Photovoltaic performances and lifetime analysis of TiO2/rGO DSSCs sensitized with Roselle and N719 dyes

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Abstract. Two titanium dioxide/reduced graphene oxide (TiO2/rGO) based dye-sensitized solar cells (DSSCs) were fabricated and separately sensitized with natural dye extracted from Roselle flowers and ruthenium-based dye of N719. The current-voltage (I-V) performances were measured using Visiontec Solar I-V tester at standard illumination of AM1.5 and irradiance level of 100 mW/cm². The lifetime of the TiO2/rGO based DSSCs were furtherly investigated by measuring the I-V performances of the cells on the 5th day and 15th day. The highest power conversion efficiency (PCE) of 1.233 % was measured for the photoanode sensitized with N719 dye on the 15th day. The PCE of Roselle dye dropped from 0.992 % on the 5th day to 0.897 % on the 15th day. Dye degradation and low electron injection have influenced the unstable photovoltaic performances of Roselle dye even with the presence of electron conducting path provided by the rGO particles.

1. Introduction
Nowadays, the primary sources of fossil fuels generate greenhouse gases which mostly carbon dioxide. Further implication of this includes environmental pollution and global temperature warming [1]. On the other hand, dye-sensitized solar cells (DSSCs) are the ideal type of solar power source to generate electrical power. The fabrication of them involve environmentally friendly process, simple fabrication work, low cost and relatively high efficiency [2, 3]. The main component of DSSCs is the dye that is capable to produce electrons. However, the usages of ruthenium complex dyes are not suitable for environmentally friendly concept of DSSC. Although the ruthenium dyes help in delivering high power conversion efficiencies of the DSSCs, they are also reported as expensive compound, hazardous and highly volatile [1, 4]. Moreover, the demand to use natural dyes which are non-toxic and cost-effective dyes need to be considered. The sources are cheaper, easy to get in abundance and workable in the third-generation solar cells. On the other hand, many reports have been published on using the natural dyes extracted from leaves, fruits, flowers and roots in the fabrication work of DSSCs [2]. For example, Al-Alwani et al. (2018) extracted Alternanthera dentata leaves and Musa acuminata bracts as sensitizers and obtained power conversion efficiency (PCE) of 0.15 % and 0.31 %, respectively [5]. Li et al. (2013), employed red cabbage as a natural dye and achieved PCE of 2.908 % for 24 h immersion time [6].
Although the PCE generated by the natural dyes is less than the DSSCs sensitized with metal-based complex dyes, the usage of it is promising and still have a room to be improved. For example, the photoanode part can be modified by adding a graphene-based material such as reduced graphene oxide (rGO) to improve the electron transport in DSSCs [7]. Ghann et al. (2019) reported that graphene materials added into TiO\textsubscript{2} paste provides a porous photoanode film and therefore increase the DSSC’s efficiency due to higher dye loading and increased photon absorption level [8]. Moreover, Ramamoorthy et al. (2017) claimed that rGO attached to the TiO\textsubscript{2} surface layer provides an electron transport channel which could prevent from recombination inside the cell [9].

In the present work, two TiO\textsubscript{2}/rGO based DSSCs were fabricated and separately sensitized with natural dye of Roselle flowers and synthetic dye of N719. Their photovoltaic performances were analyzed as per their photovoltaic parameters, current-voltage (I-V) and power-voltage (P-V) curves. Thus, the photovoltaic properties of short-circuit current density, $J_{sc}$, open-circuit voltage, $V_{oc}$, fill-factor, FF, power conversion efficiency, PCE (or $\eta$) and maximum power, $P_{max}$ of the DSSCs were furtherly measured on 5\textsuperscript{th} day and 15\textsuperscript{th} day to analyze the lifetime and stability of the cells.

2. Experimental Work

2.1. Materials
Titanium (IV) oxide nanopowder, Ethanol, acetone, poly(ethylene)glycol-block (PEG), Triton X-100 and rGO were purchased from Sigma-Aldrich Corporation. Fluorine-doped tin oxide (FTO) coated glasses (resistivity ~25Ω/sq) were purchased from Ossila (Sheffield, United Kingdom). N719 ruthenium powder, liquid electrolyte of MPN100 and platinum (Pt) paste were purchased from Solaronix SA (Aubonne, Switzerland). Roselle flowers were obtained from Malacca, Malaysia.

2.2. Preparation of Roselle Natural Dye
Roselle petals were washed with water and dried. 6 g of cleaned petals were crushed using mortar and pestle. The paste was mixed in the solution of 20 ml deionized (DI) water and 6 ml ethanol. The mixture was stirred on hotplate at 40 °C for 24 h. The red color solution was filtered through Whatman No. 43 paper to obtain an anthocyanin source. Then, the dye solution was wrapped with an aluminium foil to prevent from light and kept inside the refrigerator. Figure 1 shows the process to extract the Roselle dye.

![Figure 1. Natural dye extraction from Roselle flowers.](image)
2.3. Preparation of N719 Ruthenium Dye
17.83 mg of Ruthenizer powder was dissolved in 50 ml absolute ethanol to get 0.3 mM ethanolic solution of N719 dye. The mixture was dissolved in the glass bottle and wrapped with aluminium foil to prevent exposure from any light sources. The solution was then ultrasonicated for 30 min to fully dissolve the traces of Ru-powder. The solution was kept for 24 h in the dark cabinet before use.

2.4. Preparation of TiO$_2$/rGO Photoanodes
6 g of TiO$_2$ nanopowder was dissolved in deionized (DI) water followed by acetone and PEG. The solution was vigorously stirred on the hot plate at 60 °C for 24 h. Then, 0.1 ml of Triton X-100 were added to the mixture to improve the TiO$_2$ films adhesion on the glass substrate. The sonicated and dried of 2 mg rGO were added in the prepared TiO$_2$ paste. The paste was vigorously stirred for 24 h to obtain a gel-like solution. The obtained TiO$_2$/rGO paste were deposited on the conductive side of the cleaned FTO substrates by a doctor blade technique. The photoanodes area of 0.35 cm$^2$ were dried at room temperature for 5 min before annealed at 400 °C for 30 min in oven. After the photoanodes were cooled down to room temperature, they were separately sensitzed in the Roselle and N719 dyes for 24 h. Longer immersion time is to ensure the dyes were fully adsorbed throughout the TiO$_2$/rGO mesoporous layer. After 24 h, any excess dye on the photoanodes were cleaned with ethanol.

2.5. Fabrication of TiO$_2$/rGO based DSSC
For construction of complete DSSCs, the counter electrodes were platinized with semi-transparent platinum (Pt) paste onto the cleaned FTO substrates. The substrates were then annealed at 400 °C for 1 h in the oven. The dye-covered TiO$_2$/rGO photoanode and Pt counter electrode were assembled into a sandwich structure cell with a parafilm spacer attached in between them. Two small paper clamps were used to clamp the cell. After injection of the liquid electrolyte at the small hole of the spacer, the cell was sealed with the parafilm spacer.

2.6. I-V Measurement of TiO$_2$/rGO based DSSC
The current-voltage (I-V) parameters of the TiO$_2$/rGO based DSSCs were measured by IV Tester System (VS-6820, IVT Solar) at AM1.5 condition and under 100 mW/cm$^2$ solar light generated from Xenon arc lamp (XES Series Class AAA solar simulator, XES-1600SE-200S). After the I-V measurements, the DSSC’s power conversion efficiency were calculated by the following equations [10]:

$$\eta = \frac{V_{oc} \cdot J_{sc} \cdot FF \times 100\%}{P_{in}}$$

where $P_{in}$ is the radiation power incident on the cell, $J_{sc}$ is short-circuit current density at zero voltage, $V_{oc}$ is the open-circuit voltage at zero current density, $J_{m}$ is the maximum current density, $V_{m}$ is the maximum voltage and $FF$ is the fill factor.

In order to study the lifetime of the cells, the fabricated TiO$_2$/rGO-DSSCs based on Roselle and N719 dyes were kept in a dark container and at a room temperature. The I-V performances were measured on the 5$^{th}$ day and 15$^{th}$ day. Thus, the photovoltaic parameters were recorded for further analysis and comparison.

3. Results and Discussion

3.1. Photovoltaic Performances on the 1$^{st}$ Day
Table 1 shows the photovoltaic performances of TiO$_2$/rGO photoanode sensitized with Roselle and N719 dyes. The performances on the 1$^{st}$ day were also illustrated by J-V and P-V curves as shown in
Figure 2. It is observed that TiO$_2$/rGO based DSSC of Roselle dye achieved PCE of 0.779 % higher than the photoanode sensitized with N719 dye (PCE = 0.338 %).

Moreover, the percentage difference in $V_{oc}$ values between the two dyes are not significant which only 17.24 %. The other photovoltaic parameters that influence this increment include $J_{sc}$ and $FF$. Higher $J_{sc}$ is due to good electron transfer mechanism inside the cell. Wongcharee et al. (2007) reported that higher interaction between TiO$_2$ molecules and anthocyanin leads to a better electron mechanism due to shorter distance between dye skeleton of cyanidin and delphinidin and the juncture connected to the TiO$_2$ surface [11]. This factor is also supported by an excellent electrical conductivity of rGO that increase the amount of electron transfer from the anthocyanin molecules to the conduction band of TiO$_2$ [9, 12, 13]. Figure 3 shows chemical structures of cyanidin and delphinidin in the Roselle dye [11].

| Dye       | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (V) | $FF$ (%) | PCE (%) | $P_{max}$ (mW/cm$^2$) |
|-----------|-----------------------|--------------|----------|---------|----------------------|
| Roselle flower | 1.226                 | 0.794        | 80.0     | 0.779   | 0.779                |
| N719     | 0.951                 | 0.668        | 53.16    | 0.338   | 0.338                |

Figure 2. J-V and P-V curves of TiO$_2$/rGO photoanodes sensitized with (a) Roselle and (b) N719 dyes on the 1$^{st}$ day.

Figure 3. Chemical structures of cyanidin and delphinidin in the Roselle dye [11].

3.2. Photovoltaic Performance on the 5$^{th}$ day
In order to study the lifetime of the fabricated DSSCs, the I-V performance were measured again on the 5$^{th}$ day. Table 2 and Figure 4 show the photovoltaic performances and J-V and P-V curves of the TiO$_2$/rGO based DSSCs, respectively. It was observed that the efficiency of the photoanodes immersed
in the Roselle and N719 dyes are slightly higher compared to the results obtained on the first day of testing these solar cells. The percentage increase of PCE values were measured around 27.34 % and 60.95 % for Roselle and N719 dyes, respectively.

Moreover, the maximum power, \( P_{\text{max}} \) generated by the Roselle dye is almost 1 mW/cm\(^2\) compared to only 0.5 mW/cm\(^2\) for the N719 dye sample. On the other hand, a small percentage difference of 24.33 % on the \( J_{\text{sc}} \) values for Roselle and N719 dyes were measured. Bell et al. (2011) reported that the incorporation of rGO in the TiO\(_2\) paste extend the electron lifetime by a factor of four and generate the photogenerated current up to ten times [14]. These factors resulting in the increase of electron transfer rate and reduces electron recombination in the DSSC [12].

Table 2. Photovoltaic parameters of TiO\(_2\)/rGO based DSSC on the 5\( ^{th} \) day.

| Dye           | \( J_{\text{sc}} \) (mA/cm\(^2\)) | \( V_{\text{oc}} \) (V) | FF (%) | PCE (%) | \( P_{\text{max}} \) (mW/cm\(^2\)) |
|---------------|---------------------------------|----------------|--------|---------|-------------------------------|
| Roselle flower| 1.383                           | 0.837           | 85.71  | 0.992   | 0.992                         |
| N719          | 1.083                           | 1.009           | 49.80  | 0.544   | 0.544                         |

Figure 4. J-V and P-V curves of TiO\(_2\)/rGO photoanodes sensitized with (a) Roselle and (b) N719 dyes on the 5\( ^{th} \) day.

3.3. Photovoltaic Performance on the 15\( ^{th} \) day

The effect of incorporating of rGO in the TiO\(_2\) paste were further measured on the 15\( ^{th} \) day of their photovoltaic performance. The photovoltaic parameters and J-V and P-V curves are presented in Table 3 and Figure 5, respectively.

Table 3. Photovoltaic parameters of TiO\(_2\)/rGO based DSSC on the 15\( ^{th} \) day.

| Dye           | \( J_{\text{sc}} \) (mA/cm\(^2\)) | \( V_{\text{oc}} \) (V) | FF (%) | PCE (%) | \( P_{\text{max}} \) (mW/cm\(^2\)) |
|---------------|---------------------------------|----------------|--------|---------|-------------------------------|
| Roselle flower| 1.14                            | 0.87            | 90.46  | 0.897   | 0.897                         |
| N719          | 1.283                           | 1.25            | 76.90  | 1.233   | 1.233                         |
74x557 Figure 5. J-V and P-V curves of TiO$_2$/rGO photoanodes sensitized with (a) Roselle and (b) N719 dyes on the 15th day.

As time goes on, it was found that the $J_{sc}$ value of Roselle dye is slightly decreases to 1.14 mA/cm$^2$ compared to the value measured on the 5th day ($J_{sc} = 1.383$ mA/cm$^2$). The decreased in $J_{sc}$ value is due to high charge recombination event in the electrolyte at the TiO$_2$/dye interface [12]. Moreover, although the $FF$ value increases to 90 %, the PCE value decreases to 0.897 % after 14 days. The PCE percentage difference between the Roselle and N719 dyes were calculated around 31.55 % which is lesser than 58.33 % measured on the 5th day. Furthermore, the N719 dye sample shows tremendous PCE performance where the values increase from 0.544 % on the 5th day to 1.233 % on the 15th day. The percentage difference was calculated as large as 77.55 % between the values measured on the 15th and 5th day.

3.4. Photovoltaic Performances and Lifetime Comparison Between Roselle vs N719 Dyes

From the obtained photovoltaic performances in the previous sections, the results can be categorized for each of the photovoltaic parameters of $J_{sc}$, $V_{oc}$, $FF$ and PCE. Figure 6 shows the lifetime comparison between Roselle and N719 dyes for each of the parameters. It is observed that the values of $J_{sc}$, $V_{oc}$, and PCE for N719 are gradually increase even after 2 weeks or 336 hours. In contrast, the $FF$ value drops to 49.80 % on the 5th day before it increases back to 76.90 % on the 15th day. Higher fill factor signifies that the internal resistance inside the TiO$_2$/rGO photoanode sensitized with N719 is low. Ding et al. (2015) reported that good fill factor is referred to as having low total series resistance of the solar cell [15].

On the other hand, the photovoltaic parameters of TiO$_2$/rGO sensitized with Roselle dye were found as unstable. For example, the $J_{sc}$ and efficiency values were found increase on the 5th day but decrease on the 15th day. In general, the $J_{sc}$ parameter represents electron density in the conduction band (CB) of TiO$_2$ where it leads to higher electron population in the CB of FTO [9]. The increased of $J_{sc}$ could also be due to the increased of dye molecules that still retained in the cells even after so many days. Both phenomena indicate large amount of electron injection to the CB of TiO$_2$ that directly influences the overall power conversion efficiency [9]. Cheng et al. (2013) reported that increment of $J_{sc}$ is due to the enhancement of dye absorption amount in the photoanodes and high surface area of the photoanodes [16]. Nevertheless, the decreased of $J_{sc}$ values on the 15th day are due to low amount of electrons flow through the external circuit of the DSSC device. Another possibility includes electron recombination event by the tri-iodide ions at the TiO$_2$/dye interface where it degrades the photovoltaic performance of the cell [17].

Moreover, the $V_{oc}$ parameter for both dyes increase as the lifetime of the cells increased from day one to day fifteen although it is quite low for Roselle dye sample. $V_{oc}$ is an important parameter where it represents a difference between the conduction band (CB) of TiO$_2$ and the redox potential of electrolyte [9]. Furthermore, the presence of rGO also facilitates the photogenerated electrons in the CB
of TiO$_2$ to flow into the external circuit of DSSC where it provides as an electron conducting path that suppresses the recombination but increases the $J_{sc}$ values.

From this analysis, Roselle dye seems not stable yet in their lifetime due to dye degradation and low electron injection after 336 hours. Iqbal et al. (2019) reported that natural dyes demonstrate lower power conversion efficiencies than the ruthenium-based dyes due to the dye degradation [18]. Moreover, Tekerek et al. (2011) mentioned that weak binding energy of natural dye with the TiO$_2$ film and low charge-transfer absorption in the visible light range also degrade their photovoltaic performance [19].

![Figure 6](image1)

Figure 6. Each photovoltaic parameter of (a) $J_{sc}$ (b) $V_{oc}$ (c) FF and (d) $\eta$ versus number of days between Roselle and N719 dyes.

4. Conclusion

The anthocyanin extracted from *Hibiscus sabdariffa* L. (Roselle flowers) planted in Malacca, Malaysia was used as the natural dye for TiO$_2$/rGO based DSSCs. The photovoltaic performances and lifetime analysis of the cells were compared with the TiO$_2$/rGO photoanodes sensitized with synthetic N719 dye. The highest PCE values was achieved by the DSSC with N719 dye at 1.233 % on the 15$^{th}$ day. The PCE difference between the Roselle and N719 dyes were measured around 31.55 %. Each photovoltaic parameter of $J_{sc}$, $V_{oc}$, FF and PCE were evaluated to analyze the cell’s lifetime. After 2 weeks, the TiO$_2$/rGO DSSC sensitized with N719 dye showed improvement in the photovoltaic performances compared to the Roselle dye sample. The existence of rGO has retained the amount of dye adsorption and the photogenerated electrons flow in the TiO$_2$/rGO based DSSC. This research work requires further investigation on the structures, morphologies, optical, chemical and electrochemical impedance properties of TiO$_2$/rGO photoanodes.

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