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EFFECT OF CITRIC ACID ADDITION UPON THE PRECIPITATION PROCESS ON THE NANOSTRUCTURAL CHARACTERISTICS OF ZnO NANOPARTICLES

Imam Akbar[1], Akhmad Herman Yuwono[1,2*], Nofrijon Sofyan[1,2], Ghiska Ramahdita[1,2], Amalia Sholehah[1,2]

[1] *Department of Metallurgical and Materials Engineering, Faculty of Engineering, Universitas Indonesia, Kampus Baru UI Depok, Depok 16424, Indonesia*
[2] *Tropical Renewable Energy Center (TREC), Faculty of Engineering, Universitas Indonesia, Kampus Baru UI Depok, Depok 16424, Indonesia*

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ABSTRACT

Zinc oxide (ZnO) nanoparticles have been investigated in depth, due to their potential as a semiconductor material in dye sensitized solar cell applications. In this current research, ZnO nanostructure was synthesized using a simple precipitation technique with the addition of citric acid ($C_6H_8O_7$) as the capping agent. Various ratios of ZnO and citric acid were prepared, *i.e.* 1:1, 2:1, 4:1 and calcination temperatures of 150 and 400°C were used to investigate the effect of those parameters on the ZnO nanostructure and its crystallinity. The nanostructure characteristics, *i.e.* nanocrystallite size, crystallinity, and optical properties were determined by using x-ray diffraction (XRD), scanning electron microscopy (SEM), and ultra-violet visible (UV-Vis) spectroscopy, respectively. The investigation results showed that ZnO nanostructure was formed as spherical shapes and rods in the range of 19.8–30.8 nm with the lowest band gap energy (E_g) of 3.15 eV obtained under conditions of a 4:1 ratio and calcined at 400°C. Considering nanostructural characteristics, the ZnO nanostructures in this study would be suitable for application as a semiconductor oxide layer in a dye sensitized solar cell.

Keywords: Citric acid; Crystallinity; Dye-sensitized solar cell; Nanostructure, ZnO

1. INTRODUCTION

One of the renewable energies with a great potential in current and future usage is solar cell since it can produce "clean and sustainable energy". A dye densitized solar cell (DSSC) is one of the devices which can convert photon energy from sunlight into electricity though an electro-molecular mechanism. Since the photon-electricity conversion efficiency of the DSSC is still rather low in comparison to the silicon-based solar cell, many investigations have been conducted to increase the efficiency by modifying the photo electrode. In this context, nanostructured materials are thought to be among the alternative modifications that can be made. Metal oxides, such as titanium dioxide (TiO_2) and zinc oxide (ZnO), are the best candidates as semiconductor material. In this study, the material used as the photo electrode is ZnO, since it has direct band gap energy and high exciton binding energy around ~60 meV, (Peng & Qin, 2011; Raoufi, 2013).

ZnO nanoparticles can be synthesized through various methods, which are classified based on the process phase. Synthesis in the vapor phase, (Fan & Lu, 2005) and in the solid phase may be

* Corresponding author's email: ahyuwono@eng.ui.ac.id, Tel. +62-21-786 3510, Fax. +62-21-787 2350
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performed with three methods, such as physical vapor deposition (PVD), chemical vapor deposition (CVD), and spray pyrolysis (Turner et al., 2009). Any of the three methods may create ZnO with a complex structure; however, these methods cost too much because of the equipment and they take a relatively long time because of several stages that need to be accomplished. By contrast, liquid phase synthesis is the simplest method, easy to recreate and less costly than the other techniques. Techniques, such as precipitation, hydrothermal (Suwanboon et al., 2014), and sol–gel (Ikono et al., 2012) were commonly used in liquid phase synthesis. One of the disadvantages of this liquid phase synthesis; however, is that the methods produce mostly spherical nanoparticles; therefore, additional compounds are needed to form a structure. Citric acid is one of the compounds that can be use as a capping agent. Previous studies indicated that this substance can form some structures, such as spherical, rod, disk and flower-like shapes (Zhang et al., 2005). These structures can enhance the performance of the DSSC, such as flower-like shapes that can act as a scattering layer to improve the reflectance, (Xu et al., 2013) and rod shapes can improve the electron lifetime and transport process by making a pathway for the electron (Mor et al., 2006).

In this present study, we modified the nanostructural characteristics of the ZnO nanoparticles by varying some parameters including the ratio of citric acid as a capping agent with the calcination temperatures to obtain the desired ZnO nanoparticles. The results obtained from this work are discussed in this paper.

2. EXPERIMENTAL SETUP

2.1. Materials

The precursor material used in this study was an analytical grade of zinc acetate dehydrate, $Zn(CH_3COO)_2.2H_2O$ obtained from Sigma-Aldrich. The other starting materials were lithium hydroxide (LiOH), ethanol (C_2H_6O), and citric acid ($C_6H_8O_7$), all from Merck.

2.2. Synthesis of ZnO Nanostructure

Starting materials and precursors were prepared separately. Firstly, 2.19 g of $Zn(CH_3COO)_2.2H_2O$ were dissolved in 100 ml ethanol. Secondly, the mixture of 0.48 g LiOH and a weight variation of 2.10, 1.05 and 0.525 g $C_6H_8O_7$ were dissolved in 100 ml ethanol. Each of these mixtures was dissolved at 45°C and was magneticly stirred continuously for 2 hours. The mixture of LiOH and $C_6H_8O_7$ were then added dropwise to the first solution and mixed for about 2 hours until the precipitate was obtained. This precipitate was dried and calcined at 150°C. The resulting powders were labeled as (1:1) – 150, (2:1) – 150 and (4:1) – 150. Sample (4:1) was further calcined at 400°C, cooled and rinsed with distillated water, re-dried, and marked as (4:1) – 400.

2.3. Characterization

All synthesized powders were subject to characterization. The x-ray diffraction (XRD) pattern was obtained by using a Philips Analytical X-Ray B.V PW1710 and a SHIMADZU XRD-7000 at a range of 20–80°. UV-Vis spectra were recorded by using a SHIMADZU UV-2400 Series by diffuse reflectance spectroscopy (DRS) and this was is converted to the Kubelka-Munk function (Gooch, 2011) from the reflectance spectrograms. The nanostructure images were taken by using a SEM (FEI Inspect F50) instrument.

3. RESULTS AND DISCUSSION

3.1. Effect of Citric Acid Concentration

The citric acid concentration effect on the crystallinity of ZnO can be seen in Figure 1 below. The pattern (a) showed no obvious peak. Similar result can be seen on pattern (b), but at a certain angle some peak has begun to rise. Furthermore, a significant difference can be

observed from pattern (c) in which the diffraction peak that belongs to the ZnO wurtzite phase (ICDD code 01-075-0576) has appeared quite clearly.

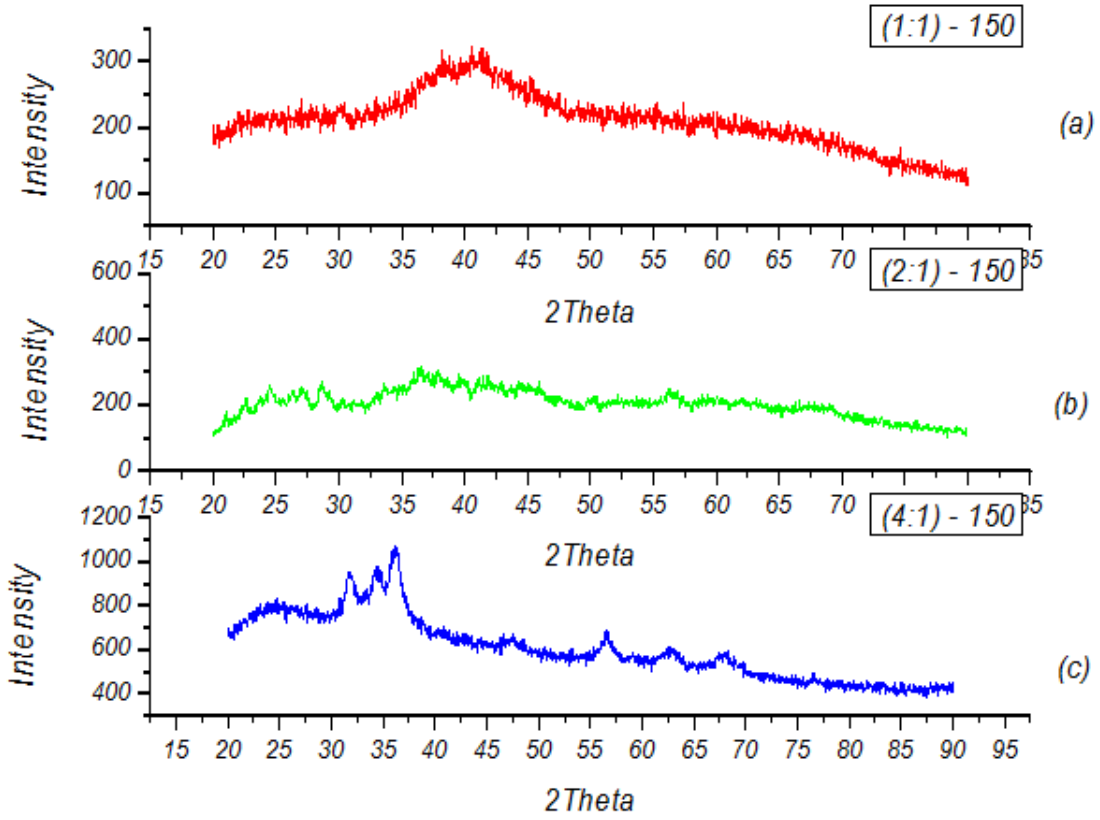

Figure 1 XRD pattern of ZnO powder calcined at 150°C synthesized with ZnO: citric acid ratios of: (a) 1:1; (b) 2:1; (c) 4:1

Based on the observed pattern, along with the increasing concentration of citric acid, the formation of ZnO will be more difficult as seen in pattern (a) and (b). The powder formed is still in the amorphous phase. The main cause of the slow growth process is the solubility of citric acid and lithium hydroxide in ethanol in which these precursors dissolve incompletely, so the supply of OH is reduced. This issue led to a failure in the formation of ZnO crystal (Cho et al., 2009, 2011).

The results from UV-Vis characterization in the form of diffuse reflectance spectroscopy are given in Figure 2. The band gap energies (E_g) were then estimated from the reflectance by using the Kubelka-Munk function (Kubelka & Munk, 1931). As can be seen from the figure, the optical properties still can be observed, which show the estimated value of the band gap energy. The exact value was obtained from the graph based on the linear part of the Tauc equation (Tauc et al., 1966). Starting from the lowest citric acid concentration, the E_g values obtained were 3.15, 3.16, 3.23, and 4.00 eV, respectively. These results indicate that the band gap energy value decreases with the increase in crystallinity, as a result of higher number of ZnO nanostructures formed under the synthesis condition.

3.2. ZnO Morphology

Based on morphological observations, only one sample shows a convincing nanostructure, i.e. the specimen calcined at 400°C (4:1 – 400). The detail picture is shown in Figure 3. The ZnO

powder morphological observation was conducted at each stage, but only sample (4:1) – 400 provides a clear image. In general, the particle forms imperfect spherical shapes.

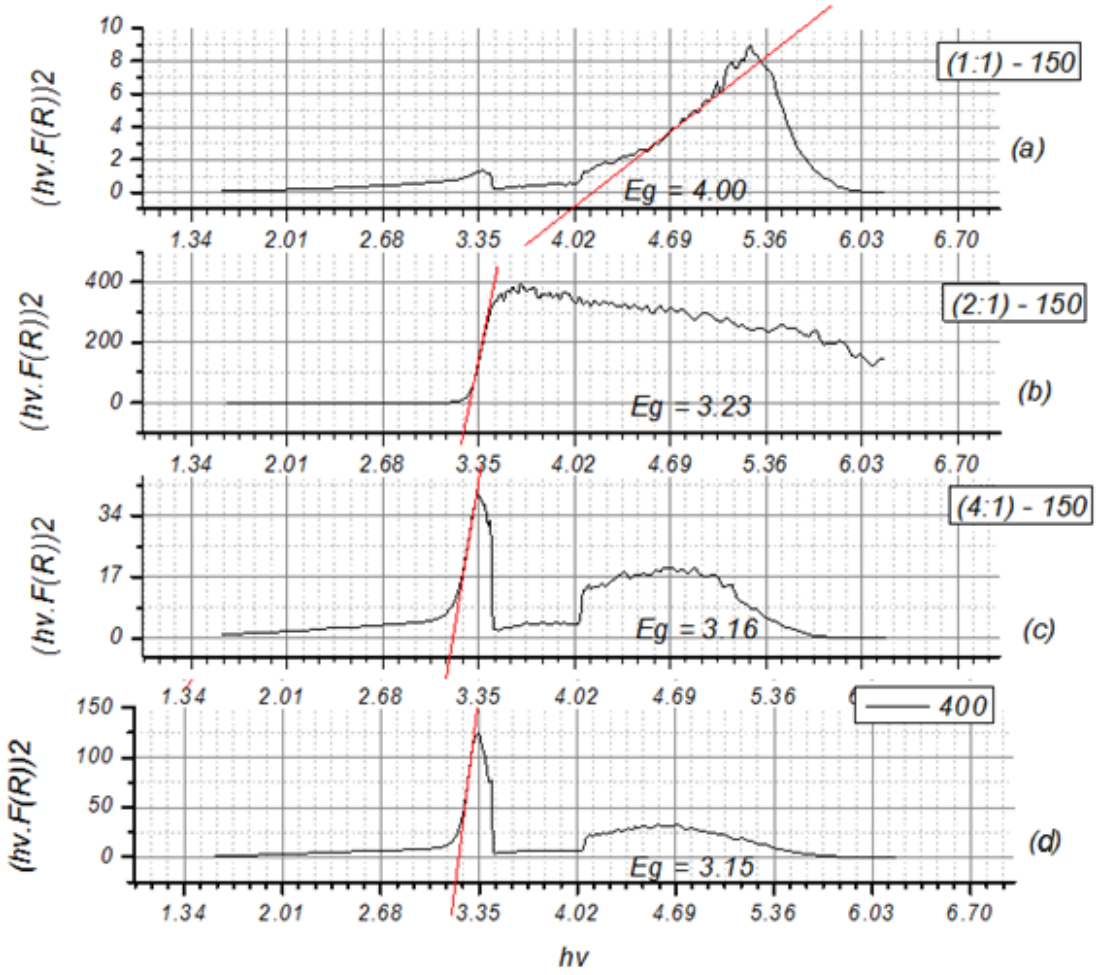

Figure 2 Estimated band gap energy (E_g) of ZnO nanoparticles calcined at 150°C and synthesized with ZnO: citric acid ratios of: (a) 1:1; (b) 2:1; (c) 4:1; and (d) with ZnO: citric acid ratios of 4:1 but calcined at 400°C

Based on the SEM image given in Figure 3, other structures can be observed. Nanorod structures can be found on the right side of the image shown by the dark arrow, but the size of this nanorod could not be determined precisely, because some of the particles stick together and form an aggregate. This nanorod structure is expected to form due to the adsorbed citric acid on the ZnO nuclei. When the temperature is high enough, the nuclei will grow, but in some directions the growth is restrained by citric acid (Cho et al., 2009; Cho et al.,2011) resulting in anisotropy growth or identical properties in all directions, without affecting the crystallinity (Suwanboon et al., 2014). However, the double effect of high temperature caused by the calcination process cannot be done for a long period, resulting in an incomplete formation of nanorod structures. In addition, citric acid will decompose at a given temperature and lose its function as a capping agent. Both of these phenomena explain why the structure was formed into a mixture of spherical and nanorod structures.

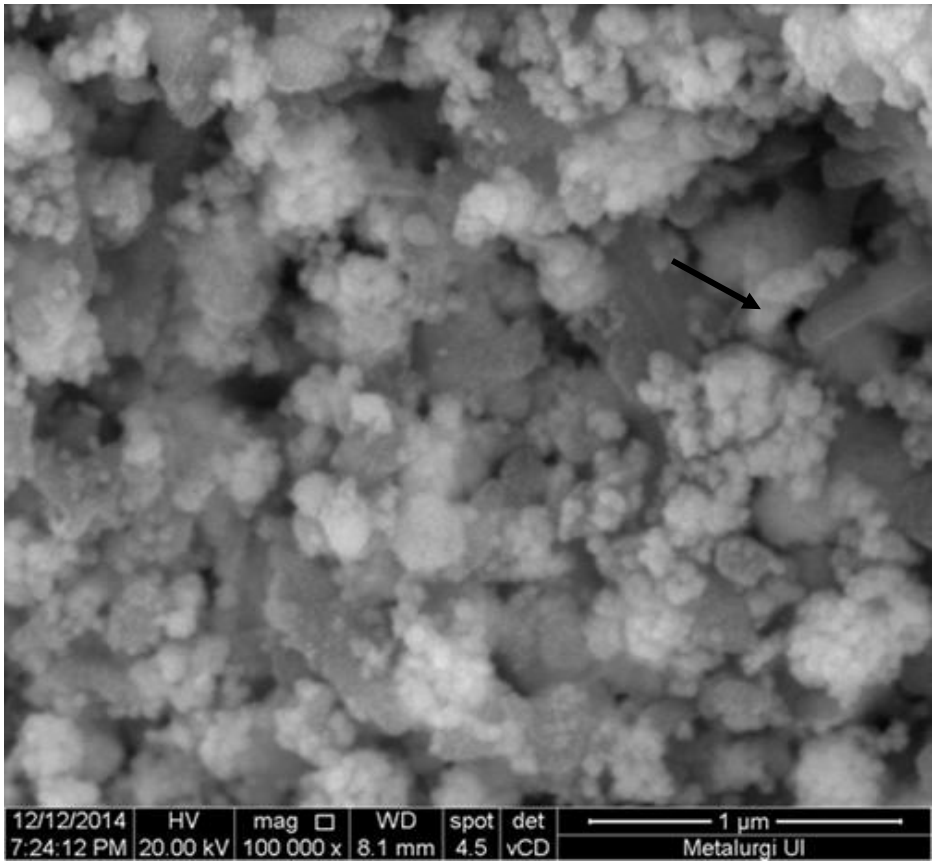

Figure 3 SEM image of nanostructural characteristic obtained by ZnO sample with citric acid ratio of (4:1) and calcination temperature of 400^{o}C. The arrow shows nanorod structure, due to an anisotropy growth.

4. CONCLUSION

In this work, the addition of citric acid affected the nanostructural characteristics of the synthesized ZnO. The obtained ZnO nanoparticle was partially formed into a nanorod structure. This was expected to be due to citric acid adsorbed on the surface of ZnO nuclei, which restrained the formation of crystalline ZnO in some directions and this resulted in anisotropy growth without affecting the crystallinity. A higher calcination temperature up to 400^{o}C has improved the crystallinity and crystallite size up to 30.81 nm with a band gap energy of 3.15 eV. The obtained ZnO nanoparticles in this study have potential usage as the semiconductor oxide layer in the sandwich structure of a DSSC device.

5. ACKNOWLEDGEMENT

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6. REFERENCES

Cho, S., Jang, J.W., Jung, S.H., Lee, B.R., Oh, E., Lee, K.H., 2009. Precursor Effects of Citric Acid and Citrates on ZnO Crystal Formation. *Langmuir*, Volume 25(6), pp. 3825–3831

Cho, S., Jang, J.W., Jung, A., Lee, S.H., Lee, J., Lee, J.S., Lee, K.H., 2011. Formation of Amorphous Zinc Citrate Spheres and their Conversion to Crystalline ZnO Nanostructures. *Langmuir*, Volume 27(1), pp. 371–378

Fan, Z., Lu, J.G., 2005. Zinc Oxide Nanostructures: Synthesis and Properties. *J. Nanosci. Nanotechnol*., Volume 10, pp.1561–1573

Gooch, J.W., 2011. Kubelka-Munk Equation. *Encyclopedic Dictionary of Polymers*, 2nd Edition, pp. 414–415

Ikono, R., Akwalia, P.R., Siswanto, Bambang, W.W., Sukarto, A., Rochman, N.T., 2012. Effect of PH Variation on Particle Size and Purity of Nano Zinc Oxide Synthesized by Sol-Gel Method, *Intl. J. Eng. Tech*., Volume 12(6), pp. 5–9

Kubelka, P., Munk, F., 1931. Ein Beitrag zur Optik der Farbanstriche. Z. *Tech. Phys*., Volume 12, pp. 593–601

Mor, G.K., Shankar, K., Paulose, M., Varghese, O.K., Grimes, G.A., 2006. Use of Highly Ordered TiO_2 Nanotube Arrays in Dye-sensitized Solar Cells. *Nano Letters*, Volume 6(2), pp. 215–218

Peng, Q., Qin, Y., 2011. ZnO Nanowires and their Application for Solar Cells, in Nanowires Implementations and Applications, Abbass Hashim (Ed.), ISBN: 978-953-307-318-7, *InTech*., pp. 157–178

Raoufi, D., 2013. Synthesis and Microstructural Properties of ZnO Nanoparticles Prepared by the Precipitation Method. *Renewable Energy*, Volume 50, pp.932–937

Suwanboon, S., Amornpitoksuk, P., Bangrak, P., Randorn. C., 2014. Physical and Chemical Properties of Multifunctional ZnO Nanostructures Prepared by Precipitation and Hydrothermal Methods. *Ceramics International*, Volume 40(1), pp. 975–983

Tauc, J., Grigorovici, R., Vancu, A., 1966. Optical Properties and Electronic Structure of Amorphous Germanium. *Phys. Stat. Sol*., Volume 15(2), pp. 627–637

Turner, S., Tavernier, S.M.F., Huyberechts, G., Blermans, E., Bals, S., Batenburg, K.J., van Tendeloo, G., 2009. Assisted Spray Pyrolysis Production and Characterization of ZnO Nanoparticles with Narrow Size Distribution. *J. Nanoparticle Research*, Volume 12(2), pp. 615–622

Xu, J., Fan, K., Shi, W., Li, K., Peng, T., 2013. Application of ZnO Micro-flowers as Scattering Layer for ZnO-based Dye-sensitized Solar Cells with Enhanced Conversion Efficiency. *Solar Energy*, Volume 101, pp. 150–159

Zhang, H., Yang, D., Li, S., Ma, X., Ji, Y., Xu, J., Que, D., 2005. Controllable Growth of ZnO Nanostructures by Citric Acid Assisted Hydrothermal Process. *Mater. Letters*, Volume 59, pp. 1696–1700