The Effects of the Concentration of Red and Yellow Gambier Fruit Dyes on the Short-Circuit Photocurrent in Dye-Sensitised Solar Cells

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Abstract. Natural dyes still have low efficiency, although there are good opportunities to apply them in dye-sensitised solar cells (DSSCs). In this research, the working-electrode was prepared from indium tin oxide (ITO) and titanium oxide (TiO\textsubscript{2}), using the doctor blade method for doping TiO\textsubscript{2} on ITO glass. Then, the working-electrode was soaked in gambier extract for 24 hours. The counter-electrode and electrolyte were made from burning a candle and mixing KI + I\textsubscript{2}, respectively. UV-vis and FTIR spectra have been made to investigate the effect of the concentration of red and yellow gambier prepared by maceration and evaporation from methanol. They were used to analyse absorbances and compounds in gambier, respectively. From UV-vis and FTIR spectra results, we obtained that the organic dyes from the red and yellow gambier fruits could have a high potential to be used as a sensitisier to absorb photons in DSSCs. From the $I\!-\!V$ measurement, we found that the efficiency tends to increase as the concentration increases. It indicates that the concentration of natural dyes could increase the performance of DSSC. Furthermore, an efficiency of 3.248\% was found to be achievable for DSSCs from a 70\% concentration of yellow gambier fruit dye.

1. Introduction

At present, most electrical energy comes from fossil fuels, including non-renewable and limited resources such as gas, coal, and oil. These cause pollution, climate change and global warming [1]. Consequently, renewable and sustainable energy resources such as solar cells, which make use of sunlight, the most abundant resource, are badly needed [2-3]. Dye-sensitised solar cells (DSSCs) were first introduced by O’Regan and Grätzel and have potential-promising low-cost and eco-friendly production, easy-to-get raw materials, and easy fabrication [4-6]. DSSCs have three important components: the working electrode, the counter electrode and the electrolyte. Simply put, a semiconductor material is coated on a conducting glass and immersed in dye as a sensitisier, and the device is completed with a platinum counter electrode and I/I\textsubscript{3} as the electrolyte. The current is produced from photons absorbed by the molecules of the dyes, supplying energy to electrons injected into the conduction band of the semiconductor materials. Then, the dye must be produced by electron transfer from the electrolyte and continue to the counter electrode [7].

In DSSCs, the dye plays an important role in absorbing photons, and commonly, two types of dye have been used, such as the dyes N179 [8], N719 [9-10]. These have achieved high efficiency (13\%) [11], but are unfortunately expensive. Recently, researchers have developed natural dyes from wood,
leaves, fruits and flowers containing pigments such as anthocyanins, carotenoids, flavonoids and tannins [5,12-13], which are abundant and inexpensive resources. Nasyori et al. used anthocyanins from caesalpinia sappan linn wood [14], imperata cylindrica [15], sappan wood, noni leaves, safflower, black rice [16], rosella, blue pea flower [17], pawpaw leaf, flame tree flower [18] and mango [19]. However, the low efficiency is still a challenge. One method used to overcome this challenge is to dope materials and modify the concentration to improve the performance of DSSCs.

In this study, we applied a new natural dye from red and yellow gambier fruits extract which has rarely been used as a sensitisier in DSSC research. We found that it worked well as a sensitisier and investigated the effect of the concentration in improving the performance of DSSCs.

2. Materials and Methods

2.1. Materials
The ITO (indium tin oxide) was purchased from Latech Scientific (Singapore) with the specification of 7–10 Ω/sq and 20 × 20 × 7 mm; TiO₂ (99%, 5-10 nm) from Titanos (Shanghai); yellow and red gambier fruit from West Sumatra (Indonesia); methanol (99%), KI and I₂ (99%, solid, ROFA), candle.

2.2. Extraction of natural dyes
The dye was prepared from yellow and red gambier fruit. The samples were rinsed for 5 minutes in aquabidest and dried at room temperature for 2 h. The samples were divided into 200 g aliquots and macerated in 300 ml of methanol for 24 h. Then the samples were evaporated for 3 h and left at room temperature 2 h. Finally, the concentrations of the original dyes were prepared in methanol of 30, 50 and 70% and measured by Agilent 8453 UV-visible spectrophotometer and Shimadzu IR prestige-21 FTIR spectrophotometer.

2.3. Fabrications of DSSCs
First, to make a working electrode, 0.5 g of TiO₂ and 0.8 ml methanol were prepared and mixed. Meanwhile, ITO glass was prepared, its resistivity was measured, and it was washed in methanol in an ultrasonic cleaner for 480 seconds. The TiO₂-methanol mixture was doped on the ITO-positive surface by the doctor blade method in a 1 cm² area on the ITO glass. It was then sintered in an oven in air at 200 ℃ for 1.5 h. Finally, the TiO₂ film was immersed in the previously-prepared dye concentrations for 24 h.

For the counter electrode, ITO glass was prepared, the resistivity was measured, and it was washed with methanol in an ultrasonic cleaner for 480 seconds. Then, the positive area of the ITO was burned with the candle, and a 1 cm² area was made on the ITO glass.

Finally, to make the electrolyte, 5 g of solid KI and 0.5 g of I₂ were prepared and mixed with Aquabidest distilled water in the ultrasonic cleaner three times for 480 seconds each.

2.4. Measurement of current and voltage
The working electrode and counter electrode were assembled into a sandwich, and doped electrolyte was placed in both electrodes. The work was carried out in full sunlight on the West Sumatra at 10.30 – 12.00 (GMT+7) using a potentiometer (10k) and a light meter to measure input power. Current and voltage measurement setups are shown in Figure 1.
3. Results and discussions

3.1. The absorption spectra of dye concentrations

Before the dye of gambier fruits extract was used in the working electrode, it was characterised. The first identification of the absorbance wavelength of red and yellow gambier fruits has been made by UV-Vis spectroscopy between 200 – 850 nm.

![Figure 2. Measurement of red and yellow gambier fruits extract by UV-Vis spectroscopy](image)

Dye concentrations of 30, 50, and 70% were measured. Figure 2 indicates that higher absorbance occurs in red gambier extract dye at 30% concentration, and additionally, in the wavelength of 250–300 nm, the dyes peak with absorbances 0.462, 0.358, 0.571, 0.746, 0.992, and 0.378. Then, the main peaks of the gambier fruits extract appear at in the wavelength range 431 – 655 nm for red gambier and 359 – 707 nm for yellow gambier. The works explain that the organic dyes from the red and yellow gambier fruits have a high potential to be used as a sensitisier to absorb photons.
3.2. FTIR
The content and functional groups of the extract of red and yellow gambier fruits were analysed using FTIR spectroscopy (Figure 3). Figure 3 shows that the peak locations are similar wavenumbers, but the transmittance is different for red and yellow gambier fruits extract. The results of peak wavenumber are shown in Table 1.

| Sample            | Wavenumber cm⁻¹ | Band   | References |
|-------------------|------------------|--------|------------|
| Yellow gambier     |                  |        |            |
| extract            | 3350.36          | O-H    | [20]       |
|                   | 2926.01          | C-H    | [20]       |
|                   | 1608.63; 1517.96; 1465.9 | C-C | [20]       |
|                   | 1369.46; 1282.66; 1195.87; 1141.86; 1101.35; 1045.42 | C-O | [20]       |
|                   | 2926.01          | -CH₂   | [21]       |
|                   | 1282.66          | -CO₂   | [21]       |
|                   | 1371             | -CH₃   | [21]       |
| Red gambier        |                  |        |            |
| extract            | 3369.64          | O-H    | [20]       |
|                   | 2926.01          | C-H    | [20]       |
|                   | 1608.63, 1521.84, 1450.47 | C-C | [20]       |
|                   | 1365.6; 1262.66; 1240.23; 1141.86; 1103.28; 1045.42 | C-O | [20]       |
|                   | 1365.6           | -CH₃   | [21]       |
|                   | 1262.66; 1240.23 | -CO₂   | [21]       |

It is evident that the content of gambier extract is tannins [22] and flavonoids [23] included in the dye compound and can act as a sensitisier in DSSCs [5].

Figure 3. FTIR spectra of red and yellow gambier fruits extract

3.3. Current and Voltage of DSSCs
The measurement of current and voltage was undertaken under sun illumination to analyse the ability of the DSSC to convert solar energy to electrical energy. Figure 1 shows a DSSC consisting of a working electrode which was immersed in red and yellow gambier fruit extracts of varying concentrations for 24 h with an ITO area of 1 cm², a counter electrode coated by candle and a KI/I₂ electrolyte. A light meter
was used to detect the input current and \( I-V \), \( FF \), the fill factor, and the efficiency, \( \eta \), were calculated using the Equations (1) and (2).

\[
FF = \frac{V_{\text{max}} J_{\text{max}}}{V_{\text{oc}} J_{\text{sc}}},
\]

\[
\eta = \frac{J_{\text{sc}} \times V_{\text{oc}} \times FF}{P_{\text{in}}} \times 100\%,
\]

where \( J_{\text{max}} \) and \( V_{\text{max}} \) are the maximum current (mA cm\(^{-2}\)) and voltage (V), \( J_{\text{sc}} \) and \( V_{\text{oc}} \) are the highest current (mA cm\(^{-2}\)) and voltage (V), \( FF \), \( P_{\text{out}} \) and \( P_{\text{in}} \) are input and output of power (mW cm\(^{-2}\)), and \( \eta \) is the efficiency.

**Table 2.** Performance of DSSCs made with the natural dye from red and yellow gambier fruit extract

| Sample            | Concentration | \( J_{\text{max}} \) mA cm\(^{-2}\) | \( V_{\text{max}} \) volt | \( J_{\text{sc}} \) mA cm\(^{-2}\) | \( V_{\text{oc}} \) volt | \( FF \) | \( P_{\text{in}} \) mW cm\(^{-2}\) | \%   |
|-------------------|---------------|-------------------------------------|-----------------------------|-----------------------------------|------------------------|--------|-----------------------------|------|
| Yellow Gambier     | 30            | 0.576                               | 0.373                       | 1.009                             | 0.649                  | 0.334  | 9.593                       | 2.280|
|                   | 50            | 0.447                               | 0.35                        | 0.834                             | 0.622                  | 0.210  | 9.593                       | 1.134|
|                   | 70            | 1.064                               | 0.236                       | 1.114                             | 0.649                  | 0.431  | 9.593                       | 3.248|
| Red Gambier       | 30            | 0.158                               | 0.757                       | 0.76                              | 0.442                  | 0.206  | 9.593                       | 0.720|
|                   | 50            | 0.258                               | 0.232                       | 0.488                             | 0.47                   | 0.062  | 9.593                       | 0.149|
|                   | 70            | 0.359                               | 0.223                       | 0.692                             | 0.1242                 | 0.446  | 9.593                       | 0.400|

Table 2 and Figure 4 show the performance of the DSSCs at different concentrations of the natural dye. Table 2 shows the \( I-V \) curves obtained from red and yellow gambier fruits dyes. Calculations show the highest efficiency value is produced by yellow gambier fruits extract with a dye concentration 70%, where \( J_{\text{sc}} = 1.064 \) mA cm\(^{-2}\), \( J_{\text{max}} = 1.114 \) mA cm\(^{-2}\), \( V_{\text{oc}} = 0.649 \) V, \( V_{\text{max}} = 0.236 \) V, \( FF = 0.431 \) and \( \eta = 3.2\% \) and the lowest efficiency value is \( \eta = 0.149 \% \) (with \( J_{\text{sc}} = 0.0488 \) mA cm\(^{-2}\), \( J_{\text{max}} = 0.258 \) mA cm\(^{-2}\), \( V_{\text{oc}} = 0.47 \) V and \( V_{\text{max}} = 0.223 \) V) from the 30% concentration of the red gambier fruit extract. The concentration in the dye is a key factor in improving the performance of DSSCs. Consequently, the more photons are absorbed by dye there are, the more electrons will flow.
Figure 4. I-V curves of DSSCs (A) red gambier fruit and (B) yellow gambier fruit

Figure 4 depicts the effects of modifying the concentration of dyes from red and yellow gambier fruits on the current and voltage curve of DSSCs. The highest efficiency of the extract of red and yellow gambier fruits was obtained 70% and 30%, respectively (Table 2). This research indicates that the concentration of the natural dye used as a sensitizer is the best method to improve the performance of DSSCs because, so far, the efficiencies of natural dyes obtained are still low (Table 3):

| Dye                             | Reference |
|---------------------------------|-----------|
| Caesalpinia Sappan Linn         | [14]      |
| Imperata cylindrica             | [15]      |
| Sappan Wood                     | [16]      |
| Noni Leaf                       |           |
| Safflower                       | 0.00007   |
| Black Rice                      | 0.0001    |
| Rosella                         | 0.37      |
| Blue pea flower                 | 0.15      |
| Pawpaw Leaf                     | 0.2       |
| Flame Tree Flower               | 0.2       |
| Mango                           | 0.43      |

4. Conclusion

In this research, we applied the new natural dye from red and yellow gambier extracts as a sensitizer in DSSCs and investigated the effect of the dye concentration on efficiency. From experimental measurements of UV-vis and FTIR spectra, we found that the organic dyes from the red and yellow gambier fruits could have a high potential to be used as a sensitizer to absorb photons in DSSCs. In addition, we found that the efficiency tends to increase with the concentration. It suggests that the concentration of natural dyes could enhance the performance of DSSC significantly. Furthermore, by optimizing the concentration of red and yellow gambier an efficiency of 3.248% was achieved at a 70% concentration of yellow gambier fruit dye.
5. References
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Acknowledgement
This research was financially supported by “Riset Desentralisasi PDUPT” research grant from Ministry of Research and Technology/National Agency for Research and Innovation, Indonesia, in the fiscal year of 2020