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Effects of thermally reduced graphene oxide in the photoanode on the properties of dye sensitized solar cells

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Abstract. This paper examines the effects of thermally reduced graphene oxide (rGO), incorporated in the titanium dioxide (TiO_2) photoanode, on the performance of anthocyanin dye sensitized solar cells (DSSCs). While anthocyanin based DSSCs are cost effective, their efficiency tends to be low. In this study, rGO-TiO_2 nanocomposites with different rGO weight fractions were synthesized. Their surface morphology was studied with Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). Electrical conductivity of these nanocomposite layers were measured with the four-point probe method. The current-voltage characteristics of the DSSCs made with these nanocomposites along with anthocyanin dye from blackberries, a carbon counter electrode, and an Iodine based electrolyte were studied. It was found that the addition of rGO, at low weight fractions, increased nanocomposite conductivity, the solar cell short circuit current, and cell efficiency. Peak efficiency, increased by 45.7% of that with no rGO, was achieved with a photoanode layer containing 0.004 wt% rGO.

1. Introduction

Graphene has attracted attention in dye-sensitized solar cells (DSSCs) due to its high electric conductivity, thermodynamic efficiency, and high transmittance in the visible light spectrum [1,2]. Incorporation of graphene in the electrodes of DSSCs has shown improvements in DSSC performance [3]. Most notable performance enhancement occurs when incorporated in the photoanode of the DSSC. The DSSC efficiency increases greatly when graphene is added in the titanium dioxide (TiO_2) photoanode at low concentrations. This is partly due to the conduction band of rGO being in between the conduction bands of TiO_2 and fluorinated tin oxide (FTO), which reduces the back electron transfer and increases the electron transport between TiO_2 and FTO. It is also speculated that the small size and honeycomb structure of graphene allow it to bond to the TiO_2 particles and facilitate the conduction of electrons [3]. However, as graphene concentration increases, it may begin to absorb light thus reducing solar cell efficiency [4]. A number of methods have been used to synthesize rGO and nanocomposites containing rGO, and different reduction methods result in different properties of the nanocomposites and therefore the properties of the DSSCs [1].

Bell et al. synthesized an rGO-TiO_2 composite by mixing suspensions of TiO_2 and GO at various GO concentrations [5]. The GO in the mixtures was reduced by ultraviolet light, resulting in the rGO-TiO_2 composites. It was demonstrated that the incorporation of rGO extended the electron lifetime of the TiO_2 films by a factor of approximately four. Additionally, the rGO-TiO_2 solar cells yielded ten times the photogenerated current of TiO_2 solar cells [5]. Cheng *et al* used a hydrothermal method to obtain anatase TiO_2 nanoparticle-decorated rGO, which increased the N719 based DSSC efficiency by approximately 60% [6]. It was proposed that the structure of rGO provides the surface for the nucleation of the TiO_2 nanoparticles due to the fact that as rGO content increases, the average crystal size of TiO_2 particles increases. Sun et al. used heterogeneous coagulation to synthesize a graphene-TiO_2 nanocomposite [7]. The graphene-TiO_2 nanocomposite increased the efficiency of the N719 based DSSCs by 59% showing that heterogeneous coagulation is an effective method in increasing charge transfer and thus performance of the solar cell.

Due to the difficulty in synthesizing ruthenium based dye, Smestad and Grätzel developed DSSCs that utilizes flavonoids and chorophyllides as sensitizers such as anthocyanin extracted from blackberries, raspberries, pomegranate seeds, or green citrus leaves [8]. Use of non-ruthenium based dye is a cost effective, non-toxic, environmentally friendly option [9]. However, the anthocyanin based DSSCs exhibit much lower conversion efficiency than that of their ruthenium based counterparts. In this study, the rGO-TiO_2 nanocomposites with varying rGO weight fractions are investigated to determine their effects on the properties of anthocyanin DSSCs.

2. Experimental

2.1. rGO-TiO_2 nanocomposites preparation and solar cell assembly

GO solution was synthesized by adding 350 mg of GO powder (Graphene Supermarket) to 70 mL of deionized water (DI) in a 600 mL beaker. The solution was placed in an ultrasonic bath (Branson Ultrasonic Bath) and was sonicated with heat for one hour to create a homogeneous brown mixture with a GO concentration of 5 g/L.

Three layers of scotch tape were used to define the borders of twenty five 8x30 cm^2 areas on the FR4 glass epoxy panel. Approximately 4 g of the GO solution was spread using a glass slide on each of the twenty five 8x30 cm^2 areas of FR4. The solution was left to air dry for 8 hours. The GO was then thermally reduced using a CO_2 50 Watt laser engraver, which was set to 14% power, 100% speed, and 300 pixels per inch [10]. The resulting rGO was extracted using a razor blade and 100 mg was measured.

Table 1. TiO_2 weight and rGO weight used in creating the nanocomposites as well as the calculated percent by weight (wt%) present in the nanocomposites.

Sample Number	TiO_2:rGO (mg)	rGO wt%
1	125:0	0
2	1000:0.02	0.002
3	1000:0.03	0.003
4	1000:0.04	0.004
5	1000:0.05	0.005
6	1000:0.08	0.008
7	1000:1	0.100
8	750:1	0.133
9	500:1	0.200
10	250:1	0.398
11	125:1	0.794
12	125:3	2.34
13	125:6	4.58

The rGO-TiO_2 nanocomposites were synthesized using different weight ratios of TiO_2 (Sigma Aldrich) to rGO ranging from 1:0 to 1:0.0458. Table 1 shows the amount of TiO_2 and rGO that was used to synthesize each composite and the rGO wt%. The TiO_2 and rGO were combined in a mortar, and a pestle was used to mix and grind the contents. To create the nanocomposite paste, 0.003 mL of acetic acid was added for each milligram of TiO_2/rGO powder. The contents were mixed until the paste became lump free. A drop of surfactant (Triton X-100) was added for every 125 mg of powder and mixed with the paste. The rGO-TiO_2 nanocomposite paste was deposited on the FTO coated glass using the doctor blade technique and annealed at 450°C for 20 minutes.

The anthocyanin dye was prepared by crushing 173 g of blackberries in 20 mL of DI water and filtering it through a filter with a pore diameter of 20 μm. The rGO-TiO_2 coated glass was placed face down in the dye for 40 minutes. The dye-loaded active electrode was rinsed with DI water and followed with an isopropyl alcohol (IPA) rinse. The DSSC was constructed by combining the rGO-TiO_2 electrode and carbon coated counter electrode as shown in figure 1. The electrolyte, synthesized by dissolving 0.127 g of 0.05 M Iodine (I_2) in 10 mL of water-free ethylene glycol and adding 0.83 g of 0.5 M potassium iodide, was introduced to the solar cell through capillary action. It is visible that the electrolyte spreads evenly through the inner surface of the photoanode.

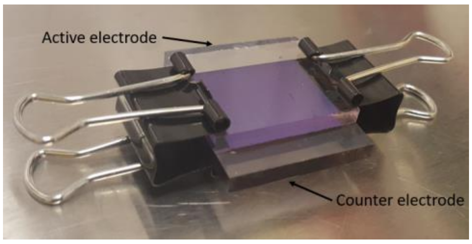

Figure 1. The DSSC assembly.

2.2. *Characterization*

The surface morphology of the rGO-TiO_2 nanocomposite layers was studied with Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). Electrical conductivity of these nanocomposite layers were measured using the four-point probe station. The current-voltage of the DSSCs was characterized using a solar simulator at air mass (AM) 1.5 in a dark chamber.

3. Results

Figure 2 shows the SEM images of the rGO-TiO_2 layers with different rGO weight fractions corresponding to those in table 1. The surface roughness of the films in Images 2 to 9, containing 0.002 to 0.2 wt% of rGO, is smaller than that in Image 1. The few large particles shown in Image 7 may be caused by the grinding process. The surface roughness of the films in Images 10 to 13, containing 0.398 to 4.58 wt% of rGO, is higher than that in Image 1. In general, the surface morphology of the nanocomposite film is improved when the rGO is less than or equal to 0.2 wt%.

Figure 3 shows the maximum size of the particles in the rGO-TiO_2 nanocomposite films measured with AFM. For the films with rGO weight fraction between 0 and 0.2 wt%, the maximum particle size remains in the range between 4.5 μm and 5.5 μm. The films, with rGO weight fraction higher than 0.2%, contain larger particles which is consistent with the results obtained from the SEM measurements.

Figure 4 shows the electrical conductivity of the rGO-TiO_2 nanocomposite films obtained with four-point probe measurements. It can be seen that as rGO weight fraction increases, conductivity also increases, reaching a maximum of 8.04 S/cm for the film with 0.2 wt% rGO. Further increase in the rGO weight fraction resulted in the decrease in conductivity. The increase in conductivity at low rGO concentration is contributed by the increased charge transfer in the TiO_2 coated rGO [6]. The decrease in conductivity at a higher rGO concentration may result from the aggregation of TiO_2 coated rGO, which can be seen from the results of SEM and AFM.

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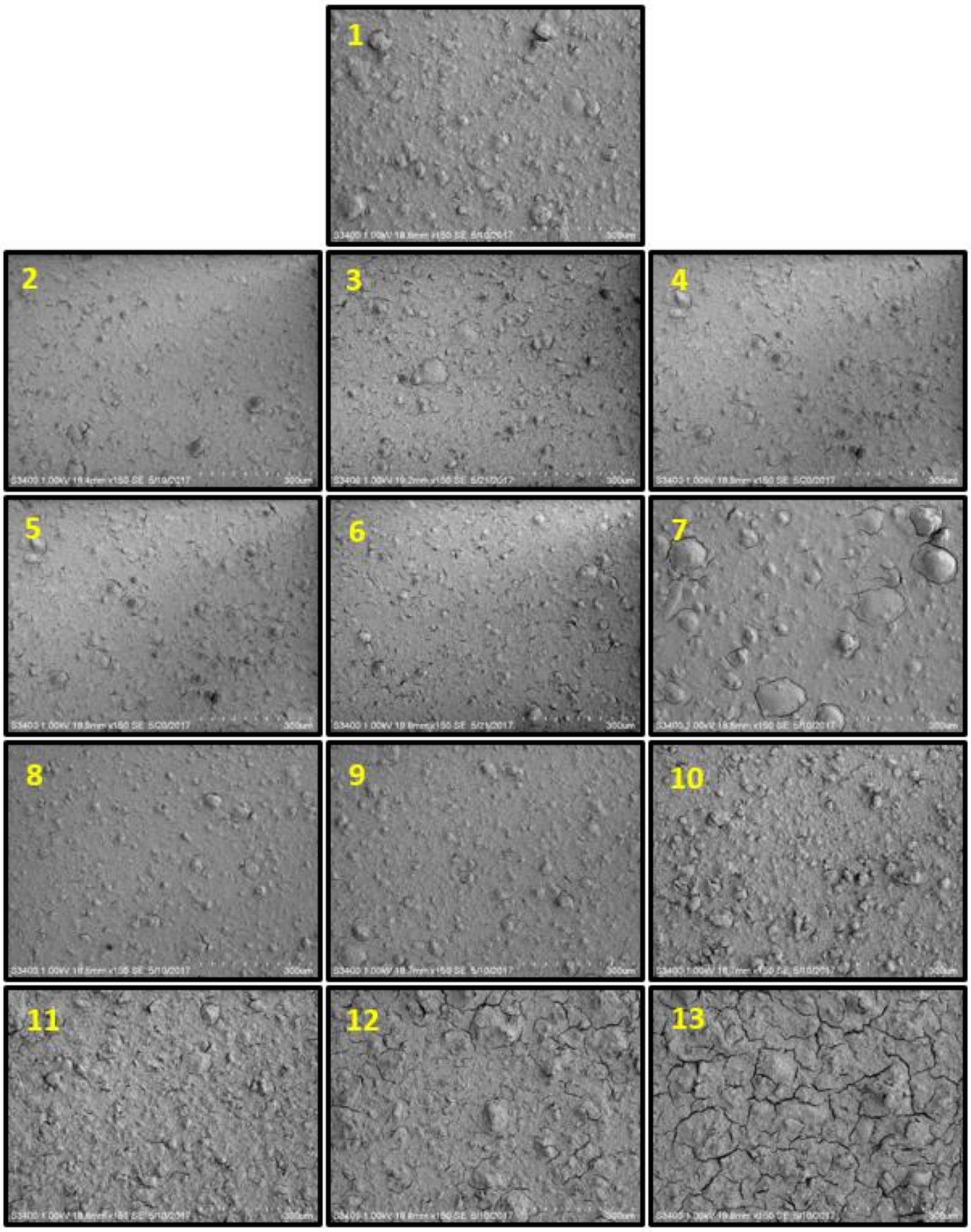

Figure 2. The SEM images of rGO-TiO_2 nanocomposite films with different rGO weight fractions.

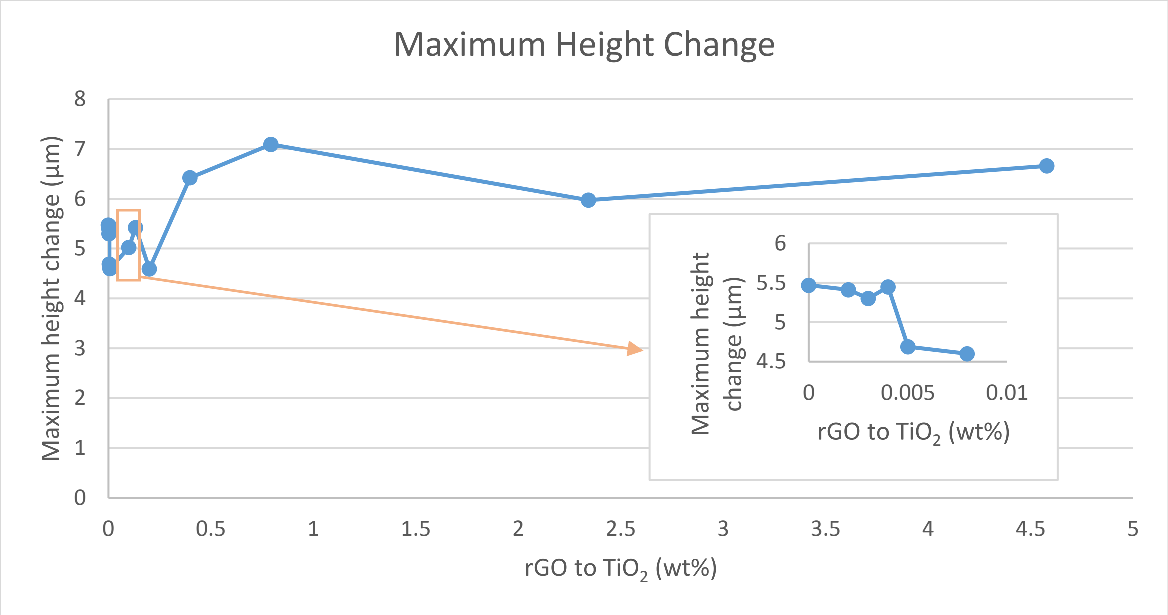

Figure 3. The maximum size of the particles in the rGO-TiO_2 nanocomposite films with different rGO weight fractions.

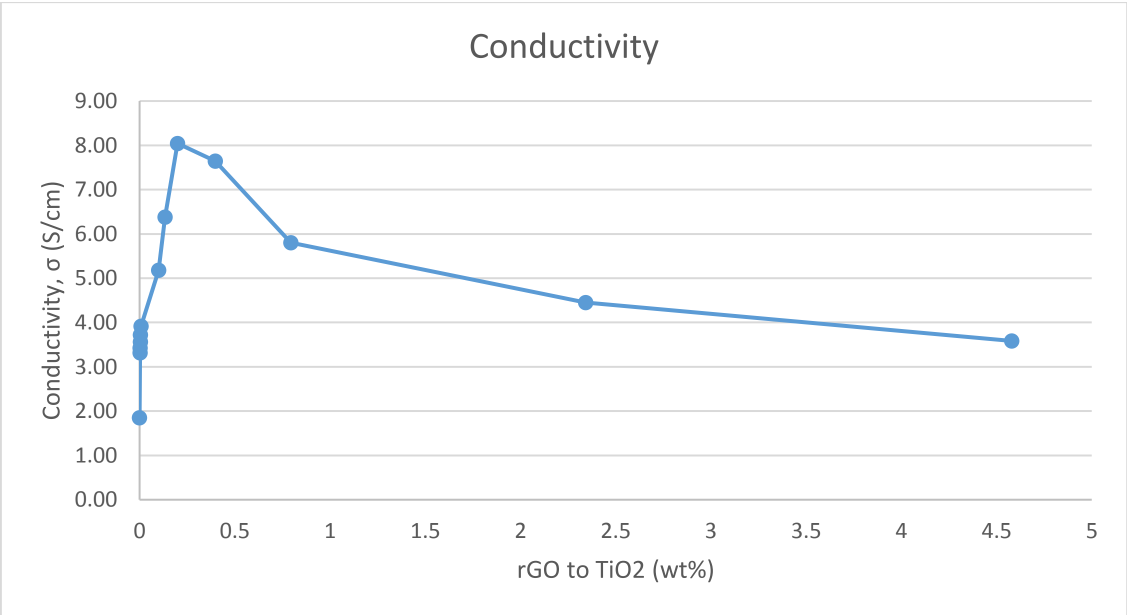

Figure 4. Conductivity of the rGO-TiO_2 nanocomposite films with different rGO weight fractions.

The performance of the rGO-TiO_2 based anthocyanin dye DSSCs is listed in table 2. The open circuit voltage (V_{oc}) remains fairly constant as the rGO wt% is below 0.133% and decreases as the rGO wt% is above 0.133%. As the short circuit current (I_{sc}), reaches the maximum at 0.004 wt% rGO, so does the power conversion efficiency (PCE). A 46% increase in PCE was achieved by incorporating 0.004% rGO weight fraction in the TiO_2 photoanode. The current-voltage characteristic of the DSSC with 0.004 wt% rGO is shown in figure 5.

Table 2. The performance of DSSCs with different rGO-TiO_2 nanocomposite photoanodes.

Sample Number	rGO wt%	I_{SC} (mA)	V_{OC} (V)	I_{MPP} (mA)	V_{MPP} (V)	PCE (%)	FF
1	0	4.601	0.4160	3.025	0.2100	0.1760	0.3319
2	0.002	4.632	0.4130	3.300	0.2540	0.2322	0.4382
3	0.003	5.516	0.4180	3.838	0.2230	0.2371	0.3712
4	0.004	5.640	0.4170	3.972	0.2330	0.2564	0.4062
5	0.005	5.050	0.4170	3.398	0.2480	0.2334	0.4002
6	0.008	4.358	0.3950	3.306	0.2450	0.2244	0.4705
7	0.100	2.855	0.4570	1.826	0.2390	0.1209	0.3345
8	0.133	1.786	0.4120	1.177	0.2490	0.0812	0.3983
9	0.200	1.185	0.2610	0.6508	0.1450	0.0261	0.3051
10	0.398	0.872	0.2120	0.5020	0.1120	0.0156	0.3041
11	0.794	0.7311	0.1370	0.3958	0.0690	0.0076	0.2520
12	2.343	0.6191	0.0680	0.3056	0.0360	0.0030	0.2613
13	4.580	0.4098	0.0480	0.2097	0.0220	0.0013	0.2345

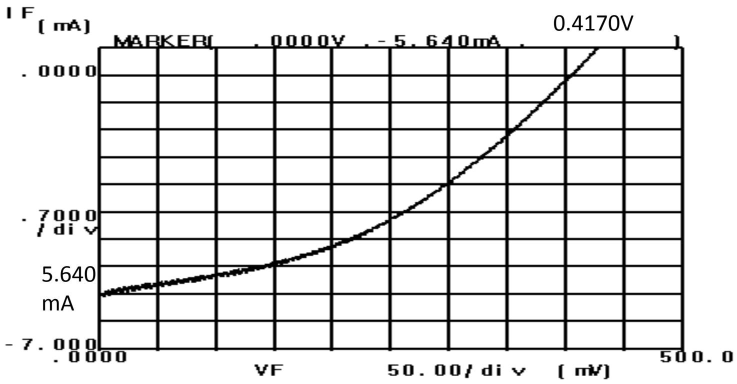

Figure 5. The I – V characteristic of DSSC with 0.004 wt% rGO.

4. Discussion

At low rGO weight fractions (less than 0.133 wt%), the open circuit voltage does not change excessively and remains between 0.39 V and 0.48 V. This exhibits a minimal effect on efficiency since the Fermi level of the TiO_2-FTO interface does not alter significantly. Efficiency is largely dependent on the short circuit current which increases from 4.60 mA (0% rGO) to 5.64 mA (0.004 wt% rGO). The increase in current could be attributed to the increase in electrical conductivity of the photoanode. As rGO content is increased to 0.004 wt%, the electrical conductivity of the nanocomposite increases from 1.85 S/cm to 3.56 S/cm, resulting in the increase of charge transfer from the nanocomposite to the FTO. This increase in charge transfer reduces carrier recombination, effectively increasing the short circuit current.

As rGO content continually increases past the optimal point of 0.004 wt%, the short circuit current and conversion efficiency start to decrease while the electrical conductivity of the nanocomposite continues to increase. The decrease in efficiency is due to the increased light absorption of rGO. This can be confirmed by the obvious coloration change of the nanocomposite films with greater than 0.2 wt% rGO. The increased light absorption of rGO results in the decreased light absorption of the dye, which lowers the electron excitation and reduces the short circuit current and efficiency. The short circuit current and efficiency of the DSSCs with higher than 0.1 wt% rGO decreased below those with 0 wt% rGO.

The low conversion efficiency of the DSSCs studied here may be caused by the low carrier generation in the anthocyanin dye and a high charge recombination in the electrolyte. The future plan for this study is to incorporate an additive, such as 4-TBP, in the electrolyte to resist the charge recombination.

5. Conclusions

The effects of incorporating rGO in the photoanode on the performance of the anthocyanin DSSCs were investigated. The surface of the rGO-TiO_2 nanocomposites becomes rougher when the rGO weight fraction is greater than 0.2 wt%. The electrical conductivity increases as rGO weight fraction increases from 0 wt% to 0.2 wt%. Incorporation of 0.004 wt% rGO resulted in a 45.7% increase in the cell conversion efficiency. The amount of rGO required to reach maximal efficiency was comparable with the 0.005 wt% rGO reported by Ha et al. who used a similar method of nanocomposite synthesis. However, the graphene was synthesized using plasma-assisted electrochemical exfoliation [11]. Additionally, the increase in efficiency was much greater than the 15% increase reported by Ha et al. Use of thermally reduced GO has shown to be effective in increasing DSSC power conversion efficiency.

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