Performance Improvement of TiO$_2$ Based Solar Cells by Coating Cu Nanoparticles into the Space between TiO$_2$

Sahrul Saehana, Rita Prasetyowati, Marina I. Hidayat, Pepen Arifin, Khairurrijal, and Mikrajuddin Abdullah

*Email: din@fi.itb.ac.id

Abstract. TiO$_2$ thin films with its pore coated by copper (Cu) nanoparticles have been developed in order to improve the TiO$_2$ based solar cells performance. Contact between Cu nanoparticles and TiO$_2$ play role in minimizing the recombination of electron-hole pairs and increasing electron transfer in TiO$_2$ based solar cells. The Cu coating on the space between TiO$_2$ has been performed by electroplating methods. It is found that the solar cells performance of Cu coated TiO$_2$ films become higher than of the pure TiO$_2$ film. The presence of Cu nanoparticles on TiO$_2$ films were confirmed from Scanning Electron Microscopy (SEM). In this study, a maximum conversion efficiency of 3.73% was achieved.

Keywords: solar cells, TiO$_2$, efficiency

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INTRODUCTION

Recently, TiO$_2$ is widely used in solar energy applications [1]. It because this material have attracted much attention because high efficiency [1], easy fabrication [2], low cost [3,4], and non-toxic materials [4], as well as long term stability [5]. However, the efficiency of TiO$_2$ based solar cells still low because the high rate of electron-hole recombination [6].

The popular method to minimize electron-hole recombination by depositing metal on the semiconductor surface or make contact between both of them [6-8]. The excited electrons are trapped at the metal surface, increasing charge carrier lifetimes. This phenomenon can be seen at Fig. 1(a).

In the previous study, we modified TiO$_2$ thin films using an interconnected metal (Cu) for electron transport by using printing methods [9-10]. However, the performance is still lower. It may caused size of nanoparticle and high internal resistance of solar cells.

In this study, we attempted to improve the efficiency of TiO$_2$ based solar cells by deposited Cu nanoparticle in the space between TiO$_2$ by using electroplating methods. In other hand, we employed a polymer electrolyte composed of polyvinyl acetat (PVA) and a lithium salt for hole transport and to increase the short circuit current [11-12]. An additional goal of the study was to demonstrate the use of simple and low-cost methods such as electroplating for depositing metal on the space between TiO$_2$.

EXPERIMENTAL

TiO$_2$ thin film was deposited on the indium thin oxide (ITO) substrate using spray methods. A suspension was prepared by dispersing 10 g TiO$_2$ in 10 mL of water and mixing with a magnetic stirrer for 45 min. The TiO$_2$ suspension was sprayed on the substrate at a temperature of 150°C [13]. The spray process was repeated 20 times. The resulting thick film of TiO$_2$ was heated on a hot plate at 250°C for 30 min to evaporate water, and then sintered at 450°C for 30 min to improve the electrical contact between the TiO$_2$ particles and the ITO. Copper coatings were prepared using a Watts-type bath containing 20 mL copper sulphate (Cu$_2$SO$_4$). A copper rod of 99.99% purity with dimensions of 5 cm was used as the anode and the TiO$_2$ film deposited on an ITO-coated glass substrate was used as the cathode. The electroplating conditions, i.e. current, voltage, deposition time, solution concentration, volume of solution, distance between anode-cathode, pH solution and bath temperature were 150 mA, 5 V, 25 s, 0.1 M, 20 mL, 15 cm, 4.6, and 25°C, respectively.

The polymer electrolyte was made by dissolving 0.5 g LiOH (Bratchem, Indonesia) in 10 mL water and adding 0.8 g polyvinyl acetat (PVA, Bratchem). The mixture was heated with stirring at 110°C for 1 hour to produce a gel-like electrolyte. The electrolyte was manually applied to the Cu/TiO$_2$ layer and an aluminum counter electrode was added.
Scanning electric microscope (SEM) (JEOL JSM-6360LA) operating at 20 kV was employed to investigate the morphology of the films. The performance of the devices was measured using a current-voltage (I-V) meter (Keithley 617). The measurements were obtained in the dark and under xenon lamp illumination. Light intensity was measured using a luxometer (Lutron LX-101).

The sandwiched structure of this solar cell is shown in Fig. 1 (b).

![Diagram of solar cell](image)

**FIGURE 1.** (a) Photoexcitation process on TiO₂ surface and (b) Design of our solar cells.

**RESULT AND DISCUSSION**

**Absorbance of TiO₂**

In this experiment, we used less pure TiO₂ powder from Brachem (Indonesia) in markets and its absorbance spectra was shown in Fig. 2. According to M. Abdullah, et al. reports that our TiO₂’s were doped Carbon about 7.13% [9]. This doping level is likely the factor responsible for widening the absorption spectra.

Fig. 2 shows that the TiO₂’s electrodes are able to absorb broad wavelength, ranging from less than 200 nm to longer than 800 nm. It indicates that this electrode is better enough to use as photoactive of solar cells. Figure 2 also shows that at wavelength around 800 nm. This result is based on Da Chen, et al. report [14] and M. Abdullah’s et al. report [13]. The doping level in our sample is higher, so the reduction in the effective band gap is expected.

**FIGURE 2.** Absorption spectra of modified TiO₂ film.

**Surface Morphology**

Figure 3(a) is a micrograph of the TiO₂ film. The film surface is smooth and uniform with distributed nanometer sized grains. It also showed that the minimum size of TiO₂ particles was approximately 200 nm. According to Ryan O’Hayre, et al., this size lead to solar cells better performance than the TiO₂ nanoparticle size to solar cells discussed detailed in [15]. The pore of TiO₂ film was large enough to electron and holes diffusing [16].

Figure 3(a) also clearly showed that the film was homogenous, so it is better enough to absorb photon and to produce excited electron. The porosity of the film was predicted the several micro-pores means the spray methods better enough to produce working electrode. This result is similar with M. Abdullah et al. report [13].

Contact between Cu nanoparticle and TiO₂ film shown in Figure 3(b) assumed play significant role to minimize recombination electron-hole pairs. The Cu film was expected to increase performance of TiO₂ solar cells [17].

**Photovoltaic Performance of TiO₂/ITO Solar Cell**

Fig. 4 shows I-V characteristics of our solar cell for different light intensity. The better performance may be caused by metal-semiconductor contact (MS) significantly inhibit recombination of charge carriers. In basic scenario, in Figure 1(b) seems running well...
FIGURE 3. (a) SEM images of TiO₂ film without Cu nanoparticles and (b) Cross-section of Cu/TiO₂ film after coating using electrophating methods.

the Figure 1(b), it was apparent that when solar cell is irradiated by sunlight, the electron-hole pair formed. The electrons of TiO₂ are excited from ground state to excited state by adsorbing photons and then transfer to the conducting glass through the interconnected Cu. In other hand, the holes diffuse to electrolyte. Meanwhile, upon reaching the TCO electrode, the electrons are conducted to the counter electrode via the external circuit. Through counter electrode, the electrons are accepted by the electrolyte. This means, that the holes in the electrolyte recombine with electrons to form the negative charge carriers [18].

However, the increasing photovoltaic performances are attributed to metal-semiconductor junction presence. Cu interconnected seems to have good electron transfer ability (as in Fig 1(b)). In this study, interconnected Cu nanoparticle acts as electron path and lead to rapid electron transfer. Further study including quantitative electron diffusion measurement is required to determine the contribution of these factors.

The lower fill factor is lack of our solar cells. It may be caused by high internal resistance of solar cells [19].

FIGURE 4. Comparison of photocurrent and voltage characteristics of: (a) Uncoated TiO₂ and (b) Cu/TiO₂ (electroplated) with substrate 100 Ω/cm², and (c) Cu/TiO₂ (electroplated) with substrate 10 Ω/cm².

Table 1 shows the comparison of uncoated and Cu coated TiO₂ solar cells. It was obtained the efficiency of the Cu coated TiO₂ film solar cell is higher than uncoated TiO₂ solar cells. This is caused by the high Schottky barrier of metals deposited on the TiO₂ that enables them to act as electron traps, facilitating electron capture. According to Hailing [20], electron capture by metals increases electron-hole pair separation lifetime by hindering the recombination of electron-hole pairs and promoting.
TABLE 1. Comparison of uncoated TiO₂ and copper coated TiO₂ performances.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Structure of solar cells</th>
<th>Intensity (mW/cm²)</th>
<th>ITO Resistance (Ω/cm²)</th>
<th>Short Circuit Current, Iₑ (mA)</th>
<th>Open Circuit Voltage, Vₑ (V)</th>
<th>Fill Factor, FF</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ITO/TiO₂/PVA:LiOH/Al</td>
<td>4.39</td>
<td>100</td>
<td>0.01</td>
<td>0.1</td>
<td>0.24</td>
</tr>
<tr>
<td>2</td>
<td>ITO/TiO₂/PVA:LiOH/Al</td>
<td>37.48</td>
<td>100</td>
<td>0.04</td>
<td>0.1</td>
<td>0.38</td>
</tr>
<tr>
<td>3</td>
<td>ITO/TiO₂:Cu/PVA:LiOH/Al</td>
<td>4.39</td>
<td>100</td>
<td>0.12</td>
<td>0.8</td>
<td>0.35</td>
</tr>
<tr>
<td>4</td>
<td>ITO/TiO₂:Cu/PVA:LiOH/Al</td>
<td>37.48</td>
<td>100</td>
<td>0.90</td>
<td>0.8</td>
<td>0.41</td>
</tr>
<tr>
<td>5</td>
<td>ITO/TiO₂:Cu/PVA:LiOH/Al</td>
<td>4.39</td>
<td>100</td>
<td>0.10</td>
<td>0.5</td>
<td>0.37</td>
</tr>
<tr>
<td>6</td>
<td>ITO/TiO₂:Cu/PVA:LiOH/Al</td>
<td>37.48</td>
<td>10</td>
<td>6.00</td>
<td>0.5</td>
<td>0.61</td>
</tr>
</tbody>
</table>

TiO₂: Cu = Cu coated TiO₂

electron transfer processes.

Table 1 also clearly shows that the increase of solar cells efficiency with reducing internal resistance. The effect of improving efficiency by reducing ITO resistance can be shown in sample 3-6. It is also observed that Iₑ, Vₑ, and FF are improved with decreasing resistance of substrate. It suggested that ITO resistance attributed to internal resistance which was important to improve performance of solar cells [19].

CONCLUSION

We have successfully developed low cost solar cells with a solar to electric energy conversion efficiency about 3.73%. Our solar cells consist of TiO₂ electrode was made using spray technique, Cu coated TiO₂ film, polymer electrolytes and Al counter electrode. These solar cells have shown better performance in terms of short circuit current (Iₑ), open circuit voltage (Vₑ), fill factor (FF) and energy conversion efficiency. Copper deposited in space between TiO₂ acts as trap of electron to minimizing electron-hole recombination and to electron path and lead to rapid electron transfer. Therefore, the our solar cells showed significant potential as a low cost alternative to currently widely-used.

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