

# Time Variation of Insertion Cu On TiO<sub>2</sub> Nanoparticles Layer Through The Electroplating Method In Dye-Sensitized Solar Cell (DSSC)

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**Abstract:** Copper (Cu) is a conductive metal. Insertion of copper on a TiO<sub>2</sub> active layer is the right choice in the effort to improve Dye-Sensitized Solar Cell (DSSC) performance. Electroplating methods were used in this study to insert copper in the TiO<sub>2</sub> layer. The device of DSSC used in this study is natural dye *Moringa Oleifera*, TiO<sub>2</sub>-Cu electrode, the counter electrode of Pt and electrolyte from NaI. The peak absorbance of dye is at wavelength 415 nm and maximum efficiency is 0,093% from the time variation electroplating of 25 s. There is increase efficiency from TiO<sub>2</sub> to TiO<sub>2</sub>-Cu electrode with time variation of electroplating. It is shown that insertion of copper in the TiO<sub>2</sub> nanoparticles layer improves the performance of DSSC.

**Keyword :** Electroplating, copper, TiO<sub>2</sub> nanoparticles, Dye-Sensitized Solar Cell (DSSC)

## 1. Introduction

Solar cell research has undergone development until now as growing demand for electrical energy. One development of solar cells is Dye-Sensitized Solar Cell (DSSC). DSSC is renewable energy that utilizes natural dyes from plants in the process of absorption sunlight to be converted into electrical energy. In addition to using natural dyes, DSSC devices are Eco-friendly, easy, and less costly in production.

The semiconductor used in the DSSC is titanium dioxide (TiO<sub>2</sub>). Titanium is one of the abundant elements in the Earth's crust of about 0,63%. TiO<sub>2</sub> consisted of rutile, anatase, brookite, and TiO<sub>2</sub> (B) which in this study used TiO<sub>2</sub> anatase with a band gap of 3.2 eV (Carp et al., 2004). The abundant availability of TiO<sub>2</sub> in the Earth's crust has an impact on cheaper production costs. TiO<sub>2</sub> has a large surface, transparent, high photosensitivity properties, and particle size of 10-20 nm (Mohammed et al., 2015). Previous research has provided good efficiency results in DSSC using TiO<sub>2</sub> semiconductors but still needs to be improved to obtain DSSC with maximum and stable results. In addition to TiO<sub>2</sub> used as a semiconductor, many studies have attempted to insert other materials in the TiO<sub>2</sub> layer in order to improve the performance of the DSSC. Other materials used in the insertion are metals and organic materials.

This study will be inserted Cu on TiO<sub>2</sub> to know the performance of DSSC. Previous studies, the insertion of Cu on TiO<sub>2</sub> layers was able to improve the performance of the DSSC because Cu was conductive (Yuliza et al., 2013). The insertion of Cu on TiO<sub>2</sub> layers can be done by several methods such as electroplating, nanocomposite, hydrothermal, sputtering, pulse plating (Saehana *et al.*: 2011; Ansari *et al.*: 2015; Gumilar *et al.*: 2014; Rokhmat *et al.*: 2017 ). The result is a performance improvement of the DSSC after insertion Cu on TiO<sub>2</sub> layers in both the solar cell and the DSSC.

This study will be inserted Cu on TiO<sub>2</sub> layers using electroplating method. Electroplating method is a method of coating metal on conductive solid material by utilizing electric current in electrolysis process (Riyanto: 2013 and Gumilar *et al.*: 2014). Study of Saehana *et al.* (2011) by the method of electroplating (the current 1 A and voltage 5 V) on solar cells provide the efficiency from Cu-TiO<sub>2</sub> of 0.78%. The result was very helpful the performance of solar cells. Another study of Saehana et al. (2012) with the electroplating method on temperature variations and current variations show that insertion of Cu with the method electroplating was able to improve the performance of solar cells. The result of the greatest efficiency is obtained at a temperature of 55 °C was 3.88% and at the current 50 mA is 4.38%. Therefore in this study wanted to know how variation of insertion time using electroplating method can influence the improvement of DSSC performance.

In addition to using TiO<sub>2</sub> semiconductors, various natural dyes have been studied to determine the performance of DSSC. One of the natural dyes used previously is *Moringa oleifera* which is high in chlorophyll. However, the efficiency result given is not maximal, that is 0,0078% (Jonathan *et al.*, 2016). Therefore in this study, will also be used dye chlorophyll from *Moringa oleifera* combined with a TiO<sub>2</sub>-Cu electrode, a counter electrode from platinum and electrolyte form NaI solution.

## 2. Experiment

The TiO<sub>2</sub> nanoparticle layer was prepared by dissolving 0.5 g of TiO<sub>2</sub> nanoparticles in distilled water of 2.5 ml, stirring for 30 min at room temperature and deposited on FTO glass by a spin coating method. The next TiO<sub>2</sub> layer furnace at 450 °C for 30 minutes. The insertion of Cu on TiO<sub>2</sub> layer is done by using electroplating method. The electrolyte solution for Cu insertion consisted of CuSO<sub>4</sub>.5H<sub>2</sub>O 1.96 gr dissolved in 120 ml distilled water and 0.1 ml H<sub>2</sub>SO<sub>4</sub>. The voltage used in the electroplating process is 3 V and the current is 8 mA. The variation of research used in the electroplating process is the variation of insertion time.

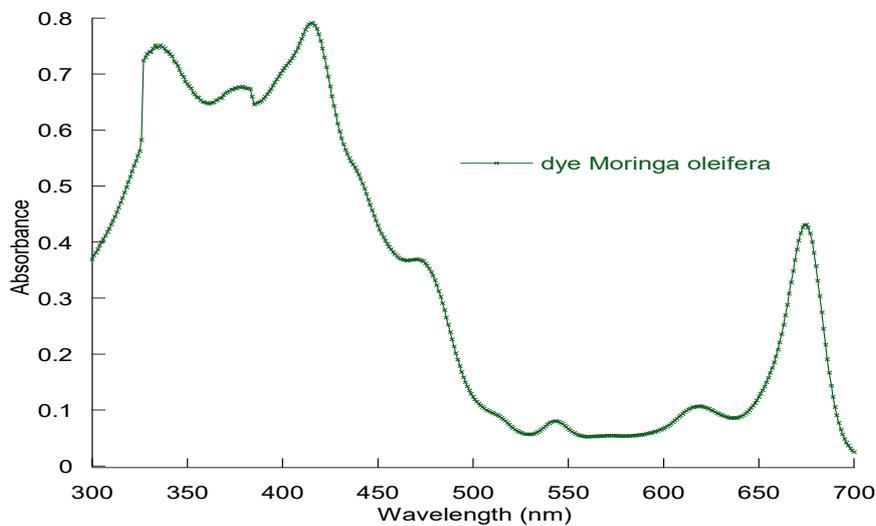
The TiO<sub>2</sub> layer which has been inserted Cu (TiO<sub>2</sub>-Cu) with a variation of insertion time then tested the absorbance spectrum using *UV-Visible Spectrophotometer*. The active layer of TiO<sub>2</sub>-Cu layer was then immersed in dye extract from *Moringa oleifera* for 24 hours and tested the voltage-current characteristic (*I-V*). Dye *Moringa oleifera* obtained from fresh leaf extract 20 g dissolved in solvent 100 ml, stirred for 1 hour subsequently silenced for 24 hours before filtered. Dye extract is also tested spectrum absorbance using *UV-Visible Spectrophotometer*.

The electrolyte used is a NaI solution and the counter electrode is Platinum (Obina *et al.*, 2017). TiO<sub>2</sub>-Cu electrode and the counter electrode are arranged like a sandwich. Next electrolyte drops between them for testing *I-V* characteristic using Keithley 2602A.

### 3. Results and Discussion

#### 3.1. Characterization of the absorbance spectrum

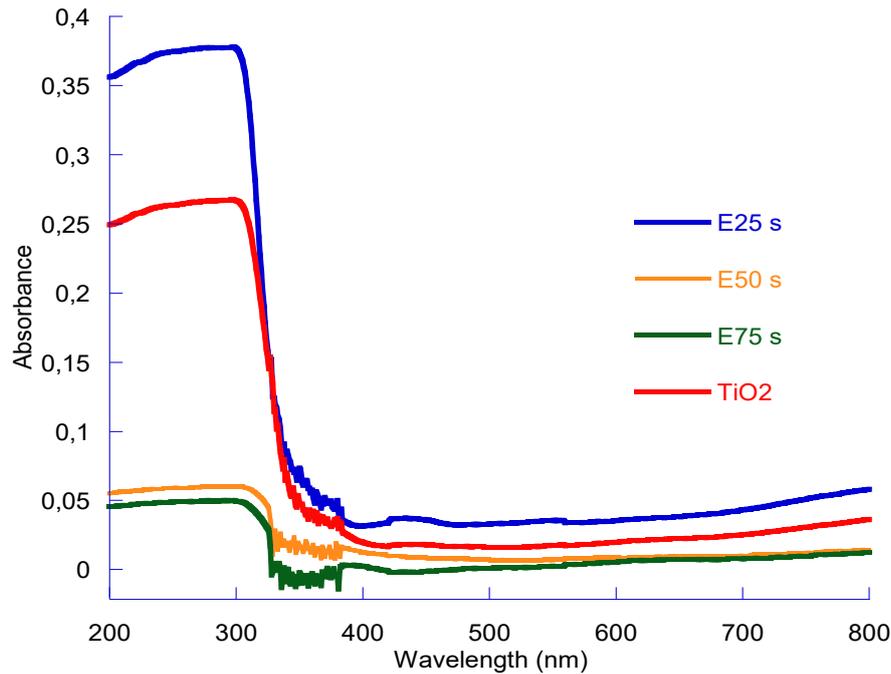
The absorbance spectrum from the extract of dye *Moringa oleifera* was measured in the wavelength range 300 nm to 700 nm which can be seen in Figure 1. The result of dye absorbance shows that there is an absorption of light in the wavelength range 300-700 nm. Where there is absorption peak at wavelength 333 nm, 415 nm, and 674 nm. The highest peak of absorbance at the wavelength of 415 nm can be seen from Table 1. It shows that the use of *Moringa oleifera* dye can help light absorption in DSSC fabrication. The absorbance of dye *Moringa oleifera* from previous studies has maximum absorption at 400 nm wavelength (Jonathan *et al.*, 2016). The difference of these results with the results of this study may be due to differences in dye and solvent concentrations used. the previous study used a solvent ratio of 1 : 2 whereas in the study was dye 1 : 5. The use of concentrations of dye and solvent can affect the absorbance of the material. The absorbance spectrum test is performed on an electrode with a variation of Cu insertion time in TiO<sub>2</sub> layer by an electroplating method. The results are seen in Figure 2 and Table 1.



**Figure 1.** Absorbance spectrum of dye *Moringa oleifera*

**Table 1.** Absorbance spectrum of materials

No.	Data	$\lambda$ (nm)
1	Dye	415
2	TiO <sub>2</sub>	296
3	Cu-TiO <sub>2</sub> 25 s	299
4	Cu-TiO <sub>2</sub> 50 s	298
5	Cu-TiO <sub>2</sub> 75 s	297



**Figure 2.** Absorbance spectrum of dye *Moringa oleifera*

Figure 2 gives information that  $\text{TiO}_2$  and  $\text{Cu-TiO}_2$  with time variations of electroplating have absorption of light in the wavelength range 200-400 nm. It shows that there is the absorption of light other than in the UV region there is also absorption in the visible light range. Maximum absorption of the material can also be seen from Table 2 which shows that maximum absorption is present in  $\text{Cu-TiO}_2$  with the variation of insertion time of 25 s at 299 nm wavelength. There was a shift from the peak of the  $\text{TiO}_2$  absorbance and the insertion time variation at 75 s, 50 s, and 25 s, but the results were not much different from the absorbance of  $\text{TiO}_2$ . This can be due to the structure of the sample layer in the test is still not flat so that the absorption of light during absorbance testing is still not perfect. So it needs to be tested several times to obtain maximum results.

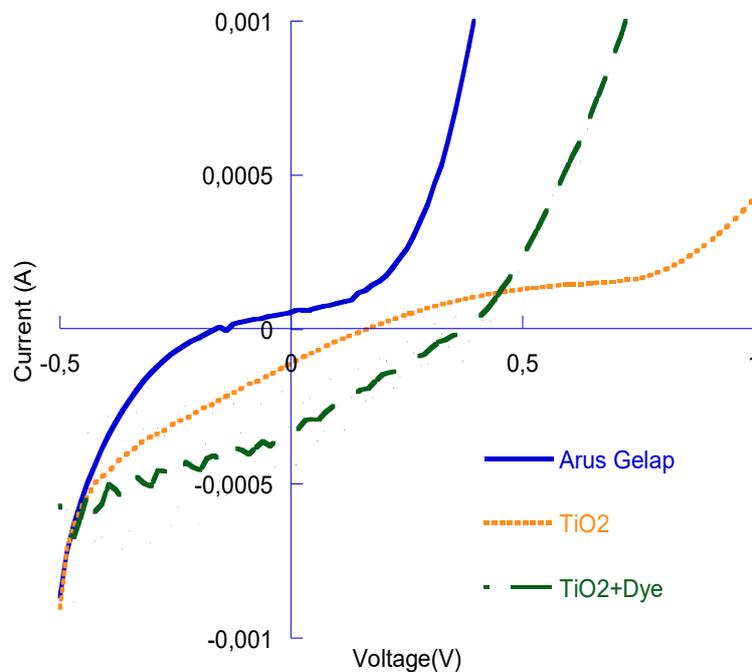
### 3.2. Characterization of I-V meter

Figure 3 shows the results DSSC of I-V characteristics with the electrode of  $\text{TiO}_2$  without dye and  $\text{TiO}_2$  with dye. The result of the picture can be seen that there is a graph shift from dark current to bright current both on  $\text{TiO}_2$  and on  $\text{TiO}_2$  which is immersed in dye. It can be seen from the picture that the widest area in quadrant four is on the  $\text{TiO}_2$  electrode which has been immersed in dye. Where the data is supported by the amount of efficiency produced can be seen in Table 2. The efficiency of  $\text{TiO}_2$  that is immersed in the dye is greater than without immersion in the dye that is respectively 0,034% and 0,004%. It shows that chlorophyll dye *Moringa oleifera* capable of binding better with  $\text{TiO}_2$  semiconductor nanoparticles. Dye has been able to increase the absorption of photons and reduce the recombination of electrons to be forwarded towards the  $\text{TiO}_2$  semiconductor. The results of the efficiency of this study are greater

than previous studies where using dye *Moringa oleifera* and TiO<sub>2</sub> nanocrystal is an efficiency of 0.0078% (Jonathan et al., 2016).

The *I-V* characteristic is performed on DSSC insertion time variation from Cu on TiO<sub>2</sub> through electroplating method shown in Figure 4. The curve formed from Figure 4 shows that the electroplating time variation of 25 s has a wider area in quadrant four than the 50 s and 75 s time variations. In the 50 s and 75 s time variations, it is seen that there is almost no difference in the area formed in quadrant four.

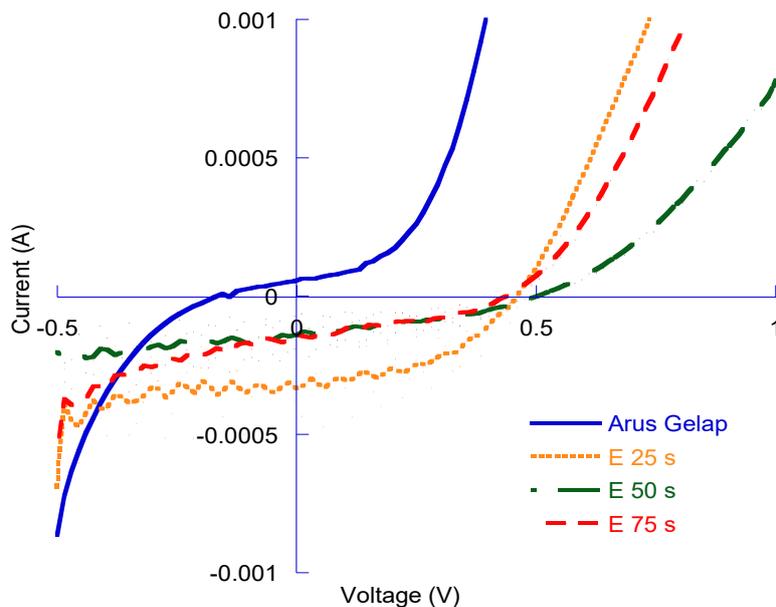
The result of the curve can also be proven from the performance result of the DSSC shown with the efficiency value in Table 2. When viewed from the results of TiO<sub>2</sub> without Cu efficiency provides information that the insertion of Cu by electroplating method can increase the efficiency of DSSC which is maximal in the variation of electroplating time 25 s. The data in Table 2 shows that the greatest efficiency in the electroplating time variation is 25 s, 0.090% and followed by the time variation of 50 s that is 0.036% and the time variation of 75 s is 0.033%.



**Figure 3.** Characterization of current-voltage (*I-V*) from TiO<sub>2</sub> and TiO<sub>2</sub>-dye

**Table 2.** Characterization of current-voltage (*I-V*)

No.	Electrode	Dye	V <sub>oc</sub> (mV)	I <sub>sc</sub> x10 <sup>-5</sup> (mA)	P <sub>max</sub> x10 <sup>-5</sup>	FF	η x10 <sup>-1</sup> (%)
1	TiO <sub>2</sub>	-	0.18	10.39	0.38	0.21	0.04
2	TiO <sub>2</sub>	<i>Moringa o.</i>	0.38	31.16	3.41	0.28	0.34
3	Cu-TiO <sub>2</sub> 25 s	<i>Moringa o.</i>	0.48	43.00	9.34	0.45	0.90
4	Cu-TiO <sub>2</sub> 50 s	<i>Moringa o.</i>	0.52	6.31	3.63	1.11	0.36
5	Cu-TiO <sub>2</sub> 75 s	<i>Moringa o.</i>	0.46	11.00	3.28	0.63	0.33



**Figure 4.** Characterization of current-voltage ( $I$ - $V$ ) from time variation Cu on  $\text{TiO}_2$  through electroplating method

Means that Cu can be inserted optimally on layer  $\text{TiO}_2$  with the help of electric current of 8 mA and voltage of 3 V in electroplating method for 25 s. Where Cu is able to bind with  $\text{TiO}_2$  and become a bridge for electron transfer. The increased efficiency of DSSC with Cu indicates that Cu can prevent electrons from dye absorption results to recombine and assist the electron transfer process or electron migration to the  $\text{TiO}_2$  semiconductor conduction bands more quickly and smoothly until it reaches the FTO substrate.

However, the increase in Cu insertion time, there is a decrease in efficiency values generated by DSSC. It is seen from the efficiency results at 50 s and 75 s. The addition of time in electroplating means the more Cu or the thicker Cu that is inserted on the  $\text{TiO}_2$  layer. Therefore it causes a metal bulk effect like the results of previous research. Excessive Cu insertion can give rise to bulk effects that can degrade the performance of the DSSC (HaiLing et al., 2009). According to research Hailing et al. (2009), Cu is the high range of bulk effects when used in large quantities. Similarly, it is shown by the results of previous research that the electroplating method is applied to insert a variety of Cu in the  $\text{TiO}_2$  / CuO layer. The result is an increase of DSSC efficiency at 5 to 20 s electroplating time, but efficiency decreases at 25 s and 40 s were in this electroplating process using 10 mA current (Rokhmat et al., 2017). The degradation of excessive DSSC performance due to Cu may also be due to the closed of the  $\text{TiO}_2$  layer by Cu. The impact is that Cu will inhibit  $\text{TiO}_2$  in capturing photons and transfer electrons so that  $\text{TiO}_2$  semiconductors can not work optimally (Rokhmat et al., 2016).

#### 4. Conclusion

Dye from *Moringa oleifera* in DSSC can improve the performance of the DSSC. Electroplating method has helped the insertion of Cu into a  $\text{TiO}_2$  layer so that the performance of DSSC can increase better than  $\text{TiO}_2$  without metal. The presence of Cu

helps in the process of electron migration to run smoothly and quickly. The maximum Cu insertion occurs at electroplating time for 25 s giving an efficiency of 0.093%. Excessive Cu insertion may lead to a decrease in DSSC performance

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