Potential Natural Dyes of Three Different Plant Parts as Photosensitizers in Dye Sensitized Solar Cells

K.A.D.N. KULASINGHE[1], W.J.S.K. WEERAKKODY[1] and G.A.K.S. PERERA[2]

[1]*Department of Plantation Management, Faculty of Agriculture and Plantation Management, Wayamba University of Sri Lanka, Makandura, Gonawila (NWP), 60170, Sri Lanka*

[2]*Department of Electronics, Faculty of Applied Sciences, Wayamba University of Sri Lanka, Kanadulla, Kuliyapitiya, 60200, Sri Lanka*

ABSTRACT

Three natural dyes were extracted using three different solvents (acetonitrile, ethanol, N-hexane) from flowers of *Clitoria ternatea* (butterfly pea), leaves of *Tectona grandis* (teak) and fruits of *Basella alba* (malabar spinch) species to use as photosensitizers in fabricating dye sensitized solar cells. The extracts were characterized by UV-visible absorption spectra. The solar cells were assembled using a fluorine doped tin oxide (FTO) conductive glass plates. The photo electrochemical performances of the dye sensitized solar cells based on these dyes showed open circuit voltage (V_{oc}) ranging from 521 mV to 715 mV, short circuit photo current densities (Jsc) ranging from 1.39×10^{-4} Acm^{-2} to 3.67×10^{-4} Acm^{-2} and the power conversion efficiencies we 0.046 to 0.152. All three plant dyes tested showed the possibility of using them in dye sensitized solar cells as photosensitizers. Among them, *Clitoria ternatea* dissolved in ethanol which had the highest Voc, Jsc and power conversion efficiency has the highest potential to use as photosensitizer in dye sensitized solar cells with improved performance.

KEYWORDS: Conversion efficiency, Dye-sensitized solar cell (DSSC), Natural dye

INTRODUCTION

The technology of converting solar energy to electrical energy for the future power requirements demands developing suitable devices (Maabong *et al.*, 2015). Dye -sensitized solar cells (DSSCs) have recently penetrated into the research and development area worldwide as a promising candidate for that purpose. Dye Sensitized Solar Cells was investigated by Gratzel in 1991 (Abdel-Latif *et al.*, 2015). Since that time it has received a considerable attention due to its promising solar energy conversion ability. Among several new energy technologies DSSC constituting third generation solar cells which mimics the natural photosynthetic process of green plants are one of the most promising new energy generation systems of photovoltalic technology. It has emerged as one of renewable energy sources as a result of exploiting several new concepts and materials such as nanotechnology and molecular devices (Attanayaka *et al.*, 2011). Dye -sensitized solar cells is formed with a dye sensitized nano-crystaline metal oxide semiconducting layer deposited on a conductive glass, a counter electrode and an electrolyte. In the assembly of DSSC, the dye plays an important role in converting solar energy into electrical energy with the aid of a semiconducting photo anode (Abdel-Latif *et al.*, 2013).

Many metal complexes and organic dyes have been synthesized and used as photosensitizers. By far, the highest efficiency of DSSC by Ruthenium-containing compounds absorbed on nanocrystaline TiO_2 reached to an efficiency of 11-12% due to their intense charge-transfer absorption over the entire visible range and highly efficient metal-to-ligand charge transfer (Kim *et al.*, 2013). Although Ruthenium complexes have provided relatively high efficiency there are some disadvantages of using them as well (Azhari *et al.*, 2015). The major drawback of Ruthenium is rarity, high cost of production, toxicity and complicated synthesis process. Therefore, researchers have focused their attention on easily available dye extracted from natural sources (Ekanayaka *et al.*, 2012). The advantages of natural dyes include their availability, environmental friendliness and low cost. However, natural dyes have problems as well. Applications of these natural dyes based solar cells appear to be limited due to low Voc and Jsc. Another major problem is instability of the dye (Zhou *et al.*, 2011).

Several natural dyes from leaves, flowers and fruits such as black rice, capsicum, *Erithrina varigata* flower, *Rosa xanthiana*, curcumin, red-perilla, rosella flower, blue pea flower, *Jathropha curcas*, *Citrus aurantium*, red cabbage *etc.* have been used as sensitizers in DSSCs. Natural pigments containing anthocyanins and carotenoids have shown overall solar energy conversion efficiencies below 1% (Calogero *et al.*, 2010). Dye -

sensitized solar cells has several advantages over rare metal complexes. In this context, anthocyanin is one such flavonoid compound present in many fruits, flowers and leaves and is responsible for the red, violet and blue colors. The advantages of anthocyanin are the binding of carbonyl and hydroxyl groups to the surface of a porous TiO_2 film. This causes electron transfers from the anthocyanin molecule to the conduction band of TiO_2 (Kim *et al.*, 2013).

In this study three different natural dyes were extracted from flowers, leaves and berries of *Clitoria ternatea* (butterfly pea), *Tectona grandis* (teak) and *Basella alba* (malabar spinach) plant species using simple extraction technique. They were used to fabricate DSSCs to explore their suitability to serve as photosensitizers.

MATERIALS AND METHODS

Preparation of Dye Solutions

The study was carried out at the Faculty of Agriculture and Plantation Management and Faculty of Applied Sciences, Wayamba University of Sri Lanka from January to May 2016.

The flowers of butterfly pea, berries of Malabar spinach and leaves of teak were collected from Makandura area. The raw materials were crushed separately using a mortar and pestle. Approximately 30 g of each crushed sample was dissolved in 60 mL of ethanol, n-hexane and acetonitrile solutions separately and kept at room temperature for adequate extraction without exposure to sun light. After extraction, the solid residues were filtered to obtain a dye solutions were characterized by UV-visible (UV-Vis.) absorption.

Titanium Dioxide (TiO_2) Electrode Preparation

A fluorine-doped tin oxide (FTO) conductive glass slides were first cleaned with a detergent, acetone, ethanol and water. Then, the plates were dried using hot air. For preparation of TiO_2 paste, TiO_2 (0.2 g) was ground using mortar and pestle about one minute. Then three drops of acetic acid were added and grinding was carried out for few minutes. After that one drop of Triton x and three drops of acetic acid were added and mixture was ground until it became a pulp. Then six drops of acetic and few drops of ethanol were added into the mixture and grinding was continued until all TiO_2 particles were ground well. After preparing the paste, electrodes were prepared by doctor blade method and they were kept to dry in open air. When paste was completely dried, 1 cm^2 area was created by scratching off excess TiO_2 paste. Finally, above electrodes were sintered at 450 °C temperature for 45 min. Sintered electrodes were dipped in natural dye solution for 24 h before assembling DSSCs.

Gel Polymer Electrolyte Preparation

For preparing the electrolyte samples, poly methyl methacrylate (PMMA; 100 mg), ethylene carbonate (EC; 150 mg), propylene carbonate (PC; 150 mg), Pr_4NI (200 mg) and Iodine (I_2; 1.65 mg) were measured using an analytical balance. Small amount of acetone was added into PMMA and then it was heated 60 °C until all the PMMA were dissolved. The weighed amount of EC, PC, Pr_4NI were added into PMMA and then temperature was increased up to 80 °C. Finally, I_2 was added to complete the process. The resulting slurry was cast on a dye absorbed FTO glass plate and pressed by a Platinum plate which was used as the counter electrode.

All the fabricated solar cells were characterized by taking I-V measurements using a computer controlled e DAQ potentiostat under 100 Wm^{-2} irradiations.

The photoelectric conversion efficiency (η) and fill factor (FF) was calculated using the following equation:

$$\eta(\%) = \frac{\text{Voc} \times \text{Jsc} \times \text{FF} \times 100}{\text{Pin}}$$

Where η is the efficiency, and Voc, Jsc and FF are the open-circuit voltage, short circuit current density and fill factor, respectively. P_{in} is the maximum light energy.

$$\text{FF} = \frac{\text{Jm} \times \text{Vm}}{\text{Jsc} \times \text{Voc}}$$

Where Jm and Vm are solar cell photocurrent and voltage at maximum power point. The maximum power point is determined from the P-V curves from which Jm and Vm can be calculated.

RESULTS AND DISCUSSION

UV-Visible Absorption Spectra

Three different plant dyes with three different solvents (acetonitrile, ethanol and N-hexane) were subjected to UV-VIS spectroscopy to confirm their suitability. In order to employ a natural dye for DSSCs, its UV-VIS absorption spectrum should have response within the visible range.

The maximum absorbance of teak dissolved in acetonitrile and ethanol, butterfly pea dissolved in acetonitrile and ethanol and malabar spinach dissolved in acetonitrile were found within the visible range (380 nm-700 nm). The dyes having peak points within the visible range were selected for fabrication of DSSC (Figures1, 2, 3, 4 and 5).

It was found that teak dissolved in acetonitrile has only one absorption peak at the wave lengths of 671 nm (Figure 2). Teak dissolved in ethanol has two absorption peaks at the wave lengths of 666 nm and 582 nm (Figure 1). Absorption peaks for Butterfly pea dissolved in acetonitrile has also two peaks at wave lengths of 624 nm and 527 nm (Figure 3). Butterfly pea dissolved in ethanol has three peaks at wave lengths of 646 nm, 466 nm and 439 nm (Figure 4). Malabar spinach dissolved in acetonitrile also has two peaks at the wave lengths of 661 nm and 551 nm (Figure 5).

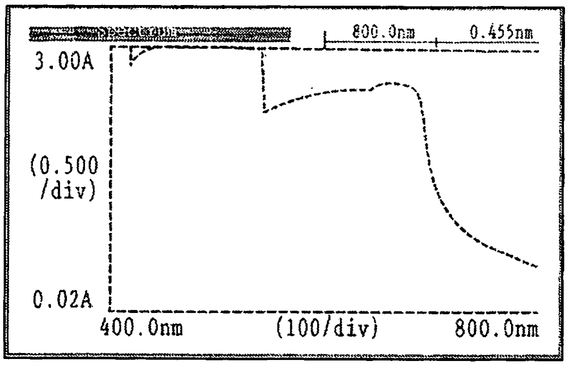

Figure 1. UV-Vis absorbtion spectra of the teak dissolved in ethanol extract

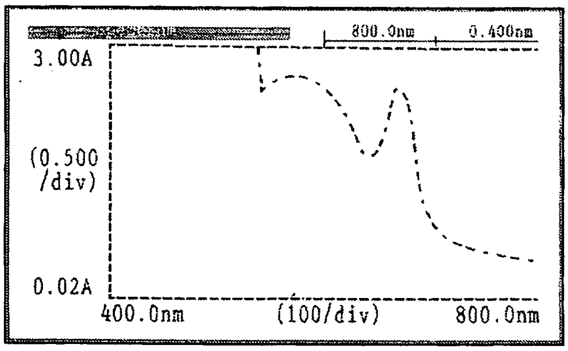

Figure 2. UV-Vis absorbtion spectra of the Teak dissolved in acetonitrile extract

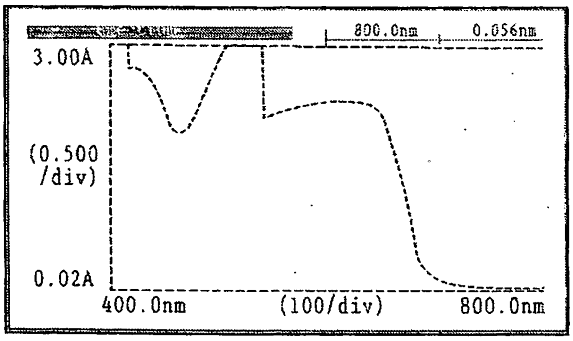

Figure 3. UV-Vis absorption spectra of the butterfly pea dissolved acetonitrile extract

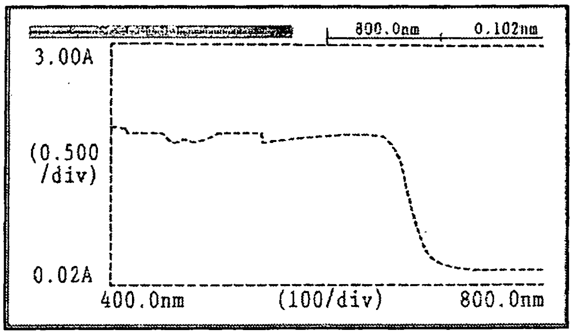

Figure 4. UV-Vis absorption spectra of the butterfly pea dissolved ethanol extract

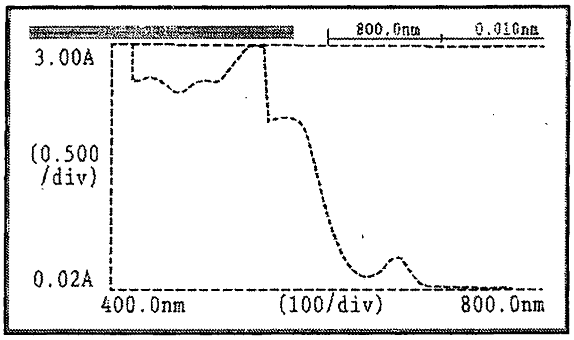

Figure 5. UV-Vis absorption spectra of the Malabar Spinach dissolved acetonitrile extract

Photo Electrochemical Performance of DSSCs

Photovolatic tests of DSSCs using these natural dyes as sensitizers were performed by measuring the current-voltage (I-V) curves under irradiation with light.

The I-V curve of a solar cell yields important photochemical properties. These include the short circuit photocurrent density (Jsc), open circuit voltage (Voc), the maximum power point (Pmax), the fill factor (FF) and the conversion efficiency (η). These five types of dye have shown the characteristic shape of the I-V curve.

Fill factor reflects the electrochemical losses occur during the operation of the DSSC. η of a DSSC is a good measure to evaluate the ability of a DSSC to convert solar energy to electricity.

The Voc varies from 521 mv to 715 mv, and Jsc were changed from 1.39×10^{-4} Acm^{-2} to 3.67×10^{-4} Acm^{-2}. The highest Voc (715 mv) and Jsc (3.67×10^{-4} Acm^{-2}) were obtained from the butterfly pea extracted from ethanol. The lower Voc (521 mv) and Jsc (1.39×10^{-4} Acm^{-2}) were obtained from teak extracted from ethanol. The fill factors of these DSSCs were mostly higher than 55%. The highest fill factor value (0.738) and lowest fill factor value (0.582) were obtained from butterfly pea dissolved in acetonitrile and butterfly pea dissolved in

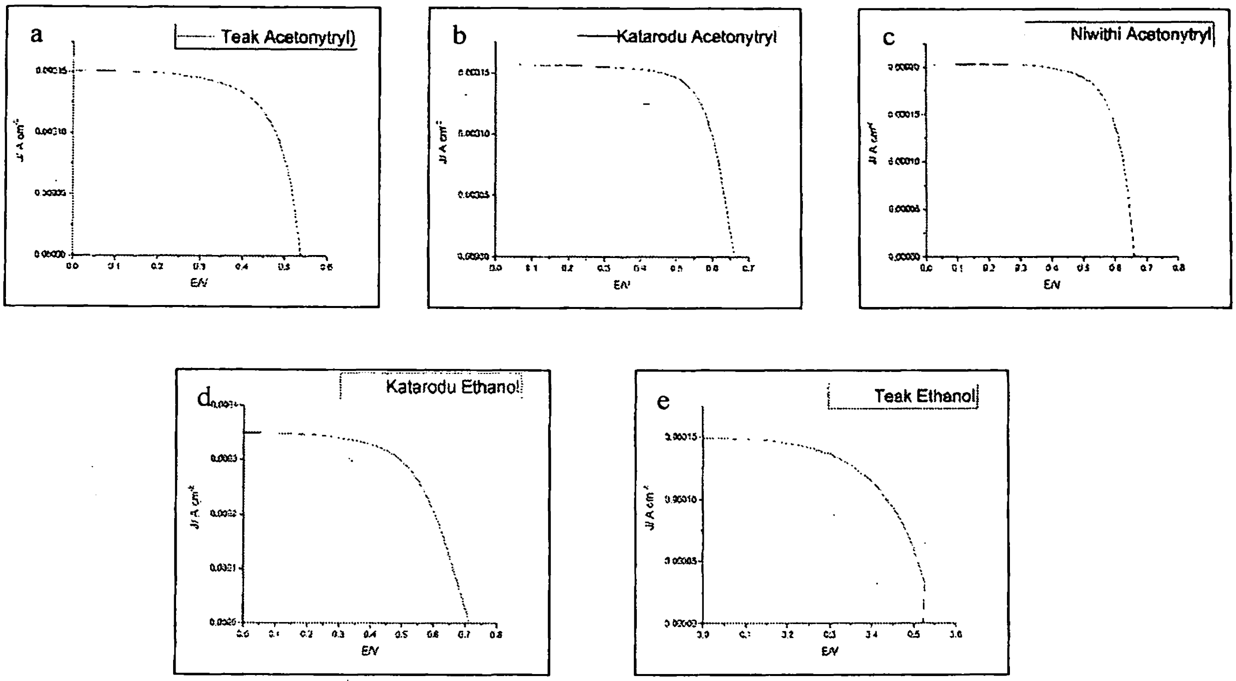

Figure 6. Current- voltage (I-V) characteristics of the photovoltaic devices sensitized with (a) teak –acetonitrile, (b) butterfly pea - acetonitrile, (c) Malabar spinach - acetonitrile, (d) Butterfly pea-ethanol, (e) teak – ethanol; *J- current, V- voltage*

Table 1. Photovoltaic performance of the DSSC sensitized with the dyes with three different solvents

Sample	Solvent	Voc (mv)	Jsc (10^{-4} Acm^{-2})	FF	η
Teak	Acetonitrile	539	1.51	0.675	0.055
Teak	Ethanol	521	1.39	0.636	0.046
Butterfly Pea	Acetonitrile	661	1.56	0.738	0.075
Butterfly Pea	Ethanol	715	3.67	0.582 .	0.152
Malabar Spinach	Acetonitrile	662	2.03	0.734	0.099

Voc- open-circuit voltage, Jsc- short circuit current density, FF- fill factor, η- efficiency; DSSC

ethanol. Efficiency was varied from 0.046 to 0.152. The highest was obtained from butterfly pea extracted from ethanol, while the lowest was obtained from teak dissolved in ethanol.

According to the values of Voc, Jsc and η, the best performance was obtained from butterfly pea dissolved in ethanol. Among these dye solutions, butterfly pea dissolved in ethanol was the darkest dye. That may be reason for demonstrating the highest performance. Evidently, (Maabong *et al.*, 2015), showed higher conversion efficiency with darker dyes. Further research is necessary for further purification to increase the performance as reported by increase the conversion efficiencies of these dyes (Zhou *et al.*, 2011).

CONCLUSIONS

Dyes extracted from teak leaves in acetonitrile and ethanol, butterfly pea flowers in acetonitrile and ethanol and Malabar spinach fruits in ethanol were shown successful performances as the photosensitizer for Dye Sensitized Solar Cells. Among them the best performing dye (Voc, Jsc and η were 715 mv, 3.67 Jsc and 0.152 respectively); butterfly pea flowers extracted in ethanol is the most promising natural dye for solar cell development.

ACKNOWLEDGMENTS

Authors wish to express their gratitude to Mr. W.A.D.S.S. Weerasinghe, Mr. Y.M.C.D. Jayathilaka and Miss K.E.C.M. Bandaranayke, Polymer Research Electronics Laboratory, Department of Electronics, Faculty of Applied Science, Wayamba University of Sri Lanka, for their encouragements and continuous support in testing and assembling solar cell during the study period. Further, non-academic staff members of the Department of Plantation Management are acknowledge with gratitude for their support in laboratory work.

REFERENCES

Abdel-Latif, M.S., Abuiriban, M.B., El-Agez, T. and Taya, S.A. (2015). Dye sensitized solar cells using dyes extracted from flowers, leaves, parks and roots of three trees. *International journal of renewable energy*, **5**, 295.

Abdel-Latif, M.S., Agez, T.M., Taya, S.A., Batniji, A.Y. and Ghamri, S.E. (2013) Plant seeds based dye sensitized solar cells, *Scientific Research.* 516.

Attanayaka, P., Silva, C., Premachandra B.A.J.K., Alwis, A.A.P. and Senadheera G.K.R. (2011). Using over 100 natural dyes as sensitizers. **4**, 2-3.

Azhari, M.A., Arith, F., Ali F., Rodzi, S. and Karim, K. (2015). Fabrication of low cost sensitized solar cell using natural plant pigment dyes. *ARPN Journal of engineering and applied sciences*, **10**, 27092.

Calogero, G., Marco, G., Caramori, S., Argazzi, R., Cario, A. and Bignozzi, C.A. (2010). Efficient dye sensitized solar cells using red turnip and purple wild Sicilian prickly pear fruits. *International journal of molecular science*, **11**, 255-257.

Ekanayake, P., Iskandar, M., Tennakoon, K., Ming, L.C., Yoong, V.N., Zain, R., Senadeera, R. and Yoshikawa, S. (2012). Fabrication of eco-friendly dye sensitized solar cells using pigments from Melastoma malabath, a native plant in Bornes, *Ceylon journal of science*, **16**, 65-70.

Kim, H., Bin, Y., Karthick, S.N., Hemalatha, S. and Vijayakumar, G. (2013). Natural dye extracted from Rhododendron species flowers as a photosensitizer in dye sensitized solar cell. *International Journal of Electrochemical Science*, **8**, 6735-6737.

Maabong, K., Muiva, C. M., Monower, P., Sathiaraj, T.S., Hopkins, M., Nguyen, L., Malungwa, K. and Thobega, M. (2015). Natural pigments as photo sensitizers for dye-sensitized solar cells with TiO_2 thin films. *International Journal of Renewable Energy Research*, **5**, 55.

Zhou, H., Wu, L., Gao, Y. and Ma, T. (2011). Dye sensitized solar cells using 20 natural dyes as sensitizers. *Journal of Photochemistry and Photobiology Chemistry*, **219**,188-193.