

PREPARATION OF DYE-SENSITIZED SOLAR CELLS USING FLOATED GRAPHITE/GRAPHENE COMPOSITE FILM AS A COUNTER ELECTRODE

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ABSTRACT

Dye-sensitized solar cells (DSCs) have attracted a lot of attention due to their low cost, ease of fabrication and reasonable photon to current conversion efficiency compared to conventional silicon based solar cells. However, further improvements are needed to enhance the performance and also to reduce the cost of production in order to produce commercially viable solar cells. In this paper, fabrication of floated graphite/graphene composite counter electrode using Sri Lankan vein graphite is described. Graphene/floated graphite counter electrode is a good substitute for platinum because of their high electrical conductivity and catalytic activities as well as its abundance. In this work, the screen printing method has been used to prepare composite counter electrodes. In order to get the maximum power conversion efficiency, the compositions of the counter electrodes and the thickness of the films are optimized. A maximum efficiency of 5.51% is obtained with 1:1 composite counter electrode while it is 8.09% with platinum counter electrode.

Keywords : Dye-sensitized solar cells, floated graphite/graphene composite films.

1. INTRODUCTION

Silicon solar cell is the most commercially available solar cell in the world due to its high efficiency and durability. But apart from these advantages, there are some disadvantages in silicon solar cells. Production cost of silicon solar cell is very high and advanced technologies are used to make silicon solar cells. Most of the highly efficient Silicon-based solar cells uses single crystal silicon. Single crystals of silicon are very expensive owing to the fact that silicon has been synthesized from pure silica and the process involves the reduction of silica at elevated temperatures using coke. This process generates tons of carbon dioxide [1]. Hence the fabrication of silicon solar cells is not environmentally friendly at all. O'Regan and Gratzel first reported high efficiency DSCs in 1991. DSCs are competitive alternatives to traditional silicon-based solar cells. DSCs are of low-cost and have convenient fabrication procedures. This electrochemical cell contains I/I₃ electrolyte, semiconductor TiO₂ mesoporous structure coated with monolayer Ru based N-719 dye and a counter electrode (CE). The highest reported efficiency for a DSC is 11.5% [2]. When compared to silicon solar cells DSCs are low cost and easy to fabricate [3]. In a DSC light is absorbed by a sensitizer, which is attached to the surface of a wide band gap semiconductor material such as TiO₂, ZnO or SnO₂ [4]. Charge separation takes place at the interface via photo-induced electron injection from the dye into the conduction band of the metal. Carriers are transported in the conduction band of the semiconductor to the charge collector. The use of sensitizers having a broad absorption band in conjunction with oxide films of nanocrystalline mesoporous morphology permits to harvest a large fraction of sunlight. DSCs also use lightly platinumized fluorine-doped tin oxide (Pt-FTO) as the counter electrodes. But the use of platinum adds a high cost to the DSC device. To overcome this problem, it is desirable to search for low-cost alternative materials for platinum that have high catalytic activity towards tri-iodide reduction [5]. Graphite has a high electronic conductivity and beneficial catalytic properties [6]. It is readily available in Sri Lanka and low cost. Graphene is another material got great attention as CEs in

DSCs due to its distinctive and unique properties [7]. Graphene used in this study was synthesized starting from Sri Lankan vein graphite of over 98.0% [8] purity using Hummers' method. Developing a low-cost, screen-printed composite material comprising of graphene and floated graphite mixture for use as CE for DSCs can be a good alternative for platinum. Floated graphite/graphene composite material was deposited on an FTO glass plate and the results obtained from a device of the configuration FTO/TiO₂/Dye/T⁺/electrolyte/Floated graphite-graphene-FTO composite counter electrode is reported. The optimization is carried out by changing the thickness of the composite layer and the mixing ratios of floated graphite and graphene.

2. EXPERIMENTAL

In this study, we developed a low-cost, screen-printed composite material comprising of graphene and floated graphite mixture for use as CE for DSCs. First, according to the modified hummers method, ball milled graphite (particle size < 45 µm) (1 g) (99%, Bogala) was added to Conc. H₂SO₄ acid (50 ml) (98%, Merck) while stirring in an ice-water bath. Then, KMnO₄ (3 g) (Sigma Aldrich) was gradually added by maintaining the temperature under 10 °C. Then, the solution was stirred at room temperature for 25 minutes followed by 5 minutes sonication in an ultrasonic bath. The stirring-sonication process was repeated for 12 times. 200 ml of distilled water was added and extra 2 hours ultrasonic treatment was carried out. Then, 1M NaOH solution (> 98%, Sigma Aldrich) was added to adjust the pH at ~ 6 and the solution was sonicated for 1 hour. Then, 20 g L-ascorbic acid (Sigma Aldrich) was dissolved in 200 ml distilled water and the mixture was slowly added to the exfoliated graphite oxide suspension at room temperature. After that, solution was heated to 95 °C for 1 hour. Then, resultant black precipitates were simply filtered by cellulose filter paper and were further washed with a 1M HCl acid solution (37%, Merck) and distilled water to neutral pH. Finally, the filtrate was freeze-dried to obtain graphene powder [9].

Floated graphite was prepared by ball milled graphite (particle size < 45 µm) (99%, Bogala). Graphite powder was added to a water beaker and it was boiled using a Bunsen burner and floated graphite on water surface was collected using a glass strip to a small beaker. Then it was heated up to 100 °C to evaporate excess water to get the floated graphite powder.

The precursor solution for counter electrode (CE) was prepared by mixing graphene, floated graphite powder (1:1 wt. ratio), distilled water, ethanol and carboxylic methyl cellulose (CMC) and grounding well in a mortar. Then the paste was screen printed on a fluorine-doped tin oxide (FTO) glass plate and sintered at 300 °C for 30 minutes. The thickness of the composite CE was varied by changing the number of screen printed layers on the FTO substrate. The working electrode (WE) of the solar cell was prepared by spraying the TiO₂ colloidal solution on a FTO glass plate by spray pyrolysis method at 150 °C and finally sintered at 500 °C in a furnace for 30 minutes [2]. The film thickness was maintained at 12-14 µm. Then, the mesoporous TiO₂ film was soaked in a 0.30 mM solution of ruthenium dye N719 in an anhydrous ethanol for 12 hours. The WE and CE are assembled by sandwiching the electrolyte I⁻/I₃⁻ as the redox couple. The current density-voltage (J-V) measurements of the DSCs were recorded under the illumination of halogen light source.

3. RESULTS AND DISCUSSION

By keeping the sintering temperature and Carboxylic methyl cellulose (CMC) amount constant, thickness of the film was varied, in order to find the optimum film thickness for different floated graphite, graphene compositions such as 1:0, 1:1, 1:2, 2:1 and 0:1. The thickness of the film was varied by applying several layers of composite pastes onto the FTO glass plate using screen printing technique and the thickness was measured using a digital micrometer.

Table 1: J-V parameters and conversion efficiencies of dye-sensitized solar cells using floated graphite : graphene in 1:1 ratio CE as a function of the thickness of the counter electrode.

Approximate Thickness (μm)	Voc (V)	Jsc (mA cm^{-2})	FF	Efficiency η (%)
30	0.562	9.40	0.43	2.26
40	0.646	9.60	0.51	3.17
50	0.683	10.74	0.60	4.39
60	0.750	11.10	0.66	5.51
70	0.754	10.31	0.62	4.81
80	0.650	8.57	0.63	3.49

Table 1 shows the J-V data and conversion efficiencies of the DSCs fabricated by changing the thickness of the composite counter electrode but keeping all other parameters constant. There is a systematic change of short-circuit current density (J_{sc}), Open circuit voltage (V_{oc}) and fill factor (FF), indicating a clear increase in efficiency as the composite electrode thickness is varied from 30 μm to 80 μm . Increasing thickness further is difficult due to the fact that a smooth film of the composite material having a large thickness cannot be fabricated without having cracks in the film. This may account for the decrease in efficiency after this optimum composite material film thickness. The best performance ($\eta = 5.51\%$) was achieved at the thickness of 60 μm and the best cell showed a short circuit current density (J_{sc}) of 11.1 mA cm^{-2} , open circuit voltage (V_{oc}) of 750 mV and fill factor 66%. When determining the performance of a solar cell, the charge transfer resistance (R_{CT}), sheet resistance (R_s) of the CE are important factors. According to the above photovoltaic parameters it can be clearly seen that the efficiency of a solar cell mainly depends on the thickness of the catalytic layer. When increasing the thickness of the films up to 60 μm the efficiencies are increased may be due to the increase of the defects and functional groups at the edge planes of the graphene layers which are highly affect to the catalytic activity of a CE. It is clear that for a thick film of CEs, the charge transfer resistance is lower than for thin layers and this directly affects the Fill factor and R_{CT} [10]. It can be seen that according to the above table at higher thicknesses the fill factor is increased than at lower thicknesses. Further, the short circuit current density (J_{sc}), increased until an optimum thickness and thereafter it dropped due to the effect of sheet resistance. As thickness increased further, the sheet resistance became prominent and starts to affect the short circuit current and reduced the cell performance.

Table 2: Photovoltaic parameters of DSCs with platinum and composite counter electrodes (CEs).

CEs	Jsc (mA cm^{-2})	Voc (V)	FF	Efficiency (%)
Pt	14.31	0.759	0.74	8.09
Composite	11.10	0.749	0.66	5.51

The DSC fabricated using usual FTO-Pt counter electrode gave an efficiency of 8.09% with a short circuit current density of 14.31 mA cm^{-2} , fill factor of 0.74 and V_{OC} of 759 mV. The maximum power conversion efficiency of the floated graphite-graphene composite CE based DSC is 5.51%, which was obtained from the contributions of a short-circuit current density of 11.10 mA cm^{-2} , fill factor of 0.66 and V_{OC} of 749 mV. Considering the costs of Pt and graphene-graphite that we prepared using Sri Lankan vein graphite 5.51% efficiency is more practical than that of 8.09% efficiency for the platinum-based counter electrode. The J-V curves obtained for the devices with composite counter electrode and Pt-FTO counter electrode are shown in Fig. 1.

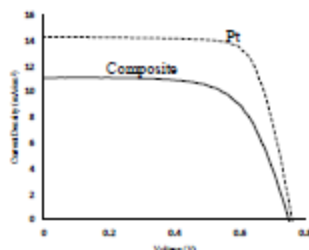


Fig. 1. The J-V Plots for Pt and 1:1 composite counter electrode solar cells.

Appearance and morphology of screen-printed carbon layers graphene, graphite, and 1:1 composite counter electrodes are shown in Fig. 2.

Scanning electron microscopy (SEM) provides morphology and structure of nanomaterials. The SEM images of the surface of the graphene counter electrodes is shown in Fig. 2 (a) and 2 (b). From the Fig. it can be observed that graphene counter electrode has layered structure, which afford to ultrathin and homogeneous graphene films. The Fig. 2 (c) and 2 (d) shows the different magnifications of SEM image of graphite counter electrode. From these SEM images it is clear that how the sheets are stalked together. The graphite counter electrode consist of small flakes and has nonhomogeneous surface compared to graphene counter electrode. The SEM images of composite counter electrode is shown in Fig. 2 (e) and 2 (f). The composite film forms an open layered structure with pores on the micrometer scale. From the three different high magnification SEM images shown in Fig. 2 (b), 2 (d) and 2 (f), it can be clearly seen that the differences of the surface morphologies of graphene, graphite and composite counter electrodes. Fig. 2 (f) simply shows the porous surface of the composite counter electrode at $1 \mu\text{m}$ magnification which highly affect to the surface area of the film. The SEM images of cross section of composite counter electrode are shown in Fig. 2 (g) and 2 (h). These images show how the layers are stack with each other.

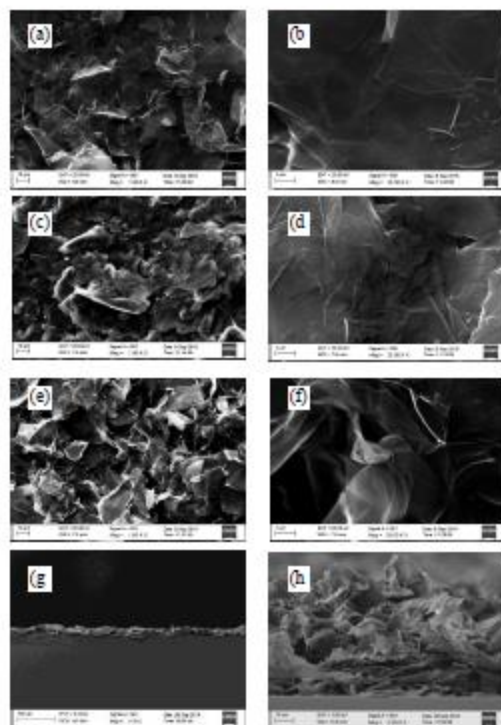


Fig. 2. SEM images of the surface of graphene counter electrode (a) 10 μm , (b) 1 μm , floated graphite counter electrode (c) 10 μm , (d) 1 μm , composite counter electrode (e) 10 μm , (f) 1 μm , cross section of composite counter electrode (g) and (h).

X-ray diffraction (XRD analysis) is a unique method in determination of crystallinity of a compound. It is the most widely used technique for general crystalline material characterization. XRD is used to measure the average spacing's between layers or rows of atoms, determine the orientation of a single crystal or grain. The XRD pattern obtained for graphene, graphite and 1:1 composite counter electrodes were given below. X-ray powder diffraction analysis was performed using Siemens D5000 Powder X-Ray diffractometer using Cu K α -radiation of wavelength $\lambda = 1.54060$ nm. The X-ray intensity was measured in the range of $15^\circ \leq 2\theta \leq 45^\circ$. The observed XRD

pattern for graphite film screen printed on a FTO glass plate is shown in Fig. 3. It shows the diffraction peak of graphite film found around $2\theta = 26.6^\circ$, corresponding to the highly organized layer structure with interlayer distance $\sim 3.35 \text{ \AA}$ along the (002) orientation.

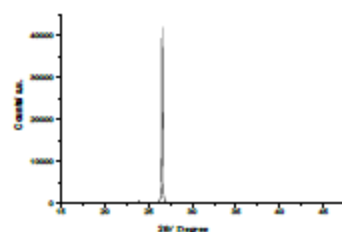


Fig. 3. XRD spectrum for fabricated graphite counter electrode.

The XRD pattern observed for graphene film screen printed on a FTO plate is shown in Fig. 4. The peaks which marked with stars are corresponding to the (110), (101) and (200) peaks of the FTO pattern. The diffraction peak found around $2\theta = 25.8^\circ$ corresponding to the graphene layer structure with average interlayer distance $\sim 3.45 \text{ \AA}$ along (002) orientation. Above two XRD spectrums show there is a significant shift in the peak position of graphene and graphite films along (002) orientation, indicating an increase in d spacing from 3.35 \AA to 3.45 \AA .

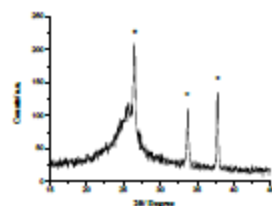


Fig. 4. XRD spectrum for fabricated graphene counter electrode.

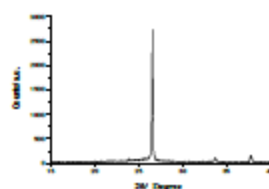


Fig. 5. XRD spectrum of composite counter electrode.

The XRD pattern observed for graphene to graphite (1:1 ratio) composite film screen printed on a FTO plate is shown in Fig. 5. The diffraction peak of graphene film found around $2\theta = 26.6^\circ$ corresponding to the graphene layer structure with average interlayer distance $\sim 3.35 \text{ \AA}$ along (002) orientation.

3. CONCLUSION

In conclusion, screen-printed floated graphite/graphene is a promising catalyst for DSC counter electrodes. A successful procedure was developed to fabricate floated graphite-graphene composite electrodes on FTO surfaces using a purposely developed screen printing technology. Graphene used was synthesized by Hummer's method starting from Sri Lankan vein graphite of over 98.0% purity. The thickness of the composite layer was varied by increasing the number of layers screen printed on successive layers. The composite electrode was used as the counter electrode in DSCs and the J-V parameters and conversion efficiencies were determined at each thickness. The best conversion efficiency of 5.51% was obtained for the composite film with 60 μm thickness. This efficiency is a result of contributions from a short-circuit current density of 11.10 mA cm^{-2} , fill factor of 0.66 and an open circuit voltage of 749 mV. Increasing the composite layer thickness beyond 80 μm was not practical due to the difficulty in smooth film formation without cracking. The SEM image of the 1:1 composition simply revealed that the high porosity of the composite counter electrode lead it to a highest efficiency and the exfoliation of graphene sheets were confirmed by the XRD and the SEM images. Also the obtained efficiency for the composite film was comparable with that of Pt electrodes. The DSC fabricated using usual FTO-Pt counter electrode gave an efficiency of 5.09 % with a short circuit current density of 14.31 mA cm^{-2} , fill factor of 0.74 and open circuit voltage of 759 mV. The lower efficiency of the low cost DSC counterweigh the higher efficiency of the expensive Pt-counter electrode based DSC.

4. REFERENCES

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