Dye-sensitized solar cell (DSSC) performance of copper on TiO₂ as a photoelectrode through nanocomposite and electroplating method

A Supriyanto*, W M Obina, T Y Septiawan, A H Ramelan, and F Nurosyid

Department of Physics, Faculty of Mathematics and Natural Science, Sebelas Maret University, Surakarta, Indonesia

*Corresponding author: agusf22@staff.uns.ac.id

Abstract. Dye-Sensitized Solar Cell (DSSC) is a generation of solar cells that utilize dye as a sensitizer and can convert solar energy into electrical energy. Components of DSSC are photoelectrode, dye, counter electrode and electrolyte. The photoelectrode is one of the devices of the DSSC. The modification of the photoelectrode is the insertion of copper on TiO₂ to improve the performance of the DSSC. The method used in this research is the nanocomposite method and the electroplating method. Nanocomposites are the process of mixing different materials or materials that are nano-sized. Electroplating is a method of metal coating with the help of electric current. The dye used is Moringa Oleifera, the counter electrode is platinum, and the electrolyte is NaI. The purpose of research can be obtained from the characterization of the absorbance spectra, XRD and current-voltage (I-V). The results of the absorbance spectrum show that there is the maximal absorption of light from the nanocomposites. The XRD results show the presence of copper on TiO₂ because there are diffraction patterns of TiO₂ anatase, TiO₂ rutile, and copper. Characterization of I-V DSSC shows that the efficiency of copper insertion on TiO₂ through electroplating method is 0.090% and nanocomposite is 0.048%. The insertion of copper on TiO₂ capable of improving the performance of DSSC is through electroplating method.

1. Introduction
The need for electrical energy is the main reason for the development of solar cells. The solar cell has a method that directly converts solar energy into electrical energy without the greenhouse effect, so it is suitable for continuous development in the use of electrical energy [1]. The principle of the photovoltaic energy conversion process is electron excitation due to light absorption events and charge separation [2]. DSSC is a device of solar cells capable of generating electrical energy. Michael Gratzel and Brian O'Regan introduced the basic principle of DSSC as a solar cell device that utilizes dye to coat semiconductors for maximum absorption of sunlight [3]. Components of DSSC are photoelectrode that has been immersed in dye, counter electrode and electrolyte of couple redox I/I³. DSSC is a device that is easy to make, low cost, eco-friendly and has resulted in efficiency is 11.1% [4].

Semiconductor often used in DSSC is Titanium dioxide (TiO₂). TiO₂ is used because it is stable, transparent, the surface is large enough to bind more dye, high efficiency, greater availability at the cheaper cost, has a refractive index of $n = 2.4-2.5$ and is eco-friendly [5]. TiO₂ is a semiconductor that has a band gap for rutile is 3.02 eV, anatase is 3.2 eV, and brookite is 2.96 eV. The anatase phase of TiO₂ has high electron mobility, low dielectric constant and low density making it suitable for use in
solar cells [6]. Copper is a conductive metal and has excellent thermal properties. The electron configuration of the copper is \([Ar]3d^{10}4s^1\), so that on the outer shell there is one valence electron. Copper is capable of transitioning due to the small orbital energy levels. It makes copper often used in semiconductor insertion.

Copper insertion in TiO\(_2\) has been done, and the result can increase the \(V_{oc}\) (The value of \(V_{oc}\) is 0.30\(V\)) and \(I_{sc}\) (The value of \(I_{sc}\) is 0.79\(mA\)) values of DSSC [7]. The efficiency of copper insertion on TiO\(_2\) through nanocomposite method is 0.40\%, by electroplating method is 0.78\% and by a sputtering method is 1.20\% [8]. The efficiency of copper insertion on TiO\(_2\) from solar cells by electroplating method is 0.045\% and by pulse plating method is 0.117\% [9]. From these studies, this research will be carried out copper insertion on TiO\(_2\) using nanocomposite method and the electrolating method. The nanocomposite is the incorporation of some nano-sized material or less than 100\( nm\) and electrolating is a method of metal coating with the help of electric current on a conductive solid object [10].

2. Methods

2.1. Preparation photoelectrode of nanocomposite method

The insertion of copper on TiO\(_2\) was prepared by dissolved 0.1\(g\) PVA in 10\(ml\) distilled water dan stirred at 80\(^\circ\)C for 2\(h\). After 2\(h\), add the powder of TiO\(_2\) 0.8 and copper (CuSO\(_4\)5H\(_2\)O) 0.3\(g\) then stirring for 2\(h\) to get a good paste. Deposition of paste on FTO conductive glass with the active area of 1\(cm\times1cm\). The layers of the nanocomposite are heated at 450\(^\circ\)C for 30\( min\) [11].

2.2. Preparation photoelectrode of the electroplating method

The paste of TiO\(_2\) was prepared by dissolving TiO\(_2\) powder 0.5\(g\) with distilled water 2.5\(ml\) and stirring for 30\( min\) at room temperature. Deposition the paste of TiO\(_2\) on the FTO with area 1\(cm\times1cm\). Heat the layer so that the solvent can evaporate at 450\(^\circ\)C for 30\( minutes\). The layer of TiO\(_2\) doped copper through electrolating method for 25\(s\) using electrolyte solution of copper. Electrolyte solution from copper is the copper powder (CuSO\(_4\)5H\(_2\)O) 1.96\(g\) dissolved in distilled water 120\( ml\) and 0.1\(ml\) H\(_2\)SO\(_4\). The current used in the electrolating process is 8\(mA\), and the voltage is 3\(V\) [8,12].

2.3. Fabrication of DSSC

The dye used is extracted from fresh Moringa oleifera leaves [13]. Photoelectrode is layers of Cu/TiO\(_2\) through nanocomposite method and the electrolating method soaked in the dye for 24\(h\). Electrolyte and counter electrode used are NaI and Pt [11]. Components of the DSSC are prepared by a sandwich system.

2.4. Characterization

The characterization done in the research is the absorbance spectrum with UV-Vis Spectrophotometer, X-Ray diffraction (XRD), Scanning Electron Microscopy (SEM) and current-voltage (I-V) with Keithley 2602A. The characterization of the absorbance spectrum is used to determine the UV-Vis absorption of the material. XRD characterization is used to determine the diffraction pattern and the sample material. SEM characterization is used to know the sample morphology and characterization of I-V to know the performance of DSSC.

3. Results and Discussion

3.1. Characterization of the absorbance spectrum

Absorbance characterization is performed in the wavelength range of 200-800\( nm\). Absorbance spectrum results show that there is an increase in light absorption when TiO\(_2\) is inserted with copper. Figure 1 is copper insertion through the nanocomposite method shows absorption at the wavelength range of 200-250\( nm\) and 300-400\( nm\). Copper insertion through electrolating method shows absorption at wavelength 200 - 390\( nm\). The absorption shift that occurs is caused by the interface charge transfer of the TiO\(_2\) valence band to the copper that has been inserted in the titania. Generally excited electrons will be transferred from the valence band to the conduction band on TiO\(_2\).
Both methods show that the maximum absorption of light at copper insertion on TiO$_2$ is through the nanocomposite method. The absorbance of both methods shows that TiO$_2$ can bind well with copper. The excited electrons entering the TiO$_2$ conduction will be trapped inside the copper to be forwarded to the FTO. It can be due to the high Schottky barrier of Cu inserted on TiO$_2$[8]. The Schottky barrier is a barrier arising from the connection of semiconductors with metals. Copper acts as a transport bridge for moving electrons faster and easier. The more electrons trapped in copper will increase the number of electron transfers to improve the performance of the DSSC. The absorption shift that occurs is caused by the interface charge transfer of the TiO$_2$ valence band to the copper that has been inserted in the titania. The difference in absorbance can be due to the presence of a defect center resulting in changes in optical absorption where there are differences in the composition of copper and titania.

3.2. Characterization of XRD

XRD characterization as shown in Figure 2 shows that there are diffraction patterns of TiO$_2$ anatase, TiO$_2$ rutile, and copper. Based on the annealing temperature used 450°C, TiO$_2$ should only show the diffraction pattern of anatase and diffraction pattern of copper. The rutile phase indicates that there is a copper inserted in TiO$_2$. Based on previous research, insertion in TiO$_2$ can increase the rutile fraction at low temperatures resulting from oxygen defect and vacancy[7]. The vacancy is the atomic void in the lattice and the defects that occur in the metal where the high mass of copper oxide catalyst inhibits the formation of anatase phase completely and accelerate the increase of the rutile phase. The presence of copper accelerates the growth of the rutile phase. Both methods show diffraction patterns that are not much different and emerging diffraction patterns of anatase, rutile, and copper where the intensity through the electroplating method is higher. This can be caused by the copper crystal structure inserted in TiO$_2$ is more homogeneous through electroplating methods (Figure 3).

3.3. Characterization of SEM

The morphology of the SEM characterization results in Figure 3 indicates that the granules of the electroplating method are more homogeneous than the nanocomposite method. Copper is better inserted between TiO$_2$ by the electroplating method so that only small pores are formed. The morphology of the electroplating results is more evenly distributed than the nanocomposite method. The average particle size through the nanocomposite method is 85-237 nm, and the electroplating method is 60-74 nm. According to XRD results show higher intensity and more regular charts.
Crystal structure through the electroplating method is more homogeneous with an average particle size smaller than using the nanocomposite method.

![Figure 2](image_url)  
**Figure 2.** XRD Characterization of copper insertion on TiO\(_2\) with: (a) electroplating method and (b) the nanocomposite method

![Figure 3](image_url)  
**Figure 3.** The Morphology of copper insertion on TiO\(_2\) with: (a) electroplating method and (b) the nanocomposite method

3.4. Characterization of I-V Meter

The purpose of voltage-current characterization (I-V) is to know the performance of DSSC with copper insertion in TiO\(_2\) through nanocomposite method and the electroplating method. Figure 4. and Table 1. shows the result of I-V characterization in which both copper insertion methods can improve the performance of the DSSC. DSSC efficiency without copper insertion is 0.034%, DSSC efficiency of copper insertion with nanocomposite method is 0.048%, and electroplating method is 0.090%. It shows that the performance of DSSC is more increased in copper insertion through the electroplating method.
method. DSSC performance improvements can be affected by the increasingly widespread electrode surface due to copper insertion through electroplating methods. It is supported by SEM results where the morphology is homogeneous from the electroplating method. The nanocomposite method and the electroplating method have been used in past copper insertion on TiO$_2$. The efficiency of the nanocomposite method is 0.40%, and the efficiency of the electroplating method is 0.78% in 1A, 5V, and 10s[8]. The electroplating method is also used in insert copper on TiO$_2$/CuO with the current of 10mA and time 20s gives efficiency that is 1.62% [14]. Insertion of copper on TiO$_2$ with nanocomposite method with the concentration of 10:1 (TiO$_2$: Cu) gives efficiency that is 0.011 [11]%. The result difference can be influenced by several factors, namely difference of material and process used from current, voltage, cathode-anode, dye, electrolyte, and the counter electrode. Accuracy and precision of the research also greatly affect the performance of the DSSC.

4. Conclusion
The insertion of copper on TiO$_2$ through nanocomposite method and the electroplating method can improve DSSC performance. Photoelectrode can work maximum because there is the diffraction pattern of rutile, anatase, and copper. The morphology of the coating by electroplating method is more homogeneous and fewer pores are formed between TiO$_2$ and copper. The electroplating method gives the biggest efficiency that is 0.090%. Insertion of copper on TiO$_2$ can prevent recombination and become a bridge in electron transfer.

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