

## rGO-SWCNT hybrid for counter electrode in dye sensitized solar cell

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### ABSTRACT

*Towards platinum free counter electrode in dye sensitized solar cells, some carbon-based materials like carbon nanotubes and graphene are fully utilized due to their extraordinary properties such as high aspect ratio and conductivity. In this paper, single-walled carbon nanotubes (SWCNT), reduced graphene oxide (rGO) and hybrid structure of rGO-SWCNT spray coated counter electrodes were compared with graphite as the reference material. The morphology of these materials was analyzed with FESEM and FTIR. The DSSC performance was then measured using solar simulator. The current-voltage (I-V) characteristics show that the rGO-SWCNT counter electrode result the excellent performance with efficiency of ~1.86 %, 95.2 % better than graphite. This higher performance was attributed by the complete oxygen-functional group removal during reduction process which offers large active surface area for electro-photocatalytic activity, higher conductivity, better structure and properties compared to the individual forms.*

**Keywords:** Graphene oxide, carbon nanotubes, hybrid materials, DSSC, materials for electronic

### 1. INTRODUCTION

The great demand on green technology makes the solar cell as one of the most required devices nowadays. Instead of high performance silicon solar cell, dye sensitized solar cells (DSSC) are promising alternatives since reported by Michael Gratzel in 1991 [1]. Considered as the third generation solar cell, DSSC have received significant attention due to their low-cost fabrication and relatively high efficiency which is up to 11.4 % [2-4]. In a conventional structure, a DSSC consists of following components: a mesoporous titanium dioxide (TiO<sub>2</sub>), a Ruthenium based dye, electrolyte as an electron mediator, and a platinum (Pt) counter electrode. Counter electrode acts as an electron carrier from the external circuit to the electrolyte and catalyzes the reduction of triiodide ions in electrolyte. Hence, a good counter electrode must possess both excellent catalytic activity and high electrical conductivity. Commonly, Pt is used in DSSC because it evinces a strong electro-photocatalytic activity for the iodide/triiodide. However, the high price of Pt, poor stability and required complex equipments were serious drawbacks for large-scale and cost-effective DSSC fabrication. Besides, by-products like PtI<sub>4</sub> and H<sub>2</sub>PtI<sub>6</sub> [5] were produced when it dissolves in the electrolyte which can be dangerous to the environment.

The potential of various carbon-based materials has been demonstrated in the search for Pt-free DSSC including carbon black [1], carbon nanotubes (CNT) [6] and graphene [4]. Carbon nanotubes which is a tube-shaped carbon in nanometer size is proved can generate electron-hole pairs when shining the light which doubled up the efficiency of DSSC [7]. Their outstanding mechanical, electrical and thermal properties resulted from their structures offer a high impact to the device performance. However, its hydrophobic nature in solution gives some challenges during CNT counter electrode preparation, hence the selection of the suspension is crucial.

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The recent use of carbon 2D material, graphene has aroused more interesting outcomes. It is claimed that graphene can improve the performance of DSSC better than CNT due to its higher electron and hole transport mobility, high electrical conductivity and large specific surface area [8]. Besides graphene, reduced form of graphene oxide is favored among DSSC researchers as this material is easy to be produced and used, cheaper and highly conducting. Graphene oxide (GO) can be produced by chemical method and further reduced either thermally or chemically to form reduced graphene oxide (rGO). Efficiencies of the DSSC with graphene and rGO are reported at 5.69 % [9], 4.04 % [10], 3.96 % [4] and others. However due to strong van der Waals between the graphene sheets, aggregation issue always happened which may reduce the active area and leads to an increase of internal resistance and diffusion resistance of redox species [11].

Inspired by the extraordinary DSSC performance contributed by these two attractive materials together with their advantages and disadvantages, hybrid structure of graphene and CNT is expected can boost up the device efficiency. Jie Ma has demonstrated the surfactant free CNT structure by using GO solution as the surfactant [12]. The restacking rGO also can be minimized by incorporating the CNT into the 2D structure which enhances the electrochemical behavior [13]. There are many convenient and efficient ways in preparing the hybrid structure such as chemical vapor deposition [14], chemical method using hydrazine [15], sodium borohydride [13], ethanol [16] and even DI water [12].

In this paper, a simple approach by incorporating single-walled carbon nanotubes (SWCNT) into GO as the counter electrode using spray pyrolysis was demonstrated. The GO was further annealed in order to form rGO-SWCNT hybrid. The performance of rGO-SWCNT DSSC was also compared with the rGO, SWCNT and graphite DSSC respectively.

## 2. MATERIAL AND METHODS

### 2.1 GO-SWCNT and counter electrode preparation

First, GO was synthesized by modified Hummers method as described in our previous study [17]. Pre-oxidized graphite flakes and 15 g of potassium permanganate ( $\text{KMnO}_4$ ) were stirred in a solution containing concentrated sulphuric ( $\text{H}_2\text{SO}_4$ ) acid for several hours. The solution reaction was then terminated by the addition of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and subsequently washed with hydrochloric (HCl) acid in order to remove the sulfate ions. The final product was washed with DI water and dried in vacuum. The acid treatment of SWCNT was performed using a mixture of  $\text{H}_2\text{SO}_4$  and nitric ( $\text{HNO}_3$ ) acids in the volume ratio of 3:1. The mixture was refluxed for several hours, after which time the acid mixture was decanted. At the end of this process, the mixture was washed repeating with DI water until the pH of the solution become neutral. In order to obtain the GO-SWCNT mixture, GO powder and acid treated SWCNT were mixed thoroughly in DI water with the ratio of 5:5 in a 200 ml beaker before subjected to sonication process for well dispersion.

Single-walled carbon nanotubes, rGO and GO-SWCNT counter electrodes were prepared by spray pyrolysis using 1 ml of centrifuged solution. The temperature of 100 °C was used during spray coating to ensure a good evaporation of the solution and adhesion were achieved. Reduction process from GO to rGO was completed by annealing both samples of GO and GO-SWCNT at 150 °C for 3 hours. For the graphite counter electrode, the electrode was coated with a thin layer of graphite pencil for the entire substrate.

## 2.2 DSSC fabrication

Titanium dioxide suspension was prepared by grinding TiO<sub>2</sub> powder (Degussa P25) with a mortar and pestle. Initially, TiO<sub>2</sub> powder was mixed with diluted acetic acid (CH<sub>3</sub>COOH) (0.035 M) in order to separate aggregated TiO<sub>2</sub> particles with high shear force. After that, the colloidal suspension was added with a few drops of surfactant (Triton X-100) which produced an uniform and lump-free suspension. Then, the working electrode was coated with TiO<sub>2</sub> suspension using doctor blade technique. The resulting layer was then annealed at 450 °C in vacuum furnace for 30 minutes. Afterwards, the annealed working electrodes were sensitized by immersing them in  $3 \times 10^{-4}$  mol L<sup>-1</sup> ethanolic solution of Ruthenium dye (cis-dithiocyanato-N,N-bis(2,2-bipyridyl-4-carboxylicacid-4-tetra-butylammonium carboxylate) ruthenium (II); N719 (Sigma Aldrich), for 24 hours at room temperature.

In the final stage of DSSC fabrication, dye-sensitized working electrode and counter electrode were sandwiched together with two binder clips on the longer edges in order to hold the counter and working electrodes together. The iodide electrolyte solution consists of 0.5 M potassium iodide mixed with 0.05 M iodine in an organic solvent. Then, it was dropped at one edge of the electrode. An assembled DSSC was kept at room temperature for 10 minutes in order to make sure that all of the stained area was contacted by the electrolytes.

## 2.3 Efficiency Measurement

The morphology of the prepared material was examined using Field Emission Scanning Electron Microscopy (FESEM) (FEI Nova NanoSEM 450). The functional group attached in the carbonaceous material was analyzed by Fourier Transform Infra-Red (FTIR). The current-voltage (I-V) curve of DSSCs performance was obtained using solar simulator which was measured under illumination by simulated solar irradiance of 100 W. A polycarbonate plastic was used to protect the cell from damage by excessive UV light. The power conversion efficiency ( $\eta$ ) was calculated using Eq. (1)

$$\text{Efficiency, } \eta = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}} 100\% \quad (1)$$

while the fill factor ( $FF$ ) was calculated using Eq. (2)

$$FF = \frac{P_{max}}{I_{sc} \times V_{oc}} \quad (2)$$

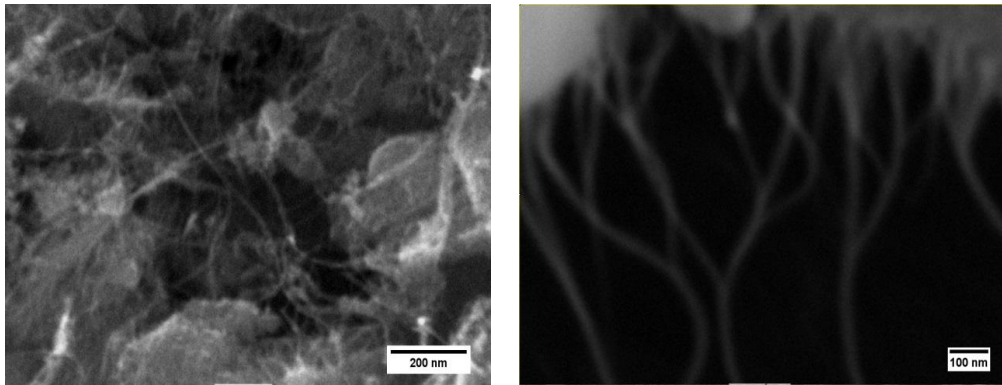
where maximum voltage (open circuit voltage,  $V_{oc}$ ), maximum current (short circuit current,  $I_{sc}$ ) and fill factor ( $FF$ ).

## 3. RESULTS AND DISCUSSION

### 3.1 Morphology analysis of carbon based materials

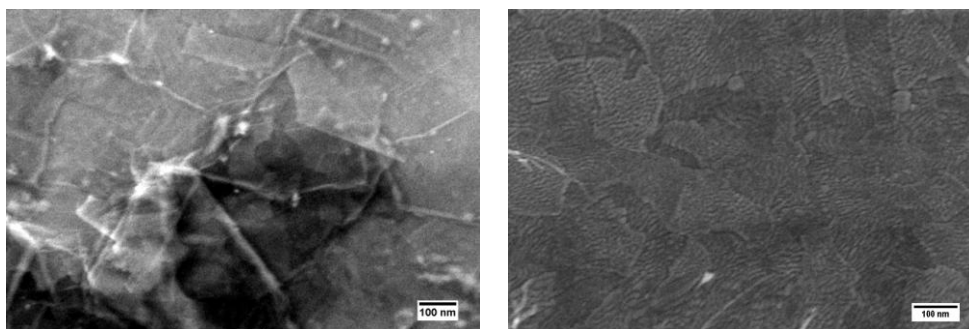
Figure 1 shows the surface morphology of pristine SWCNT and acid functionalized SWCNT. The raw SWCNT contain a large quantity of impurities such as amorphous carbon and catalytic particles. Besides, the hydrophobic nature makes SWCNT tend to agglomerate which hindering it to be dispersed in various solvent. Thus, acid treatment SWCNT is one of the established methods in order to increase solubility and the purity of SWCNT. According to the FESEM

images, it can be clearly seen that the tubes were more individual while the metal particles were removed after functionalized. As discussed by [18], during acid treatment process, the raw SWCNT were purified and a part of catalyst particles were possibly eliminated. Besides, the functional groups were attached on the sidewall tubes during oxidation which resulting improvement in its hydrophilicity and solubility.

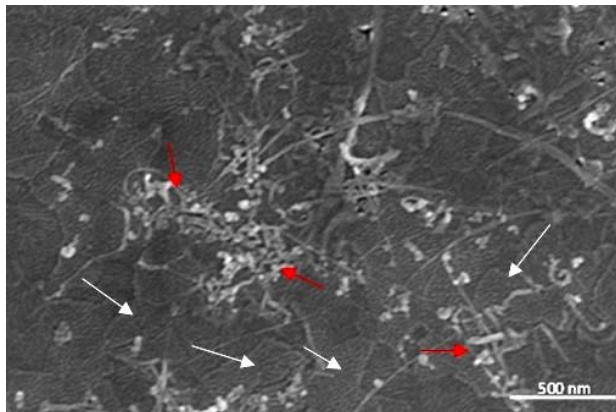


**Figure 1.** FESEM images of (a) SWCNT and (b) functionalized SWCNT

FESEM images of GO and rGO are shown in Figure 2. It was observed that the GO sheets were in stacked and overlapped. It can be attributed by the van der Waals effect. The volume of the GO sheets was affected by the solution concentration. After reduction process, the surface of rGO tends to crumpled and rippled due to the deformation upon reduction process. This is also happened because of the van der Waals interaction [19]. It was stated that, interlayer partial chemical or hydrogen bonds might be formed because of a large number of defects, dangling bonds, and O/H atoms, which are the driving force behind microscopic folding. The rGO also contains mesoporosity structures which allow faster mobility of the charge carriers and improve the electrode-electrolyte interaction, hence enhance the performance of DSSC counter electrode [4].

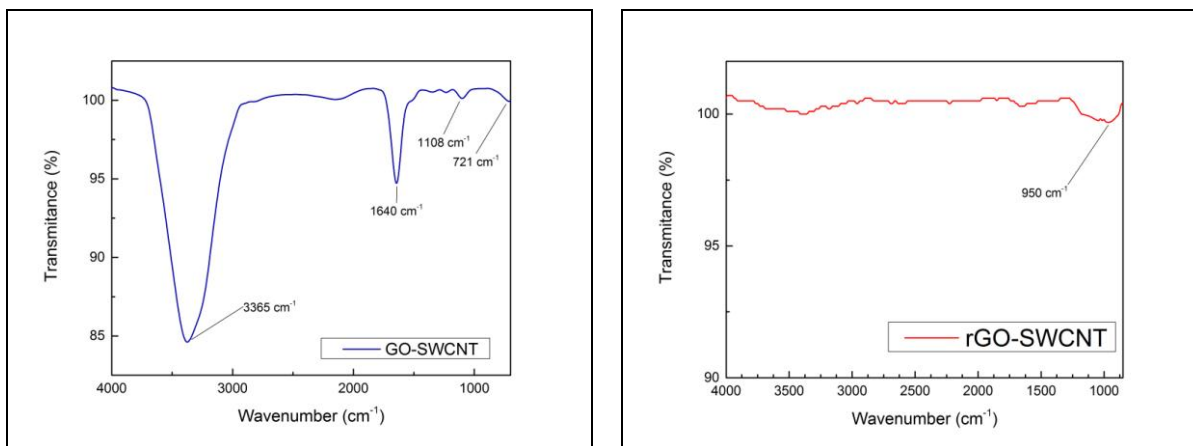


**Figure 2.** FESEM images of (a) GO and (b) rGO



**Figure 3.** FESEM images of rGO-SWCNT

Figure 3 shows the rGO-SWCNT hybrid structure in the ratio of 1:1. The SWCNT are clearly seen to be incorporated with the rGO layers. The SWCNT dispersed well between the rGO sheets due to the possible interaction between  $\pi$ - $\pi$  hydrophobic region of rGO and the side walls of functionalized SWCNT. It is preferable to have high aspect ratio of GO and SWCNT in order to create the continuous network. The presence of functional groups in GO encourages the SWCNT to be well dispersed in the DI water for relatively longer time. In another hand, it is stated that due to this strong interaction between the rGO and SWCNT [13], the dispersed behavior of the rGO is similar to an isolated conductive pad that connected by the conductive wire of SWCNT, which may improve the conductivity of counter electrode. With the rGO wrapped the SWCNT after reduction, it was expected that efficient conduction path was created and counter electrode conductivity was highly improved. It is possible to control the dispersion and mesostructure of rGO by avoiding restacking through the ratio of GO to SWCNT.



**Figure 4.** FTIR spectra (a) GO-SWCNT and (b) rGO-SWCNT

The characteristic FTIR spectrum of hybrid materials was depicted in Figure 4. According to the Figure 4(a), it was clearly seen a broad peak in the high frequency area at  $3365\text{ cm}^{-1}$  corresponds to the stretching of O-H groups which indicates that the oxygen containing groups. The absorption peak at  $1640\text{ cm}^{-1}$  and  $1108\text{ cm}^{-1}$  represent C=O and C-O, which result for stretching vibration of the carbonyl and carboxylic groups. The peak at  $721\text{ cm}^{-1}$  can be assigned to C=C stretching of aromatic rings.

The presence of functional groups reveals that the hybrid material was well oxidized. As stated by Youn et. al [20], the functional groups are favorable to the formation of a stable colloidal



suspension hybrid material due to highly negative surface charge of the as-prepared hybrid material. In Fig. 4(b), the peaks referring to the oxygen functional groups were disappeared after thermal reduction process which as a result of abrupt elimination of intercalated water and oxygen group.

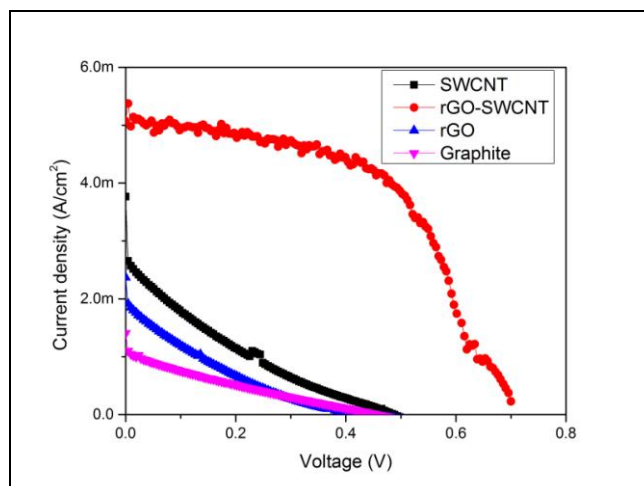
### 3.2 DSSC performance using various counter electrodes

Figure 5 shows the I-V characteristics of the DSSC fabricated using various different counter electrodes which were extracted from Table 1. Under illumination, the efficiency of conventional DSSC with graphite counter electrode was 0.09 %, indicating very poor electrical and catalytic activity and quite low as the reference sample. For the rGO DSSC, the device exhibited an open-circuit voltage ( $V_{oc}$ ) of 0.46 V, a short-circuit photocurrent ( $J_{sc}$ ) of 2.4 mA cm<sup>-2</sup>, and a fill factor ( $FF$ ) of 0.13 which yielding an efficiency ( $\eta$ ) of 0.14 %. From the oxidation process, some functional groups that attached at the basal planes and carboxylic acid at the edges of the GO sheets have decreased the conductivity of GO. Thus, thermal treatment was applied to reduce these oxygen functional groups. This rGO DSSC performance which performed an efficiency of 0.14% indicates that, the reduction process was not completely performed. Since the oxidation level is high on the graphene surface, the electron mobility is low thus increase the charge transfer resistance as only few active areas can be participated in the catalyzing reaction.

The device performance was further tested with SWCNT counter electrode where the values of  $V_{oc}$ ,  $J_{sc}$ ,  $FF$ , and  $\eta$  were 0.49 V, 3.8 mA cm<sup>-2</sup>, 0.12, and 0.22 %, respectively. It shows that the solubility of SWCNT was greatly amended after functionalized. From the result, it was observed that the rGO and SWCNT have significantly improved the  $V_{oc}$  compared to the conventional graphite counter electrode. The improved  $V_{oc}$  is a result of the decrease in the Fermi level of the redox species [21]. However, the obvious decreased  $FF$  for both electrodes might be attributed to the high electrical resistance of the ITO at the surface of the carbonaceous materials in contact with the electrolyte.

The rGO-SWCNT counter electrode shows a remarkable performance with comparable current density, higher  $V_{oc}$  and an enhanced  $FF$ , which resulting improvement in overall cell performance. As discussed by [13], the incorporating SWCNT into rGO can effectively be used to rebuild the structure of the carbon-based materials, and the active sites were also improved. The higher  $V_{oc}$  of this DSSC was attributed to the positive shift in the electrolyte energy level [4]. In another work, Hashimoto has proved that the greater  $V_{oc}$  was resulted from the faster charge injection for Ru dye on the semiconductors [22].

The performance of the cell was improved by 95.2 % (compared with the reference sample) attributed by the complete reduction of GO. The removal of oxygen groups for rGO-SWCNT electrode offers a tremendous surface area for faster and stronger redox reactions and better electro-photocatalytic activity for the reduction of triiodide ions [12]. Other than oxygen-containing groups removal, the heat treatment also improve the structure and other properties of graphene as some atomic-scale lattice defects also detached [23], thus more conductive network can be restored. The electrochemical and electrical losses happen in DSSC are performed by the  $FF$  results [24] which may also affect the counter electrode performance. The  $FF$  of rGO-SWCNT counter electrode is much higher (0.52) than SWCNT (0.12), rGO (0.13) and graphite (0.15). With a higher  $J_{sc}$  recorded for the hybrid counter electrode, it shows that higher catalytic activity for triiodide reduction and electrical conductivity were performed. Thus, these results proved that the combination of SWCNT with rGO can be superseding the graphite as a conventional counter electrode.



**Figure 5.** DSSC I-V characteristic

**Table 1** Electrical parameter from DSSC I-V curve

	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	Fill Factor (FF)	Efficiency ( $\eta$ %)
<b>Graphite</b>	0.43	1.4	0.15	0.09
<b>rGO</b>	0.46	2.4	0.13	0.14
<b>SWCNT</b>	0.49	3.8	0.12	0.22
<b>rGO-SWCNT</b>	0.7	5.1	0.52	1.86

#### 4. CONCLUSION

We demonstrated the use of spray coated carbon-based materials like graphite, SWCNT, rGO and also hybrid structure of rGO-SWCNT as counter electrode in DSSC. The unique properties of the hybrid structure have improved the electro-photocatalytic activity by offering higher active surface area, faster charge transfer and more conducting network which enhance the DSSC overall performance. Better performance of SWCNT DSSC was obtained compared to rGO due to acid functionalized method which improve the solubility of the tubes and incomplete reduction process of GO.

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