

Comparison of Titanium Dioxide (TiO₂) nanoparticle-nanofiber and nanofiber-nanoparticle on the application of dye-sensitized solar cell (DSSC)

Linda Kusumaning Tyas¹, Risa Suryana¹, Fahru Nurosyid¹, Novita Asma Ilahi¹

Physics Department of Post Graduate Program Sebelas Maret University,
Jl. Ir. Sutami 36A Kentingan Jebres Surakarta 57126, INDONESIA

E-mail: lindakusumant@gmail.com

Abstrak. Dye-sensitized Solar Cell (DSSC) is a solar cell that has great potential in the future because of the cheaper cost of fabrication and environmentally friendly basic ingredients. This study aims to determine the effect of type of screen on the TiO₂ layer as the active electrode DSSC. The active electrode TiO₂ based DSSC fabricated by the method of double layer. Efficiency Dye-sensitized Solar Cell (DSSC) can be obtained from the current-voltage curve I-V meter. Nanofiber on the nanoparticles can reach a highest efficiency of DSSC about 0,015%. The second variation of between nanofiber-nanoparticle layering, and nanoparticle-nanofiber, it appears that the nanofiber layer of nanoparticles above, no significant changes, namely in 10 minutes $\eta = 0.014965$; 15 minutes $\eta = 0.011021$ and 20 minutes $\eta = 0.013332$. This is demonstrated by the nature of the dominant nanofiber as a photon trap covered by the nature of the dominant nanoparticles absorb the dye, so that overtime does not affect the incoming electron. While the results of nanofiber layer on the nanoparticles changed significantly in the variation of 20 minutes, ie $\eta = 0.00283$. You can also see the most optimum time was 15 minutes, which is $\eta = 0.01559$. This may be due in this 15 minute nanofiber coating has a thickness that is optimum so that electrons can reach the electrode diffuse due to the interaction between photons and the dye more.

1. Introduction

Solar energy is one alternative energy that can be used by humans today. Geographically, Indonesia is located on the equator causes Indonesia can receive solar heat more than other countries, namely 4800 watt /m²/day. Based on this phenomenon, the solar energy to electrical energy is converted into solar cells [1]. Dye-sensitized solar cells (DSSCs) have been extensively researched over the past Decades due to Reviews their high energy conversion efficiency and especially low production costs as cheaper alternatives to silicon solar cells. DSSC typically consists of a nanocrystalline TiO₂ films covered by a monolayer of dye molecules, redox, electrolyte, and counterelectrode. For the formation of an efficient DSSC, photoanode materials with various morphologies such as nanoparticles [2].

Advantages of using TiO₂ that is environmentally friendly, has inert properties and photoactive, easily manufactured and inexpensive cost. TiO₂ has an energy band gap width is 3.2 eV and is only able to absorb ultraviolet light from the solar spectrum [3]. TiO₂ anatase phase that is used has to have the

¹ To whom any correspondence should be addressed.



ability photoactive high so it is often used as a photocatalyst. Anatase is thermodynamically less stable than rutile, but its formation occurs at lower temperatures [4]. In its application as a photocatalyst DSSC, commonly used in the type of anatase TiO_2 because it has the high photocatalytic ability. In addition, the nanocrystal structure and high surface area of TiO_2 can be used to improve system performance DSSC, especially in increasing the density and electron transfer [5].

Modification of TiO_2 layers needed to make the residence time of photons in layers longer than the planar shaped layer. This is because the photons coming will be trapped between the nanorod, nanowire or nanotube. Photon interaction with electron excitation dye produces further injected into the conduction band of TiO_2 . Electrons diffuse towards the electrode on the surface of TiO_2 . In addition, there is a modified form of TiO_2 nanofiber. By modifying the shape of TiO_2 layer in the form of nanofiber, the residence time of photons in a nanofiber layer will be longer than the shaped layer is because the photons coming planar. This is because the photons coming will be trapped between the nanorod, nanowire or nanotube. Photon interaction with electron excitation dye produce further injected into the conduction band of TiO_2 . Electrons diffuse towards the electrode on the surface of TiO_2 . The number of electrons in the electrodes will determine the efficiency of DSSC. The photoelectrode of the DSSC fabricate from TiO_2 Nanostructures commonly. There are many approaches for the DSSC's photoelectrode such as doctor blade method, screen printing, drop-casting, spin-coating [6], spray coating [7], chemical vapour deposition [8], chemical bath deposition [9], hydrothermal method, electrophoretic deposition (EPD) and electrospun [10]. DSSC consists of four main components, namely an n-type semiconductor such as nanoparticles of TiO_2 , a dye that is sensitive (Dye sensitizer) on the absorption of visible light, an electrolyte made in one of the semiconductor surface and a counter electrode such as platinum (Pt), carbon (C), which helps transfer electrons to the electrolyte [11].

Dye-sensitized Solar Cells (DSSC) is a photoelectrochemical solar cell that uses an electrolyte as charge transport medium. DSSC is divided into several parts consisting of nanopores TiO_2 , dye molecules adsorbed on the surface TiO_2 dan catalysts which are all deposited between two glass conductive DSSC can not be separated from the dye, by far the dye that is used as a sensitizer can be either synthetic dye and natural dye. Synthetic dye generally using ruthenium-based organic metal complex. In studies that have been done, the dye of the ruthenium complex compounds can achieve efficiencies of 11-12% [12]. However, the amount of ruthenium complex dye is limited and the price is quite expensive. For these reasons, developing research towards finding natural dyes extracted from flowers, leaves, and fruits [13]. Natural dye that is used as a sensitizer in DSSC classified as environmentally friendly, making it too easy and cheap although lifetime is low [14].

Application to the DSSC, TiO_2 used generally phase photoactive anatase because it has high ability. TiO_2 with nanopores structure that the pore size in the nanoscale will increase the performance of the system because nanopores structure has the characteristics of high surface area so that it will increase the amount of dye that has absorbing the implications of which will increase the amount of light that has absorbing. From various studies have been conducted several deposition techniques TiO_2 in DSSC, one of the DSSC fabricated using a double layer coating method electrophoretic deposition (synthesis of TiO_2) and Dr.Blade (TiO_2 nanoparticles), obtained a considerable efficiency is 5.96% [10].

2. Eksperimental

2.1 Materials

TiO_2 used in this study using two types namely TiO_2 nanofiber and TiO_2 nanoparticle synthesis with 21 nm Titanium Dioxide Anatase TiO_2 powder, 99.8% trace metals basis, Titanium (IV) Isopropoxide (TTIP) 97% purity, Acetic Acid ($\text{CH}_3\text{CO}_2\text{H}$, 99.7% Aldrich, USA), Ethanol ($\text{C}_2\text{H}_5\text{OH}$, Merck, Germany), and Polyvinyl Pyrrolidone (PVP, Mw ~ 29000 Aldrich). As the dye, dried moss, N-hexane, silica gel.

2.2 Preparation of TiO_2

There are two layers of TiO_2 , the TiO_2 nanoparticles, and TiO_2 Nanofiber.

2.2.1 TiO_2 Nanoparticles

Titanium (IV) Oxide nanoparticles, anatase titanium dioxide powder, 99.8% trace metals basis. TiO_2 of 0.5 g dissolved in 2 ml of ethanol, stirred for 30 minutes at 300 rpm using a vortex stirrer [15].

2.2.2 Synthesis of TiO_2 nanofiber

Titanium (IV) Oxide synthesis of TiO_2 Nanofiber material made of titanium (IV) Isopropoxide (TTIP), Acetic Acid, Ethanol, and Polyvinyl Pyrrolidone (PVP). 1 ml acetic acid mixing with ethanol, stirred for 10 minutes. Once it is added Polyvinyl Pyrrolidone (PVP) of 2.5 g, stirred for 1 hour. Then, after 1 hour, is added titanium (IV) Isopropoxide (TTIP) 0.5 ml, then stirred until homogeneous.

2.3 Deposition of TiO_2

2.3.1 TiO_2 nanofiber on TiO_2 nanoparticle

In the treatment of the first, the coating of TiO_2 nanofiber on top of TiO_2 nanoparticles, TiO_2 superimposed on the glass conductive Fluorine Tin Oxide (FTO) with an area of deposition of 1 cm x 2 cm using spin coating, the rotating speed is the same, 1000 rpm in 60 seconds, TiO_2 layer that has been deposited on a hot plate heated to a temperature of 30 °C/10 min. In the deposition of TiO_2 nanoparticles done 3 times coating. [3]. Furthermore, TiO_2 nanofiber layer deposited on surfaces that have been coated with TiO_2 nanoparticles using methods electrospinning. Nanofiber layer made with a variety of plating time of 10 minutes, 15 minutes and 20 minutes at a distance of 25 cm spinnerets with collectors. Voltage electricity used between 5 kV 6 kV using the same annealing temperature in each variation is 450 °C for 3 hours to evaporate the organic material [16].

2.3.2 TiO_2 Nanoparticles on Nanofiber

TiO_2 layer of nanoparticles on TiO_2 nanofiber, done in a way that is similar to the previous one, TiO_2 nanofiber deposited on glass conductive Fluorine Tin Oxide (FTO) with an area of deposition of 1 cm x 2 cm using methods electrospinning made with the time variations layering are 10 minutes, 15 minutes and 20 minutes at a distance of 25 cm spinnerets with collectors. Voltage electricity used between 5 kV-6 kV. After the deposition of TiO_2 nanofiber finish, then TiO_2 nanoparticles deposited on the fiber nanofiber TiO_2 using spin coating, the rotating speed is the same, namely 1000 rpm in 60 seconds. TiO_2 layer that has been deposited on a hot plate heated to a temperature of 30 °C/10 min. In the deposition of TiO_2 nanoparticles done 3 times coating. The second layer of TiO_2 nanofibers and nanoparticles was annealed at a temperature of 450 °C for 3 hours.

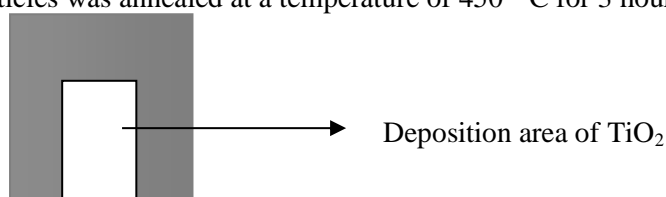


figure 1. Active cell of Fluorine Tin Oxide (FTO: 1cm x 2cm)

2.4 Extraction of Chlorophyll Dye Bryophyta

Wet moss, dried by the sun first. Once dry, moss weighed as much as 20 g and pulverized using a mortar. Moss smooth and then dissolved in 100 ml acetone (ratio 1: 5), stirred using a vortex stirrer for 1 hour. Once homogeneous, the solution was filtered using Whatman filter paper number 42. The solution was filtered, and then do the chromatographic process. This process uses a silica gel 30 g mixed with 100 ml of n-hexane, and then inserted into the chromatography column. Afterwards the solution moss, put in a column chromatography, wait to a solution of moss down until the end of the column and drips[17].

2.5 Characterization absorbance of TiO_2 double layer nanoparticles and nanofiber

TiO_2 layering with a two layering technique, was soaked in moss extract chlorophyll dye, for 24 hours at room temperature so that the dye can absorb perfectly. After the immersion, then tested absorbances using UV-Visible Spectrometer Lambda 25 [10]. The wavelength range of 300-800 nm is used. The characterization results in the form of UV-Vis absorbance wavelength curve [15].

2.6 Preparation of Electrolyte and Counter Electrodes

In making this electrolyte solution using a mixture Polyethylene Glycol (PEG) 400, potassium iodide (KI), and iodine (I_2). First, a homogeneous solution prepared from 10 ml of PEG and 0.8 g of KI. The second solution is prepared from 0.127 g I_2 and 10 ml PEG. After that, each solution was mixed and stirred using a vortex stirrer for 30 minutes. Value Molecular weight (M_w) of the PEG, KI, and I_2 respectively amounted to 380-420 g/mol, 166 g/mol and 254 g/mol [18].

Making the counter electrode using a carbon comprising 2B pencil that has been shaded in active cells evenly and layers have been shaded 2B pencil back layered with soot burning candle wax on the pitch-black color.

2.7 Fabrication of DSSC

Photoanode fabrication of DSSC is made of a two-layer structure of TiO_2 . First TiO_2 nanofiber over TiO_2 nanoparticles and TiO_2 nanoparticles over TiO_2 nanofiber. After each had been coated with two layers of TiO_2 , is the process of soaking the moss chlorophyll dye. This soaking process is carried out for 24 hours. Then the counter electrode spilled electrolyte solution 2 drops on the active cell, the active electrode positioned above the counter electrode with the active cell position facing each other, are arranged offset in order to facilitate the testing. Sandwich DSSC which has arranged by clamped using binder clips.

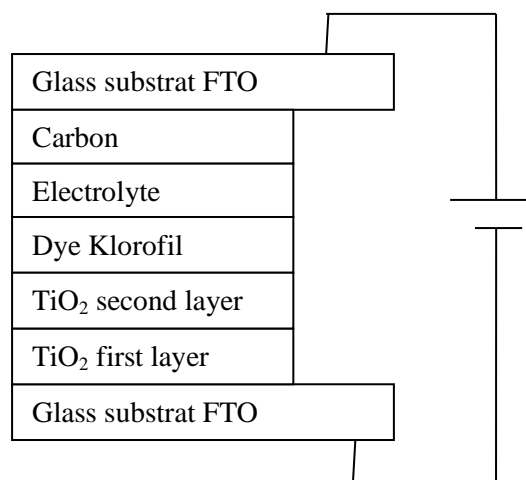


Figure 2. Illustration of the result assembling DSSC

2.8 Characterization of I-V on DSSC

I-V measurements using the tool Keithley meter 2602A System Source. Probe the positive (red) is connected to the counter electrode substrate (carbon layer) and the negative probe (black) is connected to the active electrode substrate (a layer of TiO_2 and dye). Testing I-V performed in two conditions, namely conditions of dark and bright conditions. In dark conditions, DSSC closed using aluminum foil and in bright conditions, DSSC irradiated using a xenon lamp of 1000 W / m^2 . Characterization test is indicated by the chart-circuit (I) and voltage (V) obtained from the active cell, which will show the efficiency of DSSC.

3. Result and Discussion

TiO₂ layering capability using the techniques of 2 layers of TiO₂ nanoparticles and TiO₂ nanofiber with moss extraction chlorophyll dye can be proved by the results of characterization by UV-Vis Spectrometer shown in Figure 3. In the red line (B) is TiO₂ nanofiber on top of TiO₂ nanoparticles and the blue line (D) is a layer of TiO₂ nanoparticles on the nanofiber. On the charts very visible absorbance at highest peak 6.25715 a.u with a wavelength of 348 nm. Meanwhile, back when observed high absorbance peak average currently on TiO₂ nanoparticles on the TiO₂ nanofiber coating that is a 15 minutes peak at 2.5481 a.u, a wavelength of 400 nm and 20 minutes 1.91375 a.u peak at a wavelength of 450 nm. This high absorbance can be affected because the TiO₂ layer is thick enough so that the dye absorbed is also higher. From the graph it can be seen, the layering of TiO₂ nanoparticles TiO₂ nanofiber on may affect the absorbance is higher because the dye will be absorbed more perfect in the pores of the TiO₂ nanoparticles.

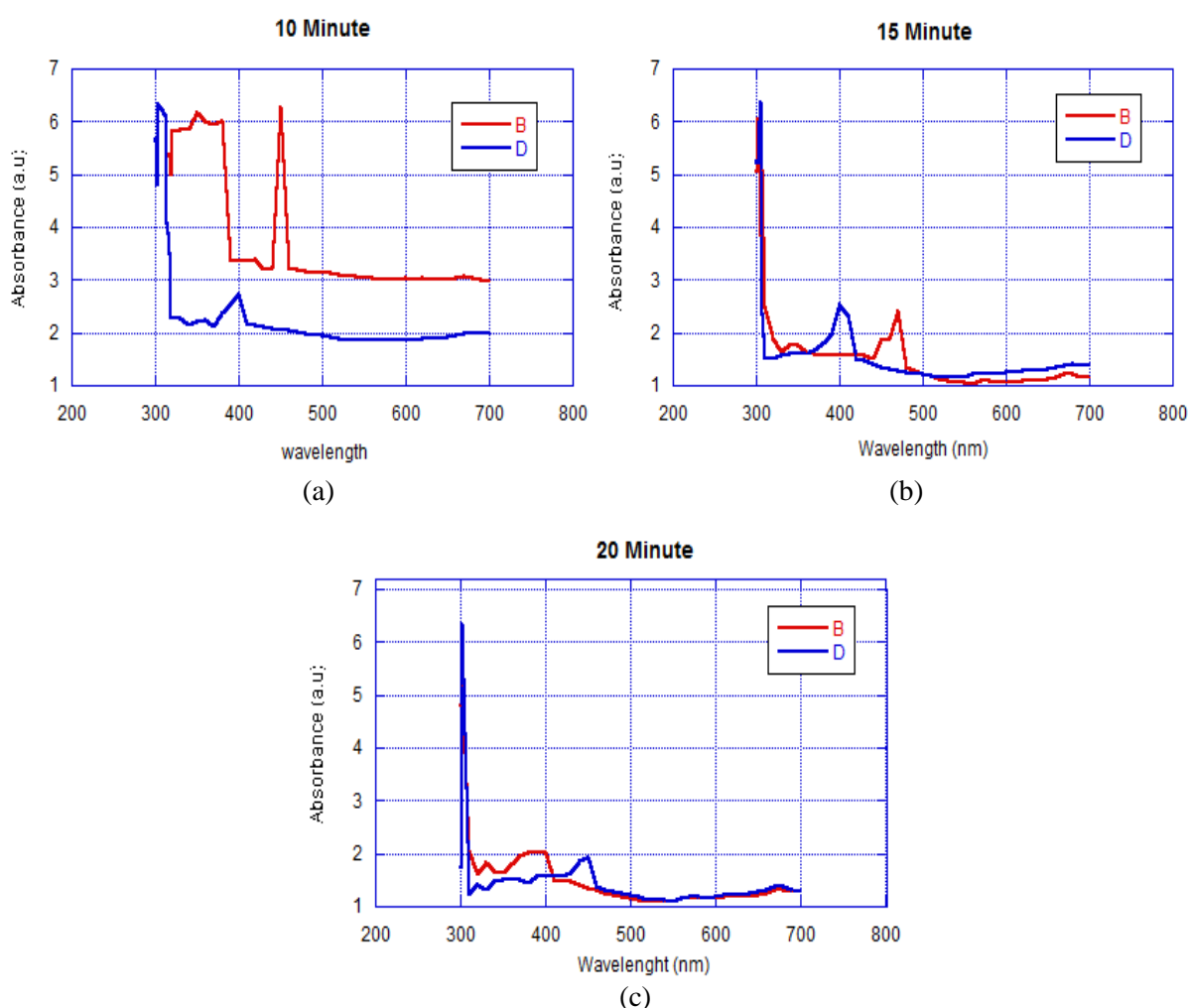
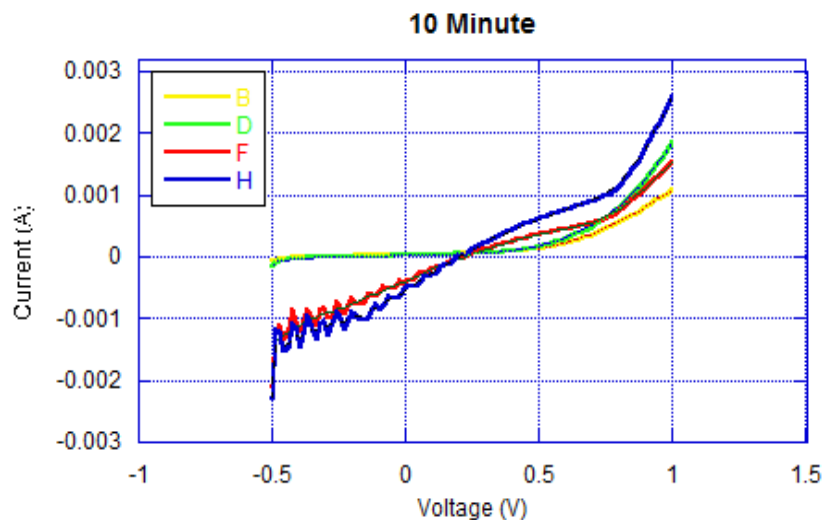


Figure 3. (a) Absorbance TiO₂ double layer, 10 minutes. (b) Absorbance TiO₂ double layer, 15 minutes. (c) Absorbance TiO₂ double layer, 20 minutes.

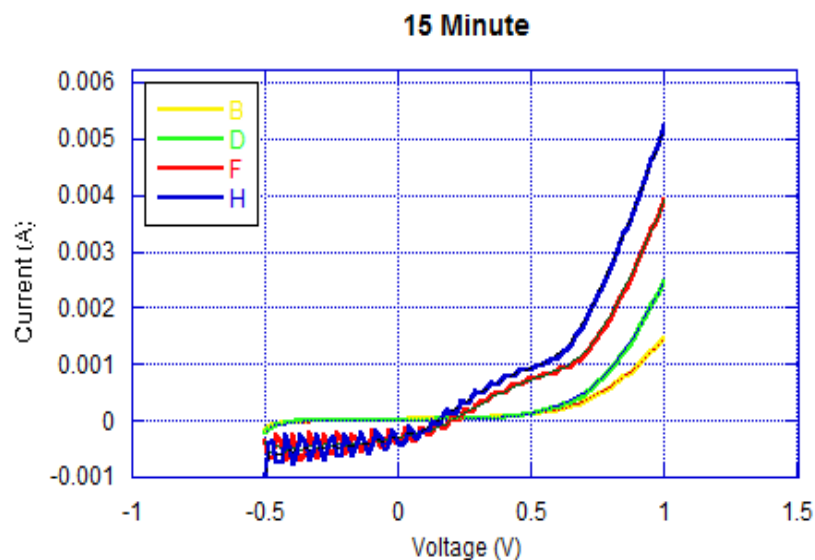
The next characterization is the current-voltage (I-V) which is a method to determine the ability of DSSC to be able to convert light into electrical energy that is expected to have a high percentage of capabilities. Measurements were made using Keithley 2602A conducted in the dark and the light. A state of light, the light coming from a xenon lamp with an intensity of 1000 W/m². Results from

testing the current-voltage variation TiO_2 double layer with a time of 10 minutes, 15 minutes and 20 minutes. In the picture, there are four colours (yellow (B), green (D), red (F) and blue (H)) The colour chart shows the I-V on each variation. To yellow (B) shows the dark state of TiO_2 nanoparticle on the TiO_2 nanofiber and green (D) indicates the dark state of TiO_2 nanoparticle on the TiO_2 nanofiber. Furthermore, there are two colours that indicate the state of the light that is, red (F) shows the light state of TiO_2 nanoparticle on the TiO_2 nanofiber and blue (H) shows the light state of TiO_2 nanoparticle on the TiO_2 nanofiber.

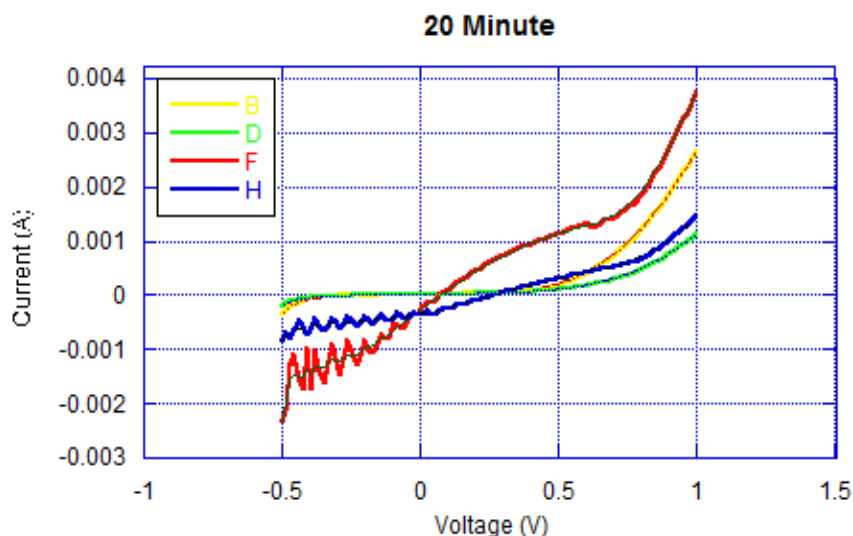
From the pictures I-V curves 10 minutes, 15 minutes and 20 minutes when the light state located in quadrant IV, located under the I-V curve when the dark state. From the I-V characteristic curve shown in Figure 4:



(a)



(b)



(c)

Figure 4. (a) I-V graph of TiO_2 double layer, 10 minutes. (b) I-V graph of TiO_2 double layer, 15 minutes. (c) I-V graph of TiO_2 double layer, 20 minutes.

From Figure 4 (a), (b) and (c) it can be determined the value of the current (I_{sc}) and voltage (V_{oc}). So based on the calculation can also know the value of maximum power (P_{max}) which can also determine the maximum current (I_{max}) and maximum voltage (V_{max}). From these calculations, it can be seen the percentage of efficiency. The results of the I-V characteristics can be seen in table 1:

Table 1. The results of the efficiency of the both TiO_2 double layer

TiO_2 Nanofiber on The TiO_2 Nanoparticle								
Nano Particle	Nano fiber	V_{oc} (Volt)	I_{sc} (Ampere)	P_{max} (Watt)	V_{max} (Volt)	I_{max} (Ampere)	Fill factor	Efficiency (%)
3 Layer (21 nm)	10 minutes	0.220029	0.000379	2.10E-05	0.084975	0.000247	0.251147	0.010477
	15 minutes	0.190025	0.000386	3.12E-05	0.115106	0.000271	0.425063	0.01559
	20 minutes	0.054994	0.000219	5.66E-06	0.039975	0.000142	0.470532	0.00283
TiO_2 Nanoparticle on The TiO_2 Nanofiber								
3 Layer (21 nm)	10 minutes	0.000488	0.190083	2.99E-05	0.100018	0.000299	0.322958	0.014965
	15 minutes	0.114995	0.000441	2.20E-05	0.070008	0.000315	0.434712	0.011021
	20 minutes	0.250036	0.000352	2.67E-05	0.114996	0.000232	0.302748	0.013332

Based on Table 1 explains that the changes efficiency on both the structure of TiO_2 layer is not too significant, for example, the results of the efficiency of a layer of TiO_2 nanoparticles on the TiO_2 nanofiber, when 10 minutes has an efficiency $\eta = 0.014\%$, 15 minutes $\eta = 0.011\%$ and 20 minutes $\eta = 0.013\%$. It can be caused by the properties of nanofiber that serves to trap photons obscured by the overlaying nanoparticles. As for the TiO_2 nanofiber on the TiO_2 nanoparticles at the time 10 minutes had an efficiency $\eta = 0.010\%$, and a 15 minutes $\eta = 0.015\%$, but seen a significant difference at 20 minutes which has an efficiency $\eta = 0.002\%$, the difference is due to the working electrode not

achieve optimum thickness so that electrons can not diffuse reach the electrodes. Based on these results the highest efficiency can be seen in the TiO₂ nanofiber on the TiO₂ nanoparticles in 15 minutes. This can happen because the plating time 15 minutes, nanofiber formed and spread evenly on the above FTO already coated with TiO₂ nanoparticles. So that photons inside nanofiber more and longer stuck. This can increase the absorption of photons, which then interacts with the dye and can generate a lot of excited electrons. The role of the TiO₂ nanoparticles on the TiO₂ nanofiber also has a very important influence. Where TiO₂ nanoparticle acts as an absorber dye while TiO₂ nanofiber role in improving the absorption of light absorbed by the dye so that photons can be trapped inside for longer[19].

In conclusion, comparison of a double layer of TiO₂ nanoparticles is a layer on the TiO₂ nanofiber had less good results because at anytime change does not significantly increase efficiency with this case due to the pure characteristic of nanofiber lost by characteristic of the nanoparticles. As for TiO₂ nanofiber layer on the TiO₂ nanoparticles better efficiency results in 15 minutes. Consider that in the 15 minutes have an optimum thickness so that electrons can reach the electrode diffuse.

References

- [1] Rakhman, D.F., Pramono, S.H., Maulana, E. Skripsi, Universitas Brawijaya, Malang, 2014.
- [2] Rapsomanikis A., Papoulis D., Panagiotaras D., Kaplani E., Stathatos E. 2014. Global NEST Journal, Vol 16 No 3, pp.485-489.
- [3] Grätzel, M. 2005. Inorg. Chem., 44(20). pp. 6841-6851. DOI:10.1021/ic0508371.
- [4] Michael Hoffmann. 1995. Journal of American Chemical Society, 95. pp.69-96
- [5] Zhang, H., Banfield, J.F. 2000. Journal of Physics Chemistry B. vol.104. pp.3481
- [6] E. Edri, S. Kirmayer, M. Kulbak, G. Hodes, D. Cahen. The Journal of Physical Chemistry Letters. 5(2014) 429-433.
- [7] S.Y. Kim, Y. Kim, K.M. Lee, W.S. Yoon, H.S. Lee, J.T. Materials and Interfaces 6 (2014) 13430-13437.
- [8] A.K. Chandiran, A. Yella, M.T. Mayer, P. Gao, M.K. Nazeeruddin, M. Grätzel, Advanced Materials. 26 (2014) 4309-4312.
- [9] E. Edri, N. Kedem, H. Cohen, P. Barnes, G. Hodes, The Journal of Physical Chemistry. 118 (2014). 16884-16891.
- [10] Pirhadi, M. Feshki, S., Marandi, M., Davarnejad, R. Journal Nanostruct., 6(1):32-37, Winter 2016. DOI:10.7508/jns.2016.01.005.
- [11] Stathatos, E. 2012. Journal of Engineering Science and Technology, Review 5, pp.9-13.
- [12] Chiba Y, Islam A, Watanabe Y, Komiya R, Koide N, Han L.Y. Japanese Journal of Applied Physics. 45: L640 (2006). DOI:10.1143/JJAP.45.L638.
- [13] Zhou, H, et al. 2011. Journal of Photochemistry and Photobiology A Chemistry, pp.188-194.
- [14] Lee, J.K. and Mengjin, Y., 2011. Material Science and Engineering B 176, pp.1142-1160
- [15] Deni Yulika, Skripsi, Universitas Sebelas Maret, Surakarta, 2014
- [16] Diah A.E, Skripsi, Universitas Sebelas Maret, Surakarta, 2016.
- [17] Dinasti D.P, Skripsi, Universitas Sebelas Maret, Surakarta, 2016.
- [18] Nafi,ah Ardhani, Skripsi, Universitas Sebelas Maret, Surakarta, 2013.
- [19] S.W. Lee, D. Zhang. I.P. Herman, Applied Physics Letters 104 (2014) 053113.
- [20] Grätzel, M. 2003. Journal of Photochemistry and Photobiology. Vol. 4, pp. 145-153.
- [21] Z. Huang. 2003. Composites Science and Technology, vol. 63, no.15, pp.2223-2253.