International Journal of Eco-Innovation in Science and Engineering (IJEISE) Vol 3 (1), 2022 (30-34)
https://ijeise.upnjatim.ac.id/ E-ISSN: 2721-8775

Article

Optimization ZnO Properties for Electron Transport Layer (ETL) of Hybrid Solar-cell Prepared with Sol-gel Method Combined with Reflux Treatment

Pardi Sampe Tola[1*]

[1] *Department of Food Engineering, Faculty of Engineering, Universitas Pembangunan Nasional "Veteran" Jawa Timur, Gunung Anyar, Surabaya 60294, Indonesia*

*Corresponding author: pardi.sampe.fisika@upnjatim.ac.id

Received: 7th February 2022; Revised: 24th March 2022; Accepted: 18th May 2022; Available online: 19th May 2022; Published regularly: May and November

---

Abstract

Electron-hole pair (exciton) generation and extraction from solar-cell photoactive layer is the main parameters determined solar-cell performance. Generally solar-cell consists of a photoactive layer sandwiched between electron transport layer (ETL) and hole transport layer (HTL). Exciton separation and extraction from photoactive layer depend on several properties: energy level match of photoactive layer and charge transport layer, surface contact area of photoactive layer and charge transport layer, and charge transport properties of charge transport layer. ETL and HTL should meet several characteristic e.g.: high transparency in UV-visible light region, high degree of crystallization to minimize charge lose and high electron or hole mobility. In this study we try to fabricate ZnO as an ETL of hybrid solar-cell with sol-gel method combined with reflux treatment. The quality of ZnO ETL highly effected by precursor solution properties; solution homogeneity, viscosity and stability. These precursor solution properties depend on chemical composition and reaction condition, reflux treatment designed to enhance precursor solution reaction time and increase solution stability. Previous study shown low solution stability of ZnO precursor prepared with sol-gel without reflux treatment which resulting on low ETL quality. Visible observation of the resulting precursor solution showed that reflux treatment enhances solution stability, while solution prepared without reflux treatment easily formed precipitation phase. Furthermore, ZnO powder prepared with reflux treatment exhibit preferable crystallization and small ZnO crystallite size. Low-temperature crystallization of ZnO prepared with sol-gel method combined with reflux treatment, make it is possible to fabricate thin film with small particle size therefore able to enhance surface contact area of photoactive layer and ETL.

Keywords: sol-gel, reflux, ZnO powder, electron transport layer (ETL).

1. Introduction

Solar-cells based on organic material (organic solar-cells) is one type of photovoltaic devices that gain consideration for future energy harvesting devices. Organic solar-cells have several advantages, such as, low cost devices fabrication due to its low temperature processing, can be fabricated on flexible surfaces because low temperature processing and based on 2-dimensional structure (thin films) which offer possibility to fabricate light mobile photovoltaic devices. Latest study reported solar-cells based on organic material have been reached around 18% of power conversion efficiency (PCE) [1]. But compare to crystalline silicon based solar-cells, organic solar-cells have stability limitations. Organic materials easily undergo structures and properties change under oxygen and moisture exposure, high temperature environment, as well as UV radiation, which consequently decreases

DOI: https://doi.org/10.33005/ijeise.v3i01.61

PCE of organic solar-cells [2], [3]. Introduction of inorganic component into organic solar-cells would able to preserve solar-cells stability as the result maintaining PCE throughout solar-cells lifetime [4]. Photovoltaic consisting of organic and inorganic material known as hybrid solar-cells. Hybrid solar-cells synergize the advantage properties of organic and inorganic materials. Hybrid solar-cell consist of organic photoactive heterojunction layer (binary combination of electron donor and acceptor) where electron-hole pair generated, and charges extraction layer (inorganic or organic charge transport layer). Effective electron-hole pair separation and extraction from photoactive layer indispensable to achieve high PCE solar-cell [5], which suggests the importance of careful design of electronic structure of hybrid solar-cell. In this study, inorganic materials will apply as electron transfer layer (ETL) and organic compound as hole transfer layer (HTL) to achieve high PCE and stable hybrid solar-cells.

Electronic structure match and contact area of photoactive layer and charge extraction layers are crucial to solar-cells performance. The electronic structure of the solar-cell is illustrated in Figures 1. Conduction and valence band match and large contact area of ETL/photoactive and photoactive/HTL interface resulting on effective excitons separation and extraction. In addition to enhance hybrid solar-cell performance, inorganic ETL is able to prevent photoactive layer from oxygen and moisture exposure. Moreover, due to acid nature of organic photoactive layer which could cause corrosion of solar-cell electrode, addition of inorganic ETL can prevent direct contact of photoactive layer and electrode [6], [7].

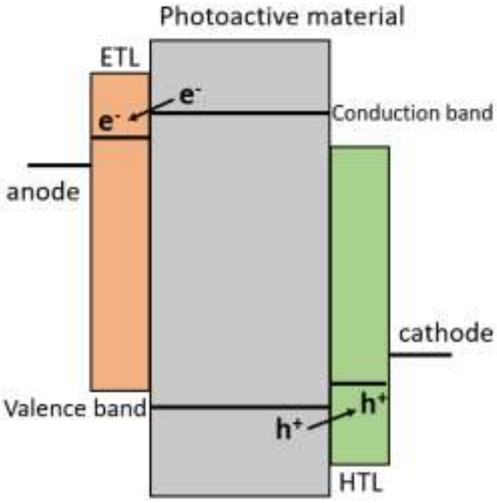

Fig. 1. Electronic structure of solar-cell, conduction and valence band match of ETL/photoactive layer/HTL junction and illustration of electron-hole pair separation and extraction process.

Transparent conducting metal oxide ZnO has been widely applied in many kinds of electronic devices, due to its advantage properties, such as; lower optical absorption at UV-visible light region, large band gap semiconductor, ~3.3-3.4 eV, high electron mobility, ~166 cm^2/Vs, large exciton binding energy, 60 meV, and high thermal stability [8]-[10]. Moreover, dependent on fabrication method ZnO have various morphologies; thin film and nanostructure, e.g. nanowires, nanorods and nanotubes [11]-[13]. Nanostructured ZnO provide large surface area that could lead to effective electron extraction [5]. Thin film ZnO can be fabricated with thermal vapor-based methods e.g. pulsed laser deposition (PLD), where highest degree ZnO crystallization is formed, but these techniques have some drawbacks such as expensive equipment, complicated processing, low yield and high vacuum and temperature processing. Solution-based method such as hydrothermal, electrochemical and sol-gel have been extensively used to grow ZnO nanostructured on ZnO-seeded layer. However, sol-gel method can be applied to deposit both ZnO-seeded layer as well as nanostructured ZnO depend on the fabrication condition and heating treatment.

Sol-gel based processing of ZnO enable to fabricate nanostructured thin film due to low temperature crystallization and easy deposition of thin film over a large area up to several square meters [14]. The quality and properties of ZnO thin film fabricated with sol-gel method depend on precursor solution parameters; viscosity, pH, concentration, stability, etc. [15]. However, due to instability of the precursor solution of ZnO at ambient condition, it easily forms precipitation phases which result in large particle size, high impurity and crystal defects. Addition of chemical stabilizer, diethanolamine (DEA) could improve precursor solution stability, but large amount of DEA addition lead to low homogeneity of ZnO thin films.

In this initial study we try to fabricate ZnO powder with sol-gel method combined with reflux treatment and small chemical stabilizer addition, study the reflux treatment effect on precursor solution stability and ZnO powder crystallization and size. Reflux treatment were designed to maintain precursor concentration during reaction. Reflux treatment offers several benefits, such as;

heating process can be held for a long period of time without change solution concentration and increasing reaction rates which may result on better ZnO crystallization and thin film morphology.

2. Experiment

ZnO powder were prepared with sol-gel method combined with reflux treatment. ZnO precursor; 0.27 g of zinc acetate dihydrate, $Zn(CH_3COO)_2.2H_2O$ dissolved into 5 ml ethanol at room temperature, followed by stabilizer addition, diethanolamine (DEA). The precursor solution continuously stirred until dilute solution of zinc acetate dihydrate obtained. The solution then transferred in to reflux system, as shown in Figures 2.

Fig. 2. Sol-gel reaction with reflux treatment set-up, consist of: mixing stirrer, hotplate, distillation tube and vacuum system.

The precursor solution steadily mixed and heated at 80 °C for 3 and 24 hours in the reflux system. After mixing and heating process, the obtained product was washed 3 times with ethanol followed by drying at 80 °C. Dried powder then annealed in air at 450 °C for 30 minutes to achieve ZnO powder. XRD characterization was carried out by using a Philip Panalytical PW 1710 diffractometer, with Cu monochromatic X-ray (λ = 0.154 nm) to confirm the reflux effect on crystallization of ZnO.

3. Result and discussion

Reflux treatments were conducted at low vacuum conditions to establish low moist environment as well as maintain the solution concentration, as shown in Figures 2. Addition of small amount DEA is important for initial nucleation and prevent formation of large particle size. Water absorption by zinc acetate dihydrate will accelerate linking process of precursor so that induce formation of precipitation phase. Due to hydrophilic character of DEA, DEA able to prevent water absorption by zinc acetate dihydrate. However, large DEA addition have negative effect on ZnO thin film formation because after solvent removal, cluster-like (inhomogeneous) thin film is formed, this may due to large boiling point difference of ethanol and DEA.

Ethanol solvent with low boiling point (78 °C) is easily evaporate during mixing and heating process. On the other hand, non-volatile molecules: DEA with 269 °C boiling point and heavy molecule (zinc acetate dihydrate) remain in the reaction chamber. Condensation of ethanol vapors and return of the condensate ethanol to the reaction chamber will enable to conduct sol-gel reaction in a long period of time without formation of precipitation.

Resulting solution was cooled in a closed container and stored at room temperature. Solution stability is visually checked regularly every 1 day by taking photos of the precursor solution.

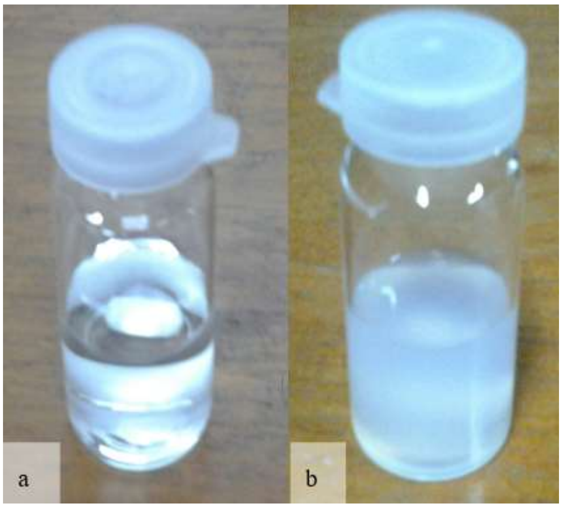

Fig. 3. ZnO solution after sol-gel reaction and stored several days at room temperature: a. with and b. without reflux treatment, respectively.

Figure 3 shows the ZnO solution after reaction and stored for several days at room temperature. Visually solution with reflux treatment stable after keeping at room temperature for a long period of time. On the other hand, solutions without reflux treatment form precipitation phase after being kept at room temperature, non-transparent solution is formed. Formation of precipitation phase will form low quality thin film in terms of morphology and crystallization.

The reflux treatment effect on the formation of ZnO crystal examined by varying the sol-gel reaction time. XRD pattern of ZnO powder with different reflux treatment time shown in Figures 4.

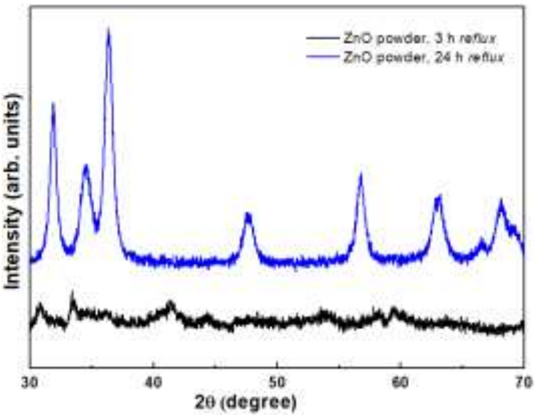

Fig. 4. XRD patterns of ZnO powder with different reflux treatment time: 3 hours and 24 hours.

The ZnO powder obtained from 3 hours reflux treatment not showing any peak of ZnO crystalline. We assume that the ZnO powder is in amorphous phase which suggests higher heating temperature required to form crystalline ZnO. However, powder obtained from 24 hours reflux treatment shows peak of ZnO crystalline with wide XRD peak. XRD peak position of ZnO powder match with ZnO XRD database, as listed in Table 1.

Table 1. ZnO peak position and crystalline parameters [16].

No	Peak angle (2θ)	Bounding distance (Å)	Miller indices		
			h	k	l
1	31.77	2.814	1	0	0
2	34.42	2.603	0	0	2
3	36.25	2.476	1	0	1
4	47.54	1.911	1	0	2
5	56.60	1.624	1	1	0
6	62.86	1.477	1	0	3
7	66.34	1.407	2	0	0
8	67.96	1.378	1	1	2
9	69.10	1.358	2	0	1

The crystallite size of ZnO crystal can be approximate by using Scherrer equation [17]:

$$D = \frac{K\,\lambda}{FWHM\ \cos\theta}$$

Full width half maximum ($FWHM$) of XRD peak inversely proportional with crystallite size of particles (D), as the crystallite size gets smaller, the peak gets broader. Here we chose the highest XRD peak at 2θ = 36.25°, λ = 0.154 nm, K is Scherrer constant = 0.9 and $FWHM$ of peak at 36.25° = 0.5°. By substituting the parameters, we estimate ZnO crystallite size is around 18 nm. The XRD result showed that reflux treatment highly affected crystallization of ZnO and also offered the possibility to fabricate thin film with small particle size due to low temperature processing.

4. Conclusions

Reflux treatment performed during sol-gel reaction exhibit potential to be applied for ZnO thin film deposition. ZnO solution treated with reflux shown stable characteristic. No precipitation phase formed after stored for long period of time indicated that precursor solution with reflux treatment will able to form homogeneous thin film. Furthermore, reflux treatment able to extended sol-gel reaction time, without change solution concentration. Reaction time highly affected the formation of ZnO crystal, our result shown solution with 24 hours reaction time able to form ZnO nanocrystalline with particle size ~18 nm. Low crystallization temperature of ZnO prepared with reflux treatment make it possible to fabricate thin film ZnO with small particle size and may increase charges separation efficiency of hybrid solar-cells. This initial study we focusing on optimization sol-gel reaction and formation of ZnO crystal powder, further study addressed to fabricate ZnO thin film and study the properties. Several adjustments may require to fabricate ZnO thin film.

References

1. Q. Liu, et al. “18% Efficiency Organic Solar Cells,” *Sci. Bull.*, vol. 6, pp. 272-279, 2020.
2. V.S. Balderrama, M. Estrada, P.L. Han, P. Granero, J. Pallarés, J. Ferré-Borrull, et al. “Degradation of Electrical Properties of PTB1:PCBM Solar Cells under Different Environments,” *Solar Energ. Mater. Solar Cell*, vol. 125, pp. 155–163, 2014.
3. L. Córcoles, J. Abad, J. Padilla, and A. Urbina. “Wavelength Influence on the Photodegradation of P3HT:PCBM Organic Solar Cells,” *Solar Energ. Mater. Solar Cell*, vol. 141, pp. 423–428, 2015.

4. A.S. Gertsen, M.F. Castro, R.R. Søndergaard, and J.W. Andreasen, "Scalable Fabrication of Organic Solar Cells Based on Nonfullerene Acceptors," *Flex. Print. Electron.* vol. 5, pp. 014004, 2020.
5. N. Asim, et al, "Nanomaterials for Green Energy, Novel Nanomaterials for Solar Cell Devices," pp. 227–277, 2018
6. S. Shobih, R. Abdillah, and E. S. Rosa, "Fabrication of Hybrid Polymer Solar Cells By Inverted Structure Based on P3HT:PCBM Active Layer," *Jurnal Elektronika dan Telekomunikasi*, vol. 17, no. 1, pp. 13-18, 2017.
7. M. Ikram, M. Imran, J. M. Nunzi, S. R. Bobbara, S. Ali, and Islah-u-din, "Efficient and low cost inverted hybrid bulk heterojunction solar cells," *Journal of Renewable and Sustainable Energy*, vol. 7, no. 4, pp. 043148, 2015.
8. A. Wei A, L. Pan, and W. Huang, "Recent progress in the ZnO nanostructure-based sensors," *Mater Sc Eng B.*, vol. 176, pp. 1409–1421, 2011.
9. F. Lu F, W. Cai, and Y. Zhang, "ZnO hierarchical micro/nanoarchitectures: solvothermal synthesis and structurally enhanced photocatalytic performance," *Adv Funct Mater.*, vol. 18: pp. 1047–1056, 2008.
10. J. Wang, E. Elamurugu, H. Li, S. Jiao, L. Zhao, R. Martins R, et al, "Effect of N and P codoping on ZnO properties," *Adv Mater Res.*, vol. 645: pp. 64–67, 2013.
11. K. Wahid, W. Lee, H. Lee, A. The, D. Bien, I. Azid, "Effect of seed annealing temperature and growth duration on hydrothermal ZnO nanorod structures and their electrical characteristics," *Appl Surf Sci.*, vol. 283, pp. 629–635, 2013.
12. Y. Li, K. Duan, and P. Shi, "Synthesis of ZnO nanoparticles on Si substrates using ZnS source," *J Cryst Growth.*, vol. 260 309–315, 2004.
13. J. Song and S. Lim, "Effect of seed layer on the growth of ZnO nanorods," *J Phys Chem C.*, vol. 111, pp. 596–600, 2007.
14. R. Schwartz, T. Schneller, and R. Waser, "Chemical solution deposition of electronic oxide films," *Comptes Rendus Chimie.*, vol, 7, no. 5, pp. 433–461, 2004.
15. B. Mridula and S. Pei-Chen, "Modern Technologies for Creating the Thin-film Systems and Coatings, Chemical Solution Deposition Technique of Thin-Film Ceramic Electrolytes for Solid Oxide Fuel Cells," Chapter 16.
16. S.T. Gautam, K.S. Ajaya, R. Singh, and G. Ashish, "Facile synthesis of flat crystal ZnO thin films by solution growth method: A micro-structural investigation," *Journal of Saudi Chemical Society*, vol. 18, no. 5, 2014.
17. B. Ingham and M.F. Toney, "Metallic Films for Electronic, Optical and Magnetic Applications," Chapter 1, 2014.

DOI: https://doi.org/10.33005/ijeise.v3i01.61