J Mater Sci: Mater Electron
DOI 10.1007/s10854-017-6466-9

Broad absorption natural dye (Mondo-Grass berry) for dye sensitized solar cell

L. Ajith DeSilva[1] · P. K. D. D. P. Pitigala[2] · A. Gaquere-Parker[3] · Ryan Landry[1] · J. E. Hasbun[1] · Victoria Martin[1] · T. M. W. J. Bandara[4] · A. G. U. Perera[2]

Received: 15 September 2016 / Accepted: 25 January 2017

Abstract Two major drawbacks in dye-sensitized solar cells (DSSC) are the narrow spectral response and the short-term stability. Research on development of artificial dyes for a broad frequency response is a major field of research today. The work presented here shows a broad response with a natural dye extracted from a Mondo-grass (*Ophiopogon japonicus*) berry. Its range of sensitivity covers the entire visible region and its tail expands to the near infrared. This is a unique situation since many natural dyes containing anthocyanin or carotenoids strongly absorbed only below 600 nm. A TiO_2 based electrode sensitized with Mondo grass berry dye DSSC was tested for its performance. An open circuit photovoltage of 495 mV and a short circuit photocurrent of 0.6 mA/cm^2 were obtained under 1 sun illumination. The broad spectral response from 400 to 750 nm was observed for the Mondo-grass berry dye. A high fill factor of 71% was achieved but energy conversion efficiency was only 0.2% for the cell. Even though cell efficiency is low with this dye, the solar cells have exhibited better stability when compared with that of the Blackberry. The thin layer chromatography results indicate that Mondo-grass berry dye contains a mixture of two or more chemical compounds belonging to both the anthocyanin and the carotenoid families.

✉ L. Ajith DeSilva
ldesilva@westga.edu

[1] Department of Physics, University of West Georgia, Carrollton, GA 30118, USA

[2] Department of Physics and Astronomy, Georgia State University, Atlanta, GA 30303, USA

[3] Department of Chemistry, University of West Georgia, Carrollton, GA 30118, USA

[4] Department of Physical Sciences, Rajarata University of Sri Lanka, Mihintale, Sri Lanka

1 Introduction

Solar cells are an attractive renewable energy source and are also promising devices for future energy needs. However, in order for solar cells to achieve their potential and penetrate into the global energy markets, it requires an expansion from the designing of high efficiency devices to the searching of new materials and methods that can deliver energy at a significantly lower cost. The dye-sensitized solar cells (DSSCs) have drawn a tremendous research interest due to their lower cost and easy fabrication compared to those of silicon solar cells [1, 2]. In DSSC, the dye is anchored to a wide band gap semiconductor. The most commonly used semiconducting material has been TiO_2 nano-sized particles. Charge separation takes place at the interface via photo-induced electron injection from the dye into the conduction band of the TiO_2. The cell properties such as fill factor (FF) and efficiency (η) are mainly dependent on the dye used as sensitizer. Generally synthesized dyes such as transition (heavy) metal compounds (ruthenium polypyridyl complexes) are very effective and the power conversion efficiencies reached thus far are about 11% with I^-/I_3^- electrolyte redox couple [3]. Not only do ruthenium polypyridyl complexes undergo an expensive and complicated synthesis process but they also contain an environmentally undesirable heavy metal. Alternatively, natural dyes can be used as the sensitizer with an adequate efficiency. There are an unlimited number of sources available to extract natural dye pigments as means of using in DSSC as sensitizer. Using natural dyes in solar cells is also advantageous due to their greener and lower cost.

Published online: 06 February 2017

Natural dyes usually have few principal pigments; the most common molecular structures are Chlorophylls, Carotenoids, Anthocyanins, and Betalains [4–9]. The pigments responsible for the several colors found in the dyes range from red to blue in fruits, flowers, leaves, seeds and roots of plants. Each pigment family has been investigated in various works including a sensitizer for DSSCs [4, 5, 7, 10, 11]. As far as the natural dye is concerned, the maximum fill factor reported to this day is 63% which is for the anthocyanin family [12]. The maximum efficiency of 2.6% was reported for the chlorophyll family [4]. For the carotenoids family the maximum reported efficiency is 0.37% while the fill factor is under 1% [4, 13].

In this study, our investigation is based on a natural dye extracted from Mondo-grass berry also known as monkey grass; the scientific name is *Ophiopogon japonicus*. This is grown as an ornamental plant for ground covering in the southern parts of North America and parts of Japan. The root of the plant has been used in traditional medicine in China [14]. Literature studies revealed that attempts have been made to identify the chemical composition of the root extract [15, 16]. To our knowledge, very few studies about this variety of berries have been published. One reported study about Mondo-grass berry dye compares carotenoids content in Mondo-grass berry species [17].

2 Experimental

Nanocrystalline TiO_2 films were deposited on conducting Fluorine doped Tin Oxide (FTO) glass plates (0.5×1.5 cm^2, active area 0.25 cm^2) as described below. FTO glass plates were purchased from Solaronics, Switzerland (sheet resistance 15 ohm/□). They were cut in to small pieces whose dimensions were 0.5 cm × 1.5 cm and were cleaned by warming in a solution of 0.1 M potassium hydroxide (KOH) solution, followed by rinsing with deionized water, and again washed with dilute 0.1 M of HNO_3 and rinsing with deionized water. Finally, the glass plates were boiled for 5 min in an aqueous solution of 50% propan-2-ol, and allowed to dry in air. It is crucial to avoid any contamination with grease, such as the natural lipids found on the hands, and special care must be taken, like wearing gloves. TiO_2 paste was screen printed [18] on top of the etched area (0.5×1 cm^2). TiO_2 paste was prepared by grinding 1 g of TiO_2 powder (Degussa P25) with a few drops of acetic acid and the surfactant Triton X100, and some ethanol to form a paste. The film was dried under ambient conditions few hours and then sintered in air at 450 °C for 20 min. The TiO_2 film thickness was estimated to be in the range of 1.5 ± 0.2 µm.

The Mondo-grass berry dye was prepared as follows. Healthy ripe berries were picked and thoroughly rinsed with deionized water. The berries were crushed in a mortar with a pestle adding 95% of methanol as needed and few drops of acetic acid until a homogeneous pulp is formed. The pulp was transferred to a closed amber glass container and kept for 24 h in a refrigerator for saturation. The pulp then was vacuum filtered twice to extract the dye. The filtered dye was used directly without further purification to soak with pre-prepared TiO_2 plates. Blackberries were purchased from local stores and the same procedure as of Mondo-grass berry was followed to extract the dyes.

For the DSSC, TiO_2 film sensitized with Mondo grass dye was used as the working electrode. The Iodine/triiodide red-ox couple as the electrolyte [19], and a Platinum plate for the counter electrode were used to test its performance. The current–voltage (IV) characteristics of the samples were measured using KETHLEY 2400 source meter. A UV-VIS-NIR monochromator, lock-inamplifier and a chopper system with higher order cutoff filters were used to ascertain the spectral response for the absorption of the dyes and action spectra of the DSSCs. Monochromator output light intensity was estimated using calibrated Si and InGaAs photodiodes.

For thin layer chromatography (TLC) data the following procedure was followed. Fifteen microliters of the extracted dyes from Mondo-grass berries and blackberries were spotted on an EMD Millipore Silica Gel 60 F_{254} Coated Aluminum-Backed (Fisher Scientific) TLC plate (4 cm × 12 cm). The plate was eluted with (99.5%, anhydrous) ethanol at 25 °C. The TLC plate was carefully removed and air-dried. The spots were visualized by illuminating with a UV light source (254 nm).

The IR absorption spectra of the dye coated TiO_2, in the range 8000–500 cm^{-1}, was obtained using the Bruker Vertex 70 FTIR. Dye coated films were prepared on Real Crystal® IR KBr sample cards.

3 Results and discussion

Figure 1 is a picture of the thin layer chromatography (TLC) plates for Mondo-grass berry (S1) and for Blackberry (S4) dyes, both eluted with ethanol. It is seen from the TLC plate that the Mondo-grass dye extract contains one main chemical compound ($R_f=0.99$) that shows a tail throughout the plate and one lower spot ($R_f=0.13$) while the blackberry extract shows one spot ($R_f=0.99$) at the top of the plate under the same eluting conditions. Both also display a colored spot ($R_f=0.04$) that did not elute with the eluent.

The differences between the TLC plates clearly show the difference in chemical compositions of the two extracts. Tailing bands on TLC plates are due to the molecular interaction between the silanol groups on the silica gel with

Fig. 1 Thin layer chromatography (TLC) picture in ethanol for Mondo-grass berry (S1) and for Blackberry (S4) dyes. TLC plate is 4 cm × 12 cm dimensions, is under UV illumination

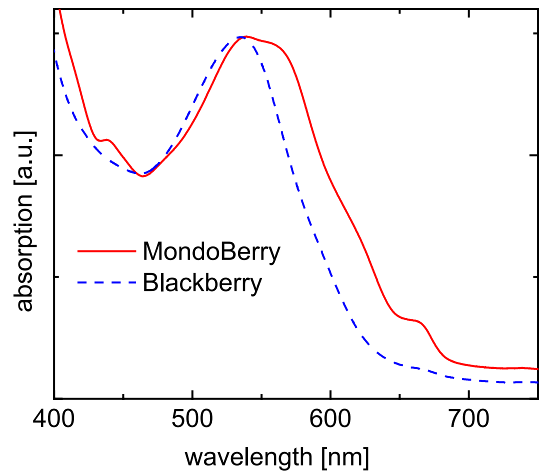

Fig. 2 Absorption of Mondo-grass berry with a large tail extending towards the longer wavelength and a maximum absorption at 550 nm and for blackberry maximum absorption at 530 nm

polar molecules, able to interact through hydrogen bonds, present in the mixture to elute. This is therefore consistent with molecules that contain many hydroxyl groups like anthocyanins. Other eluents were used such as Petroleum ether, Ethyl acetate, and dichloromethane but could not elute these highly polar molecules present in the mixtures. In addition, the differences seen by TLC could be most likely due to the presence of a mixture of two or more families of chemical compounds belonging to both the anthocyanin and carotenoid families. Attempts were made to analyze the chemical structures of the dyes present in Mondo-grass berry extract using Gas Chromatography Mass Spectrometry. Also the analysis could not identify the individual chemical compounds detected in TLC, however, the presence of high-molecular-mass compounds was revealed in the extract. To our knowledge, no such analysis has ever been conducted to analyze the chemical composition of Mondo berry extract.

Figure 2 shows the absorption spectra of the extracted Mondo-grass berry dye in ethanol. Mondo-grass dye exhibits a broad absorption from 400 to 750 nm with a peak at 550 nm. For similar conditions, the extracted blackberry dye showed a narrower absorption region than that of the Mondo-grass berry, which has also been reported in the literature [20]. Further, the peak absorption for the blackberry was at 530 nm. The difference in absorption between the Mondo-grass berry and the blackberry is attributed to the different dye families. Blackberry contains manly anthocyanin [4, 20] while Mondo-grass berry comprises mainly carotenoids [17]. The light absorption of this type of molecules typically shows a broad band covering the visible region. This is due to charge transfer transitions from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO).

Mondo-grass berries, although the carotenoids content of the grass itself, measured by High Performance Liquid Chromatography (HPLC), has been reported earlier [17]. More experiments to determine the exact composition of the berry extract using HPLC and potentially Liquid chromatography Mass Spectrometry are planned but the scope is beyond the current focus of this study.

The normalized FTIR absorption spectra shown in Fig. 3 are of the bare TiO_2, the Mondo-grass berry extract coated on TiO_2 (TiO2/MB) and the Blackberry extract coated on TiO_2 (TiO2/BB). As can be seen, in the blackberry coated TiO_2, the broad peak at 3200–3600 cm^{-1} implies existence of H-bonding between hydroxyl groups and the sharp peak next to it indicates presence of free hydroxyl groups in this sample. This implies that the blackberry is attached to TiO_2 via H-bonding and also there are free hydroxyl groups also

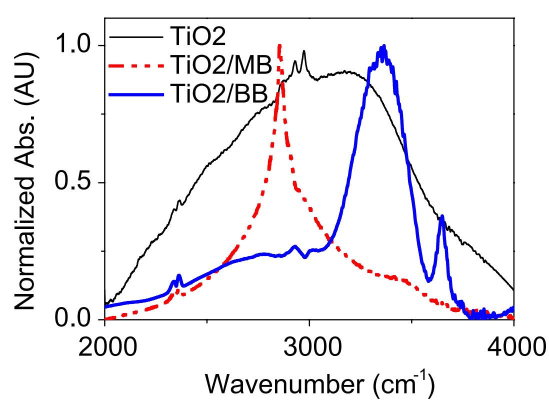

Fig. 3 The normalized FTIR absorption spectrum of the TiO_2 (TiO2), Mondo-grass berry extract coated on TiO_2 (TiO2/MB) and Blackberry extract coated on TiO_2 (TiO2/BB)

in the sample. In contrast the measurement with Mondo berry do not show these two peaks, which implies the Mondo-grass berry is attached on to the TiO_2 via hydroxyl groups, but not by the H-bonding. The strong chelation, of the Mondo-grass berry extract on to TiO_2, has resulted in the enhancements of the device. The peak at 2850 cm^{-1} is not clearly identified, but it can be a result of carbonyl groups (O=C–H stretching) in the compounds of Mondo-grass berry extract. The TiO_2 shows a very broad feature with few sharp peaks at 2934 and 2970 cm^{-1}. Broad feature is due to hydroxyl ligands on the film and the scattering effects in the film. The sharp peaks in TiO_2 are due to some organic compound residues introduced during the preparation process (methanol and acetic acid were used in preparation of the TiO_2 film for FTIR measurement).

It was also observed that the UV–Vis absorption band of the Mondo-grass berry/TiO_2 is slightly red shifted compared to that of the dye in solution (not shown). A similar behavior has also been reported and is attributed to complexation between dye molecules and metal ions (Ti^{+4}) [20]. The absorption of the Mondo-grass berry band covers the entire visible region while the tail expands to the near infrared region. This is a unique situation because many natural dyes containing anthocyanin or carotenoids strongly absorb in the region below 600 nm [21]. The extension in the absorption can be due to either one or more phenomena. One of the possibilities is extensions in the response and absorption spectra of photovoltaic devices as a result of coupling two or more pigments [22, 23]. This is so because Mondo-grass berry extracts have multiple compounds in them, as uncovered with TLC analysis. Additionally, some dye compound forms J-aggregates which result in a red shift in the absorption and response spectra [24–26]. Considering the absorption spectra of the dyes from two berries, Mondo-grass berry dye has the higher and the broader absorption with a tail in the longer wavelength region. Thus another possibility is that we can expect higher number of π electrons being excited when Mondo-grass berry dye absorbs light and generates photocurrent.

The IV characteristics of the DSSC sensitized with Mondo-grass berry and the blackberry dyes are shown in the Fig. 4. For the DSSC sensitized with Mondo-grass berry dye, an open circuit voltage of 495 mV and a short circuit photocurrent of 0.6 mA/cm^2 were observed under a simulated lamp equivalent to 1 sun illumination. A *FF* of 71% and energy conversion efficiency (η) of 0.2% is achieved for the cell. For similar conditions, DSSC sensitized with blackberry dye, an open circuit voltage of 475 mV and a short circuit photocurrent of 0.6 mA/cm^2 were observed with a *FF* of 67% and η of 0.18%. To our knowledge, this is the first time that the *FF* reported value exceeds 70% [4] for the carotenoid family DSSC. The improved *FF* also could be contributing to the coupling of multiple compounds in the berry extract and the organic aggregations of the compounds in the device [22–25]. Table 1 summarizes photo-electrochemical properties of DSSC sensitized with natural dyes used in this work.

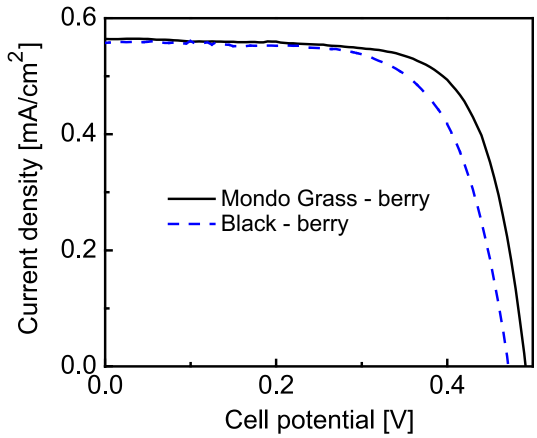

Fig. 4 IV Characteristics of the solar cells loaded with Mondo-grass berry and Blackberry dyes, the samples were measured using KETHLEY 2400 source meter

Table 1 The device properties for the solar cells loaded with Mondo-grass and Blackberry dyes

	I_{sc} /mA/cm^2	V_{oc} /V	FF	η%
Mondo-grass berry	0.564	0.495	0.71	0.20
Blackberry	0.557	0.475	0.67	0.18

Further analysis of current–voltage characteristics shows the shunt resistance and the series resistance of the device sensitized with Mondo-grass berry extract as ~31.9 kΩ and 65 Ω respectively. The relevant values for the device with blackberry extract are ~46.5 kΩ and 95 Ω respectively. It is interesting to observe that the fill factor of the Blackberry coated device was compromised merely due to the high series resistance in it, contributed by the weak dye chelation (via H-bonding). In contrast, the same cause might have contributed to the higher shunt resistance in this device. Furthermore, the better chelation of the Mondo-grass berry extract on to the TiO_2 film has led to the low shunt and series resistances in it.

The stability of the dye implies a good regeneration rate in the dye after each generation-recombination cycle. But the low carrier injection rate has resulted in the low photocurrent in it. The photocurrent will depend on the carrier injection and the generation-recombination rates of the dyes. So, a low injection rate will result in low photocurrent, even with a good regeneration rate. There is also a possibility of concentrated quenching effects in carrier injection process in the device, as the berry extract is a concentrate cocktail of different molecules. Also the weak chelation of the dye via H-bonding will also contribute to the low photocurrent.

Figure 5 shows the photocurrent action spectrum for the Mondo-grass dye-loaded film. The peak of the absorption band was found at 550 nm and showed a wide band from visible to Infrared (Fig. 2). The action spectra of the DSSC sensitized with Mondo-grass berry also shows a similar broad absorption band with a peak at 575 nm. This indicates that photocurrent generates due to the direct injection of excited electrons from the dye.

One of the major problems in dye sensitized solar cells is instability of the cells due to photo degradation of the dyes; however, some artificial dyes, for instance, ruthenium based dyes, have shown better stability though the high cost of these dyes are a drawback to fabricated low cost dye sensitized solar cells [1, 27]. The effect of instability is severe for the cells containing natural dyes and reports on stability test for natural dyes are rarely found in the literature. Thus stabilities of fabricated cells were measured by irradiating them for about 90 h. The cell potential variation with time is shown in Fig. 6. Both cells show more or less a V_{oc} that increases within about 30 h. After that period cell V_{oc} decreases; the drop however is not very significant compared to their initial values of V_{oc}. A stability comparison between the cells show a slightly better performance for the Mondo-grass berry than for the blackberry as shown in Fig. 6. For better visibility, a sloid line for Mondo-grass berry and a dashed line for blackberry DSSC are drawn in the stability graph. Even though, the efficiency of the solar cell reported in this work is low the better stability shown would be advantageous for future studies and scientific interests in other applications.

In order to confirm and test the stability of Mondo berry extract, the IR absorption was measured and compared on the sample just after coating the Mondo berry extract

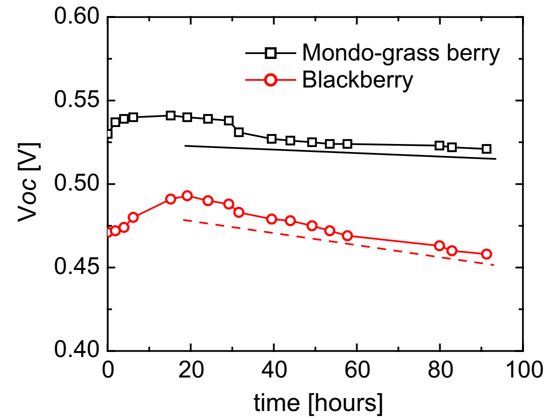

Fig. 6 The stability comparison between Mondo-grass and blackberry soaked DSSCs, Voc of each cell is monitored by refilling the electrolyte each time

on TiO_2 and after light soaking for ~8 h as shown in the Fig. 7. The IR absorption fetchers of the berry extract is still strongly visible in the sample despite the small decrement in the absorption as can be seen in the figure after light soaking of the sample. In this light soaking stability study, the electrolyte was not employed in to the device; hence the dye regeneration process was not efficient as in a complete device. Hence a higher degradation rate for the dye was expected than in a full cell configuration.

4 Conclusion

The present work reports a broad response (from 400 to 750 nm) for a natural dye extracted from a Mondo-grass (*O. japonicus*) berry. The dye is used as is, without additional purification after the extraction procedure from the pulp. A DSSC sensitized with Mondo-grass dye was tested for its

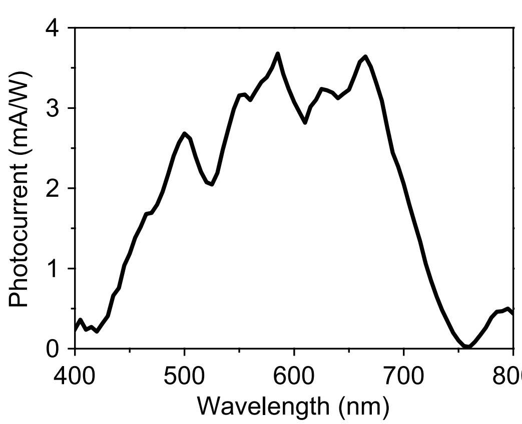

Fig. 5 The action spectrum for Mondo-grass berry dye sensitized solar cell

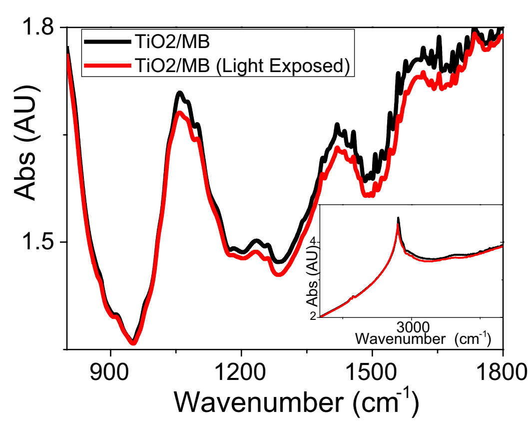

Fig. 7 The IR absorption spectra of Mondo berry extract just after coating the on TiO_2 and after light soaking (~8 h)

performance. An open circuit photovoltage of 495 mV and a short circuit photocurrent of 0.6 mA/cm^2 were observed under a 1 sun illumination. A fill factor of 71% and energy conversion efficiency of 0.2% is observed for the solar cell. Furthermore, a better stability is reported by the DSSC with Mondo-grass berry dye when compared with that of Blackberry. The thin layer chromatography results indicate that Mondo-grass berry contains a mixture of two or more chemical compounds belonging to both anthocyanin and carotenoid families.

Acknowledgements We thank Professor K. Tennekone for having fruitful discussions and providing valuable suggestions to figure out molecular composition of the dye. The authors would like to thank the *University of West Georgia Student Research Assistant Program* (SRAP) for their continued financial support for this research.

References

1. M. Grätzel, J. Photochem. Photobiol. C **4**, 2 (2003)
2. M. Grätzel, Nature **414**, 338-344 (2003)
3. A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, Chem. Rev. **110**, 6595 (2010)
4. P. Sahni, Adv. Sci. Lett. **5**, 1961 (2012). doi:10.1166/asl.2012.1961
5. H. Hug, M. Bader, P. Mair and T. Glatzel, Appl. Energy **115**, 216-225 (2004)
6. R. Ramamoorthy, N. Radha, G. Maheswari, S. Anandan, S. Manoharan, R. V. Williams, J. Appl. Electrochem. (2016). doi:10.1007/s10800-016-0974-9
7. F. Delgado-Vargas, A. R. Jimenez, and O. Paredes-Lopez, Crit. Rev. Food Sci. **40**(3): 173–286 (2000)
8. N. Gokilamani, N. Muthukumarasamy, M. Thambidurai, A. Ranjitha, D. Velauthapillai, T. S. Senthil, R. Balasundaraprabhu. J. Mater. Sci. **24**, 9 (2013)
9. N. J. Cherepy, G. P. Smestad, M. Gra1tzel and J. Z. Zhang, J. Phys. Chem. B **101**, 9342 (1997)
10. P. Vankar and R. Shanker, Color Technol. **125**, 3 (2009)
11. M. Thambidurai, N. Muthukumarasamy, D. Velauthapillai, N. S. Arul, S. Agilan, R. Balasundaraprabhu. J. Mater. Sci. **22**, 11 (2011)
12. J.M.R.C. Fernando, G.K.R. Senadeera, Res Comm. Curr. Sci. **95** 25 (2008)
13. N.M. Gómez-Ortíz, I.A. Vázquez-Maldonado, A.R. Pérez-Espadas, G.J. Mena-Rejón, J.A. Azamar-Barrios, G. Oskam, Sol. Energy Mat. Sol. C 94, 1 (2010)
14. J. Kou, Y. Sun, Y. Lin, Z. Cheng, W. Zheng, B. Yu, Q. Xu, Biol. Pharm. Bull. **28**, 7 (2005)
15. N.T.H. Anh, S. Tran Van, A. Porzel, K. Franke, L. A. Wessjohann, Phytochemistry **62**, 7 (2003)
16. Y. Min, D. Guo, Y. Guan, C. Huang, J. Am. Soc. Mass. Spectr. **16**, 2 (2005)
17. X-L. Sun, Y-S Sun, Y-F Xu, H. Zhou, Acta Agrectir Sinica **17**, 4 (2009)
18. S. Ito, P. Chen, P. Comte, M.K. Nazeeruddin, P. Liska, P. Péchy, M. Grätzel, Prog. Photovolt. **15**, 603 (2007)
19. K. Tennakone, I. R. M. Kottegoda, L. A. A. De Silva, and V. P. S. Perera, Semicond. Sci. Technol. **14** (1999)
20. G. Calogero, J.-H. Yum, A. Sinopoli, G.D. Marco, G. Michael, M.K. Nazeeruddin, Sol. Energy, **86**, 5 (2012)
21. H. K. Lichtnethaler, and C. Buschmann, *Current Protocols in Food Analytical Chemistry* (Wiely, Newyork, 2001), pp. F4.3.1–F4.3.8
22. P.K.D.D.P. Pitigala, M.K.I. Senevirathna, V.P.S. Perera, K. Tennakone, Langmuir **20**, 5100-5103 (2004)
23. V.P.S. Perera, P.K.D.D.P. Pitigala, M.K.I. Senevirathne and K. Tennakone, Sol. Energy Mat. Sol. C **85**, 91–98 (2005)
24. P.K.D. Duleepa Pitigala, M.M. Henary, E.A. Owens, A.G. Uinil Perera, K. Tennakone, J. Photochem. Photobiol. A **325**, 39–44 (2016)
25. K. Tennakone, P.K.D.D.P. Pitigala and A.G.U. Perera, RSC Adv. **3**, 2493–2832 (2013)
26. K. Rajeshwar, J. Appl. Electrochem. **15**, 1067–1082 (1985)
27. A. Hinsch, J. M. Kroon, R. Kern, I. Uhlendorf, J. Holzbock, A. Meyer and J. Ferber, Prog. Photovolt. **9**, 6 (2001)