ISSN 2250-3153

Solid State Solar Cells Based On Tio_2 Sensitized With Natural Pigment Extracted From the Anthurium

G.G.G.M.N.Hemamali [*‡], G.R.A.Kumara [**]

[*] Postgraduate Institute of Science, University of Peradeniya, Peradeniya,Sri Lanka.
[**] Postgraduate Institute of Science, University of Peradeniya, Peradeniya,Sri Lanka.

***Abstract*:** The purpose of this experiment was to create functional dye-sensitized solid state solar cells using natural pigments extracted from the blood red Anthurium as the electron donating species. Natural dye was extracted and adsorbed onto a nano-porous titania substrate. Platinum coated glass was used as the counter electrode. The cells were prepared using drop coating method to get a thickness around 10μm using 25 nm size TiO_2 particles. Using the extracted natural dye we have been able to obtain high efficiencies with CuSCN over CuI hole conductor.

The prepared cells show open circuit voltage (Voc) of 0.46 V and 0.43 of fill factor (FF) with an overall efficiency (η) of 0.34 % for CuSCN over the CuI hole conductor. Nevertheless short circuit current density (Jsc) was 2.37 mA cm^{-2} for CuI, it was 1.73 mA cm^{-2} for CuSCN.

***Key words*:** Dye Sensitized Solid State Solar Cells, Cyanidin, Anthurium, hole conductor.

1. INTRODUCTION

Dye-sensitized solar cells (DSCs) have received wide-spread research attention due to their high power conversion efficiencies over 11% under simulated standard solar emission (AM 1.5) [2,3] which make them realistic alternatives to conventional photovoltaic cells for various applications. However, DSCs, based on the liquid electrolytes, usually suffer from leakage and sealing problems, and their scalability remains challenging. By replacing the liquid electrolyte by solid hole transporting media, some of these limitations have been overcome. Concerning solid-state approaches, various inorganic [5, 10] p-type semiconductors such as CuSCN and CuI have been introduced into dye sensitized porous titanium dioxide (TiO2) electrodes.

A solid hole conductor is inappropriate because of the low mobility of ions. Obviously, the preference should be a p-type semiconductor that accepts holes from the dye cation. In this n-type semiconductor/ dye/p-type semiconductor device (NDP), light is absorbed by the surface anchored dye, leading to a photo excited state, then the photo-excited dye molecules sandwiched between the two semiconductors inject electrons into the n-type material and holes into the p-type material; that is

Dye $\longrightarrow$ Dye* Photo excitation of the dye

Dye* $\longrightarrow$ Dye^{+} + e- Electron transfer to the semiconductor

Dye^{+} $\longrightarrow$ Dye + h^{+} Electron transfer from the hole conductor.

However, in NDP type dye sensitized solid-state solar cells (DSSCs), band structures of n-semiconductor and p-semiconductor play an important role. Charge generation of a DSSC is illustrated in Fig. 1.

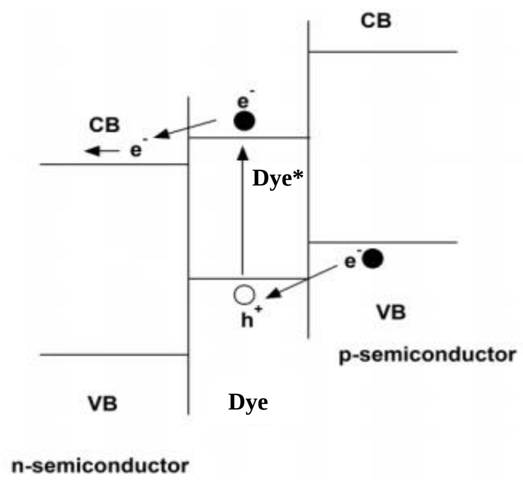

Figure 1. Charge generation of a NDP type solid-state solar cell

Resulting a photocurrent in the cell, the vacancy exists in the dye molecule is immediately neutralized from accepting an electron from the inner band of the p-type semiconductor. Several natural pigments [6] have been recognized as suitable sensitizers for fabricating DSSCs. Among them pigments based on Cyanidin was identified as a better sensitizer for DSSCs prepared using CuI and CuSCN.

In this work TiO_2 based DSSCs were prepared and have been tested for natural dyes extracted from blood red Anthurium with CuSCN and CuI hole conductors.

II. EXPERIMENT

Nano-porous layers of $Ti0_2$ were coated on fluorine-doped tin oxide (FTO) glass (1.5 cm x 2 cm) by the following method. First Titanium tetraisopropoxide (5.00ml), Glacial Acetic Acid (5.50ml), and Iso-propyl Alchohol (20.00ml) were mixed in to a ceramic motor and ground well to disperse all reagents in the medium. Then distilled water (5.00ml) was added quickly to the solution mixture. Gelatinous form was occurred in this step. P25 Degussa TiO_2 powder (0.650 g) was added to the mixture and ground until the gelatinous solution become thicker solution of TiO_2.The prepared paste was coated on an FTO glass by using drop coating method with an approximate thickness of 10-12 micrometre with $1cm^2$ cell area. Then the coated plate was annealed at 500^oC for 30 min.

The following method was used to obtain natural pigment from blood red Anthurium flowers. Petals of the flowers were freezed over night and boiled with 25% acetic acid. This process hydrolyses the glycoside yielding cyanidin acetate [5]. Absorption spectra (obtained using a Shimatzu UV 1800 spectrophotometer) also confirmed that cyanidin contained in the dye.

Nano-porous $Ti0_2$ electrodes were coated with pigment by dipping them in the extracted dye from blood red Anthurium over night in a dark and sealed place. After this treatment the electrode surface acquired a bluish-red tint due to complexation of cyanidin with Ti^{4+} ions on the $Ti0_2$ surface. Then pigment-adsorbed electrode was washed using acetonitrile and dried in air for few minutes.

CuI and CuSCN were deposited on the pigment-coated electrodes as described below. CuI solid can be dissolved in moisture free acetonitrile. Therefore a saturated solution of CuI was prepared by dissolving CuI in acetonitrile under sonification. This solution (~10.00 ml) was treated with a little amount of THT (~5 mg). To coat CuI on the photoanode, first the dye coated plate was placed on a hotplate under 110^0C temperature. Then the solution was lightly spread over the dyed surface using a dropper allowing evaporation of acetonitrile. This procedure was repeated until CuI surface gets filled just above the level of TiO_2 (can be optimized by measuring no change of *I*sc).

To prepare a structure modified CuSCN, first a pulp was prepared by mixing CuSCN (2.00g) in THT (2.0 ml) this pulp was dissolved in profile sulphide (15.00 ml). The solution was kept in a dark container. After few days, crystals were occurred in the container. Then the crystals were filtered out and mother liquor was used to fabricate in photo electrode as same as the procedure used in CuI deposition.

After depositing the CuSCN, the electrical contact was made by applying graphite powder onto the CuSCN surface. For CuI , no need to apply graphite. Then I-V measurements were carried out by applying a platinum coated glass plates on top of the CuSCN and CuI films. The current-voltage (I-V) characteristics of the cells at AM 1.5 (100 mW cm^{-2}) simulated sunlight irradiation were recorded with a calibrated solar-cell evaluation system (PE Cell-PEC L 12).

III. RESULTS AND DISCUSSION

In this work, the current voltage characteristic of solid-state dye sensitized solar cells based on CuI and CuSCN hole conductors are discussed. The influence of the TiO_2 film and natural dye extracted from blood red Anthurium are discussed as well.

Fig. 2 shows the absorption spectrum of an aqueous solution of the cyanidin contained natural dye is peaked at about 530 nm. UV-vis absorption spectrum of the dye was observed to understand the potency of the natural dye.

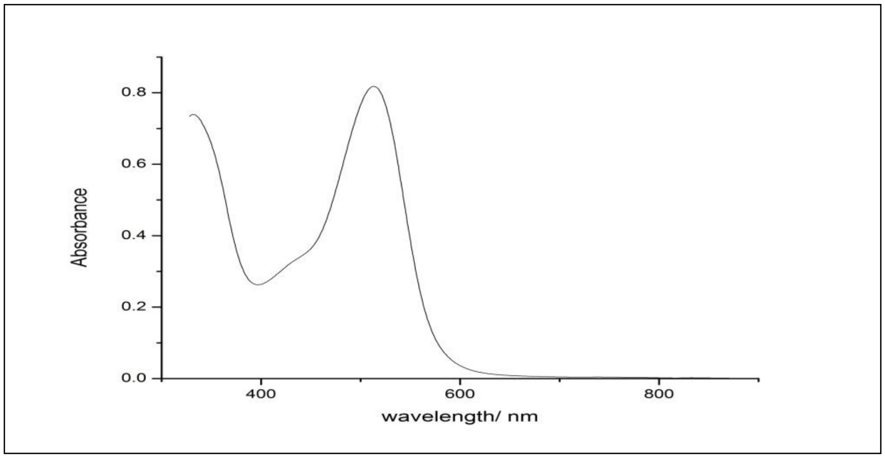

Figure 2. UV-vis absorption spectra of natural dye extraceted from blood red anthurium.

As a result of complexation with Ti^{4+} ions on the surface, cyanidin is strongly adsorbed on TiO_2. Ti^{4+} ions on the surface of TiO_2 are bonded to hydroxyl groups, thus the cyanidin cation can readily complex with the surface Ti^{4+} ions by eliminating a proton (Fig. 3). Complexation of Ti^{4+} with benzene derivatives including several hydroxyl groups is well established. The surface complex is totally insoluble in any solvent and unaffected by strong acid and weak alkalis. Strong alkalis in the presence of oxygen denature the complex. The complete removal of the film is possible only by treatment with a strong oxidizing agent.

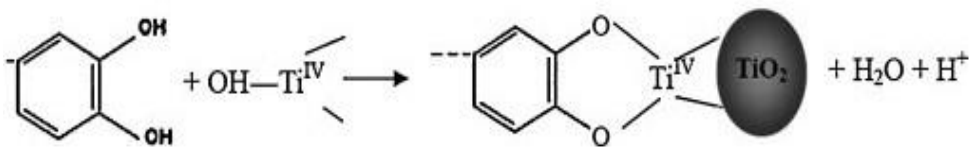

Figure 3. The mechanism of surface complexation of cyanidin with TiO_2.

Under the irradiation with white light (100 mW cm−2) from AM 1.5 solar simulator, Photovoltaic tests of DSSCs were performed. The photoelectrochemical parameters of the DSSCs sensitized with natural dye are listed in Table 1 for the CuI and CuSCN hole conductors.

Table 1: Photovoltaic performances of the cells

Dye used	Electrolyte used	J_{sc} / mA cm^{-2}	V_{oc} / V	Fill Factor	Efficiency %
Natural Dye (extracted from Anthurium)	CuSCN	1.73	0.46	0.43	0.34
	CuI	2.37	0.33	0.39	0.30

It indicates that, the prepared solid state solar cells show open circuit voltage (Voc) of 0.46 V and 0.43 of fill factor (FF) with an overall efficiency (η) of 0.34 % for CuSCN over the CuI hole conductor. Nevertheless short circuit current density (Jsc) was 2.37 mA cm^{-2} for CuI, it was 1.73 mA cm^{-2} for CuSCN.

Fig.4 shows the Variation of current-voltage curve of natural dye cyanidin based DSSCs for the two hole conductors. Experiment was conducted less than 1 sun illumination, (100 mW/cm2, and air mass 1.5).

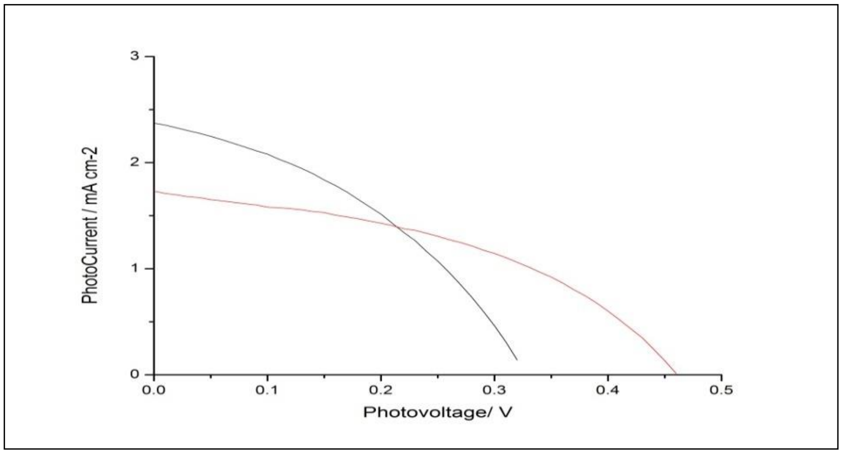

Figure 4. I-V characteristic curve of the cells (Red line for CuSCN and Black line for CuI)

However, we have found some variation in the IV curves between cells. These differences include variation in the photocurrent and fill factor, as well as changes in the open circuit voltage. It is clear that the low fill factor is a key limitation on the efficiency. The fill factor is degraded by the "flattened" shape of the IV at 1 sun. The photocurrents are also somewhat lower for the cells prepared using CuSCN, but the higher fill factor, and the higher photovoltage, result in high efficiency than cells prepared using the CuI hole conductor. As the dye and TiO_2 film were identical for the cells, the changes between the two cells must be related to differences in the CuSCN and CuI layer.

IV. CONCLUSION

In this work, the raw pigments simply extracted in acidic conditions from anthurium achieved solar energy conversion efficiency of 0.34 %, which is the highest obtained among all sensitized cells with CuSCN as the hole conductor, for the CuI hole conductor, it is 0.30%. However, Poor performance of this device may be due to inefficient charge separation at the interface caused due to penetration of fewer amounts of CuSCN/CuI. Lose of excited energy of natural dye molecules via quenching of natural dye aggregates may be another reason. We believe that the efficiency of the cell can be increased by improving a procedure to remove the lipids, carotenes, tannins and flavonols contain in the pigment solution and developing the CuI, CuSCN coating techniques. Nevertheless, the device that we have made is notable and could motivate further research into solid-state dye sensitized photovoltaic cells.

ACKNOWLEGMENT

The author thanks Mr. C.S.K.Ranasinghe for his guidance and the encouragement given to complete this study. Also wish to acknowledge Miss. E. Jayeweera and Mr. M. Wanninayaka for the support and sharing their valuable time to make this work success.

REFERENCES

[1] B. O'Regan, M. Grätzel, A low-cost, high-efficiency solar cell based on dye sensitized colloidal TiO2 films, Nature 353 (1991) 737–740.

[2] Y Chiba, A. Islam, Y. Watanabe, R. Komiya, N. Koide, L.Y. Han, Dye-sensitized solar cells with conversion efficiency of 11.1%, Jpn. J. Appl. Phys. 45 (2006) L638–L640.

[3] R. Buscaino, C. Baiocchi, C. Barolo, C. Medana, M. Grätzel, Md.K. Nazeeruddin, G. Viscardi, A mass spectrometric analysis of sensitizer solution used for dyesensitized solar cell, Inorg. Chim. Acta 361 (2008) 798–805.

[4] G. Zhang, H. Bala, Y. Cheng, D. Shi, X. Lv, Q. Yu, P. Wang, High efficiency and stable dye-sensitized solar cells with an organic chromophore featuring a binary _conjugated spacer, Chem. Commun. (2009) 2198–2200

[5] K Tennakone, G R R A Kumara, A R Kumarasinghe, K G U Wijayantha and P M Sirimanne. A dye-sensitized nano-porous solid-state photovoltaic cell. Semicond. Sd. Technol. 10 (1995) 1689-1693.

[6] Mubarak A. Khan1*,Shauk M M Khan1, Mahir Asif Mohammed2, Sabia Sultana1, Jahid M M Islam1and Jasim Uddin. Sensitization of Nanocrystalline Titanium dioxide Solar Cells using Natural Dyes: Influence of Acids Medium on Coating Formulation. American Academic & Scholarly Research Journal Vol. 4, No. 5, Sept 2012.

[7] Mounir Alhamed, Ahmad S. Issa, A. Wael Doubal*. STUDYING OF NATURAL DYES PROPERTIES AS PHOTO-SENSITIZER FOR DYE SENSITIZED SOLAR CELLS (DSSC). Journal of Electron Devices, Vol. 16, 2012, pp. 13701383.

[8] Huizhi Zhou, Liqiong Wu, Yurong Gao, Tingli Ma∗. Dye-sensitized solar cells using 20 natural dyes as sensitizers. Journal of Photochemistry and Photobiology A: Chemistry 219 (2011) 188–194.

[9] G.R.A. Kumara, S. Kaneko, M. Okuya, B. Onwona-Agyeman, A. Konno, K. Tennakone, Shiso leaf pigments for dye-sensitized solid-state solar cell, Sol. Energ. Mat. Sol. C 90 (2006) 1220–1226