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Abyan Muwaffaq, Syamsul Hadi and Zainal Arifin

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The Effect of Electrospinning Precursor Flow Rate with Rotating Collector on ZnO Nanofiber Size Results on Double-Layered DSSC Photoanode Fabrication

Abyan Muwaffaq[1,a)], Syamsul Hadi [1,b)], and Zainal Arifin[1,c)]

[1]*Department of Mechanical Engineering, Sebelas Maret University, Surakarta, 57126, Indonesia*

[a)]heyabyan@gmail.com
[b)]syamsulhadi@ft.uns.ac.id
[c)]Corresponding author: zainal_arifin@staff.uns.ac.id

Abstract. DSSC solar cells are predicted to be energy conversion devices for the next generation, therefore various developments are carried out to improve the performance of DSSC solar cells. A research is conducted in this paper on the process of making ZnO nanofiber as a DSSC photoanode using an electrospinning machine. Direct deposition method is used to directly spray ZnO precursor solution on conductive glass deposited with TiO_2. The rotating collector is used to uniform and to reduce the size of the resulting nanofiber structure. The size reduction of the resulting nanofiber can improve the performance of DSSC photoanode. Variations of precursor discharge 2, 4, 6, and 8 μL/minute are used to determine their effects on the morphological arrangement of the resulting ZnO nanofibers. From the results of this study, the most uniform nanofiber results and the smallest average size are obtained from the use of the lowest flow rate variation, which is 2 ml/min.

INTRODUCTION

The increasing need for energy use by humans demands scientists to research and develop the use of renewable energy sources as an alternative. One of the renewable energy options is solar energy due to its abundant availability and a sustainable energy supply [1]. A solar cell is a device that converts solar energy into electrical energy [2]. The latest generation of 3 generations of solar cells developed by scientists is the dye-sensitized solar cell (DSSC) which is discovered by Michael Gratzel in 1991 [3].

DSSC has several advantages such as low fabrication costs, flexibility, and the materials used are more environmentally friendly [3]. The DSSC component consists of a TCO substrate, semiconductor, dye, electrolyte, and counter electrode [4]. The working principle of DSSC utilizes photon energy to excite electrons from the dye to generate electricity from the oxidation-reduction cycle that occurs in the DSSC [5]. DSSC performance is indicated by the efficiency (η), short-circuit current density (J_{SC}), fill factor (FF), and open-circuit voltage (V_{OC}) [6].

The value of DSSC performance depends on the type of semiconductor used [7]. In general, TiO_2 and ZnO are used as DSSC semiconductors. TiO_2 has the advantages of low cost and good performance in ultaviolet light although its performance is quite poor in visible and infrared light [4]. ZnO has the advantages of higher electron mobility and is easy to modify on its morphological structure, although ZnO has a fairly low level of chemical stability and higher band gap than TiO_2 [8]. Double-layer method is used to form dye loading layer using TiO_2 and light scattering layer using ZnO, with the purpose of strengthening the bonds between semiconductor and substrate, expanding the light absorption range by using dye as a sensitizer, expanding the area of dye absorption, and increasing capture of photons [9]. Figure 1 shows DSSC with double-layered photoanode.

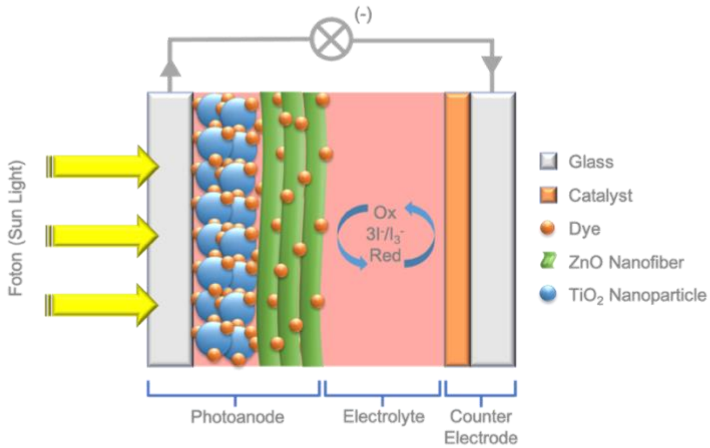


FIGURE 1. DSSC with double-layered photoanode

Nanofiber is one type of nanostructure used for DSSC photoanode. Nanofiber has a morphological structure that can provide a direct flow of electrons from the photogenerated current to its conductive substrate, and has a dendrite-like structure that results in a larger absorption surface area [10]. The electrospinning process is one way to produce nanofibers. Some of the advantages of electrospinning include a low-cost fabrication process and ability to control the morphology of the resulting fiber [11]. The working principle of electrospinning is to use electrostatic forces formed from charged particles caused by the emergence of high voltage between the needle tip and the collector. Figure 2 shows a picture of electrospinning and its components.

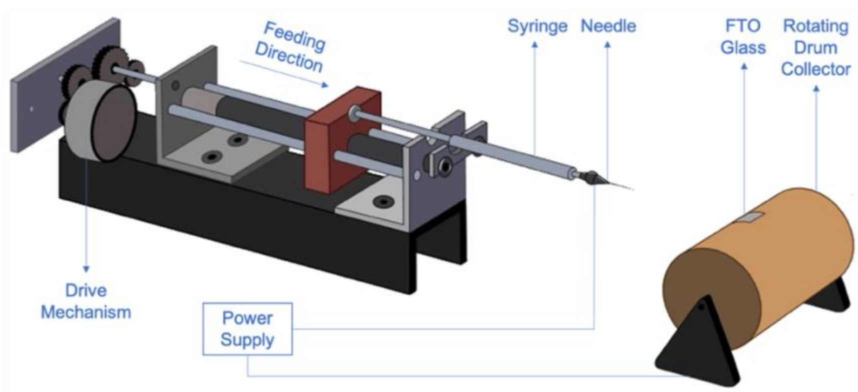


FIGURE 2. Electrospinning machine

The morphological structure of electrospinning nanofibers is influenced by several factors, one of which is the precursor flow rate during the feeding process. The higher the flow rate used, the thicker the nanofibers formed [11]. The use of a rotating collector in the electrospinning process will also provide better uniformity of the resulting nanofibers, as well as increase the rate of precursor evaporation which will affect the decrease in nanofiber diameter [12]. The smaller the size of the resulting nanofiber, the performance of the DSSC will increase [13]. Previous studies varied the precursor flow rate in the electrospinning process with a fixed collector, resulting in the smallest average nanofiber diameter at the lowest flow rate, although the use of a fixed collector resulted in poor uniformity and defects in the resulting nanofibers [14].

This study used a mixture of polyvinyl alcohol solution with zinc acetate solution as precursor solution. The direct deposition method is used to place the semiconductor to the substrate. This method is done by spraying the precursor solution directly onto the TiO_2-deposited conductive glass in the electrospinning process. The use of this method will shorten the ZnO coating process in the manufacture of DSSC and reduce damage to the nanofiber results. The variation of the precursor flow rate is used to determine its effect on the resulting nanofiber.

METHODS

Semiconductor Fabrication and Sintering Process

The process begins by synthesizing a precursor solution consisting of a mixture of polyvinyl alcohol (PVA, made by Merck) solution with zinc acetate solution. PVA solution is prepared by dissolving 1 gram of polyvinyl alcohol ($(C_2H_4O)_x$) with 10 ml of distilled water, then stirring for homogenization process for 4x60 minutes at a temperature of 158°F. $Zn(CH_3CO_2)_2$ solution is synthesized by dissolving 2 grams of zinc acetatedihydrate ($(CH_3COO)_2Zn.2H_2O$, made by Merck) with 8 ml of distilled water, then stirring for homogenization process for 60 minutes at 158°F. Next, the PVA solution is mixed with $Zn(CH_3CO_2)_2$ solution in a ratio of 4:1 wt%, then stirred for the homogenization process for 8x60 minutes at a temperature of 158°F. Then the mixed solution is left at room temperature for 24 hours to remove the resulting foam. The result is a solution of PVA/$Zn(CH_3CO_2)_2$ which can be used to compose ZnO nanofibers by electrospinning machine.

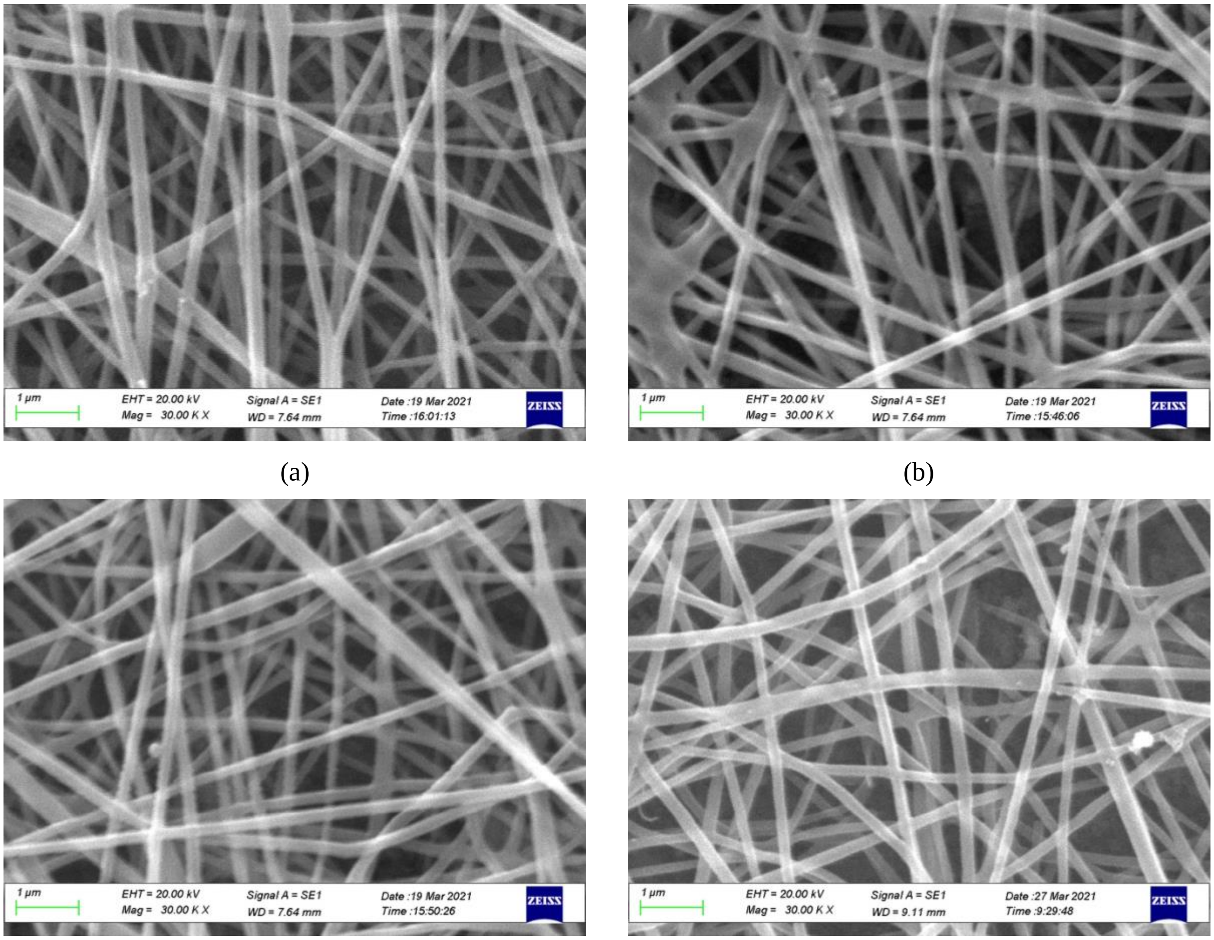
The PVA/$Zn(CH_3CO_2)_2$ solution is then put into a syringe pump with a capacity of 1 ml, then installed in electrospinning machine. The syringe containing the solution is connected to the positive pole of a 15 kV high voltage and placed at a fixed distance of 8 cm from the FTO (fluorine doped tinoxide) glass on the rotating collector connected to the negative pole. FTO glass that has been deposited with TiO_2 nanoparticles is used in this study. Precursor flow rate as independent variable in the electrospinning process uses variations of 2, 4, 6, and 8 μL/minute. The solution that is sprayed from the syringe has been subjected to high voltage, so that the electrostatic field on the negatively charged collector will attract the solution to the FTO glass. The solution then automatically adheres to the collector surface in the form of nanofibers. After the spraying process, the samples are then sintered at a temperature of about 932°F for 60 minutes to dissolve organic matter and form ZnO in the form of crystals.

RESULTS AND DISCUSSION

DSSC Characteristic Test

The Scanning Electron Microscope (SEM) test produces graphic data in the form of structure and dimensions of ZnO semiconductor nanofibers. The results of the SEM test of the double-layer DSSC photoanode are shown in Figure 3. From the photo of the SEM test results, it can be observed that the lower the use of the precursor flow rate, the smaller the diameter of the nanofiber resulted. The SEM test results from the DSSC photoanode with the electrospinning process using a rotating collector drum are much more uniform than using a fixed collector as in previous studies [14]. This proves previous research which explains that the use of a rotating collector will produce nanofibers with good uniformity [12].

However, some defects are still found in the nanofiber results. This is because the stretching process of the solution that comes out of the syringe tip is influenced by whether or not the voltage used in the electrospinning process is constant. The stretching process of the solution will also take more time as the flow rate of the precursor used increases, which in turn causes some of the solution to not adhere perfectly to the substrate. This proves previous research which explains that the uniformity of the resulting nanofiber will be better with the use of a lower flow rate of precursor [15], while the possibility of defects in the resulting nanofiber will be greater along with the magnitude of the flow rate of the precursor used [16].



(a) (b)

(c) (d)

FIGURE 3. Double-layer photoanode SEM test results for precursor flow rate variation (a) 2 μL/minute, (b) 4 μL/minute, (c) 6 μL/minute and, (d) 8 μL/minute

The results on nanofiber diameter measurements using ImageJ software can be seen in Table 1. This data shows that the use of a larger precursor flow rate will produce nanofibers with a larger diameter. The results of this measurement are in accordance with previous studies which explained that the thickness of the nanofiber produced from the electrospinning process is directly proportional to the amount of flow rate of the precursor used [11]. The use of a rotating collector also increases the evaporation rate of the precursor so as to produce nanofibers with a smaller diameter compared to the use of a fixed collector in previous studies [14]. This proves the previous study which explained that the use of a rotating collector will affect the nanofiber diameter to be relatively smaller [12]. The size reduction of the nanofiber produced either from the use of low flow rate variations or the use of a rotating drum collector will increase the dye absorption area by the semiconductor which has an impact on increasing the performance of the DSSC [13].

TABLE 1. Measurement of the diameter of ZnO nanofibers for each variation of precursor flow rate

Precursor flow rate variation	Average diameter (nm)	Maximum diameter (nm)	Minimum diameter (nm)	Standard deviation (nm)
2 μL/minute	127.078	139.022	114.683	5.992
4 μL/minute	186.266	194.906	179.428	4.386
6 μL/minute	224.657	239.798	207.959	9.017
8 μL/minute	287.052	298.299	271.92	6.729

CONCLUSIONS

The use of variations in the precursor flow rate in electrospinning process with a rotating collector using direct deposition method affects the characteristics and performance of the resulting double-layered DSSC photoanode. The use of rotating collector also affects the size of the resulting nanofiber to be relatively smaller than the use of a fixed collector. The lower the flow rate of the precursor used, the smaller the resulting nanofiber diameter and the wider the dye absorption area, which can lead to an improved DSSC performance.

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