

Photovoltaic Performance of Platinum-Graphene Based Counter Electrode for Dye Sensitized Solar Cells

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Abstract Dye-sensitized solar cells were fabricated using graphene on platinum-based counter electrodes, electrolyte and titanium dioxide thin films deposited on fluorine-doped tin oxide, FTO, using doctor-blade technique. The prepared CE's were characterized using UV-Vis spectrophotometer and four-point probe for optical transmittance and sheet resistance respectively. Transmittance of single and double layers graphene on platinum was noted to be high at visible wavelength. Each layer increase in graphene corresponds to decrease of 2.41% in the optical transmittance of graphene films. Sheet resistance was found to reduce with increase in number of graphene layers with 1150, 550 and 201 Ω/sq for monolayer, bi-layer and MLG on FTO respectively. The solar cell was then characterized by analyzing the photocurrent-voltage characteristics obtained through applying external bias on the solar cell and the results showed incorporation of graphene layers in platinum based CE's increase the short circuit current density and the photoelectric conversion efficiency (η). However, incorporation of MLG on platinum based CE led to reduction of η . Pt/single Layer-Gr, Pt/double Layer-Gr, Pt/multilayer graphene CE's had a conversion efficiency of 3.42, 3.58 and 2.25 % respectively. Pt/double Layer-Gr based CE's showed the highest conversion efficiency and improvement of 6.87 % on η as compared to that of reference platinum-based CE's.

Keywords: graphene layers, sheet resistance, transmittance, Platinum/Gr counter electrode, DSSC

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1. Introduction

Dye-sensitized solar cell (DSSC) is the third generation of solar cell which has been developed by O'Regan and Gratzel in 1991 [1]. Photovoltaic device works by converting photon from solar energy to electrical energy, based on sensitization of wide bandgap semiconductor, dyes and electrolyte [2,3]. DSSCs have attracted considerable attention as a viable alternative to conventional silicon-based photovoltaic cells because of their low- production cost, high conversion efficiency, environmental friendliness, and easy fabrication procedure [4,5,6]. A typical DSSC is comprised of a titanium dioxide semiconductor, an electrolyte with redox couple (I_3^-/I^-), and the transparent conducting oxide (TCO) glass coating with platinum as the counter electrode (CE) to collect the electrons and catalyze the redox couple regeneration [7]. TiO_2 is the most suitable material for the photoanode since the edge of the conduction band is located where it allows electron injection from the excited state of the dye [8]. The photoanode plays an important role in improving light to energy conversion efficiency of DSSCs by increasing two parameters, a short-circuit current density (J_{sc}) and an open circuit voltage (V_{oc}).

TiO_2 exist in three crystalline phases namely; anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic) [9]. TiO_2 has a wide application and this has been possible since heat treating leads to a wide variation in structural, optical and electrical properties. Thus, optimization of the annealing temperature is very crucial for the application of these TiO_2 films [10,11,12]. Surface roughness of the TiO_2 thin films has been reported to have a great effect on the optical transmittivity, particularly for films annealed at high temperatures [13]. Various methods for depositing TiO_2 thin films have been reported. These methods include magnetron sputtering [14], RF sputtering [9], electron beam evaporation [15], sol-gel [16], and doctor-blade technique [17]. In this work, doctor-blade technique has been preferred due to its ease and low cost, large area of deposition, good uniformity, and high thickness control [18].

Platinum is the most common material used as the CE in DSSCs due to its high catalytic activity and resistance against iodine corrosion [19]. However, the cost of Pt which increases the cost of DSSCs and the PtI_4 setback after reacting with the electrolyte limits the application of Pt on DSSCs [20]. It is viable to find alternative materials with the characteristics of low cost, simple fabrication process, and good reduction ability to the electrolyte so that the amount of Pt applied is reduced and the

performance of DSSC is enhanced. In recent years, many researchers have been putting efforts on investigating the alternative materials to replace Pt, especially the carbon materials, such as carbon nanotubes, carbon black, mesoporous carbon, cobalt, and graphite [21-26]. Graphene is a new kind of carbon material which has a structure composed of one-atom-thick planar sheets of carbon with sp^2 hybridization that are packed densely in a benzene ring structure or honeycomb lattice [27]. Graphene has many outstanding properties such as electron transport, mechanical properties, and high surface area [28,29]. Furthermore, graphene is easily synthesized at low production cost [30,31]. Nowadays, composite materials of graphene with other materials, such as metals and polymers, enjoy a tremendous increase in interest because graphene plays a significant role in improving physical and electrochemical properties when working synergistically with other materials [27,32,33].

In this work, the effect of incorporation of graphene layers to the platinum based counter electrode to the performance of DSSC was investigated. The use of graphene on Pt-based CE is found to enhance the photo catalytic activity of the solar cell that resulted in higher conversion efficiency.

2. Experimental Procedure

In preparation of the working electrode, FTO SnO_2 : F glass substrates (Melting point $<1000^\circ C$, Xinyan Technology Co. Limited, China) were cut into 1.5×2 cm pieces using the diamond cutter. The as cut SnO_2 : F glass substrates then cleaned. A 1×1 cm² window was cut from a scotch magic tape and placed on the conductive side of the FTO glass substrates. The titanium nanoxide T/SP (18% wt, 15-20 nm, Solaronix, Switzerland) was stirred manually before use using a clean glass rod. Thin film of nano-crystalline TiO_2 films was applied by slot-coating (doctor blading) the titanium nanoxide paste on the conductive side of the FTO substrates using the cleaned tempered glass. The scotch tape was removed carefully and the coated glass was then covered by Petri dish for 30 minutes. The thicknesses of the films were controlled through applying uniform pressure in the pasting region. The samples were kept in a dark box for 20 minutes to enhance homogeneity. The samples were annealed at $1^\circ C/min$ then sintered at $450^\circ C$ for 30 minutes in a KL20 furnace. They were let to cool in the furnace

While preparing the platinum CE, the SnO_2 : F glass substrates (2.0×1.5 cm, $7 \Omega/sq$) and the tempered glass were cleaned using acetone (purity 99.5%), ethanol (purity 99.5%) and deionized water sequentially for five minutes in each step. The glass substrates were then dried using pressurized warm hair. A scotch tape was cut into 1×1 cm² window and placed on the conductive side of the FTO SnO_2 : F glass substrates. A thin layer of Platisol T/SP (Solaronix, Switzerland) was doctor bladed on the conductive side. The films were then kept for 20 minutes in a clean dark box to enhance homogeneity after which they were heat treated at annealing rate of $2^\circ C/min$ and sintered at $400^\circ C$ for 30 minutes to activate the Pt film. They were let to cool in the furnace after which they were instantly used to fabricate the DSSCs.

In preparation of Pt on graphene based CEs, the CVD graphene (coverage $> 98\%$), in which gaseous carbonaceous precursor, methane, was flowed at $1000^\circ C$ over FTO SnO_2 : F glass substrates (1.5×2 cm), (Graphene Laboratories Inc., USA) were used [34, 35]. Films were soaked in ethanol for five minutes and then thoroughly rinsed with deionized (DI) water for 5 minutes. The films were then dried using pressurized air and placed in a hot air furnace $50^\circ C$ where they were retrieved for coating. A scotch tape was cut into 1×1 cm² window and placed on the conductive side of the graphene coated FTO SnO_2 : F glass substrates. A thin layer of platisol T/SP (Solaronix, Switzerland) was doctor bladed on the graphene side which was identified using a multimeter. The films were then kept for 20 minutes in a clean dark box to enhance homogeneity after which they were heat treated at an annealing rate of $2^\circ C/minute$ and sintered at $400^\circ C$ for 30 minutes to activate the Pt on graphene film. They were let to cool in the furnace after which they were instantly used to fabricate the DSSCs. CE samples were analyzed using UV-Vis spectrophotometer.

A dye-sensitized solar cell was assembled by sealing the dye-coated TiO_2 electrode with the platinum-coated FTO counter electrode using a dupont surlyn (meltonix 1170-25 solaronix) a thermal plastic hot-melt sealant with a thickness of $50 \mu m$ leaving a small space for the electrolyte introduction. The electrolyte was then introduced into the space between the electrodes via the small space that was left during sealing, which was later sealed by already melted plastic hot-melt sealant at $70^\circ C$. Solar cell was then characterized by analyzing the I-V characteristics obtained through applying an external bias on the cell in a dark room. A 450 W halogen lamp adjusted to an intensity of $100 mW/cm^2$ was used. The irradiance on the DSSC's was maintained at $100 mW/cm^2$ with the use of a solar power meter TM206 and single crystal Si photoanode. During characterization, the cells were covered with a black-printed paper with a hole measuring $1 cm^2$ for the active area. The following parameters were taken; open circuit voltage, short circuit current, and fill factor.

3. Results and Discussion.

3.1. Optical Properties of Graphene Films on FTO

Transmittance spectra of bare FTO, single layer graphene, double layer graphene and multi-layer graphene layers on FTO CEs was obtain from 280 nm to 800 nm. The transmittance of both bare FTO and Gr on FTO CEs increases with the change in wavelength from 290 nm to 800 nm. At shorter wavelengths, below 280 nm, the transmittance is observed to be low for all samples. With the increase in graphene layers from monolayer, bi-layer then few layers on FTO, the optical transmittance is noted to reduce as shown in Figure 1.

At 575 nm, all sample show maximum transmittance with bare FTO, monolayer, bi-layer and multi-layer on FTO having 83.5, 81.1, 78.7, and 64.5 % respectively. The transmission of graphene displays the expected optical density of about 2.3% with reference to the bare FTO.

Further, the transmittance trend of graphene on FTO to that of the bare FTO is similar depicting that graphene-FTO interface does not cause optical interference. The transmittance of graphene was noted to drop with the increase in the number of layers, with multilayer graphene on FTO giving the lowest transmittance that is below 70%. Single layer and bi-layer on FTO is highly transparent in the visible-UV range. High transmittance of few layers of graphene on FTO is significant for DSSC in allowing the movement of incident sunlight down to the active region of DSSC photoanode. Graphene can absorb light of wavelength range from 200 to 800 nm and therefore the addition of graphene layers caused an increase of light absorbance thus reducing the transmittance as observed.

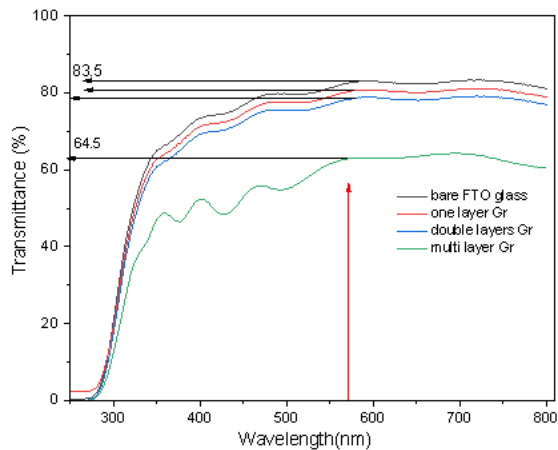


Figure 1. Transmittance spectra of bare FTO glass, single, double and multi-layer graphene on FTO glass

Platinum on graphene-based CE's transmittance spectra were obtained from 280-800 nm and all samples exhibit similar trend. At shorter wavelength the transmittance is observed to be low. However, with the change in wavelength, from 300 nm to 800 nm, the transmittance of all samples increases as shown in Figure 2.

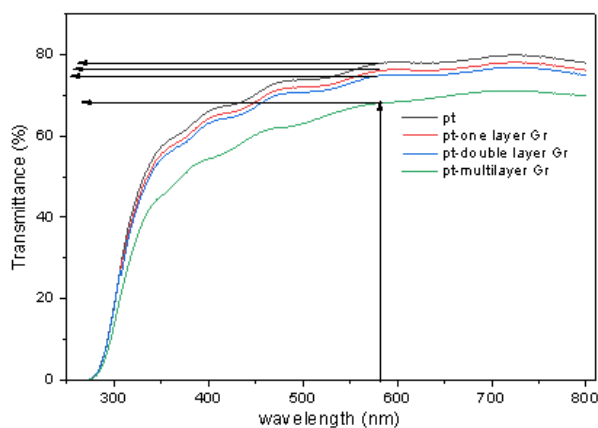


Figure 2. Transmittance spectra of bare FTO, platinum deposited on FTO and Pt on single, double and multilayer graphene using doctor blade method

From 350-400nm, all the four samples indicate transient instability, caused by excitation and cross relation of the FTO atoms. Beyond 450 nm, the three samples experienced dynamic stability. The average transmittance obtained at wavelength of 575 nm is 79.6%, 77.2%, 74.8% and

62.5% for Pt on FTO, Pt /one layer Gr, Pt/ bi-layer graphene and Pt/ multi-layer Gr on FTO respectively. Incorporation of platinum on Gr/ FTO was noted to slightly lower the transmittance as illustrated in Table 1.

Table 1. Transmittance of Gr on FTO and Pt/Gr on FTO glass CE's

Gr layers	Transmittance (%)	
	FTO/Glass	Pt/FTO/Glass
Bare	83.5	79.6
Monolayer	81.1	77.2
Bi-layer	78.7	74.8
Multi-layer	64.5	62.5

It can be observed that there is no optical interference that occurs when platinum is interface with graphene within the visible and NIR range (400-850 nm). The transmission curves however coincide at the extremes, both within the ~300nm range and the ~850 nm range indicating reduced transmission of ultraviolet and NIR radiation (beyond 850 nm). This is mainly caused by the FTO glass substrate which undergoes transient instability within these wavelength ranges hence absorbing almost all the incident radiations. The highest optical transmittance of graphene and Pt/Gr CE's is maximum at 750 nm with the Pt CE indicating a transmission of 78.5% whereas Pt/ one layer Gr CE and Pt/ bi-layer Gr having a transmission of 77.3% and 75.4% respectively. The high and constant transmittance of 70% in the most of the visible range indicates that platinum on graphene layers CE's can be used for rear illumination and in window application.

3.2. Sheet Resistance of Graphene Layers on FTO Substrate

The sheet resistance of graphene layers deposited on FTO substrate was evaluated using four-point probe. This was done by taking four equally spaced, co-linear probes to make electrical contacts on graphene deposited on FTO. Direct current was applied between the outer two probes (1 and 4) and voltage drop measured between the inner probes (2 and 3) then R_s obtained. Sheet resistance was observed to be high on single layer graphene on FTO and low on multi-layer graphene on FTO as given in Figure 3.

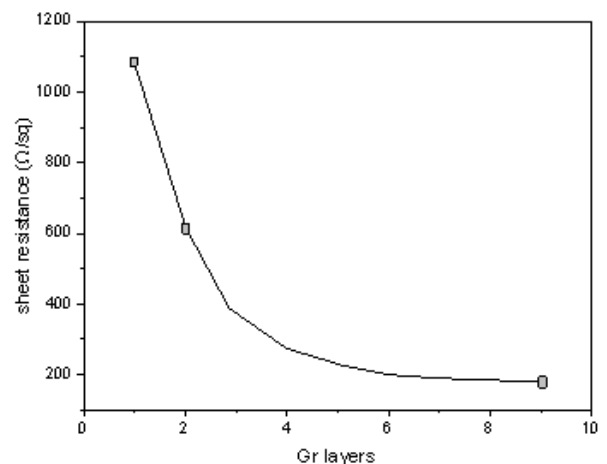


Figure 3. Variation of sheet resistance (Ω/sq) with graphene layers

Single layer graphene on FTO is noted to have the highest sheet resistance of $1150 \Omega/\text{sq}$. With the increase in graphene layers, the sheet resistance reduces with double layer and multi layer graphene on FTO having 550 and $201 \Omega/\text{sq}$ respectively. Surface resistance of the graphene sheets is very important in an electrochemical cell, as the sheet resistance determine the resistance of the electrons in the cell, influencing directly on the efficiency of the DSSC. The comparison of transmittance of platinum on graphene layers CE's with obtained sheet conductance is shown in Figure 4. Sheet conductance of graphene based CE's is noted to increase with number of graphene sheets.

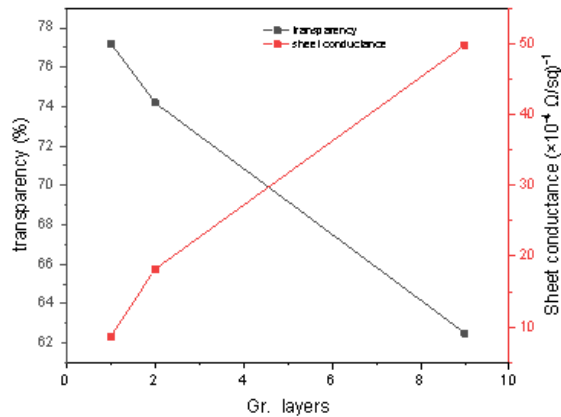


Figure 4. Variation of transparency and sheet conductance as function of graphene layers supporting Pt

3.3. I-V Characteristic Curve for DSSC Fabricated Using Platinum on Gr CE's

DSSCs were fabricated to evaluate the power conversion efficiencies of the solar cells with Pt deposited on different number of graphene layers. The current density- voltage curves of both graphene based CE's and reference Pt-based CE's DSSCs recorded under 1000 Wm^{-2} , A.M 1.5 irradiation are given in Figure 5. The I-V curves obtained are observed to follow typical trend for DSSCs.

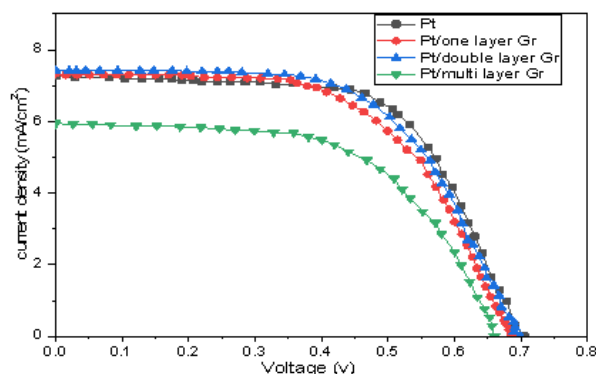


Figure 5. The photovoltaic current density-voltage curves of Pt/graphene layers CE's and reference Pt DSSCs

The solar cell parameters, including open-circuit (V_{OC}), short-circuit photocurrent density (J_{sc}), fill factor (FF), and power conversion efficiency (η) were obtained and summarized in Table 2. Incorporating graphene on

platinum-based CE's is observed to affect J_{sc} , V_{OC} , FF and η of DSSCs.

Table 2. Photovoltaic parameters Pt/graphene layers and Pt based CE's DSSCs

Sample	V_{OC} (v)	J_{sc} (mA/cm^2)	FF (%)	P_{max} (mW/cm^2)	η (%)
Pt	0.72	7.27	0.64	5.23	3.35
Pt/bi-layer Gr	0.71	7.63	0.66	5.42	3.58
Pt/single layer Gr	0.70	7.52	0.65	5.26	3.42
Pt/multi-layer Gr	0.66	5.98	0.57	3.95	2.25

The reference DSSC fabricated with Pt as counter electrode has V_{OC} , J_{sc} , FF and efficiency of 0.72V, $7.27 \text{ mA}/\text{cm}^2$, 0.64 and 3.35 % respectively. Incorporation of graphene based CE's seem to affect the characteristics of the prepared DSSCs. Pt on double layer Gr CE's was noted to improve J_{sc} , FF and η to $7.63 \text{ mA}/\text{cm}^2$, 0.66 and 3.58 % respectively with slightly lower value of V_{OC} to that of Pt reference counter electrode. The improved performance of the solar cells with Pt on double layer Gr electrodes is related to the improved electron transfer of graphene on the counter electrode. Comparing the maximum output power, Pt on bi-layer Gr CE's gives the highest maximum power of $5.42 \text{ mW}/\text{cm}^2$. Pt on single layer Gr CE's improves J_{sc} from 7.27 to $7.52 \text{ mA}/\text{cm}^2$, FF slightly changing from 0.64 to 0.65 and also conversion efficiency improving from 3.35 to 3.42%. Incorporation of multi-layer Gr on Pt CE's, give relatively low values of V_{OC} , J_{sc} , FF and overall conversion efficiency. The observable difference in the DSSCs fabricated is on J_{sc} , FF and PCE but there is no significant variation in both the V_{OC} . Pt on few layers Gr, single and double layers, improve on the J_{sc} and hence on the overall conversion efficiency. This improvement can be attributed to better electrons conductivity and enhanced catalytic activity for the reduction Γ_3 in both single layer and bi-layers of graphene CE's. The conversion efficiency of DSSC is observed to increase with increase in graphene layers from monolayer to bi-layer then drop with MLG on pt counter electrode. Incorporating single layer graphene on platinum improves η from 3.35 to 3.58 % and double layer improve from 3.35 to 3.42%. Pt on double graphene increases the conversion efficiency by 6.86 %.

In the I-V curve, the tangent slope of vertical part near the V_{OC} is proportional to the reciprocal of the series resistance ($1/R_s$) [36]. I-V curves demonstrate a direct relationship between the R_s and J_{sc} in that the lower the series resistance, the higher the J_{sc} .

From the R_s obtained, Pt on bi-layer graphene with low sheet resistance has the highest J_{sc} and improved performance of the cell. Based on sheet resistance, sheet conductance and high transparency of CE's, the performance of a solar cell can be determined. For maximum DSSC efficiency, the sheet resistance should be small and optical transmittance should be large as noted in Pt/bi-layer graphene CE's. With an increase in the number of graphene layers, both the optical transmittance and sheet resistance decrease (sheet conductance increases) as earlier noted. Thus, sheet resistance and optical transmittance are two competing parameters for high

efficiency of graphene-based CEs. The enhanced conductivity of graphene film is good for the increase of J_{sc} and reducing the internal resistance (R_s) of the solar cell. The observed drop in sheet resistance from monolayer to bi-layer Gr on FTO is beneficial to the performance of solar cell, because it improves the J_{sc} , FF and η . In this work, Pt/bi-layer Gr was found to have good conductivity and appropriate transparency that is required for better performance of a solar cell.

This is consistent with reports by Wang et al who demonstrated a proportional decrease in optical transparency (transmittance) with an increase in graphene layer number from 1 to 8 [37]. Reports have also noted the decrease in series and sheet resistance of graphene structure with graphene's rising number of layers [37,38,39]. However, although the nature of variation remains the same, the exact amount of reduction in transmittance, variation in R_s , series resistance, shunt resistance, V_{OC} , J_{sc} , FF and η with graphene thickness is purely subjective to the consecutive layers of graphene layer. Bi-layer and tri-layer graphene, in most cases, offer high efficiency attributed to their adequate transparency as well as sheet conductance [40,41,42].

4. Conclusion

Incorporation of Gr on Pt based CEs improved J_{sc} , FF , and η . Pt on double layer Gr improves J_{sc} from 7.27 to 7.63 mA/cm², FF from 0.64 to 0.66 and η from 3.35 to 3.58% from Pt reference solar cell. Pt on single layer Gr improved overall conversion efficiency from 3.55 to 3.42%. Addition of graphene layers reduces the sheet resistance and improves the sheet conductance of Pt based CEs enhancing the efficiency of DSSCs. Platinum/bi-layer graphene on FTO was found to have improved sheet resistance, sheet conductance and appropriate transparency for better performance of a DSSC. Incorporation of graphene to platinum thus increases availability of the metal particles for electron transfer in the CE. Furthermore, graphene could also provide a fast diffusion pathway for the electrolyte and ensure excellent electrode-electrolyte contact, which improves the electron transfer rate at the interface thus improving the performance of the solar cell.

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