Structural and luminescent properties of ZnO flower-like microstructures synthesized using the chemical bath deposition method

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Abstract. Crystalline zinc oxide (ZnO) flower-like nanostructures were synthesized by the chemical bath deposition (CBD) method. The temperature of the bath was maintained at 80°C. The effect of different mol % of zinc acetate and different synthesis time on the structure, morphology and optical properties of microstructures were obtained. The X-ray diffraction (XRD) pattern for the ZnO flower-like microstructures showed crystalline peaks corresponding to a hexagonal wurtzite ZnO structures. The average diameter sizes calculated using the XRD spectra were found to be 48, 45 and 42 nm for particles synthesized for 10 minutes, 5 minutes and 1 minute, respectively. Scanning electron microscopy (SEM) observations showed the presence of microcrystallites forming microflower-like aggregates. In the case where a higher mol concentration of zinc acetate was used in the preparation process the microflower-like structures were larger in size than that of the lower mol percentages used. The shape however did not change. Transmission electron microscopy (TEM) micrographs of the ZnO powder revealed the formation of ZnO flower-like microstructures. Energy dispersive X-ray (EDS) analysis showed all expected elements. The ZnO powder revealed good optical properties with high absorptions properties in the UV region. The band gap energies increased slightly with an increase in the mol concentration of the zinc acetate and again in synthesizing time. The calculated band energy gaps were 3.2 eV for samples synthesized for 10 minutes and 3.3 eV for ZnO synthesized for 5 minutes and 1 minute, respectively which were lower than that of bulk ZnO (3.37eV). The photoluminescence measurements reveal a strong emission peak at around 606 nm.

1. Introduction

Zinc oxide (ZnO) has been intensively studied in the past decade and it is a wide, direct band gap (3.37 eV) semiconductor, which crystallizes in both the cubic and hexagonal form. It is commercially used as a phosphor for cathode ray tubes in flat panel displays [1] and is widely used in photovoltaic devices [2]. ZnO has attracted much attention because of different properties in nano forms in comparison with those of the bulk materials. Size dependence on optical properties of nanocrystalline semiconductors makes them an interesting candidate for phosphor applications [3]. Numerous attempts of synthesizing one dimensional zinc oxide nanostructures have been reported [4-6]. The chemical bath deposition (CBD) method is a simple, cheap and convenient process to prepare semiconducting materials. The more recent interest in all things 'nano' has provided a boost for CBD, since it is a low temperature, solution (almost always aqueous) technique, crystal size is often very small and it gives better homogeneity. Moreover CBD takes advantage of the controlled and continued

release of metal sulfide ions in the aqueous phase. The aim of this paper was to investigate the effect of different preparation parameters on the particle size of the ZnO.

2. Experimental

The ZnO microstructures were prepared by changing different mol concentrations of zinc acetate and holding thiourea and ammonia constant. The preparation of ZnO was carried out using the following procedure: Different mol concentrations of zinc acetate solutions were taken in a 200 ml beaker. Then, a certain volume of thiourea solution was then added in the reaction bath and the mixture was stirred for a few minutes, following that, a certain amount of ammonia solution was added slowly into the mixture, while continuing stirring for different times (for few minutes or immediate after the precipitates has formed, 5 and 10 minutes). The temperature of the bath was then allowed to increase up to 80^0C. After the precipitates were formed the pH was measured and the precipitates were filtered and washed with 50 ml of ethanol. The obtained particles were dried at ambient conditions for several days. After that the powders were ready to be characterized. The particle size and morphology and the structural and luminescent properties of the as-synthesized phosphors were examined by means of scanning electron microscopy (SEM), X-ray diffraction (XRD), Uv-vis spectroscopy and Photoluminescence (PL).

3. Results and Discussion

3.1 Structural analysis and Composition analysis

Figure 1 (a) shows the XRD patterns of the ZnO microstructures synthesised at constant mol concentration of zinc acetate of 0.56M but for different synthesizing times. The average calculated values of the cell constants of a and c are 3.257 and 5.215 Å, which matched perfectly with standard data available in JCPDS card no. (36-1451, a = 3.24982 and c= 5.20661 Å). The XRD results (broad peaks) indicate that the ZnO microparticles were composed of single hexagonal wurtzite nanocrystallites.
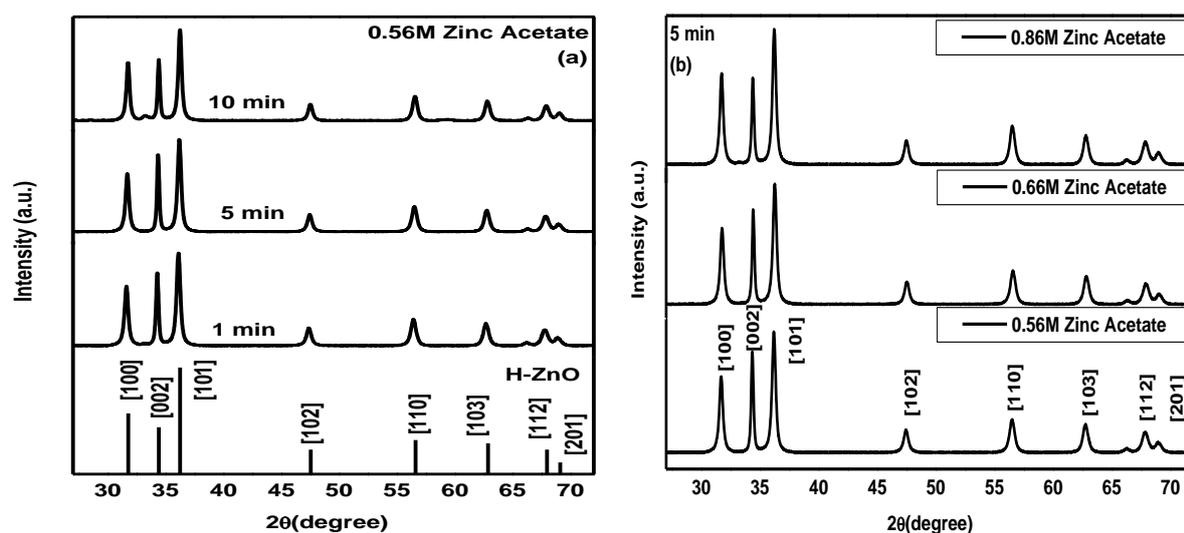

Figure 1. X-ray powder diffraction patterns for ZnO structures prepared at (a) different synthesizing times but constant mol concentrations and (b) different mol concentrations of lead acetate at constant synthesizing time.

No structural dependence on the synthesis time and precursor concentration were observed, figure 1 (a) and (b). The average size of the as-prepared crystals can be calculated from the Full Width Half Maximum (FWHM) of the diffraction peaks using the Debye-Scherrer formula [7]. The average diameter sizes calculated using the XRD spectra are found to be 48, 45 and 42 nm for particles synthesized for 10 minutes, 5 minutes and 1 minute, respectively. In Figure 2 the calculated average grain sizes are plotted for the samples prepared at different mol concentrations of zinc acetate synthesized for 10 minutes and 5 minutes, respectively, it is clear that the calculated average crystallite size increases with an increase in the zinc acetate concentration.
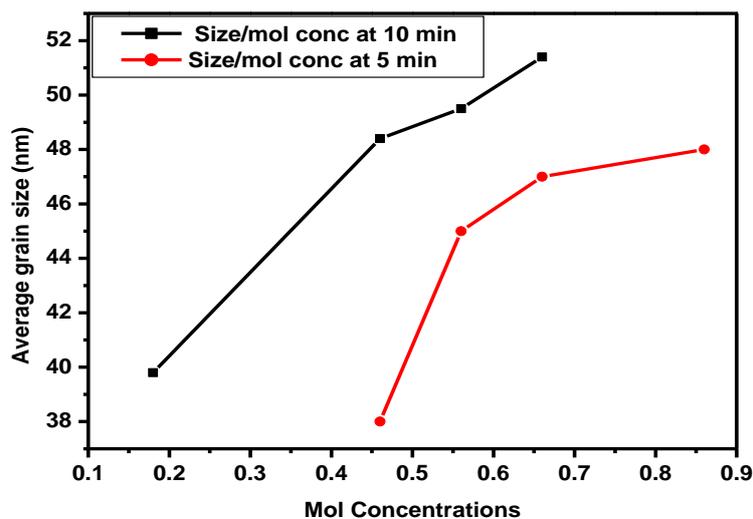

Figure 2. The dependence of average particle sizes of the ZnO on the zinc acetate concentration for different synthesis time.

3.2 Surface morphological analysis

Figure 3 (a) and (b) show SEM images of the as prepared ZnO microstructures prepared at different mol concentrations of zinc acetate but synthesized at constant time. The surface aspects of all the SEM images are composed of flower-like structures. It is clear that the flower-like structures are clustered with some surrounded by spherical nanoparticles. By comparing the SEM micrographs it is clearly seen that by increasing the mol concentration of zinc acetate there is an increase in the diameter and the length of the microrods.
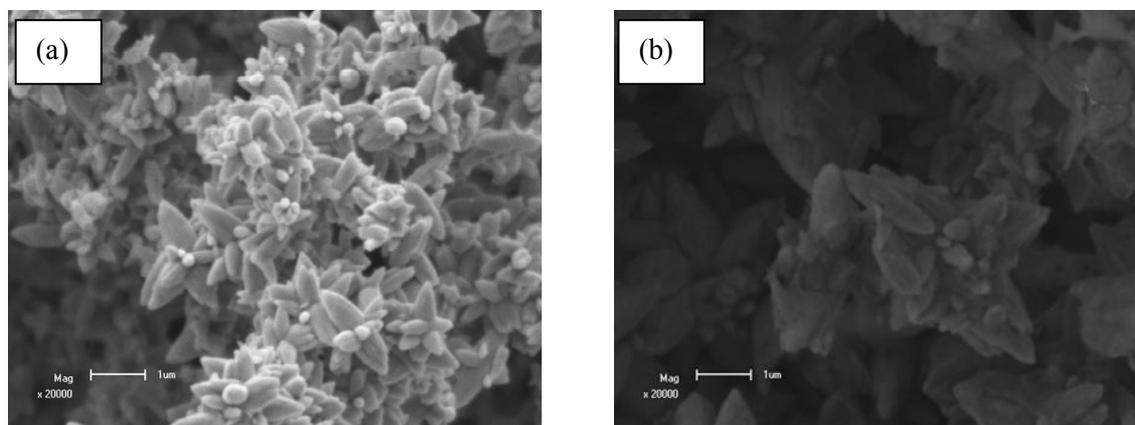

Figure 3. SEM images of ZnO microstructures for (a) 0.56M and (b) 0.86M Zinc acetate concentration synthesized at constant time.
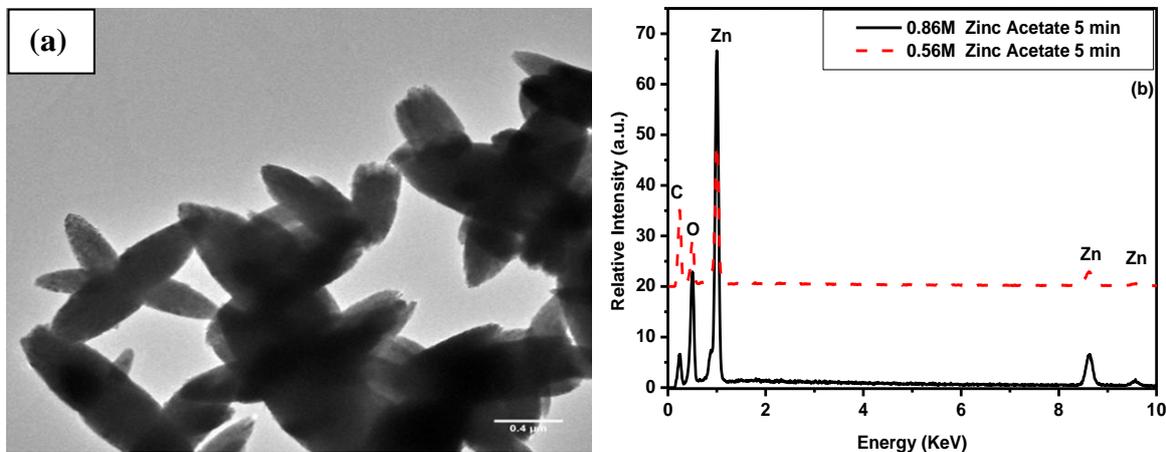
Figure 4. (a) and (b) representative TEM and EDS spectra of the ZnO microflower-like structures prepared at different mol concentration of Zinc acetate for a constant time of 5 min.

The TEM micrograph of ZnO synthesized for 5 minutes using 0.56M zinc acetate is shown in figure 4(a). The presences of ZnO flower-like microstructures are clearly visible in the TEM images. The microstructures are aggregated. The elemental composition of the ZnO samples were analysed using EDS. From Figure 4 (b) the elemental analysis of the ZnO flower-like microstructures suggests the existence of Zn and O (from the cores and the outside shell) and C (from the C double sided tape).
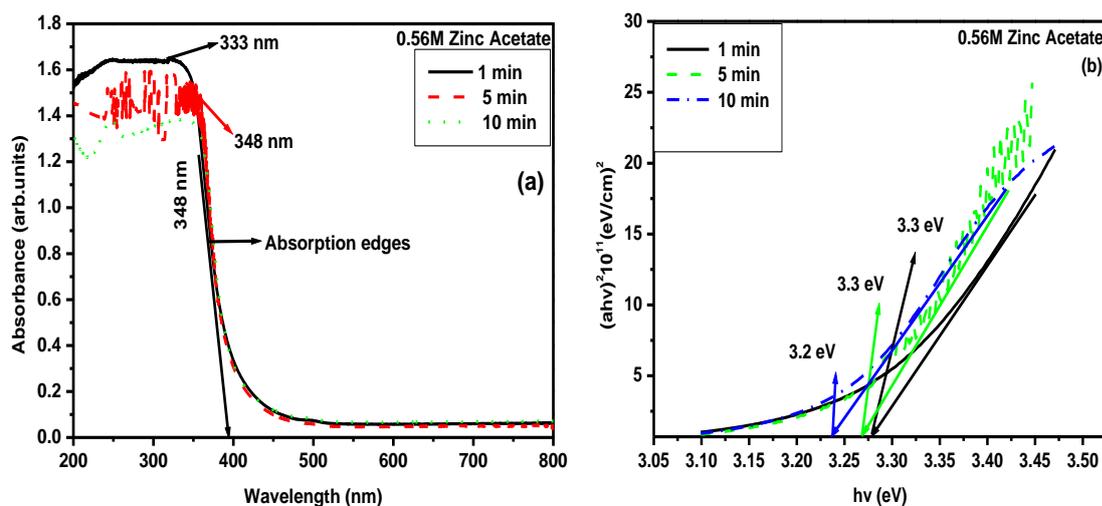
3.3 Optical properties

Figure 5. The absorbance spectra (a) and the band gap energy (b) of ZnO structures prepared at different synthesizing times and at constant zinc acetate concentration.

The absorption spectra exhibit a shoulder peaks at around 333 nm for sample synthesized for 1 minute 348 and 341 nm for samples synthesized for 5 and 10 minutes, respectively, which are attributed to the exitonic absorption corresponding to 3.5 eV [8], figure 5. By increasing the synthesizing time the absorption peak shoulders shift slightly to higher wavelengths. This shift from 333 to 348 nm may be due to the particles sizes that were decreasing as the synthesizing time decreases [9]. The absorption edges were not affected by the synthesizing time. This may be due to the morphology which was homogeneous. The ZnO is a direct bandgap material. The energy band gaps of these materials were estimated using the Tauc relation [10],

$$\alpha = (h\nu - E_g)^n \qquad (1)$$

where α is the absorption coefficient, $h\nu$ is the photon energy, E_g is the band gap n=2 for direct transitions. The energy band gaps were measured with the help of absorption spectra plotting graphs of $(\alpha h\nu)^2$ versus $h\nu$, and the corresponding band gaps obtained from extrapolating the straight portion of the graph on the $h\nu$ axis at $\alpha = 0$. All the calculated band gap energies were below the theoretical band gap value of 3.37 eV. This may be due to the particle sizes which are bigger than the exciton Bohr radius of ZnO [11]. From figure 5 (b) it is clear that the band gap energy of ZnO structures decreases slightly (band gap energy do not change a lot) with an increase in synthesizing time. Even as the mol concentration of zinc acetate increased the band gap energy slightly increased which is not shown here. This decrease in band gap energy is in accordance with the particle size that is increasing as the synthesizing time increased as confirmed by SEM and XRD results.

3.4 Photoluminescence

The photoluminescence (PL) measurement of the ZnO microflower-like structure was carried out at room temperature with 325 nm excitation. Figure 6(a) shows strong and broad emission spectrums, which are mainly located in the orange region with its maximum luminescence intensity at around 606 nm. It has been suggested that the orange band emission correspond to the oxygen interstitials, showing excess of oxygen in the ZnO microflower-like [12]. Comparing the three patterns, the maximum luminescence intensity is reached at the ZnO synthesized for 5 minutes, by increasing the synthesizing time further the luminescence intensity decreases. Even as the mol concentration of zinc acetate increases the luminescence intensity decreases which is not shown here. This decrease in luminescence intensity may be due to the increase in particle size as confirmed by the XRD. There was no shift in the luminescence band of ZnO flower-like microstructures for samples prepared at different synthesizing times and constant mol concentration of zinc acetate; this may be due to the uniform particle sizes as observed with the SEM.
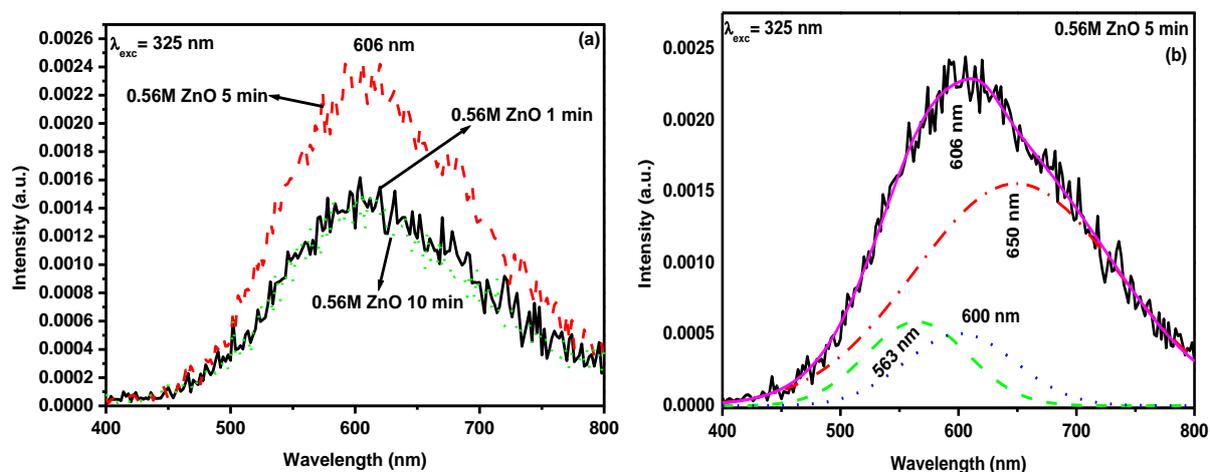

Figure 6. The PL spectra of ZnO microstructures, prepared at (a) different synthesizing times but synthesized at constant mol concentration of zinc acetate and (b) fits to the 5 min sample luminescence spectra of ZnO microflower-like prepared by the CBD method.

After Gaussian simulation (figure 6(b)) it was suggested that the orange emission at around 606 nm is composed of mainly three peaks at around 563, 600 and 650 nm, respectively. The green emission at around 563 nm corresponds to the single ionized oxygen vacancy in the ZnO microflowers [13]. The orange emission at around 600 nm corresponds to the oxygen interstitials [12]. The infrared luminescence band (ILB) at around 650 nm may be due to the numerous defects located at deeper levels in the ZnO band structure, though the exact reason behind the origin of this red emission is not clear at this moment.

4. Conclusion
The ZnO microstructures have been successfully synthesized by the chemical bath deposition technique at 80°C. XRD showed that the structure of the material obtained is hexagonal wurtzite ZnO. UV spectroscopy showed that the band gap energy of the ZnO microflower-like decreased with an increase in the synthesizing time. PL showed that the emission intensity of the microstructures depends on the synthesizing time and the mol concentration of the zinc acetate.

References
[1] Prevenslik T V 2000 *J. Lumin.* **1210** 87-89
[2] Ghosh P K, Mitra M K and Chattopadhyay K K, 2005 *Nanotech.* **16** 107–112
[3] Ntwaeabora O M, Kroon R E, Kumar V, Ahn J-P, Park J-K and Swart H C 2009 *J. of Phys and Chem of solids* **70** 1438-1442
[4] Shen G, Hee Cho J, Juang S I1 and Lee C J 2005 *Chem. Phys. Lett.* **401** 529-533
[5] Sun Y, Fuge G M and Ashfold M N R 2004 *Chem. Phys. Lett.* **396** 21-26
[6] Hu J Q, Li Q, Meng X M, Lee C S and Lee S T 2003 *Chem. Mater.* **15** 305-308
[7] Cullity B D1978, 1956 *Elements of X-ray Diffraction (2nd Ed)*, (Addison Wesley) 285-284
[8] Valle G G, Hammer P, Pulcinelli S H and Santilli C V 2004 *J. of the European Ceramic Society* **24** 1009-1013
[9] Wang Y and Herron N, 1991 *J. Phys. Chem.* **95** 525-532
[10] Sharma T P, Patidar D, Saxen N S and Sharma K 2006 *Indian J Pure and Appl. Phys*. **44** 125-128
[11] Gu Y, Igor L, Igor L K, Yin M, O'Brien S and Neumark G F, 2004 *App. Phys. Lett.* 85 3833-3835
[12] Ong H C, and Du G T, 2004 *J. Cryst. Growth* **265** 471
[13] Lyu S C, Zhang Y, Ruh H, Lee H J, Shim H W, Suh E K and Lee CJ, 2002 *Chem. Phys. Lett.* **363** 134-138