

## Morphology and Optical Properties of Zinc Oxide Nanoparticles Synthesised by Solvothermal Method

Widiyastuti Widiyastuti<sup>\*,a</sup>, Siti Machmudah<sup>a</sup>, Tantular Nurtono<sup>a</sup>, Sugeng Winardi<sup>a</sup>, Ratna Balgis<sup>b</sup>, Takashi Ogi<sup>b</sup>, Kikuo Okuyama<sup>b</sup>

<sup>a</sup>Department of Chemical Engineering, Institut Teknologi Sepuluh Nopember, Kampus ITS Sukolilo, Surabaya, Indonesia

<sup>b</sup>Department of Chemical Engineering, Hiroshima University, Higashi-Hiroshima, Japan

widi@chem-eng.its.ac.id

Zinc oxide (ZnO) nanoparticles were successfully synthesised in solvothermal batch reactor using zinc acetate as precursor and ethanol as solvent, without any surfactant addition. Commercial batch Teflon reactor of 21 mL was used and filled 80 % capacity with 0.1 M zinc acetate solution. The reactor was heated in an oven and held at a constant temperature for 12 h. In order to investigate the temperature effect on the characteristics of the generated particles, the reactor temperatures were varied at 120, 140, 160, and 180 °C. The powder was characterised by its morphology, crystallinity, and photoluminescence spectra via scanning electron microscopy (FE-SEM, Hitachi), x-ray diffraction (XRD, Phillips), and photoluminescence spectrometer (Simadzu) respectively. Spherical nanoparticles were generated for particles synthesised without LiOH addition into precursor. By adding 0.14 M LiOH into the precursor, rod particles were obtained with an aspect where the ratio (length to diameter) of particle increased with temperatures. Based on the X-ray diffraction analysis, wurtzite structure of ZnO in a hexagonal phase was formed. Neither impurities nor other crystalline phases were observed in the samples. The crystalline size increased from 19 to 28 nm by increasing the reactor temperature from 120 to 180 °C. LiOH addition led to decrease in the crystalline size at the same reactor temperature. Their crystalline size increased from 16 to 23 nm by increasing the reactor temperature from 120 to 180 °C. Photoluminescence intensity increased with temperatures. LiOH addition was able to shift the photoluminescence emission spectra peak from wavelength of 421 nm to 457 nm by excitation at wavelength of 250 nm. It corresponded to the dominant emission shifted from violet to blue by adding LiOH during the synthesis.

### 1. Introduction

ZnO particles have been widely applied in the field of optics and optoelectronics because they have wide bandgap semiconductor compound ( $E_g = 3.37$  eV) with a large exciton binding energy (60 meV) (Morkoç and Özgür, 2009). Comparing to that of the thermal at room temperature at 26 meV, ZnO particles exhibit a strong exciton binding energy correspond to a valuable photonic material in the UV-blue region (Ghoshal et al., 2008). Due to its good electrical and optical properties, thermal and chemical stability, non-toxicity, and relatively low price as metal-oxide semiconductors, ZnO particles have been applied as photocatalyst, solar cell windows, sensor for volatile organic compound (Saito et al., 2014) and specifically, sensor for nitro-organic compound (Casa et al., 2016). These wide range of electrical and optical properties highly depend on both the shape and size of nanostructured particles.

Many methods have been developed to control the properties of ZnO nanostructured particles. Fine spherical particles were produced by spray pyrolysis method. Aluminium as dopant was selected to control the electrical properties of ZnO film (Widiyastuti et al., 2012). Nano-sized ZnO particles have been synthesised using low pressure spray pyrolysis (Hidayat et al., 2008) and pulse combustion spray pyrolysis (Widiyastuti et al., 2007). ZnO nanostructured using green process of sonochemical reaction method was also reported that pulse wave of ultrasonic irradiation affected the photoluminescence intensity and photocatalytic activity (Widiyastuti et al., 2015).

Another green process to produce ZnO nanostructures is solvothermal method. A solvothermal process can be defined as a chemical reaction in a closed system in the presence of a solvent at a temperature higher than that of the boiling point of such a solvent. Solvothermal process has been of interest due to its mild synthesis conditions, simple processes, low cost and simple equipment, and inherent stability. The size and morphology of ZnO nanoparticles can be controlled by adjusting the ratio of the two selected solvents, in the template-free solvothermal method (Lian et al., 2012). Solvothermal method can produce pencil-like ZnO microrod (Liu et al., 2012). Other experimental parameters such as reaction temperature, reaction time, and solvent, precursor, and additive/surfactant types might affect the growth of novel nanostructures of ZnO which led to the controlled characteristics of the generated ZnO particles.

In this study, the effect of temperature in producing ZnO nanoparticles in a solvothermal method on the generated particle morphology and photoluminescence properties was investigated. Ethyl alcohol and zinc acetate dihydrate were selected as the solvent and the precursor. The effect of lithium hydroxide added in the solution was also examined.

## 2. Experimental

Zinc acetate dihydrate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  99.5 %, Merck) was dissolved in ethanol by stirring to prepare zinc salt solution. In order to prepare zinc salt solution with lithium hydroxide addition, zinc acetate and lithium hydroxide solutions were mixed to obtain the final solution containing 0.1 M zinc acetate and 0.14 M lithium hydroxide. Commercial batch Teflon reactor of 21 mL was used and filled 80 % capacity with precursor solution. Reactor was heated in an oven and held at a constant temperature for 12 hours. The oven was turned off for natural cooling to room temperature. The oven temperature was set at 120, 140, 160 and 180 °C to investigate the effect of temperature. The generated particles were separated from the liquid by centrifugation. Then, they were washed by distillate water for three time to make sure the contaminants were eliminated. After that, the particles were placed in crucible boat and were dried in oven at temperature 60 °C for 6 h. The powder was characterised by its morphology, crystallinity, chemical bonding, and photoluminescence spectra via field emission scanning electron microscopy (FE-SEM, Hitachi), x-ray diffraction (XRD, Phillips), and photoluminescence spectrometer (Simadzu).

## 3. Results and discussion

The morphologies of the generated ZnO particles at various temperatures were analysed by FE-SEM. Figure 1(a) - (d) show the morphology of particles synthesised at 120, 140, 160, and 180 °C, without LiOH addition. The temperatures were selected under subcritical condition, in which the synthesis temperature was larger than that of normal boiling temperature of ethyl alcohol (78.37 °C) as a solvent and lower than that of its critical temperature (241 °C). Spherical particles were produced and the sizes increase with temperatures. In addition, for temperature of 180 °C, the particle sphericity decreased. The average size are 32, 38, 42, and 60 nm for synthesis temperatures of 120, 140, 160, and 180 °C.

The particles morphology was deformed from spherical to nanorod when LiOH was added to the precursor as depicted in Figure 2(a) - (d) for synthesis temperatures of 120, 140, 160, and 180 °C. The diameter and length of nanorod increased by increasing the temperature from 120 to 140 °C. The size decreased steeply with the increase of temperature from 140 to 180 °C. Table 1 shows the length, width, and ratio of length and width (L/W) for particles synthesized by adding LiOH at varied temperatures.

In the solvothermal process, the formation of ZnO nanostructures follows two consecutive stages, nucleation and secondary growth processes. Nucleation process is indicated by the formation of  $\text{Zn}(\text{OH})_2$  colloids from the reaction of  $\text{OH}^-$  ions and  $\text{Zn}^{2+}$  ions in the ethyl alcohol. As the supersaturation reaches,  $\text{Zn}(\text{OH})_2$  colloids precipitates and then decomposes into ZnO nuclei at elevated temperature. It is assumed that LiOH is involved in the secondary growth of ZnO nuclei in elongating structures. The addition of LiOH can increase the supersaturation degree. This process led to the growth of elongated structures and the roughness of the surface (Hu et al., 2010).

*Table 1: Length, width, and ratio of length and width (L/W) for particles synthesised by adding LiOH at varied temperatures*

Temperature (°C)	Average Length, L (nm)	Average Width, W (nm)	L/W
120	17.21	50.53	2.93
140	36.04	87.75	2.43
160	25.14	59.19	2.35
180	23.24	55.11	2.37

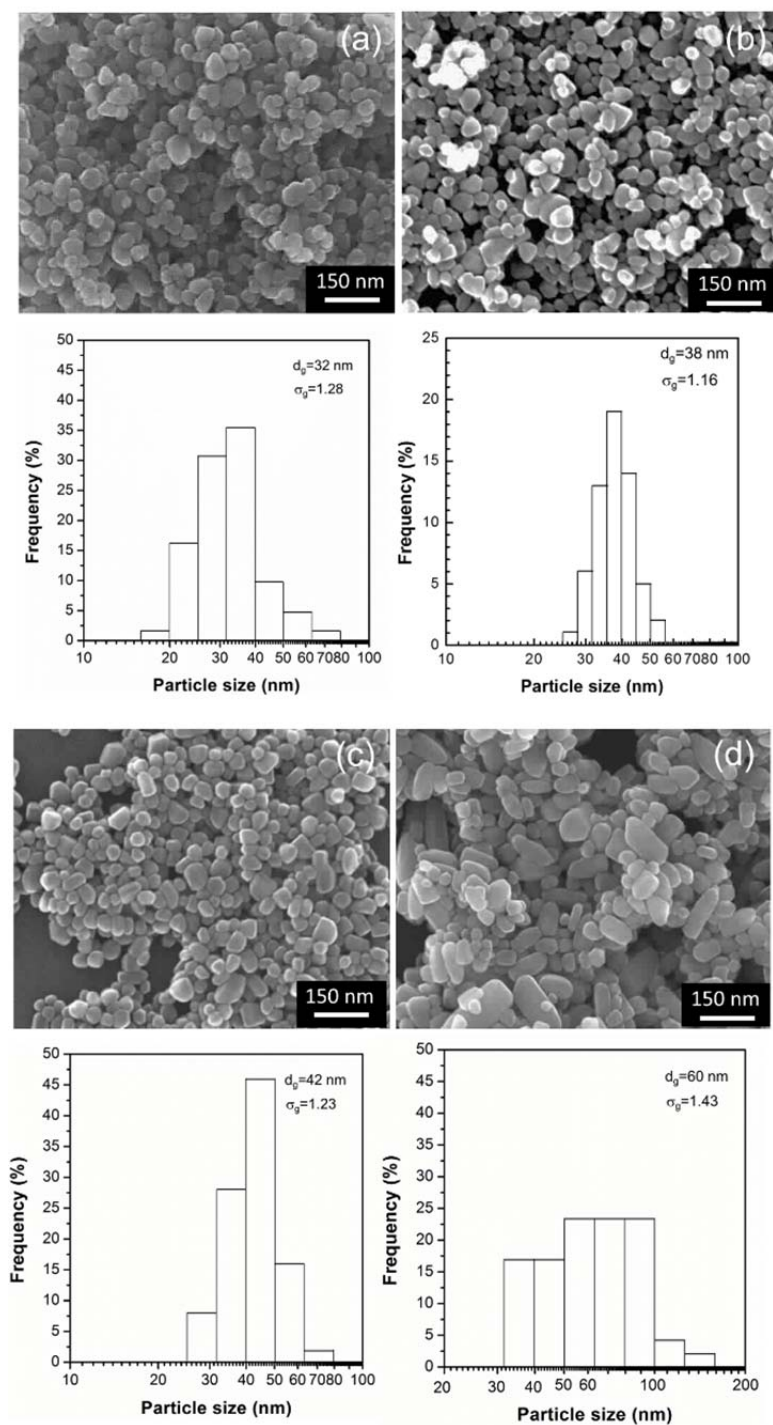


Figure 1: SEM images of the generated particles using precursor without LiOH addition for reactor temperatures of (a) 120 °C, (b) 140 °C, (c) 160 °C, and (d) 180 °C

Figure 3(a) and 3(b) show the XRD diffractograms of ZnO particles prepared at varied temperatures without LiOH addition and with LiOH addition. It can be shown that the diffractograms were in good agreement with that of JCPDS 36-1451 corresponding to the hexagonal wurtzite crystal structure of ZnO. No other impurities peaks observed in the XRD diffractograms revealed that the crystalline ZnO formed well for all samples. The addition of LiOH did not affect the diffractograms which agreed well with the ZnO standard of JCPDS 36-1451. However, LiOH addition caused the (0 0 2) lattice plane at  $2\theta = 34.364^\circ$  was higher than that of (1 0 0) lattice

plane at  $2\theta = 31.732^\circ$ . The presence of  $\text{Li}^+$  in the precursor can slow down the growth speed in one direction and increase it in another direction (Ehrentraut et al., 2006).

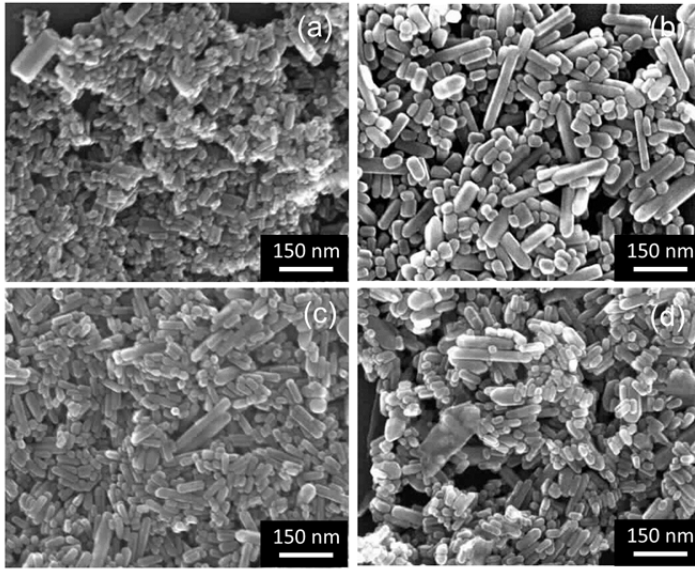


Figure 2: SEM images of the generated particles using precursor with 0.14 M LiOH addition for reactor temperatures of (a) 120 °C, (b) 140 °C, (c) 160 °C, and (d) 180 °C

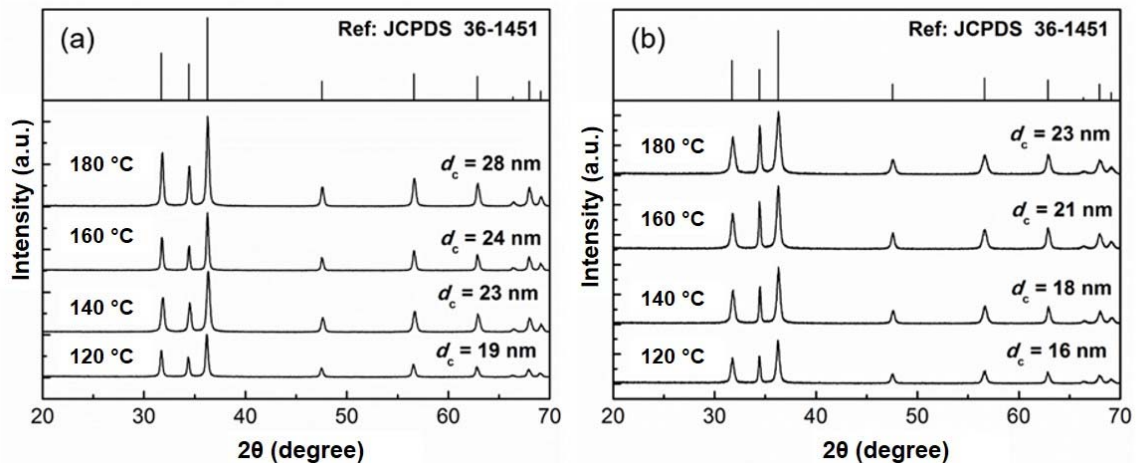


Figure 3: XRD patterns of the generated particles synthesised at various temperatures (a) without LiOH addition and (b) with 0.14 M LiOH addition

The crystalline size,  $d_c$ , was estimated using Scherrer equation based on the highest peak in XRD diffractograms correspond to (1 0 1) lattice plane at  $2\theta = 36.252^\circ$ . The crystalline size of the generated ZnO nanostructures increase with temperature. The addition of LiOH inhibited the growth of ZnO crystal resulting in smaller crystalline size than that of ZnO without LiOH addition. Figure 4 shows the effect of synthesis temperature on the crystalline size of the generated ZnO particles.

Photoluminescence emission spectra of ZnO samples that excited at wavelength of 250 nm are shown in Figure 5. ZnO particles synthesised without LiOH addition have the highest emission peak at 421 nm corresponding to violet emission spectra. The photoluminescence intensities have linear correlation with synthesis temperature. LiOH added into the precursor was able to shift the photoluminescence emission peak to 457 nm corresponding to blue emission spectra. Besides photoluminescence spectra can be used to evaluate the optical properties, it can be used to study the defect characteristics. The characteristic of near-band-edge emission of free exciton recombination process causes ultra-violet/violet emissions whereas blue emission was caused by association with oxygen vacancies.

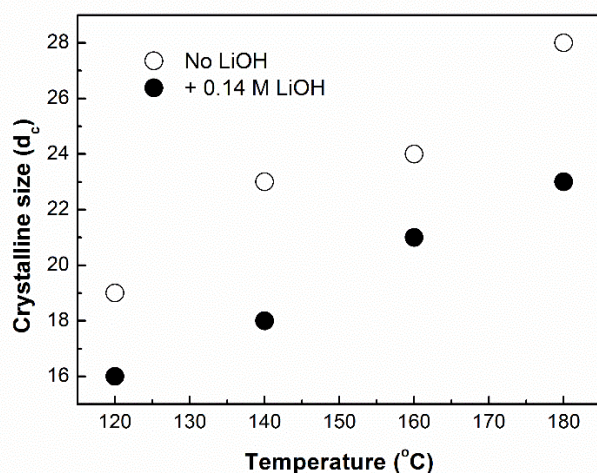


Figure 4: Effect of LiOH addition and solvothermal temperature on the crystalline size of the generated particles

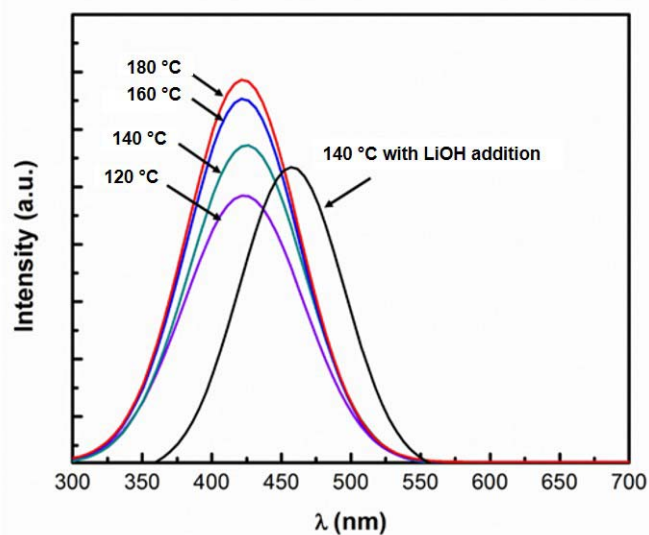


Figure 5: Photoluminescence spectra of the generated particle at varied temperature and compared to particles that generated by LiOH addition during the synthesis

#### 4. Conclusions

ZnO nanoparticles were produced using solvothermal method. Particles characteristics were affected by synthesis temperature and addition of LiOH into the precursor. Spherical and nanorod nanoparticles were produced by without LiOH and with LiOH, added into precursor. XRD analysis of all the generated particles was in good agreement with hexagonal wurtzite crystal structure of ZnO. The size of particles and the crystalline increased with temperatures and decreased with the addition of LiOH. Photoluminescence emission spectra peak was shifted from wavelength of 421 to 457 nm corresponding to violet to blue emission by adding LiOH into precursor when they were excited at wavelength of 250 nm.

#### Acknowledgments

The authors want to thank Ms. Hikmatul Auliyah and Ms. Palupi Nisa for assistance in the experiments. Research Grant sponsored by Ministry of Research Technology and Higher Education, Republic Indonesia under research collaborations and international publications scheme (No. 078/SP2H/LT/DRPM/II/2016) is gratefully acknowledged.

**Reference**

- Casa M., Sarno M., Paciello L., Revelli M., 2016, Synthesis and Characterization of Water Stable ZnO Quantum Dots Based-Sensor for Nitro-Organic Compounds, *Chem. Eng. Trans.* 47, 7-12.
- Ehrentraut D., Sato H., Kagamitani Y., Sato H., 2006, Solvothermal growth of ZnO, *Prog. Cryst. Growth Ch.* 52, 280-335.
- Ghoshal T., Kar S., Ghatak J., Chaudhuri S., 2008, ZnO nanocones: Solvothermal synthesis and photoluminescence properties, *Mater. Res. Bull.* 43, 2228-2238.
- Hidayat D., Ogi T., Iskandar F., Okuyama K., 2008, Single crystal ZnO:Al nanoparticles directly synthesized using low-pressure spray pyrolysis, *Mat. Sci. Eng. B – Solid.* 151, 231-237.
- Hu Q.R., Wang S.L., Jiang P., Xu H., Zhang Y., Tang W.H., 2010, Synthesis of ZnO nanostructures in organic solvents and their photoluminescence properties, *J. Alloy. Compd.* 496, 494-499.
- Lian J., Liang Y., Kwong F., Ding Z., Ng D.H.L., 2012, Template-free solvothermal synthesis of ZnO nanoparticles with controllable size and their size-dependent optical properties, *Mater. Lett.* 66, 318-320.
- Liu Z., Zhang, Q., Li Y., Wang H., 2012, Solvothermal synthesis, photoluminescence and photocatalytic properties of pencil-like ZnO microrods, *J. Phys. Chem. Solids* 73, 651-655.
- Morkoç H., Özgür Ü., 2009, Zinc Oxide: Fundamentals, Materials and Device Technology. Zinc Oxide: Fundamentals, Materials and Device Technology, Wiley-VCH Verlag GmbH and Co. KGaA, Weinheim, Germany.
- Saito N., Matsumoto K., Watanabe K., Aubert T., Grasset F., Sakaguchi I., Haneda H., 2014, Solvothermal synthesis of ZnO spherical particles and VOC sensor application, *J. Ceram. Soc. Jpn.* 122, 488-491.
- Widiyastuti W., Machmudah S., Kusdianto K., Nurtono T., Winardi S., 2015, Characteristics of ZnO nanostructures synthesized by sonochemical reaction: Effects of continuous and pulse waves, *AIP Conf. Proc.* 1699, ID: 040001, DOI: 10.1063/1.4938316.
- Widiyastuti W., Setiawan A., Winardi S., Nurtono T., Madhania S., Susanti D., 2012, The influence of Al dopant precursors on the characteristics of ZnO fine particles prepared by ultrasonic spray pyrolysis, *Procedia Eng.* 50, 152-158.
- Widiyastuti W., Wang W.N., Purwanto A., Lenggono I.W., Okuyama K., 2007, A pulse combustion-spray pyrolysis process for the preparation of nano- and submicrometer-sized oxide particles, *J. Am. Ceram. Soc.* 90, 3779-3785.