

BINDING AGENT AFFECT ON THE STRUCTURAL AND OPTICAL PROPERTIES OF ZnO NANOPARTICLES

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Abstract. In this study, different concentrations of hydroxyl-footed methylresorcinarene (HFMR) are selected to bind zinc acetate in order to investigate its role on the formation of ZnO nanoparticles. Accordingly, the size of produced ZnO nanoparticles are affected by the existence of the binding agent as observed by XRD and TEM analysis. The particle size increases from 28 to 43 nm with increasing amounts of binding agent. The SEM and TEM micrographs show hexagonal morphology. The UV-vis absorption and PL spectra show that the absorption edge shifts to red.

1. INTRODUCTION

Zinc oxide is one the most promising materials for optoelectronic applications because of its wide band gap (3.37 eV) and large excitation binding energy (60 meV). ZnO also has great potential applications in room – temperature UV lasers [1], sensors [2] and photocatalysis [3,4] due to its unique electrical and optical properties, such as low dielectric constant, high chemical stability, and good photoelectric and piezoelectric behaviors [5]. Different synthetic methods have been used to prepare ZnO nanoparticles, such a hydrothermal [6], sol-gel [7], precipitation [8], microemulsion [9], and thermal decomposition [10].

Of these methods, ZnO nanomaterials can be obtained easily by thermal decomposition of a zinc salt such as $Zn(CH_3COO)_2$. The high solubility and low temperature of decomposition make zinc acetate an attractive precursor [11]. Investigations into the kinetics and mechanism of the thermal decomposition process have been carried out [1,12]. It has been observed that with zinc acetate organic additives affect the shape and size of the ZnO nanoparticles [13,14]. This process eliminates the addition of base or acid solutions. Theoretical con-

siderations suggest that the growth of the nanocrystals could be either controlled by the diffusion of particles, by the reaction at the surface, or by both factors [15]. Thus, Viswanatha et al. [16] observe the growth of the ZnO nanocrystals in water to follow a growth mechanism intermediate between diffusion-control and surface reaction-control. The effect of capping agents on the growth of nanocrystals have been examined by a few workers [17-21].

The aim of this study is to present a method based on thermal decomposition that creates zinc oxide nanoparticles of different size and shape. We present our findings on the affect of adding different amounts of a binding agent on the structure, shape, and optical properties of ZnO nanoparticles.

2. EXPERIMENTAL

Zinc acetate dehydrate, $Zn(CH_3COO)_2 \cdot 2H_2O$ and hydroxyl-footed methylresorcinarene (HFMR) [22] were dissolved in 50 ml methanol. The solution was stirred for 60 min at room temperature and then evaporated under vacuum at 40 °C to remove the solvent. The resulting solid was dried under vacuum and grounded into a powder. It was then heated at

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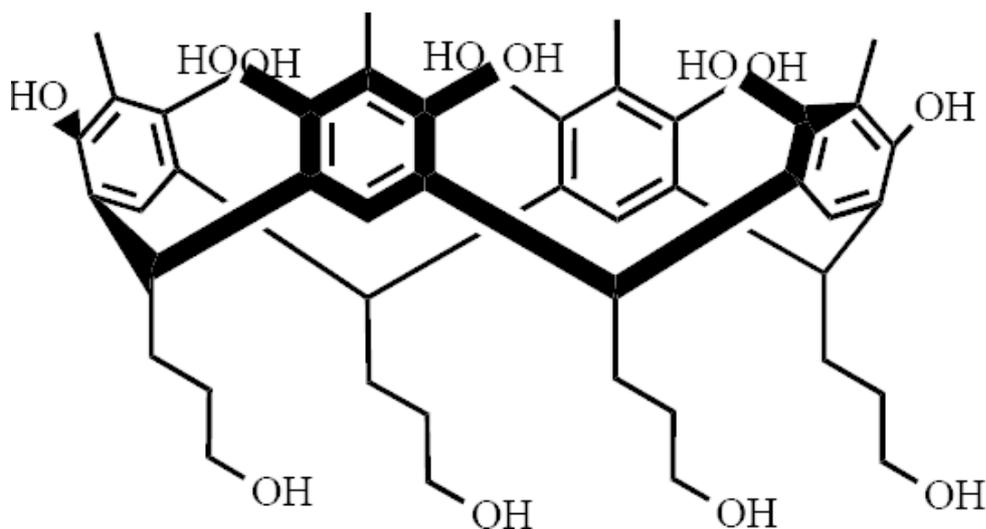


Fig. 1. Hydroxyl-footed methylresorcinarene (HFMR) binding agent.

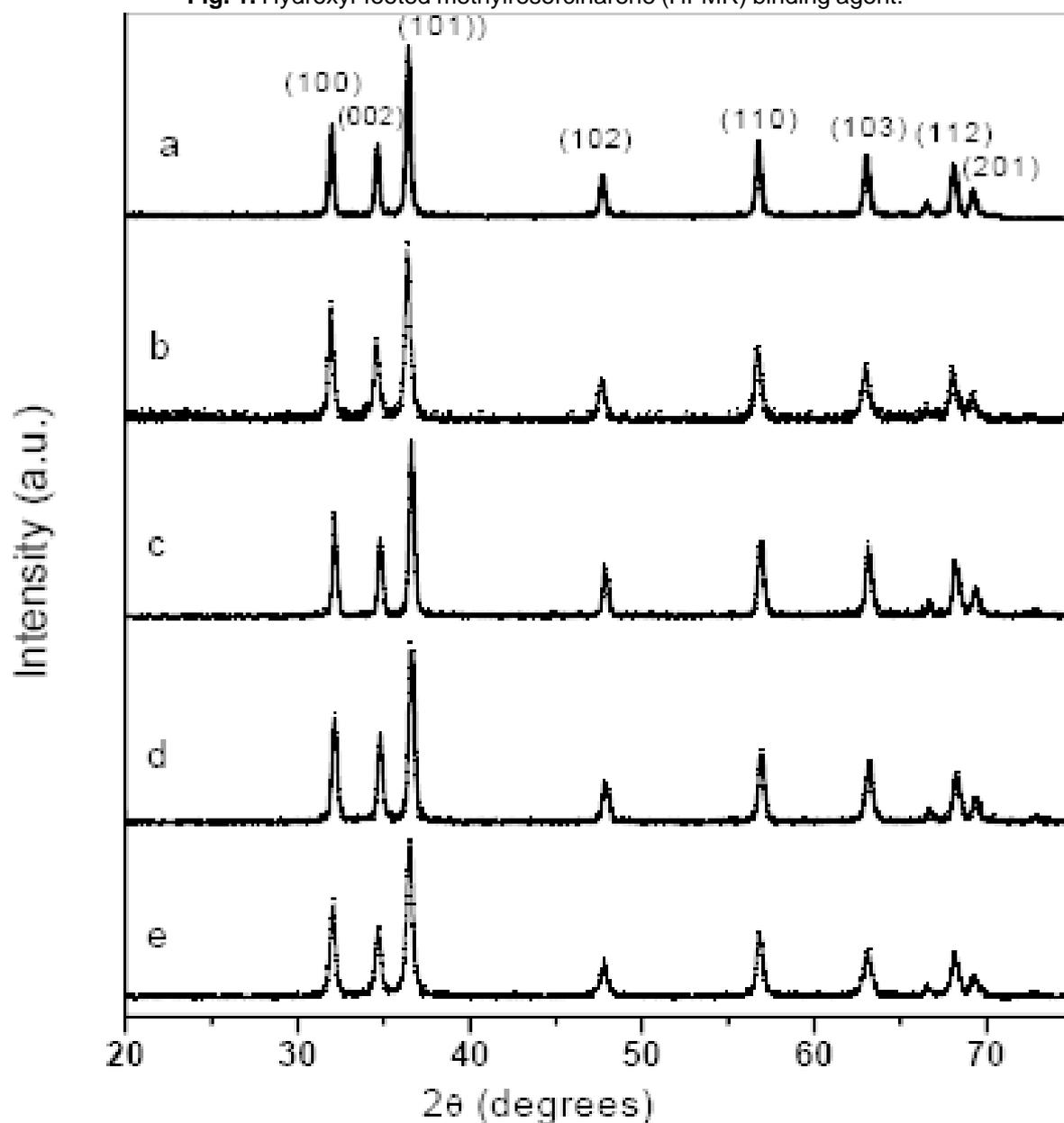


Fig. 2. XRD patterns of ZnO products prepared from zinc acetate and (a) 0 HFMR, (b) 0.015 M HFMR, (c) 0.023 M HFMR, (d) 0.035 M HFMR, and (e) 0.045 M HFMR.

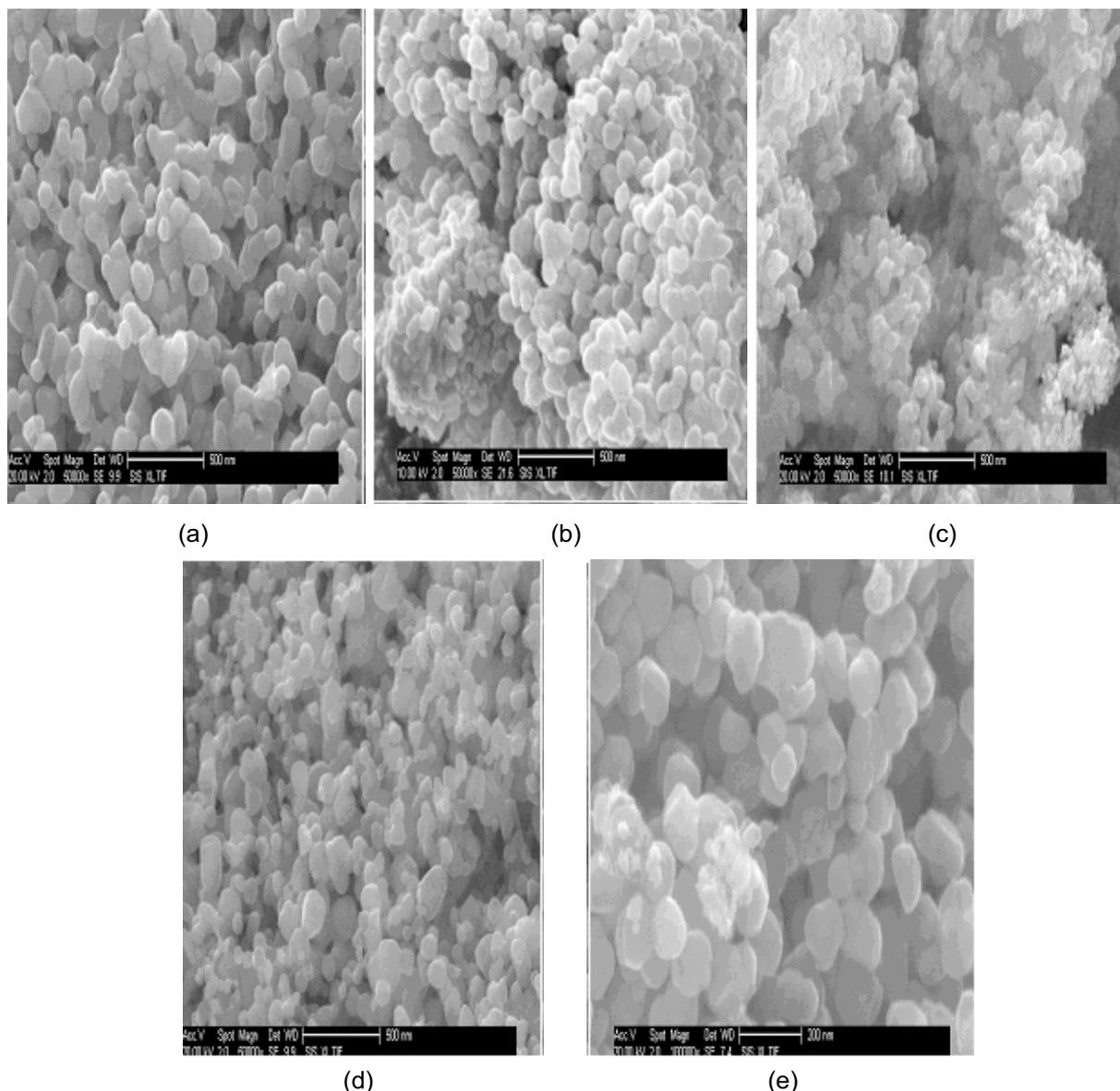


Fig. 3. SEM micrographs of ZnO nanoparticles prepared from zinc acetate and (a) 0 HFMR, (b) 0.015 M HFMR, (c) 0.023 M HFMR, (d) 0.035 M HFMR, and (e) 0.045 M HFMR.

500 °C for 2h. The molar concentration of zinc acetate was 0.091 mol/l for each experiment, but the molar concentrations of HFMR were 0, 0.015, 0.023, 0.035, and 0.045 M. HFMR concentrations above 0.045 mol/L produced precipitates during mixing.

3. CHARACTERIZATION

The UV-vis absorption spectra were taken with a Hewlett Packard8453 spectrometer of ethanolic nanoparticle solutions made by sonication of the products in ethanol. The fluorescence measure-

ments were also done with ethanolic solutions of nanoparticles but with a Perkin – Elmer LS 50B luminescence spectrometer and with a 250 nm excitation wavelength. The SEM was done with a Philips XI30 ESEMFEQ. The TEM analysis was done with a Tecnai F300 transmission electron microscope, images taken after suspending the nanoparticles in 95% ethanol. Crystal structure identification and crystal size analysis were performed with a X-ray diffractometer XDS 2000, Scintac Inc., USA with $\text{CuK}\alpha$ radiation source and scan rate of 2°/min.

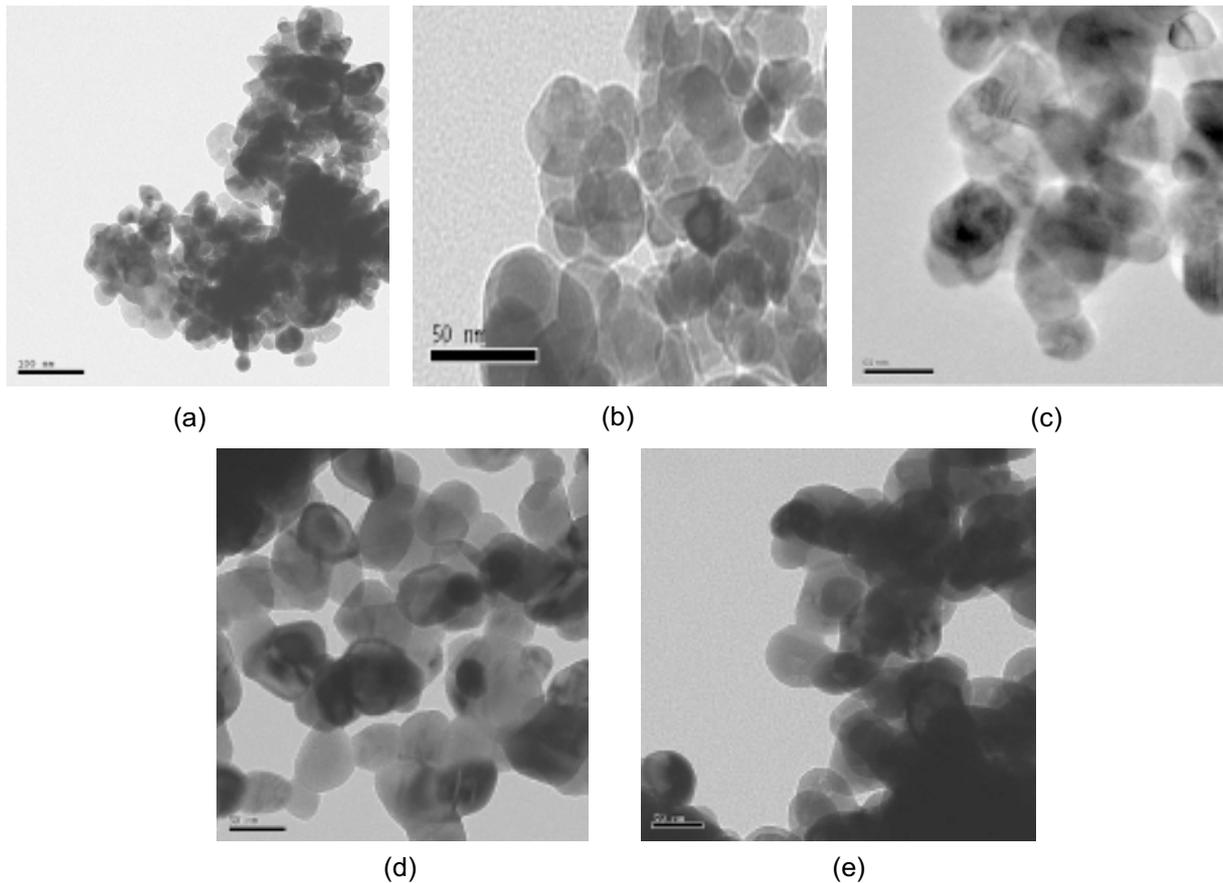


Fig. 4. TEM micrographs of ZnO nanoparticles prepared from zinc acetate and (a) 0 HFMR, (b) 0.015 M HFMR, (c) 0.023 M HFMR, (d) 0.035 M HFMR, and (e) 0.045 M HFMR.

4. RESULT AND DISCUSSION

Hydroxyl-footed methylresorcinarene (HFMR) has eight hydroxyl groups on one of its rims and four on its other (Fig. 1). These oxygens can bind zinc cations and potentially alter the size of ZnO nanoparticles during crystal growth. Once the zinc acetate and HFMR are heated the carbons and hydrogens will be burned away, leaving ZnO nanoparticles.

XRD analysis after heating showed that all of the ZnO products have the wurtzite structure [23]. The XRD patterns of the products show good crystallinity for all of the different amounts of HFMR (Fig. 2). The XRD peaks correspond to the (100), (002), (101), (102), (110), (103), (200), (112), and (201) planes of ZnO in the wurtzite structure corresponding with JCPDS (Card Number 36-1451). At the same time, no diffraction peaks from other species could be detected, which indicates that all the precursors have been completely decomposed and no other crystal products have been retained after

the decomposition process. All samples have a preferred orientation along the (101) plane. It is observed that the preferred orientation of (101) for the ZnO nanoparticles, are slightly shifted to the right when HFMR was present when compared to ZnO prepared without HFMR (Fig. 2).

The particle size D of the samples was determined using the Scherrer formula [24]:

$$D = \frac{0.9\lambda}{(B \cos \theta)}$$

where D is the particle size, λ the X-ray wavelength, θ the Bragg's angle in radians, and B the full width at half maximum of the (101) peak in radians. The average particle size of the products was found to be 26-44 nm. It is observed that the particle size increases as the amount of HFMR increases.

The SEM micrographs clearly show the spherical shape of the ZnO nanoparticles whether prepared with or without HFMR (Fig. 3). They also show the morphological homogeneity of the mate-

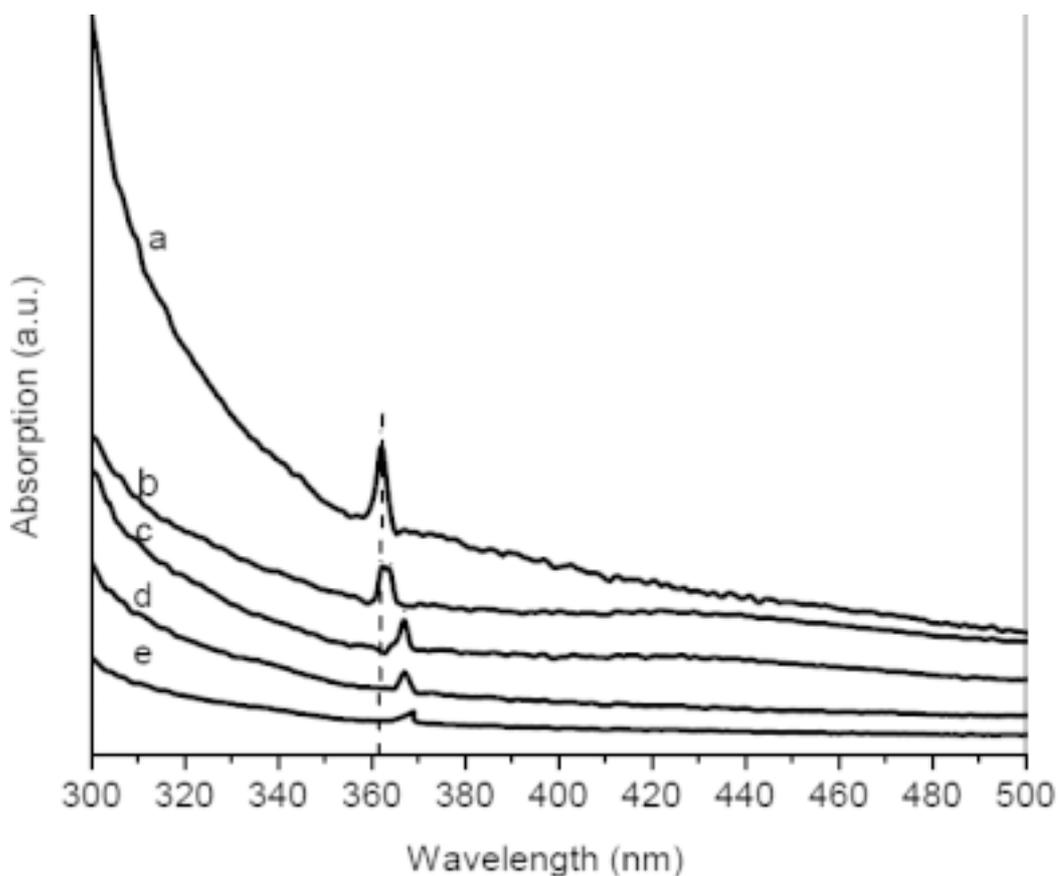


Fig. 5. UV-vis spectra of ZnO nanoparticle solutions prepared from zinc acetate and (a) 0 HFMR, (b) 0.015 M HFMR, (c) 0.023 M HFMR, (d) 0.035 M HFMR, and (e) 0.045 M HFMR.

rial. The TEM images show the distribution of nanoparticle sizes (Fig. 4). The images show a hexagonal nanoparticles, which in accord with the XRD. The average particle size of the samples was found of 24 - 43 nm. Addition HFMR to the zinc acetate doesn't change ZnO nanoparticles shape, but it does cause an increased in nanoparticle size especially for higher amounts of HFMR. There was observed a small difference between nanoparticle size measured by XRD and TEM. The reason for this is well known.

HFMR in methalonic solution may form long chains through hydrogen bonding between HFMR molecules. This long chains are well-known to be flexible. Therefore, HFMR with flexible long chains is not able to confine the dimensions of produced ZnO. So the produced ZnO is easy to form agglomeration as shown in Figs. 4b - 4d. For this reason HFMR is not suitable to bind zinc acetate for preparing controlled -size ZnO nanoparticles by thermal decomposition method. The difference in the obtained values of the particle size of produce

ZnO nanoparticle is due to the fact that TEM measurements is based on the difference between the visible grain boundaries. while XRD calculations measure the extended crystalline region that diffracts X-rays coherently. So, the XRD method has a more stringent criterion and leads to smaller sizes [25].

The optical properties of the ZnO nanoparticles, prepared without and with HFMR were studied by UV-Vis absorption spectroscopy. The inset in Fig. 5 shows the room temperature optical absorption spectra of the ZnO nanoparticles, prepared without and with HFMR. The UV-vis absorption spectra of the ZnO nanoparticles, prepared without and with HFMR, have absorptions from 362 - 369 nm (Fig. 5). A clear shift in the absorption onset is discernible in ZnO nanoparticles prepared with HFMR (see Fig. 5). The absorption edge cut off increases from 362-369 nm for 0-0.045 M HFMR, respectively. The observed red shift of ZnO nanoparticles implies that the particle size increases with increased added HFMR. Band gaps of 3.43-3.37 eV

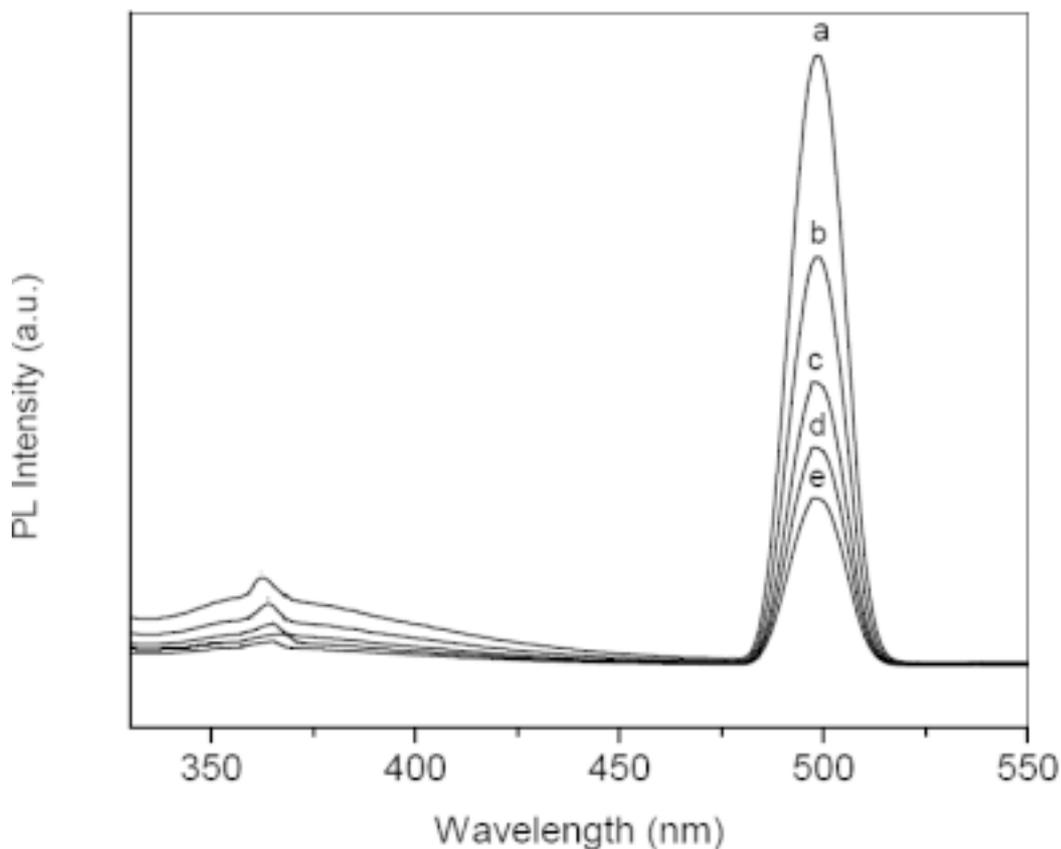


Fig. 6. PL spectra of ZnO nanoparticle solutions prepared from zinc acetate and (a) 0 HFMR, (b) 0.015 M HFMR, (c) 0.023 M HFMR, (d) 0.035 M HFMR, and (e) 0.045 M HFMR.

are calculated for the ZnO nanoparticles obtained from 0 to 0.045 M HFMR. It is reasonable to expect the band gap, E_g , to decrease with increasing the particles size of ZnO prepared with HFMR. Compared to the bulk ZnO, the observed red shift in ZnO nanoparticles may be due to the size effect [26].

Fig. 6 displays the photoluminescence spectra at room temperature of ZnO nanoparticles prepared without and with HFMR. The PL measurements were performed at excitation wavelength of 250 nm. The original ZnO nanoparticles without binding agent (HFMR) showed the highest emission, while the binded nanoparticles showed gradually decreasing intensity by increasing the concentration of HFMR. For all the samples, a blue-green emission peak (500 nm) and a UV emission peaks at 362, 364, 361, 370, and 372 nm for ZnO nanoparticles prepared with 0, 0.015, 0.023, 0.035, or 0.045 M HFMR, respectively. The highest energy peak corresponds to the absorption peak in the UV-vis measurements and the band-gap of

ZnO. The band edge emission shifts to the red with increasing the concentration of binding agent HFMR, reflecting the change in the exciton energy in the absorption spectra and an increasing in particle size of ZnO nanoparticles (see Fig. 6). It moves to larger wavelength as the nanoparticle size increases. The blue-green emission at 500 nm has been extensively investigated [27]. A single ionized oxygen vacancy results in green emission of ZnO nanoparticle, because of recombination of a photo-generated hole with a single ionized electron in the valence band [28].

5. CONCLUSIONS

ZnO nanoparticles have been successfully synthesized from zinc acetate by thermal decomposition. Changing the amount of zinc binding agent, HFMR, caused an increase in ZnO nanoparticle size. XRD results reveal a hexagonal crystal structure for the ZnO and a nanoparticle size range from 24-40 nm. The nanoparticle size range observed by TEM im-

ages was a little larger, 28-43 nm. The SEM and TEM micrographs clearly show microstructural homogeneities with hexagonal shape for the nanoparticles prepared without and with HFMR binding agent. HFMR is not suitable to bind zinc acetate for preparing well-controlled ZnO nanoparticles through this thermal decomposition method. Optical absorption spectra is also confirmed that the binding agent was not effective in confining ZnO nanoparticles. The UV-vis and absorption spectra show that the absorption-edge is shifted to the red with increased amounts of binding agent, which is due to an increase in nanoparticle size.

REFERENCES

- [1] M. H. Huang, S. Mao, H. Feick, H. Q. Yan, H. Hind, R. Russo and P. D. Yang // *Science* **292** (2001) 1897.
- [2] E. Comini, G. Faglia, G. Sberveglieri, Z. W. Pan and Z. L. Wang // *Appl. Phys. Lett.* **81** (2003) 1869.
- [3] G. Marci, V. Augugliaro, M. Lopez-Munoz, M. Schiavello, R. J. D. Tilley and A. M. Venezia // *J. Phys. Chem.* **B 105** (2001) 1026.
- [4] D. Han, X. L. Ren, D. Chem., F. Q. Tang, D. Wang and J. Ren // *Photogr. Sci. Photochem.* **23** (2005) 414.
- [5] X. Y. Kong and Z. L. Wang // *Nano. Lett.* **3** (2003) 1625.
- [6] C.H. Lu and C.H. Yeh // *Ceram. Int.* **26** (2000) 351.
- [7] M. S. Tokumoto, S. H. Pulcineli, C. V. Santilli and V. Briois // *J. Phys. Chem.* **B 107** (2003) 568.
- [8] A. P. A. Oliveira, J. F. Hochepped, F. Grillen and M. H. Berger // *Chem. Matter.* **15** (2003) 3202.
- [9] J. Zhang, L. D. Sun, X. C. Jiang, C. S. Liao and C. H. Yan // *Cryst. Growth Des.* **4** (2004) 309.
- [10] Y. Yang, H. Chen, B. Zhao and X. Bao // *J. Crystal Growth* **263** (2004) 447.
- [11] T. J. Gardner and G. J. Messing // *Thermochim. Acta* **78** (1984) 17.
- [12] X. Y. Zhao, B. C. Zheng and C. Z. Li // *Powder Technol.* **100** (1998) 20.
- [13] J. Zhang, L. D. Sun, H. Y. Pan, C. S. Liao and C. H. Yan // *New J. Chem.* **26** (2002) 33.
- [14] N. S. Pesika, Z. Hu, K. J. Stebe and P. C. Searson // *J. Phys. Chem.* **B 106** (2002) 6985.
- [15] D. V. Talapin, A. L. Rogach, M. Haase and H. Weller // *J. Phys. Chem.* **105** (2001) 12278.
- [16] R. Viswanatha, P. K. Santra, C. Dasgupta and D. D. Sarma // *Phys. Rev. Lett.* **98** (2007) 255501.
- [17] X. Peng, J. Wickham and A. P. Alivisatos // *J. Am. Chem. Soc.* **120** (1998) 5343.
- [18] L. Qu, W. W. Yu and X. Peng // *Nano Lett.* **4** (2004) 465.
- [19] R. Viswanatha and D.D. Sarma // *Chem. Eur. J.* **12** (2006) 180.
- [20] N. S. Pesika, Z. Hu, K. J. Stebe and P. C. Searson // *J. Phys. Chem.* **106** (2002) 6985.
- [21] C. R. Bullen and P. Mulvaney // *Nano Lett.* **4** (2004) 2303.
- [22] W. W. Yu and X. Peng // *Angew. Chem., Int. Ed.* **41** (2002) 2368.
- [23] B. C. Gibb, R. G. Chapman and J. C. Sherman // *J. Org. Chem.* **61** (1996) 1505.
- [24] B. D. Cullity, *Elements of X-ray Diffraction* (Addison-Wesley Publishing Company, Inc., London, 1978).
- [25] S. Bandyopadhyay, G. K. Paul, R. R. Roy and S.K. Sen // *Chem. Phys.* **74** (2002) 83.
- [26] C. Wang, E. Shen, E. Wang, L. Gao, Z. Kang, C. Tian, Y. Lan and C. Zhang // *Materials Lett.* **59** (2005) 2867.
- [27] K. Vanheusden, W. L. Waaen, C. H. Seager, D. R. Tallant and J. A. Voigt // *J. Appl. Phys.* **79** (1996) 7983.
- [28] S. Monticone, R. Tufeu and A. V. Kanaev // *J. Phys. Chem.* **B 102** (1998) 2854.