Fabrication and variation layers of Cu/TiO$\textsubscript{2}$ nanocomposite and its applications in Dye-Sensitized Solar Cell (DSSC)

Wilfrida Mayasti Obina$^{1,2}$, Cari$^{1}$, Agus Supriyanto$^{1}$, Sri Sumardiasih$^{1}$, Trio Yuda Septiawan$^{1}$, Khairuddin$^{1}$

$^{1}$Physics Departement of Post Graduate Program Sebelas Maret University, Jl. Ir. Sutami 36A Kentingan, Surakarta 57126, INDONESIA

$^{2}$Email: wilfridakiki@gmail.com

Abstract. Fabrication of Cu/TiO$\textsubscript{2}$ nanocomposite had been successfully performed. A nanocomposite was prepared by the insertion of metal (copper) in the TiO$\textsubscript{2}$ nanoparticles. Cu/TiO$\textsubscript{2}$ nanocomposite was deposited on the FTO glass used the spin coating method. Layers of Cu/TiO$\textsubscript{2}$ nanocomposite were prepared in variations at 1, 2 and 3 layers. Spektrofotometer UV-VIS Lambda 25 was used to determine the optical characteristics and the energy gap of DSSC materials. El kahfi 100/I-V Meter and Keithley 2602A was used to determine the electrical properties of Cu/TiO$\textsubscript{2}$ nanocomposite. UV-VIS result was showed that there increased absorption wavelength of Cu/TiO$\textsubscript{2}$ nanocomposite and were able to decrease the energy gap. El kahfi was showed that the conductivity of the Cu/TiO$\textsubscript{2}$ nanocomposite was $3.71 \times 10^{-2}$ ($\Omega^{-1} \text{m}^{-1}$). Keithley was showed that the highest efficiency in the 3 layers of Cu/TiO$\textsubscript{2}$ nanocomposite of 0.011%.

1. Introduction
Dye-Sensitized Solar Cell (DSSC) was one of the solar cells devices which used natural dyes to convert solar energy into electrical energy. DSSC was consists of a dye, counter electrode, the active layer, electrolyte, and FTO glass as a substrate [1]. The performance of DSSC was increased if the performance of its constituent materials increased. For example, the active layer of TiO$\textsubscript{2}$ was modified. TiO$\textsubscript{2}$ was a semiconductor that stable, transparent, environmentally friendly and large surface [2]. The results showed that TiO$\textsubscript{2}$ had an energy gap of 3.2 $eV$ [3]. TiO$\textsubscript{2}$ was selected for the insertion of metal because it had the large surface. Large Surface would cause the hole or gap between the particles of TiO$\textsubscript{2}$. Metal was inserted between the particles to overcome these gaps. Metals had good conductivity properties. The purpose was to facilitate the transfer of electrons when passed a layer of TiO$\textsubscript{2}$. Research had been done about metal doped on TiO$\textsubscript{2}$ through several methods such as hydrothermal, sputtering, electroplating and nanocomposite [4,5]. Fabrication of Au/TiO$\textsubscript{2}$ nanocomposite could improve the efficiency of up to 6% [6]. Gold (Au) and silver (Ag) had electrical conductivity properties were better, but they were expensive and limited supply in nature.

In this study was used metal of copper (Cu). Copper doped into natural dye could increase the efficiency from DSSC of 71% [7]. Copper was good thermal conductivity and there was approximately 68 ppm in the earth's crust [8]. Copper had a size of 128 $pm$ or 0.128 $m$ and TiO$\textsubscript{2}$ nanoparticles had a size of 21 $nm$. So that copper would be inserted on TiO$\textsubscript{2}$ through the fabrication of Cu/TiO$\textsubscript{2}$ nanocomposite. The nanocomposite was a merger of nano-sized material and had a different phase. Research had been made a Cu/TiO$\textsubscript{2}$ nanocomposite and could lower the value of electric
resistance. The resistance value of TiO$_2$ layer was 7.714-kilo ohm and Cu/TiO$_2$ nanocomposite layer was 6.624-kilo ohm [9].

Variations at 1 layer, 2 layers and 3 layers of Cu/TiO$_2$ nanocomposite was made in this study. Spin coating method was used in the deposition of Cu/TiO$_2$ nanocomposite. The spin coating method was a method shed a solution of the film on the substrate and rotated at a certain speed. In this research would be tested the absorbance, the energy gap, conductivity and efficiency of Cu/TiO$_2$ nanocomposite. Fabrication of Cu/TiO$_2$ nanocomposite was expected to increase the performance of the DSSC.

2. Experimental Details

2.1. Preparation of Cu/TiO$_2$ nanocomposite

Cu/TiO$_2$ nanocomposite was prepared by dissolved 0.1 g of Polyvinyl Alcohol (PVA) in 10 ml of distilled water while stirred with heated at 80°C for 2 h. TiO$_2$ as much as 1 g and 0.1 g of copper (CuSO$_4$·5H$_2$O) was added to the mixture while stirred for 2 h.

2.2. Extraction of Natural Dyes

*Moringa oleifera* leaves of 10 g were smoothed by porcelain mortar. Ethanol of 50 ml was added in the leaves. Dye was extracted by a magnetic stirrer for 1 h and then allowed to stand for 24 h at room temperature. The result of the soaking was filtered to obtain the pure extract dye.

2.3. Fabrication of DSSC

The conductive glass was Fluorine Tin Oxide (FTO) by the active cell area of 1 cm x 1 cm. FTO glass was cleaned with distilled water for 15 minutes and alcohol 70% for 15 minutes by the ultrasonic bath. Variation of layers was made by varying the scotch tape to make the active areas. A number of variation layers were equal to the variation of scotch tape. The active layer was the layer of Cu/TiO$_2$ nanocomposite. Deposition of Cu/TiO$_2$ nanocomposite was done by varying 1, 2, and 3 layers. Layers of Cu/TiO$_2$ nanocomposite on FTO glass was heated at 100°C for 30 minutes to evaporate the distilled water and 450°C for 30 minutes. Next, the active layer was soaked in the dye for 24 h. The counter electrode was used 2.5 ml solution of platinum. The platinum solution was obtained by mixing 1 ml Hexachloroplatinic (IV) acid 10% (Platinum) with 207 ml of isopropanol stirred for 30 minutes. The electrolyte solution has used a mixture of 2 g of Natrium Iodid (NaI) with 3.68 ml of acetonitrile, 1 ml Propylene Carbonate, 14.56 ml Polyethylene glycol and 0.2 g of Iodine (I$_2$) which stirred for 1 h. Last was assembled DSSC with the sandwich method.

2.4. Characterization

The absorbance of materials was tested by a *UV-Visible Spectrophotometer Shimadzu 1601 PC*. The result of absorbance was used to determine the energy gap. The calculation could follow the energy gap in equation (1) [10]. Where $h$ was Planck's constant ($h = 6.63 \times 10^{-34}$ Js), $c$ was the speed of light ($c = 3 \times 10^8$ m/s), $\lambda$ was the wavelength, and $E$ was the energy gap ($1eV = 1.6 \times 10^{-19}$ J).

$$E = \frac{hc}{\lambda}$$

(1)

The electrical characteristics (conductivity) was tested by *Elkahfi 100 / I-V Meter* and *I-V* characteristics of DSSC by a *Keithley 2602A*. The intensity of the light (Keithley) was used of 1000 W/m$^2$ from halogen lamps. The test results of Keithley was calculated by Equation (2-3). Where $V_{max}$ = maximum voltage (V); $I_{max}$ = maximum current density (mA/cm$^2$); $V_{oc}$ = Open circuit voltage (V) and $P_{in}$ = power of the incoming light.

$$FF = \frac{P_{max}}{P_{in}} = \frac{I_{max} \times V_{max}}{I_{sc} \times V_{oc}}$$

(2)

$$\eta = \frac{FF \times I_{sc} \times V_{oc}}{P_{in}} \times 100\%$$

(3)
3. Results and Discussion

Figure 1 showed the optical characteristics of dye, TiO$_2$ paste, Cu/ TiO$_2$ nanocomposite, Cu/TiO$_2$/dye (1 layer) and Cu/TiO$_2$/dye (2 layers). There were three absorbance peaks by the dye which located in the wavelength range 333 nm - 674 nm. The highest absorbance peak of the Moringa oleifera was a wavelength of 415 nm and the highest absorbance peak of pure TiO$_2$ was 341 nm. This means that TiO$_2$ was also able to absorb visible light very well. Absorbance peak of Cu/TiO$_2$ nanocomposite was the wavelength of 344 nm. It was seen that the light absorption increased from the range of 341 nm to 344 nm. This showed the highest absorption by Cu/TiO$_2$ nanocomposite. The highest absorbance peak of Cu/TiO$_2$ nanocomposite for 1 layer was 343 nm and 2 layers were 345 nm. From the results of the absorbance and the layers could be seen that the increased of the member of layers causes increasing the absorbance. If more light was absorbed, then more electrons could be transferred dan the performance of the DSSC increased.

| Table 1. Energy gap of Cu/TiO$_2$ nanocomposite |
|-----------------|-------|-----|
| Materials       | $\lambda$ (nm) | $E_g$ (eV) |
| Dye             | 415   | 2.99|
| TiO$_2$         | 341   | 3.64|
| Cu/TiO$_2$      | 344   | 3.61|
| Cu/TiO$_2$/dye (1 layer) | 343 | 3.61|
| Cu/TiO$_2$/dye (2 layers) | 345 | 3.60|

Table 1 showed that the doped copper on TiO$_2$ nanoparticles through fabrication nanocomposite could lower energy gap. The energy gap was the energy required by an electron to jump to the conduction band [11]. The presence of copper doped would help facilitate the transferred of electrons from the dye (LUMO) to the conduction band (CB). From the results could be seen that the energy gap of TiO$_2$ decreased after was made Cu/TiO$_2$ nanocomposite. It was from 3.64 eV to 3.61 eV. Energy gap decreased of 0.03 eV would show that copper had been successfully inserted between the TiO$_2$ nanoparticles. Could also be said that the fabrication of Cu/TiO$_2$ nanocomposite serves to trap electrons from the dye to be forwarded to the FTO glass.
Figure 2. Electrical Characteristics for; (a) TiO$_2$ and Dye, (b) Cu and Cu/TiO$_2$ Nanocomposite

Table 2. Electrical conductivity of Cu/TiO$_2$ nanocomposite

| Material     | Conductivity of Dark Condition ($\Omega^{-1}m^{-1}$) | Conductivity of Light Condition ($\Omega^{-1}m^{-1}$) | $\Delta$ Conductivity ($\Omega^{-1}m^{-1}$) |
|--------------|-----------------------------------------------|-----------------------------------------------|------------------------------------------|
| Dye          | $0.13 \times 10^{-2}$                        | $0.18 \times 10^{-2}$                        | $0.05 \times 10^{-2}$                   |
| TiO$_2$      | $0.07 \times 10^{-2}$                        | $0.08 \times 10^{-2}$                        | $0.01 \times 10^{-2}$                   |
| Cu           | $16.21 \times 10^{-2}$                       | $18.99 \times 10^{-2}$                       | $2.78 \times 10^{-2}$                   |
| Cu/TiO$_2$   | $2.93 \times 10^{-2}$                        | $3.71 \times 10^{-2}$                        | $0.78 \times 10^{-2}$                   |

Figure 2 showed the electrical characteristics of the materials in the dark condition or light condition. From the graph showed that all the materials had the ability to conduct electricity in the dark condition or light condition. Figure 2 and Table 2 showed that there were an increased in conductivity from the dark condition to light condition for all materials. The highest conductivity in the condition of light was copper of $18.99 \times 10^{-2} \Omega^{-1}m^{-1}$. This showed that the copper had good conductivity properties, so the right to insert in the TiO$_2$ nanoparticles. The conductivity of the Cu/TiO$_2$ nanocomposite increased by $3.63 \times 10^{-2} \Omega^{-1}m^{-1}$ from the conductivity of the TiO$_2$ was $0.08 \times 10^{-2} \Omega^{-1}m^{-1}$. This showed that the Cu/TiO$_2$ nanocomposite had a good ability to conduct electricity. So it could help increased the performance of DSSC.

Figure 3. $I-V$ characteristics from DSSC for 1 layer, 2 layers and 3 layers of Cu/TiO$_2$ nanocomposite
Tabel 3. $I-V$ characteristics from DSSC

| Various layers of Cu/TiO$_2$ nanocomposite | $V_{oc}$ (mV) | $I_{sc}$ (mA) | FF | $\eta$ (%) |
|------------------------------------------|--------------|--------------|----|----------|
| 1 layer                                  | 2.35 x 10$^{-4}$ | 4.77 x 10$^{-3}$ | 4.58 x 10$^{-1}$ | 0.005 |
| 2 layers                                 | 2.95 x 10$^{-1}$ | 5.83 x 10$^{-5}$ | 4.99 x 10$^{-1}$ | 0.008 |
| 3 layers                                 | 2.04 x 10$^{-1}$ | 4.23 x 10$^{-5}$ | 12.93 x 10$^{-1}$ | 0.011 |

Characteristics of $I-V$ could be seen in Figure 3 and Table 3. From the graph showed that there was an increased the area formed from 1 layer to 3 layers. Efficiency from 1 layer of Cu/TiO$_2$ nanocomposite was 0.005%, 2 layers of Cu/TiO$_2$ nanocomposite was 0.008% and 3 layers of Cu/TiO$_2$ nanocomposite was 0.011%. Copper doped TiO$_2$ nanoparticles had been increased the performance of DSSC [5,9,11]. Efficiency increased from 1 layer until 3 layers of Cu/TiO$_2$ nanocomposite. The highest efficiency was the 3 layers of Cu/TiO$_2$ nanocomposite of 0.011%. Results efficiency explained that there was good contact between the copper and TiO$_2$ nanoparticles in the fabrication of nanocomposite.

4. Conclusion
Fabrication of nanocomposite with TiO$_2$ nanoparticles was inserted by copper had been successfully performed. Copper could occupy the space between the TiO$_2$ particles very well. It was seen from the results of the optical characterization of Cu/TiO$_2$ nanocomposite had the absorbance peak at 345 nm and decreased energy gap until 3.60 eV. The results electrical characteristics of Cu/TiO$_2$ nanocomposite had a conductivity value of 3.71 x 10$^{-2}$ ($\Omega^{-1}$ m$^{-1}$) and the highest efficiency in the 3 layers of Cu/TiO$_2$ nanocomposite of 0.011%. Efficiency from 1 layer of Cu/TiO$_2$ nanocomposite was 0.005%, 2 layers of Cu/TiO$_2$ nanocomposite was 0.008% and 3 layers of Cu/TiO$_2$ nanocomposite was 0.011%.

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