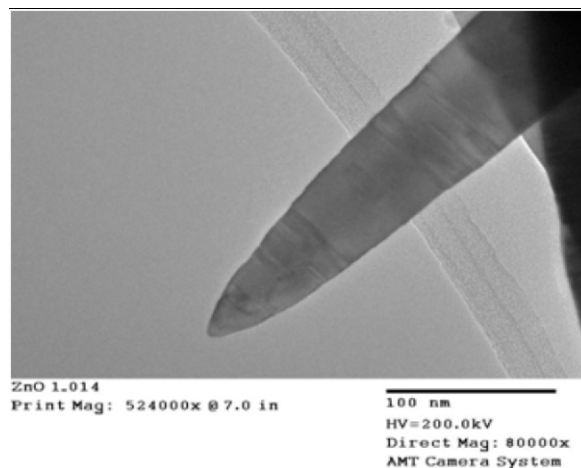
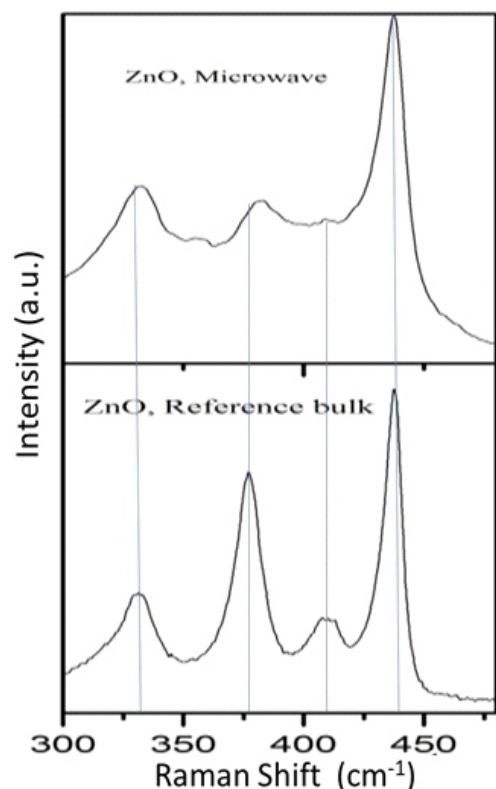


Figure 3. TEM image of zinc oxide sample obtained at 1 minute.

ZnO is a semiconductor with wurtzite crystal structure. Wurtzite structure belongs to the space group  $C_{6v}^4$  with two formula units per primitive cell, where all atoms occupy  $C_{3v}$  sites. The Raman active zone-center optical phonons predicted by the group theory are  $A_1+2E_2+E_1$ . The phonons of  $A_1$  and  $E_1$  symmetry are polar phonons and, hence, exhibit different frequencies for the transverse-optical TO and longitudinal-optical LO phonons. Nonpolar phonon modes with symmetry  $E_2$  have two frequencies,  $E_2$  (high) is associated with oxygen atoms and  $E_2$  (low) is associated with Zn sublattice. All described phonon modes have been reported in the Raman-scattering spectra of bulk ZnO [18,19].

The measured nonresonant Raman spectra of ZnO microcrystals and bulk samples are shown in Figs. 4a and 4b, respectively. All spectra in Figure 4 were taken under the laser spot area of 1.6  $m^2$  while the excitation laser power was kept at 15 mW. Comparing the spectra, we can conclude that in the bulk ZnO spectrum the peak at 379  $cm^{-1}$  corresponds to  $A_1$  TO, 410  $cm^{-1}$  corresponds to  $E_1$  TO, and 439  $cm^{-1}$  corresponds to  $E_2$  high. In the microstars spectrum, the peak at 436  $cm^{-1}$  corresponds to  $E_2$  high, which is shifted by 3  $cm^{-1}$  compared to bulk. The broad peak at about 330  $cm^{-1}$  seen in both spectra in Fig. 4 is attributed to the second-order Raman processes. Since the microcrystal size is relatively large, the observed redshift of the  $E_2$  high phonon cannot be ascribed to the optical-phonon confinement by the nanorods boundaries [20,21].



**Figure 4.** Nonresonant Raman spectra for a) ZnO nanocrystals; for b) bulk ZnO a plane. Photoluminescence background is subtracted from the bulk ZnO spectrum.

#### 4. Conclusions

In this work, has been demonstrated that a facile and inexpensive microwave treatment of a zinc nitrate precursor led to the crystalline ZnO microstars shaped particles when zinc nitrate and methenamine solution was used. One minute was enough in order to obtain the synthesis of ZnO with wurtzite arrangement.

High crystalline materials were readily obtained without the need of a post-synthesis treatment. This method can also be used for the preparation of other metal oxide powders.

#### 5. Acknowledgments

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#### 6. References

1. Bhooloka Rao B. *Mater Sci Phys* 2000;64: 62-5.
2. Lei Luo, Yanfeng Zhang, Mao Samuel S, Liwei Lin. *Sens Actuators A* 2006; 127, 201-6.
3. Gardeniérs JGE, Rittersma ZM, Burger GJ. *J Appl Phys* 1998; 83, 7844-54.
4. Dutta S, Jackson HE, Boyd JT, Hickernell FS, Davis RL. *Appl Phys Lett* 1981, 39 206-8.
5. Chang SJ, Su YK, Shei YP. *J Vac Sci Technol A* 1995, 13 385-8.
6. Horsthuis WHG. *Thin Solid Films* 1986, 137, 185-92.

7. Liu M, Kitai AH, Mascher P. *J Lumin* 1992, 54, 35-42.
8. Krishnakumar T, Pinna Nicola, Prasanna Kumari K, Perumal K, Jayaprakash R. *Mater Lett* 2008, 62, 3437-40.
9. Clavel Guylhaine, Willinger Marc, Zitoun David, Pinna Nicola. *Adv Funct Mater* 2007, 17, 3159-69.
10. Iwasaki M, Inubushi Y, Ito S. *J Mater Sci Lett* 1997, 16, 1503-5.
11. Lauf RJ, Bond WD. *Am Ceram Soc Bull* 1984, 3, 278-81.
12. Eilers H, Tissue BM. *Mater Lett* 1995, 24, 261-5.
13. Nishizawa H, Yuasa K. *J Mater Sci Lett* 1998, 7, 985-7.
14. Milosevic O, Uskokovic D. *Mater Sci Eng A* 1993, 168, 249-52.
15. Jezequel D, Guenot J, Jouini N, Fievet F. *J Mater Res* 1995, 10, 77-83.
16. J. Yang, J. Lang, L. Yang, Y. Zhang, D. Wang, H. Fan, H. Liu, Y. Wang, M. Gao, *J. Alloys Compd.* 2008, 450, 521-24.
17. Vaezi MR, Sadrnezhad SK. *Mater Des* 2007, 28, 515-9.
18. N. Ashkenov et al., *J. Appl. Phys.* 2003, 93, 126.
19. J. F. Scott, *Phys. Rev. B* 1970, 2, 1209-211.
20. V. A. Fonoberov and A. A. Balandin, *Phys. Rev. B* 2004, 70, 195410-16.
21. V. A. Fonoberov and A. A. Balandin, *Phys. Status Solidi C* 2004, 1, 2650-53.