

Performance Improvement of Cu₂O/TiO₂ Heterojunction Solar Cell by Employing Polymer Electrolytes

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Abstract -- We report performance improvement of Cu₂O/TiO₂ heterojunction solar cells by employing polymer electrolyte which containing Li⁺ ion. Cu₂O were deposited on a TiO₂ film using the electrochemical deposition (ECD) method. Based on the SEM result, the particles of Cu₂O seemed to penetrate the space between TiO₂ particles and were deposited close to the TiO₂/indium tin oxide (ITO) substrate interface. The film was confirmed to be a Cu₂O/TiO₂ composite by XRD, SEM and EDX measurements. We assumed that polymer electrolyte, containing Li⁺ ion, improving electronic transport by diffusing to TiO₂ conduction band. Moreover, the counter electrode was formed by evaporating Al for I-V characterization, and the fabricated cell showed improving of photovoltaic properties.

Index Term-- polymer electrolyte, Cu₂O/TiO₂, heterojunction solar cells, electrochemical deposition.

1. INTRODUCTION

TiO₂, an n-type semiconductor with a bandgap energy of 3.0–3.2 eV, has attracted a great deal of attention in solar energy applications [1-3] due to its relatively high efficiency [2-4], easy fabrication [5], low cost [6,7], low toxicity [7], and long term stability [8]. On the other hand, cuprous oxide (Cu₂O) is a non-toxic p-type semiconductor with direct band gap of 2.0 eV, which makes it a promising material for solar light absorption [9-11]. Cu₂O/TiO₂ p-n junction has already developed as potential solar cells [12–15]. The Cu₂O with absorption in visible light spectrum, associated with the favorable band energy alignment with TiO₂, leads to an efficient pathway for charge transfer. Moreover, low cost of TiO₂ and Cu₂O provides the feasibility to build large scale photovoltaic devices.

Very recently, Zainun et al. reported about Cu₂O/TiO₂ heterojunction solar cells made by using electrochemical deposition (ECD) [12]. They demonstrated simple and low cost of solar cells by used ECD methods. However, its efficiency is still lower (less than 0.1%). We assumed that its electron transport, especially in Cu₂O/TiO₂ junction, was still poor. On the other hand, we assumed that electrode pair should be used different metal. It is very important because it correspond to electronic transport [16-18].

Many study about TiO₂ based solar cells reports that the use of polymer electrolyte containing cation, such as Li⁺, could improve the performance of solar cells. In this case, Li⁺ ion plays an important role in the improvement of

photoelectric performance of solar cells. As we know, ion diffusion, which diffused in conduction band of TiO₂, has strongly correlated with electron transport in TiO₂ network. Moreover, the small-radius Li⁺ could deeply penetrate into the TiO₂ film and form an ambipolar Li⁺-e⁻ with the electrons in the conduction band of TiO₂, which increases the transport speed of electrons innanocrystalline TiO₂ network and enhances the short current of solar cells [16-18].

In this study, we report the improvement efficiency of Cu₂O/TiO₂ heterojunction solar cells by employing polymer electrolytes, which containing Li⁺ ion. Improvement of our solar cells may caused by using of polymer electrolyte as electron transport medium. In this research, Cu₂O/TiO₂ composite thin films were generated through a combination of electrochemical deposition (ECD) and spray methods, and a cell was fabricated by forming metal electrodes on the film. Through ECD, we observed that the particles of Cu₂O penetrated the nanoporous layer of the TiO₂. The structural of the films were also characterized, and the photo response of the cell was measured.

2. EXPERIMENTAL PROCEDURES

The ITO-coated glass substrate (1 cm²) was sonicated in water for 15 min, followed by 70% alcohol for 30 min. A suspension was prepared by dispersing 10 g TiO₂ in 10 mL of water and mixing with a magnetic stirrer for 45 min. The TiO₂ suspension was sprayed on the substrate at a temperature of 150°C [19]. The spray process was repeated 20 times. The resulting thick film of TiO₂ was heated on a hotplate 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 TiO₂ particles and the ITO.

The deposition of Cu₂O on the TiO₂ film by ECD was accomplished using an aqueous solution containing 1 mol/L copper (II) sulfate in 20 mL of pure water. The plating bath was operated at temperatures 95°C and the plating current was maintained at 300 mA. A copper rod of 99.99% purity with length dimensions of 5 cm was used as the anode. The electroplating voltage was 5 V, the deposition time was 25 s, the anode-cathode separation was 15 cm, and the pH was 4.6.

The polymer electrolyte was prepared by dissolving 0.5 g of LiOH in 10 mL of water and adding 0.8 g of polyvinyl acetate (Bratachem, Indonesia). The mixture was

stirred and heated to 110 °C for 1 hour to produce a gel-like electrolyte. The electrolyte was manually applied to the Cu₂O/TiO₂ layer and an aluminum electrode was added.

The crystal structures of the films were analyzed using Cu K α radiation in a PW1710 X-ray diffractometer (XRD), and the patterns were recorded between 20 and 80° (2 θ). A scanning electron microscope (SEM) (JEOL JSM-6360LA) operating at 20 kV was employed to investigate the morphology and elemental analysis of the films. Device performance was measured using a current-voltage (I-V) meter (Keithley 617). Measurements were obtained in the dark and under xenon lamp illumination. Moreover, light intensity was measured using a luxmeter (Lutron LX-101).

3. RESULTS AND DISCUSSIONS

Chemical reaction which occurred in this experiment was formation of copper nanoparticle and formation of Cu₂O. The formations of Cu₂O on ITO electrode were caused by oxidation of Cu which following reaction 1 [21-24].



The morphology and structure of Cu₂O/TiO₂ film was determined using scanning electron microscope and electron dispersive X-ray analysis. The particles are sub-micrometer in size, with a minimum value of approximately 192 nm. Figure 1(a) and (b) are a micrograph of the TiO₂ and Cu₂O/TiO₂ electrode. Cross sectional of TiO₂ film is smooth and uniform with equally distributed nanometer sized grains. According to the theory of Usami and Ozaki the grains could also improve conversion efficiency through multiple scattering events [20]. The porous TiO₂ electrode formed using the spray method provides pore sizes of 50-300 nm and a thickness of 5-6 μm . Figure 1(b), which was morphology of Cu₂O/TiO₂ film, illustrated that Cu₂O nanoparticles take place in the space between TiO₂ particles. Inside the film there is not much difference in grain size between TiO₂ and Cu₂O. On the other hand, Figure 1(c) depicts our design of solar cells which employed polymer electrolyte as electron transport medium.

At inset of Figure 1(b), the substrate side shows the colors of Cu₂O turned orange after its was deposited. Figure 1(b) depict the Cu₂O seemed to grow at space between TiO₂ particle and was mainly deposited near the TiO₂/ITO interface. We assumed that Cu₂O progressively filled the pore of TiO₂ from the bottom, as shown in inset of Figure 1(b). Deposition process of Cu₂O in TiO₂/ITO interfaced was similar with Zainun et al result [12]. It is also shown that the diamond-shaped Cu₂O grains are larger than the TiO₂ particles and make contact with each other. It is assumed that p-n junction has been formed by TiO₂ and Cu₂O.

Figure 2 shows X-ray diffraction patterns for Cu₂O/TiO₂ composite films. All of the peaks observed for TiO₂ can be attributed to the TiO₂ anatase structure, and the peaks observed for Cu₂O can be attributed to the Cu₂O cubic structure. For the composite film, in addition to the TiO₂ peaks, Cu₂O peaks were also observed. On the other hand, Figure 2 is also depicting the presence of copper (Cu) nanoparticle in Cu₂O/TiO₂ composite.

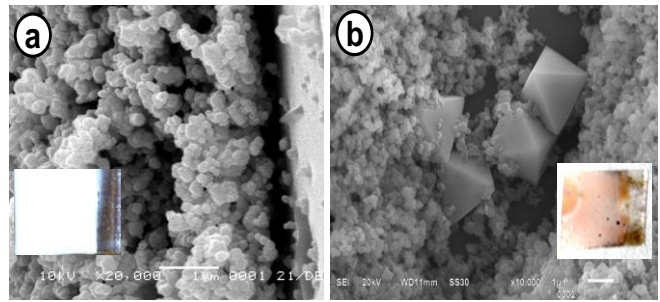


Fig.1. (a) SEM image of TiO₂ film, (b) SEM images of deposited Cu₂O on TiO₂, (c) model of the Cu₂O/TiO₂ film structure.

The presence of Copper (cu) also probably made highly Schotky junction which can inhibit electron-hole recombination in Cu₂O or TiO₂ surface. In this case, Cu₂O/Cu or TiO₂/Cu junction also play significant role to enhance current densities and improving performance of our solar cells [25-31].

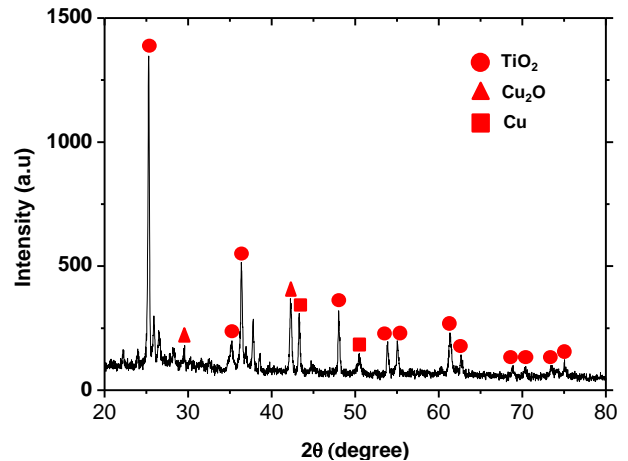


Fig. 2. X-ray diffraction patterns of Cu₂O/TiO₂ composite films.

Elemental analyses of TiO₂ films based on EDX analysis were also performed using the JEOL JSM-6360LA. Figure 3 contains the EDX spectra of Cu₂O/TiO₂ film. The peaks in figure 3 correspond to Ti, O and Cu demonstrating that the TiO₂ films were successfully coated with Cu₂O to the extent of 48.94%, 36.40, or 14.66%.

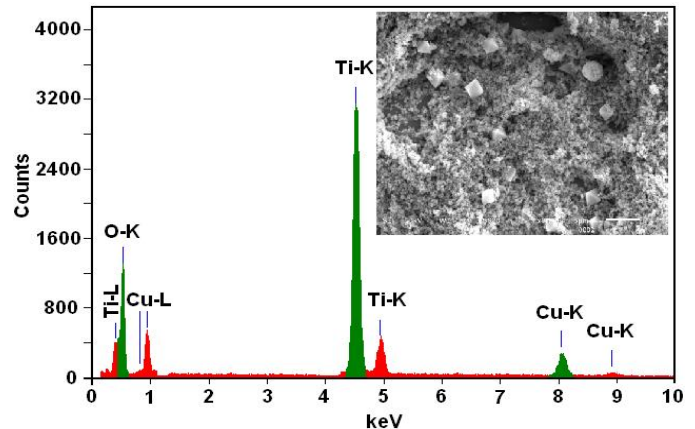


Fig.3. Elemental analysis of Cu₂O/TiO₂ films.

Figure 4(a) depicted our solar cells structured which employing polymer electrolyte with Li^+ ion. Moreover, Figure 4(b) and 4(c) shows the photovoltaic behavior of the $\text{Cu}_2\text{O}/\text{TiO}_2$ composite films measured during illumination through the indium tin oxide (ITO) glass substrate. One sample with different intensity were prepared and measured. The xenon lamp light intensity was varied at $4.39 \text{ mW}/\text{cm}^2$ and $37.48 \text{ mW}/\text{cm}^2$ for all of the measurements. For the low intensities, the short-circuit current was $0.05 \text{ mA}/\text{cm}^2$, the open-circuit voltage was 0.85 V , fill factor was 0.40 , and the efficiency was 1.05% . On the other hand, high intensities has the short-circuit current was $1.28 \text{ mA}/\text{cm}^2$, the open-circuit voltage was 0.86 V , fill factor was 0.56 , and the efficiency was 1.05% . We believed that p-n junction was formed, with the Cu_2O was acting as ap-type semiconductor and TiO_2 was acting as an n-type semiconductor. This structured possible occurred because the contact between TiO_2 and Cu_2O was shown in Figure 3(b).

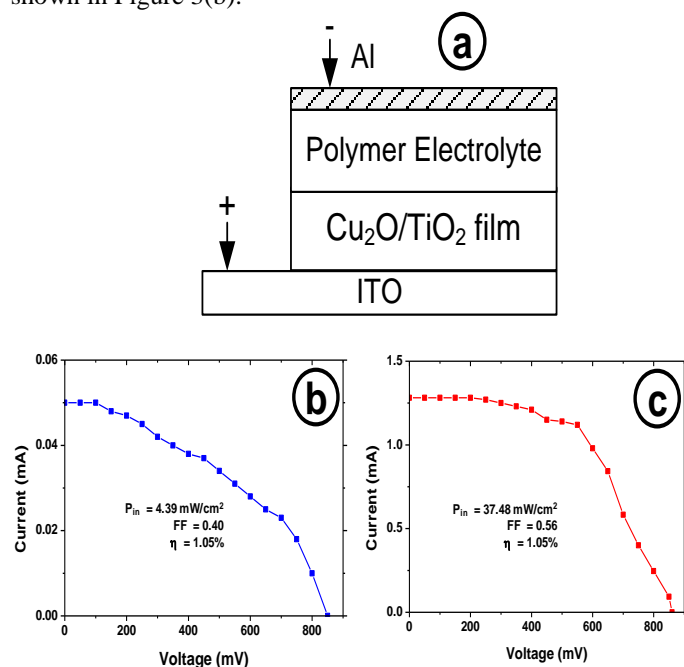


Fig.4. (a) Structure of $\text{Cu}_2\text{O}/\text{TiO}_2$ solar cells and position of the electrodes for the I-V measurement, and (b) I-V curves for $\text{Cu}_2\text{O}/\text{TiO}_2$ films with different intensity.

In this study, we employ a polymer electrolyte containing Li^+ to improve performance of $\text{Cu}_2\text{O}/\text{TiO}_2$ solar cells. The use of a gel polymer electrolyte with a conductivity of $0.16 \text{ S}/\text{cm}$ increased the speed of electron migration in TiO_2 and enhanced the short-circuit current and open-circuit voltage of the solar cells [16,17]. According to Wang et al. [18], Li^+ ion creates new trapping states that contribute to electron injection into the TiO_2 conduction band. Increases in electrolyte conductivity increase the short-circuit current. However, in this study conductivity optimization was not performed.

4. CONCLUSIONS

A $\text{Cu}_2\text{O}/\text{TiO}_2$ heterojunction solar cell which was employing polymer electrolyte was successfully fabricated

with a power conversion efficiency of 1.05% . Polymer electrolyte containing Li^+ ion provide significant photovoltaic response and have the potential to be used as electronic transport in solar cells. This may lead to high efficiency and lower costs for $\text{Cu}_2\text{O}/\text{TiO}_2$ heterojunction solar cells.

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