Characteristics of ZnO nanofiber in double Layer (TiO$_2$ / ZnO) DSSC results of direct deposition electrospinning manufacturing: Variation of tip to collector distance

Zainal Arifin *, Syamsul Hadi, Suyitno, Singgih Dwi Prasetyo
Department of Mechanical Engineering, Faculty of Engineering, Sebelas Maret University
Ir. Sutami 36, Jebres, Surakarta, Indonesia
*Email: zainal_arifin@staff.uns.ac.id

Abstract Solar energy is obtained from sunlight. Solar cells are harvesters of solar energy that are converted into electrical energy through the photovoltaic process. One of solar cell types are Dye-sensitized solar cells (DSSC) based on double layer photoanode which is very attractive to researchers because of its high performance, cheaper, and availability of mass production. The two-layer TiO$_2$-ZnO semiconductor obtained with the nanofiber ZnO semiconductor was deposited directly with the TiO$_2$ nanoparticle semiconductor. The addition of the nanofiber ZnO semiconductor layer is known to reduce the semiconductor band gap value. This present study is to determine the effect of direct deposition of the ZnO layer using electrospinning with variation of the tip distance of the collector. The results showed that the use of ZnO nanofiber layers made by direct deposition on the tip distance is 7 cm to the collector, which produced a small diameter size and uniform morphology. Small and uniform morphology allows DSSC to have better electron excitation. This is directly proportional to the high efficiency of DSSC double layer.

Keywords: tip distance to collector, direct deposition, electrospinning, double layer DSSC

1. Introduction
Solar energy is energy obtained from sunlight. Utilization of solar energy has enormous potential to be developed in Indonesia. The International Renewable Energy Agency (IRENA) estimates that it can produce electrical energy of 532.6 GW. Electrical energy is obtained from the conversion of solar energy through the photovoltaic process using solar cells [1]. Silicon solar cells, thin layer type solar cells, and Dye-sensitized solar cells (DSSC) are three generations of solar cells.

DSSC type solar cells are easy in fabrication and are lower cost than silicon solar cells or thin layer type solar cells [2]. The performance of DSSC in general can be characterized by several parameters namely the value of efficiency, fill factor (FF), short-circuit photocurrent density (JSC), and open-circuit voltage (VOC). DSSC is composed of two electrodes: the Photoanode electrode and the photo inert counter electrode [3]. Photoanode electrodes are made of semiconductors that have absorbed dyes and deposited on Transparent Conductive Oxide. Meanwhile the photo inert counter electrodes are made of a platinum layer superimposed on Transparent Conductive Oxide [4].
Semiconductors in the DSSC photoanode function as converters of photon energy from solar radiation through the process of electron excitation based on the gap in material energy or band gap [5]. TiO₂ and ZnO as semiconductors have potential as electrodes in photovoltaic technology, electroluminescence devices and ultraviolet transmitter devices[6]. TiO₂ semiconductors have higher photovoltaic performance in the visible light region compared to ZnO semiconductors. However, ZnO semiconductors have a lower electron charge recombination effect than TiO₂. TiO₂ and ZnO semiconductors have been used in many research of nanomaterial engineering because they have a better energy gap, which is 3.20-3.61 eV with efficiencies of 0.26% and 0.13% [7].

The photoanode layer engineering was carried out with a TiO₂ nanoparticle semiconductor added with a ZnO nanofiber semiconductor layer as a double layer photoanode. The TiO₂ layer functions as a photon trap because it has a large surface area. Besides, ZnO functions as the absorption of photons to enter DSSC. Double layer photoanode engineering is intended to improve DSSC performance, which is also be proportional to the band gap value of 2.5 - 3 eV [8]. Double layer photoanode arranged to form a sandwich can strengthen the semiconductor bond with the substrate (adhesive properties) [9], as Figure 1.

![Figure 1. DSSC double layer photoanode structure](image)

From the statements that have been disclosed, this research focuses on engineering double layer photoanode with direct deposition of ZnO layers on the TiO₂ layer. The nanofiber ZnO layer was obtained from a direct deposition process using the electrospinning process on TiO₂ semiconductors in the form of particles that had been deposited on Fluorine doped tin oxide (FTO) glass[10]. The use of direct deposition methods using the electrospinning process can reduce fabrication time, can prevent damage to nanoparticle and nanofiber structures, and can improve DSSC performance[11]. However, for direct deposition, the electrospinning process depends on the distribution of molecular weight, the surface viscosity of the solution, the temperature, the distance between the tip and the collector, and the flow rate of the solution[12]. Using distance between tip to the collector in the electrospinning process is known to greatly affect the particle size of the semiconductor morphology[13]. Therefore, this study reveals the effect of the variation of tip distance to the ZnO semiconductor direct deposition collector on the performance of the DSSC double layer photoanode which is also reviewed through the DSSC band gap value.
2. Method

2.1. Material
ZnO semiconductors are formed using Zinc acetate dihydrate ((CH$_3$COO)$_2$Zn.2H$_2$O, Merck) material; The carrier material in the electrospinning process uses PVA or polyvinyl alcohol (CH$_2$CH(OH)$_n$, MW = 72,000, Merck) material; aquades used as a solution for zinc acetate and PVA to form a homogeneous solution; A 2 x 2 cm FTO glass of dyesol deposited with TiO$_2$ nanoparticles; Synthetic dyes used N719 from dyesol; Iodide (I$^-$) EL-HPE electrolyte solution from Dyesol.

2.2. DSSC photoanode double layer fabrication
Preparation of the solution for the semiconductor ZnO nanofiber was carried out by a homogenization process between the precursor solution and the Zn(Ac)$_2$ solution for 8 hours at 70°C at a ratio of 4: 1 wt%. The precursor solution was obtained by mixing 2-gram PVA with 20 ml of distilled water (H$_2$O) at 70°C for 4 hours. Zn(Ac)$_2$ solution was made by mixing 2 grams of zinc acetatedihydrate and 8 ml H$_2$O for 1 hour at a temperature of 70°C.

The homogenization of the solution was carried out by electrospinning process to form ZnO nanofiber on DSSC double layer TiO$_2$ / ZnO. The solution is inserted into the syringe and is connected to an electrospinning machine in the Nanobioenergy Lab, Sebelas Maret University, Surakarta. The injection pump tip is connected to the positive terminal high voltage 15 kV at varying distances (3, 5 and 7 cm) horizontally from the collector plate of the FTO that has deposited TiO$_2$ with the negative terminal using the direct deposition method. The flow rate of the solution through the needle is 4μL / min based on the rate at the electrospinning machine. FTO glass that has been deposited with TiO$_2$ nanoparticles and ZnO nanofibers is sintered at a temperature of around 500°C with a detention of 1 hour using Digital Muffle Furnace model XD-1700M. The results of the semiconductor deposition sintering can be used as a double layer DSSC photoanode.

Double layer DSSC photoanode soaked with N719-synthetic dye that has been dissolved with a sensitizer solution. Photoanode soaked for 24 hr, it can absorb the solution perfectly. The results of the DSSC double layer photoanode immersion are combined and bonded with a counter electrode. Next iodide solution (I$^-$) as an electrolyte is added to the counter electrode and covered with a dyesol plaster. The components of the FTO substrate, colorants, electrolytes, and counter electrodes form a unified DSSC.

2.3. Testing
DSSC performance is known through observations with the Scanning Electron Microscope (SEM) test to determine the morphology and size of semiconductor nanofibers. Semiconductors band gap values can be determined through the Tauc graph, band gap values are obtained by extrapolating the linear curves formed by $(\alpha.hv)^{1/2}$ to hv, where $\alpha$ is the absorbance coefficient and hv is the photon energy, as in equation 1 [14]. DSSC performance testing was performed with a Solar Simulator Machine with a light intensity of 100 mW/cm$^2$ with a surface area of 1 cm$^2$.

In the voltage current curve (IV) there is a maximum power point (PMAX) which is the product of the maximum current and voltage. Another performance shown by DSSC is the value of fill factor (FF) which has the meaning as a comparison between maximum power (PMAX) against ISC and VOC multiplication as shown in equation 2. DSSC efficiency is obtained from a comparison between maximum power (PMAX) and power that is light emitted in the active area of the solar cell (Plight). The light rays produce power which is the result of the multiplication of the intensity of sunlight with the area of the active region, so that the solar cell efficiency is obtained as shown in equation 3.
\[ E = hV = \frac{hc}{\lambda} \]  
\[ FF = \frac{V_{MAX} \times I_{MAX}}{I_{SC} \times V_{DC}} \]  
\[ \eta = \frac{P_{MAX}}{P_{light}} = \frac{P_{MAX}}{I \times A} = \frac{I_{SC} \times V_{DC} \times FF}{I \times A} \]  

3. Results and discussion

3.1 Analysis of scanning electron microscope (SEM)

SEM images observed from direct deposition of ZnO nanofibers on DSSC double layer variations in the distance of the tip and collector electrospinning process are shown in Figure 2. It can be seen that the use of a 7 cm distance has a more uniform morphology and has a smaller average diameter of 92 nm. This is because the closer the tip distance to the collector accelerates the jet / whip of the solution bubble sticks to the collector and becomes fiber. The overlapping fibers do not stretch and evaporate. Therefore, the nanofiber has an irregular size and shape [16]. Giving the small size of the nanofiber will expand the surface of the semiconductor. Thus, it can reduce the value of the semiconductor band gap.

![Figure 2. ZnO semiconductor SEM photo results on double layer DSSC for each distance: a) 3 cm, b) 5 cm, c) 7 cm electrospinning process](image)

3.2 Band gap value

Figure 3 shows the band gap values for each variation. The results show that the farther the tip to the collector will decrease the band gap value. Decreasing the band gap is an indication of a shrinking semiconductor size. The value of the band gap decreases, allowing for easier electron excitation when getting energy from outside. However, it can reduce the magnitude of the difference in solar cell potential due to differences in energy levels with the redox potential of electrolytes [14].
Figure 3. Tauc’s plot method in determining the ZnO semiconductor band gap on DSSC double layer

3.3 DSSC performance
The performance of double layer photoanoda for the variation of tip distance to the collector can be seen in the curve in Figure 4 and Table 1. The results of DSSC with direct deposition of ZnO nanofiber with a distance of 7 cm from the tip to the collector have the highest photovoltaic conversion efficiency. According to SEM test on the tip distance, it is 7 cm to the collector, which is produced a small diameter size and uniform morphology. ZnO nanofiber semiconductor diameter which is small reduced the value of the band gap, so it will be easier to absorb photons from solar energy[17]. It can be seen, that the distance of the tip collector to the needle as far as 7 cm has the highest efficiency of DSSC which is 1.69%.

Figure 4. Curve I-V of each tip distance variation to the DSSC double layer photoanode collector

| Tip Distance to Collector Variations | VOC (V) | JSC (mA cm⁻²) | Fill Factor (%) | Efficiency (%) | Dye Loading (x 10⁻⁷ mol cm⁻²) |
|-------------------------------------|---------|---------------|----------------|---------------|-------------------------------|
| 3 cm                                | 0.56    | 3.44          | 52             | 1.00          | 0.44                          |
| 5 cm                                | 0.52    | 6.65          | 45             | 1.66          | 0.81                          |
| 7 cm                                | 0.55    | 6.29          | 47             | 1.69          | 0.86                          |
4. Conclusion

Making DSSC double layer photoanode has been successfully carried out. Direct deposition of ZnO nanofiber semiconductors on Fluorine doped tin oxide (FTO) glass coated with TiO₂ nanoparticles using the electrospinning process. It can be seen that the process of direct deposition of ZnO layers using electrospinning reduces fabrication time, prevents damage to nanoparticle and nanofiber structures, and improves DSSC performance. The direct deposition process with a tip distance to the 7 cm collector using the electrospinning process produces nanofibers that are uniform and smaller in diameter than other variations. Therefore, the value of the band gap decreases resulting in electron excitation by high photons. Performance of the DSSC is based on JSC value. The higher the JSC value generated, DSSC efficiency will increase. The highest efficiency that was obtained is the tip distance to the collector of 7 cm by 1.69%.

5. Acknowledgment

This work is partially supported by the grant of PDUPT from the Ministry of Research, Technology, and Higher Education, the Republic of Indonesia with contract number 719 / UN.27.21 / PN / 2020 for FY 2020.

6. References

[1] Dang M 2017 Solar Energy Potential in Indonesia 19th International Conference of Young Scientists 199
[2] Halme J 2002 Dye-sensitized nanostructured and organic photovoltaic cells: technical review and preliminary tests Solar Cells
[3] Arifin Z, Soeparman S, Widhiyanuriyawan D and Suyitno S 2017 Performance Enhancement of Dye-Sensitized Solar Cells Using a Natural Sensitizer International Journal of Photoenergy 2017
[4] Shalini S, Balasundara Prabhu R, Prasanna S, Mallick TK and Senthilarasu S 2015 Review on natural dye sensitized solar cells: Operations, materials and methods Renewable and Sustainable Energy Reviews 51 1306-25
[5] Dobrzański LA, Mucha A, Prokopowicz MP vel, Szindler M, Drygała A and Lukaszkowicz K 2016 Characteristics of dye-sensitized solar cells with carbon nanomaterials Materiali in Tehnologije 50 649–54
[6] Gu P, Yang D, Zhu X, Sun H and Li J 2018 Fabrication and characterization of dye-sensitized solar cells based on natural plants Chemical Physics Letters 693 16–22
[7] Sinha D, De D, Goswami D, Mondal A and Ayaz A 2019 ZnO and TiO2 Nanostructured Dye sensitized Solar Photovoltaic Cells Materials Today: Proceedings 11 782–8
[8] Yang M, Dong B, Yang X, Xiang W, Ye Z, Wang E, Wan L, Zhao L and Wang S 2017 TiO2 nanoparticle / nanofiber-ZnO photoanode for the enhancement of the efficiency of dye-sensitized solar cells RSC Advances 7 41738–44
[9] The L and Leung WWF 2014 Optimizing scattering layer for efficient dye sensitized solar cells based on TiO2 nanofiber Polyhedron 82 7–11
[10] Boyadjiev SI, Kéri O, Bárdos P, Firkala T, Gáber F, Nagy ZK, Baji Z, Takács M and Szilágyi IM 2017 TiO 2 / ZnO and ZnO / TiO 2 core / shell nanofibers prepared by electrospinning and atomic layer deposition for photocatalysis and gas sensing Applied Surface Science 424 190-7
[11] Jati HN, Khusaini MZ, Sutanto H and Arifin Z 2019 Application of direct deposition method for dye-sensitized solar cell manufacturing process AIP Conference Proceedings 2097 1–6
[12] Katoch A, Kim JH and Kim SS 2014 TiO2 / ZnO inner / outer double-layer hollow fibers for improved detection of reducing gases ACS Applied Materials and Interfaces 6 21494–9
[13] Arifin Z, Hadi S, Jati HN, Prasetyo SD and Suyitno 2020 Effect of electrospinning distance to
fabricate ZnO nanofiber as photoanode of dye-sensitized solar cells

[14] Kumari N, Gohel J V. and Patel SR 2018 Optimization of TiO2 / ZnO bilayer electron transport layers to enhance the efficiency of perovskite solar cells Materials Science in Semiconductor Processing 75 149-56

[15] Supriyanto A, Furqoni L, Nurosyid F, Hidayat J and Suryana R 2016 Effects of sintering temperatures and screen printing types on TiO2 layers in DSSC applications AIP Conference Proceedings 1717

[16] Hekmati AH, Rashidi A, Ghazisaeidi R and Drean JY 2013 Effects of needle length, electrospinning distance, and solution concentration on morphological properties of polyamide-6 electrospun nanowebs Textile Research Journal 83 1452–66

[17] Samanta P, Bagchi S and Mishra S 2015 Synthesis and Sensing Characterization of ZnO Nanofibers Prepared by Electrospinning Materials Today: Proceedings 2 4499–502