The Photovoltaic Performance of Doped-CuI Hole Conductors for Solid State Dye-Sensitized Solar Cells

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Abstract. The iodine doped copper (I) iodide (I₂: CuI) at different weight of iodine dopant have been prepared to investigate its thin films properties and photovoltaic performance. A novel method of mist atomization technique has been used for the deposition of CuI materials. The structural and electrical properties of CuI thin films deposited on the glass substrates were studied. The thin films morphology examined by FESEM shows a variation of crystal size and structure. Brick-like structure with smooth faces and sharp edges were seen for the doped thin films. The CuI thin films at 30 mg of iodine doping shows the highest resistivity of 4.56 x 10¹ Ω cm which caused by the surface traps create by iodine doping. The photovoltaic performance of ss-DSSC on the effect of variation iodine doping was investigated. The ss-DSSC fabricated with undoped CuI materials shows the highest efficiency of 1.05% while the 40 mg I₂ content shows the lowest conversion efficiency of 0.45%. The crystals size of CuI and its degree of crystallization are greatly contributed to the high filling fraction of the porous TiO₂ layer and hence the cells performance.

Keywords: iodine doping; dye sensitized solar cells; hole transport material; pore filling; copper (I) iodide

1. Introduction
Photovoltaic is a promising alternative renewable energy that utilizes the sunlight energy to obtained electricity which has pronounced potential to solve the future energy problem faces worldwide. Dye sensitized solar cells (DSSC) is one of the auspicious technology in the photovoltaic fields. It offers two separate function of light harvesting and charge transport which only uses low cost materials with less stringent procedure in device fabrications [1]. Generally, there are two types of DSSC which are liquid based and solid state DSSC. The efficiency of over 11% has been achieved for DSSC using the redox couple (I⁻/I³⁻) liquid electrolytes [2]. This organic liquid electrolyte is however, highly corrosive, volatile and photo reactive [3]. Besides that, it is also facing a leakage problem due to the interaction between the electrolytes and the sealing materials [3]. Therefore, in the quest of replacing the liquid electrolytes, the solid-state DSSC (ss-DSSC) is the promising option by exploiting the hole conductor to perform the dye regeneration. The recent progress of ss-DSSC has reached the power conversion
efficiency of about 4-4.8% [4-6]. The solid state hole transport material (HTM) includes inorganic and organic material such as CuBr, CuSCN, CuI, poly (3,4-ethylenedioxythiophene) (PEDOT). The inorganic material such as copper based material is likely to be used since it is able to be deposited with low temperature which helps to preserve the dye materials [7]. Furthermore, the CuI has good conductivity of $10^2$ Scm$^{-1}$, which expedites the hole conducting ability [8]. Solid state DSSC employing the inorganic hole transport material (HTM) of copper (I) Iodide have first fabricated by K.Tennakone and had achieved efficiency of 2.4% [9]. Despite the advantages of using HTM to fabricate ss-DSSC, the low efficiency of ss-DSSC compared to the liquid based DSSC is mainly contributed by two factors which are (1) poor light harvesting efficiency due to the thinner electrode use (~2-3 μm) and (b) rapid recombination dynamics between the hetero-junction of ss-DSSC [10].

Some approaches have been proposed to improve the overall efficiency of ss-DSSC. These includes a study done to reduce a recombination rate between the electron, oxidized dye and the hole conductor. The recombination rate can be reduced by improved the pore filling fraction between the nano porous layer of TiO$_2$ and the HTM and also by increasing the hole mobility of the HTM. Various methods had been done to improve the pore filling penetration, including solution casting, soaking in precursor solution, spin coating and many more [9, 11, 12].

Therefore, in this research, we are targeting to study the effect of doped hole conductor which in this case is copper (I) iodide (CuI) to the photovoltaic performance of TiO$_2$/dye/CuI solar cells. In this paper, the iodine is chosen as the dopant that act as an electron acceptor that creates holes in the valence band [13]. The anionic nonmetal dopants are favorable than cationic dopants in this case, because the related impurity states are near the valence band edge and do not act as charge carriers [14]. Furthermore, their function as recombination centers might be minimized as compared to cation doping [14]. Other than that, this research also proposed a new method to deposit hole conductor which is by mist atomizer technique that will hope to improve the pore filling problem between the porous layer of dyed TiO$_2$ and HTM. The I$_2$ dopant concentrations were varied and the ss-DSSCs were fabricated at different dopant concentration. The thin film characteristic which includes surface morphology and electrical properties at different doping concentration were studied. Then, further investigation was done to see the doping effect to the photovoltaic performance of TiO$_2$/dye/CuI solar cells.

2. Experimental Details

2.1 Preparation of CuI thin film

Glass substrates of 2.5cm x 2.5 cm were used as the substrate for the CuI deposition. The glass substrates were cleaned by using sonication in acetone, methanol and de-ionized water respectively for 10 min. The deposition of CuI films were taken at room temperature by atomization technique. Mist-atomization is a process similarly known as spray pyrolysis which involves the process of spraying precursor solution onto heated surface and the constituents react to form the intended products [15]. The CuI solution was formed by mixing the precursor of copper (I) iodide powder (ALDRICH, 98%) with acetonitrile as a solvent. All chemicals were used without any further purification. The iodine which acts as dopant was varied at 10, 20, 30 and 40 mg. The prepared solutions were stirred for 3 hours at room ambient condition. Before the deposition, the substrates were preheated at 50°C in the furnace before the deposition process. This solution was then deposited by mister atomizer to form fine droplets using argon as a carrier gas. The solution volume sprayed was 50 ml for all samples. Then, after the completion of the deposition process, the films were heated for about 5 min at 50°C to evaporate the solvent. All other parameters, including, the flow rate, solution molarity, height between substrate and nozzle were kept constant during the deposition to obtain a uniform thin films throughout the experiment process.
2.2 Fabrication of TiO$_2$/dye/CuI solar cells

The indium tin oxide (ITO) coated glass (10 Ω /□) was used as the conducting substrate. The mesoporous layer of TiO$_2$ was coated on the ITO coated glass by the following method. The TiO$_2$ paste was made by adding 0.6g TiO$_2$ nanopowder (<25nm, Sigma Aldrich) to the 5 ml absolute ethanol (99%). Then, 200 µl of titanium isopropoxide (TTIP, 99.99%) and 0.24 g of polyethylene glycol (PEG) 20000 were added and the mixture was stirred for 1 day to obtain a well dispersed solution. The TiO$_2$ deposition was carried out by spin coating technique at 500 rpm and 2000 rpm for 15s and 45s respectively. The TiO$_2$ film was then annealed at 450 °C for 60 min. The TiO$_2$ thin film was immersed into an ethanolic solution of 0.5mM N719 dye and was kept at room temperature for 24 hours. The CuI was deposited onto the dyed TiO$_2$ thin film at varied doping concentrations of 10, 20, 30 and 40 mg. The Au sputtered ITO coated glass substrate was used as the counter electrode the device active area is 0.28cm$^2$.

2.3 Characterization of CuI thin film and TiO$_2$/dye/CuI solar cells

The characterizations of CuI thin films were done for structural and electrical properties. The surface morphology of the films was observed with a field emission scanning electron microscope (JEOL JSM- J600F. The electrical properties of CuI thin films have been characterized by 2 point probe current-voltage (I-V) measurement by solar simulator CEP 2000 Spectral Sensitivity Analyzing System. Au was used as metal contacts for I-V measurement and deposited using sputter coater (EMITECH K550X). The DSSCs performance was measured using solar simulator device (CEP 2000). The current density-voltage ($J$-$V$) characteristics of the solar cells were measured under illumination at 100 mW/cm$^2$ by using an AM 1.5 solar simulator CEP 2000 Spectral Sensitivity Analyzing System. All of the measurements were done in room ambient.

3. Results and Discussion

3.1 Surface Morphology and Electrical Properties of CuI Thin Film

Fig. 1 shows surface morphology of SEM images of CuI thin films at various doping concentration for undoped and doped thin films. From the figures, it could be seen that the surface morphology of CuI films are crystalline in nature. The undoped thin films in fig. 1 (a) shows a good uniformity with crystal grains of about 80 nm – 150 nm. When the CuI solution was doped from 10 mg to 40 mg, there morphology of all the doped thin films was very much affected by the doping process. The SEM images of doped films revealed that there are existence of brick – like crystals with smooth facets and sharp corners. For 10 mg and 20 mg, the crystal grains are much larger than the undoped films. The 20 mg films show poor uniformity of films by having large and small CuI brick-like crystals in the films. When the I$_2$ dopant increases to 40 mg, the films composed of small brick-like crystals with sharp edges with sizes of about 75-90 nm compared to other doping concentration. By comparing between the undoped and doped thin films, the undoped thin films had a grain crystal structure of CuI while the doped thin films generally had brick – like crystals with smooth facets and sharp corners structures. The reasons of this to happened is due to the CuI nuclei formed simultaneously when the iodine concentration was higher, which preferred the growth of the integrated polyhedral CuI crystals on the surface [16]. The CuI crystal size obtained in this research was in the good agreement by Y. Yan et.al which also used spraying method for CuI deposition [17]. For application as a hole conductor in ss-DSSC, the pore penetration of HTM into TiO$_2$ which will limit the efficiency of the device. There are several ways studied by other researchers to overcome the pore penetration issues, including by using crystal growth inhibitor and melt infiltration [18-21]. The used of crystal growth inhibitor to the precursor solution might be tedious since it may change the properties of the deposited materials. While, the melt infiltration technique is not suitable for CuI since it has very high melting temperature of 878K [22]. Therefore, we proposed a new deposition method of CuI by using mister atomizer that hope to lessen the pore filling problem in ss-DSSC.
The effects of iodine doping of CuI thin films to the electrical properties are presented in fig. 2. The electrical measurement of CuI films were carried out by using 2 point probe I-V measurement with a constant voltage in the range of -5V and 5V. The metal contact used for the measurement is aurum (gold). From the I-V curves the resistivity, $\rho$ of CuI thin film was calculated using following equation (1):

$$\rho = \left(\frac{V}{I}\right) \frac{wt}{l}$$

where $V$ is supplied voltage, $I$ is measured current, $t$ is the film thickness, $w$ is the electrode width and $l$ is the length between electrodes.

Figure 2 shows the plot of resistivity of CuI films deposited at various doping concentration. It is observed that the resistivity first increased with increased of doping concentration up to 30 mg and then decreased at doping concentration of 40 mg. The resistivity of CuI thin films at various doping concentration showed resistivity ranging from $1.8 \times 10^{-1}$ $\Omega$cm to $4.56 \times 10^1$ $\Omega$cm. The p-type conductivity of CuI is depends on the excess of iodine in the stoichiometric excess which due to the acceptor-type copper vacancies ($V_{Cu}$). In this investigation, the doped thin films have much higher resistivity compared to the doped thin films. This is because as the $I^-$ atoms increases consequently the increasing of hole concentration, the number of free electron carrier is reduced due to the attraction between the electron and hole. Hence, the reduction of free charge carrier of electron will significantly increase the resistivity value of the doped CuI thin films. Other than that, the increment of resistivity for doped thin films may be due to surface traps created above the valence band upon the introduction of iodine atoms. The excess of $I_2$ atoms in the lattice will create layer of electrons charge trapping and thus will reduce its mobility. Perera et al had described that the surface trapping sites is 0.2 eV above the valence band of CuI [23]. However, the low resistivity of CuI thin films at 40 mg of doping concentration may be due to the morphology of the thin film itself which was attributed to the improvement of grain boundaries that lead to better less carrier scattering and enhances the carrier mobility of CuI atoms.
3.2 Photovoltaic Performance of Solid State DSSC

The $J$-$V$ curves of TiO$_2$ based DSSC at different weight of I$_2$ dopant was shown in fig. 3. The cells were illuminated under AM 1.5 (100mW/cm$^2$) with cells area of 0.28 cm$^2$. Good rectification behaviour is observed for all samples which are a key function required in solar cells. The summarized photovoltaic efficiency for TiO$_2$/dye/ CuI cells fabricated at weight of I$_2$ content has been tabulated in table 1. The best device efficiency was achieved for undoped CuI thin films with a current density of $J_{SC} = 3.51$ mA/cm$^2$, open circuit voltage of $V_{oc} = 0.65$V, a fill factor of 0.46 and a power conversion efficiency of $\eta = 1.05\%$. While the lowest conversion efficiency was obtained for solar cells device with the I$_2$ content of 40 mg with efficiency of 0.45%. The $J$-$V$ curve for 40 mg of I$_2$ content for the fabricated DSSC is contradictory to the finding of I-V characterization of 40 mg of I$_2$ content in CuI thin film.
Table 1. Photovoltaic performance of TiO2/dye/CuI solar cells at different weight of I2 dopant

| Weight of I2 dopant (mg) | JSC (mA/cm²) | Voc (V) | FF (%) | η (%) |
|--------------------------|--------------|---------|--------|-------|
| 0                        | 3.51         | 0.65    | 0.46   | 1.05  |
| 10                       | 4.30         | 0.54    | 0.38   | 0.87  |
| 20                       | 2.46         | 0.57    | 0.42   | 0.59  |
| 30                       | 2.85         | 0.55    | 0.31   | 0.48  |
| 40                       | 1.54         | 0.64    | 0.46   | 0.45  |

The resistivity curves as shown in fig. 2 shows a low resistivity value of undoped and 40 mg I2 dopant content CuI thin films. However, the same trend was not observed for the DSSC fabricated at different I2 weight. The reasons of this to happen are maybe due to the high crystallization of CuI doped at 40 mg weight of I2. Although, the low resistivity of CuI thin films was observed at this condition, which means high hole transfer yield, these 40 mg of I2 content showed strong tendency to crystallize compared to undoped thin films. The high crystallization of CuI atoms attributed to the formation of crystal boundaries which will act as barriers of hole transport [24]. Even though the 40 mg fabricated DSSC shows low conversion efficiency, the fill factor of this device is same as the DSSC fabricated for undoped CuI which is 0.46 and is the highest fill factor among other samples. Basically, the fill factor is defined by the ratio of the current and the voltage at the maximum power point to the short circuit current and the open circuit voltage. The squareness of the J-V curves indicates low recombination reaction caused by the high conductivity observed for these (undoped and 40 mg of I2 content) CuI thin films. From table 1, it could be seen that, as we increased the amount of dopant, the overall performance of the device was slightly decreased. The main factor contributes to the decrease of cell performance is attributed to the pore penetration of CuI onto the dyed TiO2 layer. The bigger crystallite size of CuI at 10, 20 and 30 mg of I2 content will results poor pore filling of porous TiO2 layer and hence increase the recombination reaction thus less device efficiency was perceived.

4. Conclusion
In summary, we have demonstrated the study on I2 doped CuI thin films deposited by mist atomization technique at different weight of I2 dopant. The surface morphology and electrical properties shows an effect towards the doping process. The FESEM images reveal the structure of brick-like crystal with smooth faces and sharp edges as the I2 amount increases. The undoped and 40 mg doped films shows smaller grain sizes compared to others. This morphology affects the electrical resistivity of the doped films. The smallest resistivity of 10⁴ Ωcm was shown for undoped thin films and sample doped at 40 mg of I2 content. For the electrical device performance, the results shows that, as the I2 dopant increases from 0 mg- 40 mg, the cells efficiency decreases with the highest efficiency obtained for undoped CuI of 1.05%. The strong tendency of CuI crystallization for sample doped at 40 mg I2 weight attributed to the low device performance.

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