Dyes extracted from Hibiscus Sabdariffa flower and Pandanus amaryllifolius leaf as natural dye sensitizer by using an alcohol-based solvent

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Abstract. The efficiency improvement of Dye sensitized solar cells (DSSC), the fabrication of DSSC by using metal-free organic natural dyes with a different type of solvents for the extraction of dye sensitizer was investigated. The metal-free organic Dye which comes from anthocyanin and chlorophyll dyes were dissolved by using different solvents, which are ethanol, methanol and mixture of ethanol and methanol. Anthocyanin dye was extracted from the petals of Hibiscus Sabdariffa (Roselle), and chlorophyll dye was extracted from the epidermal leaves of Pandanus amaryllifolius (Pandan). The purpose of using different solvents from alcohol-based was to determine which solvents that produce the highest effect in term of efficiency for DSSC. To confirm which solvents that produce the highest efficiency to the DSSC, the photovoltaic measurement was conducted, and the data was collected. From the photovoltaic analysis, the J-V characteristics under illumination are recorded. The sample that used anthocyanin dye extracted from Roselle flower diluted with methanol solvent gave the highest efficiency which is 0.0005% with the following parameters – Voc = 0.419 V, Jsc = 0.0057 mA/cm² and FF = 0.24. Meanwhile, the sample that used chlorophyll dye extracted from Pandan leaves diluted with a mix of ethanol and methanol solvents gave the highest efficiency which is 0.00014% with the following parameters - Voc = 0.347 V, Jsc = 0.0016 mA/cm² and FF = 0.25.

1. Introduction

Dye-Sensitized Solar Cell (DSSC) is one of a device to convert light energy into electrical energy by using a photovoltaic effect that is introduced by Gratzel in 1991 [1]. Starting from 1991, DSSC has attracted the attention of researchers for its advantages compared to Silicon Solar Cell (SSC). Until now, many kinds of research had been done to improve the efficient [2] of the DSSC. The low cost of fabrication for DSSC, simple fabrication to be done in ambient condition and the availability of the material used in DSSC had made it popular among the researchers.

There are four important parts in the basic structure of DSSC; working electrode or photoanode, dye sensitizer, an electrolyte and counter electrode or photocathode. In order to improve the efficiency of DSSC, researchers had focused on to improve every part of the DSSC. DSSC started to function when the sunlight enters the cell through the transparent Indium Tin Oxide (ITO) substrate, striking the dye
sensitizer in the working electrode [3]. Dye sensitizer hits the photons from the sunlight, and an electron can be injected directly into the conduction band of a surface that is called Titanium Dioxide (TiO$_2$) layer. The electron moved by diffusion to the transparent substrate on top, which is known as a counter electrode. Meanwhile, the dye molecule from dye sensitizer had lost an electron, and the molecule will break down if another electron is not provided. The dye sensitizer strips one from iodide in the electrolyte and oxidizing it into triiodide.

![Figure 1 Dye-sensitized solar cell working principle.](image)

To prevent the recombination process that can lead to short circuit, the reaction occurs quite fast compared to the time that it takes for the electron that has been injected to recombine with the oxidized dye molecule. The triiodide then recovered the missing electron by mechanically diffusing to the bottom of the cell, where the counter electrode reintroduces the electrons after flowing through the external circuit. From the observation, for every sample of DSSC, the main part that plays a crucial role is dye sensitizer as it is highlighted in Figure 2.

![Figure 2 Dye-sensitized solar cell basic structure](image)

The usage of dye sensitizer in Dye-Sensitized Solar Cell (DSSC) is very important as it is one of the primary keys to ensure that DSSC is operated. Dye sensitizer needs several characteristics to ensure that it is a suitable dye sensitizer such as can smoothly injecting electrons to the conduction band of Titanium Dioxide (TiO$_2$) [4], firmly bonded to the TiO$_2$ surface [5] and can absorb light below a wavelength of 920 nm [6].

For dye sensitizer, it is categorized into two groups; metal complex [7] and metal-free organic dye [8]. The metal complex dye is the common Dye used by researchers as it has high stability [9] and gives high efficient conversion efficiency to DSSC [10]. The popular metal complex dye used is Di-tetramethylammonium cis-bis(isothiocyanato)bis(2,2’–bipyridyl-4,4’-dicarboxylate)ruthenium (II) or known as N719 or commonly called as ruthenium dye. N719 Dye gives a high impact on the efficiency of DSSC as it has several advantages like high stability [11] and has excellent photoelectrochemical properties [7]. However, the trend nowadays had changed the researchers to replace their usual method of using metal complex dye to metal-free organic Dye as a metal complex dye is expensive [12] and
limited [13]. The researcher uses Metal-free organic Dye as it is having a higher extinction coefficient [14] and can be purified and synthesized easily [14] and environmental friendly [15] to nature.

In this study, we used metal-free organic Dye which can be obtained from the extraction of fruits, vegetables and plants. Several groups of metal-free organic Dye has been used, such as anthocyanin [16], chlorophyll [17] and carotenoid [18]. For this study, anthocyanin and chlorophyll group are chosen to be used as metal-free organic Dye as it is easy to get. Anthocyanin is the natural pigment that gives colours to plants, fruits and vegetables, which are blue and purple colours [19]. For this group, the absorption spectrum of anthocyanin in the visible range is between 450 to 580 nm, and it usually gives colour in blue to the purple range [20]. Zhang et al., investigated the natural dye sensitizers with more than 20 different natural dyes such as bacteria, vegetables and insects in DSSC and achieved the best performance with the red cabbage extracts with the efficiency of 1.51% and purple sweet potatoes with the efficiency of 1.1% and both of it are from the anthocyanin group [21].

Chlorophyll group is a pigment which is found in the leaves mostly green plants, and it absorbed the light from red, blue and violet wavelengths and obtained its colour by reflecting green [22]. The absorption spectrum of chlorophyll group is between 600 to 700 nm [23]. Cho et al., investigated the usage of chlorophyll dye extracted from sweet potato leaf with the efficiency obtained is 0.391% [24]. In this study, the Roselle (Hibiscus Sabdariffa) flower from the anthocyanin group and Pandan (Pandanus amaryllifolius) leaves are used as organic natural dye sensitizer. The DSSC samples were prepared with the use of natural dyes extracted from the petal of Hibiscus Sabdariffa flower and extracted of epidermal part of Pandanus amaryllifolius leaves. Both of it is used freshly and stored in the room temperature.

The study is conducted by varying the type of solvent, which is alcohol-based used in dye sensitizer. The solvent used are ethanol, methanol and mix of ethanol and methanol, and the result is evaluated by the result of the efficiency of DSSC by using the organic natural dye sensitizer.

2. Experimental method

2.1. Preparation of working electrode

The process started with the cleaning of the substrate (Indium Tin Oxide – ITO glass) for the working electrode by using acetone and ethanol. It was sonicated in the sonicated bath for 10 minutes for each solvent. The resistivity of ITO glass was checked by using a multimeter, and the resistivity was recorded. 250 mg of Degussa P25 powder was weighed and added with the stabilizer. The stabilizer is the mixture of acetic acid and distilled water (DI water). The product obtained was white paste which is Titanium Dioxide (TiO₂) paste. The ITO glass then was covered with Scotch tape to obtain an active area of 1.5 cm x 1.5 cm. TiO₂ paste was spread over on the surface of the ITO glass by using Dr Blade’s technique. Then the samples were annealed in the furnace for 450°C [25] for 1 hour and were kept in the dark place after the annealing process.

2.2. Preparation of dye sensitizer

In this study, the dye sensitizer used were from the anthocyanin group (Roselle/Hibiscus Sabdariffa) flower and chlorophyll group (Pandan/Pandanus amaryllifolius) leaf. For anthocyanin extraction, the petals of Roselle flower were cleaned by washing and drying in an oven for 60°C until it became thoroughly dried. After the samples cooled down, it was crushed by using mortar pestle until a fine powder was formed. 10g of Roselle powder obtained from the previous process was weighed and diluted with 10 ml of ethanol. It was followed by 10 g of Roselle powder with 10 ml of methanol and 10 g of Roselle powder with 10 ml of mix ethanol and methanol. It was then being stirred by using a magnetic stirrer for 10 minutes to ensure that the Roselle powder was diluted. For chlorophyll extraction, the step was repeated like Roselle powder, and the same amount was used in diluting the Pandan leaf powder.
Six samples of the working electrode that has been annealed were soaked into six solutions of dye sensitizer for 30 minutes. The samples were kept in the dark place to maintain the humidity for dye sensitizer and to keep the dye sensitizer from a light source.

2.3. Preparation of counter electrode
For the counter electrode, the substrates with the resistivity area were covered with the Scotch tape. Platinum paste by Dyesol was dropped at the end of the surface and was spread all over the glass by using Dr Blade’s technique. The substrates were then annealed for 350°C for 30 minutes. A transparent substrate will be obtained after the annealing process.

2.4. Assemble of device
In the last step of fabrication for DSSC, the working electrodes that have been soaked in dye sensitizer for 24 hours were dried before it was assembled with the counter electrode. The working electrode and counter electrode were clipped together by using a clip at the end of the substrate. A few drops of electrolyte were dropped between the substrate until it was fully covered with the electrolyte. In this study, we were using iodine as our electrolyte. The complete device was tested by using a solar simulator machine, and the efficiency was obtained and calculated.

3. Results and discussion
For this section, the efficiency for Dye-Sensitized Solar Cell is discussed. To evaluate the DSSC, whether it is functioning well with the dye sensitizer or not, the efficiency of DSSC is calculated. The result for the efficiency is tabulated in Table 1. For this study, six samples with the different type of solvents used in the dye sensitizer were tested, and the experiment was repeated three times to get an average for each result and to determine which solvent was the best for it to be used for the future research.

The conversion efficiency of DSSC can be obtained by using the equation one stated below:

\[ \eta = \frac{J_{sc} \times V_{oc} \times FF \times 100\%}{Pin} \]  

(1)

where the \( J_{sc} \) is the short circuit current density, \( V_{oc} \) is the open-circuit voltage, \( FF \) is the fill factor and \( Pin \) is the intensity of incident light that is used in the experiment. \( J_{sc} \) and \( V_{oc} \) is the result that can be obtained during the experiment; meanwhile, for \( FF \), it is needed to be calculated by using equation two below:

\[ FF = \frac{V_{m} \times I_{m}}{V_{oc} \times J_{sc}} \]  

(2)
Figure 3 shows that the J-V curve of the anthocyanin group (Roselle) as dye sensitizer in three different types of solvents which are ethanol, methanol and mix of ethanol and methanol. It shows that the mix of solvent (ethanol and methanol) has the highest curve compared to the other two solvents. Methanol solvent is known for its highly toxic [26], and that is why the curve for methanol is stable and then dropped at the end of the graph as the lowest.

Figure 4 shows that the J-V curve of the chlorophyll group (Pandan) as dye sensitizer in three different types of solvent, which is ethanol, methanol and mix of ethanol and methanol. It shows that by using methanol as a solvent for chlorophyll (Pandan), it has the highest curve of current density compared to ethanol and mix of ethanol and methanol because methanol is more stable compared to the other two solvents.

Table 1 Efficiency of DSSC by using a different type of solvent

| Device             | Voc (V) | Jsc(mA/cm²) | Fill Factor (FF) | Efficiency, $\eta$ (%) |
|--------------------|---------|-------------|------------------|------------------------|
| Roselle (Anthocyanin) |         |             |                  |                        |
| Ethanol            | 0.451   | 0.0042      | 0.170            | 0.0003                 |
| Methanol           | 0.419   | 0.0057      | 0.240            | 0.0005                 |
Table 1 shows the photovoltaic test (efficiency) of DSSC by using anthocyanin (Roselle) and chlorophyll (Pandan). As in the table, there are three samples each for two groups of dye sensitizer by using a different solvent. The photovoltaic parameters like open-circuit voltage ($V_{oc}$), short circuit current ($J_{sc}$), fill factor (FF) and the conversion efficiency of DSSC, $\eta$ (%) are listed in Table 1.

Based on Table 1, the highest efficiency obtained by using methanol as a solvent in the dilution for anthocyanin is 0.0005% with the $V_{oc}$ of 0.419V, $J_{sc}$ of 0.0057mA/cm$^2$ and FF is 0.240. Meanwhile, the ethanol gives the efficiency by 0.0003% with the $V_{oc}$ of 0.451V, $J_{sc}$ of 0.0042mA/cm$^2$ and FF is 0.170. Eli et al., investigated the natural dye sensitizer by using Roselle flower, and the efficiency obtained is 0.022% [27]. Besides, Adamu et al. investigated the effect of annealing temperature for DSSC using the anthocyanin group ($Hibiscus Sabdariffa$) flower. It gave the efficiency of 0.0005% at the annealing temperature of 450°C [28] while Danladi et al. investigated the characterization of DSSC based on natural pigment by using anthocyanin group ($Hibiscus Sabdariffa$) with the efficiency obtained is 0.0067% [29]. Adamu et al. also investigated the effect of degradation for $Hibiscus Sabdariffa$ DSSC with the efficiency obtained is 0.0000023% [30]. The huge difference between the experiment result and the reference result is due to the short time during the soaking process for working electrode in the dye sensitizer as the reference results stated that they soaked the working electrode for 24 hours [27] whereas we soaked it for only 30 minutes and due to the short time during the soaking process, less photon can be trapped from the sunlight by the dye sensitizer. Less electron was injected to the conduction band of TiO$_2$ meanwhile the longer time of soaking for the working electrode, more photon can be trapped, and more electron can be injected to the conduction band of TiO$_2$ that lead to higher efficiency for DSSC. Yongcharree et al. reported that anthocyanin groups are more soluble in ethanol due to the aggregation of the dye molecule are less expected [31], and due to that, the efficiency of DSSC using ethanol solvent is less than methanol.

For chlorophyll dye extracted from the Pandan leaf, the highest efficiency obtained is by using a mix of ethanol and methanol as the solvent for dilution with the efficiency of 0.00014% followed by methanol solvent with the efficiency of 0.0001%. Mahmoud et al., investigated the DSSC by using chlorophyll dye extracted from Pandan leaf and give the efficiency of 0.1% [32] meanwhile Huda et al. also investigated the usage of chlorophyll (Pandan) dye in DSSC and it provides the efficiency of 0.0006% [33]. The reference result is higher than the experimental result as the soaking time for the working electrode in dye sensitizer is 24 hours meanwhile the soaking time in this experimental is only 30 minutes that affect the number of the electron in the conduction band of TiO$_2$.

4. Conclusion

In this paper, the dyes extracted from the anthocyanin group ($Hibiscus Sabdariffa$) and chlorophyll group ($Pandanus amaryllifolius$) are demonstrated. By using ethanol, methanol and mix of ethanol and methanol as a solvent to dilute the dyes, it gives two highest efficiencies from both that is 0.0005% by using methanol as a solvent for anthocyanin ($Hibiscus Sabdariffa$) and 0.00014% by using a mix of methanol and ethanol as solvent chlorophyll ($Pandanus amaryllifolius$) respectively. Both of the results show that the methanol yielded the best efficiency if it was used as it is more stable [32] and have a
lower boiling point which helps in slowing the evaporation of the solvent as the solvent is known as the one which evaporates fast.

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