

Temperature Dependence of Structural and Optical Properties of ZnO Nanoparticles Formed by Simple Precipitation Method

Christian Mark Pelicano^a, Eduardo Magdaluyo^b, Atsushi Ishizumi^c

^{a,b}Department of Mining, Metallurgical and Materials Engineering, University of the Philippines, Quezon City Philippines
^cGraduate School of Materials Science, Nara Institute of Science and Technology, Ikoma Nara Japan

Abstract. ZnO nanoparticles were successfully synthesized by a simple precipitation method. The effect of growth temperature on the structural and optical properties of the resulting nanoparticles was investigated by transmission electron microscopy (TEM), ultraviolet-visible spectroscopy (UV-VIS) and photoluminescence (PL) spectroscopy. TEM images and selected area electron diffraction (SAED) pattern showed that the nanoparticles were polycrystalline ZnO having hexagonal wurtzite structure. The average size of the nanoparticles were 4.72nm to 7.61nm synthesized at room temperature to 80°C. This result is also consistent with the calculated sizes using effective-mass approximation model. From the optical absorption data, the band gap energy of nanoparticles blue-shifted due to the quantum confinement.

1 Introduction

Particles of semiconductor materials in nanoscale have recently gained much interest due to their unique physical and chemical properties, which are different from the bulk materials. Among these materials, ZnO nanoparticles have been consistently studied due to its several possible applications in sensors [1], catalysis [2], photovoltaics [3-4] and piezoelectric transducers [5], among others. ZnO is an n-type semiconductor with a direct wide band gap of 3.37 eV and a large exciton binding energy of about 60 meV at room temperature [6]. It also has a high absorption coefficient, good carrier mobility and flexible synthesis techniques. The properties of nanostructured ZnO depend strongly on its structural morphology and crystal size [7]. Thus, a deep understanding of these properties is necessary for fundamental study and utilization for commercial applications.

Various synthesis methods have already been developed for ZnO nanoparticles such as metal organic chemical vapor deposition (MOVCD) [8], sol-gel [9], flame spray pyrolysis [10], thermal decomposition [11] and precipitation [12]. However, these methods require controlled reaction systems such as high temperature, high cost materials and complicated equipment [13] except for the precipitation route which offers a simple and economical method for large scale production. In this study, a simple precipitation method was utilized to synthesize ZnO nanoparticles. The effect of growth temperature to the structural and optical properties of the resulting nanoparticles was also examined using

transmission electron microscope (TEM), (UV-VIS) and photoluminescence (PL) spectroscopy.

2 Experimental

Dimethyl sulfoxide (DMSO, (CH₃)₂SO) and ethanol (CH₃CH₂OH, 99.5%) were used as solvents; zinc acetate dehydrate (Zn(CH₃CO₂)₂·2H₂O) as precursor; tetramethylammonium hydroxide (N(Me)₄OH·5H₂O) for hydrolysis. In a typical preparation, 6 ml of 0.55M N(Me)₄OH in ethanol was added dropwise at approximately 0.6 mL/min to 0.1M Zn(CH₃CO₂)₂·2H₂O dissolved in DMSO under constant stirring. The nanoparticles were precipitated and washed twice by centrifugation for 30 min in ethyl acetate to eliminate excess reactants. After which the nanoparticles were redissolved in 3 ml ethanol for storage. The morphology and structure of ZnO nanoparticles were examined by transmission electron microscope (TEM, JEM-3100FEF) and selected area diffraction (SAED). For optical characterization, the UV-VIS transmittance and photoluminescence (PL) spectra were measured by JASCO V-530 and FP 750 spectrometer, respectively.

3 Results and discussion

Figure 1 shows the TEM images of ZnO nanocrystals formed at different temperatures. At room temperature, monodispersed ZnO nanocrystals with a mean diameter of 4.72nm were formed as seen in Figure 1(a). Increasing the temperature to 40°C, the mean diameter of the

Corresponding author: ^acopelicano@upd.edu.ph, ^bedmagdaluyo@gmail.com

nanocrystals increased to about 5.24nm. As can be observed, the particles have started to agglomerate due to Oswald ripening process which could be induced by increasing supply of thermal energy. At higher temperatures of 60°C and 80°C, larger particles with mean diameters of 6.70 and 7.61nm developed, respectively, as seen in Figure 1(c) and 1(d). When the growth temperature is increased the critical particle radius increased as well resulting to the disappearance of the smaller particles to supplement the growth of the larger ones [14]. Here, the following chemical reactions govern the growth stages of ZnO nanoparticles:

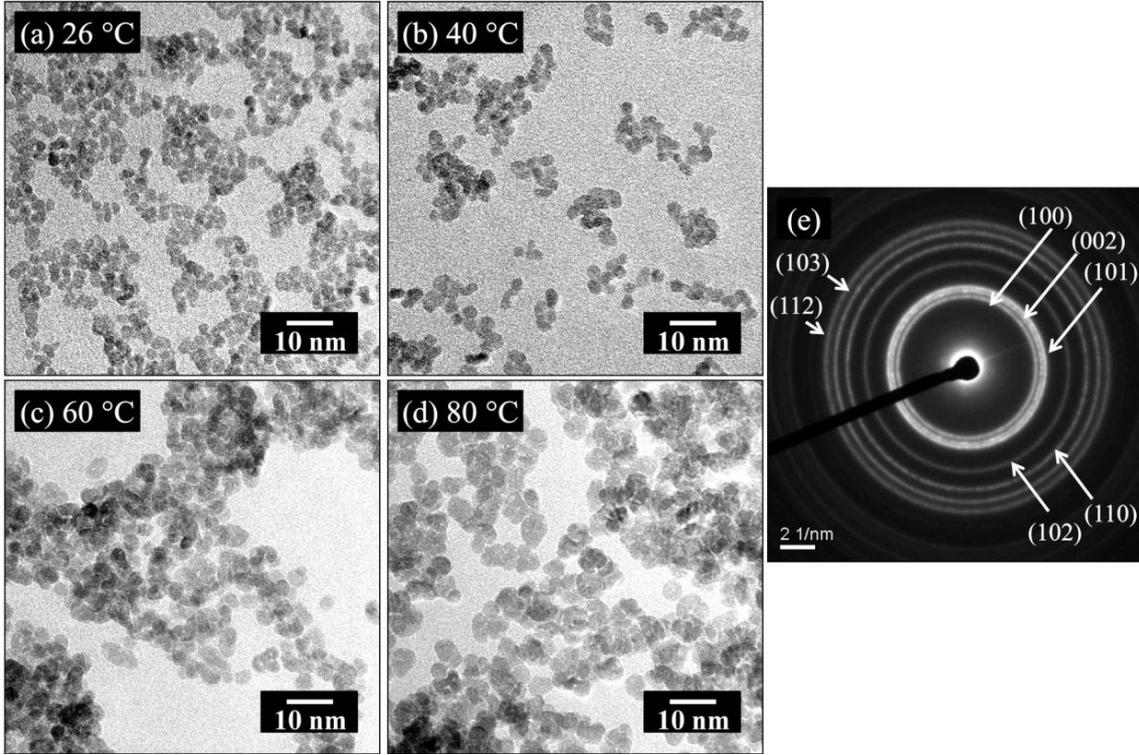
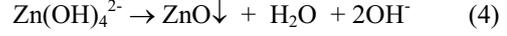
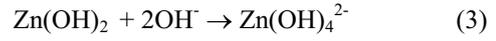


Figure 1. TEM images of ZnO nanocrystals synthesized at different temperatures: (a) 26°C, (b) 40°C, (c) 60°C, (d) 80°C and (e) SAED pattern for 80°C sample

When the $\text{N}(\text{Me})_4\text{OH} \cdot 5\text{H}_2\text{O}$ in ethanolic solution was slowly added into the $\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$ in DMSO solution, $\text{Zn}(\text{OH})_2$ precipitated instantaneously, as illustrated reaction (2). Further addition of hydroxyl ions (OH^-) resulted in the conversion of $\text{Zn}(\text{OH})_2$ into soluble $\text{Zn}(\text{OH})_4^{2-}$. As the reaction proceeded, $\text{Zn}(\text{OH})_4^{2-}$ is dehydrated into ZnO following crystal growth. Figure 2 shows the UV-VIS absorption spectra of the synthesized ZnO nanocrystals for different temperatures. As the reaction temperature is decreased, the characteristic absorption peaks of the synthesized ZnO nanocrystals blue-shifted from 3.54 to 3.71 eV due to quantum confinement effect. On the other hand, these energy band gap values can be used to calculate estimation of size variation from the absorption spectra through the effective mass approximation model [15]:

$$E_g^* = E_g^{\text{Bulk}} - R_y^* + \frac{2\pi^2\hbar^2}{MD^2} \quad (5)$$

where $E_g^{\text{Bulk}} = 3.37$ eV is the energy of band gap of the bulk ZnO, M is the effective mass, \hbar is Planck's constant, $R_y^* = 0.04$ eV is the Rydberg's constant, D is the diameter of the nanoparticles and E_g^* is the energy band gap in eV that can be calculated from the excitonic absorption peak using Equation 6:

$$E_g^* = \frac{1240}{\lambda_{\text{excitonic}}} \quad (6)$$

Table 1. Measured and calculated nanoparticle size aBy UV-VIS, bBy TEM

Temperature (°C)	Band Gap (eV)	Diameter Size ^a (nm)	Diameter Size ^b (nm)
26	3.71	5.86	4.72
40	3.60	6.88	5.24
60	3.57	7.27	6.70
80	3.54	7.73	7.61

The size values using the effective mass model are given in Table 1. The results are in agreement with those measured using TEM having the same trend of increasing size as growth temperature is increased. Figure 3 shows the PL spectra of the ZnO nanoparticles at different temperatures. It has been well established that nanostructured ZnO with small size and defects demonstrates strong visible emission [17], attributed to defects such as oxygen (V_o) and zinc (Zn_i) interstitials. Here, only a strong visible emission can be observed at room temperature synthesis. At the same time large size and crystalline in nature nanoparticles exhibit stronger UV emission [16] which is related to a near band-edge transition of ZnO, specifically, the recombination of the free excitons. When the temperature is increased to 40°C and 60°C, both UV and visible emissions can be seen due to the development of larger particles in this temperature regime. Defects present decreased as the surface area of the nanoparticles increased due to Ostwald ripening. At reaction temperature of 80°C, only UV emission was observed and could indicate increased crystallinity of the nanoparticles. It should be noted that the emission peaks also red-shifted to higher wavelength supporting the earlier results of an increase in the diameter of the nanoparticles at higher temperatures.

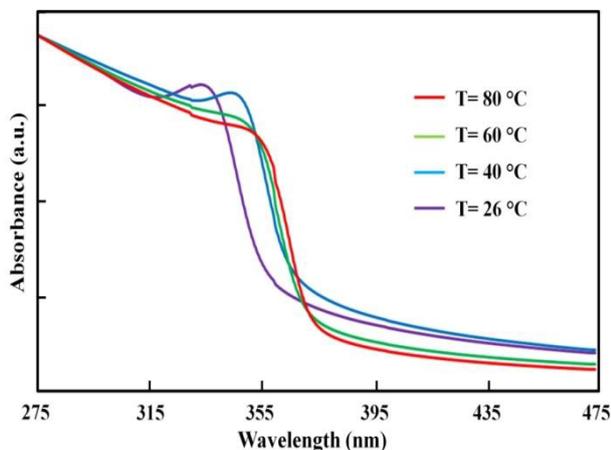


Figure 2. UV-VIS Absorption spectra of ZnO nanoparticles synthesized at different temperatures

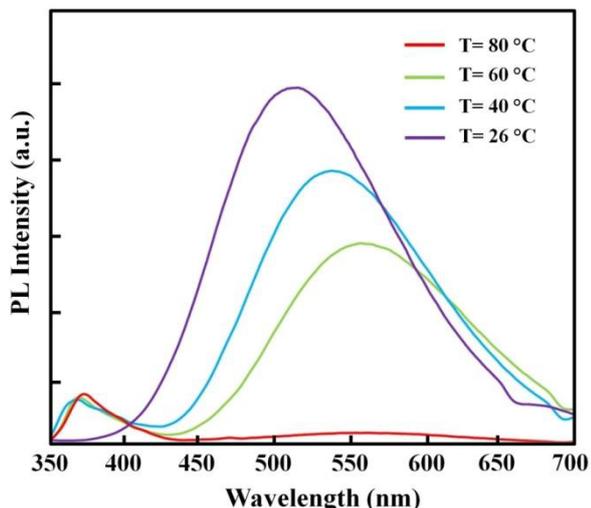


Figure 3. Photoluminescence spectra of ZnO nanocrystals for different temperatures

4 Summary

We demonstrated a simple precipitation method for the preparation of ZnO nanoparticles using zinc acetate and tetramethylammonium hydroxide as precursors. The particles were hexagonal ZnO with average sizes of 4.72-7.61nm for increasing reaction temperatures. This trend is consistent from calculations using effective mass approximation model. From absorption data, the band gap values blue-shifted to lower temperatures revealing quantum confinement at smaller diameters. These size-controlled properties of ZnO nanoparticles exhibit good utilization for various commercial applications.

References

- Haiqin Bian et al., "Improvement of acetone gas sensing performance of ZnO nanoparticles", *Journal of Alloys and Compounds* 658 (2016) 629e635
- Chayma Abed et al., "Mg doping induced high structural quality of sol-gel ZnO nanocrystals: Application in photocatalysis", *Applied Surface Science* 349 (2015) 855-863
- E. Gondek et al., "Organic hybrid solar cells—Influence of ZnO nanoparticles on the photovoltaic efficiency", *Materials Letters* 131 (2014) 259-261
- Muhammad Ikram et al., "Hybrid organic solar cells using both ZnO and PCBM as electron acceptor materials", *Materials Science and Engineering B* 189 (2014) 64-69
- Van Son Nguyen et al., "Influence of cluster size and surface functionalization of ZnO nanoparticles on the morphology, thermomechanical and piezoelectric properties of P(VDF-TrFE) nanocomposite films", *Applied Surface Science* 279 (2013) 204-211
- Y. I. Ozgur, Alivov, C. Liu et al., "A comprehensive review of ZnO materials and devices," *J. Appl. Phys.* 98 (2005), 1-103.
- J. Z. Yin, et al., Water Amount Dependence on Morphologies and Properties of ZnO nanostructures in Double-solvent System. *Sci. Rep.* 4, 3736.
- Jie Jiang et al., "Effects of phosphorus doping in ZnO nanocrystals by metal organic chemical vapor deposition", *Materials Letters* 68 (2012) 258-260
- E Moghaddam et al., "Preparation of surface-modified ZnO quantum dots through an ultrasound assisted sol-gel process", *Applied Surface Science* 346 (2015) 111-114
- Okorn Mekasuwandumrong et al., "Effects of synthesis conditions and annealing post-treatment on the photocatalytic activities of ZnO nanoparticles in the degradation of methylene blue dye", *Chemical Engineering Journal* 164 (2010) 77-84
- Mutasim I. Khalil et al., "Synthesis and characterization of ZnO nanoparticles by thermal decomposition of a curcumin zinc complex", *Arabian Journal of Chemistry* (2014) 7, 1178-1184

12. K. Jeyasubramaniana,, G.S. Hikkua, R. Krishna Sharma,"Photo-catalytic degradation of methyl violet dye using zinc oxide nano particles prepared by a novel precipitation method and its anti-bacterial activities", *Journal of Water Process Engineering* 8 (2015) 35–44
13. C.Wang,W.X. Zhang, X.F. Qian, X.M. Zhang, Y. Xie, Y.T. Qian, A room temperature chemical route to nanocrystalline PbS semiconductor, *Mater. Lett.* 40 (1999) 255–258.
14. Ronald Buckley,"Solid State Chemistry Research trends", Nova Science Publishers Inc., 2007
15. L.E. Brus, *J. Chem. Phys.* 80 (1984) 4403.
16. Sun, T. J.; Qiu, J. S.; Liang, C. H. *J. Phys. Chem. C* 2008, 112, 715–721.
17. Djuris'ic', A. B.; Choy, W. C. H.; Roy, V. A. L.; Leung, Y. H.; Kwong, C. Y.; Cheah, K. W.; Rao, T. K. G.; Chan, W. K.; Surya, C. *AdV. Funct. Mater.* 2004, 14, 856–864.