GLOBAL ENGINEERS & TECHNOLOGISTS REVIEW
www.getview.org

SYNTHESIS AND FABRICATION OF AN EFFECTUAL DYE SENSITIZED SOLAR CELL

MATHISUTAN MURUGIAH[1], JAMIL HASHIM[2], UMAR NIRMAL[3] and YUHAZRI[4], M.Y.

[1, 2, 3] Faculty of Engineering and Technology
Multimedia University
Jalan Ayer Keroh Lama, 75450, Melaka, MALAYSIA
[1]mathi_suthan@yahoo.com
[2]jamil.hashim@mmu.edu.my
[3]nirmal@mmu.edu.my

[4] Faculty of Manufacturing Engineering
Universiti Teknikal Malaysia Melaka
Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, MALAYSIA
[4]yuhazri@utem.edu.my

ABSTRACT

This paper is the result of an experimental study on using zinc oxide (ZnO) as an alternative material to titanium oxide (TiO_2) in the fabrication of dye sensitized solar cell (DSSC). The zinc oxide thin film was prepared using sol-gel route technique. ZnO powder was annealed separately at 250°C and 500°C. ZnO powder annealed at 500 °C was found to be more effective compared to the one annealed at 250°C. Higher temperature annealing condition has given significant result in producing higher grade ZnO with reduced impurity and increased absorption intensity. Scanning Electron Microscope (SEM), X-ray Diffraction (XRD), Particle Size Analyzer and Energy Dispersive X-ray Spectrometry (EDS) were used to study the microstructure of the material. Fabrication of DSSC was carried out using ZnO porous, natural dye, graphite, sulphuric acid and ITO glasses. Tests were conducted using natural sunlight and the results revealed that the DSSC produced has an efficiency of 25.0%., very comparable with results from other studies. Thus, an effectual DSSC has been achieved.

Keywords: *Indium Tin Oxide, ITO glass, Zinc Oxide, Dye-Sensitized Solar Cell, DSSC.*

1.0 INTRODUCTION

The development of finding clean alternatives to power generation is crucial due to the raising global demand for green energy sources as an alternative to depleted fossil fuels (El-Badri, 2010). Photovoltaic or solar energy is an emerging alternative that has a potential of clean solution to this issue. Moving toward the latest technology, earlier studies were deployed in developing solar cell technology using crystalline. Crystalline materials were thought to have a prospect as an alternative source of energy but it was costly. The idea of thin film materials was later discovered and soon it has captured the attention of many solar cell developers (Olivia, 1998). Dye sensitized solar cell (DSSC) was such an attempt of using thin film materials in solar cell. It was first developed by O'Regan and Gratzel (Lanlan *et al.*, 2010) and later it has attracted more interests due to its low cost and simple fabrication process. This was followed by rigorous studies to improve the cost of solar cell development. Further progress was made with the invention of DSSC using titanium dioxide (TiO_2) thin film, thus, generating a new technology for converting light energy into electrical energy (Lanlan *et al.*, 2010). It has been recorded that DSSC using TiO_2 as a thin film substance showed up to 7.1 % in efficiency (i.e. solar cell output efficiency) under solar illumination with dye photo physics and electrolyte redox chemistry (Yeji *et al.*, 2010).

Currently, TiO_2 material is widely adopted as the best alternative material in producing electrode for the DSSC. DSSC device comprises a large band gap semiconductor nanocrystalline electrode. The band gaps of the bulk TiO_2 are 3.0eV for rutile phase and 3.2eV for anatase phase. The porous TiO_2 film has achieved energy conversion efficiency of about 11.1% (Yeji *et al.*, 2010) and (Tsokos, 2008). In regard to this and due to its high refractive index, TiO_2 have been widely used in painting, coatings, plastics and optical industries (Stucky and Bartl, 2010) and (Reijnders, 2009). Beside TiO_2, investigations on amorphous silica (SiO_2) nanoparticles (particles< 100 nm) have been carried out in determining its performance and level of energy efficiency. However, in considering its environmental effects, research on this material has been aborted as the material is hazardous to mankind (Reijnders, 2009). Further research was conducted to develop another alternative

material for DSSC fabrication using zinc oxide (ZnO) nanoparticles. Findings from the research show that ZnO has the potential to be an alternative electrode material because of its wide band gap (i.e. 3.37eV) which is comparable to TiO_2 material. Moreover, ZnO with flat band potential, higher than TiO_2, is very much beneficial for enhancing the cell's open circuit photo voltage at 60Mv of excitation binding energy (Pawar *et al.*, 2009). ZnO is also known for its electrical and optical properties, low cost, non-toxicity, and relatively low deposition temperature (Shen *et al.*, 2010) making it a promising alternative.

In lieu to the above, the current work initiates to explore on the possibility to develop an alternative material for fabrication a low cost DSSC. Zinc acetate dehydrate was used as a starting or precursor material to producing zinc oxide. This was followed with the study on thin film application. There are several techniques available to produce thin film for the solar cell such as magnetron sputtering, pulsed laser deposition, spray pyrolysis, thermal evaporation and sol-gel route (Musil *et al.*, 2005), (Bao *et al.*, 2005), (Nakaruk *et al.*, 2010), (Shah *et al.*, 2009), (Rani *et al.*, 2008), (Micheal *et al.*, 1982), (Fouad *et al.*, 2006), (Hench and West, 1990). In this work, the study has focused on synthesized zinc oxide powder by using sol-gel route technique. This technique was chosen since it is cheap, processing can be done at low operating temperature while offering high uniformity and easy controlled reaction (Brinker and Scherer, 1990). Microstructure analysis was carried out for two different heat treated samples (i.e. ZnO treated at 250ºC and 500ºC) to determine the annealing condition of the samples. These samples were further analyzed using particle size analyzer, X-RAY Diffractometer (XRD) XPERT-PRO with Cu-Kα radiation (λ=1.54060) and Energy Dispersive X-Ray Spectrometry (EDS). Energy Dispersive X-Ray Spectrometry (EDS) was conducted using a scanning electron microscope (SEM) machine, EVO 50 ZEISS-7636.

Dye is normally used to excite the photon junction semiconductor mechanism. The most efficient sensitizer dye that has been used for the fabrication of DSSC is ruthenium polypyridyl complex (Grätzel, 2003). Other sensitizer dyes widely used are N719 ethanol dye (Lanlan *et al.*, 2010) and Eosin-Y dye (Rani *et al.*, 2008). Recent researches have shown that natural dyes can be used as a sensitizer replacing the ruthenium complex (Grätzel, 2003) and (Nazeeruddin *et al.*, 2011). This includes leaves and flowers with colour pigment detectable in red-to-blue spectrums. Good examples of source of natural dye are dragon fruit (Hylocereus costaricensis) and raspberries (Riyaz and Nafarizal, 2010). Therefore, for the current work, dragon fruit was used in extracting the natural dye due to its high availability factor in Malaysia.

2.0 MATERIALS AND METHODS

2.1 Preparation of Zinc Oxide Powder

The zinc oxide porous solution was prepared by dissolving zinc acetate dehydrate, $Zn(CH_3COO)_2 2H_2O$ in an acetic acid solution at room temperature (28 ± 5°C). A milky solution was formed and by using sol-gel route technique, clear solution was obtained by magnetic stirring. The prepared solution was found to be stable and colourless without turbidity. The heating was done at 90 ± 5°C until the solution evaporated leaving white particles in the beaker. During this period of time, white ZnO precipitates were slowly formed by settling down at the bottom of the beaker. The heating process was continued (90 ± 5°C) until formation of particles in gel-like paste was observed. The gel-like paste was then annealed in the oven at 90 ± 5°C for approximately 8 hours to form ZnO porous. This sample was then divided into two and given further annealing treatment at two different temperatures; i.e. 250ºC and 500ºC. A detailed elucidation of the structure and composition was carried out using various characterization techniques. Surface morphology and the particle size of the ZnO substance were analyzed through SEM (model: EVO 50 ZEISS-7636) and particle size analyzer. Before taking the SEM images, the samples were coated with a thin layer of gold using ion sputtering (model: JEOL, JFC-1600). All observing conditions were performed at room temperature of 28 ± 5 °C and at humidity level of 80 ± 10 %. X-ray diffraction (XRD) of the samples was obtained using a XPERT-PRO with Cu-Kα radiation (λ=1.54060). Quantitative analysis of elements was done by energy-dispersive X-ray (EDX) measurements.

2.2 Preparation of ZnO Electrodes and Counter Electrode

ZnO powder was chunked into small particles followed by 15ml addition of ethanol. The mixture (i.e. ZnO powder and ethanol) was mixed uniformly until it produced a well uniform ZnO paste. The paste was carefully deposited onto a 2 x 2 cm^2 indium tin oxide (ITO) glass to form the electrode, Figure 1(a). By means of using a hot place, the ZnO electrode was heated up to 150 ± 5°C for approximately 15 minutes. This was done to harden the ZnO paste on the ITO glass while indirectly enhancing the bonding characteristics (i.e. ZnO paste against the ITO glass). For the purpose of preparing the natural dye, pieces of fresh dragon fruit flesh with weight approximately 50 grams is mixed into 50 ml distilled water at room temperature of 28 ± 5°C, Figure 1(b). The mixture is further blended using an electric blender (model: Braun AG, type 4-172) for 10 minutes until a homogenous colour (i.e. dark pink) is seen by the naked eye. When this is achieved, the harden ZnO electrode is dipped into the dye solution for 24 hours, Figure 1(c).

For the purpose of preparing the counter electrode, graphite is deposited on the conducting surface of another virgin ITO glass, Figure 1(d). This was followed by treating both the opposite surfaces of the electrode and counter electrode with sulphuric acid. The two sides of ITO glasses that had been treated with sulphuric acid were then sandwiched securely together, Figure 1(e). The whole DSSC is left to dry at room temperature at 28 ± 5°C for about one hour before it was evaluated.

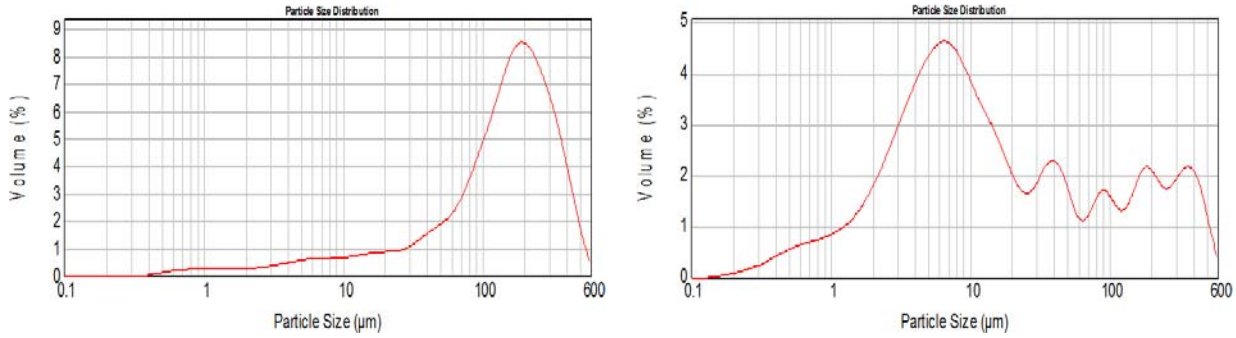
(a) (b) (c) (d) (e)

Figure 1: Preparation of the Dye Sensitized Solar Cell, **(a)** ZnO electrode preparation, **(b)** Fresh dragon fruit, **(c)** ZnO electrode coated with dragon fruit dye, **(d)** Counter electrode preparation, **(e)** Prepared DSSC.

3.0 RESULTS AND DISCUSSION

3.1 Particle Size Analyzer

Particle size analysis test was conducted on two samples of ZnO treated at different temperatures of 250ºC and 500ºC. The results of the particle size and its distribution are presented in Figure 2. From Figure 2(a) & Figure (b), ZnO sample at 250ºC shows the average size of the particle was between 100µm to 500µm. For the ZnO sample at 500ºC, the average size of particle was between 2µm to 20µm. From the result, it shows that ZnO sample annealed at 500ºC gave far finer particle than the one annealed at 250ºC. Consequently, the 500ºC annealed samples with smaller particle size gave large surface area of contact and large absorptive character compared to ZnO sample annealed at 250ºC. Based on this observation, ZnO annealed at 500ºC was selected for further fabrication of dye sensitized solar cell.



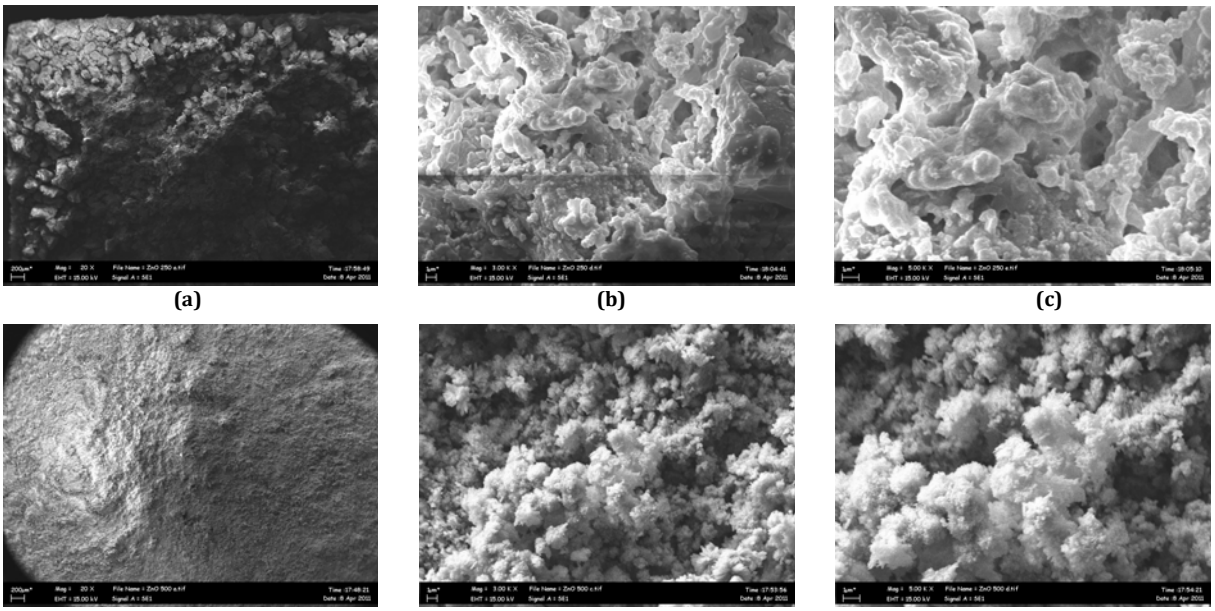
(a) (b)

Figure 2: Particle size distribution of ZnO at different temperatures, **(a)** 250ºC, **(b)** 500ºC.

3.2 Scanning Electron Microscope analysis

Based on the images obtained by SEM, the ZnO particles were thin flakes of very fine particles that were agglomerated jointly. This was due to the formation of carbonates or carboxylate ions from the acetic acid or other hydroxyl ions. This finding was similar to other findings as reported by Rani *et al.*, (2008). The ZnO powder which was annealed at 250ºC [c.f. Figure 3(a)] shows the morphology was rougher as compared to ZnO annealed at 500ºC, Figure 3(d). At higher magnifications, the amount of synthesising reaction that occurs for both samples can be seen clearly [c.f. Figure 3(b), Figure 3(c), Figure 3(e) and Figure 3(f)].

Upon SEM anaylsis, it was found that ZnO powder sample annealed at 500ºC had smaller particle size and the reaction growth was more symmetrical as compared to ZnO sample at 250ºC. The uniformity in particle size and finer surface area makes ZnO annealed at 500ºC [c.f. Figure 3(f)] in better advantage compared to sample annealed at 250ºC [c.f. Figure 3(c)].



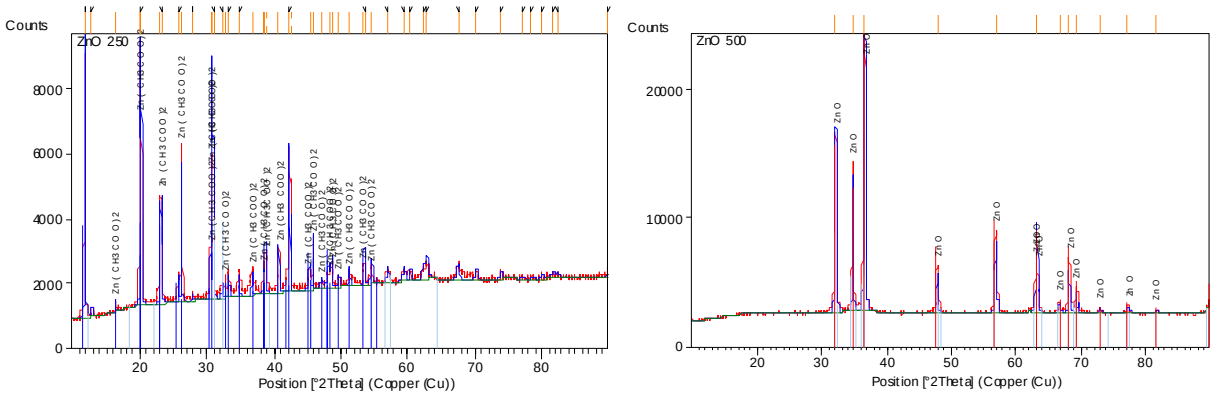
(a) **(b)** **(c)**

(d) **(e)** **(f)**

Figure 3: SEM images of ZnO at different temperatures and magnifications, **(a)** ZnO at 250ºC, 20X, **(b)** ZnO at 250ºC, 3000X, **(c)** ZnO at 250ºC, 5000X, **(d)** ZnO at 500ºC, 20X, **(e)** ZnO at 500ºC, 3000X, **(f)** ZnO at 500ºC, 5000X.

3.3 XRD Pattern Analysis

From Figure 4(a) ZnO sample annealed at 250ºC gave a non uniform diffraction pattern compared to ZnO powder annealed at 500ºC. However, ZnO at 250ºC did not exhibit any true character. Part of it was transformed back to the zinc acetate. This is due to the insufficient annealing heat which was not high enough to fully oxidize the sample, and the sudden exposure to the environment had caused the intermolecular structure to return to its initial condition. ZnO oxide powder annealed at 500ºC gave a more promising result as shown in the X-RAY diffraction, Figure 4(b). From the figure, it shows that the intensity of absorption of ZnO sample annealed at 500ºC lies between position 30º to 40º on a hexagonal plane at º2Theta measurement. Therefore, ZnO sample at 500ºC was selected as a thin film material to fabricate the DSSC.

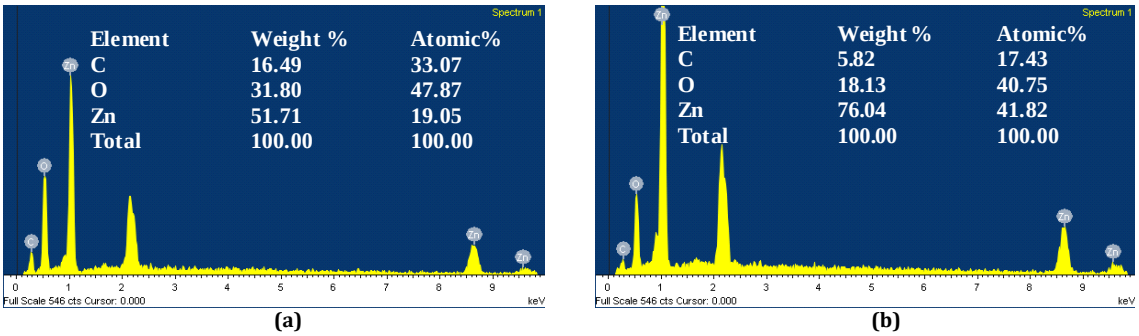


(a) **(b)**

Figure 4: XRD patterns of ZnO powder at different temperatures, **(a)** 250ºC, **(b)** 500ºC.

3.4 Energy Dispersive X-Ray Spectrometry Analysis

From the results obtained in Figure 5(a) and Figure 5(b), it was found that there was carbon impurity in both samples. For ZnO sample at 250ºC, the weight by percentage of carbon impurity was about 16.49% while the atomic weight was about 33.07%. For ZnO sample at 500ºC, the weight by for carbon impurity was about 5.82% and atomic weight was about 17.43% which is significantly lower than 250ºC ZnO sample. This shows that the amount of the impurities can be reduced when the sample is heat treated at a higher temperature. The above results also show that the 500ºC ZnO sample has a higher atomic percentage of Zn and O composition in the sample as compared to ZnO sample at 250ºC. In other words, ZnO sample at 500ºC gives better quality amount of ZnO which is vital in producing an effective thin porous film of ZnO for DSSC. Thus, this is the main reason ZnO sample at 500ºC was selected as the substrate for producing a thin porous film of DSSC.



(a) **(b)**

Figure 5: EDS spectrums of ZnO at different temperatures, **(a)** 250ºC, **(b)** 500ºC.

3.5 I-V Curve Analysis

The testing for the DSSC was carried out to determine the voltage and current generated by the solar cell. Theoretically, short circuit current (I_{sc}) and open circuit voltage (V_{oc}) represents the maximum photocurrent and photovoltage of the fabricated DSSC. The maximum power of a solar cell can be found using Equation 1.

$$P_{max} = I_{max} \text{ x } V_{max} \quad (1)$$

The fill factor (FF) of a solar cell is expressed using Equation 2.

$$FF = P_{max} / (I_{sc} \text{ x } V_{oc}) \quad (2)$$

Thus, the efficiency of the solar cell is the measurement of the electrical power generated by DSSC divided by the solar power distributed on the surfaces of DSSC. Taking the solar power (i.e. natural sunlight intensity) per unit area square to be 1mW/mm^2 and the surface size of the DSSC to be 20 x 20 mm^2, the nett solar power in mili Watts is expressed in Equation 3.

$$P_{solar\ nett} = 1mW/mm^2 \text{ x } 20mm \text{ x } 20mm = 400mW \quad (3)$$

Correspondingly, the measurements of voltage and current were taken at every 5 minutes of time interval for a total duration of 30 minutes where the DSSC was subjected to direct sunlight (i.e. DSSC was placed 90 degrees below the sun light). From Figure 6, theoretically, it can be said that the transient photocurrents generated are almost consistent per unit time. The transient current decreased proportionately with increase in its resistance. The instantaneous current was at maximum with zero internal resistance and decayed when the internal load resistance becomes very large.

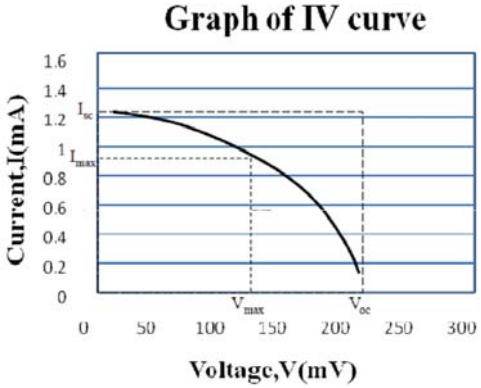


Figure 6: Theoretical graph of I-V curve showing I_{sc}, V_{oc}, I_{max} & V_{max} for determining P_{max} and FF

By merging all the values into a single graph as per Figure 7, the graph shows that the current and voltage of DSSC are found to be consistent with varied times. The efficiency (η) of the fabricated DSSC is expressed in Equation 4.

$$\eta = P_{max} / P_{solar\ nett} \quad (4)$$

Making P_{max} as the subject in Equation 2 and substituting it in Equation 4 the following is obtained:

$$\eta = (FF \text{ x } I_{sc} \text{ x } V_{oc}) / P_{solar\ nett} \quad (5)$$

Knowing the values of I_{max} and V_{max} from Figure 6, P_{max} is computed using Equation 6 which is as follow:

$$P_{max} = I_{max} \text{ x } V_{max} = 1mA \text{ x } 100mV = 100mW \quad (6)$$

In regard to this, values of I_{sc} and V_{oc} are determined from Figure 6 and the field factor is computed using Equation 2 where:

$$FF = (1mA \text{ x } 100mV) \,/\, (1.3mA \text{ x } 275mV) = 0.28 \quad (2')$$

Lastly, with I_{sc} = 1.3mA, V_{oc} = 275mV, FF = 0.28 and $P_{solar\ nett}$ = 400mW, the efficiency of the fabricated DSSC is computed using Equation 5 where η = 25%.

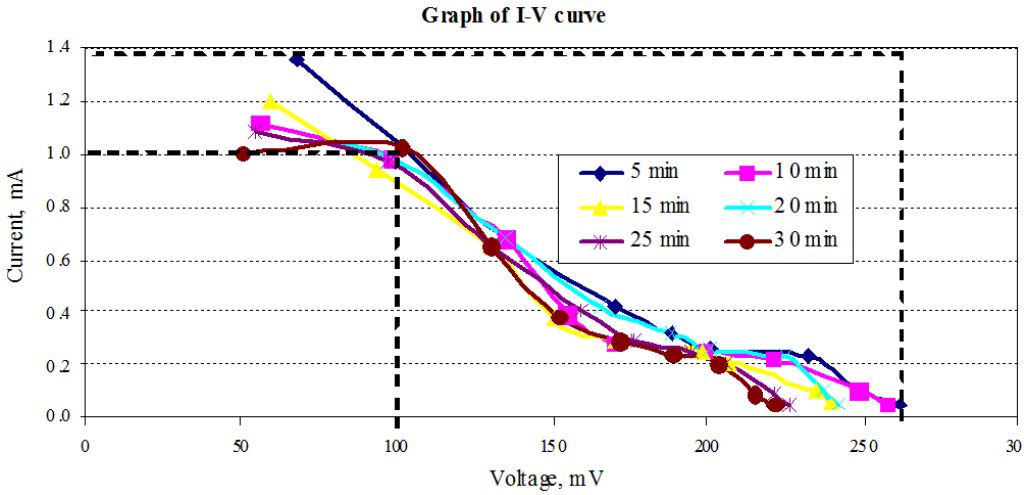


Figure 7: I–V curves for the fabricated DSSC using two ITO glasses with one electrode coated with graphite and the other coated with ZnO powder annealed at 500ºC and treated with natural dragon fruit dye

4.0 CONCLUSION

This work has successfully established the cost effective method of producing an effectual dye sensitized solar cell using ZnO and natural dye. The synthesis of ZnO was carried out using sol- gel route technique in producing zinc acetate dehydrates that was successfully transformed into ZnO material. The DSSC produced had an efficiency of about 25%, a positive result as compared to other findings. This clearly shows that the ZnO material has the ability to be an alternative material to TiO_2 in fabricating a low cost DSSC. ZnO powder annealed at 500 ºC was found to be more effective compared to one annealed at 250ºC. Higher temperature annealing condition gave significant outcome in producing higher grade of ZnO with reduced impurity and increased absorption intensity. The result shows that ZnO and natural dye have a promising application in the fabrication of dye sensitized solar cell.

REFERENCES

[1] El-Badri, A.S. (2010): *World Oil Outlook*. Yearly report of Organization of The Petroleum Exporting Countries, pp.1-281.

[2] Bao, Q., Chen, C., Wang, D., Ji, Q., Lei, T. (2005): Pulsed Laser Deposition and its Current Research Status in Preparing Hydroxyapatite Thin Films. *Applied Surface Science*, *Vol.252, Iss.5*, pp.*1538-1544.*

[3] Brinker, C.J. and Scherer, G.W. (1990): *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*. Academic Press.

[4] Fouad, O.A., Ismail, A.A., Zaki, Z.I., Mohamed, R.M. (2006): Zinc Oxide Thin Films Prepared by Thermal Evaporation Deposition and Its Photocatalytic Activity. *Appl. Catal. B: Environ*, Vol.62, p.144.

[5] Grätzel, M. (2003): Dye-Sensitized Solar Cells. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, Vol.4, Iss.2, pp.145-153.

[6] Hench, L.L. and West, J.K. (1990): The Sol-Gel Process. *Chemical Reviews*, Vol.90, No.1, pp.33–72.

[7] Lanlan, L., Renjie, L., Ke, F. and Tianyou, P. (2010): Effects of Annealing Conditions on the Photoelectrochemical Properties of Dye-Sensitized Solar Cells Made With ZnO Nanoparticles. *Solar Energy*, Vol.84, No.5, pp.845-853.

[8] Micheal, R.S. and Waltham M. (1982): Method to Synthesize and Produce Thin Films by Spray Pyrolysis. *U.S. patent 4336285*.
[9] Musil, J., Baroch, P., Vlček, J., Nam, K.H. and Han, J.G. (2005): Reactive Magnetron Sputtering of Thin Films: Present Status and Trends. *Thin Solid Films*, *Vol.475, Iss.1*, pp.*208-218.*
[10] Nakaruk, A., Ragazzon, D. and Sorrell, C.C. (2010): Anatase Thin Films by Ultrasonic Spray Pyrolysis. *Journal of Analytical and Applied Pyrolysis*, Vol.88, Iss.1, pp.98-101.
[11] Nazeeruddin, M.K., Baranoff, E., Grätzel, M. (2011): Dye-Sensitized Solar Cells: A Brief Overview. *Solar Energy*, Vol.85, Iss.6, pp.1172-1178.
[12] Olivia, M. (1998): Fundamentals of Photovoltaic Materials. Technical report by National Solar Power Research Institute, pp.1-8.
[13] Pawar, B., Dukhohama, G., Mane, R., Ganesh, T., Anilghule, S.R., Jadhava, K.D. and Sung-Hwanhan. (2009): Preparation of Transparent and Conducting Boron-Doped Zno Electrode for Its Application in Dye-Sensitized Solar Cells. *Solar Energy Materials & Solar Cells*, Vol.93, pp.524-527.
[14] Rani, S., Suri, P., Shishodia, P.K. and Mehra, R.M. (2008): Synthesis of Nanocrystalline ZnO Powder Via Sol–Gel Route For Dye-Sensitized Solar Cells. *Solar Energy Materials and Solar Cells*, Vol.92, Iss.12, pp.1639-1645.
[15] Reijnders, L. (2009): The Release of TiO2 and SiO2 Nanoparticles from Nanocomposites. *Polymer Degradation and Stability*, Vol.94, No.5, pp.873-876.
[16] Riyaz, A.M.A. and Nafarizal, N. (2010): Fabrication and Analysis of Dye-Sensitized Solar Cell Using Natural Dye Extracted From Dragon Fruit. *Issue on Electrical and Electronic Engineering,* Vol.2, Iss.3.
[17] Shah, N.M., Panchal, C.J., Kheraj, V.A., Ray, J.R. and Desai, M.S. (2009): Growth, Structural and Optical Properties of Copper Indium Diselenide Thin Films Deposited by Thermal Evaporation Method. *Solar Energy*, Vol.83, Iss.5, pp.753-760.
[18] Shen, L., Ma, Z.Q., Shen, C.F., He, B. and Xu, F. (2010): Studies on Fabrication and Characterization of a ZnO/p-Si-based Solar Cell. *Superlattices and Microstructures*, Vol.48, No.4, pp.426-433.
[19] Stucky, G.D. and Bartl, M.H. (2010): Mesostructured Thin Film Oxides. Chapter 8 of Thin Film Metal-Oxides: *Fundamentals and Applications in Electronics and Energy*, Springer, pp.255-279.
[20] Tsokos, K.A. (2008): *Physics for the IB Diploma*, 5th edition, Cambridge, Cambridge University Press, pp.800-835.
[21] Yeji, L., Jinho, C. and Misook, K. (2010): Comparison of the Photovoltaic Efficiency on DSSC for Nanometer Sized TiO_2 using a Conventional Sol–gel and Solvothermal Methods. *Journal of Industrial and Engineering Chemistry*, *Vol.16, Iss.4*, pp.*609-614.*