Fruit based Dye Sensitized Solar Cells

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Abstract. Dye Sensitized Solar Cell (DSSC) was first discovered in 1991 by O’regan and Gratzel. This new type of solar cell was reported to have lower production cost with efficiency as high as 12% which is comparable to conventional silicon solar cell. Initially, it uses ruthenium dye as light sensitizer for the operation. However, DSSC with ruthenium dyes are facing environment friendly issues due to the toxic chemicals and costly purification in processing ruthenium dye. Regardless of the poor performance in DSSC, natural dyes which are easy to prepare, cheap and environmental friendly still appear to be an alternative as dye sensitizer. In this study, dye sensitized solar cells (DSSCs) were fabricated using anthocyanin source dyes extracted from several local fruits. All the extracts absorb a wide range of the visible light and ultraviolet spectrum. Therefore, all of the natural dyes show light absorption properties which is important for a dye sensitizer. A DSSC is comprised of conductive substrate, nanoporous semiconductor TiO² layer, dye sensitizer, electrolyte with redox couple and a counter electrode with catalyst. In this study, the effect of different light source and different counter electrode are been investigated. However, it is vital to know that further research need to do more on the locally Borneo sourced dyes to evaluate and enhance their performance in Dye Sensitized Solar Cell.

1. Introduction

Dye Sensitized Solar Cell (DSSC) was first published in 1991[1]. This new type of solar cell was reported to have lower production cost with efficiency as high as 12%. Initially, it uses ruthenium dye as light sensitizer for the operation. However, DSSC with ruthenium dyes are facing environment friendly issues due to the toxic chemicals and costly purification in processing ruthenium dye. Regardless of the poor performance in DSSC, natural dyes which are easy to prepare, cheap and environmental friendly still appear to be an alternative as dye sensitizer.

Dye sensitizers are chemicals which can absorb energy from visible light, which then produces excited electrons to be injected to the wide band gap semiconductor [2]. There are few characteristics for an efficient dye sensitizer. Firstly, it must have an intense absorption ability in the visible region under the illumination of the sunlight. Furthermore, the dye molecules should contain hydroxide groups or carboxyl groups which will firmly graft to the Titanium (IV) sites on the TiO² surface.
Moreover, it should also have the ability of efficient electron injection into the conduction band of the semiconductor [3].

In 1997, it was found out that the subgroup of flavonoid which is anthocyanin's works well with DSSC system. Anthocyanins are weak acids and occur naturally in all tissues of the plants such as flowers, fruits, leaves, stem and roots. Dabai (Black Olive) is one of the exotic fruit in Sarawak. The major phenolic component found in the peel of Canarium Odontophyllum is anthocyanin [4]. On the other hand, Both Mangosteen and Wild Mangosteen are tropical fruit widespread over Borneo and they are seasonal. Their fruit peel contains anthocyanin [5].

In this work, the photoelectrochemical results obtained by using natural photosensitizers such as Black Olive (Canarium Odontophyllum), Mangosteen (Garcinia mangostana), Wild Mangosteen (Garcinia Hombroniana) are presented. Furthermore, Blueberry (Vaccinium Myrtillus) was prepared as standard natural dye. The objective of this research is to find out the photoelectrochemical properties of the DSSC using anthocyanin as dye sensitizer. Moreover, the effect of different light source, dye concentration and counter electrode on the DSSC efficiency was investigated.

2. Methodology

2.1. Preparation of Photosensitizers

The natural samples shown in Figure 1 were cut into small pieces to the size of about 0.5cm x 0.5cm. The natural dye solutions were prepared by crushing the samples with distilled water and then the solid residues were removed from the solution. Next, the samples were crushed in a mortar and pestle together with distilled water until the solution turns to colour solution. The solid residues were removed from the solution and the remaining solution was prepared as dye sensitizer. N719 dye (0.3mM) was prepared as standard.

\[ \text{The anthocyanin sources used as photosensitizers in DSSC} \]

2.2. Preparation of Photoanode

The TiO\textsubscript{2} solution is prepared by the adding of 1.0g colloidal P25 Degussa TiO\textsubscript{2} powder and 0.50g of polyethylene glycol 10,000 (PEG 10,000) into the mortar. Then, the paste was blended with 2.0ml nitric acid (HNO\textsubscript{3}) solution (0.1M) and 1 ml of nonionic surfactant, Triton X-100. After that, the paste was blended by pestle in the mortar continuously for 15 minutes until the paste becomes thick and free of aggregates. The paste was left to equilibrate in the fume chamber for another 15 minutes. Next, the paste was deposited on the FTO glass using a doctor blade method until the uniform layer was achieved.

The paste was allowed to be dry first before heat at high temperature. When the paste becomes dry, the scotch tape was removed and the FTO glass was heated on a hot plate at the sintering temperature of 450\textdegree C for 30min to achieve nanoporous structure in semiconductor thin film as shown in figure 2. After 30 minutes, the FTO glass was allowed to be cool to room temperature before immersed in the natural dye extract for 24 hours.
Figure 2. Deposition of the TiO$_2$ paste on the Fluorine doped Tin Oxide (FTO) glass via doctor blade method.

2.3. Preparation of Electrolyte
The polymer gel electrolyte was prepared by using 3.25g Potassium iodide (KI), 0.5g iodine (I$_2$) 30ml propylene carbonate (PC) and 20.0 ml of polyethylene glycol 400 (PEG 400). Firstly, KI and I$_2$ were put in the 250ml conical flask together with 30ml propylene carbonate (PC). The mixture was stirred on the magnetic stirrer for 30 minutes at room temperature then PEG400 was added. The mixture is then reacted at 100°C for 24hr. Finally, the colloidal liquid was cooled to 60°C to form a polymer gel electrolyte after 24 hours. The polymer gel electrolyte was then stored in bottle as shown in figure 3.

Figure 3. Polymer gel electrolyte used in DSSC

2.4. Preparation of Counter Electrode
The FTO glass was coated as carbon soot layer counter electrode by using a candle flame. Then the slide was heated on a hot plate at 150°C for 15min. For carbon paste counter electrode, the carbon paste was prepared with 0.1g of TiO$_2$, 1mL of HNO$_3$ mixed in beaker for 5 minutes. Afterwards, 0.1g of carbon was added and mixed for another 5 minutes. Next, 0.05g PEG10000 was added in the mixture and blended for 5 minutes. Then, 20µL triton-X was added into the mixture. The carbon paste was heated on a hot plate at the sintering temperature of 300°C for 1hour. Following that, deposition of the carbon paste on the Fluorine doped Tin Oxide (FTO) glass was done by using doctor blade method until the uniform layer was achieved. After the paste becomes dry, the scotch tape was removed from FTO glass. Figure 4 shows the carbon soot and carbon paste counter electrode.

Figure 4. Types of the counter electrode: Carbon soot (left) and Carbon Paste ( right)
2.5. Fabrication of Dye Sensitized Solar Cell (DSSC)

The slide was allowed to cool to room temperature before assembly of the cell. The slide that stained with natural dye was left dry and the electrolyte was dropped on the semiconductor slide and heat at 60°C for 30 minutes as shown in figure 5.

![Figure 5. Deposition of electrolyte on the semiconductor slide](image)

Subsequently, the two slides that coated carbon and semiconductor respectively were clipped together. Then the alligator clips were used to clip the glass and connected to multimeter as shown in figure 6. The circuit was constructed by using DSSC, potentiometer or variable load resistor and multi-meter. The complete circuit was tested using sunlight and metal halides lamp as light sources.

![Figure 6. DSSC cell assembly](image)

3. Result and Discussion

3.1. Absorption Spectra of Natural Dye

Figure 7 shows the UV-Vis absorption spectra of Black Olive, Blueberry, Mangosteen and Wild Mangosteen. It has been known that all the extracts absorb a wide range of the visible light. Therefore, they fulfil the characteristics to become potential dye sensitizers which absorption ability in the visible region under the illumination of the light source and also the conversion ability from light energy to electrical energy. The absorption characteristics for each extracts are dissimilar attributable to different types of anthocyanins that contained in the natural extract. It was found out that the absorption of Black Olive is the broadest among other extracts.

![Figure 7. The absorption spectra of the natural anthocyanin sources](image)
3.2. Photocurrent and Photovoltage Measurement

Overall performance of the anthocyanin source as sensitizer in DSSCs was evaluated in terms of the open circuit voltage (Voc), short circuit current (Jsc), fill factor (FF) and energy conversion efficiency (ŋ). Dyes obtained from the Black Olive, Mangosteen, and Wild Mangosteen are all capable to promote light harvesting ability and electron injection to the conduction band of TiO₂ (Table 1). Obviously, the efficiency of DSSC sensitized with Black Olive was significantly higher than the standard natural dye, Blueberry. This is due to the higher intensity and broader range of the light absorption ability as referred to Fig 7(a). Moreover, the Black Olive cell has the highest fill factor (in Table 1), thus low equivalent series resistance and promotes efficient electron transfer. Therefore, the Black Olive extract should be an alternative anthocyanin source for DSSC and Black Olive was chosen for further study since it gave a better sensitizing performance compared to other extracts.

| No. | Samples               | Voc (mV) | Jsc (mA) | FF    | ŋ, % |
|-----|-----------------------|----------|----------|-------|------|
| 1   | Ruthenium N719        | 708      | 0.54     | 0.26  | 0.25 |
| 2   | Black Olive           | 543      | 0.11     | 0.54  | 0.08 |
| 3   | Mangosteen            | 432      | 0.12     | 0.30  | 0.04 |
| 4   | Wild Mangosteen       | 430      | 0.11     | 0.24  | 0.03 |
| 5   | Blueberry             | 390      | 0.11     | 0.39  | 0.04 |

3.3. Effect of different light source

Sunlight has a very broad spectrum of light if compared to the metal halide light which has a narrow spectrum. Therefore, the metal halide light releases lower frequencies of light which means less energy created in the DSSC and resulted in low efficiency. When the photons from sunlight strike the dye molecule, more electrons are released from ground state of dye molecule to excited state. Hence, it produces higher current under illumination of sunlight (in Table 2).

| No.  | Light Source   | Voc (mV) | Jsc (mA) | FF     | ŋ, % |
|------|----------------|----------|----------|--------|------|
| 1    | Sunlight       | 569      | 0.26     | 0.34   | 0.13 |
| 2    | Metal halides lamp | 543   | 0.11     | 0.54   | 0.08 |

3.4. Effect of different counter electrode

The function of the counter electrode is to transfer electrons from the external circuit to triiodide/iodide in the redox electrolyte. The use of carbon paste counter electrode facilitates the electron transfer process to regenerate the electrolyte thus higher efficiency achieved (in Table 3). Consequently, carbon paste counter electrode obtained higher open circuit voltage and short circuit current as well as fill factor over carbon soot layer counter electrode. This may due to the attachment of the carbon paste onto FTO glass substrate are stronger than carbon soot layer. Therefore, the electron transfer process becomes more efficient.

| No.  | Counter Electrode | Voc (mV) | Jsc (mA) | FF    | ŋ, % |
|------|-------------------|----------|----------|-------|------|
| 1    | Carbon Paste      | 543      | 0.11     | 0.54  | 0.08 |
| 2    | Carbon Soot       | 507      | 0.08     | 0.36  | 0.04 |
4. Conclusion
In conclusion, the Black Olive extract has higher photosensitization performance as compared to other extracts. This is due to broader absorption ability and better charge transfer between the Black Olive extract and TiO$_2$ surface. Black Olive extract obtained higher efficiency under illumination of sunlight due to sunlight has broader spectrum of light which contribute to more energy created in DSSC. The photovoltaic performance of fabricated DSSCs operated with carbon paste coated counter electrode over carbon soot layer coated counter electrode has shown an increase in $V_{OC}$, $J_{sc}$, FF and energy conversion efficiency.

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