The Electrical Properties of TiO_2/Dye/CuI Solar Cell at Different Concentration of CuI as the Hole Conductor

Siti Zawani Binti Roslan, Norulhuda Abd Rasheid
University Technology MARA (UiTM),
40450 Shah Alam, Selangor, Malaysia

ABSTRACT—This research focusses on the performance of solid-state dye-sensitized solar cell by varying the molar concentration of CuI thin film as hole conductor. Nanoporous semiconductor TiO_2 acted as n-type in solid-state dye-sensitized solar cell which is deposited with dye to absorb the light. The correlation between thickness of the thin film and the efficiency of solar cell was investigated. The incomplete pores filling of TiO_2 leads to the bad efficiency due to the increase in recombination and series resistance in solar cell. Thus, mister atomizer method was used to increase the pores filling of TiO_2. The result shows the thickness of thin film and particle size of CuI increase as the molar concentration increases. The efficiency of solid-state DSSC is strongly related to the thickness thin film, filling fraction of TiO_2, and the photon absorption of dye.

Keyword-CuI, mister atomizer, pore filling TiO_2

I. INTRODUCTION

Recently, dye-sensitized solar cells (DSSC) have received international research focus on their high power conversion efficiency and low-cost [1-2]. By using liquid electrolyte it can reach the efficiency around 11.5%. However, by using liquid based DSSC have occurred some problems such as potential leakage, low stability, solvent evaporation and reaction of the sealant with the electrolyte [3-4]. These problems have sparked research in solid-state dye-sensitized solar cell which has solid-state holes transport material by utilizing p-type semiconductor to improve the long time stability of the cell. Bandara et.al was using CuI as hole conductor in their research and reported that the efficiency are 0.12% for dense TiO_2 layer while for dense TiO_2 layer coated with porous TiO_2 layer, the efficiency are 1.74% [5].

The copper compound such as CuI, CuBr, and CuSCN was found suitable to be used in solid-state solution [6]. In this present study, Copper (I) Iodide (CuI) is used as p-type hole conductor. CuI is a p-type high bandgap material of 3.1eV which belongs to group I-VII semiconductors [7] that support of choosing CuI as p-type hole transport materials in solid-state dye-sensitize solar cell. CuI exists in three crystalline phases of α, β, and γ. The high temperature (above 392°C) α-phase of cubic structure is a mix conductor, where the charge carriers is predominantly Cu^{2+} ions [8]. The main problem in solid-state DSSC is this cell suffers a bad contact between the dyed TiO_2 porous film surface and the p-type semiconductor which is CuI [7].

The basic element of dye-sensitized solar cell is a nanostructured material, composed of porous layer of titanium dioxide (TiO_2) and covered with molecular dye that can absorb sunlight. In recent years, TiO_2 has been extensively studied due to their potential applications in a wide range of fields such as solar cell, gas sensors and dielectric capacitors [9]. TiO_2 is preferred material since it has high photocatalytic activity and having a high bandgap of 3.2eV which lies in the near UV region (388nm) [10]. However, TiO_2 has a weakness structure which is the random porous structure. This weakness leads to the undesired characteristic such as low conductivity and charge density that may be caused by the incomplete filling of the porous TiO_2 film.

The technology of deposition techniques such as spin coating and solution casting are not suited well enough since it cannot solve the problems of pore filling of TiO_2 network [7]. M.N Amalina et al. studied the technique to fulfill the porous structure of TiO_2 by using mister atomizer method. The result has shown that the CuI thin film is successfully grown by using the mister atomizer method at different precursor concentration. Thus, in this present study, mister atomizer method was used to overcome the bad contact between porous structure of TiO_2 and CuI. This technique is the same concept of spray pyrolysis which used atomizer to convert the liquid into the form of mist.

In this present study, the different precursor concentration from 0.01M to 0.09M was studied to investigate the performance of solar cell in term of efficiency and the filling of pores TiO_2 structure. The obtain result regarding I-V curve, incident photon conversion efficiency (IPCE), thickness of thin film, surface morphology, and element arrangement in thin film were discussed.

II. EXPERIMENT PROCEDURE

The ITO coated glass is used as a substrate in solid-state DSSC. The ITO was cleaned with acetone, and followed with methanol and finally de-ionized water for 30 minutes each. All stages were put in ultra sonic cleaner and after that, the cleaned substrate was blown quickly by Argon to ensure that the remaining particles were removed. The next step is the preparation of Titanium Dioxide (TiO_2) paste. 99.7% TiO_2 nano powder were added with Absolute Ethanol and stirred for half an hour and then added with 99.99% TTIP. After 2 hours, PEG20000 was added into paste and sonicate the paste for 30 minutes and stirred for 24 hours. After being stirred for 24 hours, TiO_2 paste were deposited onto ITO coated glass by using spin coating technique at 500rpm for 15 seconds and followed by 45 seconds at 2000rpm. The first layer was dried at room temperature before proceed to the second layer. After second layer was done, the thin film was baked at 450^0C for 1 hour to make sure the thin film was dried and solid thus easy for dye absorption. Then the samples were immersed into the dye solutions for 24 hours. In this research, 0.05mM of dye N3 was used and mixed with Absolute Ethanol. Copper (I) Iodide (CuI) powder was used to mix with Acetonitrille at room temperature as preparation of CuI solution. The solutions were stirred for 3 hours before deposited onto TiO_2 layer. The parameters investigated in this present research work are the molar concentration of CuI from 0.01M, 0.03M, 0.05M, 0.07M, and 0.09M. The molarity can be calculated by using following equation (1):

$$Molarity = \frac{grams}{Molecular\ \ Weight}\ X\ Volume \qquad (1)$$

This solution was then sprayed in fine droplets using argon as a carrier gas and all the samples were sprayed in 100ml CuI solutions. The substrate temperature during the depositions was between 70^0C to 80^0C. The last step is cell assembly. The dyed TiO_2 deposited with CuI solution substrate and counter electrode with Pt coating substrate are attached together and sealed with sealant at temperature between 80^0C to 90^0C.

The solar cell has been characterized by current-voltage measurement by using solar simulator (CEP 2000) at the range voltage between -0.1v to 0.7v. The area solar cell under illumination is $0.28cm^2$. Pt was used as metal contacts for I-V measurement and deposited using sputter coater (EMITECH K550X). The IPCE were characterized by CEP 2000. The wavelength for IPCE measurement was measured between 300nm - 800nm. The surface morphology of the films was observed with a field emission scanning electron microscope (JEOL JSM- J600F). The thickness of the thin film is characterized using surface profiler (VEECO DEKTAK 150). The EDS was measured using OXFORD Instrument (X-MAX) attached with FESEM machine. All of the measurements were done in room ambient.

III. DISCUSSION

A. Structure Properties of TiO_2/Dye/CuI Thin Film

The thickness of thin film was measured using surface profiler (VEECO DEKTAK 150). The optimum thickness is important to investigate in solid-state DSSC because it will contribute to the Voc and Jsc which reflect the efficiency of solar cell [11]. From the Table 1, the thickness of TiO_2 thin film is 2.60177um. 0.01M gives the lowest reading of thickness thin film which is 4387.61nm and the highest thickness is 10.16025um at 0.09M concentration.

Table 1: thickness of TiO_2 thin film

Thin film	Thickness (um)
TiO_2	2.60177

Table 1: Thickness of thin film at different molar concentration

Concentration (M)	Thickness (um)
0.01	4.38761
0.03	4.65873
0.05	4.85075
0.07	5.67507
0.09	10.16025

From the results shown in Table 2, the thickness thin film is around 4.3um to 4.8um through 0.01M to 0.05M concentration. At 0.07M, the thickness of thin film is 5.67507um and the thickness is sharply increased at 0.09M. The thicker thin film can increase the resistivity of solar cell due to the less electron movement across the thick layer [11]. Moreover, a thicker thin film also affects the efficiency due to series resistance and incident photon absorption [12]. It is confirm that, as the solution concentration increases, the amount of CuI particles that involves in forming the deposited film increases which lead to the increasing in the film thickness [13]. Besides that, increasing the solution concentration can increase the crystallite size that can cause the increase in thin film thickness [14].

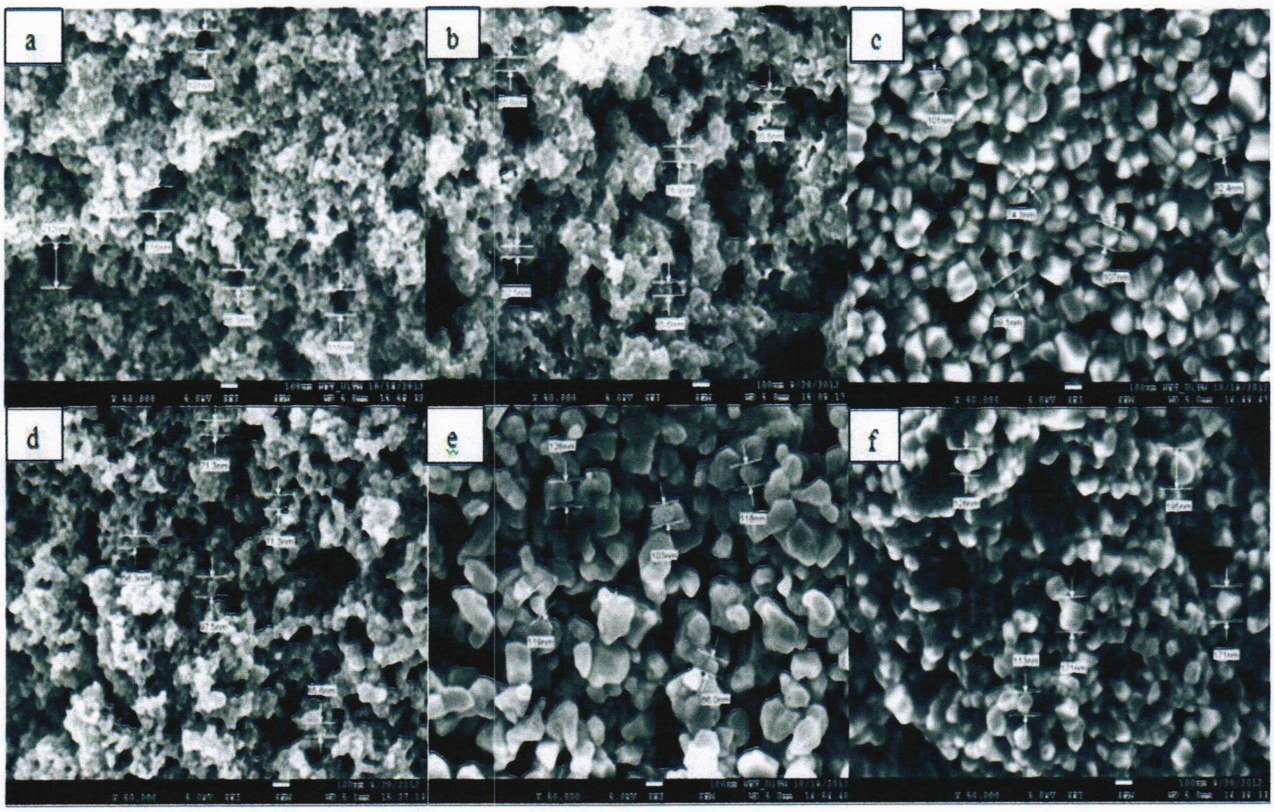

Figure 1: FESEM image of (a) porous TiO_2 thin film, (b) 0.01M, (c) 0.03M, (d) 0.05M, (e) 0.07M, (f) 0.09M

Surface morphology of thin film was measured using FESEM JEOL (JSM-7600F). All the measurements were taken at 5kV with 50000 magnifications. The porous size distribution of TiO2 is varied in the range 86.3nm to 212nm. Figure 1(b) shows the particle size of CuI is around 50nm to 80nm. FESEM image in Figure 1(c) shows the surface was the densest and uniform continuous path compare with Figure 1(b). The particle size also increase which is around 80nm to 100nm and same with 0.05M which is the particle size is around 50nm to 100nm. At 0.07M and 0.09M, the particle size of CuI becomes bigger than porous size of TiO2. The particle size of CuI increases as the molar concentration increases. The result from the FESEM images shows the porous structure of TiO2 is less as the molar concentration is higher. This shows that the CuI thin film is successfully grown by using mister atomizer method at different precursor concentration.

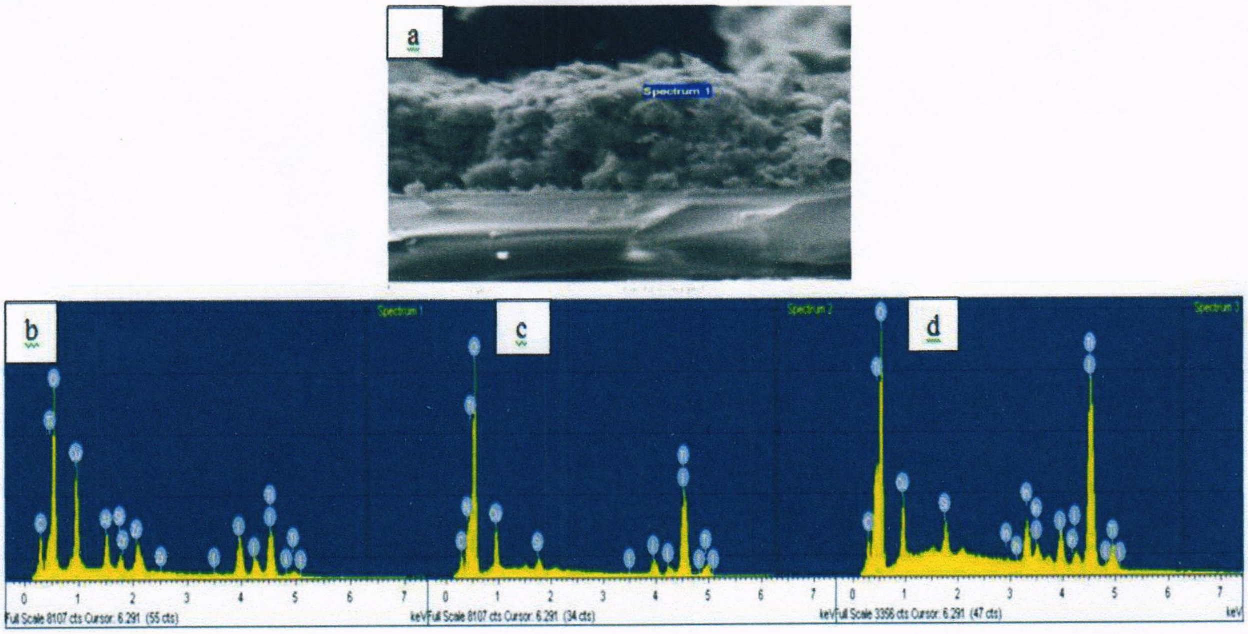

Figure 2: (a) FESEM image of cross sectional of thin film, the EDS spectra of 0.01M at (b) top layer, (c) middle layer, (d) bottom layer

The EDS spectra was taken from cross section of thin film. The spectrum was measured using OXFORD Instrument (X-MAX) attached with FESEM machine. The main reason EDS ware taken is to investigate the element arrangement in the thin film. Figure 2 shows the EDS spectra for 0.01M concentration. The main element found in EDS is Titanium (Ti), Oxygen (O) and Iodine (I). The EDS spectra shows the element arrangement of CuI has in three spectrums which is spectrum 1 is top layer as shows in Figure 2(b), spectrum 2 is in the middle layer (Figure 2(c)), and spectrum 3(Figure 2(d)) is bottom layer of thin film. The EDS spectra show that element CuI is successfully filled the porous structure of TiO_2 by using mister atomizer method. The pore filling is importance to investigate because it relates to the efficiency of solid-state DSSC which is the efficiency of solar cell increased with increasing filling fraction [15].

B. Electrical Properties

The graph of I-V solar cell in Figure 3 is from 0.01M, 0.03M, 0.05M, 0.07M, and 0.09M concentration. Current-voltage (I-V) characteristics were measured using solar simulator (CEP 2000) from -0.1V to 0.7V under dark and illumination.

Table 2 show the I-V characteristic of solid-state dye-sensitized solar cell. The efficiency of solar cell can be calculated by using following equation (2):

$$\eta = \frac{\text{Vmpp X Jmpp}}{\text{Pin}} \text{ X } 100\% \qquad (2)$$

Where Pin is incident light power, Jmpp is current in I-V curve respective to the point of maximum power output, and Vmpp is voltage in I-V curve respective to the point of maximum power output.

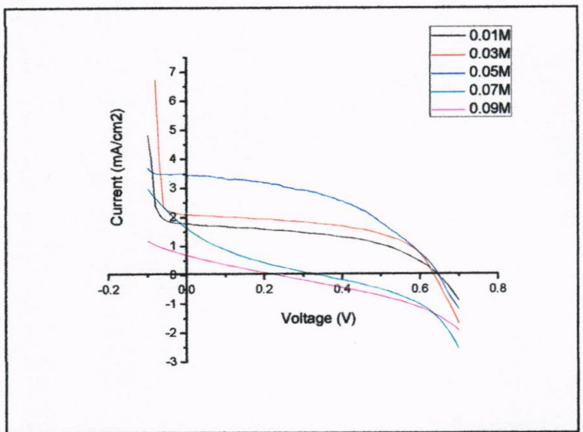

Figure 3: Current-voltage (I-V) curve of solid-state dye-sensitized solar cell under illumination

Table 2: I-V characteristic of solar cell at different molar concentration

Molar Concentration (M)	Jsc (mA/cm^2)	Voc (V)	Fill Factor (FF)	Efficiency (n)
0.01	1.784077	0.646157	0.476279	0.549052
0.03	2.145305	0.638088	0.544369	0.745185
0.05	3.510622	0.650209	0.46132	1.053028
0.07	1.698393	0.363711	0.167756	0.103627
0.09	0.745999	0.255242	0.231464	0.044073

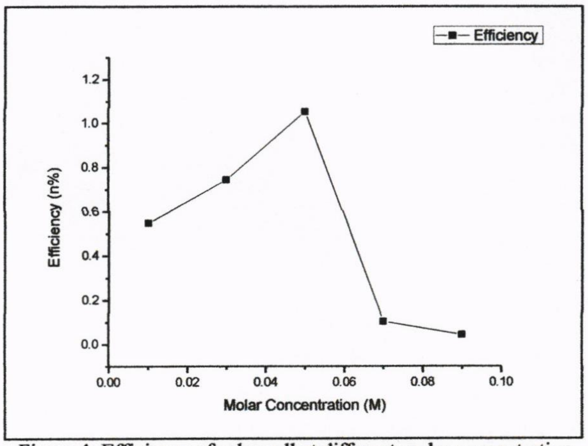

Figure 4: Efficiency of solar cell at different molar concentration

Figure 4 shows 0.05 molar concentration of CuI has the highest efficiency among to the others molar concentration which is above 1%. This result related to the particle size of CuI which is smaller than porous size of TiO_2 surface structure. The FESEM image of 0.05M support to the best result in term of efficiency which is the porous structure of thin film is less compared to 0.01M. The photon absorption of dye also gives the impact to the efficiency which is the higher absorption of dye gives the higher efficiency due to more photons are absorbed near the surface of the CuI films and thus the electron collections are more efficient [15]. Increasing the molar concentration in CuI solution can improve the efficiency of solid-state solar cell as shows in Figure 4 from 0.01M to 0.05M. However, the thickness of thin film also become thicker and makes the efficiency of solar cell becomes lower. At 0.07M concentration to 0.09M concentration, the efficiency of solar cell becomes lower. This factor contributed to the thickness reported earlier. Moreover, the incomplete pores filling because of the bigger particle sizes of CuI also causes an increase in recombination and series resistance and limits the number of dye molecules that can transfer holes in solid-state DSSC [14].

Internal photon to conversion efficiency (IPCE) of the solar cell with wavelength between 300nm to 800nm was measured. The result of IPCE is shown in Figure 5. The graph in Figure 5 shows it had two humps. The first hump is the photon absorption of TiO_2 while the second hump is photon absorption of dye. The wavelength of TiO_2 photon absorption is between 300nm to 450nm and the maximum wavelength photon absorption of dye is 550nm. IPCE is conversion of photon absorption to electric current [7]. At high photon absorption, the thickness of thin film is smaller as shown in Table 1. The lowest absorption photon at 0.09M concentration has the highest thickness of thin film which leads to the lower efficiency that has been discussed. These results contributed to the absorption properties where thicker thin films shows less absorption due to the difficulty of electron movements resulting in high resistivity in thicker thin films [10]. Thus, the result of IPCE are closely related with efficiency of solar cell which is the efficiency is higher when IPCE higher [16].

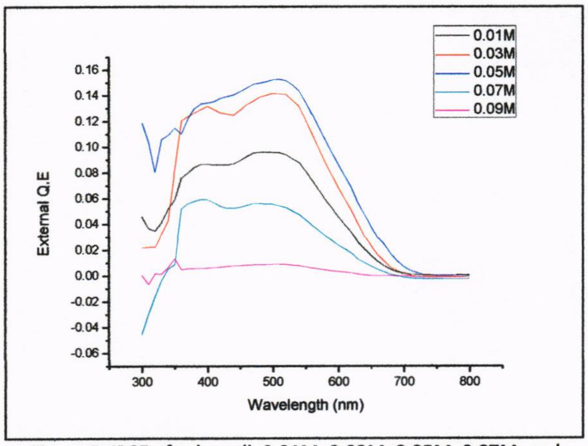

Figure 5: IPCE of solar cell, 0.01M, 0.03M, 0.05M, 0.07M, and 0.09M.

IV. CONCLUSIONS

Solid-state DSSC characteristics were investigated at different precursor concentration. The current-voltage of solid-state dye-sensitize solar cell were investigated by using two point probe I-V measurement. The I-V curve shows the highest efficiency at 0.05M and the lowest efficiency at 0.09M. Increasing molar concentration of CuI gives good efficiency of solar cell due to the filling porous structure of TiO_2 but at the same time increase the thickness of thin film which leads to the poor efficiency because of the less electron movement in the thicker film. The thickness of thin film is related to the solar cell performance which is thicker film leads to the low efficiency of solar cell. Poor filling of CuI into the porous TiO_2 structure also leads to the worse performance of solar cell due to the bad contact between n-type and p-type semiconductor. Increasing the filling fraction may slow the recombination by increasing the separation distance between holes in CuI and electrons in TiO_2 [14] which can increase the efficiency of solar cell.

ACKNOWLEDGEMENT

This study was supported by NANO-ElecTronic Center (NET) and NANO-SciTech Centre of Universiti Teknology MARA, UiTM.

REFERENCES

[1] I-Kang Ding , John Melas-Kyriazi, Ngoc-Le Cevey-Ha, Kethinni G. Chittibabu, Shaik M. Zakeeruddin, Michael Grätzel, Michael D. McGehee,"Deposition of Hole-Transport Materials in Solid-State Dye-Sensitized Solar Cells by Doctor-Blading", *Organic Electronics*, 11 (2010) 1217–1222, 2010.

[2] S. Khemthong, S. Cabaniss, J. Zhao, A. Wang, "Low Cost Silicon Solar Cells with High Efficiency at High Concentrations", *IEEE*, CH2953-8/91/0000-0268,1991.

[3] A.F. Nogueira, C, Longo, M.A De Paoli, "Polymers in dye sensitized solar cells", overview and perspectives, Coord. Chem. Rev. 248,1455-1468, 2004.

[4] A.R. Zainun, M. Rusop, U.Z. Noor, "Photoluminescence Characterization of Nanostructured Copper (I) Iodide (CuI) Incorporatewith Bidentate Ligand*", International Conference on Electronic Devices, Systems and Applications (ICEDSA2010)*, 2010.

[5]J. Bandara, H. C. Weerasinghe, "Efficient solid-state dye-sensitized solar cells fabricated on a compact TiO_2 barrier layer preventing short-circuit current", *Sri Lanka Journal of Physics*, Vol 5 (2004) 27-35.

[6] A. R. Zainun, U. M. Noor, M. Ruso, "Electrical and optical properties of nanostructured copper (I) iodide (CuI) incorporated with ligand agent for dye sensitized solar cell applications (DSSC*)", International Journal of the Physical Sciences* Vol. 6(16), pp. 3993-3998, 2011.

[7] M.N. Amalina, M.Rusop, "Effect of the Precursor Solution Concentration of Copper (I) Iodide (CuI) Thin Film Deposited By Mister Atomizer Method,*" IEEE Symposium on Industrial Electronics and Application*, pp, 440-441, 2011.

[8] M. Rusop, P.M. Sinmame, T. Shirata, T. Soga, T. Jimbo, "Characterization of transparent CUI films and charge generation in dye-sensitized CuI/Dye/$Ti0_2$ solar cells", IEEE, 0-7803-7578-5/02, 2002.

[9] Swati S. Pradhan, S. K. Pradhan, P. K. Barhai, "Structure and morphology evolution of TiO2 films grown by sputtering", *IEEE*, 978-1-4577-2037-6/11, 2011.

[10] Madhusmita Sahoo, Tom Mathews S. Dhara, S. Dash, A. K. Tyagi, "Ultrasonic spray pyrolytic synthesis and characterisation of ZnO-Ti02 nanocomposite thin films", IEEE, 978-1-4673-0074-2/11, 2011.

[11] M.N. Amalina, M.Z Musa, M. Rusop, "Electrical and Optical Properties of Nanostructured Copper (I) Iodide Thin Filmsfor DSSC*", International Conference on Electronic Devices, Systems and Applications (ICEDSA)*, 2011.

[12] Michael D. Irwin, D. Bruce Buchholz, Alexander W. Hains, Robert P. H. Chang, and Tobin J. Marks, " P-Type semiconducting nickel oxide as an efficiency-enhancing anode interfacial layer in polymer bulk-heterojunction solar cells," Proceedings of the National Academy of Sciences, vol. 105, pp.2783–2787, 2008.

[13] Nur Amalina Muhamad, Muhammad 'Atiq Azman, Mohamad Rusop Mahmood, "Effect of the Precursor Solution Concentration of CuI Thin Film Deposited By Spin Coating Method", Advanced Materials Research Vol. 364, pp 417-421, 2012.

[14] Alaa A. Akl, "Effect of solution molarity on the characteristics of vanadium pentoxide thin film", Applied Surface Science 252, 8745–8750, 2006.

[15] I-Kang Ding, Nicolas Te´treault, Je´re´mie Brillet, Brian E. Hardin, Eva H. Smith, Samuel J. Rosenthal, Fre´de´ric Sauvage, Michael Gra¨tzel, and Michael D. McGehee, "Pore-Filling of Spiro-OMeTAD in Solid-State Dye Sensitized Solar Cells: Quantification, Mechanism, and Consequences for Device Performance," *Journal of Advanced Functional Materials*, vol. 19, pp, 2431-2436, 2009.

[16] Meng Ni, Michael K. H. Leung and Dennis Y. C. Leung, "Theoretical Modeling of the Electrode Thickness Effect on Maximum Power Point of Dye-Sensitized Solar Cell", *The Canadian Journal of Chem Eng,* Vol 86, 2008.

[17] Christian Graziani Garcia, Adelino Kaoru Nakano, Cornelis J. Kleverlaan, Neyde Yukie Murakami Iha, "Electron injection versus charge recombination in photoelectrochemical solar cells using cis-[(dcbH2)2Ru(CNpy)(H2O)]Cl2 as a nanocrystalline TiO2 sensitizer", *Journal of Photochemistry and Photobiology A: Chemistry 151*, 165–170, 2002.