Concentrating yellow and red gambier fruit (Uncaria) in isopropyl alcohol to improve the performance of dye-sensitised solar cells

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Abstract. The organic dyes used in dye-sensitised solar cells (DSSCs) possess a low efficiency, leading to problems in the development of more efficient and cheaper DSSCs. In this work, we analysed the effect of the concentrations of organic dye from yellow and red gambier (Uncaria) fruits. The concentrations were prepared with isopropyl alcohol at concentrations of 30, 50 and 70%, respectively. Titanium oxide (TiO$_2$) is a semiconductor which was used in this work by utilising the method of the doctor blade, and indium tin oxide (ITO) was used as the conductive glass. The counter electrode and electrolyte were fabricated by burning candle and mixing KI + I$_2$, respectively. The characteristic spectra of UV-Vis and FTIR were used to analyse the gambier fruit. We obtained that the tannins from red and yellow gambier fruit extract are highly potential to apply as a sensitisier in DSSCs. Furthermore, the measurement of current and voltage was employed under sun irradiation. We obtained that the highest efficiencies were 0.819924 % and 1.747999 % for red and yellow extract, respectively. It indicates that the concentration of the organic dye could improve the performance of DSSCs.

1. Introduction

The source of electrical energy has become a paramount issue since most electrical energy is generated using limited fossil fuels such as coal, gas, and petroleum [1]. Consequently, renewable and sustainable energy resources are urgently needed. Recently, dye-sensitised solar cells (DSSCs) have attracted tremendous attention due to their low cost and eco-friendly production, readily available raw materials, and ease of fabrication [2, 3]. Commonly, DSSCs consist of three important items: a working electrode, a counter electrode and an electrolyte. Simply, a glass conductor is coated with a thin film of semiconductor material and immersed in a sensitisier dye, and the DSSC is completed with a platinum counter electrode and I$_2$/I$^-$ as the electrolyte. The current is produced from photons absorbed by dye molecules supplying energy to electrons injected into the conduction band of the semiconductor materials. Then the energy must be produced by electron transfer from the electrolyte and continued to the counter electrode [4]. Unfortunately, the low efficiency and stability of DSSCs still present a challenge for large-scale production and deployment.

To answer this challenge, researchers have studied numerous dyes and doped many materials. Several scientists have focused on using natural dyes to improve the performance of DSSCs, using plants such as Caesalpinia sappan Linn. wood [5, 6], the leaves and fruit of Mimosa pudica Linn [7], black rice, Pterocarpus indius Willd. leaves [8], and doping with Fe [9] and Cu [10]. Not only do the
dyes improve the performance of DSSCs, but also the semiconductor materials used are also important. TiO$_2$ and ZnO are the semiconductor materials typically used; they have small band gaps of 3.0 eV and 3.3 eV [11], respectively. The highest efficiencies reported in DSSCs to date are 12% and 13% [12, 13].

In this research, we have investigated a natural dye from the extracts of red and yellow gambier fruits which have rarely been studied; however, it has promising applications as a sensitizer in DSSCs. Our results show that the effect of the concentration of the sensitizer plays a crucial role in improving the performance of the DSSCs.

2. Method

2.1. Material preparations

Indium tin oxide (ITO) was purchased from Latech Scientific (Singapore) with the specification of 7–10 Ω/sq and 20×20×7 mm; TiO$_2$ (99%, 5–10 nm) from Titanos (Shanghai); yellow and red gambier fruit from West Sumatra (Indonesia); isopropyl alcohol (99%), KI and I$_2$ (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 distilled water and dried at room temperature for 2 h. The fruits were divided into 200 g aliquots and macerated in 300 ml of isopropyl alcohol for 24 h. Then the samples were evaporated for 3 h and left at room temperature for 2 h. Finally, concentrations of 30, 50 and 70% in isopropyl alcohol were prepared from the original dye.

2.3. Fabrication of DSSCs

First, 0.5 g of TiO$_2$ and 0.8 ml isopropyl alcohol were prepared and mixed to make a working electrode. Meanwhile, the ITO glass was prepared, its resistivity was measured, and it was washed in isopropyl alcohol in an ultrasonic cleaner for 480 seconds. The TiO$_2$-isopropyl alcohol mixture was doped on the ITO-positive surface using the doctor blade method in a 1 cm$^2$ area on the ITO glass. It was then sintered in an oven in air at 200 °C for 1.5 h. Finally, the TiO$_2$ film was immersed in the previously-prepared dye concentrations for 24 h.

For the counter electrode, the ITO glass was prepared, the resistivity was measured, and it was washed with isopropyl alcohol in an ultrasonic cleaner for 480 seconds. Then, the positive area of the ITO was burned with the candle, and a 1 cm$^2$ area was made on the ITO glass.

Finally, to make the electrolyte, 5 g of solid KI and 0.5 g of I$_2$ 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 the doped electrolyte was placed in both electrodes. The work was carried out in full sunlight in 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. FTIR Spectroscopy

After the red and yellow gambier fruit extracts were processed by maceration and evaporation, the gambier extracts were examined with a Shimadzu IRPrestige-21 FTIR spectrophotometer. The functional groups and content of the gambier extracts were characterised using their FTIR spectra. Figure 2 shows many peaks with different transmittances and wavenumbers. The key wavenumber regions of the gambier extracts are $1608.63 - 520.78 \text{ cm}^{-1}$ and $1608.63 - 459.06 \text{ cm}^{-1}$ for red and yellow fruits respectively. More detail about these peaks is given in Table 1.

Figure 1. (a) measurement of current and voltage, (b) structures of DSSCs

Figure 2. FTIR spectra of the red and yellow gambier fruit extracts
Table 1. Characteristic FTIR peaks of red and yellow gambier fruit extracts

| Sample          | Wavenumber cm⁻¹ | Band   | References |
|-----------------|-----------------|--------|------------|
| Red gambier     | 3371.57         | O–H    | [14]       |
| extract         | 2974.23; 2927.94| C–H    | [14, 15]   |
|                 | 1718.58         | C–O    | [14]       |
|                 | 1608.63; 1521.84| C–C    | [14]       |
|                 | 1195.87; 1141.86| C–O    | [14]       |
|                 | 1047.35         |        |            |
|                 | 1379.1          | -CH₃   | [15]       |
|                 | 1284.59         | -CO⁻   | [15]       |
| Yellow gambier  | 3385.07         | O–H    | [14]       |
| extract         | 2972.31; 2927.94| C–H    | [14, 15]   |
|                 | 1608.63; 1517.98| C–C    | [14]       |
|                 | 1143.79; 1118.71| C–O    | [14]       |
|                 | 1080.14; 1031.92|        |            |
|                 | 1379.1          | -CH₃   | [15]       |
|                 | 1286.52         | -CO⁻   | [15]       |

Table 1 shows the functional groups and content of red and yellow gambier fruit extract. It is evident that the tannin compound is dominant [16], followed by flavonoids [17], which are the compounds applied as a sensitiser in DSSCs [3].

3.2. The absorption spectrum of dye concentrations

The tannin extract was extracted from red and yellow gambier fruit using isopropyl alcohol and has been tested using an Agilent 8453 UV-visible spectrophotometer between 200 – 850 nm. The values of the absorbance and wavelength in Figure 3 from yellow and red gambier fruit were determined.

Figure 3. Measurement of red and yellow gambier fruit extracts by UV-Vis
Figure 3 shows that the 70% concentration of yellow gambier has the highest absorbance value. Additionally, at a wavelength of 280 nm, the dyes peak with absorbances 0.674, 0.555, and 0.516 for red and 0.311, 0.448, and 0.755 for yellow of gambier fruit extracts.

3.3. Measuring the current and voltage of DSSCs

Measurements of current and voltage have been made under direct solar illumination. A light meter was used to detect the input current. The \(I-V\) curve, the fill factor, \(FF\), and the efficiency, \(\eta\), were calculated using Equations (1) and (2).

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

Where \(J_{\text{max}}\) and \(V_{\text{max}}\) are the maximum currents (mA cm\(^{-2}\)) and voltages (V), \(J_{\text{sc}}\) and \(V_{\text{oc}}\) are the highest currents (mA cm\(^{-2}\)) and voltages (V), and \(P_{\text{in}}\) and \(P_{\text{out}}\) are the input and output powers (mW cm\(^{-2}\)), respectively.

Table 2. Performance of DSSCs made with natural dyes from red and yellow gambier fruit extracts

| 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            | 0.414                            | 0.163                    | 0.552                            | 0.267                    | 0.4579 | 9.52                          | 0.708842|
|                | 50            | 0.413                            | 0.189                    | 0.623                            | 0.443                    | 0.2828 | 9.52                          | 0.819924|
|                | 70            | 0.457                            | 0.157                    | 0.609                            | 0.342                    | 0.3445 | 9.52                          | 0.753664|
| Red Gambier    | 30            | 0.645                            | 0.258                    | 0.984                            | 0.523                    | 0.3234 | 9.52                          | 1.747999|
|                | 50            | 0.764                            | 0.208                    | 1.12                             | 0.349                    | 0.4065 | 9.52                          | 1.669238|
|                | 70            | 0.621                            | 0.255                    | 1.028                            | 0.349                    | 0.4414 | 9.52                          | 1.663388|

Table 2 and Figure 4 show the current and voltage of the DSSCs made with different concentrations of red and yellow gambier fruit extract. Table 2 depicts the current and voltage values obtained. These calculations show that the highest efficiency value is obtained by red gambier fruit extract with a dye concentration of 30%, where \(J_{\text{sc}} = 0.984\) mA cm\(^{-2}\), \(J_{\text{max}} = 0.645\) mA cm\(^{-2}\), \(V_{\text{oc}} = 0.523\) V, \(V_{\text{max}} = 0.258\) V, \(FF = 0.3234\) and \(\eta = 1.748\%\) and the lowest efficiency value is \(\eta = 0.7088\%\) (with \(J_{\text{sc}} = 0.552\) mA cm\(^{-2}\), \(J_{\text{max}} = 0.414\) mA cm\(^{-2}\), \(V_{\text{oc}} = 0.267\) V and \(V_{\text{max}} = 0.163\) V) from the 30% concentration of the yellow gambier fruit extract. The dye plays a key role by absorbing photons because the number of absorbed photons is linear with the current and voltage generated. In other words, the more photons absorbed by the dye, the more electrons will flow.
Figure 4. $I-V$ curves of DSSCs (A) yellow gambier fruit and (B) red gambier fruit

Figure 4 shows the $I-V$ curves obtained from different concentrations of red and yellow gambier fruit extracts in isopropyl alcohol. The highest efficiencies obtained were 1.747999% and 0.819924%, from 30% red and 50% yellow gambier extracts respectively (Table 2). This work has been successfully performed and indicated that the effect of the concentration of natural dye is crucial to improve the performance DSSCs, because all efficiencies are still low (Table 3).
Table 3. The efficiency of DSSCs based on organic dye

| Dye                                      | %            | Reference |
|------------------------------------------|--------------|-----------|
| Caesalpinia sappan Linn.                 | 0.196629     | [5]       |
| Caesalpinia sappan Linn.                 | 0.04108      | [6]       |
| Flower of Mimosa pudica Linn.            | 0.16         | [7]       |
| Leaf of Mimosa pudica Linn.              | 0.12         |           |
| Leaf of Pterocarpus indicus Willd.       | 0.035084     | [8]       |
| Oriza sativa glutinosa                   | 0.148        | [9]       |
| Oriza sativa Linn.                       | 0.0846       | [10]      |

4. Conclusion
In this work, we investigated a new natural dye from tannin extracts of red and yellow gambier fruits and measured the effect of changing the concentration in isopropyl alcohol of the sensitisers in DSSCs. From UV-Vis measurements and FTIR spectra, the red and yellow gambier fruit extracts have been determined to have a high potential for successful use as sensitisers in DSSCs. Additionally, we found that the highest efficiency is 1.747999% from the red gambier fruit extract at 30% concentration, and it is evident that this concentration of natural dyes could significantly enhance the performance of DSSC.

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