The application of sensitizers from red frangipani flowers and star gooseberry leaves in dye-sensitized solar cells

Wan Almaz Dhafina¹, Hasiah Salleh²*, Muhamad Zalani Daud¹ and Nora’aini Ali¹

¹School of Ocean Engineering, Universiti Malaysia Terengganu, 21030 Kuala Nerus, Terengganu, Malaysia
²Centre for Fundamental and Liberal Education, Universiti Malaysia Terengganu, 21030 Kuala Nerus, Terengganu, Malaysia

Corresponding author: hasiah@umt.edu.my

Abstract. Nowadays natural based dyes for dye-sensitized solar cells (DSSCs) have been in research field attention due to its advantages over other type of dyes such as low-cost, low-toxicity, completely biodegradable and abundance of resources. Natural dyes can be produced via the simple extraction method of pigments from plant parts such as flower, fruits, leaves, tuber etc. In this feature article, the natural dyes which composed of anthocyanin pigment from red frangipani flowers and chlorophyll from star gooseberry leaves were applied in zinc oxide, (ZnO) based-DSSC. The ZnO photoanode of the DSSCs sample were sensitized in each dye with different duration. It was observed that DSSCs which has chlorophyll pigment as dye had better performance with power conversion efficiency (PCE) of 0.007%.

1. Introduction

DSSCs is among third generation solar cell that works with the same principal with photochemical cell, but depends on the photon from sunlight to make chemical reaction and generates energy. It was pioneered by Gratzel’s group which its architecture consists of nanoparticle of titania, ruthenium based dye and iodide species electrolyte [1]. For the record, N3 dye (one of ruthenium dye) shows constant high PCE compared to the other kind of dyes until now. However, the ruthenium dye is high-cost due to the lack of ruthenium resource, complex synthetic route and purification requirement [2]. Due to this problem, researches searched new ways to substitute ruthenium based dye and lead to the finding of alternative dyes which are organic dye and natural dye. These two dyes are low-cost and rather environmental friendly. Unfortunately, the synthetic route of organic dye is very complicated, and the yield is very low [3]. In other hand, natural dye is easy to be produced via simple extraction of plant pigments [4] using conventional solvents. Mostly, metal oxide of choice used in DSSC is titania but several studies have attempted to use zinc oxide (ZnO) due to low-cost [5], higher electron mobility [6] and higher conduction band energy level that prompt the better electron injection. It has been reported that ZnO is the first material used in experimental design to proof the irreversible electron injection from organic molecules into the conduction band of metal oxide [7]. Basically, DSSC architecture composed of photoanode and cathode that sandwiched together with electrolyte fillings. Several requirements need to be met regarding the energy level of every materials in DSSC: 1) The highest occupied molecular orbital (HOMO) of chosen dye must be lower than redox level, 2) the lowest unoccupied molecular orbital (LUMO) of chosen dye should be sufficiently higher than
conduction band of metal oxide of choice and 3) catalyst metal of choice in electrode must not chemically reactive with electrolyte and dye.

In this feature article, we discussed about sensitization of ZnO nanoparticles and natural dyes from red frangipani flowers, noted as red frangipani dye (RFD) and star gooseberry leaves, noted as star gooseberry dye (SBD). To the best of our knowledge, there is no research has been done to investigate the potential of combination between ZnO and RFD and there are no reports has been made regarding SBD.

2. Experimental

2.1. Fabrication of ZnO thin film
The indium tin oxide (ITO) glass substrate with dimension of 2cm x 2cm was use as a base to fabricate active materials in photoanode. The ITO glasses were cleaned ultrasonically in distilled water, acetone (R&M Chemicals) and ethanol (95%, HmbG Chemicals) for 5 min, respectively and dried with hairdryer [8]. The ZnO nanopowder, Sigma-Aldrich (0.025M) in methanol, (R&M Chemicals) was spin-coated with spin-coater, MODEL WS-400B-6NPP/LITE on ITO glass with ten repetitions at velocity of 2000rpm for 20s [9]. After that the ZnO thin film was dried with hair dryer and kept in dry box.

2.2. FRD and SBD preparation
Both RFD and SBD were prepared via simple extraction method using ethanol with the ratio between flowers and leaves over ethanol was 1/10. The flowers of red frangipani and star gooseberry leaves (Figure 1) were cut into small pieces, washed with distilled water several times and blow dried with hairdryer. After that the flowers and leaves were immersed respectively in ethanol and heated at 40°C for 2 hours and stirred at 350 rpm. After that the solution were filtered and the crude dye was used as it is (Figure 1(c)). The structure of anthocyanin pigment from RF flowers and chlorophyll from SB leaves are showed in Figure 1(d) and 1(e) respectively [10].

![Figure 1.](image)

**Figure 1.** (a) red frangipani flowers, (b) star gooseberry leaves, (c) extracted dyes solution (the green one is SBD while the red one is RFD), (d) Chemical structure of anthocyanin and (e) chemical structure of chlorophyll [11].
2.3. Dye sensitizing on ZnO thin film
The ZnO thin films were sensitized by dipping them in RFD and SBD respectively in dark environment. The sensitization process was varied from 2h-8h with 2h interval. After that, sensitized thin film was taken out, rinsed with ethanol several times and dried with hairdryer.

2.4. Penetration of cathode and electrolyte
To prepare cathode, clean ITO glass was sputtered with aurum with thickness of 0.001nm. Electrolyte solution was prepared by mixing 0.5M of Lithium Iodide (LiI), Sigma-Aldrich, 99.9% trace metals basis and 0.05 Iodine (I2), Fluka Analytical in acetonitrile, (Merck KGaA) and kept in the dark environment.

2.5. Assemble of DSSC
Both electrodes (cathode and photoanode) were sandwiched together (Figure 2) with a piece of parafilm that have punched hole with diameter of 6mm inserted between electrodes. The electrolyte was dropped through parafilm hole on photoanode before covered with cathode. After that both electrodes were clipped together with mask with punched hole of 6mm diameter.

![Figure 2](image)

**Figure 2.** Sandwiched cathode and photoanode of DSSC. Where cathode was ITO/Au and anode was ITO/ZnO/dye+ electrolyte.

2.6. Characterization
RFD and SBD were characterized in several aspects. UV-Vis spectrometer (Model Lambda 25 with UV Winlab V2.85 software, Perkim Elmer) was employed to characterize optical properties of RFD and SBD while, the functional group of RFD and SBD were investigated via Fourier transform infrared (FTIR). The HOMO and LUMO level of RFD and SBD were investigated through cyclic–voltammetry (C-V) from METROHM AUTOLAB and lastly the power conversion efficiency (PCE) of DSSCs were studied by employing KEITHLEY 4200-SCS SEMICONDUCTOR CHARACTERIZATION SYSTEM.

3. Results and discussion

3.1. UV-Vis absorption and determination of Functional Groups via Fourier Transforms Infra-Red of RFD and SBD
Absorption spectra of RFD and SBD are shown in Figure 3(a). Max absorption peak of RFD was at 542nm which proved the existent of anthocyanin pigment content [12-13] while absorption spectra pattern of SBD was matched with results reported by [14] which proved it was chlorophyll pigments that consist of chlorophyll a and chlorophyll b.
Figure 3. (a) UV-Vis absorption spectres and (b) Fourier Transforms Infra-Red spectres of RFD and SBD.

Maximum absorption peak of SBD was 480.5nm. Chlorophyll absorbs blue and red light strongly and transmits green light which make them looked green in colour, while RFD which was anthocyanin pigment absorbs green light. The band gap of RFD and SBD were determined using eq (1) [15]. Where $E_g$ is band gap, $h$ is plank constant, while $c$ is speed of light and $\lambda_{max}$ is wavelength of maximum peak of UV-Vis absorption spectra.

$$E_g = \frac{hc}{\lambda_{max}}$$  

The calculated band gap of RFD was 2.29eV while SBD was 2.58eV. The collected Fourier Transforms Infra-Red (FTIR) spectra of RFD and SBD are shown in Figure 3(b).

The FTIR spectrum of RFD exhibits most of the characteristic of the anthocyanin. Peak 3334 cm$^{-1}$ represented aromatic O-H-H while peak 2962 cm$^{-1}$ corresponded to C-H stretching. Other peaks like 1639cm$^{-1}$ was corresponding to characteristic of C=O stretching vibration of anthocyanin and peak 1053cm$^{-1}$ corresponded C-O stretching. Lastly, the peak at 557cm$^{-1}$ corresponded to C-Cl bond in anthocyanin [10]. The FTIR spectrum of SBD exhibits most of characteristic of chlorophyll. Peak 3346.5 cm$^{-1}$ represented NH stretch and peak 2974.2 cm$^{-1}$ corresponded to CH stretch. Peak 1651.1 cm$^{-1}$ represented C=C while peak 1535.3 cm$^{-1}$ corresponded to NH out of plane. Other peaks were 1415.8 cm$^{-1}$, 1384.9 cm$^{-1}$, 1327 cm$^{-1}$ and 1085.9 cm$^{-1}$ corresponded to aromatic C-C stretch, CH3, aromatic-N and C-O stretch respectively [16].

3.2. Cyclic-voltammetry of RFD and SBD

The Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) were evaluated from oxidation onset and reduction onset of cyclic-voltammetry (C-V) plot in Figure 4. The characterization was executed with Platinum. Pt mesh and potassium chloride (KCl) as counter and references electrodes, respectively. The electrochemical measurement was carried out with the scan rate of 0.05V/s and step potential of 0.01V. All measurement was done at room temperature.
The HOMO and LUMO of RFD and BSD were calculated using eq(2) and (3), where $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ represent energy level of HOMO and LUMO respectively, while $E_{\text{Oxidation}}^\text{Onset}$ and $E_{\text{Reduction}}^\text{Onset}$ are the value of oxidation and reduction coordinates in C-V plot respectively and 4.4 is adjustment factor [17-18].

\begin{align}
E_{\text{HOMO}} &= e[E_{\text{Oxidation}}^\text{Onset} + 4.4] \\
E_{\text{LUMO}} &= e[E_{\text{Reduction}}^\text{Onset} + 4.4]
\end{align}

The obtained LUMO value for RFD was -3.54eV while SBD was -3.50eV. The HOMO value for RFD was -5.83eV and for SBD was -5.96eV. Band gap value of RFD and SBD was calculated using eq (4) [20].

\[ E_g = E_{\text{LUMO}} - E_{\text{HOMO}} \]

The band gap values that were obtained through C-V characterization for RFD was 2.30eV while for SBD was 2.5eV. These band gap values were congruent with one that was obtained from UV-Vis spectroscopy characterization, hence, proved the calculated band gap of RFD and SBD were valid. From the calculation of HOMO and LUMO of RFD and SBD, the energy level alignment of every materials in proposed ZnO and RFD/SBD based DSSC can be elucidated.

**Figure 4.** Cyclic-voltammetry plot of RFD and SBD.

**Figure 5.** Energy level diagram and mechanism of photocurrent generation in ZnO based DSSCs with (a) RFD and (b) SBD.
By referring to Figure 5 the four steps of carrier movement in this DSSC can be assumed that upon incident photons from light illumination on DSSC, firstly the RFD/SBD molecule will gain enough energy to photoexcite its electron from HOMO to LUMO. Secondly, at LUMO the electron injects into the conduction band of ZnO and thirdly, diffuses into ITO conductive layer of glass substrate. After that, the electron will transfer back into the counter electrode (cathode) and diffused into the layer of catalyst metal then into the iodide electrolyte. The iodide electron will have redox reaction and donates electron to the oxidized RFD/SBD. The molecule of RFD/SBD will be back to its original state and theoretically, all of this mechanism will be repeated and sustained [19-21].

3.3. Dye-sensitized solar cell performances

DSSC samples that have been tested through I-V characterization exhibited the photodiode properties. The parameters of interest are open circuit voltage ($V_{oc}$), short circuit current ($I_{sc}$), maximum voltage ($V_{max}$), maximum current ($I_{max}$), fill factor (FF) and PCE as displayed in Table 1. The FF and PCE were calculated using eq (5) and (6)

$$FF = \frac{I_{sc}V_{oc}}{I_{max}V_{max}}$$

$$PCE = \frac{I_{max}V_{max}}{A_{active}P_{in}} \times 100$$

where $A_{active}$ is active area that has been illuminated with light source which is $2.8274 \times 10^{-5}$ m$^2$ and $P_{in}$ is the intensity of light which is 100 W/m$^2$. I-V curves of DSSCs that have been sensitized with RFD in different duration is shown in Figure 6(a). The performance of RFD DSSCs increased up to sensitization time of 4h, then, gradually decreased when the sensitization duration increases to 6h and 8h. Therefore, the best sensitization duration in RFD was 4h. ZnO is sensitive to acidic media. RFD is anthocyanin that naturally acidic in nature (pH of RFD was 5.5) and it was suspected that Zn(II) complexes was formed after 4h that reduced electron injections and increased carrier combination that dampened the DSSC performance [21].

Figure 6(b) shows I-V curves of DSSCs that have been sensitized with SBD in different duration. The best I-V performance was from the sensitization of DSSC with SBD in 6h dipping duration. It was believed that, after 6h the SBD aggregated on ZnO nanoparticles and formed blocking layer for electron injection and mobility of it in DSSC and the most ideal of sensitization process is only monolayer of dye molecules required to anchor to metal oxide [22].

The changes pattern in $I_{sc}$, $V_{oc}$, FF and PCE of DSSC through different sensitization time by RFD and SBD can be understood more by referring to Table 1. DSSCs that have been sensitized with SBD had better performance than that of have been sensitized with RFD overall. It was assumed that since SBD is chlorophyll which absorb two range of visible light (red and blue regions), it harvested more photons from light compared to RFD which is anthocyanin that only absorb green light. Furthermore, chlorophyll is less acidic than anthocyanin (pH of SBD was 5.78) and less prone to form Zn(II) complexes that dampened the electron injection which will reduce the PCE value of DSSCs and allowed ZnO to be sensitized in longer period.
Table 1. I-V parameters of the fabricated DSSCs sensitized by RFD and SBD at different duration.

| Dye | Sensitization duration (h) | $V_{oc}$ (mV) | $I_{sc}$ (µA) | $V_{max}$ (mV) | $I_{max}$ (µA) | FF | PCE (%) |
|-----|----------------------------|---------------|--------------|---------------|---------------|----|--------|
| RFD | 2                          | 205           | 1.06         | 100           | 0.57          | 0.38 | 0.002  |
|     | 4                          | 250           | 1.46         | 140           | 0.78          | 0.33 | 0.004  |
|     | 6                          | 105           | 0.87         | 55            | 0.44          | 0.34 | 0.001  |
|     | 8                          | 35            | 0.50         | 30            | 0.36          | 0.16 | -      |
| SBD | 2                          | 115           | 1.51         | 65            | 0.65          | 0.41 | 0.002  |
|     | 4                          | 245           | 1.43         | 135           | 0.75          | 0.35 | 0.004  |
|     | 6                          | 250           | 4.43         | 130           | 1.61          | 0.53 | 0.007  |
|     | 8                          | 75            | 0.54         | 45            | 0.30          | 0.30 | 0.001  |

Figure 6. Figure 6: I-V curves of DSSCs that have been sensitized with (a) RFD and (b) SBD in different duration.

4. Conclusion

In summary, ZnO and RFD/SBD based DSSCs were successfully fabricated. ZnO acted as electron collector active material while RFD/SBD served as electron donor active material in photoanode of DSSCs. RFD and SBD are two different plant pigments which are anthocyanin and chlorophyll respectively that harvested light at different region in visible range. SBD-DSSCs had better performance than RFD-DSSC due to the ability of chlorophyll to harvest red and blue light compared to that of RFD which is anthocyanin that only can harvest green light only. Another reason of better performance in SBD-DSSCs was due to less acidic nature of chlorophyll compared to anthocyanin, which less formation of Zn(II) complexes that hindered better performance of DSSCs.

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