

Optical Properties of Some Selected Fruit Juices and their Usage in Photovoltaic Cells as a Sensitizer

P. M. Sirimanne¹, P. N. Dissanayake²

Department of Science and Technology, Uva Wellassa University, Badulla, Sri Lanka

Abstract: Use of natural pigments in photo-electrochemical cells, as a sensitizer is a cost effective approach compare to that of ruthenium based metal centered dyes. Different pigments extracted from fruits were utilized as a sensitizer in solar cells. However, ruthenium based metal centered dyes exhibit much higher power conversion efficiency in dye-sensitized solar cells, due to excellent matching of band-gap with HOMO, LUMO levels of dye and charge transfer process.

Keywords: photo-electrochemical solar cells, photosensitization, quinonoidal, cole-cole plot.

1. Introduction

The history of photovoltaic began with the investigation of photo-effects on silver halides in 19th century. Becquerel demonstrated the first photovoltaic cell, which was composed of silver chloride coated metal electrode immersed in an electrolyte in 1838 [1]. Significant progress in sensitization process was ascertained after another few decades by Gerischer and Tributsch [2]. The major break through out of dye-sensitized solar cells was usage of highly porous titanium dioxide film with a large photoactive area by a Swiss research group in 1991 [3]. Since then several hundreds of research publications have been aroused in the field of dye sensitization. Most of these investigations were based with ruthenium based metal centered dyes. Several environmental problems are encountered in the usage of with ruthenium based metal centered dyes in this type of solar cells. Hence, scientists have chosen environmental friendly sensitizers (organic dye and natural pigments) in the fabrication of sensitized solar cell [4,5]. However, efficiencies of these cells are much lower than ruthenium based solar cells. In this viewpoint, finding a stable, environmental friendly organic dye or natural pigment is one of the scientific hurdles. In this manuscript, we discussed the properties of different types of pigments extracted from natural fruits and their applications in sensitized solar cells.

2. Experimental Section

2.1 Preparation of screen printing TiO₂ pastes

2.1.1. Nano-crystalline TiO₂ paste

An amount of 12 g of acetic acid was added to 58.6 g of titanium iso-propoxide while stirring at room temperature. The mixture was poured into 290 ml water, as quickly as possible, with vigorous stirring (700 rpm). The hydrolysis reaction was stirred for one hour. 5.4 ml of 65% nitric acid was added to the mixture and heated from room temperature to 78 °C, within 40 min, and peptized for 75 min. Water was added to the mixture until 370 ml. The suspension was kept in a titanium autoclave and heated to 250 °C for 12 h. 2.4 ml of 65% nitric acid was added and the particles dispersed with a 200 W ultrasonic titanium probe at a frequency of 15 pulses per sec. The resultant colloid was concentrated with a rotary-

evaporator. The solution was centrifuged and washed with ethanol three times to produce a precipitate of TiO₂ in ethanol. An amount of 16 g of TiO₂ precipitate was mixed with 64.9 g of a solution of terpineol and ethyl cellulose in ethanol. The precipitate was well mixed and rotary-evaporated.

2.1.2. Micro-crystalline TiO₂ paste

400 nm particles (in aqueous solution) are transferred into ethanol by centrifuging and removing supernatant then topping up with pure ethanol. 5 parts of 400 nm titania paste and 1 part of 18 nm titania paste were mixed with 3.5 parts of ethyl cellulose and 30.5 ml of terpineol. The mixture was rotary-evaporated until ethanol is removed.

2.2 Preparation of TiO₂ films

Conducting glass plates (FTO) were cut into 1 x 2.5 cm² pieces, cleaned by detergent, thoroughly washed with distilled water and dried in an oven. One of the edges of FTO (1 x 1 cm²) was covered with 3M-tape and placed horizontally on a hotplate facing the conducting side to air. Temperature of the hotplate was gradually increased up to 450 °C. A solution of titanium diisopropoxide bis(acetylacetonate) (Sigma-Aldrich) in isopropanol (1:9) was sprayed over the FTO quickly at the thermal equilibrium at 450 °C and allowed to reach to room temperature by disconnecting power of the hotplate. This procedure results compact nano-crystalline TiO₂ layer on FTO. The microcrystalline TiO₂ paste was coated on the compact TiO₂/FTO substrates by screen-printing. The TiO₂ coated films (0.5 cm x 0.5 cm) were backed at 450 °C for 30 min. Finally TiO₂ substrates were wetted from a 0.05 M TiCl₄ (aq) in 20% HCl is diluted from a 2.0 M stock solution and again backed at 450 °C for another 30 min.

2.3 Pigment coating procedure on TiO₂ film

Different types of natural pigments were extracted by squeezing the ripe fruits. The juice was concentrated at 60°C in atmospheric condition. Pigment was coated on TiO₂ electrodes as follows: TiO₂ coated glass plates were kept immersed in a mixture of pigment solution. The temperature of the pigment was maintained as 40 °C. The amount of

pigment on TiO₂ electrodes was controlled by varying the immersion time in the pigment solution.

2.4 Assembling of the cell

2.4.1. Preparation of Pt coated electrodes

10 mM H₂PtCl₆ in isopropanol solution was prepared. One drop of this solution was put onto the conductive side of FTO electrode and allows drying. FTO counter electrode (active side up) was inserted into ceramic tube, gradually heated up to 400 °C leave for 15 min., allowed to cool electrode. A hole with a diameter of 1 mm was made on the Pt coated FTO electrode.

2.4.2. Preparation of electrolyte solution

An electrolytic solution was prepared by maintaining 0.03 M iodine, 0.5 M 4-tertbutylpyridine, 0.6 M 1-butyl-3-methylimidazolium iodide and 0.1 M guanidinium thiocyanate in a mixture of acetonitrile/valeronitrile 85:15 by volume.

2.4.3. Sealing of the cell

A rectangular hole with the dimension of 0.5 cm x 0.5 cm was made the center of 1 cm x 1 cm Surlyn film (thickness is 25 μm). This film was placed on the dye coated TiO₂ film as the rectangular hole superimpose with the dyed TiO₂ film (0.5 cm x 0.5 cm). A Pt coated FTO electrode hole with a diameter of 1 mm was placed on this TiO₂ electrode with the Surlyn film and heated by applying pressure on glass electrodes as Surlyn film melts and adhesive with two electrodes. The electrolyte was filled in to the device from the back hall and hall was sealed.

2.5 Measurements

Absorption spectra of dye solutions and dye coated TiO₂ films were measured by using UV-VIS-NIR spectrometer (Jasco V-570). Morphology of the cell was studied using scanning electron microscope. Photo-effects of the cell were studied by illuminating the cell through TiO₂ layer. The variation of photocurrent of the cell with the wavelength was measured using monochromator (Jasco) coupled with single-phased lock-in amplifier (NF Instrument-5600 A), under constant photon energy illumination mode. Current-voltage characteristics were recorded with a solar simulator (Wacom) coupled with semiconductor parameter analyzer (Hewlett Packard HP 4145B), under 1.5 AM condition. Scan speed was maintained as 0.01 Vmin⁻¹. The interfacial electrical properties of the cells were studied natural bias under a three-electrode configuration with the same electrolyte, by using a multi-channelled potentiostat (Princeton Applied Research) coupled with a computer. The charge transfer resistance at the electrolyte-electrode interface was evaluated from EClab software.

3. Results and Discussion

TiO₂ electrodes used in the present experiment are prepared as producing maximum photo-performance, as reported previously [6]. These TiO₂ electrodes are composed with three components, namely (a) dense TiO₂ layer, (b) nano-

crystalline TiO₂ layer and (c) meso-porous TiO₂ layer. These three layers can be easily distinguished by the nature of the morphology of the layers. The morphology of each TiO₂ layer is shown in Fig. 1. The cross-sectional image of the electrode is also shown image d in Fig. 1. The average thickness of the electrode was evaluated as 20 μm from a thickness meter (Fig. 2).

Capability of using different types of natural fruit juices extracted from pomegranate (*Punica granatum*), red-flesh dragon (*Hylocereus costaricensis*), prickly pear cactus

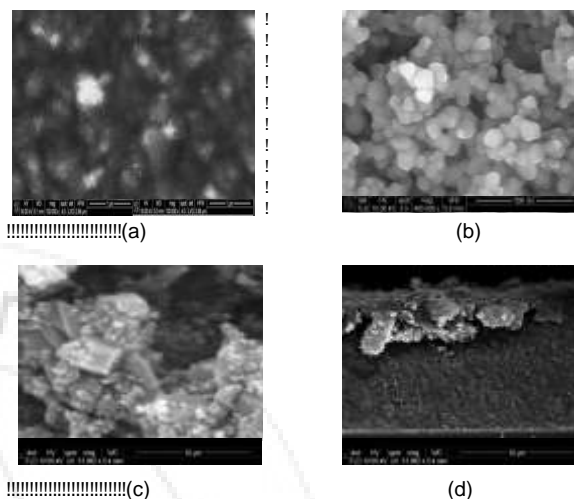


Figure 1: The morphology of TiO₂ electrodes a) dense TiO₂ layer, (b) nano-crystalline TiO₂ layer and (c) microcrystalline TiO₂ layer and (d) cross section of TiO₂ electrode.

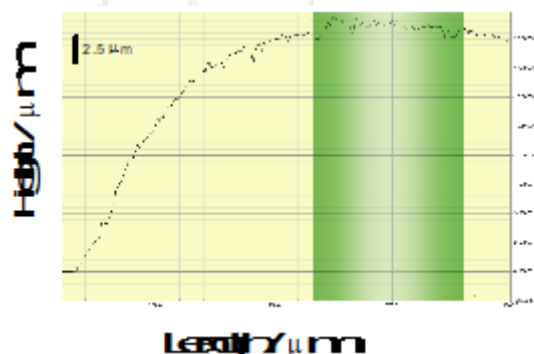


Figure 2: The variation of thickness of the electrode

(*Opuntia*), and red ginger lily (*Etilingera Elatior*) was used as sensitizer in photovoltaic cells. These fruit juices can keep several hours without fermentation in atmospheric condition. However, concentrated fruit juices were able to keep several weeks under refrigerate. Absorption spectrum of natural fruit juice (a) pomegranate (b) red-flesh dragon (c) prickly pear cactus and (d) red ginger lily is shown in Fig. 3.

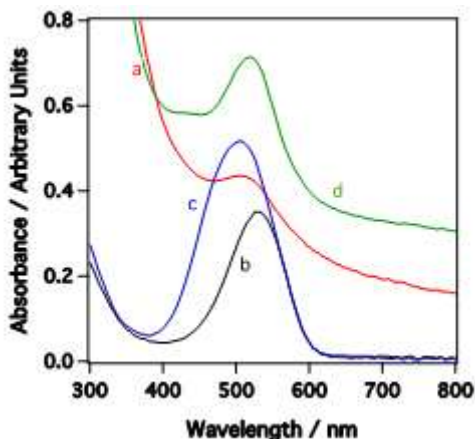


Figure 3: Absorption spectrum of natural fruit juice (a) pomegranate (b) red-flesh dragon (c) prickly pear cactus and (d) red ginger lily

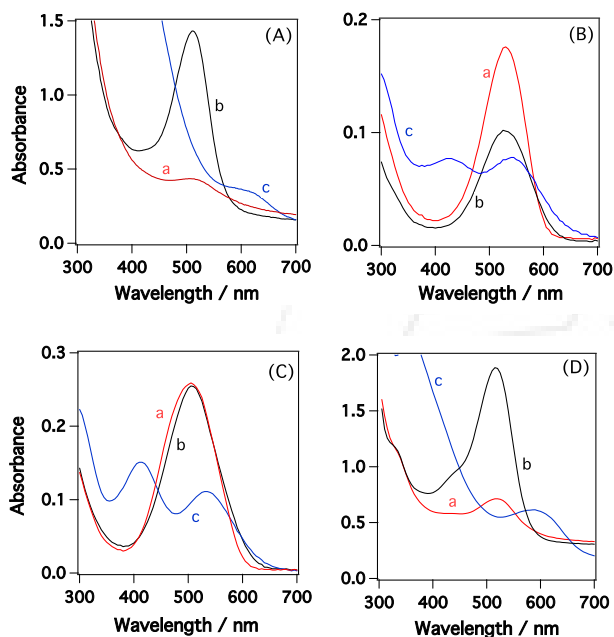


Figure 4: Absorption properties of fruit juices for (A) pomegranate (B) red-fleshed dragon (C) prickly pear cactus and (D) red ginger lily as (a) natural, (b) acidic and (c) basic solutions

These fruit juices absorb different regions of visible light due to their structures. Absorption properties of fruit juices (A) pomegranate (B) red-fleshed dragon (C) prickly pear cactus and (D) red ginger lily were studied under acidic and basic media and results are shown in Fig. 4. Natural pomegranate juice absorbs visible light with a maximum at 510 nm (curve a in Fig. 4(A)). However, addition of several drops of acid to the natural juice enhanced the intensity of absorption maximum by several fractions (hyperchromic shift) (curve b in Fig. 4(A)). However, a bathochromic shift with a magnitude of 100 nm was observed in the absorption spectrum of basic pomegranate juice compared to that of the natural juice. Absorption spectrum for natural juice of red-flesh dragon fruit (a) natural (b) acidify and (c) basic juices is shown in Fig. 4(B). A significant reduction in absorption properties (hypochromic shift) of acidify medium was observed. This result is contrast with the result observed by adding acid in to pomegranate juice. No significant change was observed in the absorption by adding acid into prickly

pear cactus juice (curve b in Fig. 4 (C)). A shift and split with a reduction in the intensity in the absorption band were observed by adding base in to red-flesh dragon, prickly pear cactus fruit juice (curves c in Fig. 4(B&C)). Red ginger lily fruit juice also behaves in a similar manner to that of pomegranate juice, with the acid and base treatments. However, an unpredictable enhancement in the absorption band was observed by adding base in to methanol extraction of red ginger lily fruit juice (curve c in Fig. 5). Absorption spectrum of (a) natural and (b) acidic red ginger lily fruit juice extracted into methanol is also shown in Fig. 5. FTIR spectroscopy of these samples was performed for better understanding. FTIR spectrum of natural fruit juice (a) pomegranate (b) red-flesh dragon fruit (c) prickly pear cactus and (d) red ginger lily is shown in Fig. 6 (A). Though intensity of characteristic peaks varies, characteristic peaks were situated at 3400, 2930, 1639 and 1053 cm^{-1} in FTIR

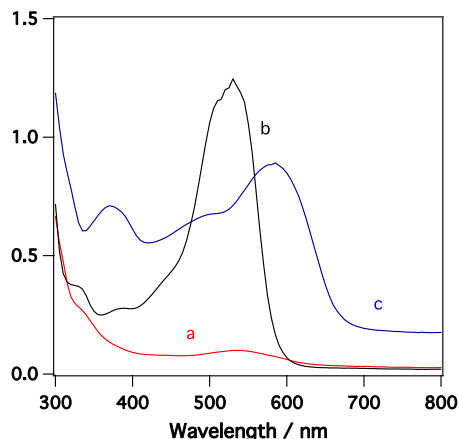


Figure 5: Absorption spectrum of (a) natural, (b) acidic and (c) basic red ginger lily fruit juice extracted into methanol

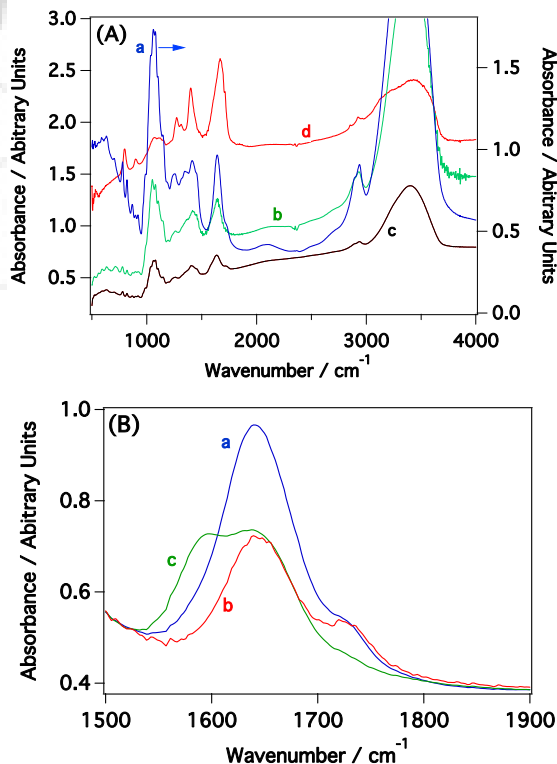
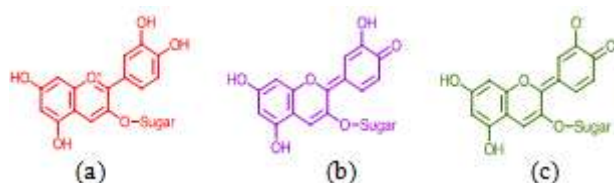


Figure 6: (A) FTIR spectra for (a) pomegranate (b) red-flesh dragon fruit (c) prickly pear cactus and (d) red ginger lily and

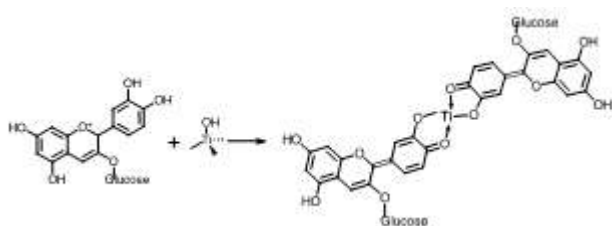
(B) FTIR spectra for (a) acid, (b) natural and (c) base added pomegranate juice spectra, for all samples. These peaks are due to stretching of H bonds, aliphatic hydrogen, C=O groups and C-O-C bond, respectively [7,8]. FTIR spectra for acid and based added juice samples were also studied. For an example, FTIR spectra for (a) acid, (b) natural and (c) based added pomegranate juice is shown in Fig. 6(B). A clear splitting of the peak at 1639 cm^{-1} (curve c in Fig. 6(B)) was observed for base added fruit juice. No detectable deviation on the FTIR spectrum was observed for acid added juice (curve a in Fig. 6(B)) compare to that of natural juice (curve b in Fig. 6(B)). It is known that dye molecules behave in different manner in different environments, probably due to enforcement of Van der Waals interaction between dye molecules and solvents depending on their polarity [9].



Scheme 1: Structure of (a) acidified, (b) natural and (c) basic pomegranate juice

The composition and structure of red-flesh dragon, prickly pear cactus and red ginger lily is not known, to the best of our knowledge. However, pomegranate fruit juice contains with several anthocyanins, and other phenolic compounds [10]. Cyanadin 3 glucoside is the most known compound in pomegranate fruit juice. These molecules mainly composed from benzopyril group and phenolic group [11]. Color of the compound strongly depends on the numbers of substituents in phenolic rings [12]. Molecular structure of (a) flavylium form (acidify), (b) quinonoidal form (natural) and (c) basic forms of cyanadin-3-glucoside are shown in scheme 1 [13].

We have made an attempt to coat acidified, natural and basic fruit juices on TiO_2 electrodes. Degree of absorption of red-flesh dragon, prickly pear cactus and red ginger lily fruit juice on TiO_2 electrodes was feeble except pomegranate juice. Acidified and natural pomegranate juices coated TiO_2 electrodes exhibited purple color and basic pomegranate juice coated TiO_2 electrodes exhibited green color for naked eye. Chelating of flavylium form of cyanadin-3-glucoside with TiO_2 results quinonoidal form of cyanadin-3-glucoside [14]. Recently, it has been confirmed that cyanadin-3-glucoside bonds with metal ions via bidentately in the pH range of 1-3 [15]. Therefore, we propose following mechanism for chelation of cyanadin-3-glucoside with TiO_2 in acidic medium.



Scheme 2: Chelation of cyanadin-3-glucoside with TiO_2

When the electrode potential of pomegranate juice coated electrode swept toward negative direction a colour change (purple to green) of the electrode was observed at potentials less than -0.8 V (versus SCE). Again purple colour was appeared on the TiO_2 electrode when the electrode is anodically polarized. Reduction and oxidation of the pigments attached to the TiO_2 electrode might be a reason. Similar colour change was observed on pomegranate pigments coated TiO_2 films by immersing in basic and acidic solutions, alternatively.

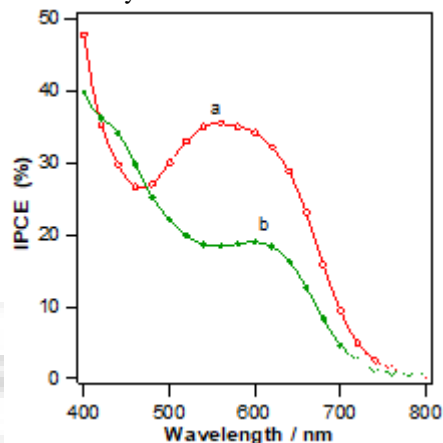


Figure 7: IPCE Spectrum for the cells prepared by using (a) acidified and (b) basic pomegranate fruits juice.

The maximum IPCE (incident photon to current conversion efficiency) of 38% was observed for the cells prepared by using acidified pomegranate fruits juice at the wavelength of 570 nm (curve a, Fig. 7). IPCE action spectrum of the cell fabricated by using a basic pomegranate dye coated TiO_2 electrode is shown as curve b in Fig. 7. Clear red shift with a magnitude of 50-60 nm was observed in the absorption spectrum of pomegranate juice (acid or natural) coated TiO_2 electrode compare to that of the basic pomegranate juice coated TiO_2 electrode. The maximum IPCE of 19% was observed for the cells prepared by using basic pomegranate fruits juice at the wavelength of 610 nm (curve b, Fig. 7).

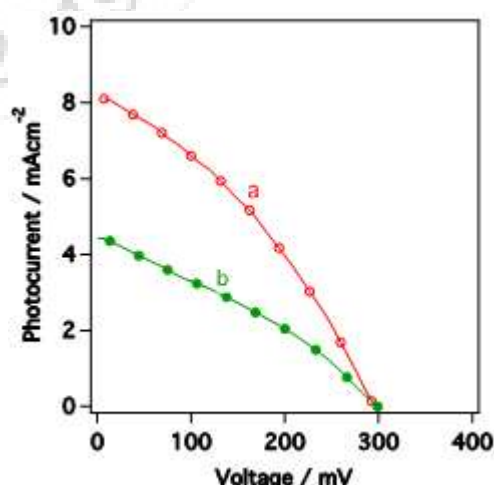


Figure 8: Current–voltage characteristics of TiO_2 |pomegranate|electrolyte cell (a) acidified and (b) basic pomegranate fruits juice

Current–voltage characteristics of TiO_2 |pomegranate pigments electrolyte cell is shown in Fig. 8. We have

observed a maximum photocurrent of $8 \pm 0.5 \text{ mA cm}^{-2}$ and a photovoltage of $300 \pm 40 \text{ mV}$ with a higher reproducibility for TiO_2 |pomegranate pigments|electrolyte cells and results are compared with the cell prepared with Ru-metal centered dye with same configuration. Approximately two times greater photo-performance is observed for Ru-metal complex based photovoltaic cells compare to that of pomegranate juice based cells [3,16].

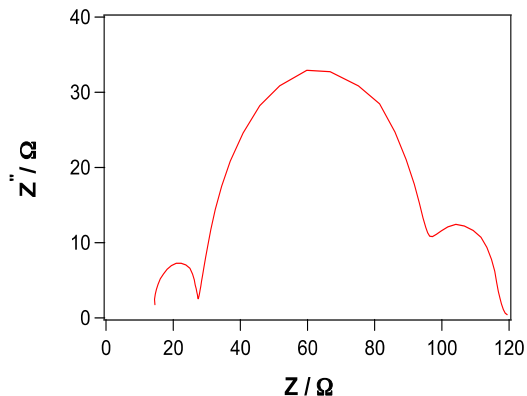


Figure 9: Nyquist diagram of TiO_2 |pomegranate|electrolyte cell

Fig. 9 represents the Nyquist diagram of pomegranate pigment coated electrode. A typical Nyquist diagram for glass-based DSCs normally features three semicircles. The semicircle corresponding to the higher range of frequencies (the left semicircle, with diameter R_1), the middle range of frequencies (the middle semicircle, diameter R_2) and the lower range of frequencies (the right semicircle, diameter R_3) represent I_3^- transport in the electrolyte, electron recombination at the TiO_2 |electrolyte interface together with electron transport in the TiO_2 network and the redox reaction at the platinum counter electrode, respectively [16]. The high frequency intercept with the real axis is the ohmic resistance (R_0) and is related with the sheet resistance of the substrate of the working electrode. Values of $R_0 - R_3$ were evaluated as 14, 10, 35 and 18 Ω from the ECLab software.

4. Conclusion

Capability of using different types of natural fruits juices as sensitizer in photovoltaic cells was studied. The maximum photo-performance was observed for the cell prepared with pomegranate juice among tested natural pigments extracted from fruits.

5. Acknowledgments

Technical assistance from Mr. G.M.M.S. Duminda is acknowledged by authors.

References

- [1] R. W. Gurney, N. Mott, "The Theory of the Photolysis of Silver Bromide and the Photographic Latent Image", Proc. R. Soc. A, 164, pp. 151-167, 1938.
- [2] H. Gerischer, H. Tributsch, "Elektrochemische Untersuchungen zur Spektralen Sensibilisierung von

ZnO-Einkristallen", Ber. Busenges Phys. Chem. 72, pp. 437-445, 1968.

- [3] B. O'Regan, M. Gratzel, "A Low Cost High-Efficiency Solar Cell Based on Dye Sensitized Colloidal TiO_2 Films", Nature, 353, pp. 737-739, 1994.
- [4] S. Ito, S.M. Zakeeruddin, R. Humphry-Baker, P. Liska, R. Charvet, P. Comte, M.K. Nazeeruddin, P. Pechy, M. Takata, H. Miura, S. Uchida, M. Gratzel, "High-Efficiency Organic-Dye-Sensitized Solar Cells Controlled by Nanocrystalline- TiO_2 Electrode Thickness", Advanced Materials, 18(9), pp. 1202-1205, 2006.
- [5] Q. Dai, J. Rabani, "Photosensitization of Nanocrystalline TiO_2 Films by Pomegranate Pigments with Unusually High Efficiency in Aqueous Medium", Chemcomm, pp. 2142-2143, 2001.
- [6] S. Ito, T. N. Murakami, P. Comte, P. Liska, C. Gratzel, M.K. Nazeeruddin, M. Gratzel, "Fabrication of Thin Film Dye Sensitized Solar Cells with Solar to Electric Power Conversion Efficiency over 10%", Thin Solid Films, 516, pp 4613-4619, 2008.
- [7] R.A. Mohomad Ali, N. Nayan, "Fabrication and Analysis of Dye Sensitized Solar Cell Using Natural Dye Extracted from Dragon Fruit", Electrical and Electronic Engineering, pp. 55-62, .
- [8] J.K. Ahamad, Z.J.A. Amer, M.J.M. Al-Bahate, "Effect of Chlorophyll and Anthocyanin on the Secondary Bonds of Poly Vinyl Chloride", Int. J. Mater. Sci. and Appl., 4(2-1), pp. 21-29, 2015.
- [9] M.S. Zakerhamdi, A. Ghanadzadeh, M. Moghadam, "Solvent Effect on the UV/visible Absorption Spectra of Some Aminoazobenzene Dyes", Chem Sci Trans., 1(1), pp. 1-8, 2012.
- [10] A.M. Gomez Caravaca, V. Verarda, A. Sequera Carretero, A. Fernandez Gutierrez, M.F. Caboni, "Determination of the Major Phenolic Compounds in Pomegranate Juices by HPLC-DAD-ESI-MS", J Agric Food Chem., 61(22), pp. 5328-5337, 2013.
- [11] Y. Espinosa Morales, J. Reyes, B. Hermosin, J.A. Azamar Barriou, "Characterization of a Natural Dye by Spectroscopic and Chromatographic Techniques", Mater. Res. Soc. Symp. Proc., pp. 1374, 2012.
- [12] R. Myjavcova, P. Marhol, V. Kren, V. Simanek, J. Ulrichova, I. Palikova, B. Papoukova, K. Leme, P. Bednar, "Analysis of Anthocyanin Pigments in Lonicera (caerulea) Extracts using Chromatographic Fractionation Followed by Microcolumn Liquid Chromatography-Mass Spectrometry", J. of Chrom A, 1217, pp. 7932-7941, 2010.
- [13] N.J. Cherepy, G.P. Smestad, M. Gratzel, J.Z. Zhang, "Ultrafast Electron Injection: Implications for a Photoelectrochemical Cell Utilizing an Anthocyanin Dye Sensitized TiO_2 Nano-crystalline Electrode", J. Phys. Chem. B 101(45), pp. 9342-9351, 1997.
- [14] O. Dangles, M. Elhabiri, R. Bouillard, "Kinetic and Thermodynamic Investigation of the Aluminium-Anthocyanin Complexation in Aqueous Solution", J. Chem. Soc. Perkin Trans., 2, pp. 2587-2596, 1994.
- [15] J.K. Ahamed, H.A.M. Salih, A.G. Hadi, "Anthocyanins in Red Beet Juice Act as Scavengers for Heavy Metal Ions such as Lead and Cadmium", Inter. J. Science and Technol., 2(3), pp. 269-274, 2013.

- [16] D. Kuang, C. Kelin, Z. Zhang, S. Ito, J.E. Moser, S.M. Zakeeruddin, M. Gratzel, "Stable, High-efficiency ionic-liquid-based mesoscopic dye sensitized solar cells", *Small*, 3(12), pp. 2094-2102, 2007.

Author Profile



Prasad M. Sirimanne was born in Matara, Sri Lanka, in 1964. He has received the B.Sc. Degree (Honors), the M.Phil. Degree in Physics, and the D. Eng. Degree in Electronic-chemistry from the Ruhuna University, Matara, Sri Lanka, Sri Jayawardenapura University, Nugegoda, Sri Lanka, Tokyo Institute of Technology, Tokyo, Japan, in 1987, 1996, and 2001, respectively. He was a Research Fellow at Toyota Institute of Technology, Tempaku, Japan, Visiting Researcher at Nagoya Institute Technology, Nagoya, Japan, Guest Scientist at Hahn-Meitner Institute, Berlin, Germany, Senior Research Fellow at Institute of Fundamental Studies, Kandy, Sri Lanka, JSPS Fellow at Gifu University, Gifu, Japan, Research Fellow of Victorian Government, Australia from 2001- 2010. He gained both IBC top hundred engineers of the world in 2013 and IBC leading engineers of the world in 2013 awards. He also won presidential award for scientific research conduct in Sri Lanka for 2005-2009 and NRC merit, awards for research publications in 2011, 2012. Currently, he works as a Professor attached to the Uva Wellassa University, Badulla, Sri Lanka. He is engaging in research in preparation of thin films and development of alternative power sources for silicon solar cells since 1992. He has obtained five international patents for the finding of plastic based dye sensitized solar cells and published over sixty five peer reviewed articles in scientific journals.



Pubudu Nuwan Dissanayake was born in Hambanthota, Sri Lanka, in 1991. He has received the Special Degree in Bachelor of Technology in Science and Technology from the Uva Wellassa University, Badulla, Sri Lanka in 2017.