

A COMPREHENSIVE STUDY ON THE STRUCTURE AND SPECTROSCOPY OF ZINC OXIDE NANOPARTICLES

Dr. Henry Phillips*¹ & Olivia Morgan²

^{1,2} Department of Economics, University of Copenhagen, Denmark

ABSTRACT

In this study, zinc oxide nanoparticles (ZnO) have been synthesized by a simple chemical route. Stability of the size has been achieved by using 2-mercaptoethanol as surface capping molecules. TEM, X-ray Diffraction (XRD), Fourier transform infrared spectrometer (FT-IR), UV-visible and photoluminescence (PL) studies were used to investigate the effect of capping agent on the size, morphology and optical properties of the ZnO nanoparticles.

Key words: Photoluminescence, UV-vis absorption Spectroscopy, TEM, XRD, ZnO nanoparticles.

I. INTRODUCTION

Nanoparticles of II-IV group semiconductors have shown in the past very interesting size-dependent properties such as reduction in the melting point, scaling of energy gap with particle size and corresponding change in the optical properties and so on. The dramatic changes in the properties of nanoparticles are mostly attributed to size effects, although surface effects cannot be neglected. Size effects are due to quantum confinement of charge carriers in nanoparticles and particle sizes can be correlated with observed energy gap variations [1-3]. It is therefore very likely that semiconductor nanoparticles, especially with a wide band gap like ZnO is attracting tremendous attention due to its interesting properties and thus has been the subject of study by many researchers. ZnO is an important wide-band-gap semiconductor that has a direct bandgap (3.37 eV) with a high exciton binding energy (60 meV), good piezoelectric properties, high chemical stability, and bio-compatibility. It can be synthesized in various morphologies allowing a fine tuning of its size- and shape-dependent properties [4,5]. In addition, it is a promising material used for various applications such as solar cells, light emitting diodes, gas sensors, biosensors, transparent conductors, varistors, chemical sensors, surface acoustic wave devices, ultraviolet nano optoelectronic devices, antireflection coatings, degradation of pollutants and random lasers etc. [6-11]. From the literature survey, it was found that various approaches for the synthesis of ZnO nanoparticles have been developed, viz. spray pyrolysis, electrodeposition, ultrasonic, sol-gel, micro emulsion, microwave-assisted techniques, facile pyrolysis mediated synthesis, chemical vapor deposition, and hydrothermal and precipitation methods [12-17]. Most of these techniques were not widely used on a large scale, but chemical synthesis route is considered to be one of the most important and best techniques, due to its simplicity and inexpensiveness. In the present study, an attempt is made to synthesize ZnO nanoparticles by a simple chemical route. Stability of the size has been achieved using mercaptoethanol as surface capping molecules. Here, the characterization of ZnO nanoparticles using X-ray diffraction, FT-IR, TEM, UV-Vis absorbance, and photoluminescence spectra is discussed.

II. EXPERIMENTAL

ZnO nanoparticles were synthesized by a simple chemical route. Basically, the nanoparticles are prepared by hydrolyzing zinc chloride in NaOH/ methanol using chemical method. Zinc oxide (ZnO) NPs about ~3-5 nm sizes were synthesized. Different solutions were prepared by dissolving 20 ml of zinc chloride (2×10^{-1} M), 100 ml of sodium hydroxide (2×10^{-1} M) and mercaptoethanol (X M) all in methanol. Zinc chloride solution, is taken in a reaction vessel and continuously stirred using a magnetic stirrer at room temperature. Varying amount of mercaptoethanol (X M) for obtaining different particle sizes was added to the above reaction mixture. Finally NaOH dissolved in 100 ml methanol was added drop wise to the solution of ZnCl_2 and mercaptoethanol under stirring condition. Growth of the colloidal ZnO could be accelerated by addition of 1.3 ml (1% to the total volume of methanol) of double distilled water to the solution. After three hours of constant stirring we got a resultant solution. The precipitate was washed in methanol and methanol was allowed to evaporate at room temperature to obtain ZnO nanoparticles in white powder form. Powder could be used directly for some measurements or redispersed in methanol for analysis. Particles with various sizes can be obtained with the above procedure by changing the mercaptoethanol concentration. As an illustration we give results on four samples of different sizes viz. Sample A (10^{-1} M), Sample B (10^{-2} M), Sample C (10^{-3} M) and Sample D (10^{-4} M). The freshly prepared ZnO nanoparticles were thoroughly characterized by XRD, FT-IR Spectroscopy, PL, TEM and UV-Vis absorption Spectroscopy.

III. RESULTS AND DISCUSSION

Synthesizing stable nanoparticles of narrow size distribution is very important. A sharp absorption should result if the particles are of uniform size. Figure 1 shows the UV absorption spectra for ZnO nanoparticles with 2-mercaptoethanol as an organic stabilizer. The excitonic peak appears quite sharp without any noticeable tailing. By changing the amount of mercaptoethanol, ZnO nanoparticles with various sizes were obtained.

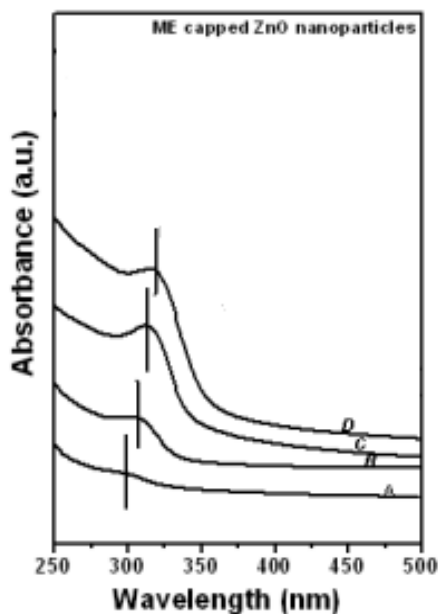


Figure 1 UV-Vis absorption spectra of ZnO nanoparticles

The results obtained show that the absorption spectra for all the samples viz. A, B, C and D are not only blue-shifted but also exhibit sharp excitonic peaks. The particle sizes calculated for the samples A-D using effective mass approximation (EMA) [18,19] varies from ~ 2.6 nm to 3.5 nm resp. Synthesized particles are found to be stable over a long time. The sizes obtained here are smaller than Bohr diameter of exciton (5.1 nm) for ZnO. This result has also been confirmed by the TEM pictures [Figure 2]. Transmission electron microscopy was performed on the sample C. TEM image of the sample C is shown in Figure 2.

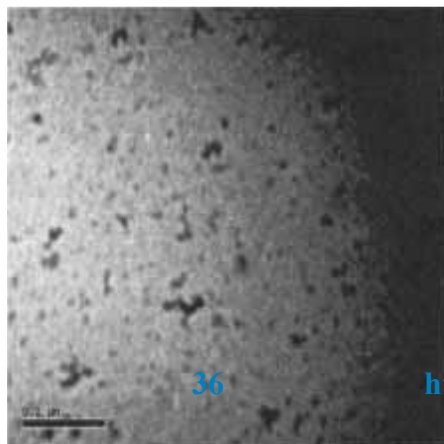


Figure 2 TEM micrograph of ZnO nanoparticles

TEM pictures confirm the formation of ZnO nanoparticles. The particles are not highly dispersed but they are distinct and almost spherical in shape. An average diameter of ~ 5 nm of spherical nanocrystalline ZnO particles can be seen which was in good agreement with the particle size calculated from XRD results. X-ray diffraction patterns obtained for the samples A-D are shown in figure 3. Diffraction patterns reveal that zinc oxide nanoparticles synthesized are of hexagonal wurtzite phase.

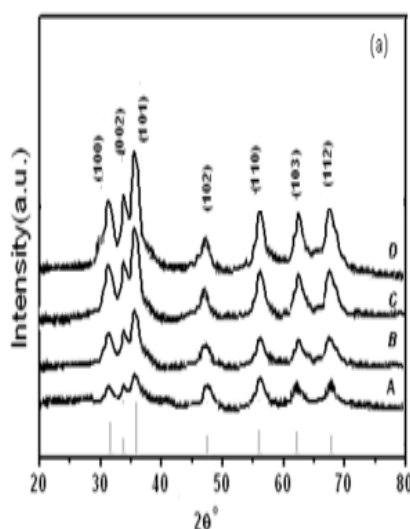


Figure 3 XRD spectra of ZnO nanoparticles

The 'd' values corresponding to the peaks appearing from the planes (100), (002), (101), (102), (110), (103) and (112) were compared with the standard data [JCPDS Card No.36-1451] [20]. By comparison with d_{hkl} values for ZnO bulk it is clear that our samples indeed are of ZnO with hexagonal wurtzite phase with lattice constants $a = b = 0.32$ nm and $c = 0.521$ nm [21]. From the figure 3 it is clearly seen that by increasing the concentration of capping agent, the peaks are broadened (A-D) suggesting the decrease in particle size. By using the Scherrer formula $d = 0.9\lambda / \beta \cos \theta$ the sizes of nanoparticles for the samples (A-D) were estimated from ~ 2.8 to 4.1 nm respectively. Particle size calculated from the XRD and that from the optical absorption is comparable to each other. Optical properties of the capped ZnO nanoparticles were investigated using room temperature photoluminescence measurements. For the PL experiment samples in the colloidal form were prepared by dispersing the particles in methanol with sonication for $\sim$ half hour. Figure 4 depicts the photoluminescence spectra recorded for samples B, C and D. Excitation wavelength used was 345 nm for all the samples.

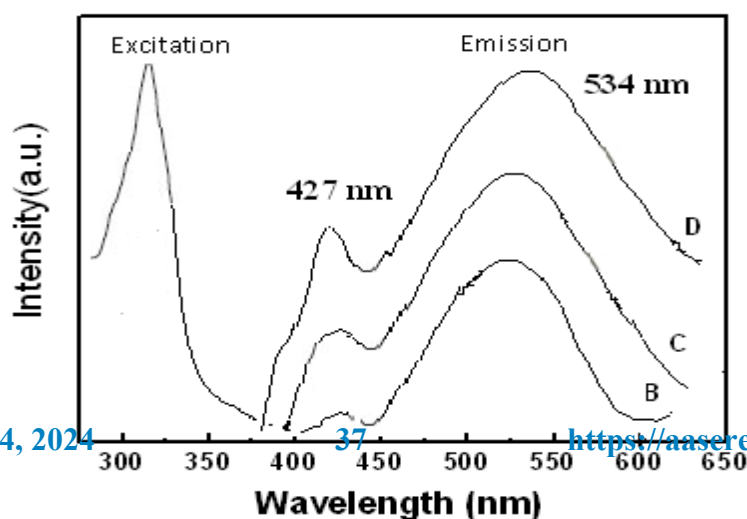


Figure 4 Room temperature Photoluminescence spectra for ZnO nanoparticles

The spectrum exhibits two peaks in the emission spectrum one at ~ 427 nm and second at ~ 534 nm. The peak at ~ 427 nm is due to the band to band transition [22, 23]. The second broad band at ~ 534 nm with minor shoulders attributed to the presence of an anion vacancy trap level within the forbidden gap. [24]. These recombination centers are considered to be due to interstitial zinc or oxygen vacancies [22, 25] present in the nanoparticles. Further in order to study the presence or absence of the various vibrational modes present in ZnO nanoparticles and to investigate the effect of the surfactant, FT-IR spectra of ZnO nanoparticles were recorded. Figure 5 gives the FTIR spectra for mercaptoethanol capped ZnO nanoparticles and spectrum of bare mercaptoethanol for the comparison. Comparison of spectrum due to mercaptoethanol with those of capped ZnO clearly indicates the presence of mercaptoethanol on the nanoparticle surfaces. The band at ~ 435 cm^{-1} to ~ 490 cm^{-1} is correlated to Zinc oxide [26]. The sharp peak for -SH stretching was observed at 2563 cm^{-1} in case of mercaptoethanol. It completely disappeared in quantum ZnO, which was attributed to the breaking of -SH bond. Presence of a broad peak in the region 3370 cm^{-1} to 4200 cm^{-1} [27] in all the samples can be attributed to -OH group in mercaptoethanol. There might be some contribution to this peak from the hydroxide which is generally present on the surface of ZnO nanoparticles. The peak at ~ 2350 cm^{-1} indicate the presence of C=O residues probably due to CO_2 . The presence of other bands at ~ 880 , ~ 1380 and 2360 cm^{-1} are probably due to the carbonate moieties which is generally observed when FT-IR samples are measured in air [28].

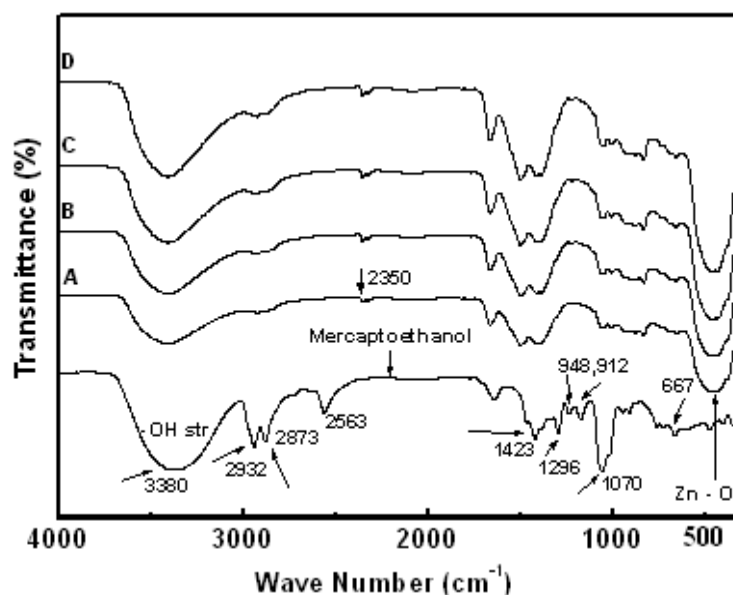


Figure 6 FT-IR spectra for ZnO nanoparticles

It seems, from these curves, that the nature of the bonds in sols changes with higher concentration of mercaptoethanol. These results and the similarity between spectra for mercaptoethanol capped nanoparticles and that with bare mercaptoethanol confirms that mercaptoethanol is present on the ZnO nanoparticle surface protecting it from agglomeration.

IV. CONCLUSION

ZnO nanoparticles of different sizes have been synthesized using wet chemical route. The formation of prepared ZnO nanoparticles was confirmed by X-ray diffraction (XRD) analysis. Using Scherrer's formula, the particle sizes were estimated to be in the range of ~2.8 to 4.1nm. The functional groups of ZnO and mercaptoethanol were identified by FT-IR analysis. The size and morphology of the samples were characterized using transmission electron microscopy (TEM). The particles are not highly dispersed but they are distinct and almost spherical in shape. An average diameter of ~5 nm of spherical nanocrystalline ZnO particles can be seen. The UV absorption peaks were blue shifted which confirmed Quantum confinement effect. Strong green photoluminescence was observed at ~534nm from all the nanoparticles. The synthesis procedure can be extended further to prepare doped ZnO nanoparticles.

REFERENCES

1. Ramakrishna, M. V.; Friesner, R. A. *J. Chem. Phys.* 1991, 95,8309
2. Lippens, P. E.; Lanoo, M. *Phys. Rev. B* 1989, 39, 10935.
3. Murray, C. B.; Norris, D. B.; Bawendi, M. G. *J. Am. Chem. Soc.* 1993, 115, 8706.
4. Z. L. Wang, *Mater. Today* 7, 2004, pp.26.
5. S. A. Akhoun, S. Rubab, M. A. Shah, 2015 , *Int Nano Lett* 5: 9–13.
6. Y. Hames, Z. Alpaslan, A. K'osemen, S. E. San, and Y. Yerli, *Solar Energy*, vol. 84, no. 3, 2010, pp. 426–431.
7. X. L. Cheng, H. Zhao, L. H. Huo, S. Gao, and J. G. Zhao, *Sensors and Actuators, B*, vol. 102, no.2, 2004, pp. 248–252.
8. P. X. Gao, Y. Ding, W. Mai, W. L. Hughes, C. Lao, and Z. L. Wang, *Science*, vol. 309, no. 5741, 2015, pp. 1700–1704.
9. Zohra N.Kayani, Farhat Saleem iIffat Batool, *Materials Today proceedings*, Volume 2, Issue 10, Part B, 2015, pp. 5619-5621.
10. P. Sharma, K. Sreenivas, and K. V. Rao, *Journal of Applied Physics*, vol. 93, no. 7, , 2003. pp. 3963–3970.
11. Nanda, J.; Sapra, S.; Sarma, D. D.; Chandrashekharan, N.; Hodes, G. *Chem. Mater.* 2000, 12, 1018.
12. Koch, U.; Fojtik, A.; Weller, H.; Henglein, A. *Chem. Phys. Lett.* 1985, 122, 507.
13. Spanhel, L.; Weller, H.; Henglein, A. *J. Am. Chem. Soc.* 1987, 109, 6632.
14. Ying Chen, Hao Ding and Sijia Sun, *J. of Nanomaterials* 2017, 7, 217
15. A. B. Moghaddam, T. Nazari, J. Badraghi, and M. Kazemzad, *International Journal of Electrochemical Science*, vol. 4, no. 2, 2009, pp. 247–257,
16. Arora,Devi,Jaswal,J.Singh,,M.Kinger,andV.D.Gupta,*Oriental Journal of Chemistry*, 2014, Vol. 30, No. (4): pp. 1671-1679
17. Pranjali P.Mahamuni, Pooja M.Patil, Maruti J.Dhanavade, Manohar V.Badiger, Prem G.Shadija, Abhishek C.Lokhande, Raghvendra A.Bohara, *J.of Biochemistry and Biophysics Reports*, Volume 17, March 2019, pp.71-80
18. S. Shionoya and W. M. Yen, Eds., *Phosphor Handbook*, CRC Press, Boca Raton, Fla, USA, 1998.
19. L. I. Berger, *Semiconductor Materials*, CRC Press, Boca Raton, Fla, USA, 1997
20. JCPDS, *Powder Diffraction File, Alphabetical Index, Inorganic Compounds*, International Centre for Diffraction Data, Newtown Square, Pa, USA, 1977.
21. Z. M. Khoshhesab, M. Sarfaraz, and M. A. Asadabad, 'Synthesis and Reactivity in Inorganic, Metal-Organic and Nano-Metal Chemistry, vol. 41, no. 7, 2011, pp. 814–819.
22. M. H. Huang, Y. Wu, H. Feick, N. Tran, E. Weber, and P. Yang, *Advanced Materials*, vol. 13, no. 2, 2001, pp. 113–116,
23. Spanhel, L.; Anderson, M. A. *J. Am. Chem. Soc.* 1991, 113, 2826.
24. G. Williams and P. V. Kamat, *Langmuir*, vol. 25, no. 24, 2009. pp. 13869–13873.
25. J. R. Heath and J. J. Shiang, *Chemical Society Reviews*, vol. 27, no. 1, pp.65–71, 1998.
26. Nagao M. *J Phys Chem.* 1971, 75:3822-8.
27. D. Shindo, T. Oikawa, *Analytical Electron Microscopy for Material Science*, Springer- Verlag Tokyo 2002
28. Lili WU, Youshi WU, Yuanchang SHI, et al. *Rare Metal.* 2006, 25: pp.68-73.