

Significant Influence of Annealing Temperature and Thickness of Electrode on Energy Conversion Efficiency of Dye Sensitized Solar Cell: Effect of Catalyst

Jasim Uddin², Jahid M. M. Islam¹, Shauk M. M. Khan¹, Enamul Hoque²,
Mubarak A. Khan^{1,*}

¹Institute of Radiation and Polymer Technology, Bangladesh Atomic Energy Commission,
P.O. Box 3787, Dhaka - 1000, Bangladesh
*Fax: +880 2 7789343, *Phone: +880 2 7788245

²Department of Physics, Jahangirnagar University, Savar, Dhaka - 1342, Bangladesh
*E-mail address: makhan.inst@gmail.com

ABSTRACT

Dye sensitized solar cell (DSSC) shows great promise as an alternative to conventional p-n junction solar cells due to their low fabrication cost and reasonably high efficiency. DSSC was assembled by using natural dye extracted from red amaranth (*Amaranthus Gangeticus*) as a sensitizer and different catalysts for counter electrode were applied for maximum energy conversion efficiency. Annealing temperature and thickness of electrode were also investigated and optimized. Catalyst, annealing temperature and thickness were optimized by the determination of cell performance considering photoelectrochemical output and measuring current and voltage; then calculating efficiency and other electrical parameters. The experimental results indicated that samples having 40 μm electrode thickness and prepared at 450 °C annealing temperature showed the best performance.

Keywords: Dye Sensitized Solar Cell; Sensitizer; catalyst; annealing temperature and thickness

1. INTRODUCTION

Most of the power generated nowadays is produced using fossil fuels, which emit tons of carbon dioxide and other pollution every second. More importantly, fossil fuel will eventually run out. So people are looking for new source of substitute clean energy in order to make the development of our civilization sustainable and cause less harm to our environment. Although the photovoltaic devices promise to offer a clean solution to these problems, current silicon-based photovoltaic technologies are hindered by serious combustion pollution and high production cost. As a novel renewable and clean solar-to-electricity conversion system, dye-sensitized solar cells (DSSCs) have attracted the attention of researchers since they were introduced by O'Regan and Gratzel [1].

Since then, DSSCs have been widely explored as a matter of tremendous interest to academic and commercial researchers due to their low cost fabrication and relatively high conversion efficiencies (>10 %) [2-4]. These cells are extremely promising because they are

made of low-cost materials and do not need elaborate apparatus to manufacture. Conventional DSSCs consist of mainly five components: (1) a conductive and transparent mechanical support, (2) a wide band gap semiconductor film, (3) a sensitizer, (4) redox couple (usually I_3^-/I^-) in an organic solvents and (5) a counter electrode. The successful combination of the materials involved in cell fabrication, as well as the precise methods used, will determine the final cell performance. In order to further improve the performances of DSSCs, extensive efforts are on-going for each of its constituent components and conditions including dye for sensitizer, electrolyte, paste formulation, catalyst for counter electrode [5], thickness of electrode [6-8] and annealing conditions [9-11] etc. In this paper our concentration is on catalyst, thickness and annealing temperature. Among these parameters the counter electrode is one of the most important components in the dye sensitized solar cell (DSSC).

The task of the counter electrode is the reduction of the redox species used as a mediator in regenerating the sensitizer after electron injection or collection of the holes from the conducting material in a solid-state DSSC [12]. Recently, some carbon materials and conducting polymers were used as efficient catalysts on the counter electrode of DSSCs [13,14]. To make an inexpensive cell one should consider a low cost material such as a carbon catalyst for counter electrode. Here our objective is to find out a low cost suitable carbon catalyst for DSSC. On the other hand another parameter that influences the performance of DSSC significantly is thickness.

Therefore, it is necessary to analyze the influence of various TiO_2 film thickness values on electron transport to improve DSSC efficiency. A number of studies on the influence of TiO_2 film thickness have focused on the transition of open circuit voltage, current density, fill factor, and efficiency and it is found that the cell's overall energy conversion efficiency strongly depends on the surface and electronic properties of the electrode with thickness varying from several hundred nanometers up to $20\ \mu m$ [15,16]. Recently, Shin et al. analyzed the effect of TiO_2 film thickness on DSSC characteristics using electrochemical impedance spectroscopy [17]. Kao et al. and Barglio et al. reported the effect of TiO_2 film thickness on DSSC performance and electrochemical behaviour [18,19].

K. Park et al. concluded that an excessively thick TiO_2 is not good for DSSC performance because of the electron recombination and the maximum photovoltaic conversion efficiency was achieved for a TiO_2 film thickness of $9\ \mu m$ [20]. Again another most important parameter that affects Dye-Sensitized Solar Cell (DSSC) characteristics is porosity. There are many aspects that can influence the porosity such as particles size of TiO_2 , annealing temperature and processing parameter or fabrication itself. In this paper, one of important parameter will be discussed, i.e., effect of annealing on characterization of TiO_2 thin layer.

Several researchers investigated the effect of annealing conditions and concluded that it has an important role in the efficiency of DSSC [21,22]. It is assumed that annealing process will improve electrical properties of this cell due to porosity effect. Annealing process can remove the binding and solvent which can increase electrically-connected network of TiO_2 particles [23]. This condition will increase TiO_2 performance as the electron transport. According to Chang-Ryul et al. [24] porosity is related with annealing duration and temperature, which affecting photocurrent density and the amount of absorbed dye.

Now our objective of this research is to optimize annealing temperature and thickness of electrode and find out available suitable catalyst for counter electrode and then fabricate a complete DSSC. For this purpose firstly we searched a suitable catalyst keeping thickness and annealing temperature remained unchanged. After choosing catalyst thickness is optimized keeping temperature remain unchanged. Finally annealing temperature is optimized. Optimal

parameters were determined by measuring current and voltage with the help of a precision multimeter and then calculating maximum power point, fill factor and cell efficiency.

2. EXPERIMENTAL

2. 1. Materials

Materials used in this experiment were Indium Tin Oxide (ITO) coated glass plate (Dyesol, Australia), TiO₂ (Degussa P25, USA) Citric acid (C₆H₈O₇), Polyethylene Glycol (PEG), Titanium IV Isopropoxide (TTIP) (Merck, Germany), Triton X-100 (Merck, Germany), Acetone (BDH, UK), Ethanol (BDH, UK), Methanol (BDH, UK), Dye extracted from red amaranth (*Amaranthus gangeticus*, local Bangladeshi name *lalshak*) in our lab, Carbon, Potassium Iodide and Iodine.

2. 2. Preparation of TiO₂ Paste

2 g of Degussa P25 powder was deposited in a beaker mixed with 0.1 M, 6 mL citric acid, 0.2 mL polyethylene glycol, 0.2 mL titanium (IV) isopropoxide and 0.1 mL nonionic surfactant triton X-100. The mixture was well mixed with the help of a glass rod and then kept in an ultrasonic bath for half an hour for the production of suspension with a consistency of a thick paint produced. The prepared paste was coated on ITO glass with surface resistance of 10-30 ohms by using doctor blade technique.

2. 3. Controlling the Thickness

The thickness of the coating was controlled using the simplest and most widely used doctor-blade method. With this technique, the thickness of the paste layer is determined by the thickness of a spacer placed on both sides. Using the Scotch tape which has a thickness of 20 μm, 2 Layer = 40 μm, 3 Layer = 60 μm, 4 Layer = 80 μm and 5 Layer = 100 μm, with the conductive side facing up, apply two parallel strips of tape on the edges of the glass plate. The area of the middle of the glass is uncovered and where the TiO₂ paste will be deposited. After depositing the paste remove the scotch tape. Two bare edges masked by the tape will give then room for future sealing and electrical contacts.

2. 4. Annealing electrode

The electrodes were annealed at temperature ranging from 200 °C – 550 °C (200 °C, 250 °C, 300 °C, 350 °C, 400 °C, 450 °C, 500 °C, 550 °C) for half an hour with the help of a furnace. After the annealing was completed, the TiO₂ coated conductive glass was allowed to cool slowly at room temperature and then the TiO₂ coated glass plate was prepared for dye soaking.

2. 5. Extraction of natural dye and staining the electrode

Red amaranth leaves were collected from local market and then washed and kept them some times for dried. 100 g of leaves were weighted and crushed in a mortar and pestle adding 50 mL of solvent. The extracted dye was filtered three times with a cotton cloth and stored in a dark bottle covered with aluminium foil paper. The TiO₂ coated glass plate was soaked in dye and was kept at a dark place. The glass plate was washed by distilled water and then ethanol and dried in air for 30 minutes

2. 6. Preparing counter electrode and Electrolyte

Carbon from various available sources has been collected to investigate its effect as a catalyst. Wood coal, char coal, soft pencil, hard pencil, carbon from recycled battery and tip of candle flame were used as catalyst. To prepare electrolyte 8.3 g of 0.5 M potassium iodide and 1.27 g of 0.05 M iodine was mixed in ethylene glycol until it is 100 mL. The solution was stored in a black bottle and was used when necessary.

2. 7. Assembling the Cell

Electrode and counter electrode were combined together keeping TiO₂ paste coated surface and the carbon coated surface face to face. 2/3 drops of electrolyte solution was given in the contact of two glasses and by the capillary action the electrolyte was uniformly distributed throughout the stained TiO₂ film. Excess electrolyte from the exposed area of the glass was wiped off by using cotton or tissue. The complete cell was then taken to sunlight for harvesting energy.

2. 8. Measuring electric properties

Electrical properties were measured by using two digital multimeter keeping the cell in sunlight of approximately 100 mW/cm² illumination. Current and voltage were measured by multimeters changing with resistance with the help of a variable resistor. Based on I-V curve, the fill factor (FF) was defined as

$$FF = (I_{\max} \times V_{\max}) / (I_{sc} \times V_{oc})$$

where I_{\max} and V_{\max} are the photocurrent and photovoltage for maximum power point (P_{\max}). I_{sc} and V_{oc} are the short-circuit photocurrent and open-circuit photovoltage respectively. The overall energy conversion efficiency (η) is defined as

$$\eta = (I_{sc} \times V_{oc} \times FF) / P_{in}$$

where P_{in} is the power of incident light.

3. RESULTS AND DISCUSSION

3. 1. Effects of Catalyst for Counter Electrode

Counter electrode (CE) of dye-sensitized solar cell (DSSC) can be prepared with different materials and methods. Here we prepared six samples of different catalyst and one for no catalyst. The photovoltaic performances of the DSSC based on different carbon catalysts counter electrode are shown in **Fig. 1**.

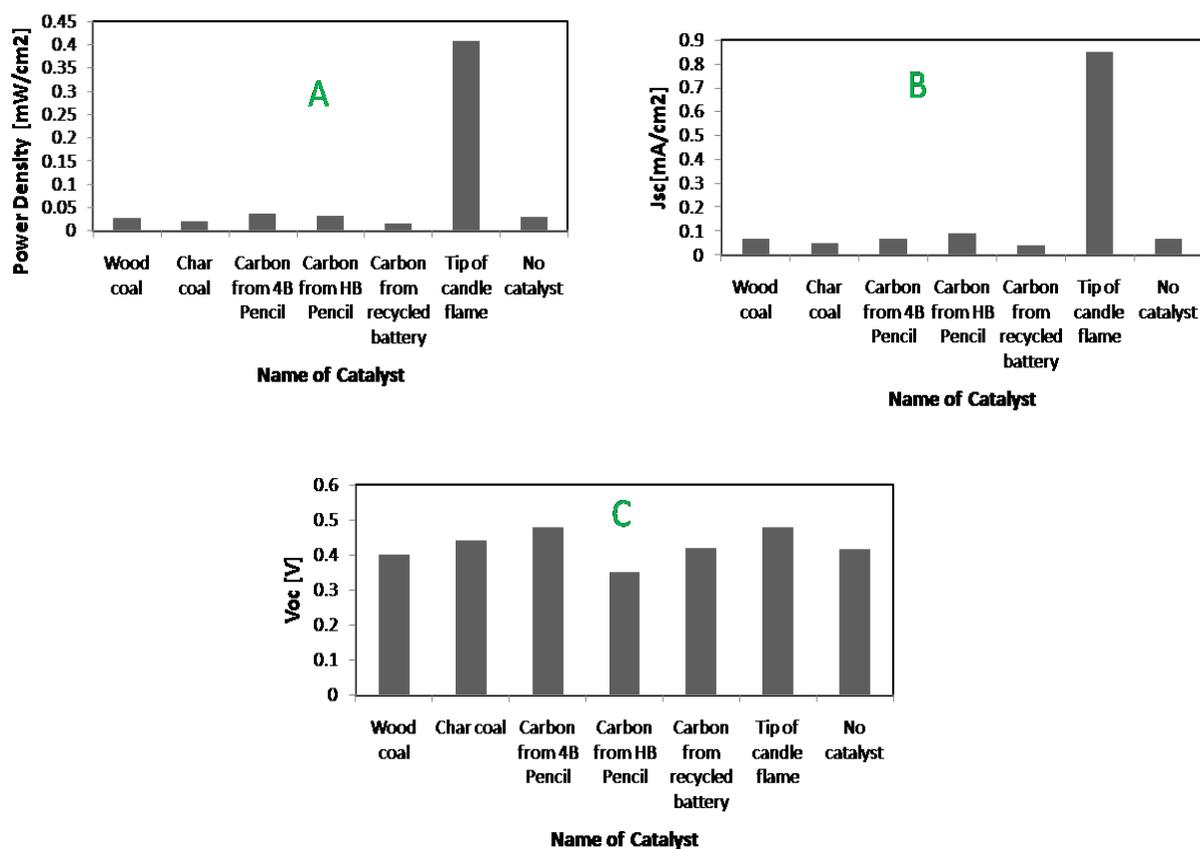


Fig. 1. Photovoltaic characteristic parameters of the DSSC with different Catalysts for counter electrode (A) Power density (B) Short circuit current density (C) Open circuit voltage.

Open circuit voltage (V_{oc}), short circuit current density (J_{sc}) and power density obtained for each DSSC are summarized in **Table 1**. Amongst the different catalyst of counter electrode the DSSC with tip of candle flame has shown maximum open circuit voltage 0.480 V and short circuit current density 0.85 mA/cm² resulting maximum power density 0.408 mW/cm². This indicates that tip of candle flame has strong catalytic activity toward the reduction of iodine electrolyte.

Table 1. Photovoltaic parameters of the DSSC made with different Carbon catalyst for counter electrode.

Name of Catalyst	V _{oc} [V]	J _{sc} [mA/cm ²]	Power Density [mW/cm ²]
Wood coal	0.402	0.07	0.029
Char coal	0.442	0.05	0.022
Carbon from 4B Pencil	0.480	0.07	0.037
Carbon from HB Pencil	0.350	0.09	0.032

Carbon from recycled battery	0.420	0.04	0.017
Tip of candle flame	0.480	0.85	0.408
No catalyst	0.418	0.07	0.030

3. 2. Effects of Thickness of TiO₂ Film on Electrode

TiO₂ layer is the carrier of electron after it is excited by the organic dye. So it is necessary to recognize the semiconductor layer thickness dependency. In this experiment the thickness of TiO₂ was controlled by the thickness of tape.

Thus, by layering several pieces of tape on both sides of the ITO glass and then following the same rolling procedure as used for a normal cell, we can control the thickness of TiO₂ in this simple way. However, it was only possible to measure several distinctive data point, i.e the integer times of thickness of the tape, because it is impossible to tape any decimal layer of tapes on the glass.

All of the measurements were taken at the same temperature, amount of illumination and pressure. **Fig. 2.** shows the photovoltaic performances of the DSSC based on different thickness (20-80 μm) of TiO₂ film. Open circuit voltage (Voc), short circuit current density (J_{sc}), fill factor (F.F.) and efficiency obtained for each DSSC are summarized in **Table 2.** The DSSC shows linear increase in efficiency, short circuit current density and fill factor with increase in thickness up to 40 μm and then decrease slightly as shown in **Fig. 2.(A-C)**, respectively.

Fig 2D shows that open circuit voltage decrease with increase in thickness. The efficiency, fill factor and short-circuit current density are maximum at the thickness of 40 μm and they are 0.20 %, 63 % and 0.70 mA/cm² respectively. Therefore, the thickness was optimized and it was 40 μm .

Table 2. Photovoltaic parameters of the DSSC for different thickness of TiO₂ film.

Sample number	Thickness (μm)	Voc[V]	Jsc [mA/cm ²]	P _{max} [mW]	F.F.	η %
1	20	0.485	0.62	0.186	0.62	0.19
2	40	0.455	0.70	0.200	0.63	0.20
3	60	0.377	0.32	0.067	0.56	0.07
4	80	0.362	0.24	0.047	0.54	0.05
5	100	Film was not stable				

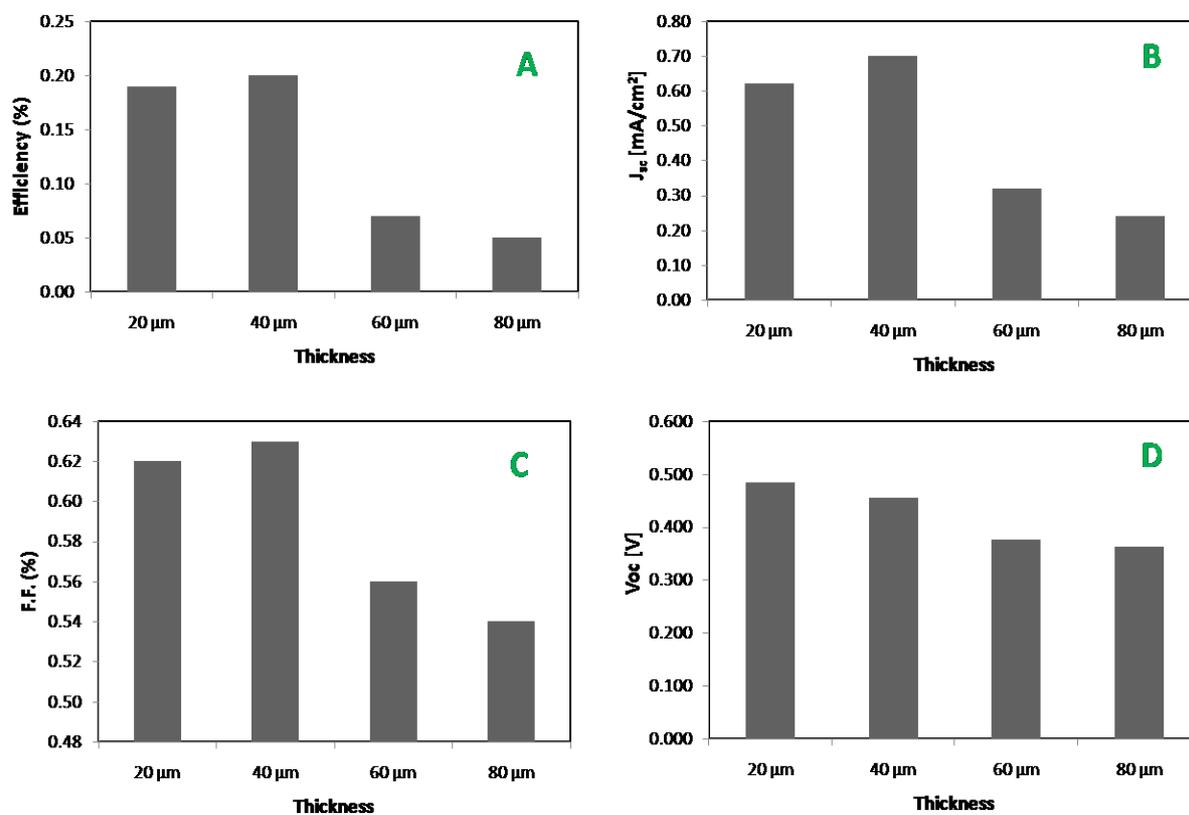


Fig. 2. Photovoltaic characteristic parameters for the DSSC with various thickness of TiO₂ film (A) Efficiency (B) Short circuit current density (C) Fill factor (D) Open circuit voltage.

3. 3. Effects of Annealing Temperature of Electrode

Table 3. Photovoltaic parameters of the DSSC annealed the electrode at various temperatures.

Sample number	Temperature [°C]	Voc[V]	Jsc [mA/cm ²]	P _{max} [mW]	F.F.	η %
1	250	0.255	0.05	-----	-----	-----
2	300	0.360	0.09	-----	-----	-----
3	350	0.448	0.40	0.099	0.55	0.10
4	400	0.473	0.52	0.150	0.61	0.15
5	450	0.479	0.64	0.212	0.69	0.21
6	500	0.477	0.45	0.130	0.61	0.13
7	550	0.480	0.40	0.116	0.60	0.12

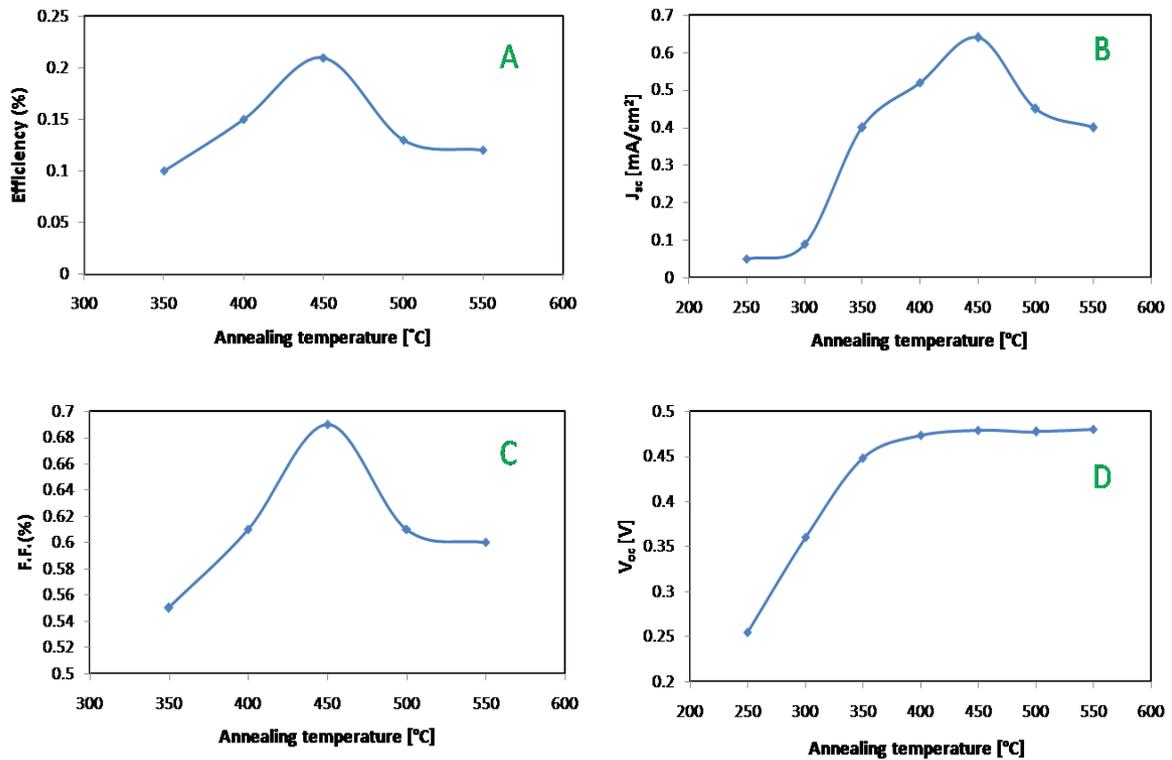


Fig. 3. Photovoltaic characteristic parameters for the DSSC with various Annealing temperature of TiO₂ film (A) Efficiency (B) Short circuit current density (C) Fill factor (D) Open circuit voltage.

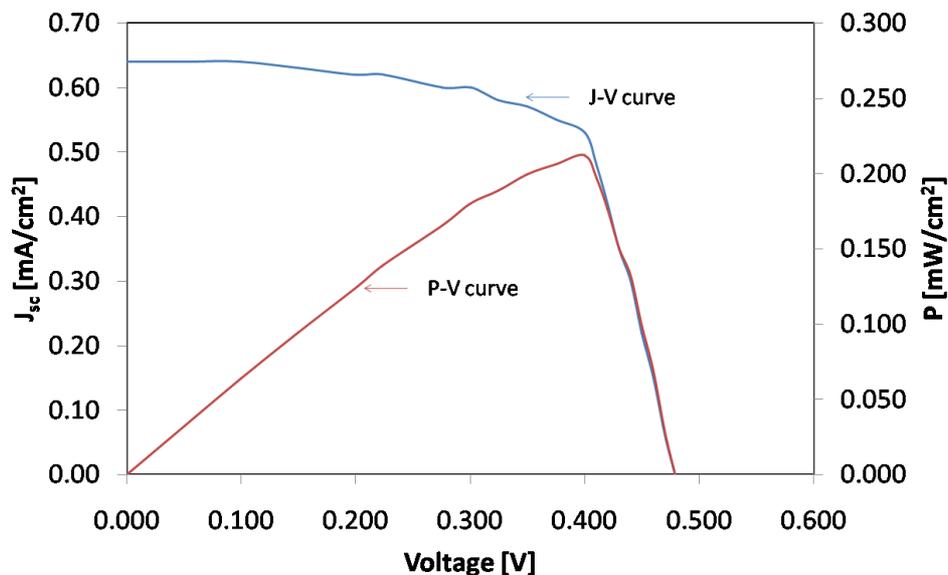


Fig. 4. J–V and P–V curves of DSSC for maximum efficiency of 0.21 % using tip of candle flame as a catalyst for counter electrode, film thickness of electrode is 40 μ m and annealing temperature was 450 °C.

Fig. 3. shows the photovoltaic performances of the DSSC based on different annealing temperature (250-550 °C) of the electrode. Open circuit voltage (V_{oc}), short circuit current density (J_{sc}), fill factor (F.F.) and efficiency obtained for each DSSC are summarized in **Table 3.** **Fig. 3 (A-C)** shows that efficiency, short circuit current density and fill factor increase with temperature up to 450 °C and then decrease.

Fig. 3D shows that open circuit voltage increase with increase in temperature up to 400 °C and after that V_{oc} was almost constant in spite of increasing temperature. It was found that annealing temperature had significant effects on the cell performance. Maximum cell efficiency was 0.21 % and it was for the temperature of 450 °C.

4. CONCLUSION

In summary, counter electrodes for DSSC with different carbon materials were fabricated using the doctor blade method and was found that tip of candle flame is a suitable catalyst for energy conversion. Fabrication of photo-electrodes of different thicknesses (20 μm , 40 μm , 60 μm , 80 μm and 100 μm) revealed that an excessively thick TiO_2 is not good for DSSC performance because of the electron recombination. The maximum photovoltaic conversion efficiency was achieved for a TiO_2 film thickness of 40 μm . The influence of annealing temperature (250-550 °C) on the performance of DSSC with TiO_2 films was studied and it was optimized at 450 °C. So, this paper describes a low cost and effective technique to fabricate dye sensitized solar cell using a novel locally available natural dye having promising energy conversion efficiency.

ACKNOWLEDGEMENTS

This work was funded by Ministry of Science and Technology, Government of Bangladesh and supported by the University Grand Commission of Bangladesh and Ministry of Education, Bangladesh. This work was carried out in Institute of Radiation and Polymer Technology (IRPT) lab of Bangladesh Atomic Energy Research Establishment (AERE) and Department of Physics of Jahangirnagar University.

References

- [1] B. O'Regan, M. Grätzel, *Nature* 353 (1991) 737-740
- [2] N.G. Park, K.M. Kim, M.G. Kang, K.S. Ryu, S.H. Chang, Y.J. Shin, *Advanced Materials* 17 (2005) 2349-2353.
- [3] K. Lee, S.W. Park, M.J. Ko, K. Kim, N.G. Park, *Nat. Mater.* 8 (2009) 665-671.
- [4] W. Lee, S.J. Roh, K.H. Hyung, J. Park, S.H. Lee, S.H. Han, *Sol. Energy* 83 (2009) 690-695.
- [5] U. Rehman, A. U. Asar, N. Ullah, R. Ullah, M. Imarn, *International Journal of Engineering & Technology* 12(05) (2012).
- [6] K.H. Park, T.Y. Kim, J. H. Kim, H.J. Kim, C. K. Hong, J.W. Lee, *Journal of Electroanalytical Chemistry* 708 (2013) 39-45.

-
- [7] J. Kr'ysa, M. Baudys, M. Zlámal, H. Kr'ysová, M. Morozová, P. Kluso, Photocatalytic and photoelectrochemical properties of sol-gel TiO₂ films of controlled thickness and porosity, *Catalysis Today* xxx (2014) article in press.
- [8] M. Fitra, I. Daut, M. Irwanto, N. Gomesh, Y.M. Irwan, *Energy Procedia* 36 (2013) 278286.
- [9] L. Lu, R. Li, K. Fan, T. Peng, *Solar Energy* 84 (2010) 844-853.
- [10] K.C. Huang, Y.C. Wang, P.Y. Chen, Y.H. Lai, J.H. Huang, Y.H. Chen, R.X. Dong, C.W. Chu, J.J. Lin, K.C. Ho, *Journal of Power Sources* 203 (2012) 274-281.
- [11] C.M. Chen, Y.C. Hsu, S.J. Cherng, *Journal of Alloys and Compounds* 509 (2011) 872-877.
- [12] T.N Murakami, M Gratzel, *Inorganica Chimica Acta* 361 (2008) 572-580.
- [13] S. Ahmad, J.H. Yum, Z. Xianxi, M. Gratzel, H.J. Butt, M.K. Nazeeruddin, *J. Mater. Chem.* 20 (2010) 1654-1658.
- [14] J.D.R. Mayhew, D.J. Bozym, C. Punckt, I.A. Aksay, *ACS Nano.* 4 (2010) 6203-6211.
- [15] M. Grätzel, *J. Photochem. Photobiol. C.* 4 (2003) 145-153.
- [16] L. Yang, Z.X. Zhang, S.H. Fang, X.H. Gao, M. Obata, *Solar Energy* 81 (2007) 717-722.
- [17] Shin, H. Seo, M.K. Son, J.K. Kim, K. Prabakar, H.J. Kim, *Curr. Appl. Phys.* 10 (2010) S422-S424.
- [18] M.C. Kao, H.Z. Chen, S.L. Young, C.Y. Kung, C.C. Lin, *Thin Solid Films* 517 (2009) 5096-5099.
- [19] V. Baglio, M. Giolamo, V. Antonucci, S. Aroco, *Int. J. Electrochem. Sci.* 6 (2011) 3375-3384
- [20] K.H. Parka, T.Y. Kim, J.H. Kim, H.J. Kim, C.K. Hong, J.W. Lee, *Journal of Electroanalytical Chemistry* 708 (2013) 39-45.
- [21] L. Lu, R. Li, K. Fan, T. Peng, *Solar Energy* 84 (2010) 844-853.
- [22] C.M. Chen, Y.C. Hsu, S.J. Cherng, *Journal of Alloys and Compounds* 509 (2011) 872877.
- [23] A.F. Nogueira, C. Longo, M.A. Paoli, *Coordination Chemistry Reviews* 248 (2004) 1455-1468.
- [24] C.R. Lee, H.S. Kim, N.G. Park, *Front. Optoelectron. China.* 4 (1) (2001) 59-64.