Effect of reduced graphene oxide addition on the performance of zinc oxide nanorod based dye-sensitized solar cell

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Abstract. As one of third generation photovoltaic device, dye-sensitized solar cell (DSSC) plays important part in search for new and renewable energy resources. As part of this device, dye has a very critical function due to its responsibility in absorbing the photon energy from the sunlight. The more light can be absorbed, the higher the value of photon to electricity conversion efficiency can be obtained. For increasing the absorption capacity of the dye, this work investigated the effect of reduced graphene oxide (rGO) addition into the dye solution with rGO to dye weight % ratio of 1:100; 3:100; and 5:100 respectively. On the basis of investigation, it was found that the ratio of 3:100 produced a higher power conversion efficiency (PCE) of about 0.02% as compared to the reference cells which displayed a value of 0.005%. It confirms that introducing rGO into the dye can enhance the DSSC performance, though several fabrication handling procedures still need to be improved as well.

1. Introduction
The dye-sensitized solar cell (DSSC) has become one of the most important generation photovoltaic cell since it has been initially found in 1991 by O’Regan and Graetzel [1]. DSSC consists of five components: (1) a transparent conductive oxides (TCO) which serves as electron conductor to dye; (2) an active semiconductor film/layer such as titanium dioxide (TiO₂) and zinc oxide (ZnO); (3) a dye sensitizer as the location of electron excitation when being exposed to the sunlight; (4) an electrolyte which functions as electron mediator between semiconductor photoanode with counter electrode, e.g. iodine; and (5) a counter electrode functioning as a cathode material to regenerate the redox shuttle, e.g. platinum (Pt) [2, 3].

ZnO has been used in DSSC with various morphologies [4], despite the fact that power conversion efficiencies (PCE) formed is relatively lower [2] compared to TiO₂-based cells. ZnO is a promising candidate to be used as semiconductor photoanode, owing to its higher electron mobility to TiO₂. Its value is about 200–300 cm² V s⁻¹ as bulk material and ~1000 cm² V s⁻¹ in the form of single crystal nanowire. By contrast, TiO₂ only provides roughly a value of 0.1–4 cm² V s⁻¹, and indeed this difference gives significant effects to the electron transport rate in the photoanode film [5-7].

Recently, graphene-based nanomaterials have been introduced into DSSC [3, 8-10]. Graphene has interesting characteristics where its crystal structure consists of two-dimensional honeycomb with large surface area [10, 11], high chemical stability and optical transmittance, as well as good electrical
conductivity [12, 13]. Graphene has been used with TiO$_2$ based DSSC, as means to obtain much higher sunlight absorption, and thus the resulted electrons to be captured from the dye molecules and subsequently donated to the external surface of the semiconductor film [14-16].

In this work, a similar approach was taken, however we utilized ZnO nanorod thin film as a compact layer for the photoanode and modified the dye through the addition of reduced graphene oxide (rGO). ZnO nanorod was fabricated by chemical bath deposition (CBD) method while rGO was obtained by chemically reducing graphene oxide (GO). The rGO was mixed into dye with a variation of the wt% ratio of rGO-dye: 1:100; 3:100; and 5:100 respectively. It is expected that rGO can improve DSSC device performance.

2. Experimental details

2.1. Fabrication of the Zinc Oxide (ZnO) nanorod

A ZnO thin film was fabricated on indium transparent oxide (ITO) glass substrate (2.5 cm x 2.5 cm) using the CBD method. Prior to fabrication, ITO glass was ultrasonically cleaned in acetone, alcohol, and aquades. Briefly, 1.3 g Zn(NO$_3$)$_2$·4H$_2$O/Zn-nitrate and 0.7 g C$_6$H$_{12}$N$_4$/HMTA were added into 100 mL aquades. The mixture solution was stirred under immersion in ice bath for 1 hour. Subsequently, the solution was dropped onto ITO glass and then being aged for 10 minutes. Afterward, it was rotated by spin coating technique at 2000 rpm for 20 seconds, and furthermore subjected to annealing process in oven at 200°C for 5 minutes. These steps were repeated three times to obtain a homogeneous thickness. Finally, the sample was annealed in oven 90°C for three hours. Figure 1 shows the schematic illustration of thin film fabrication procedures involving spin coating and CBD.

![Figure 1](image_url) (a) Spin coating process; (b) CBD.

2.2. Synthesis of Graphene Oxide (GO)

The synthesis process of GO in this work is based on Hummer’s method [17]. Briefly, 1 g solid of graphite was poured in the beaker glass, then 46 mL H$_2$SO$_4$ solution and 0.5 g NaNO$_3$ solid were mixed slowly and stirred at 350°C for 5-10 minutes. The mixture was continuously stirred in an ice bath until the temperature reached 0°C for 15-20 minutes. Moreover, 3 g KMnO$_4$ was added carefully to avoid the temperature raise not more than 20°C. Subsequently, the solution was further stirred continuously and held at a temperature of 35°C for 6 hours. As further step, 3 g KMnO$_4$ was added again step by step to the solution and continuously stirred at temperature of 350°C for 12 hours. As part of further procedure, 150 mL H$_2$O solution which has content of 6 ml of H$_2$O$_2$ was added slowly while keeping the temperature stable at 800°C and stirred roughly 10-15 minutes. Finally, the solution was filtered using Whatman filter paper and then dried in the oven at 80-900°C for 8 hours.
2.3. reduced Graphene Oxide (rGO)
To obtain reduced graphene oxide (rGO), the resulted graphite oxide (GO) powder from the above process was mixed with H₂O to obtain a concentration of 3 mg/ml. Then this dispersion solution was sonicated for 3 hours. Subsequently, 1uL hydrazine 80% was poured to the solution and stirred for 3 hours at 70°C until the color dispersion turns to black. Finally, to obtain rGO powder, the dispersion was dried for 8 hours at 90°C in the oven [18].

2.4. Fabrication of dye-sensitized solar cell (DSSC)
To start the device fabrication, the rGO solution was obtained by adding 0.076 g rGO into 52 mL aquades; then the dispersion was sonicated for 1 hour. On the other hand, the dye was prepared by addition of 0.1 g of ruthenium complex into 20 mL ethanol. Then this rGO solution was dropped into the dye solutions forming rGO: dye wt% ratio of 1:100, 3:100, and 5:100. Subsequently, the modified dyes were stirred approximately for 15 minutes. The resulted ZnO nanorod thin film from procedure 2.1 was then immersed in this modified dye solution and aged for 12 hours. The device based in sole dye was utilized as the reference. Platinum (Pt) was used as the counter electrode. It was done by dropping pt solution onto ITO glass and followed by doctor blade technique. The counter electrode and ZnO nanorod photoanode were assembled likely a sandwich model and clamped firmly together, and then an electrolyte solution (iodine, Solaronix) was dropped into the system and was left itself scatter in all area of glass.

3. Characterization
ZnO nanorod and rGO thin films were analyzed by using X-ray diffractometer (XRD), scanning electron microscope (SEM), and UV-vis spectrophotometer, while the current density versus voltage (J-V) producing IV-curve was measured by a computer-controlled 100 mW/cm² illumination of the solar simulator using an AM1.5G filter.

4. Results and discussion
Figure 2 shows the SEM image of ZnO nanorods where the hexagonal structures were clearly observed and the whole nanostructures showed dense and uniform coverage. Figures 3 (a) and (b) show SEM images of graphite and GO, respectively where the sheet appeared being folded forming continuous films.

![Figure 2](image-url)

**Figure 2.** SEM top-view images of zinc oxide nanorods on ITO substrates with different magnification of: (a) 10.000X and (b) 200.000X.
Figure 3. SEM top-view images of: (a) graphite; and (b) graphene oxide, both at magnification of 10.000X.

Figure 4 provides XRD results of ZnO nanorod thin film showing clear (002) crystal plane peak and several others confirming the wurtzite structure of ZnO phase [4], while Figure 5 compares the diffraction patterns of graphite, GO, and rGO. Based on the 2θ position of a very sharp peak at 26° in Figure 5(a) and its d-spacing calculation, the diffractogram confirmed the graphite characteristic, while the diffraction peaks at 2θ of 26.45° in Figure 5(b) and the calculation of d-spacing which provided a value of 7.54 Å were found to be a clear characteristic of GO material, as a result of the increased amount of oxygen in each layer[19]. Moreover, the reduction of GO to rGO also resulted in structural change, as obviously demonstrated by the peak rGO 2θ of 26.45° corresponding to the (002) diffraction plane and indicated that oxygen content was decreased. The main peak of (002) crystal plane looked shifted back to the original one belong to graphite and this result is in agreement with the previously reported in the literatures [2, 4, 19].

Moreover, our study was expanded to investigate the effect of rGO: dye wt% ratio on their UV Vis spectra as shown in Figure 6. It can be seen that all pure and modified dyes showed a peak at a wavelength of about 300 nm. However, it is interesting to note that rGO: dye wt% ratio of 3:100 shows the highest absorbance compared to other ratios.

Figure 4. XRD result of ZnO nanorod.
Figure 5. XRD result of: (a) Graphite, (b) GO and, (c) rGO.

Figure 6. UV-Vis spectra of pure dye and modified dyes with different rGO wt.% loading.

Figure 7. J-V characteristics solar cell devices based on four different dye configurations.
The result of PCE measurement was shown as J-V curve in Fig 7, while the resulted short-circuit current density (Jsc), open circuit voltage (Voc), and fill factor (FF) of devices were presented in Table 1. By adding rGO into the dye solution from 1:100 rGO: dye wt% ratio up to 3:100, the PCE value increased from 0.009 and reached the maximum value of 0.02 %, but further increase of the rGO has adversely effect on the declination of PCE result. It can be seen in the DSSC device with the ratio rGO: dye wt% of 5:100 produced the lowest value, i.e. 0.007. However, they are still higher than that of the reference which only gave a value of 0.005.

| Dye Configuration | Isc (mA cm$^{-2}$) | Voc (V) | FF   | PCE (%) |
|-------------------|-------------------|---------|------|---------|
| 1:100             | 3.28 x 10$^{-5}$  | 0.21    | 0.0359 | 0.009   |
| 3:100             | 5.86 x 10$^{-5}$  | 0.32    | 0.0440 | 0.020   |
| 5:100             | 3.58 x 10$^{-5}$  | 0.16    | 0.0275 | 0.007   |
| reference         | 5.06 x 10$^{-5}$  | 0.05    | 0.0123 | 0.005   |

5. Conclusion
In summary, the device performance of DSSC has been enhanced by introducing rGO into the dye. The dye modification by adding rGO has been found to increase light absorption, leading to increase the Jsc, Voc, FF, and finally overall PCE of improvement higher than reference. The maximum PCE about 0.02% is obtained with rGO: dye wt% ratio of 3:100.

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