Natural dyes extracted from leaves, fruits, and roots of *Piper Betel*, *Adonidia Merrillii* and *Morinda Citrifolia* as photosynthesizers for dye sensitized solar cells

T S Eop¹, A W Azhari¹² and D S C Halin²

¹Water Research Group (WAREG), School of Environmental Engineering, Universiti Malaysia Perlis 02600 Arau, Perlis, Malaysia.
²Centre of Excellence Geopolymer & Green Technology (CEGeoGTech), School of Material Engineering, Universiti Malaysia Perlis 02600 Arau, Perlis, Malaysia.

E-mail: ayuwazira@unimap.edu.my

Abstract. In this study, the fabrication of dye sensitized solar cell (DSSCs) using the leaves of *Piper Betel* (PB), fruits of *Adonidia Merrillii* (AM) and roots of *Morinda Citrifolia* (MC) and combination of these three dyes (PB/AM/MC) had been conducted. Fabrication of the DSSCs was conducted using layered system, which involved sandwiching of a working electrode (TiO₂ semiconductor) and counter electrode (platinum paste). The chemical and electrochemical characteristic of natural dye extracts were determined using pH meter, Fourier transform infrared (FT-IR) spectroscopy and ultra violet (UV-Vis) spectroscopy. From the study, it was observed that PB dyes showed the highest efficiencies (0.0712 %) followed by the combination dyes (0.0065 %) while AM and MC dyes showed the lowest efficiency (1.0x10⁻⁹ % and 0% respectively.

1. Introduction

Dye sensitized solar cell (DSSC) is a unique device for the conversion of visible light into electricity based on the wide gap semi-conductor sensitization. The quest for cleaner and cost effective renewable energy has lead more research attention to be focused on dye-sensitized solar cells (DSSCs), also known as Gratzel cells [1]. In DSSCs, the dye as a sensitizer plays a key role in absorbing sunlight and transforming solar energy into electric energy [2].

In comparison with silicon solar cell, the materials used in DSSCs are more environmental friendly. Typically, a standard DSSC consist of a dye-sensitized mesoporous semiconductor photoanode, an iodine/tri-iodide (I_3/I⁻) redox electrolyte, and a catalytic counter electrode [3]. The fabrication of DSSCs involve the deposition of titanium dioxide (TiO₂), a semiconductor which is normally used as paint based in industry as the photoanode and platinum as the counter electrode. The main attraction for the DSSC is not only about it low production cost but also its efficiency. It can work well even during darker condition, for example, in the dawn, dusk or in cloudy weather. This capability of effectively utilizing diffused light made this DSSC unique than the traditional solar cell as it is not limited by space (roof), but it can be installed on windows and sunroof [4].

The interest in this study is the quest for an effective natural sensitizers. A number of studies have been conducted on various plant parts, such as flowers, leaves, barks, and roots, in search of effective natural sensitizers. However, most of these studies are conducted on the individual dye sensitizers and
did not investigate the potential of mixing the sensitizers. Hence, the exploration on the potential of mixing these natural dyes is deemed necessary. The present study introduces sensitizers extracted from *Piper betel* (PB) leaves, *adonidia merillii* (AM) fruits and roots of *morinda citrifolia* (MC) and a mixture of all three dyes and examines their optical properties and performance in DSSCs.

2. Materials and method

2.1. Preparation of the sensitizers

*Piper betel* (PB) leaves, *adonidia merillii* (AM) fruits and roots of *morinda citrifolia* (MC) were collected from around Perlis, Malaysia. Fresh *piper betel* leaves were washed with clean water and dried at room temperature. To extract dye from the *piper betel*, cold extraction technique was used with ethanol as the organic solvent. The *piper betel* leaves were first crushed with mortar and pastel followed by soaking in ethanol (1:5 w/v ratio) and stored in dark area for two days.

The glassware used to store the dyes were covered with aluminium foil to minimize photooxidation. Soxhlet extraction process were then conducted to obtain the extractive compound. The crude extract was stored in a refrigerator (4 °C) until further used. The same procedure were used to prepare the *adonidia merillii* fruits and root of *morinda citrifolia*.

Apart from the individual sensitizers, mixture of the sensitizers was also prepared by mixing all three dyes (1:1:1 ratio).

2.2. Dye Sensitized Solar Cells Fabrication

Photo electrodes were prepared by depositing TiO$_2$ paste (Ti-nanoxide, Solaronix) into fluorine-doped tin oxide (FTO) conductive glasses (15 Ω) using the doctor blade technique followed by sintering at 450°C for 10 min. The photo electrodes were subsequently dipped in the sensitizers at room temperature and left overnight to allow sufficient time to graft the dye molecules on the TiO$_2$ surface. Preparation of the counter electrode was done similarly, where platinum paste (Platisol, Solaronix) were deposited onto the FTO conductive glass and sintered at 450°C for 10 min.

The DSSCs were assembled by introducing the redox electrolyte between the dyed TiO$_2$ electrode and the platinum counter electrode. The electrolyte solution was prepared by mixing acetonitrile with potassium iodide and iodine. The mixture was then stirred for about half an hour and ready to be used. The samples were characterized by using pH meter, Fourier Transform Infrared (FT-IR) spectroscopy & Ultraviolet-Visible (UV-Vis) spectrophotometry to determine the properties and characteristic of the dye that include its pH value, chemical compound and absorption peak of the dye respectively.

3. Results and discussion

3.1. pH Analysis

A pH meter was used to measure the hydrogen-ion in the sensitizer solutions obtained from the extraction process. As shown in Table 1, the average pH for each sensitizer was slightly different from each other due the condition of its pigment types.

Desorption of dye from TiO$_2$ film will occur if the pH value is higher than 9 [5, 6]. Since the pH value of the dyes obtained is lower than pH 9, no adjustment is needed as to prevent desorption of colour occur.

| Sample | Natural Dyes          | Average pH Level |
|--------|-----------------------|-----------------|
| 1      | *Piper Betel*, PB     | 5.9             |
| 2      | *Adonidia Merillii*, AM | 5.3            |
| 3      | *Morinda Citrifolia*, MC | 6.0          |
| 4      | Mixed sensitizers     | 5.9             |
3.2. Functional Group Analysis

The functional group for the sensitizers were measured using a FTIR spectroscopy. The results are as shown in Figure 1. Apparently, all sensitizers were showing the same peak pattern and it was believed that this was due to the fact that the functional group for all samples were about the same. For *Piper betel* (PB) based sensitizers (Figure 1 (a)), board absorption peak was detected at 3335.77 cm\(^{-1}\) representing strong vibration of the free hydroxyl group of phenol O-H stretch. This finding is compliment by those of Muruganandam et al. [7] who conducted the FTIR analysis on *Piper Betel* leaves where the results showing board absorption at 3311.78 cm\(^{-1}\). Another intense peak was also observed at 2975.65 cm\(^{-1}\) which attributed to the stretching of the carboxylic acid O-H stretch. In addition, the peak at 1645.67 cm\(^{-1}\) corresponding to the strong amide C=O stretch, showed the present of carbonyl stretching absorption in amide compared to the previous study which have peak at the 1707.00 cm\(^{-1}\) which represent C=O stretch but in carboxylic acid. Moreover, there was a long intense peak at 1044.23 cm\(^{-1}\) which represent a strong C-O bond and apart from that, the PB sensitizers were also showing the C-H bending peak at 878.66 cm\(^{-1}\).

As for the *Adonidia Merillii* (AM) (Figure 1 (b)), the same phenol O-H stretch vibration peak was observed at 3323.96 cm\(^{-1}\). AM dye also shows the intense broad 2976.65 cm\(^{-1}\) which attributed to the stretching of carboxylic acid O-H stretch, while the peak at 1645.80 cm\(^{-1}\) corresponds to the strong amide C=O stretch which represent the carbonyl stretching absorption. There was another long intense peak at 1044.02 cm\(^{-1}\) which denoted as the present of strong C-O bond and another C-H bending was present at peak 878.20 cm\(^{-1}\).

The FTIR analysis for *Morinda Citrifolia* (MC) (Figure 1 (c)) matched another study conducted by Suman et al. [8]. Broad absorption detected at 3333.43 cm\(^{-1}\) and 3420 cm\(^{-1}\) in both study respectively represented the strong phenol O-H stretch. Moreover, another intense vibration peak were observed at 2975.39 cm\(^{-1}\) and at 2985.52 cm\(^{-1}\) attributed to the stretching of the carboxylic acid O-H stretch. The peak at 1645.83 cm\(^{-1}\) corresponds to the strong amide C=O stretch which indicate the present of carbonyl stretching absorption in amide and another intense peak at 1044.27 cm\(^{-1}\) which represent strong C-O bond.
The mixed sensitizer (Figure 1 (d)) was showing the same peak pattern as the above mentioned individual sensitizers with broad absorption peak at 3335.84 cm\(^{-1}\) indicating the present of strong phenol O-H stretch group, followed by another broad 2975 cm\(^{-1}\) and 2897 cm\(^{-1}\) peak which attributed to the stretching of carboxylic acid O-H stretch. The peak at 1645.87 cm\(^{-1}\) corresponds to the strong amide C=O stretch which represent the carbonyl stretching absorption. Next, there is a long intense peak at 1044.19 cm\(^{-1}\) which represent as a strong C-O bond. Lastly, the mix sensitizer showed the C-H bending presented at peak 878.63 cm\(^{-1}\). From the previous literature, it was reported that the functional group required to interact with TiO\(_2\) surface was either a carboxylic group or other peripheral acidic anchoring groups [9].

3.3. DSSC’s Performance Analysis

The performances of individual and mix sensitizer is tabulated in Table 2. The interaction between dye molecule and TiO\(_2\) nanoparticle surface structure are important in enhancing DSSCs conversion energy. From the result, it was observe that the best cell performance was exhibited by the PB sensitizers with conversion efficiency (\(\eta\)) of 0.071%, given an open circuit voltage (\(V_{oc}\)) of 6.44 x 10\(^{-3}\) V, short circuit current density (\(J_{sc}\)) of 0.012 mA cm\(^{-2}\) and a fill factor of 88817.3. This is followed by MC sensitizers where the conversion efficiency (\(\eta\)) was 0.05%, an open circuit voltage (\(V_{oc}\)) of 0.002 V, short circuit current density (\(J_{sc}\)) of 0.03 mA cm\(^{-2}\) and a fill factor of 625.257. The lowest performance was shown by the AM sensitizers with conversion efficiency (\(\eta\)) of 1.0x10\(^{-9}\)%, given an open circuit voltage (\(V_{oc}\)) of 0.573 V, short circuit current density (\(J_{sc}\)) of 2.48x10\(^{-5}\) mA cm\(^{-2}\) and a fill factor of 0.323. It is believed that the low performance is contributed by the presence of oily substance in the AM dye sensitizers. The mix sensitizers also showed quite low performance, where it is believed to be contributed by the presence of AM sensitizers. For the mix sensitizers, the conversion efficiency (\(\eta\)) was 0.0065%, an open circuit voltage (\(V_{oc}\)) of 0.039 V, short circuit current density (\(J_{sc}\)) of 0.47 mA cm\(^{-2}\) and a fill factor of 0.349.

| Sensitizer                  | \(V_{oc}\) (V) | \(J_{sc}\) (mA cm\(^{-2}\)) | FF        | \(\eta\) (%) |
|----------------------------|----------------|-----------------------------|-----------|-------------|
| \textit{Piper Betel}, PB   | 6.44 x10\(^{-3}\) | 0.012                       | 88817.3   | 0.071       |
| \textit{Adonidia Merillii}, AM | 0.573         | 2.48x10\(^{-5}\)          | 0.323     | 1.0x10\(^{-9}\) |
| \textit{Morinda Citrifolia}, MC | 0.002       | 0.03                        | 625.257   | 0.05        |
| Mixed sensitizers         | 0.039          | 0.47                        | 0.349     | 0.0065      |

4. Conclusions

Three natural pigments were extracted from three plant species; \textit{Piper Betel}, PB, \textit{Adonidia Merillii}, AM and \textit{Morinda Citrifolia}, and was used as sensitizer in the fabrication of DSSCs. The sensitizers functional group were confirmed using FTIR. These dyes showed a similar structure with those of functional groups. The best cell performance was achieved by the PB dye sensitizers with conversion efficiency of 0.071% followed by MC (0.05 %) and the mix sensitizers (0.065 %) while AM sensitizers showed the lowest efficiency of 1.0x10\(^{-9}\) %. Although the efficiencies obtained from these sensitizers were quite low for large-scale practical applications, but the results may serve as a reference for future studies on these new natural sensitizers.

5. References

[1] O’regan B and Gratzel M 1991 \textit{A low-cost, high-efficiency solar cell based on dye-sensitized}. Retrieved April 6, 2018 from http://www.energygert.rutgers.edu
[2] Zhou H, Wu L, Gao Y and Ma T 2011 \textit{Journal of Photochemistry and Photobiology A: Chemistry} 219(2-3) 188-194
[3] Jumeri F A, Lim H N, Zainal Z, Huang N M, Pandikumar A and Lim S P 2015 Journal of Power Sources, 293(1) 712-720
[4] Gong J, Sumathy K, Qiao Q and Zhou Z 2017 Renewable and Sustainable Energy Reviews 68 234-246
[5] Hug, H., Bader, M., Mair, P., & Glatzel, T. (2014). Applied Energy, 115, 216-225.
[6] Munawaroh H, Saputri L N M Z, Hanif Q A, Hidayat R and Wahyuningsih S 2016 The co-pigmentation of anthocyanin isolated from mangosteen pericarp (Garcinia Mangostana L.) as Natural Dye for Dye-Sensitized Solar Cells (DSSC). In IOP Conference Series: Materials Science and Engineering 107 (1) 012061
[7] Muruganandam L, Krishna A, Reddy J and Nirmala G S 2017 Resource-Efficient Technologies 3(4) 385-393
[8] Suman T Y, Rajasree S R, Ramkumar R, Rajthilak C and Perumal P 2014 Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 118 11-16
[9] Galoppini E 2004 Coordination Chemistry Reviews 248(13-14) 1283-1297

Acknowledgments
The author would like to acknowledge the support from the Fundamental Research Grant Scheme (FRGS) under a grant number of 9003-00619 from the Ministry of Higher Education Malaysia and TSTRG grant from Tin Industry (Research And Development) Board.