DYE- SENSITIZED SOLAR CELL WITH NUT GRASS (*Cyperus rotundus*) LEAVES, MALABAR SPINACH (*Basella alba*) BUDS, and MAYANA (*Plectranthus scutellarioides*) LEAVES EXTRACTS AS PHOTOSENSITIZERS

Mary Rose T. Sullano,*, Rengel Cane E. Sia***
Department of Chemistry, University of Science and Technology of Southern Philippines,
9000, Cagayan de Oro City, Philippines
For correspondence; *sullano.maryrose@gmail.com, ** rengelcane.sia@ustp.edu.ph

***ABSTRACT**: Plants, through photosynthesis, are capable of converting sunlight into a useable form of energy. This natural process is imitated to produce electrical energy through the use of Dye-Sensitized Solar Cell (DSSC). In this research, the DSSCs were fabricated using the natural dyes extracted from mayana leaves, malabar spinach buds, and nut grass as the photosensitizers. The highest recorded open-circuit voltage (VOC) in this study is 108.1 mV which is from the DSSC fabricated with malabar spinach methanol extract; the DSSC fabricated with malabar spinach petroleum ether extract has exhibited the highest maximum power (Pmax) with 0.733 mW and a short-circuit current (ISC) of 0.015 mA. Furthermore, the DSSC with nut grass acetone extract has a fill factor (FF) that ranges from 0.9885 to 0.9889. The effects of the different photosensitizers and extraction solvents were carried out. It was found out that Malabar spinach is a better sensitizer and the effect of the solvent is dependent on the type of plant sample used.*

Keywords: Dye-sensitized solar cell, photosensitizers, nut grass, Ramayana plant, Malabar spinach

1. INTRODUCTION

Non-renewable energy, despite being affordable, is limited and can easily be depleted and fully relying on this type of energy is putting the world energy demand at risk. Thus, there is a need for a cleaner and renewable source of energy.

Solar energy is one of the most promising sources of renewable energy which can be captured through the use of solar panels. However, the conventional silicon solar cells are expensive to manufacture. This leads scientists to search for alternative solar cells which include the dye-sensitized solar cell. This solar cell made use of a dye as photosensitizers; however, synthetic photosensitizers are limit by their toxicity [1].

Plants, through photosynthesis, are capable of converting sunlight into a usable form of energy. This natural process made plants as a competitive alternative source for synthetic photosensitizers. The molecules in the plants that facilitate the capture of certain wavelengths of visible light which in turn produce excited electrons are the plant pigments, thus, plant extracts are potential photosensitizers for the dye-sensitized solar cell [2].

A Dye-Sensitized Solar Cell (DSSC) usually has a transparent conductive oxide substrate, nanostructured semiconductor, visible-light absorber dye, electrolyte, and a counter electrode. Electrons in the plant pigment molecules reach an excited state upon absorption of light. These excited electrons are injected into the conduction band of the semiconductor and into the external load which causes the pigment molecule to become oxidized. Addition of an electrolyte, which is a redox couple, is necessary to regenerate the pigment molecule. The excited electrons enter the cell again through the counter electrode which is coated with a conductive material and the cycle continues [3].

In this study, a DSSC was fabricated using a methanol, petroleum ether, and acetone dye extract from Ramayana leaves, Malabar spinach buds, and nut grass.

2. EXPERIMENTAL DETAILS

The plant samples were rinsed with tap water followed by distilled water, dried for one week, and the Ramayana leaves and nut grass was cut to small pieces and ground while the purple Malabar spinach buds were picked and pound. A mass of 10 g of each plant samples was weighed and soaked in 100 mL solvent at room temperature for 24 hours then filtered. Additional soaking was done twice separately with 100 mL of each of the solvents for 1 hour with occasional shaking. The extracts were then partially concentrated using rotary evaporator operated at 40-45 ^oC and stored in dark amber bottle in a refrigerator for later use. Paper chromatography was then employed for the possible identification of the plant pigments through the use of an ether: acetone solvent mixture [4]. The absorption spectra of the plant extracts in the visible light spectrum (400 – 700 nm) were measured using the DR 5000 HACH UV-Vis spectrophotometer.

The DSSCs were fabricated using a zinc oxide (ZnO) nanopowder (10-30 nm) suspension prepared by making a watery shampoo-like consistency paste with 1 g ZnO nanopowder and dilute nitric acid (1:1000). The ZnO suspension was deposited on the conductive side of the Indium Tin Oxide (ITO) glass by doctor blade's method and sintered by heating the slide for 30 minutes through the use of a bunsen burner. After cooling, the ZnO electrode was submerged in the natural dye extracts for 3 hours. A counter electrode was prepared by coating the conductive side of an ITO glass with graphite from a pencil. Two (2) drops of the iodide/triiodide redox couple [5] were placed on the graphite slide. The ZnO electrode was then placed on top of the counter electrode while allowing each side of the glass to hang off for further testing. The Solar cell was then sealed using 2 binder clips. Since upon sintering of the ITO, resistance increases, and electrons will find it difficult to travel, thus an aluminium foil is inserted to the edges of the electrodes of the solar cell to make electron transport from the ZnO electrode to the outer circuit easier.

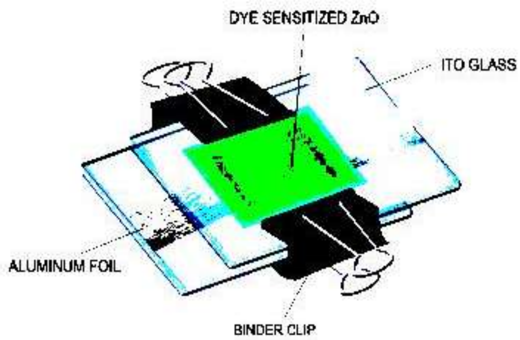

Figure (1) fabricated dye-sensitized solar cells

The dye-sensitized solar cell was evaluated through the circuit shown in Figure 2. The circuit follows the principle of Ohm's Law wherein a halogen lamp was used as light source, a potentiometer was used to vary the resistance in the circuit and two (2) multitesters were used to measure the current and the voltage simultaneously.

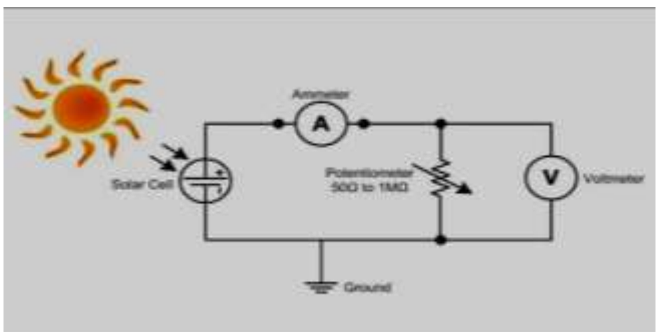

Fig (2) experimental set-up for measuring the current-voltage characteristics of DSSC

3. RESULTS AND DISCUSSION

Paper chromatography and optical measurement were employed for the possible identification of the different plant pigments. Table 1 shows that chlorophyll a is present in all the extracts. This could be due to its unique and crucial role as the only pigment in the chloroplast that can pass excited electrons to a series of proteins located in the thylakoid membrane which in turn drives photosynthesis [1][6]. Aside from chlorophyll a, accessory pigments like xanthophylls, β-carotene, anthocyanin, and betacyanin were found to be present also in the extracts in which will allow the absorption of a broader range of wavelengths to complement with the certain wavelengths captured by the chlorophyll molecule. Since excited electrons are crucial in the operation of DSSC, thus the more plant pigments present in a plant extract, the more energy it can absorb to produce excited electrons for the effective operation of the dye-sensitized solar cell.

The absorption spectra of the plant extracts provide basic information about the portion of the solar output that is absorbed to fuel photosynthesis and the needed amount of energy to boost an electron from its ground state to its excited state [7,8].

Table (1) the identified plant pigments for the different plant extracts

	Malabar Spinach Buds	Mayana Leaves	Nut Grass
Acetone Extract	Chl a, BC, XT	Chl a, β-carotene, AC, XT	β-car, Chl a, XT
Methanol Extract	Chl a, BC, XT	Chl a, XT, AC	Chl a, XT
Petroleum Ether Extract	Chl a	Chl a, β-car, AC	β-car, Chl a,

Chl a – chlorophyll a
BC – betacyanin
AC – anthocyanin
XT – xanthophyll
β-car - β-carotene

The difference in energy levels between the electron energy states is the band gap energy. This can be related to the performance of the DSSC since a low band gap means that the electrons in the ground state needed less energy to go to the excited state and become free electrons that will travel from the DSSC toward the external load to perform work.

Table 2 shows the lowest calculated bandgap energies that each specific pigment possesses. Higher band gap energies are caused by the presence of the accessory pigments since these pigments absorbed in the higher energy portion of the visible region while the lowest bandgap energy calculated was that of the pigment chlorophyll a. This means that a photon with energy higher than the bandgap energy of 1.87-1.88 eV can excite an electron in the chlorophyll a molecule. The low band gap energy of the pigment chlorophyll a is may be due to its crucial role as the pigment that donates electrons to a nearby protein which is needed for photosynthesis [1][6].

Table (2) the lowest estimated band gap energy for each plant pigment

Plant Pigment	Band Gap Energy (eV)
Chlorophyll a	1.87-1.88
β-carotene	2.76
Xanthophyll	2.80
Anthocyanin	2.16
Betacyanin	2.35

The electrical characteristics of the dye-sensitized solar cell that were observed are the open-circuit voltage, the short-circuit current, the maximum power output, and the fill factor.

The results in Table 3 showed that each plant extracts exhibit different electrical performance for each extraction solvent used. This can be related to the ability of each solvent to extract varying amounts of the different plant pigments in the samples. More plant pigments extracted by a solvent, the wider the range of wavelengths a fabricated DSSC can absorb and the more plant molecule can contribute to giving off excited electrons, thus, producing a better electrical performance. However, the DSSC fabricated from the petroleum ether extract of nut grass exhibit no electrical output which might be due to the absence of a pigment that can anchor better to the ZnO surface. The hydrocarbon-abundant nature of chlorophyll a and β-carotene, which is present in the petroleum ether extract, decreases their ability to anchor in the ZnO surface which could result to the difficulty of injecting an electron unto the ZnO [9]. Since the results of the different electrical performance of the DSSCs fabricated from each different extracts cannot generally state which solvent is more effective from the three solvents used, the effect of extraction solvent to the electrical output may be attributed to the nature of the plant samples because the three plant samples have varying abundance of the different plant pigments. A solvent that can extract pigments with good anchoring group and pigments with low band gap might be considered a desirable extraction solvent. However, in this study, methanol and acetone were effective as solvents for extraction because of the observed electrical output from its fabricated DSSCs.

Table (3) the photoelectrical properties of the fabricated DSSCs

DSSC from the Following Extracts	V_{oc} (mV)	I_{sc} (mA)	P_{max} (mW)	FF
Mayana Acetone	70.6	0.014	0.396	0.4006
Mayana Methanol	6.2	0.005	0.0126	0.4065
Mayana Petroleum Ether	9.4	0.004	0.016	0.4269
Malabar Spinach Acetone	56.2	0.004	0.0844	0.3757
Malabar Spinach Methanol	108.1	0.009	0.2847	0.2926
Malabar Spinach Pet. Ether	104.45	0.015	0.733	0.4678
Nut Grass Acetone	8.95	0.001	0.0088	0.9888
Nut Grass Methanol	85.9	0.008	0.2844	0.4138
Nut Grass Pet. Ether	0	0	0	0

Photosensitizers, being the source of the excited electrons, were found to have a significant effect on the electrical properties of the DSSC wherein the extracts of Malabar spinach buds exhibit excellent electrical properties compared to the other two photosensitizers and thus a better photosensitizer. This can be due also to the plant pigments present in the extracts while taking consideration of the band gap energy of each plant pigment molecule and the anchoring group which contributes to the better binding to the ZnO semiconductor [9]. Table 1 shows that the Malabar spinach and Ramayana extracts have the presence of the more polar plant pigments which can contribute to the better binding of the pigments to the ZnO surface while nut grass has only hydrocarbon-concentrated plant pigments that lack the needed anchoring group, thus, affecting their respective electrical outputs [10].

4. CONCLUSIONS

Based on the paper chromatographic identification of plant pigments and through optical measurements, the plant pigments found in the plant extracts, in which probable electron donors, are chlorophyll a, xanthophyll, β-carotene, anthocyanin, and betacyanin. Methanol and acetone were effective as solvents for the extraction of the plant pigments, however, the solvent's effect on the electrical performance of the DSSCs are dependent on the type of plants used. Furthermore, the band gap energies calculated ranges from 1.87 to 2.80 eV which is quite low, thus, less energy is required to produce excited electrons. And thus, the locally-found plants: Ramayana, Malabar spinach, and nut grass can be used as effective sensitizers for dye-sensitized solar cells.
The low cost, easy fabrication and environmental friendliness of dye-sensitized solar cell is a good factor to use DSSC as a device for converting solar energy into electrical energy.

5. REFERENCES

[1] Maabong, k, Muiva, C. M., Monowe, P., Sathiaraj, T. S., Hopkins, M., Nguyen, L., Thobega, M.. 'Natural Pigments as Photosensitizers for Dye-Sensitized Solar Cells with TiO2 Thin Films'. International Journal of Renewable Energy Research, 5(1), 54 – 60 (2014)

[2] Rabinowitch, E., & Govindjee. Photosynthesis. John Wiley & Sons, Inc. (1969)

[3] Bella, F., Gerbaldi, C., Barolo, C., & Gra¨tzel, M. Aqueous dye-sensitized solar cells. Chemical Society Reviews, 44(11), 3431-3473. doi:10.1039/c4cs00456f (2014)

[4] BOYER , R. F. Isolation and Spectrophotometric Characterization of Photosynthetic Pigments . Biochemical Education, 18(4), 203-206. doi:10.1016/0307-4412(90)90137-D (1990)

[5] Maulana, E. , Pramono, S. , Fanditya, D. , Julius, M. 'Effect of Chlorophyll Concentration Variations from Extract of Papaya Leaves on Dye-Sensitized Solar Cell'. World Academy of Science, Engineering and Technology, International Science Index 97, International Journal of Electrical, Computer, Energetic, Electronic and Communication Engineering, 9(1), 49 - 52. (2015)

[6] Raven, P., & Johnson, G. "Biology (6th ed.). Boston, Massachusetts: The McGraw Hill Companies. (2002)

[7] Ördög, V. "Plant Physiology" (2011)

[8] Syafinar, R., Gomesh, N., Irwanto, M., Fareq, M., & Irwan, Y. "Chlorophyll Pigments as Nature Based Dye for Dye-Sensitized Solar Cell (DSSC)". Energy Procedia, 79, 896 -902, . doi:10.1016/j.egypro.2015.11.584 (2015)

[9] Hug, H., Bader, M., Mair, P., & Glatzel, T. "Biophotovoltaics: Natural pigments in dye-sensitized solar cells" Applied Energy, 115, 216-225. doi:10.1016/j.apenergy.2013.10.055 (2014)

[10] Hasoon, S. A., Al-Haddad, R. M. S., Shakir, O. T., & Ibrahim, I. M. "Natural Dye-Sensitized Solar Cell Based on Zinc Oxide". International Journal of Scientific & Engineering Research, 6(5), 137 – 142. (2015)