CHARACTERIZATION OF ZnO NANOFIBER ON DOUBLE-LAYER DYE-SENSITIZED SOLAR CELLS USING DIRECT DEPOSITION METHOD

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KARAKTERISASI ZnO NANOFIBER PADA SEL SURYA TERSENSITISASI PEWARNA DENGAN LAPISAN GANDA MENGGUNAKAN METODE *DIRECT DEPOSITION*

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ABSTRACT Characterization

Solar cells are capable of harvesting energy by converting solar heat into electrical energy through the photovoltaic process. A type of solar cell, namely dye-sensitized solar cells (DSSCs) which based on double-layer photoanode is attracting researchers and engineers considering its characteristics, e.g., high efficiency, low cost, and available mass-production. The TiO₂-ZnO double-layer semiconductor can be obtained from a nanofiber ZnO semiconductor which is deposited with a TiO₂ nanoparticle semiconductor. In this study, the direct deposition method was applied using an electrospinning machine. The intention is to directly capture the liquid of electro-jet spun from PVA/Zn(Ac)₂ solution onto fluorine-doped tin oxide (FTO) glass. The glass itself is coated with a TiO₂ nanoparticle semiconductor. The investigation was addressed to obtain the best tip distance to the collector and the best flow rate in the electrospinning process. The subject environment was designated on the manufacturing process of nanofiber ZnO semiconductors used as double-layer DSSC photoanodes. Variations in flow rates of 3, 4, 5, 6, 7, and 8 µL/minute were applied in the observation. Furthermore, collaboration with the tip to collector distances using a variation of 3, 4, 5, 6, 7, and 8 cm was also considered in this study. Based on these parameters, the effects of the electrospinning process on the morphology of the directly deposited ZnO nanofiber semiconductor were obtained. The results showed that a flow rate of 4 µL/minute and a tip distance to the collector of 8 cm produced a small diameter and uniform morphology. This morphology allowed ZnO nanofibers to have better color absorption and electron excitation. Thus, it was directly proportional to the high efficiency of double-layer DSSCs. The performance value for the 4 µL/min discharge was 2.39%, and the performance value for the 8 cm needle tip distance to the collector was 1.61%.

Keywords: *semiconductors, double layer, direct deposition, dye-sensitized solar cells (DSSCs)*

ABSTRACT

Solar cells are capable of harvesting energy by converting solar heat into electrical energy through the photovoltaic process. A type of solar cell, namely dye-sensitized solar cells (DSSCs) which based on double-layer photoanode is attracting researchers and engineers considering its characteristics, e.g., high efficiency, low cost, and available mass-production. The TiO₂-ZnO double-layer semiconductor can be obtained from a nanofiber ZnO semiconductor which is deposited with a TiO₂ nanoparticle semiconductor. In this study, the direct deposition method was applied using an electrospinning machine. The intention is to directly capture the liquid of electro-jet spun from PVA/Zn(Ac)₂ solution onto fluorine-doped tin oxide (FTO) glass. The glass itself is coated with a TiO₂ nanoparticle semiconductor. The investigation was addressed to obtain the best tip distance to the collector and the best flow rate in the electrospinning process. The subject environment was designated on the manufacturing process of nanofiber ZnO semiconductors used as double-layer DSSC photoanodes. Variations in flow rates of 3, 4, 5, 6, 7, and 8 µL/minute were applied in the observation. Furthermore, collaboration with the tip to collector distances using a variation of 3, 4, 5, 6, 7, and 8 cm was also considered in this study. Based on these parameters, the effects of the electrospinning process on the morphology of the directly deposited ZnO nanofiber semiconductor were obtained. The results showed that a flow rate of 4

$\mu\text{L}/\text{minute}$ and a tip distance to the collector of 8 cm produced a small diameter and uniform morphology. This morphology allowed ZnO nanofibers to have better color absorption and electron excitation. Thus, it was directly proportional to the high efficiency of double-layer DSSCs. The performance value for the 4 $\mu\text{L}/\text{min}$ discharge was 2.39%, and the performance value for the 8 cm needle tip distance to the collector was 1.61%.

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ABSTRAK

Sel surya merupakan alat pemanen energi dengan mengubah panas matahari menjadi energi listrik melalui proses fotovoltaiik. Salah satu jenis sel surya, yaitu sel surya tersensitisasi pewarna (*dye-sensitized solar cells* atau DSSC). Fotoanoda DSSC dengan struktur lapisan ganda menarik para cendekiawan untuk melakukan observasi dan riset, karena memiliki efisiensi tinggi, biaya produksi rendah, dan kemampuan produksi secara massal. Semikonduktor dengan struktur lapisan ganda berupa $\text{TiO}_2\text{-ZnO}$ dapat diperoleh dari semikonduktor nanofiber ZnO yang dideposisikan dengan semikonduktor nanopartikel TiO_2 . Pendeposisian dapat dilakukan dengan metode *direct deposition* menggunakan bantuan mesin elektrospinning. Tujuannya adalah untuk secara langsung menangkap cairan elektro-jet yang dipintal dari larutan $\text{PVA}/\text{Zn}(\text{Ac})_2$ ke gelas oksida timah yang didoping fluor (FTO) yang terlapis semikonduktor nanopartikel TiO_2 . Studi ini ditujukan untuk mendapatkan jarak ujung jarum ke kolektor dan debit aliran terbaik dalam proses elektrospinning secara *direct deposition*. Eksperimen dilakukan pada proses pembuatan semikonduktor nanofiber ZnO yang digunakan sebagai fotoanoda DSSC dengan struktur lapisan ganda. Debit aliran dengan nilai 3, 4, 5, 6, 7, dan 8 $\mu\text{L}/\text{menit}$ diterapkan sebagai variasi parameter dalam eksperimen. Selain itu, jarak ujung ke kolektor juga divariasikan dengan nilai 3, 4, 5, 6, 7, dan 8 cm. Berdasarkan konfigurasi parameter yang ditetapkan, efek dari proses elektrospinning secara *direct deposition* yaitu pada perubahan morfologi semikonduktor nanofiber ZnO. Hasil penelitian menunjukkan bahwa debit aliran 4 $\mu\text{L}/\text{menit}$ dan jarak ujung ke kolektor 8 cm menghasilkan morfologi dengan diameter kecil dan seragam. Morfologi ini memungkinkan serat nano ZnO memiliki penyerapan warna dan eksitasi elektron yang lebih baik, dimana berbanding lurus dengan efisiensi tinggi DSSC dengan struktur lapisan ganda. Nilai kinerja untuk debit 4 $\mu\text{L}/\text{menit}$ adalah 2,39%, dan untuk jarak ujung jarum ke kolektor sejauh 8 cm adalah 1,61%.

Keywords: *semikonduktor, struktur lapisan ganda, metode direct deposition, sel surya tersensitisasi pewarna (dye-sensitized solar cells-DSSC)*

1. INTRODUCTION:

Solar cells harvest solar energy that is converted into electrical energy through the photovoltaic process (Grätzel, 2006; Valaski *et al.*, 2007). There have been three generations of solar cells, including silicon solar cells, thin layer type solar cells, and dye-sensitized solar cells (DSSCs) (Ali *et al.*, 2016). The DSSCs are easy to fabricate and have a lower cost than silicon solar cells or thin layer type solar cells (Qadir *et al.*, 2015). The performance of DSSCs, in general, can be characterized by several parameters, namely efficiency value, short-circuit photocurrent density (JSC), fill factor (FF), and open-circuit voltage (VOC). DSSCs are composed of two electrodes, a photoanode electrode and a photo inert counter electrode.

Photoanode electrodes are made of semiconductors that have absorbed dyes and are deposited on transparent conductive oxide. The photo inert counter electrodes are made of a platinum layer superimposed on transparent conductive oxide (Grätzel, 2003; Tobin *et al.*,

2011). Semiconductors in DSSCs' photoanodes function as converters of photon energy from solar radiation through the process of electron excitation based on the gap of material energy (bandgap) with an average of 1 to 5 eV. Some of the photoanode constituent semiconductor materials used for DSSCs are titanium oxide (TiO_2), zinc oxide (ZnO), and nickel (II) oxide

(NiO) (Grätzel, 2003; Tobin *et al.*, 2011). TiO_2 semiconductors have higher photovoltaic performance in the visible light region compared to ZnO semiconductors.

However, ZnO semiconductors have a lower electron charge recombination effect. In increasing electron mobility, nanomaterial engineering improves the properties of semiconductor materials with shapes such as nanoparticles, nanofibers, nanowires, nanorods, nanobelts, nanospirals, nanorings, and nanotubes, because nanomaterial engineering can increase chemical reactivity through the expansion of the relative area. ZnO and TiO_2 semiconductors have gone through a large amount of nanomaterial engineering because they have a better energy gap, i.e., 3.61 and 3.24

eV, respectively. These gaps can increase the semiconductor absorption of the dye and subsequently the excitation of electrons by photons (Bakr *et al.*, 2019; Khan *et al.*, 2019; Rani and Tripathi, 2015; Suprayogi *et al.*, 2019).

Engineering photoanode layers with TiO₂ nanoparticle semiconductors results in a higher surface area than other nanomaterial semiconductors because semiconductor nanoparticles can absorb dye molecules optimally (Chang and Lo, 2010; Seo *et al.*, 2007). However, the morphology of nanoparticles can reduce the mobility of electrons between particles and spread randomly (Mintcheva *et al.*, 2020). By contrast, the semiconductor ZnO nanofiber layer can bond directly with the substrate and dye 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 (Saidin *et al.*, 2017; Sorayani Bafqi *et al.*, 2015). To increase the electron mobility of TiO₂ nanoparticle semiconductors, two layers of photoanodes can be engineered as follows: TiO₂ nanoparticle semiconductors are deposited with ZnO nanofiber semiconductors, where the first layer of semiconductor TiO₂ nanoparticles functions as a layer of dye loading (DL) and the second layer of semiconductor ZnO nanofibers functions as a layer of light scattering (LS). The use of a two-layer photoanode could increase the efficiency of DSSCs by up to 2.1 times that of using a single photoanode layer. This is also proportional to the bandgap value of 2.5–3 eV. The two-layer photoanode layer arranged to form a sandwich could strengthen the semiconductor bond with the substrate (adhesive properties), as shown in Figure 1 of Appendix (Cao *et al.*, 2017; Ghanbari Niaki *et al.*, 2014; Humayun *et al.*, 2019; Zhou *et al.*, 2019).

Manufacturing modification of the two layers of photoanode can consist of ZnO semiconductors deposited directly on TiO₂ semiconductors. Particulate TiO₂ semiconductors can be created using the doctor blade method (Dobrzański *et al.*, 2016), in which a TiO₂ paste is deposited on fluorine-doped tin oxide (FTO) glass and sintered. Subsequently, ZnO nanofiber semiconductors can be obtained from the direct deposition process on FTO glass that has been coated with a TiO₂ semiconductor using the electrospinning process. The use of direct deposition methods in the two-layer photoanode engineering is intended to reduce fabrication time and prevent damage to the nanoparticle and nanofiber structures, and can improve DSSCs'

performance (Yang *et al.*, 2017). However, the use of the electrospinning process depends on the distribution of molecular weight, the surface viscosity of the solution, and temperature (Panthi *et al.*, 2015; Sorayani Bafqi *et al.*, 2015).

The flow rate and the distance of the tip to the collector in the electrospinning process greatly affect the diameter size in nanofiber morphology. Therefore, this paper investigates the effect of variations in the distance of the tip to the collector and in the discharge of the direct deposition of ZnO semiconductors on the performance of DSSC double-layer photoanodes. The use of a flow rate of 4 µL/min and a distance of 8 cm in the electrospinning process were found to provide morphological results with a small and uniform diameter. Semiconductor morphology determines the dye loading value. The amount of dye loading value can affect the DSSC performance value (Alrikabi, 2017; Hekmati *et al.*, 2013; López-Covarrubias *et al.*, 2019). Therefore, flow rates of 3, 4, 5, 6, 7, and 8 µL/min and distances of 3, 4, 5, 6, 7, and 8 cm were examined.

2. MATERIALS AND METHODS:

2.1. Materials

In this study, the main reagents used were zinc acetate dihydrate ((CH₃COO)₂Zn·2H₂O, Merck) as the main material forming ZnO semiconductors; polyvinyl alcohol (PVA) (CH₂CH(OH)_n, MW = 72,000, Merck) as a carrier material in the electrospinning process; aquades as a solvent applied to the zinc acetate and PVA to form a homogeneous solution; a glass plate with 28 test working electrodes printed with TiO₂ opaque paste (160 mm x 80 mm x 3.2 mm); synthetic dyes—N719 ([RuL₂(NCS)₂]:2TBA (L = 2,2'-bipyridyl-4,4'-dicarboxylic acid; TBA = tetra-*n*-butylammonium)) and Iodide (I³⁻) EL-HPE electrolyte solution (Hongsih *et al.*, 2015).

2.2. Fabrication of ZnO Nanofibers

The addition of precursor solutions was used to produce the morphology of the nanofibers. The precursor solution was prepared using 2 g of PVA (Merck, MW = 72,000) mixed with 20 ml of H₂O (pH = 7). The homogenization process was carried out by stirring for 4 h at a 70 °C solution temperature. The Zn(Ac)₂ solution was synthesized using 2 g of zinc acetate dihydrate ((CH₃COO)₂Zn·2H₂O, Merck),

and 8 ml of H₂O, and then the homogenization process was carried out by stirring for 1 h while keeping the solution at 70 °C. Subsequently, the homogenization process between the PVA solution and Zn(Ac)₂ was carried out in a ratio of 4:1 wt% at 70 °C for 8 h. The entire solution was mixed in a closed container using a magnetic stirrer.

Following the above, the PVA/Zn(Ac)₂ solution was left in a closed room at room temperature for 24 h so that the foam formed could be lost. The result is a PVA/Zn(Ac)₂ solution, which is used to produce the ZnO nanofiber fibers using an electrospinning machine (Zhou *et al.*, 2019).

The PVA/Zn(Ac)₂ solution was used to form ZnO nanofibers on the TiO₂/ZnO double-layer DSSCs through an electrospinning process (Katoch *et al.*, 2014). As much as 1 mL of the solution was injected into a syringe pump and connected to the electrospinning machine at the Nanobioenergy Lab, Universitas Sebelas Maret Surakarta, as shown in Figure 2 of Appendix. Electrospinning machine specifications: collector; voltage power supply: 15 kV; injection pump tip distance to the collector: 10–200 mm; injection pump solution output: 2.237 ml/h. The tip on the syringe pump was connected to a high voltage positive terminal at varying distances (3, 4, 5, 6, 7, and 8 cm) located horizontally relative to the collector plate of the fluorine-doped tin oxide glass deposited with TiO₂ with negative terminals using the direct deposition method. The flow rate of the solution through the needle was varied (3, 4, 5, 6, 7, and 8 µL/min) based on the rate at the electrospinning machine. The fluorine-doped tin oxide glass deposited with TiO₂ nanoparticles and ZnO nanofibers was sintered at a temperature of 500 °C with a retention time of 1 h using a Digital Muffle Furnace model XD-1700M. The semiconductor deposition sintering results can be used as double-layer DSSC photoanodes (Hegazy *et al.*, 2016).

2.3 Assembling double-layer DSSCs

Double-layer DSSC photoanodes were soaked with synthetic dye N719 ([RuL₂(NCS)₂]: 2TBA (L = 2,2'-bipyridyl-4,4'-dicarboxylic acid; TBA = tetra-n-butylammonium) manufactured by Dyesol that was dissolved with a sensitizer solution. The sensitizer solution was prepared by dissolving 0.02 g N719 powder into 100 ml of ethanol. The resulting double-layer DSSC photoanodes were immersed in N719 dye for 24

h. The double-layered photoanode can absorb the solution completely (Sakai *et al.*, 2013). The results of the DSSC double-layer photoanode immersion were combined and bonded with a perforated counter electrode. Subsequently, EL-HPE Iodide (I³⁻) solution manufactured by Dyesol, which was used as an electrolyte, was injected through a hole in the counter electrode and covered with a Dyesol plaster. The FTO substrate components, colorants, electrolytes, and counter electrodes form unified DSSCs (Kouhestanian *et al.*, 2016; Wei and Hu, 2015).

2.4 Testing

DSSCs performance was examined using scanning electron microscopy (SEM) to determine the morphology and size of semiconductor nanofibers; absorbance testing with a UV 1800 UV-VIS spectrophotometer was used to measure the bandgap energy value using Tauc's plot method, as shown in Equation 1 (Alrikabi, 2017; Firdaus *et al.*, 2012). The bandgap energy function is the value of VOC, as shown in Equation 2 (Bakr *et al.*, 2019); the dye-loading ability of each sample was measured using the desorption method and the Lambert–Beer equation, which tests the solution's absorbance, as shown in Equation 3 (Asib *et al.*, 2018).

$$E = h\nu = \frac{h \cdot c}{\lambda} \quad (\text{Eq. 1})$$

$$V_{OC} = \frac{E_{CB}}{e} + \frac{k_B T}{e} \ln \left(\frac{n}{N_{CB}} \right) - E_{redox} \quad (\text{Eq. 2})$$

$$A = \varepsilon \cdot c \cdot l \quad (\text{Eq. 3})$$

The performance of the DSSCs was tested using a Solar Simulator Machine with a light intensity of 100 mW/cm² and a surface area of 1 cm². The DSSC performance was evaluated by measuring the following: open-circuit photovoltage (VOC), photocurrent voltage curve (IV curve), fill factor (FF), short-circuit photocurrent density (JSC), and efficiency (η). Voltage and current curves were obtained from measurements' results, as shown in Figure 3 of Appendix (Humayun *et al.*, 2019).

In the voltage–current curve (IV), was a maximum power point (P_{MAX}) could be observed, which is the product of the maximum current and voltage. The fill factor (FF) value arises from a comparison between maximum power (P_{max}) and the multiplication of ISC and VOC values, as shown in Equation 4. The

DSSCs' efficiency was obtained from the ratio between maximum power (P_{max}) and light emitted in the solar cell (P_{light}). Light emission produces power, which is the result of the multiplication of the intensity of sunlight with the area of the active region, so that solar cell efficiency was obtained as shown in Equation 5 (Chou *et al.*, 2007; Hongsith *et al.*, 2015; Junger *et al.*, 2018).

$$FF = \frac{V_{MAX} \times I_{MAX}}{I_{SC} \times V_{OC}} \quad (\text{Eq. 4})$$

$$\eta = \frac{P_{MAX}}{P_{light}} = \frac{P_{MAX}}{I \times A} = \frac{I_{SC} \times V_{OC} \times FF}{I \times A} \quad (\text{Eq. 5})$$

3. RESULTS AND DISCUSSION:

3.1. Analysis of Scanning Electron Microscope (SEM) Results

3.1.1. Variation of Flow Rate

Figure 4 in Appendix shows the morphological forms of ZnO nanofiber semiconductors on double-layer DSSCs fabricated with various flow rates using the electrospinning process. It can be seen that lower flow rates produced more uniform shapes and diameters of the nanofibers. This is due to the fact that the lower flow rate emitted smaller solution bubbles through the injection pump tip onto the electrospinning machine. The emitted bubbles showed better stretching characteristics for the same electrostatic field. Additionally, faster stretches make it easier to dry and form fibers in the collector (Benekohal and Demopoulos, 2012; Dissanayake *et al.*, 2016).

Solution which has flow rate of 4 $\mu\text{L}/\text{min}$ in the fabrication process, causes smaller and more uniform nanofiber diameter. This was influenced by operational conditions (solution rate, tip distance to the collector, potential difference, and syringe needle size) and the solution (viscosity, conductivity, and surface tension). Because in this study the flow rate was varied and all other conditions were equal, the differences in diameter can be attributed to changes in the flow rate in the electrospinning process. As can be seen in Table 1 of Appendix, the flow rates of 4 $\mu\text{L}/\text{min}$ produced an average diameter that was 118.335 nm smaller than the flow rates of 3, 5, 6, 7, and 8 $\mu\text{L}/\text{min}$. The smaller and more uniform the diameter of the nanofiber morphology, the more

active will the surface area be in the process of absorbing the dye, which will, in turn, increase the absorption of light (Firdaus *et al.*, 2012; Grätzel, 2003; López-Covarrubias *et al.*, 2019; Saidin *et al.*, 2017).

3.1.2. Variations in Tip Distance to Collectors

SEM images of the ZnO nanofiber semiconductors on double-layer DSSCs that resulted from varying the distance between the tip and the collector during the electrospinning process are shown in Figure 5 of Appendix. All of the conditions of the fabrication of the ZnO semiconductors using the electrospinning process were constant except for the tip distance to the collector, which was varied. The figure shows that the larger the distance between the tip and the collector was, the more uniform were the results' morphological shape and size. This is because a closer distance of the tip to the collector causes the jet/whip to accelerate while the solution bubbles stick to the collector and turn into fibers. The overlapping fibers then do not stretch and may evaporate. Therefore, with closer distances, the resultant nanofiber had an irregular size and shape (Firdaus *et al.*, 2012; Saidin *et al.*, 2017).

As shown in Table 2 of Appendix, using a tip-to-collector distance of 8 cm resulted in an average diameter that was smaller than the other variations by 92.70 nm. The small size of the nanofiber expanded the surface of the semiconductor, thus increasing the absorption of dyes. A high absorption value of the dye facilitates the entry of light and thus the electron flow, as observed from the performance of DSSCs (Sorayani Bafqi *et al.*, 2015).

3.2. Characterization of Light Absorbance and Transmittance

The absorbance value of the DSSCs was obtained using the desorption method by releasing the bonds between the semiconductor and the absorbed dye using a base solvent. In this study, the double-layer DSSC photoanode was soaked in 8 ml alkaline solution (0.1 M NaOH) for 1 h. The bond between the semiconductor surface and the carboxylic acid could thus be broken, then the OH^- ions bonded to the dye molecules. Hence, the dye was separated from the semiconductor entirely. The released dye solution was tested for its absorbance value using UV-VIS (Asib *et al.*, 2018; Marimuthu *et al.*, 2018).

3.2.1. Flow Rate Variation

Figure 6a of Appendix shows the magnitude of the absorbance value for each flow rate variation in the electrospinning process. It can be seen that based on the trend of the N719 dye, at a wavelengths of 450–550 nm, the use of 4 $\mu\text{L}/\text{min}$ discharge had a higher absorbance value compared to other flow rate variations (Alrikabi, 2017). This is related to the shape and size of the morphology that resulted from the flow rate of 4 $\mu\text{L}/\text{min}$, which was uniform and had a smaller average diameter compared to other flow rates. As a result, it had a better dye loading ability, which was $1.25 \times 10^{-7} \text{ mol}/\text{cm}^2$. A high absorbance value increases the current density (JSC), which affects the efficiency of the DSSCs (Lee *et al.*, 2015). As the dye trend we used is at a wavelengths of 450–550 nm, the transmittance value is inversely proportional to the absorbance value (Marimuthu *et al.*, 2017). As shown in Figure 6b of Appendix, the use of 4 $\mu\text{L}/\text{min}$ discharge resulted in the lowest transmittance value. This is because of the large absorption ability of the dye using a discharge variation of 4 $\mu\text{L}/\text{min}$.

3.2.2. Tip Distance to Collector Variations

Regarding tip-to-collector distance variations, the usage of a distance of 8 cm resulted in the double-layer DSSCs with the highest absorbance values at wavelengths of 450–550 nm. As shown in Figure 7a of Appendix, the farther the tip's distance to the collector, the higher the absorbance value that was obtained. Based on the double-layer photoanode's characteristics, a high absorbance value indicated a higher light absorption ability. This was also corroborated by the large value of dye loading calculated according to the Lambert–Beer equation. The usage of an 8 cm tip-to-collector distance resulted in a dye loading value of $1.25 \times 10^{-7} \text{ mol}/\text{cm}^2$, thus increasing the amount of electric current received from the DSSCs (Kabir *et al.*, 2019; Marimuthu *et al.*, 2017). The light transmitted from or exited by the photoanode was identified through the results of the transmittance test. The lower the transmittance value, the less light which came out. As can be seen in Figure 7b of Appendix, the use of an 8 cm tip-to-collector distance resulted in the lowest transmittance value at the 450–550 nm wavelengths. This indicates that the ZnO semiconductor nanofiber produced by direct deposition using the electrospinning process helped the dye loading by blocking the amount of light that came out.

3.3. Band Gap Testing

The bandgap energy value was determined through absorbance spectrum testing in ultraviolet rays and visible light, i.e., the wavelengths of 200 to 800 nm. Through the graph derived by Tauc plot method, the value of the bandgap was obtained by extrapolating the linear line of the curve formed by $(\alpha \cdot hv)^{1/r}$ to hv , where α is the absorbance coefficient and hv is the photon energy. Figures 8a and 8b of Appendix show the bandgap values for each variation. The results show that the larger the tip-to-collector distance and the smaller the flow rate, the lower the obtained bandgap value. A decrease in the value of the bandgap is an indication of a shrinking semiconductor size. This allows for easier electron excitation when obtaining energy from outside (Bakr *et al.*, 2019; Ghanbari Niaki *et al.*, 2014).

3.4. Performance of DSSCs

3.4.1. Flow Rate Variation

The curve in Figure 9a of Appendix indicates the photocurrent vs. photovoltage (IV) density for each DSSCs variation of discharge with an intensity of $100 \text{ mW}/\text{cm}^2$. Table 3 of Appendix illustrates the performance of DSSCs according to VOC, JSC, FF, and efficiency values for the discharge variations. The results show that the morphological changes to the ZnO nanofiber semiconductors had a large influence on JSC and a small effect on the VOC of DSSCs. This shows that the 4 $\mu\text{L}/\text{min}$ precursor discharge in the nanofiber electrospinning process produced a small nanofiber size and the maximum electrical conductivity. Higher conductivity values were found to reduce electrical resistance in DSSCs (Seo *et al.*, 2007). With a greater dye loading ability for light absorption and optimal electrical conductivity, the variation of the 4 $\mu\text{L}/\text{min}$ precursor discharge had the maximum value of DSSCs efficiency among the variations examined. It can be seen that the discharge of 4 $\mu\text{L}/\text{min}$ had the highest efficiency of DSSCs at 2.39%. VOC, JSC, and FF values were 0.58 V, $9.14 \text{ mA}/\text{cm}^2$, and 45.18%, respectively.

3.4.2. Tip Distance to Collector Variations

The performance characteristics of the double-layer photoanodes as a function of variation of tip-to-collector distance can be seen in Figure 9b and Table 4 of Appendix. DSSCs with direct deposition of ZnO nanofibers with a distance of 8 cm from tip to the collector had the highest photovoltaic conversion efficiency. As

seen from the SEM test results, the 8 cm tip-to-collector distance resulted in the smallest nanofiber size. The small ZnO nanofiber semiconductor diameter increased the DSSCs' photovoltaic performance due to the higher surface area for absorbing dye molecules (dye loading), resulting in higher light absorption (Hekmati *et al.*, 2013; Ramli *et al.*, 2019; Sorayani Bafqi *et al.*, 2015). It can be seen that the 8 cm tip-to-collector distance resulted in the highest efficiency of DSSCs at 1.61%. VOC, JSC, and FF values were 0.56 V, 6.41 mA/cm², and 44.920%, respectively.

4. CONCLUSIONS:

Double-layer TiO₂-ZnO DSSCs were obtained using nanofiber ZnO semiconductors deposited directly on fluorine-doped tin oxide (FTO) glass coated with a TiO₂ nanoparticle semiconductor using an electrospinning machine. The use of a solution flow rate of 4 µL/min and a distance of 8 cm from the tip of the needle to the collector in the direct deposition process using an electrospinning machine produced better nanofibers than other variations, whose morphology had a small and uniform diameter of 118.35 and 85.6 nm, with a dye loading value of 1.25×10^{-7} mol/cm². The performance value for the discharge of 4 µL/min was 2.39%, and for the 8 cm tip-to-collector distance the value was 1.61%.

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APPENDIX

Figure 1. DSSCs double-layer photoanode structure.

(a)

(b)

Figure 2. (a) Scheme process (b) electrospinning machine.

Figure 3. Voltage–current curves (IV curves) found on DSSCs (Tobin et al., 2011)

(a)

(b)

(c)

(d)

(e)

(f)

Figure 4. Semiconductor SEM photo results for variations of (a) 3 $\mu\text{L}/\text{min}$ (b) 4 $\mu\text{L}/\text{min}$ (c) 5 $\mu\text{L}/\text{min}$ (d) 6 $\mu\text{L}/\text{min}$ (e) 7 $\mu\text{L}/\text{min}$ (f) 8 $\mu\text{L}/\text{min}$.

Figure 5 ZnO semiconductor SEM photo results for variations of (a) 3 cm (b) 4 cm (c) 5 cm (d) 6 cm (e) 7 cm (f) 8 cm.

Table 1. ZnO semiconductor diameter size for variations in flow rate.

Flow Rate Variation ($\mu\text{L}/\text{minute}$)	Average diameter (nm)	Maximum diameter (nm)	Minimum Diameter (nm)	Standard deviation (nm)
3	122.18	150.15	94.33	16.25
4	118.35	158.82	80.88	17.24
5	125.43	175.52	100.23	15.16
6	129.37	176.47	107.94	18.85
7	134.45	175.50	95.45	16.20
8	141.39	169.11	98.76	16.18

Table 2. ZnO semiconductor diameter size for variations in distance.

Tip to collector distance (cm)	Average diameter (nm)	Maximum diameter (nm)	Minimum Diameter (nm)	Standard deviation (nm)
3	140.4	170.21	97.80	16.28
4	115.3	155.83	79.88	17.24
5	107.3	141.49	67.59	17.52
6	96.7	140.57	63.29	15.33
7	92.7	126.20	49.45	16.12
8	85.6	114.57	62.17	14.33

(a)

(b)

Figure 6. (a) The results of ZnO semiconductor absorbance tests for flow rate variations; (b) the results of ZnO semiconductor transmittance tests for flow rate variations.

(a)

(b)

Figure 7. (a) ZnO semiconductor absorbance test results for distance variations; (b) ZnO semiconductor transmittance test results of distance variations.

(a)

(b)

Figure 8. (a) Tauc's plot method used in determining the ZnO semiconductor band gap for variations in flow rate; (b) Tauc's plot method used in determining the ZnO semiconductor band gap for distance variations.

Figure 9. (a) IV curve of each flow rate variation; (b) IV curve of each tip-to-collector distance variation.

Table 3. DSSCs characteristics for flow rate variations.

Flow Rate Variation (µl/minute)	VOC (V)	JSC (mA/cm ²)	Fill Factor (%)	Efficiency (%)	Dye Loading (x 10 ⁻⁷ mol/cm ²)
3	0.56	8.84	45.80	2.27	1.17
4	0.58	9.14	45.18	2.39	1.25
5	0.53	7.14	45.09	1.71	0.74
6	0.53	6.65	45.72	1.61	0.65
7	0.55	6.29	44.13	1.53	0.35
8	0.52	5.31	42.97	1.19	0.28

Table 4. DSSCs characteristics for tip-to-collector distance variations.

Distance Variation (cm)	VOC (V)	JSC (mA/cm ²)	Fill Factor (%)	Efficiency (%)	Dye Loading (x 10 ⁻⁷ mol/cm ²)
3	0.56	2.71	52.02	0.79	0.44
4	0.56	2.85	52.09	0.85	0.47
5	0.55	4.49	44.13	1.09	0.81
6	0.53	4.89	45.72	1.18	0.85
7	0.54	5.66	45.45	1.39	0.86
8	0.56	6.41	44.92	1.61	1.25