The Effect of Different Solvents in Natural Dyes from Roselle (Hibiscus Sabdariffa) and Green Tea Leaves (Camellia Sinensis) for Dye-Sensitized Solar Cell

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Abstract. A dye-sensitized solar cell (DSSC) fabricated using anthocyanin or chlorophyll natural dye extract coming from Roselle (Hibiscus Sabdariffa) and Green Tea leaves (Camellia Sinensis). Both dye pigmentation were extracted using different alcohol-based solvent, namely, ethanol, methanol and mixed (ethanol + methanol) to identify whether the different solvents give the effect during the dye extraction. The performance of the electron transfer interaction between the natural dye and Titanium Dioxide (TiO2) was determined. The photovoltaic response of DSSC was collected by recording the data of I-V characteristic under illumination. The DSSC using the Roselle dye extract yielded the following results; Voc = 0.001 V, Jsc = 0.00868 (mA/cm²), FF = 0.3554 and η = 0.00142% which is coming from the mixed solvent. On the other hand, the green tea dye extract yielded the following results; Voc = 0.3985, Jsc = 0.000797 (mA/cm²), FF = 0.3985 and η = 0.0000752% which is coming from the methanol solvent.

1. Introduction

Nowadays, many researchers have recognized the ability of the Dye-Sensitized Solar Cell (DSSC). As the third generation of a solar cell, it is still are not comparable with silicon solar cell [1]. Due to many modifications that can make on it, DSSC is slowly improving in terms of quality and performances [2]. DSSC is well known for its lightweight and portable characteristics, low cost of the production process, and also have less risk towards environmental impact. The DSSC structure contains three layers of components. The components are photoanode, electrolyte and photocathode, as shown in Figure 1.
Each component contributes to a different function that influences the performance of DSSC itself. Among these three components, many researchers have a focus on modifications of photoanode [2]. It is because photoanode consists of three primary materials that can be altered to get an excellent performance of DSSC [3]. Photoanode consists of Indium Tin Oxide (ITO) glass acts as a substrate, Titanium Dioxide (TiO$_2$) that acts as a dye holder, and dye sensitizer that use to excite electron and generate electricity. Photoanode can be modified in a few ways, such as the doping of polymer-based or organic material on Titanium Dioxide (TiO$_2$) surface [4], replacement of TiO$_2$ material with other metal oxide material [5], and many more. The other important component is a photocathode, which consisted of ITO glass coated with platinum.

Figure 2 shows the flow of the electrons in the DSSC. Movement of the electrons is essential to generate the electricity inside the DSSC [6]. The DSSC produces power through electrons moving from the conductive glass (photoanode) to the conductive glass (photocathode). Light will go straightforward from conductive glass (photoanode) to the TiO$_2$. TiO$_2$ is the place where the absorption of the dyes occurred and functioning to release a photon [7]. The dye in the photoanode will retain the photon of light, and one of the photons from the dye will go from ground expressed to energized state. The energized electrons will bounce to the TiO$_2$ layer and goes over the film. The electron at that point goes through the path of the electron and arrives at the photocathode. After that, the dye lost an electron as the TiO$_2$ is oxidized. After the oxidation occurs, the dye gets an electron back from the iodine electrolyte. The new electrons finally are back to the ground state. The initially lost electron arrives at the photocathode, it gives the electrons back to the electrolyte. These flows of electrons generate the electricity for the solar cell.

Other than that, the performance of the DSSC also depends on the photoanode dye of the molecule. The dye will react as a sensitizer, which means that the more sensitive the dye to the light, the more photons will be captured and trapped and the higher the current will be produced [8]. DSSC with
proper dye molecules composition is used to sensitize the bandgap of the photoanode. During the absorption of the light, the dye molecule will go to the surface of the TiO$_2$ nanostructured and get oxidized and excites the electron to be injected into the electron path to generate electricity [9].

Dye sensitizers are essential to make DSSC function well. It will generate the photon-induced electrons and injecting them into the conducting band of the TiO$_2$ semiconductor [10]. Dye sensitizer divided into two groups; (1) metal complex dye and (2) metal-free organic dye [11].

Metal Complex Dye has specific properties to achieve high conversion efficiency for DSSC. Previous researchers stated that the highest was up to 13.4% [12]. However, the metal complex dye has a complicated synthesis route, limited extinction coefficients in the visible region [13], high costs and also not environmentally friendly. All these are making strong reasons for the researcher to find another alternative to get a metal-free complex dye [14]. One of the promising metal complex dye is Ruthenium [15]. The molecular of Ruthenium has been investigated by many researchers for its characteristic as a charge transfer sensitizer [9].

The metal-free organic dye is considered as the promising materials to replace metal complex dye [16] because it has reached the highest record of 14.3% [17]. Metal-free organic dye also has been proved as it environmentally friendly, low cost compared to metal complex dye, economical purification [12], even simple and easy to synthesis. The simplest organic dye came from fruits. There are two main types of natural dye extracts that are divided based on the pigmentation of the colour; anthocyanin and chlorophyll.

Anthocyanin is a pigment that gives the colour of red, purple, blue or black [18]. Anthocyanin is quite popular as natural dye sensitizer because of carboxyl and hydroxyl group present in anthocyanin can be bound efficiently to the surface of TiO$_2$ [19]. In this experiment, Roselles used as an anthocyanin extraction. Roselle, with its scientific name, Hibiscus Sabdariffa was chosen due to its properties that are rich in anthocyanin [20]. Figure 3 shows delphinidin and cyanidin complexes that are the source of the anthocyanin in the Roselle [20]. Another strong reason to add why Roselle was chosen because it grows a lot in tropical countries such as Malaysia and therefore, it is easy to get.

Figure 3. Structure of anthocyanin in the Roselle [20]

Chlorophyll is a pigment that is found in plants and usually gives green colour [21]. Previous researches stated that the conversion efficiency of cells with chlorophyll as sensitizer is more than two per cent. In this experiment, Green tea is used as a chlorophyll extraction. Green tea, with its scientific name Camellia Sinensis, was chosen because of the strong presence of chlorophyll. Previous researches stated that in 1 g of green tea, it consists of 1.12 to 1.89 mg chlorophyll [22].

The structure of the natural dye extraction is used as a sensitizer to determine the strength of its attachment on the TiO$_2$ surface. The presence of the carboxyl and hydroxyl functional groups can
bind strongly on the surface of the TiO$_2$ [19]. This interaction between the dye structure and the TiO$_2$ can lead to the electrons transfer to generate electricity in the DSSC.

Extraction parameters are vital to obtaining an excellent natural dye extract. Previous research, have been investigated three different extraction parameters, based on their pH, boiling point and the extraction temperature [23]. Different extractions show a different performance of DSSC as it affects the functional group of the natural dye.

However, different properties of the solvent may also affect the extraction of the dye. The influence of the solvent on the dye precursor and dye stability may be investigated [24]. The measurement of photovoltaic properties is measured.

In this research, two different natural dyes (Roselle and green tea leave) were selected to determine the reaction towards the alcohol-based solvent. Different alcohol-based solvents are used (ethanol, methanol and mixtures of ethanol and methanol). The effects of the different solvent were studied to be used in the further experiment of DSSC with a natural dye sensitizer. As for the anthocyanin, they are more soluble in ethanol, but the aggregation of the dye molecule is less due to the properties of the solvents. Solvents properties are expected to improve the dye molecules dispersion adsorption on the porous active site of the TiO$_2$. Methanol properties are excellent in the dispersion of the anthocyanin that can boost the result of the mixed solvent to give the highest efficiency [25].

Since natural dyes consist of hydroxyl and carboxyl functional group, there are some differences in performance in DSSC for anthocyanin and chlorophyll. For anthocyanin, the difference is mainly due to the number of OH- and OCH$_3$ groups. Based on the previous studies, it is reported that the chemical adsorption of anthocyanins on the TiO$_2$ surface is the result of alcoholic bound protons [25]. For chlorophyll, the presence of the alkyl group resulted in the strong steric hindrance of the chlorophyll to bind with TiO$_2$ film [26]. Different type of solvent is important because it has different solubility reaction towards different materials.

2. Methodology

In order to make a DSSC device, the method will be divided into two parts. The first part is the preparation of the photoanode and the second part is the preparation of the photocathode.

2.1. Preparation of Photoanode

2.1.1. Cleaning Process

The preparation started with the clean process of the substrates to get rid of any contaminations. ITO glass was cut into 2 cm x 2 cm. After that, it was immersed in the ethanol for 10 minutes in the ultrasonic bath, and the glass was put to dry on the hot plate for 5-10 minutes. The steps were repeated using acetone and DI water. Lastly, the resistivity part will be used for fabrication and was checked using a multimeter. The ITO glasses have an average resistance of 15 Ω.
2.1.2. Preparation of Titanium Dioxide

35 ml of Nitric Acid (purchased from Aldrich) was mixed with 0.1 ml of distilled water to make a stabilizer. 250 mg of TiO$_2$ Degussa P25 powder was mixed with the stabilizer in the mortar. The stabilizer was dropped slowly until white paste-like paint was obtained. The cleaned ITO glass was covered with scotch tape side by side to get 1.5 cm x 1.5 cm active area. Sufficient amount of TiO$_2$ paste was applied on the glass using Dr Blade’s technique to get a uniform thickness layer of TiO$_2$ thin film. After that, the samples are annealed in the furnace for 450°C for 1 hour.

2.1.3. Preparation of Natural Dye Extract

In this experiment, Roselle was chosen for anthocyanin pigmentation, and green tea leaves were selected for chlorophyll pigmentation. For the extraction method, the solid-liquid extraction method will be used. First, the dye powder was obtained by heating the Roselle petals via microwave at 60°C for two hours. The dried crude is then crushed using mortar and pestle to form a dye powder. One dye weight:1 solvent volume ratio was used in this experiment, so, 10 ml of solvent (ethanol, methanol and mixed) was used to dissolve 10 gm of dye powder. The extracts were heated and stirred using a magnetic stirrer for 10 minutes. The dye extract was then put into the centrifuged machine at the speed of 800 rpm for two minutes to separate any contamination and the extract. The solution was finally filtered to extract anthocyanin and also chlorophyll. The weight was measured using the powder instead of the raw material, so the raw material was not measured beforehand.
2.1.4. Preparation of Photoanode

The annealed samples were then immersed in the dye extraction of anthocyanin, which is from Roselle and dye extraction of chlorophyll which is from the Green tea. This process was done for 30 minutes in the dark. After 30 minutes, the samples were taken out and cleaned using acetone.

2.2. Preparation of the Photocathode and Device Assembled

The platinum paste was applied on the cleaned resistivity part of the ITO glass as preparation of photocathode. After that, it was annealed at 180OC for 30 minutes in the oven. After that, the photocathode and photoanode were sandwiched together with electrolyte in the middle of it for the current flow, as shown in Figure 4.

![Figure 4. Sandwiches arrangement of the DSSC device](image)

3. Results and Discussion

The devices were brought to the Solar Simulator test. The anode wire was connected to photoanode while the cathode wire was connected to the photocathode. The power was provided as the same amount of sunlight intensity. The data was collected by creating the I-V curve under the irradiation of solar light (1000 mW/cm²). The photoelectrochemical of both Roselle and green tea are summarized in Table I.

| Device                      | $V_{oc}$ (V) | $J_{sc}$ (mA/cm²) | Fill Factor (FF) | Efficiency (%) |
|-----------------------------|--------------|-------------------|------------------|----------------|
| **Roselle (Anthocyanin)**   |              |                   |                  |                |
| Ethanol                     | 0.475        | 0.0069            | 0.2857           | 0.000959       |
| Methanol                    | 0.00116      | 0.0088            | 0.3320           | 0.00116        |
| Mixed                       | 0.00142      | 0.00868           | 0.3554           | 0.00142        |
| **Green Tea Leaves (Chlorophyll)** |          |                   |                  |                |
| Ethanol                     | 0.129        | 0.0000257         | 0.22414          | 0.0000257      |
| Methanol                    | 0.3985       | 0.000797          | 0.3985           | 0.0000752      |
| Mixed                       | 0.0845       | 0.000565          | 0.2329           | 0.0000111      |
Typically, metal-free of natural organic dyes that were used as a sensitizer in DSSCs were showing low conversion efficiency compared to the metal complex dye because the natural dye doesn’t have a specific functional group as dye [26]. Metal complex dye, have a specific functional group that are specially made for DSSC as that what makes it boosts the efficiency of the DSSC. However, they are costly and not environmentally friendly. Based on previous research, it is stated that anthocyanin is suitable for the DSSC and can be attached to TiO₂ thin film. Furthermore, it has a visible region at 450-580 nm [19]. As for the chlorophyll, it plays an important role in the photosynthesis process. However, both anthocyanin and chlorophyll probably could not yield sunlight to electricity conversion in DSSC process due to the lack of available bond in between the dye molecules and TiO₂ surface [26]. This is because the electron transportation cannot be as smooth as the DSSC that is using metal complex dye. This could be one of the reasons the efficiency percentage for both anthocyanin and chlorophyll is not as high as a metal-complex dye. Open circuit voltage (Voc) and short circuit current (Isc) is determined based on the difference between the Fermi level of TiO₂ and the potential of redox electrolyte, where it is dependent on the electron recombination rate of sensitizer absorption [26].

As Table I stated, six devices were tested using the Solar Simulator machine. Three from Roselle dye extracts and three from Green tea leaves dye extracts. Both Roselle and Green tea dye extracts are dissolved in three different solvents which are ethanol, methanol and mixed (ethanol and methanol). Based on the Table, it represents the value of the open-circuit voltage (Voc), short-circuits current...
density ($J_{sc}$), Fill Factor ($FF$) and efficiency percentage ($\eta$). Table I shows that for the Roselle natural dye extract, the device that uses mixed solvent has the highest efficiency of 0.00142%. For the Green tea dye extract, the device that uses methanol solvent has the highest efficiency of 0.0000257%. The $V_{oc}$ is the maximum voltage produced by a solar panel with no load on it. The anthocyanin in ethanol produced the highest $V_{oc}$ among others. However, the average voltage produced is not as high as the others resulting in low-efficiency value.

Figure 5 shows the photocurrent-voltage curve for DSSC sensitized by Roselle (anthocyanin) extract. For the mixed solvent (Ethanol + Methanol), although the initial current density is lower than both ethanol and methanol solvents, it hit the highest current at 0.3 V. This yielded the highest efficiency compared to the ethanol and methanol solvents. Ethanol and methanol solvents also degrade faster compared to the mixed solvent.

Figure 6 shows the photocurrent-voltage curve for DSSC sensitized by Green tea (chlorophyll) extract. Opposite from Roselle’s curve, the highest efficiency of Green tea (methanol) was boosted its performance from the initial voltage, compared to the mixed solvent and ethanol. Figure 5 and figure 6 do not correlate because it is only to see which solvent gave the best IV-curve pattern.

The comparison between Roselle (anthocyanin) dye extracts and Green tea (chlorophyll) dye extracts show that Roselle has higher efficiency and higher photosensitized performance. This might be due to the better electron charge transfer between the anthocyanin dye and the TiO$_2$ surface [27].

4. Conclusion

In this paper, a dye extracted from the Roselle was found to be highly soluble in mixed solution ethanol and methanol followed by methanol and ethanol, respectively. For dye extracted from the Green tea extract, it is found to be highly soluble in the Methanol solvent. Both results are proven based on the various photovoltaic parameters such as Voc, $J_{sc}$, $FF$ and $\eta$.

From the observation, dye extracts with the presence of the methanol will give a proper extraction and therefore boost the performance of the DSSC. For future research, the methanol-based solvent will be used for the cocktail process between anthocyanin and chlorophyll. This paper does not make a comparison between Roselle and green tea, but the contrast between the solvents in each dye. However, the reason why the research on the chlorophyll was conducted is to be the guide for the next research. The next research will be about cocktail dye between the anthocyanin and chlorophyll. Hence, why the best solvents in each dye group should be determined.

Acknowledgements

The authors are grateful to the School of Microelectronic, School of System Electric, Universiti Malaysia Perlis (UniMAP) for the use of their research facilities. This study was supported by Malaysia Ministry of Higher Education FRGS-RACER (9027-00026).

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