Polyaniline (PANI)/reduced graphene oxide (rGO) composite as a counter electrode for dye solar cells.

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Abstract. Polyaniline (PANI)-reduced graphene oxide (rGO) based transparent counter electrodes have been fabricated for dye sensitized solar cells as an alternative to the expensive platinum (Pt) counter electrodes. Here, the graphene oxide (GO) added during the polymerization of PANI will subsequently reduce to rGO. The concentration of graphene oxide (GO) was varied in PANI matrix to optimize the performance of dye solar cell (DSC). With 1% GO addition in PANI, 9.68% current density was increased, consequently, 13.9% photocurrent density was found to be increased as compared to pure PANI. Electrochemical impedance spectroscopy (EIS) disclosed that the incorporation of 1% GO in PANI caused the double-layer capacitance to increase by 10 times compared to pure PANI. This implies that graphene is capable of enhancing the specific surface area and catalytic capacity of PANI. Optical transparency of PANI-1% GO counter electrode was found to be ~67% between the wavelengths of 500 to 600 nm. Such transparency enables the construction of bifacial DSCs. Although the photo conversion efficiency (PCE) of DSC with PANI-1% GO counter electrode is still not comparable to the one with Pt counter electrode but it is sufficient to be considered as the replacement as it exhibits good photovoltaic performance and optical characteristics together with an exceptionally low cost material.

1. Introduction

Fossil fuels are the major source of energy utilized to meet current energy demands. However, these sources are non-renewable, and their increasing consumption caused imminent depletion of fossil fuels and serious environmental issues that has stimulated the advancements in renewable technology. Solar energy is recognized as the most promising energy source that is naturally available and could be utilized anywhere in the world [1, 2].

Dye Solar Cells (DSCs) are recognized as a potential alternative to conventional silicon solar cells due to their low cost, optical tunable characteristics such as color transparency and relatively high efficiency [3-5]. The number of advantages of DSCs over conventional silicon solar cells provoked
interest to enhance the performance of DSC by optimizing its various components, such as photo-electrode, dye, electrolyte and counter electrode [6-8].

Three main components of DSSC are namely photo-electrode, electrolyte and counter electrode. Photo-electrode is composed on mesoporous wideband gap semiconducting layer such as TiO$_2$ that is deposited on conducting glass FTO (Fluorine doped Tin Oxide) [7, 8]. The high surface area of TiO$_2$ layer permits the absorption of photosensitizer dye. This sensitizer is responsible for light absorption and the excitation of electron from highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LOMO). The photo-generated electron transfers to the conduction band of TiO$_2$ and percolate to FTO. The oxidized dye is regenerated by redox electrolyte solution typically iodide/triiodide ions. Iodide ions on semiconducting surface donate the electron to triiodide ion. These tri-iodide ions further diffused into the platinum counter electrode surface and reduced to iodide ions again by accepting electrons from the outer surface. This process frequently repeats itself as long as light is incident on the cell [9-11].

The role of counter electrode is crucial in DSC as it governs the regeneration of iodide ions. Mostly, platinitized counter electrodes are used due to high catalytic activity, optical transparency and good conductivity of platinum. Since, platinum is highly expensive, therefore, various materials have been studied such as carbon materials including graphite, activated carbon, carbon nanotubes and graphene [12-14] have been studied for replacement in order to make DSC more cost-effective.

However, most of carbon materials produce opaque counter electrode, thus could not be preferred as solar power windows, especially for application of building integrated photovoltaic (BIPV) [12]. Amongst the carbon materials, graphene has attracted much more attention due to its excellent electronic, optical and catalytic properties. Recently, polyaniline has been incorporated as an alternative to Pt counter electrode in DSC due to its extremely low production cost, high catalytic activity and color transparency [15]. The conductivity and catalytic characteristics of polyaniline can be further enhanced by incorporating graphene in its matrix.

There are fewer studies on fabrication of counter electrode based on reduced graphene oxide (rGO)/polyaniline (PANI) for DSCs. However, in majority reports the effect of the amount of rGO in PANI matrix upon performance of DSCs is not explored [12, 16-20]. Therefore, in this study, rGO-PANI composite is incorporated as a counter electrode and the effect of rGO concentration in DSSCs is investigated.

2. Methodology
2.1. Materials
Graphite flakes (Sigma Aldrich), Sulphuric acid (Sigma Aldrich), phosphoric acid (Merck), Potassium permanganate (Sigma Aldrich), Hydrogen peroxide (Merck), Hydrochloric acid (Merck), Aniline (Sigma Aldrich), Ammonium persulphate (Sigma Aldrich). All chemicals were used without further purification.

2.2. Preparation of Graphene Oxide
Graphene oxide was prepared by modified Hummer’s method. Typically, 3g graphite powder was added into 27 ml of H$_2$SO$_4$ and 3 ml of Phosphoric acid (H$_3$PO$_4$) were mixed and stirred for several minutes in ice bath. Then 0.225 g of graphite power was added into the solution under stirring. Later 1.32 g KMNO$_4$ was added slowly under agitation. The reaction mixture was stirred for 6 h until it became dark green. Further 0.675 ml of hydrogen peroxide (H$_2$O$_2$) was added to get rid from excess KMnO$_4$ and stirred for 10 minutes. Then the mixture was transferred to oil bath under vigorous stirring at 40°C for overnight. Afterwords 10 ml of Hydrochloric acid (HCl) and 30 ml of DI water was added and centrifuged at 8000 rpm for 30 minutes. The supernatant was decanted away, residual washed again with HCl and Deionized (DI) water mixture. Later washed GO solution was dried in an oven at 60 °C for 24 hours to get power GO.
2.3. Preparation of Polyaniline and Polyaniline-GO composite
Polyaniline was prepared by previously reported method [12]. In a typical procedure, 0.11 ml aniline was first dissolved in 50 mL of 0.4 M HCl solution, then another 50 mL of 0.4 M HCl containing 94 mg ammonium persulfate (APS) was added under vigorous stirring. For preparing PANI-GO composite, GO (1 to 5) % wt of aniline was added into the solution. After few minutes of stirring, brown color of graphene oxide turned into black color reduced graphene oxide. Then solution was transferred to ice bath kept at 4 °C for 30 min till the solution turned into blue precipitates (emeraldine base), to convert into conductive emeraldine salt it was further treated with 1 M HCl solution for 24 h till all precipitates turned green. Finally, green precipitates of emeraldine salt were collected by centrifuge at 8000 rpm for 15 minutes. Fig.1 shows polyaniline in different stages of preparation.

![Figure 1](image)
Figure 1 Polyaniline (a) before polymerization (b) after polymerization (c) after centrifuge

2.4. Fabrication of polyaniline and polyaniline-GO thin film
The collected PANI and PANI-GO precipitates were tape cast onto cleaned FTO glass. Before tape casting, electrolyte filling holes were prepared via a programmable sand blasting machine. After tape casting, electrodes were dried at 60°C on hotplate for 10 mins.

2.5. Fabrication of Devices
For the preparation of photo-electrode, commercial TiO₂ paste was printed on FTO glass via 48T mesh. After printing, samples were kept at room temperature in closed box for 10 mins to avoid irregularities in the films. After that samples were dried in a furnace at 125 °C. The printing and drying were repeated three times, to achieve required thickness of layer, followed by the sintering step. The sintered photo-electrodes were then soaked overnight in N719 dye solution at room temperature. Later, the reference counter electrodes were prepared by screen printing of commercial Dyesol Pt paste over cleaned FTO glass via 100T mesh, followed by drying at 110°C and sintering at 400°C. The working electrodes and the counter electrodes (Pt, PANI and PANI/1%GO, PANI/2%GO and PANI/5%GO) were sandwiched by thermoplastic sealant using the hot press at 170°C and 60 bar pressure for 9 s. The electrolyte was injected through the sand blasted holes in a vacuum back filling desiccator. Finally, the holes were sealed with aluminum tape and the contacts were soldered.
3. Results and Discussions
Raman spectroscopy is the powerful tool to analyze structural properties of carbon materials. It was employed to characterize prepared GO, PANI and PANI-GO composite. The Raman spectra for GO is shown in Fig. 2 (a). Raman spectrum exhibited D peak (disorder) at 1349.65 cm\(^{-1}\) and G graphitic peak at 1591.85 cm\(^{-1}\). It is well known fact that ID/IG ratio indicates the condition of crystallite dimensions. Here the value of ID/IG is calculated 0.91 which is lesser than 1 that indicates the degree of disorder is relatively small. However, it confirms the presence of functional groups over graphene plane [21].

Raman spectra for our prepared PANI and PANI-1%GO (rGO) composites is given in Fig.2 (b). Raman spectroscopy is extremely sensitive to electronic structure changes in PANI. Typically, it allows to distinguish between the various states of PANI including conductive emeraldine salt and non-conductive emeraldine base [22]. According to Lourn et al [23] the existence of peaks between 1300 - 1350 cm\(^{-1}\) associated with the protonation process which directly indicates the existence of emeraldine salt, the conductive state of PANI. Therefore, it is concluded that our synthesized PANI and PANI-rGO composite exist in conductive emeraldine salt phase of PANI. Moreover, for PANI-rGO composite both given characteristics peaks are slightly shifted to higher frequency that might be
attributed to the presence of graphene. During polymerization process for PANI-rGO composite graphene oxide reduced automatically, its functional groups utilized in polymerization process. However, rGO was not detected clearly by Raman due to the very small amount. The crystal structure of pure polyaniline and PANI-rGO composite was characterized by X-ray diffraction (XRD).

XRD patterns for pure PANI and PANI-rGO composite is given in Fig.3. The sharp peak at 27.3° indicates (200) plane of polyaniline that confirms the presence of crystalline PANI [24]. The diminishing peak at 27.3° for PANI-1%GO (rGO) might be due to the presence of rGO between the planes of PANI.

The morphology of the PANI and PANI-rGO electrodes were observed by FESEM given in Fig. 5. In Fig. 5 (a), a PANI film is shown to be homogeneous with smooth fibrous structure. Fig. 5 (b) shows PANI-rGO composite films, it seems that rGO is coated uniformly with PANI, generated a highly porous structure. Moreover, the magnified image in Fig 5 (c) clearly reveals the highly porous fibrous structure of PANI. Consequently, such type of morphology will provide high surface area which is favorable for good catalytic activity. Fig. 5 (d) displays the average film thickness determined to be ~220 nm.

The optical transparency of PANI 1%GO and Pt counter electrodes is given in Fig 4. Pt is transparent in the whole part of the optical region. It reached to 97% at 800 nm wavelength. PANI-1%GO displays good transparency between 500 to 600 nm wavelengths. Interestingly, in this wavelength region N719 dye absorbs maximum light [25], therefore devices that composed of PANI-GO electrodes can be used as bifacial solar cells.

Figure 6 (a) shows the representative I-V characteristics curves and Table 1 depicts detail parameters of the DSCs with PANI, PANI-1%GO, PANI-2%GO, PANI-5%GO and Pt counter electrodes (CE) under 1 sun illumination (1.5 A.M). The device employing PANI CE shows a short circuit current density ($J_{sc}$) of 8.47 mA/cm$^2$, an open circuit voltage ($V_{oc}$) of 0.68 V, and a fill factor (FF) of 0.461, resulting in a power conversion efficiency (PCE) of 2.65%. For PANI-1%GO CE, FF and Jsc improves from 0.461 to 0.472 and 8.47 mA/cm$^2$ to 9.29 mA/cm$^2$ respectively, which indicates
that graphene increases the catalytic ability of PANI. With further increase in GO concentration 2%GO, FF seems to be further improved from 0.472 to 0.486. However, short circuit current density decreases. The same trend is found with 5% GO where FF improved but short circuit current density further decreases. The improvement in FF might be due to the reduction in the electron transfer resistance. Possible reason for the decrease in current density by further increase in GO amount is the agglomeration of rGO flakes during reduction [26].

The device based on platinum CE gives better efficiency of 3.7% with 10.9 mA/cm² current density. Electrochemical impedance spectroscopy (EIS) is an established technique to investigate the electrical characteristics of interfaces involved in DSCs. Nyquist plots for the prepared devices using various CEs are given in Fig 6 (b). There are mainly two semicircles, the intercept of small semicircle with x-axis indicates the series resistance (Rs) which is relevant to FTO/TiO₂/electrolyte interface and this small semicircle corresponds to the charge transfer impedance at the counter electrode. Whilst, the large semicircle is relevant to the charge transfer at TiO₂/electrolyte interface. The relevant parameters of the Nyquist plots for PANI with 1%, 2%, and 5% GO and Pt counter electrode can be determined by fitting the appropriate model using Gamry Echem Analyst software.

![Figure 6](image)

**Figure 6** (a) J-V curves (b) Nyquist plots of DSSCs

The Rs value of PANI CE device is dramatically reduced by incorporating GO in PANI matrix. However, for other devices it remains almost the same. The R_{CT} value for Pt CE is recorded to be 1.14 ohm, which is relatively higher than PANI CE based device, which is 0.14 ohm. For DSC with further increase of GO content in PANI, R_{CT} values remains almost the same. The capacitive property of counter electrodes is a crucial factor since it is related to the specific surface area and catalytic activity [27]. The double layer capacitance (Cdl) for PANI CE based device is recorded as 1.08 x 10^{-6} F which is an increase by almost ten times (1.17 x 10^{-5} F) by incorporating 1%GO in PANI matrix, believed to be attributed to the higher surface area and catalytic sites. For DSC with further increase in GO concentration, namely 2% and 5%, the double layer capacitance is decreased as a result of the agglomeration of reduced graphene oxide. On the other hand, double layer capacitance for Pt is 1.86 x 10^{-5} F is comparable with the PANI-1%GO device.
4. Conclusion

In this study, PANI-rGO composite counter electrodes were employed for DSCs as a cost effective alternative to Pt counter electrodes. GO was incorporated in PANI matrix which ultimately reduced to rGO during polymerization. It was found that by incorporating 1%GO in PANI, an increase of 13.9% PCE compared to pure PANI based device can be achieved. EIS study revealed that the enhancement in performance is attributed to the increase in double-layer capacitance. This double layer capacitance was enhanced due to the increase in specific area of PANI caused by the incorporation of GO. With further increase in GO concentration, PCE was decreased, believed to be due to the agglomeration of rGO flakes in PANI matrix. Moreover, approximately 67% optical transparency of PANI-1%GO counter electrode was found between 500 to 600 nm wavelength, enabling the electrodes to be developed for bifacial DSCs. Despite having the overall PCE of Pt counter electrode higher by 18% than PANI-1%GO based device, the achieved photovoltaic performance, optical characteristics and exceptionally low cost of PANI based counter electrode is still sufficient to develop low cost DSCs.

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