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Enhanced electrical conductivity of counter electrode using hybrid of reduced graphene oxide assisted with customised triple-tail surfactant with multiwalled carbon nanotubes

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Abstract. The fluorine-doped tin oxide (FTO) was utilized as a substrate in counter electrode (CE) fabrication using spray coating method. Hybrid of reduced graphene oxide (rGO) assisted by custom-made triple-tail sodium 1,4-bis(neopentyloxy)-3-(neopentyloxycarbonyl)-1,4-dioxobutane-2-silphonate (TC14) and commercially available single-tail sodium dodecyl sulphate (SDS) surfactants with multiwalled carbon nanotubes (CNTs) were developed as CE in dye sensitized solar cells (DSSCs) application. The rGO was fabricated by using reduction process from GO solution synthesized by electrochemical exfoliation method. During the reduction process, the reducing agent of hydrazine hydrate was utilized to reduce the oxygen functional group in synthesized GO solution. Hybrid of TC14-rGO and MWCNTs presented better structural and electrical properties than pure TC14-rGO. Higher electrical properties of TC14-rGO/MWCNTs hybrid was believed makes faster electron transport for the dye regeneration in DSCCs measurement. Therefore, the TC14-rGO/MWCNTs hybrid CE thin film showed suitable to be applied and developed in DSSCs application.

1. Introduction

Counter electrode (CE) shows a key role in dye sensitized solar cells (DSSCs) performance. Platinum (Pt) was a popular CE material for CE application due to its high electrical conductivity and stability [1]. However, Pt included in expensive material, thus should be replaced with another materials. Carbonaceous materials such as graphene [2], carbon [3] and carbon nanotubes (CNTs) [4] demonstrate a good materials for CE in DSSCs application because of its cheap and abundance in nature. Among all, graphene shows a promising alternative for Pt. Graphene presents a low cost production, high electrical conductivity, high surface area, high mechanical robustness, high optical transparency and high electrocatalytic activity [5-6].

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In the recent years, the derivatives of graphene such as graphene oxide (GO) and reduced graphene oxide (rGO) were developed as CE for DSSCs application. Easy fabrication and low cost production of GO leads a high development in research area. The GO can be synthesized by using electrochemical exfoliation [7-8] and Hummers' method [9]. High cost and long time production of Hummers' method caused an inefficient in GO production. Electrochemical exfoliation demonstrates better method than Hummers' method because of its low cost production, easy fabrication, environmentally friendly and can produce in large scale for single production [10-11].

The custom-made triple-tail sodium 1,4-bis (neopentyloxy) -3- (neopentyloxycarbonyl)-1,4 dioxobutane-2-silphonate TC14) and commercially available single-tail sodium dodecyl sulphate (SDS) surfactants were used to assist the water-based electrochemical exfoliation process. In electrochemical exfoliation method, triple-tail TC14 surfactant presents better intercalation process than single-tail SDS surfactant during the GO synthesis because it offers triple interaction. Triple-tail TC14 surfactant also resulted better quality of produced GO and less agglomeration [12]. However, the produced GO contains high oxygen functional group thus can be decreased using reduction process in order to produce rGO. Reducing agent of hydrazine hydrate is used during reduction process which helps in oxygen functional group reduction [13].

The produced rGO was composited with multiwalled CNTs (MWCNTs) in order to increase the electrical and structural properties of CE thin film. In this study, MWCNTs are produced from waste palm oil (WPO) which is easily found in the environment [14]. The MWCNTs presents high optical, high electrical conductivity and high mechanical properties [4, 15]. Actually, based on the roll walls number, CNTs have three structures including single-walled carbon nanotubes (SWCNTs), double-walled carbon nanotubes (DWCNTs) and multi-walled carbon nanotubes (MWCNTs). Among all, the MWCNTs are widely used as CE material due to its better in electronic properties. The spray coating method was used to fabricate the CE samples such as SDS-rGO, TC14-rGO and TC14-rGO/MWCNTs hybrid thin films. Spray coating method presents simple, easy, low cost and can produce in large scale production [16].

2. Method

The CE thin films can be fabricated by using five steps. Firstly, preparation of FTO substrate. The FTO substrates (2x2) cm^2 were cleaned in Power Sonic410 ultrasonic cleaner which was operated at temperature of 50°C. The FTO substrates were immersed in acetone, methanol and deionized (DI) water for 5 mins, respectively. The immersed substrates were then dried for 15 mins at 90°C.

Secondly, the synthesis of GO by using electrochemical exfoliation method in an electrolyte solution containing surfactant. The custom-made triple-tails TC14 and commercially available single-tail SDS surfactants were utilized to synthesize GO which the GO solution was prepared by using 0.1 M electrolyte. Two pieces of graphite rods with high purity (99.99%) were used in this exfoliation process. In this study, graphite rods have diameter and length of around 10 and 150 cm, respectively. The electrochemical exfoliation method used two graphite rods which were partially immersed in the electrolyte solution and connected to 7 V potential for 24 hours at room temperature. The electrolyte was prepared by mixing dissolve custom-made TC14 and commercially available SDS surfactant in DI water, then the direct current (DC) voltage was connected between the graphite electrodes.

Thirdly, the synthesized TC14- and SDS-GO was then reduced by using reduction process to produce TC14-and SDS-rGO. During the reduction process, reducing agent utilized hydrazine hydrate (80% soluble in water), an approximate ratio with GO solution was 1:100. The reduction process was carried out at ~95˚C for 24 hours. Fourthly, the produced TC14-rGO solution was composited with MWCNTs by using 1 weight % of MWCNTs that was prepared from 25 ml of TC14-rGO solution and 0.254 gram of MWCNTs powder. The TC14-rGO/MWCNTs hybrid solution was stirred for 1 hour and sonicated for 30 mins at room temperature.

Fifthly, transfer process of TC14-rGO, SDS-rGO and TC14-rGO/MWCNTs hybrid solution were done by using spray coating method. Prior to transfer process, the FTO substrate pre-heated on a hot plate at 120°C for 5 mins. An airbrush system with diameter size 0.25 mm was utilized in this method and FTO substrate was sprayed with constant distance of around 10 cm from the nozzle. Finally, the TC14-rGO, SDS-rGO and TC14-rGO/MWCNTs hybrid thin films were annealed for 1 hour at 400°C in argon ambient.

3. Result and Discussion

Figure 1 present FESEM images and EDX analysis of CE thin films. The TC14-rGO (Figure 1(a)) shows a thin layer and sheet-like structure in the edge. Less agglomeration is also demonstrated by fesem image of TC14-rGO. The triple-tail TC14 surfactant promotes a better exfoliation, dispersion and stabilization as compared to single tail of SDS surfactant. The performance of triple-tail TC14 surfactant during the GO synthesis can be confirmed by EDX analysis. Figure 1(b) presents the EDX analysis of TC14-rGO that revealed higher atomic percentage of carbon (C) of 53.43% than oxygen (O) of 46.57%. This indicated successful reduction process in rGO production. The thick layer of SDS-rGO is shown in Figure 1(c). The EDX analysis of SDS-rGO also shows lower atomic percentage of C of 51.83% as compared to TC14-rGO of 53.43%. Based on these results, the triple tails TC14-rGO presents better structural properties for CE in DSSCs application.

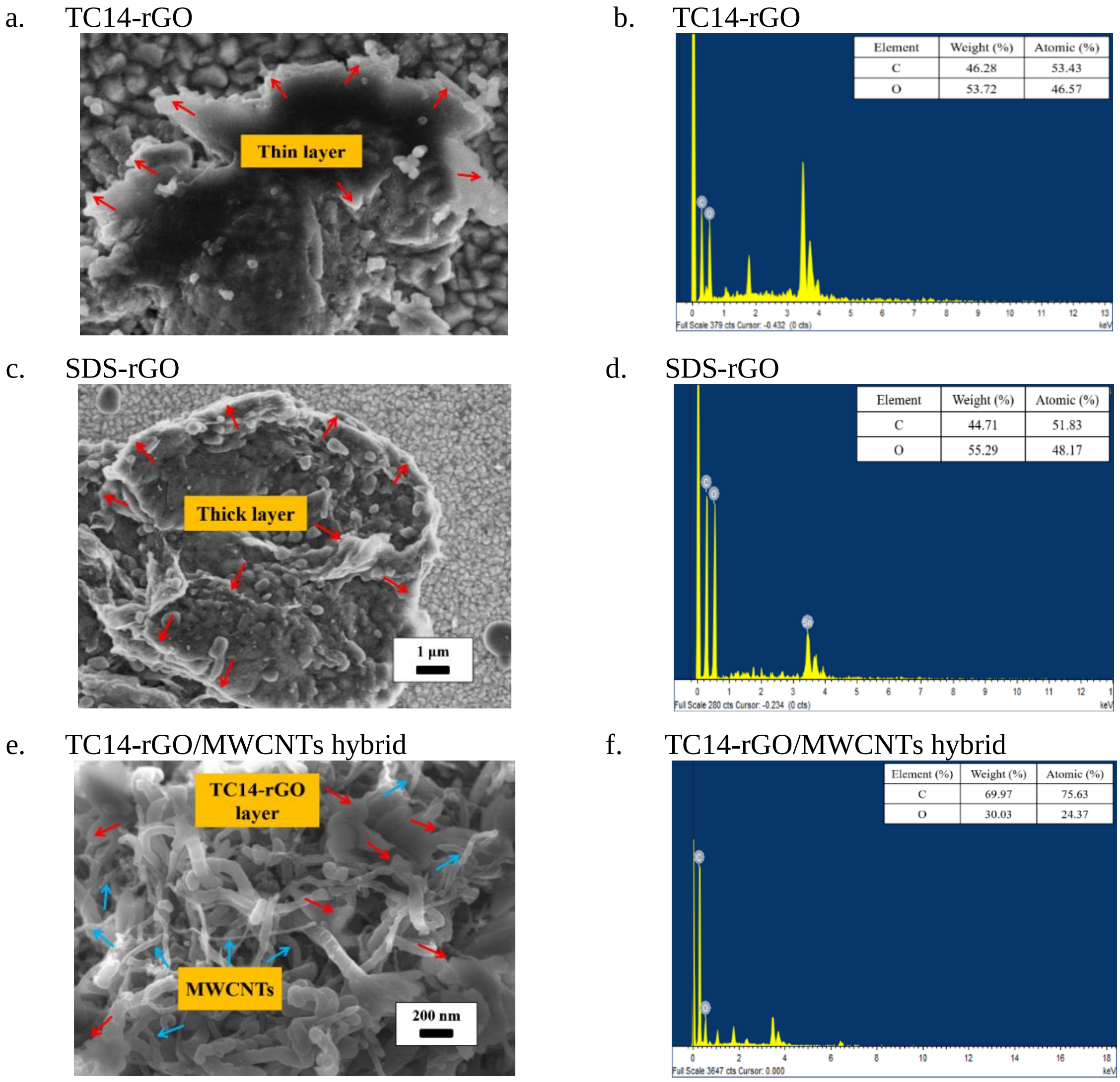

Figure 1. Fesem images with EDX analysis of (a)-(b) TC14-rGO, (c)-(d) SDS-rGO and (e)-(f) TC14-rGO/MWCNTs hybrid

The fesem image of TC14-rGO/MWCNTs hybrid (Figure 1(e)) demonstrates a well-dispersed and scattered on FTO substrate. The vacancies between TC14-rGO layers (red arrows) are connected by conjugated network of MWCNTs (blue arrows) [4]. The successful composite of TC14-rGO and MWCNTs is proved by EDX analysis in Figure 1(f). The TC14-rGO/MWCNTs hybrid reveals higher atomic percentage of C (75.63%) as compared to pure TC14-rGO thin film (53.43%).

The micro-Raman spectra of TC14-rGO, SDS-rGO and TC14-rGO/MWCNTs hybrid CE thin films are demonstrated in Figure 2. This analysis can be also used to determine the disordered structure of carbonaceous CE materials. The D- and G-band of TC14-rGO at 1368 and 1590 cm^{-1}, respectively. The defects in carbon lattice can be obtained from the value of D-band [17]. The D-band also presents vibrations of sp^3 carbon atoms. Moreover, the G-band reveals the exfoliated sheet layers during the GO synthesis by using electrochemical exfoliation method and shows the vibrations of sp^2-bonded carbon atoms [18]. The TC14-rGO demonstrates higher D-band peak intensity as compared to SDS-rGO which indicates higher defects in the TC14-rGO film. Meanwhile, the SDS-rGO shows D- and G-band at 1355 and 1587 cm^{-1}, respectively.

From the Figure 2, the I_D/I_G ratio can be also determined to predict the presence of defects and size of the sp^2 domains on the CE samples [19]. High I_D/I_G ratio of TC14-rGO (0.92) also indicates the amount of new form graphitic crystallites and increasing number of sp^2 domain [20]. Higher I_D/I_G ratio (0.92) of TC14-rGO than SDS-rGO (0.75) was believed due to more successful reduction process which presents higher reduction of O content in the TC14-rGO solution [21]. The 2D-band is also observed in all samples which can be also utilized to distinguish the number of rGO layers [22]. The 2D-band of TC14-rGO and SDS-rGO is observed at 2766 and 2716 cm^{-1}, respectively. A broad of 2D-band of TC14-rGO demonstrates that the produced rGO shows higher defect level after reduction process, this also proven by higher I_D/I_G ratio.

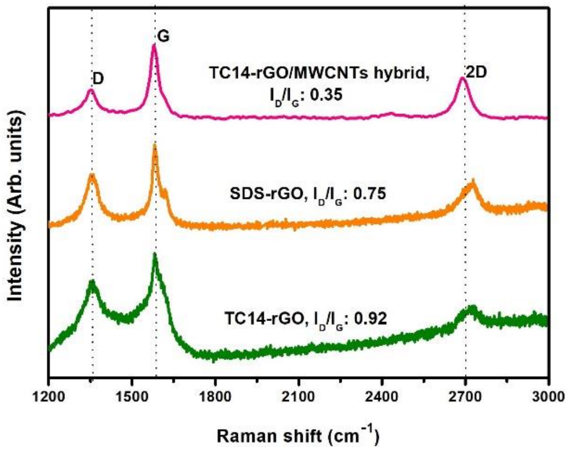

Figure 2. Micro-Raman spectra of TC14-rGO, SDS-rGO and TC14-rGO/MWCNTs hybrid thin films

The I_D/I_G ratio decreases to be around 0.35, this was affected by addition of MWCNTs in TC14-rGO sample. Its lower I_D/I_G ratio was believed contributed from a low I_D/I_G ratio of pure MWCNTs that consist of higher sp^2 structure [23]. The MWCNTs material also shows low O content, so it exhibits a small defect and this causes a decrement of I_D/I_G ratio. After the TC14-rGO was composited with the MWCNTs, the D-, G- and 2D-bands shifted to a lower wavelength when was compared to pure TC14-rGO. The summary of micro-Raman analysis of TC14-rGO, SDS-rGO and TC14-rGO/MWCNTs hybrid thin films are tabulated in Table 1. This shifting was believed due to the π-stacking interaction between the TC14-rGO sheets and side-walls of MWCNTs [24]. Based on the I_D/I_G ratio, it can be concluded that the TC14-rGO/MWCNTs hybrid reveals lower disorder structure than pure TC14-rGO and indicates a good CE sample.

Table 1. Micro-Raman analysis results of TC14-rGO, SDS-rGO and TC14-rGO/MWCNTs hybrid thin films

Sample	D-peak (cm^{-1})	G-peak (cm^{-1})	I_D/I_G ratio	2D-peak (cm^{-1})
TC14-rGO	1368	1590	0.92	2766
SDS-rGO	1355	1587	0.75	2716
TC14-rGO/MWCNTs hybrid	1352	1581	0.35	2690

Figure 3 shows the electrical properties of TC14-rGO, SDS-rGO and TC14-rGO/MWCNTs hybrid thin films which can be determined using four-point probe measurement. Higher electrical conductivity is presented by TC14-rGO of ~5.6 x 10^{-1} $S.cm^{-1}$ as compared to SDS-rGO (~5 x 10^{-1} $S.cm^{-1}$). Lower electrical conductivity of SDS-rGO was believed due to thicker layer and agglomerated structure which decelerates the electron movement in the sample. The electrical conductivity of TC14-rGO greatly increases when it was composited with the MWCNTs to be around ~6.5 x 10^{-1} $S.cm^{-1}$. This was believed due to a good electrical conductivity of pure MWCNTs produced from palm oil precursor. Based on these results, the TC14-rGO/MWCNTs hybrid demonstrates better electrical conductivity as compared to pure TC14-rGO and SDS-rGO thus suitable to be applied as CE sample for DSSCs application. The details of electrical properties of TC14-rGO, SDS-rGO and TC14-rGO/MWCNTs hybrid are listed in Table 2.

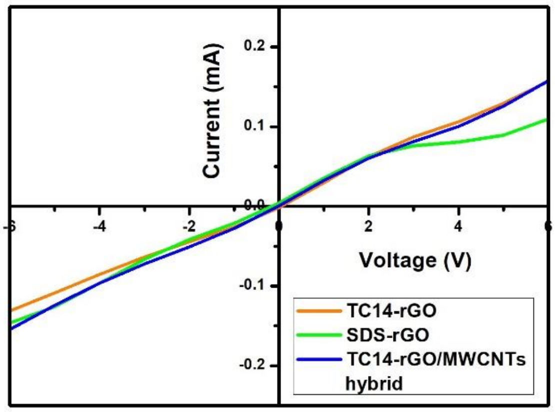

Figure 3. I-V curves of TC14-rGO, SDS-rGO and TC14-rGO/MWCNTs hybrid thin films

Table 2. Four-point probe measurement results of TC14-rGO, SDS-rGO and TC14-rGO/MWCNTs hybrid thin films

Sample	Resistivity, ρ (Ω.cm)	Conductivity, σ ($S.cm^{-1}$)
TC14-rGO	1.76	5.6 x 10^{-1}
SDS-rGO	1.99	5 x 10^{-1}
TC14-rGO/MWCNTs hybrid	1.53	6.5 x 10^{-1}

4. Conclusion

The best structural and electrical properties of CE sample is shown by TC14-rGO/MWCNTs hybrid thin film. The TC14-rGO presents less agglomeration and TC14-rGO/MWCNTs hybrid demonstrates a well-dispersed and scattered on FTO substrate. The vacancies between TC14-rGO layers (red arrows) are connected by conjugated network of MWCNTs (blue arrows). The TC14-rGO/MWCNTs hybrid also demonstrates higher atomic percentage of C (75.63%) as compared to pure TC14-rGO thin film (53.43%). The lowest I_D/I_G ratio of TC14-rGO/MWCNTs hybrid of 0.35 was believed due to low O content of pure MWCNTs material, so it exhibits a small defects and low disorder structure. In electrical properties, the TC14-rGO/MWCNTs hybrid thin film also presents the highest electrical conductivity of ~6.5 x 10^{-1} S.cm^{-1}. This finding shows that the composite of TC14-rGO with the MWCNTs from WPO presents a good structural and electrical conductivity properties, thus suitable to be applied as CE materials for DSSCs application.

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