The effect of Cu$_2$O thickness in Perovskite Solar Cell to Power Conversion Efficiency and Its Stability

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Abstract. Perovskite Solar Cell (PSC) methylammonium halide (CH$_3$NH$_3$PbI$_3$) base is one of promising solar cell that has inexpensive materials, relatively simple and versatile fabrication high power conversion efficiency (PCE). However, perovskite CH$_3$NH$_3$PbI$_3$ has relatively low stability due to very sensitive to polar solvents such as water, where this compound will easily decompose into PbI$_2$ quickly. Some attempts have been made by researchers to increase the stability for example by adding Hole transport material (HTM) to prevent corrosion of the sensitizer, enhance the resistance to degradation CH$_3$NH$_3$PbI$_3$ and improve the stability against moisture. Cuprous oxide (Cu$_2$O) is ones of p-type semiconductor with low electron affinity and very high hole mobility that is a potential for hole transport material in heterojunction based solar cells. The aim of this research is to investigate the effect of Cu$_2$O thickness as HTM in PCE and stability of perovskite solar cell. The electron transport layer (ETL) of TiO$_2$ was synthesized by a screen-printing method on fluorine tin oxide (FTO) substrate. Perovskite CH$_3$NH$_3$PbI$_3$ was deposited on ETL by one step spin coating, while Cu$_2$O was synthesized by Chemical Bath Deposition (CBD) on another FTO substrate with 5 times and 10 times dip. The stability of PSC measured by a comparison between PCE after synthesized and after stored for two months. The increasing of HTM Cu$_2$O Thickness raise the PCE and stability of PSC.

Keywords: PSC, HTM, Cu$_2$O, thickness, stability.

1. Introduction
Perovskite solar cells (PSC) have attracted much attention of photovoltaic technology in recent years [1] due to its good capability of the solution process, high carrier mobility, good optical properties, and large absorption coefficients [2]. In general, the design of PSC consists mainly of three components: compact layer, perovskite layer and HTM (Hole Transport Material) layer [3]. In the PSC architecture, the compact layer quality plays an important role for the transport electrons in perovskite devices [4]. The compact layer acts as a selective collection layer of electrons and a blocking layer of holes in solar cells that have an important influence on the performance of photovoltaics [5]. One attention focused on electron transport layer materials to obtain films with high carrier mobility,
suitable conduction bands, and good compact morphology in order to improve the efficiency of PSC [1].

PSC is one of the most promising candidates for obtaining cheap and easy solar cells fabrication. This is because the perovskite material can be easily manufactured by a simple method such as spin coating or dip coating. The discovery of the first perovskite solar cell by Kojima, et al. with a 3.5% efficiency [6]. In 2012 found a solid-state dye-sensitized solar cell with 10.2% efficiency by Chung, et al. used CsSnI3 as sensitizer and hole conductor [7]. In the same year, Lee, et al. reported the use of N719 as a sensitizer and perovskite CH3NH3PbI3 on the Al2O3 layer yielded a 10.9% conversion efficiency [8]. From the results of this invention gave birth to a new era of perovskite solar cell. In the last five years, conversion efficiency has increased to 15% in 2013 [9], to 20.1% in 2014 [10].

In general, the Perovskite solar cell has the formula ABX3, where A is methyl ammonium, B is Pb2+ or Sn2+ and X is halogen elements Cl, Br, and I. The perovskite optical properties can be tuned by varying the concentration ratio between halogens. Synthesis of perovskite solar cell can be done by one stage or two stages methods. For one stage synthesis, CH3NH2I with PbI2 is mixed together with γ-butryolactone, N, N-dimethylformamide (DMF), or dimethyl sulfoxide (DMSO) at a given temperature and time. The highest efficiency achieved by the one stage method is 19.3% in the perovskite CH3NH3PbI3.xClx system. In two stages of synthesis, PbI2 is coated first and then CH3NH2I. In general, the two-stage method has better efficiency [10]. Another method is vacuum deposition [11].

One of the weaknesses of perovskite is its relatively low stability, so its efficiency decreases with time. This is because of CH3NH3PbI3 is very sensitive to polar solvents such as water, where this compound will easily decompose into PbI2 quickly. Some attempts have been made by researchers for example by adding hole transport material (HTM) to prevent corrosion of the sensitizer and also to improve the stability against moisture.

The Cu2O semiconductor is a p-type semiconductor that is considered a promising material for the manufacture of low cost solar cell applications, therefore cuprous oxide semiconductor (Cu2O) one of a potential candidate for replacement of spiro-OMeTAD [12]. The Cu2O semiconductor has several advantages, such as can be used as a semiconductor material, non-toxic, relatively easy synthesis process, cheap production cost and energy band gap can be used for solar cell energy conversion with band gap 2.137 eV. Various techniques of Cu2O file synthesis is continue developed by simple methods such as Chemical Bath Deposition (CBD). However, the investigation of Perovskite Solar cell (PSC) stability is relatively rare. Therefore, in this report, we investigate the stability of PSC at different Cu2O thickness. The research opportunity about PSC is still wide open before wide application.

2. Materials and Methods

2.1. Materials

TiO2 nanoparticles, Sodium Dodecyl Sulphate (SDS), Polyethylene Glycol 6000 (PEG 6000), Acetylacetone and distilled water for ETL TiO2 paste. Hydroiodic acid, Monoethanolamine C2H3NO (MEA), Hydriodic acid 99.95% (Sigma-Aldrich), DMF (dimethylformamide), DMSO, PbI2 99% (Sigma-Aldrich), Methylamine (Sigma-Aldrich) for perovskite materials. Fluorine doped Tin Oxide (FTO) (Sigma-Aldrich) as a substrate. Deionized Water, Acetone, Ethanol C2H5OH (EtOH) to wash the substrate and Diethyl ether as an anti-solvent. NaOH, CuSO4 and Na2S2O3 as materials for HTM Cu2O.
2.2. **Methods**

2.2.1. **FTO substrate leaching**

FTO leaching was performed using three solutions. First, the FTO was immersed in acetone and then in Ultrasonic bath for 10 minutes. Then, the substrate immersed in ethanol in an ultrasonic bath for 10 minutes and finally cleaned by DI water.

2.2.2. **Synthesis of TiO₂ paste**

The solution for making TiO₂ paste is prepared by dissolving SDS and PEG 6000 into distilled water and then stirring until homogeneous. Then acetylacetone was added and the stirring process is continued until the homogeneous solution. TiO₂ nanoparticles were then spilt with the prepared solution and the ETL coating was made by screen printing using an FTO substrate. The FTO/TiO₂ film is then calcined at 450 °C for 2 hours.

2.2.3. **Synthesis of CH₃NH₃I**

The CH₃NH₃I powder is made by mixing Hydroiodic acid and methylamine then stirred at 0 °C for 2 hours. After 2 hours, the solution evaporated at 50 °C. to form a precipitate. The resulting precipitate then washed by diethyl ether stirred for 30 minutes (for 3 times) then filtered to form a white powder precipitate. The powder furnace for 24 hours at vacuum and dried at oven at 50 °C for 1 hour.

2.2.4. **Synthesis of CH₃NH₃PbI₃ and fabrication of FTO/TiO₂/CH₃NH₃PbI₃**

The CH₃NH₃I solution was made by mixing CH₃NH₃I powder, PbI₂ powder, DMF and DMSO stirred for 1 hour. The solution deposited on the ETL TiO₂ layer using a spin coating method. The FTO/TiO₂/CH₃NH₃PbI₃ film was then preheated for 60 seconds at a temperature of 40 °C and grounded at 100 °C.

2.2.5. **Synthesis of Cu₂O**

Synthesis of Cu₂O film was done by dip method using first and second solution. The first solution is 1M NaOH at a temperature of 70 °C, while the second solution is mixing between 1M CuSO₄ and 1M Na₂S₂O₃. The FTO substrate was immersed in the first solution and the second solution alternately for 20 s in each solution ant 5 times and 10 times.

2.3. **Characterization of samples**

Samples were characterized by means of XRD to see the crystal structure, the solar cell performance of PSC measured with PEC-CEL software and photoresponse characterized by electrometer under ON/OFF light illumination.

3. **Results and Discussion**

3.1. **Diffraction pattern**

XRD characterization used to know the crystal structure of the sample. The diffraction pattern of TiO₂ and CH₃NH₃I showed in Figure 1 (a) then PSC thickness variation of Cu₂O showed in Figure 1. (b).

Based on Fig 1 (a), TiO₂ diffraction pattern have wide and high-intensity peaks that related with small crystal size and good crystallinity respectively. TiO₂ has anatase phase in 10°, 25°, 37°, 47°, 53°, dan 62°. This diffraction pattern similar to TiO₂ synthesized by Ingale, et al. [13]. Based on Rietveld analysis using Rietica, we found the lattice parameters of a=b= 3.7892Å and c= 9.4745 at I 41/a m d space group. In Figure 1 (b) PSC show XRD pattern with different Cu₂O thickness between 5x and 10x dip. The (111) plane at 36.9 increase at the sample 10x dip indicate that Cu₂O layer oriented along (111) direction, while the sample of 5x dip more oriented along (311) direction. Moreover, the crystallinity of 10 x dip higher rather than 5 x dip due to increasing the thickness of Cu₂O film.
Figure 1. The diffraction pattern of (a) CH₃NH₃I and TiO₂ powder (b) PSC with different Cu₂O thickness

3.2. Solar cell performance

PSC performance measured by solar simulator using PEC Cell software with LED 17.32 mW/cm² intensity. PSC performance affected by some parameters such as short circuit current ($J_{sc}$), voltage open circuit ($V_{oc}$), fill factor (FF), and efficiency ($\eta$) than can be derivated from $J$ vs $V$ curve. Every parameter has relation as showed in Equation 1. The J-V curve of PSC at different Cu₂O thickness after fresh synthesized and after stored for two months are shown in Figure 3.1.

$$\eta = FF \frac{V_{oc} J_{sc}}{P_m} \times 100\%$$  \hspace{1cm} (1)

Table 1. The parameter of PSC Performance at different thickness and times

| No. | Sample       | $V_{oc}$ (V) | $J_{sc}$ (mA/cm²) | Fill factor | Efficiency (%) |
|-----|--------------|--------------|-------------------|-------------|----------------|
| 1.  | 5 x          | 1.557        | 0.038             | 0.486       | 0.143          |
| 2.  | 5 x (after 2 month) | 0.719        | 0.027             | 0.495       | 0.048          |
| 3.  | 10 x         | 1.549        | 0.071             | 0.543       | 0.354          |
| 4.  | 10 x (after 2 month) | 1.283        | 0.088             | 0.392       | 0.260          |

Table 1 shows the $V_{oc}$, $J_{sc}$, and efficiency of PSC at 10 x higher than 5x dip for both after fresh synthesized or after two month stored. This phenomenon shows that Cu₂O with thicker layer can increase the efficiency of PSC. Moreover, the stability of PSC improves by increasing the thickness of HTM Cu₂O also affect its stability.
Figure 2. J-V curve of PSC at different Cu$_2$O thickness of (a) 5 times 10 times dip (b) 5 times an 10 times dip after stored in 2 months.

3.3. Photoresponse

Furthermore, the PSC with different Cu$_2$O thickness investigated by measuring photoresponse under light illumination and dark conditions at a particular interval in order to get reproducibility of data with time. the light illumination source is turned on and off at 20 second interval, as shown in Figure 3. Uniform photocurrent responding to each switch-on and switch-off, confirming the excellent reproducibility of the samples. Time response of PSC in both 10x dip and 5x dip is shorter comparing to time decay. This phenomenon due to the illumination of light in PSC more easily to excited from the valence band to conduction band and producing electron-hole pairs \( \text{hv} \rightarrow e^- + h^+ \). At the same time, the hole at the surface will oxidize the oxygen ions to form O$_2$. when the light turns off, time decay longer than time response because the hole that reacted with oxygen ions is difficult to release. This is because the oxidation process also takes times to oxidize [14].

Figure 3. Photoresponse of PSC at different Cu$_2$O thickness in illuminated and dark condition at 20 intervals.
4. Conclusion
In this study, Electron-Transporting Layer (ETL) TiO₂ was successfully synthesized by a screen-printing method on FTO substrate. The hole transporting material (HTM) Cu₂O was successfully synthesized by chemical bath deposition with the variation of Cu₂O thickness. In general, the increasing Cu₂O thickness can improve the power conversion efficiency (PCE) and stability of perovskite solar cell. The photoresponse of PSC with HTM Cu₂O has good stability and reproducibility to each switch-on and switch-off light illumination.

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