The use of direct deposition electrospinning process in ZnO nanofiber fabrication as double layer (TiO$_2$/ZnO) DSSC: variation of solution flow rate

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Abstract The development of the use of Dye-sensitized solar cells (DSSC) types is increasingly studied. DSSC type solar cells are easy in fabrication and cheaper than silicon solar cells or thin layer type solar cells. DSSC engineering is manufactured by adding a semiconductor layer. Addition can be conducted by direct deposition of ZnO semiconductor layer on the TiO$_2$ nanoparticle layer by electrospinning process so as to create a double layer DSSC photoanode. The liquid electro-jet spun from ZnAc/PVA on FTO glass coated TiO$_2$ nanoparticles semiconductor was captured by direct deposition method using an electrospinning machine. This study was to investigate the effect of direct deposition of ZnO layers using electrospinning with variations in the distance of the tip to the collector and the flow rate. The results showed that the use of ZnO layers made by direct deposition at a flow rate 3μl / min produces a small diameter and uniform morphology. Small and uniform morphology allows ZnO nanofibers to have color absorption to produce a better DSSC double layer photoanode efficiency.

Keywords: solution flow rate, direct deposition, electrospinning, double layer DSSC

1. Introduction

The development of the use of Dye-sensitized solar cells (DSSC) types is increasingly studied. The fabrication of DSSC solar cells is easy and cheaper [1]. The absorption of sunlight which contains photons with a certain degree of energy regarding the semiconductor material present in the DSSC solar cell, so that electrons located in the crystal structure of the material can be freed from bonds between atoms and produce an electric current. The performance of DSSC is characterized by parameters of efficiency values, short-circuit photocurrent density (JSC), fill factor (FF), and open-circuit voltage (VOC) [2].

Some of the semiconductor materials making up photoanode used for DSSC type solar cells are titanium oxide (TiO$_2$), zinc oxide (ZnO), and nickel (II) oxide (NiO). In increasing electron mobility, nanomaterial engineering is used to improve the properties of semiconductor materials with shapes such as nanoparticles, nanofiber, nanowire, nanorods, nanobelts, nanospirals, nanorings and nanotubes, because nanomaterial engineering can increase chemical reactivity caused by the expansion of the relative area[3].
Semiconductor TiO$_2$ nanoparticles have a higher surface area than other nanomaterial semiconductors, because semiconductor nanoparticles can absorb dye molecules optimally. However, the morphology of nanoparticles can reduce the mobility of electrons among particles [4]. In contrast to the semiconductor ZnO nanofiber layer is able to adhere directly to the substrate and dye so as to facilitate the mobility of excited electrons. Another advantage of fiber morphology is the effect of scattering photons in a photoanode thereby increasing electron excitation [5].

Increasing electron mobility in TiO$_2$ nanoparticle semiconductors can be done by making double layer photoanoda engineering, namely ZnO nanofiber semiconductors deposited with TiO$_2$ nanoparticle semiconductors in which the first layer of semiconductor TiO$_2$ nanoparticles has a function as a layer of dye loading (DL) and the second layer of semiconductor ZnO nanofiber functions as a layer of light scattering (LS) [6]. Double layer photoanoda arranged to form a sandwich as Figure 1. Adding ZnO layer as a double layer photoanode can increase DSSC efficiency up to times from using one layer [6].

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

Double-layer photoanoda engineering can be done by direct deposition of ZnO semiconductor layers on TiO$_2$ nanoparticles by electrospinning [8]. Using of electrospinning process by direct deposition semiconductor is influenced by flow rate solution on the machine [9]. Thicker nanofiber fibers produced by electrospinning are affected by the high solution flow rate. So the nanofiber DSSC hard to excite electrons [10]. Based on the statement that has been disclosed, this research reveals the effect of variations in the flow rate of the solution on the direct deposition of ZnO nanofiber semiconductors in double layer photoanode. The use of a small solution flow rate is indicated to have better DSSC performance [11]. The use of direct deposition methods using the electrospinning process is intended to reduce fabrication time, preventing damage to nanoparticle and nanofiber structures and improving DSSC performance. DSSC performance improvement is characterized with high absorbance values of the double layer photoanode [12].

2. Method

2.1. Material
In this study the main ingredients which are used were Zinc acetate dihydrate ((CH$_3$COO)$_2$Zn.2H$_2$O, Merck) as the main material forming ZnO semiconductors, PVA or polyvinyl alcohol (CH$_2$CH (OH) n, MW = 72,000, Merck) as a carrier material in the electrospinning process, quades as a solution of 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 - N719 from dyesol, Iodide (I$^-$) EL-HPE electrolyte solution from Dyesol.
2.2. ZnO fabrication

PVA / Zn (Ac)₂ solution was synthesized with adding precursor solution to Zn(Ac)₂ solution. The precursor solution was prepared by mixing 2-gram PVA (Merck, MW = 72,000) with 20 ml of distilled water (H₂O) at 70°C for 4 hours. Afterwards, Zn (Ac)₂ solution was prepared by mixing 2 grams of zinc acetatedihydrate ((CH₃COO)₂Zn·2H₂O, Merck) and 8 ml H₂O for 1 hour at 70°C. The homogenization process was then carried out between the precursor solution and the Zn(Ac)₂ solution for 8 hours at 70°C at a ratio of 4: 1 wt%.

The PVA / Zn(Ac)₂ solution was carried out by an electrospinning process to form nanofiber ZnO on a DSO double layer TiO₂ / ZnO. The solution is inserted into the syringe and is connected to an electrospinning machine in the Nanobioenergy Lab, SebelasMaret University, Surakarta. The tip on the injection pump is joined to the positive terminal high voltage 15 kV at a distance of 8 cm horizontally against the collector plate of the FTO that has deposited TiO₂ with the negative terminal utilising the direct deposition technique[13]. The flow rate of the solution through the needle is varied (3, 5, and 7,μL / min) based on the rate of the solution on the electrospinning machine. FTO glass that has been deposited with TiO₂ 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.

2.3. DSSC assembly

Double layer DSSC photoanoda soaked with synthetic dye -N719 ([RuL₂(NCS)₂]: 2TBA (L = 2,2'-bipyridyl-4,4'-dicarboxylic acid; TBA = tetra-n-butylammonium)) from Dyesolyamg has been dissolved with a sensitizer solution.0.02-gram N-719 powder was dissolved into 100 ml of ethanol to produce a sensitizer solution. Photoanode is soaked in the solution dye for 24 hours to absorb it perfectly.

The results of the DSSC double layer photoanode immersion are combined and bonded with a perforated counter electrode. Furthermore, the EL-HPE Iodide (I³⁻)solution from Dyesol as an electrolyte is added to another electrode. The components of the FTO substrates, colorants, electrolytes, and counter electrodes form a unified DSSC.

2.4. Testing

![Figure 2. I-V curve on DSSC [15]](image)

DSSC performance is known through observations with the Scanning Electron Microscope (SEM) test to determine the morphology and size of semiconductor nanofibers. The desorption method has a function to assess the amount of dye taken by semiconductors [14]to find out the linearity
The relationship between absorbance and concentration of a solution through the Lambert-Beer equation as in Equation 1. The DSSC performance test was performed with a Solar Simulator with light intensity of 100 mW cm\(^{-2}\) with a surface area of 1 cm\(^2\). Open circuit photovoltage (VOC), photocurrent voltage curve (IV curve), fill factor (FF), short-circuit photocurrent density (JSC), and efficiency (\(\eta\)) are DSSC performances. Figure 2 shows the voltage and current curves of DSSC performance.

In the voltage current curve (IV) there is a maximum 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. Comparison between the maximum power (PMax) with the power resulted from a light in the active area of the solar cell (Plight) shows the form of DSSC performance. The light rays produce power which is the result of sunlight intensity with the active region, so that the solar cell performance is obtained as shown in Equation 3.

\[
A = \varepsilon.c.l
\]
\[
FF = \frac{V_{MAX} \times I_{MAX}}{I_{SC} \times V_{OC}}
\]
\[
\eta = \frac{P_{MAX}}{P_{light}} = \frac{P_{MAX}}{I \times A} = \frac{I_{SC} \times V_{OC} \times FF}{I \times A}
\]

3. Results and Discussion

3.1 Scanning electron microscope results
Figure 3 shows a morphological form of ZnO nanofiber direct deposition on double layer DSSC with variations in flow rates using the electrospinning process. The average diameter of nanofiber for rates 3, 5, and 7 is 122, 125, and 141 nm respectively. It can be seen that the flow rate 3 \(\mu\)L min\(^{-1}\) results in smaller and more uniform nanofiber diameter sizes than other flow rate variations. This is influenced by the smaller flow rate which resulted smaller solution bubbles in the injection pump tip on the electrospinning machine. The bubbles that are drawn have a better stretch for the same electrostatic field[16]. In addition, a faster stretch will facilitate drying. Giving the small size of the nanofiber will expand the surface of the semiconductor so that it can increase the absorption of dyes. The high absorption value of the dye facilitates the entry of light [17].

Figure 3. ZnO semiconductor SEM photo results on double layer DSSC for each flow rate: a)3 \(\mu\)L min\(^{-1}\), b) 5 \(\mu\)L min\(^{-1}\), c) 7 \(\mu\)L min\(^{-1}\) electrospinning process

3.2 Absorbance value
Figure 4 shows the amount of absorbance in each flow rate variation in the electrospinning process. It can be seen that based on the N719 coloring trend, which has a wavelength of 450-550 nm, the use of 3 \(\mu\)L min\(^{-1}\) discharge has a higher absorbance value than other flow rate variations. This is related to the shape and size of the morphology of the flow rate of 3\(\mu\)L min\(^{-1}\) which is uniform and
has a smaller average diameter. Thus, it has a better dye loading ability. The high absorbance value increases the current density (JSC) which affects the efficiency of DSSC [2,18].

![Graph of ZnO semiconductor absorbance test on double layer DSSC for each variation in the flow rate of the electrospinning process](image)

**Figure 4** The results of ZnO semiconductor absorbance test on double layer DSSC for each variation in the flow rate of the electrospinning process

### 3.3 DSSC performance

![Graph of photocurrent versus photovoltage (IV) density for each DSSC variation](image)

**Figure 5** Photocurrent versus photovoltage (IV) density for each DSSC variation

The curve in Figure 5 is the photocurrent versus photovoltage (IV) density for each DSSC variation of discharge with an intensity of 100 mW cm$^{-2}$. In addition, table 1 illustrates DSSC performance with Voc, Jsc, FF, and efficiency values for discharge variations. The results showed that the morphological changes of ZnO nanofiber semiconductors had a large influence on JSC and had a small effect on VOC DSSC. This shows that the precursor discharge 3μL min$^{-1}$ produced a small size of nanofiber so as to produce maximum electrical conductivity from the nanofiber electrospinning process results. Higher conductivity values compared to other precursor discharge reduced electrical resistance in DSSC. High ability to deliver electrons causes the electric current generated by DSSC to be more optimal with the ability of dye loading in light absorption and optimal
electrical conductivity [19]. Variations in the precursor discharge 3μL min⁻¹ have the highest DSSC efficiency of 2.36%.

| Flow Rate Variation | VOC (V)  | JSC (mA cm⁻²) | Fill Factor (%) | Efficiency (%) | Dye Loading (x 10⁻⁷ mol cm⁻²) |
|---------------------|---------|---------------|-----------------|----------------|-------------------------------|
| 3 μL / minute       | 0.58    | 9.24          | 42              | 2.36           | 1.17                          |
| 5 μL / minute       | 0.52    | 6.65          | 45              | 1.66           | 0.74                          |
| 7 μL / minute       | 0.48    | 4.75          | 46              | 1.05           | 0.35                          |

4. Conclusion
DSSC photoanode double layer TiO₂-ZnO has been obtained by nanofiber ZnO deposited directly on Fluorine doped tin oxide (FTO) glass coated with TiO₂ nanoparticles using an electrospinning machine. The direct deposition process of ZnO layers using electrospinning can reduce fabrication time, preventing damage to nanoparticle and nanofiber structures, and can improve DSSC performance. Improved photoanoda efficiency occurs in the treatment of electrospinning variations given. It is known that the use of variations in the flow rate of solution 3μL / min direct deposition electrospinning process produces nanofibers that are uniform and smaller in diameter than other variations. Therefore, the ability of dye loading for light absorption and electron excitation by photons is high. Generating DSSC efficiency at solution flow rate 3μL / minute is 2.36%.

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6. References
[1] Shalini S, Balasundara Prabhu R, Prasanna S, Mallick T K and Senthilarasu S 2015 Review on natural dye sensitized solar cells: Operation, materials and methods Renewable and Sustainable Energy Reviews51 1306–25
[2] 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 Letters693 16–22
[3] Wei W and Hu Y H 2015 Synthesis of carbon nanomaterials for dye-sensitized solar cells International Journal of Energy Research39 842–50
[4] Kabir F, Bhuiyan M M H, Hossain M R, Bashar H, Rahaman M S, Manir M S, Ullah S M, Uddin S S, Mollah M Z I, Khan R A, Huque S and Khan M A 2019 Improvement of efficiency of Dye Sensitized Solar Cells by optimizing the combination ratio of Natural Red and Yellow dyes Optik179 252–8
[5] Kumar R, Umar A, Kumar G, Nalwa H S, Kumar A and Akhtar M S 2017 Zinc oxide nanostructure-based dye-sensitized solar cells Journal of Materials Science52 4743–95
[6] Arifin Z, Suyitno S, Hadi S and Sutanto B 2018 Improved performance of dye-sensitized solar cells with TiO₂ nanoparticles/Zn-Doped TiO₂ hollow fiber photoanodes Energies11
[7] Lee J H, Ahn K, Kim S H, Kim J M, Jeong S Y, Jin J S, Jeong E D and Cho C R 2014 Thickness effect of the TiO₂ nanofiber scattering layer on the performance of the TiO₂ nanoparticle/TiO₂ nanofiber-structured dye-sensitized solar cells Current Applied Physics14 856–61
[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] Ghafari E, Feng Y, Liu Y, Ferguson I and Lu N 2017 Investigating process-structure relations of ZnO nanofiber via electrospinning method Composites Part B: Engineering 116 40–5
[10] Jati H N, Khusaini M Z, Sutanto H and Arifin Z 2019 Application of direct deposition method for dye-sensitized solar cell manufacturing process AIP Conference Proceedings 2097 1–6
[11] Khusaini M Z, Jati H N, Suyitno, Hadi S and Arifin Z 2020 The influence of electrospinning flow rate parameter on ZnO nanofiber as photoanode of dye-sensitized solar cell AIP Conference Proceedings 2217
[12] Suyitno, Agustia Y V, Hidajat L L G, Kristiawan B and Wibowo A H 2018 Effect of light and temperature on the efficiency and stability of curcumin-dye-sensitized solar cells International Energy Journal 18 53–60
[13] Arifin Z, Hadi S, Jati H N, Prasetyo S D and Suyitno 2020 Effect of electrospinning distance to fabricate ZnO nanofiber as photoanode of dye-sensitized solar cells AIP Conference Proceedings 2217
[14] Yavuz Ö, Zehra Ö and Yaşar T N 2018 Modelling, simulation and optimization of solar-assisted absorption cooling systems Green Energy and Technology pp 1047–71
[15] Sokolský M and Cirák J 2010 Dye-Sensitized Solar Cells: Materials and Processes Acta Electrotechnica et Informatica 10 78–81
[16] Sun G, Sun L, Xie H and Liu J 2016 Electrospinning of nanofibers for energy applications Nanomaterials 6
[17] Chattopadhyay S, Basu S and Saha S 2019 Solar driven photocatalytic activity of TiO 2-ZnO nanocomposite AIP Conference Proceedings 2087
[18] Prasetyo S D, Harsito C, Sutanto and Suyitno 2019 Energy consumption of spray dryer machine for producing red natural powder dye and its stability AIP Conference Proceedings 2097 1–7
[19] Marimuthu T and Anandhan N 2017 Growth and characterization of ZnO nanostructure on TiO2-ZnO films as a light scattering layer for dye sensitized solar cells Materials Research Bulletin 95 616–24