Fabrication of Titanium Dioxide-reduced Graphene Oxide (TiO$_2$/rGO) nanocomposites as the Photoanode in Dye Sensitized Solar Cells

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Abstract. One of the photovoltaic cells generation promising for low-cost fabrication is dye-sensitized solar cell (DSSC). However, it has a drawback—low efficiency because of electron recombination occurrence and low transparency of photoanode. Graphene-based materials show the potential to overcome this problem. In this work, we have investigated the integration of reduced graphene oxide (rGO) into the titanium dioxide (TiO$_2$) photoanode in DSSC. A simple Hummer’s method has been used to synthesize graphene oxide flakes. The nanocomposite of rGO/TiO$_2$ has been formed by varying the percentage of rGO between 1% and 5%. The result shows that the percentage of rGO in nanocomposite affected device performance. The efficiency decreases along with the increase in rGO. The best result was obtained with 2 wt% addition of rGO into TiO$_2$ photoanode that resulted in 0.9 % efficiency.

1. Introduction
The search for new and renewable energy has been lasting for decades. Many resources have been developed where the energy is generated from wind, water, biofuel, and sunlight. The sunlight energy is converted into electricity using the device called photovoltaic or solar cells [1]. To date, there are three generations of solar cells where the third one is called dye-sensitized solar cell (DSSC) [2-3]. DSSC uses dye as a sensitizer to harvest sunlight’s energy and its creation was inspired by the working principle of photosynthesis [4]. Therefore, with its simplicity and low-cost fabrication route, this solar cell is considered as very potential as the new energy generation resource. However, it has some drawbacks due to the low efficiency and instability of its component. In 1991, the 7.1% photoconversion efficiency (PCE) was obtained by converted 80% photon energy into electrical current. The DSSC’s development lasted for many years until it reached PCE of about 14% in 2016 [3, 5-6].

Several efforts have been devoted to increase DSSC performance in terms of the efficiency and stability issues. The development in photoanode, counter electrode, dye, and electrolyte have been to find the optimum effect to increase the efficiency of DSSC. X. Liu et al. [7] used polystyrene-titanium paste as an active layer that resulted in 5.58% efficiency. The use of natural pigment as a dye to reduce cost production although the efficiency produced is still relatively low [3]. The use of organic material as a dispersant and conductive channel type have been used in many variations that resulted in the
highest efficiency of 10.29% [8]. However, the result is not sufficient heighto move DSSC into the commercial product.

One of the emerging materials for DSSC improvement is graphene, which is well known as two-dimensional form of graphite. It has very interesting characteristics, i.e. very high strength per mass unit [9] and high conductivity of 10^6 S/cm, so that it can be expected to contribute in improving the device performance [10]. It has been reported that the use of graphene for photoanode has successfully enhanced the fill factor but adversely reduced efficiency [11]. Graphene has also been used as a counter electrode with different forms through several processes of production, resulting in efficiency that raises from 0.5% to 7.7% [12].

The production of graphene varies from micromechanical, liquid-phase exfoliation, mechanical milling, electrochemical exfoliation and chemical exfoliation [9]. A well-known Hummer’s method is usually used to synthesize graphene oxide from graphite, followed by reduction to produce reduced graphene oxide (rGO) [13]. Motivated by the above consideration, in this work we have investigated the effect of rGO concentration in the nanocomposite photoanode on the DSSC device performance. The rGO concentration was varied as 0, 1, 2, 4 and 5 wt% within titanium oxide (TiO2) matrix as photoanode.

2. Method

2.1. Fabrication of reduced Graphene Oxide (rGO).

To start the synthesis of rGO, graphene oxide (GO) was derived from Hummer’s method [9, 13-15]. Briefly, 1 g graphite powder was mixed with 46 ml H2SO4 and 0.5 gram NaNO3 and further stirred at temperature of 35 °C for 2 minutes. The mixture was then subsequently stirred for 5 minutes in an ice bath until it reached 0 °C. Afterward, 3 g potassium permanganate (KMnO4) was added slowly and the temperature must be kept stable below 20 °C. The mixture was further stirred for 6 hours at 35 °C. Then, 3 gram KMnO4 was added again slowly and the temperature must be kept under 50 °C in order to avoid explosion. It was stirred again for 18 hours at 35 °C. The oxidation was stopped by adding slowly 150 ml distilled water that contained 6 ml solution of 30% H2O2, so the temperature must be below 80 °C. In this step, the residue of KMnO4 and MnO2 were reduced to Mn2+ and the color of the solution changed from black-brown to bright yellow, indicating that graphene oxide (GO) has been formed.

The bright yellow solution was poured out and separated by the centrifuge, prior to washing process by distilled water several times until neutral pH was reached. The solution was further filtered using vacuum pump filter to obtain the GO flakes residue. These flakes were dried at 90 °C temperature for 12 hours to result in dried graphene oxide. The graphene oxide was mixed with water to form a concentration of 1 mg/ml. The reduction is performed by mixing the GO solution with 1 ml hydrazine at 100 °C temperature for 12 hours. The reduced graphene oxide has been formed and finally dried for 24 hours.

2.2. Fabrication of TiO2-rGO nanocomposites.

To start with, TiO2 nanopowder (P25 Degussa) was dispersed in distilled water with weight ratio of 100:1. Then, it was stirred for 30 minutes to obtain a homogenous mixture. Further step for nanocomposite photoanode production was conducted by integrating the resulted rGO into TiO2 colloidal dispersion, adopting the procedure reported in the literature [16]. In this work, the concentration of rGO in TiO2 matrix was varied as 0, 1, 2, 4 and 5 wt%.

2.3. Fabrication of solar cell devices.

The photoanode deposition was prepared using the doctor blade method. In this step, 1 ml of TiO2-rGO nanocomposite colloid was put onto structured ITO glass. Subsequently, it was annealed on top of the hot plate for 1 hour at a 450 °C. After annealing, the nanocomposite layer was immersed to ruthenium (Rk1) dyes for 12 h. The counter electrode (CE) was prepared with Pt (Platisol) and also annealed at the same temperature. The photoanode was then assembled with the previously fabricated CE by binder.
clips. Finally, the electrolyte of iodine was injected to the gaps of photoanode and counter and the device was ready to be measured.

2.4. Measurement and characterization.
The rGO, TiO$_2$ and its nanocomposites samples were characterized by Fourier Transform Infra-red (FTIR) and Ultraviolet-Visible (UV-Vis) spectroscopies, x-ray diffraction (XRD) and scanning electron microscope (SEM). The DSSC device performance was investigated by IV curve measurement using a computer-controlled 100 mW/cm$^2$ illumination of the solar simulator with an AM1.5G filter.

3. Results and discussion

3.1. rGO formation.
The SEM images in Figures 1 (a-c) shows that the layer of graphene oxide has been formed as the result of the exfoliation process of graphite. It can be clearly seen that its appearance is similar to a sheet of wet tissue paper with area of about 40 $\mu$m$^2$.

![SEM images of resulted graphene oxide (GO) under magnification of: (a) 5000 X, (b) 10000 X, and (c) 25000 X.](image)

Figure 2 shows the FTIR spectra of graphite, graphene oxide and reduced graphene oxide. It is confirmed that the OH vibration shift from graphite appears between 3400-3600 cm$^{-1}$ for graphene oxide only. This is because the -OH group was produced from the oxidation, thus it does not exist in the original graphite and the resulted rGO. It indeed disappeared in rGO as a result of the reduction process of graphene oxide. This is in agreement with many reports [4,17-18].

Figure 3 is the results of XRD for graphite, graphene oxide and reduced graphene oxide. It can be observed that oxidation and reduction process has resulted in the shifting of 2$\theta$. The plane distance (d-spacing) of the first peak in the XRD can be used to investigate the whole process. [19]. The first peak of graphite can be found at 2$\theta$ of 20-30° with d-spacing of about 3.9 Å. In GO, the first peak was found at 2$\theta$ of 9-10° with the d-spacing was extended to 8.8 Å, as result of the graphite exfoliation. In rGO, the peak position was back to initial 2$\theta$ of 20-30° with d-spacing which was also compressed again to 3.6 Å. This phenomenon of d-spacing transformation agrees well with literature [20].

Figure 4(a) shows diffuse reflectance-ultraviolet visible (DRS-UV-Vis) spectroscopy results of graphite, GO and rGO. The absorbance edge of those sample was observed around 350 nm wavelength. The relevant Tauc plot to obtain band gap energy ($E_g$) is shown in Figure 4(b) resulting the value for graphite, GO and rGO of 4.42, 4.47, and 4.62 eV respectively. The bandgap become larger when it was oxidized and reduced.
3.2. TiO$_2$-rGO nanocomposite formation.

Figures 5(a-c) shows the SEM images of TiO$_2$-rGO nanocomposite with rGO loading of 4 wt% under different magnification. The presence of TiO$_2$ phase appeared as small-fine particles agglomerates embeded on the surface of rGO layers, which look like as bright tissue paper.

![Figure 2. FTIR spectra of graphite, GO and rGO.](image)

![Figure 3. XRD s of graphite, GO and rGO.](image)

![Figure 4. (a) UV-Vis spectra with DRS mode and (b) band gap estimation of graphite, GO and rGO are 4.47, 4.49 and 4.62 by Tauc plot.](image)

![Figure 5. SEM images of TiO$_2$-rGO nanocomposite with rGO loading of 4 wt% under different magnification of: (a) 500 X, (b) 10000 X, and (c) 50000 X.](image)
3.3. Device performance.
The J-V curve of DSSC fabricated using different TiO$_2$-rGO nanocomposites was shown in Figure 6. Figure 7 summarizes it as a function of increase rGO wt% to the efficiency of the device without rGO (standard DSSC). It can be observed that all devices rGO-based displayed decreased efficiencies adversely. It could happen due to the electron recombination as a consequence of a rather excessive rGO addition. However, the nanocomposite photoanode with a concentration of 2% show the highest efficiency among other rGO addition.

![Figure 6. J-V Curve for different nanocomposite.](image)

![Figure 7. Efficiency of DSSC for different rGO concentration.](image)

4. Conclusion
An attempt to incorporate the rGO into nanocomposite photoanode in the DSSC has been performed. The most optimum value of device performance based on rGO-TiO$_2$ nanocomposite was obtained by rGO loading of 2 wt %. An initial PCE efficiency of 0.9 % showed promising compared to other ratios, however, higher loading of rGO resulted in lower efficiency. It can be caused by ineffective electron transfer in photoanode of devices. On the basis of the current results, it can be suggested that the optimization of rGO for improvement of DSSC performance need to further investigated.

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