Enhanced Photovoltaic Parameters of Titania/Graphene Nanocomposites Based Dye Sensitized Solar Cells

G E Khedra, T Abdallah, R E Morsi and H Talaat*

*Corresponding Author E-mail: hassantalaat@hotmail.com

Abstract. The efficiency of carbon-based dye sensitized solar cells (DSSCs) is improved by mixing titania with graphene (GR) sheets. The composite films of GR sheets and TiO2 were characterized using field emission scanning electron microscopy (SEM). The grinding of GR with TiO2 leads to smaller size TiO2 nanoparticles which increases their surface area. The photovoltaic efficiency varied with the mixing ratio giving the highest efficiency at a ratio of 1 wt. % of GR to TiO2. The increase in the photovoltaic efficiency is more than doubled the one without GR under the same conditions. Mesoporous carbon from candle flame and N3 dye were used instead of Pt and N719 dye to reduce the cost.

1. Introduction
Dye sensitized solar cells (DSSCs), were presented firstly in 1991, where electrons are produced when the dye molecules joined to electrodes were excited by exposing to sun rays. To obtain enough power, the mesoporosity of the photo-electrode of a DSSC maximize the amount of the adsorbed molecules of dye. At the same time it reduces the resistance to diffuse of electrolyte to the molecules of dye. The photo-electrode based on titanium dioxide nanoparticles (TiO2) nanoparticles, coated on a conductive glass such as fluorine-doped tin dioxide (FTO) is the most known and common mesoporous ones. There are many semi-conducting nanomaterials that have been used such as those composed of zinc oxide (ZnO) 2-4 tin oxide (SnO2)5 and niobium pentoxide (Nb2O5)5 nanoparticles. A common problem with these nanomaterials is the charge recombination resulting from reaction between the photo-excited electrons which diffuses slowly towards them, and the oxidized parts of electrolyte at the surface of the electrode. This problem has forced scientists to find alternative solutions. They used other photo-electrode materials, such as those containing carbon such as carbon particles, carbon nanotubes and, most recently, graphene (GR). GR is a monolayer. Its thickness is 0.35 nm, i.e., as thick as an atom6,7 and has high flexibility and stiffness, impressive thermal stability and a large specific surface area8,9. It has high charge carrier mobility (2x105 cm²V⁻¹s⁻¹) and high conductance because it has low band-gap10,12. GR has been applied to photo-electrodes because it has fast electron transfer, its unique properties as high thermal conduction and high optical transmittance13. These characteristics can be utilized to enhance the performance of DSSCs where the photo-excited electron is transferred from the...
dye to the metal oxide and moves to the current collector. Losses of electrons happen for many causes such as the difference in voltage between LUMO level of the dye and the Fermi level of the semiconductor, also from the ohmic resistance in the metal oxide layer. Several approaches have been created to reduce these losses. Then, as a good approach, several teams have decided to apply GR materials to enhance the performance of the metal oxide part in DSSCs. The incorporation of GR into the metal oxide layer took several ways such as grinding of powders, ball milling, colloidal aggregation, and electrospinning. Using GR with the special dye N719 and platinum electrode resulted in an increased efficiency up to 23%.

Basically, figure 1 shows the diagram of the energy band of the relative positions of the CB and the valence band (VB) and LUMO, HOMO of the dye. The light penetrates the solar cell through FTO absorbed by the dye sensitizer which loaded on the TiO₂ layer, causing electron excitation then the electron injected to the CB of the neighbouring TiO₂ atoms then the electron moves to the current collector. The electron moves to the cathode then moved to the electrolyte. Finally, the electrolyte gives an electron to the dye sensitizer, regenerating the dye and completing the circuit. The incorporation of GR into the composite resulted in reducing the band gap about 0.3 eV rendering the GR-TiO₂ hybrid material sensitive to visible light irradiation. On joining TiO₂ nanoparticles and GR, excited electrons could move to the CB of the composite via a percolation mechanism. As a result, the photo-induced electrons can easily move to the GR moiety, resulted in the best isolation and prolonged recombination time of charge carriers.

![Figure 1. Energy diagram for a DSSC, VB and CB refer to the valence band and conduction band, respectively. LUMO and HOMO levels are the least unoccupied and highest occupied molecular orbitals of the sensitizer. Blue arrows represent the energy transfer. E_F is Fermi level of GR.](image)

In this work, GR has been used in the TiO₂ scaffolding to improve electrons transport, adsorption of dye and light scattering. Since the cost of the elements in the production of solar cells, plays an important role, we have replaced the expensive Pt with carbon (candle flame) which possess mesoporous surface. Furthermore, Carbon films have high catalytic activity and chemical stability against the corrosive electrolyte in the DSSCs. Further reduction of the cost was carried out by using N3 dye instead of the costly N719 also used for reducing the recombination reaction. The photovoltaic efficiency η defined as
\[ \eta = \frac{P_{\text{max}}}{P_{\text{in}}} = \frac{V_m J_m}{P_{\text{in}}} = \frac{FF V_{\text{oc}} J_{\text{sc}}}{P_{\text{in}}} \]  \hspace{1cm} (1)

where \( P_{\text{max}} \) is the maximum output power and \( V_m, J_m \) are the maximum output voltage and output current density respectively.

\[ FF = \frac{V_m J_m}{V_{\text{oc}} J_{\text{sc}}} \]  \hspace{1cm} (2)

where \( FF \) is the fill factor and \( V_{\text{oc}}, J_{\text{sc}} \) are the open circuit voltage and short current density respectively.

2. Experimental
2.1. Materials
Powdered graphite, sodium nitrate, fluorine doped tin oxide coated glass slide (FTO) 3mm, surface resistivity 10 \( \Omega \) sq, iodine (I\(_2\)), potassium iodide (KI), TiO\(_2\) nanopowder (21 nm) and cis-bis(isothiocyanato) bis (2-2-bipyridyl-4,4-dicarboxylato) ruthenium (II) synonym; (N-3 dye) were of analytical grade and purchased from Sigma–Aldrich (Germany). All of the other chemicals were of analytical reagent grade and used without further purification.

2.2. Synthesis of GR:
Graphene oxide (GO) was synthesized from graphite (powder < 20 \( \mu \), synthetic, Sigma–Aldrich) by a modified Hummers method\(^2^\). In a brief, 4 g of graphite powder and 2 g of NaNO\(_3\) were put in a glass beaker. After that, 92 mL concentrated H\(_2\)SO\(_4\) was added and stirred slowly in an ice water bath. 16 g of KMnO\(_4\) was added gradually under stirring over 60 min and kept stirring for another 120 min. The mixture was then stirred at 35 \( ^\circ \)C for 120 min, and then 24 mL of H\(_2\)O\(_2\) (30 wt. %) was added and the mixture was stirred for 120 min at room temperature. The mixture was centrifuged and then washed with H\(_2\)O. GR was prepared by the reduction of GO by hydrazine according to the modified Hummers method, as following: 100 mg GO was put in a 250-mL round-bottom flask then 100 mL water was added, A heterogeneous yellow-brown dispersion was obtained. This mixture was sonicated until it became apparent with no visible particles. Hydrazine hydrate was added (1.00 mL, 32.1 mmol) and the solution was heated at 100 \( ^\circ \)C under a water-cooled condenser for 24 hours. GO Gradually precipitated as a solid black material. This product was isolated by filtration, washed with water (5 × 100 ml) and methanol (5 × 100 ml), and dried at 60 \( ^\circ \)C.

2.3. Preparation of the TiO\(_2\)-GR Paste:
We prepared The paste by grinding TiO\(_2\) powder and the prepared GR with different concentrations; 0.5, 0.75, 1, 1.5, 2, 2.5, 3 and 5 wt. % of GR with 1 ml of dis. H\(_2\)O containing (10 % v:v) acetyl acetone. The slurry is then further diluted by adding 1 ml of dis. H\(_2\)O and a few drops of triton X-100 to the suspension. The mixing between TiO\(_2\) and GR is completed by a long and vigorous mixing of GR and TiO\(_2\) in solution using an ultrasonic treatment during the paste preparation. The obtained paste is stored in a dark bottle until use, and whenever used, it is sonicated for 15 minutes. Subsequently, the layer is thermally annealed to get a composite porous film.

2.4. Electrolyte preparation
Polycarbonate (60 wt. %), polyethylene glycol M.wt. (4000) (40 wt. %), potassium iodide (0.65 M) and iodine (0.065 M) were mixed in sonicator for 15 min. It is worth mentioning the observation that that higher current and fill factor are obtained when using fresh electrolyte.
2.5. DSSC fabrication procedure
The working electrodes in this study were prepared using spin coating of TiO$_2$ and GR/TiO$_2$ composites on fluorine doped tin oxide (FTO) conducting transparent glass substrate. Electrodes of more than one layer of the coat were fabricated on FTO. Each layer was made by spin coating 0.025 ml of the paste at 7000 rpm for 3 sec. The coated FTO were sintered at 450 °C for 30 min to remove organic compounds and to improve interconnections between nanoparticles. The sintered electrodes were placed in N3 dye dissolved in ethanol (0.006 M) for 24 h., drops of fresh electrolyte were added to GR/TiO$_2$ electrode. The counter electrodes were coated with a thin film of carbon (candle flame). The dye coated GR/TiO$_2$ electrode and carbon coated counter electrode were sandwiched together with clips using Parafilm.

2.6. Characterization
We got scanning electron microscopy (SEM) images using SEM Model Quanta 250 FEG (Field Emission Gun) with attached Energy Dispersive X-ray (EDX) Analyses Unit, with an accelerating voltage of 30 KV., and magnification up to $10^5$. X-ray diffraction (XRD) patterns were carried out on a powder X-ray diffractometer at 40 kV and 40 mA in the range of $2\theta = 10–80^\circ$ using Cu Kα radiation (Model XPert pro). The photovoltaic performance of all prepared devices was measured using a Class 3A Sun Simulator (in the visible and near-infrared range) at AM 1.5, 100 mW cm$^{-2}$ calibrated with a standard solar cell, and a Keithley 2635A as a source-meter in ambient conditions. The active area of each device was designed to be 1 cm$^2$.

3. Results and Discussion
The XRD patterns of the GO and GR sheets are shown in figure 2 (a and b), respectively. The GO displays a (001) diffraction peak at $2\theta = 11.4^\circ$ as shown in figure 2.a. After the reduction of graphene oxide by hydrazine hydrate to GR, a new (0 02) diffraction peak appears at about $2\theta = 26.4^\circ$ which is clearly seen in Figure 2.b according to an interplanar distance of 0.42 nm. This means that the periodic structure of GO was reduced and the conjugated GR network was successfully formed.

![Figure 2. XRD patterns the graphene oxide (a) and the graphene sheets (b)](image-url)

Figure 3.a shows the TEM image for TiO$_2$ before mixing with GR and figure 3.b shows the TEM image for thin layered nano-sheets of GR. The surface morphology of both TiO$_2$ and GR-TiO$_2$ film have been examined using SEM as shown in figure 4.a and 4.b, respectively. Close examination shows that, the TiO$_2$ particles are spherical and the particle sizes of TiO$_2$ are ~17-25 and of GR/TiO$_2$ are ~15-22 nm. It appears that grinding GR with TiO$_2$ nanoparticles decreases the TiO$_2$ particle size, hence increasing the specific surface area and amount of dye that would enhance the absorption. The SEM image of GR/TiO$_2$,
in Figure 4.b, presents the incorporation of GR sheet between the TiO$_2$ particles. The optical absorption of our dye is shown in

![TEM images](image1)

**Figure 3.** TEM images of TiO$_2$ nanoparticles (a) and graphene sheets (b)

![SEM images](image2)

**Figure 4.** SEM images of TiO2 nanoparticles (a) and graphene/TiO2 composites (b)

Figure 5, it has absorption band (450–550 nm) that is centered at ~503 nm. At first, cells with layers of TiO$_2$ photoelectrodes only, were tested with different thickness. The fabricated TiO$_2$ different layers ranged from one to four. The test showed that the photovoltaic efficiency was highest for cells with 3 layers, this configuration gives 0.23 % conversion efficiency as shown in table 1.
### Table 1: Performance parameters of the DSSCs with different layers of TiO$_2$

| Thickness | $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | $P_{max}$ (Watt) | F.F % | $\eta$ % |
|-----------|--------------|-----------------------|------------------|-------|---------|
| 1 layer   | 0.522        | 0.97                  | 0.1              | 0.21  | 0.1     |
| 2 layers  | 0.5          | 0.32                  | 0.03             | 0.19  | 0.03    |
| 3 layers  | 0.516        | 1                     | 0.23             | 0.44  | 0.23    |
| 4 layers  | 0.516        | 0.3                   | 0.03             | 0.21  | 0.03    |

Photo-electrodes with fewer layers don’t load enough dye while electrode with more layers limit the diffusion of electrolyte redox molecules, resulting in an optimum number of three layers. Then, porous nanocrystalline TiO$_2$ photo-electrodes and nanocomposite porous layers of the same TiO$_2$ anatase nanoparticles mixed with different ratios of GR sheets from 0.5 to 5 wt.% were tested.

![Figure 5. UV-Vis absorption spectrum of N3 dye](image)

The I–V characteristics of DSSCs with TiO$_2$ mixed with the different ratios of GR measured under one sun (AM 1.5, 100 mW cm$^{-2}$) is shown in Figure 6. The photovoltaic performance parameters: the open-circuit photovoltage ($V_{oc}$), short-circuit photocurrent density ($J_{sc}$), maximum output power ($P_{max}$), fill factor (FF) and photoelectric conversion efficiency ($\eta$) of the DSSC with different GR ratios, are tabulated in table 2. As the GR content in the mixture increased, the current shows a slight change as observed in table 2. There is an increase in the efficiency for TiO$_2$ film with increasing contents of GR (0.5, 0.75 and 1 wt %), then there is a gradual decrease with increasing the GR ratios between (1.5, 2, 2.5, 3 and 5 wt. %). The above results show that incorporating the GR ratio in TiO$_2$ film for photo anode electrode up to 1 wt. % helps to increase the electro-catalytic reaction and intake of N3 dye.
Table 2: Performance parameters of the DSSCs with different GR ratios

| Percentage of GR% in sample | $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | $P_{max}$ (Watt) | F.F % | $\eta$ % |
|-----------------------------|--------------|----------------------|------------------|-------|---------|
| 0                           | 0.755        | 0.96                 | 0.26             | 35.70 | 0.26    |
| 0.5                         | 0.635        | 1.11                 | 0.36             | 51.07 | 0.36    |
| 0.75                        | 0.661        | 1.10                 | 0.31             | 42.64 | 0.31    |
| 1.0                         | 0.658        | 1.04                 | 0.54             | 78.91 | 0.54    |
| 1.5                         | 0.641        | 1.06                 | 0.44             | 64.76 | 0.44    |
| 2.0                         | 0.616        | 1.09                 | 0.37             | 55.11 | 0.37    |
| 2.5                         | 0.618        | 1.10                 | 0.34             | 50.01 | 0.34    |
| 3.0                         | 0.623        | 1.04                 | 0.47             | 72.54 | 0.47    |
| 5.0                         | 0.612        | 1.06                 | 0.42             | 64.74 | 0.42    |

The corresponding energy conversion efficiency of the DSSCs using the GR-TiO$_2$ composite film was measured to be 0.54 % and the $J_{sc}$, FF and $V_{oc}$ are higher than those of the DSSCs without GR (0.26 %). The addition of GR more than 1 % diminished the crystallization of particles on the surface of photoelectrodes, that may result in decreasing adsorption of the dye and lowering the efficiency of the DSSCs.

Figure 6. The photovoltaic ($J$–$V$) curves of DSSCs with working electrode with different ratios of graphene to titania.
The increase in $\eta$ with increasing the contents up to 1 wt. % of GR is due to the improvement in dye adsorption. Furthermore, such an increase may result from the high specific surface area and a lot of chemical disorders of GR sheets causing more dispersion and adsorption of the dye $^{30,31}$.

4. Conclusions.
Different thickness of TiO$_2$ layers were first optimized giving highest conversion efficiency for three layers. Layers of GR/TiO$_2$ composites with different GR's ratios between (0.5 and 5 wt. %) have been fabricated. The presence of GR sheets in the prepared composites and the complete mix with TiO$_2$ were confirmed using TEM, SEM and XRD analyses. The counter electrode was fabricated as carbon film (candle flam) instead of platinum and the dye employed was the inexpensive N3 dye. The electrode made of 1 wt. % GR and TiO$_2$ gives the highest photovoltaic efficiency 0.54%. This procedure will enable paving the way to the development of carbon-based DSSC technology. GR as a composite material for the preparation of working electrode and using the mesoporous amorphous carbon as a counter electrode. Furthermore, the use of N3 dye instead of the expensive N719 as well as the carbon counter electrode as an alternative to Pt will lower the cost of fabrication of the DSSCs.

Acknowledgment
The authors greatly appreciate the generous support of the Egyptian STDF grant ID 377.

References
1. ORegan B and Gratzel M 1991 Nature 353 737.
2. Environ E, Xu F and Sun L 2011 Energy & Environmentalal 4 818.
3. Xu J, Chen Z, Zapien J, Lee A and Zhang C W 2014 Adv.Mater.
4. Environ E, Bendall J S, Etgar L, Tan S, Cai N, Wang P, Zakeeruddin S, Gratzel M, Well and M E 2011 Energy Environ. Sci. 4 2903.
5. Cavallo C, Pascasio F D, Latini A, Bonomo M and Dini D 2017 J. Nanomater. 2017.
6. Raimond J M, Brune M, Computation Q, Martini F and De Monroe C E, 2004 306 666
7. Zhong J, Jun Y, Carter K and James M T 2011 Acs.Nano 5 4112.
8. Pan X, Zhao Y, Liu S, Korzeniewski C, Wang S and Fan Z 2012 ACS Appl. Mater. Interfaces 4 3944.
9. Tongxiang C, Ruitao L, Zheng-Hong H, Shuxiao C, Zexia Z, Xin G, Yi J, Xinning L, Kunlin W, Dehai W and Feizu K 2013 J. Mater. Chem. A 1 5736.
10. Madhavan A A, Kalluri S, Chucko D K, Arun T A, Nagarajan S, Subramanian K R V, Nair A S, Nair S V and Balakrishnan A 2012 RSC Advances 2 13032.
11. Kusumawati Y, Martoprawiro M A and Pauporte T 2014 J. Phys. Chem. C 118 9974
12. Guoab S and Dong S 2011 Chem Soc Rev 40 2644.
13. Wang J T, Ball J M, Barea E M, Abate A, Alexander-Webber J, Huang J, Saliba M, Mora-Sero I, Bisquert J, Snaith H and Nicholas R J 2014 Nano Lett. 14 724.
14. Roy-mayhew J D and Aksay I A 2013 Chem. Rev.
15. Kim, A, Kim J, Kim M, Ha S, Tien N and Kang M 2012 Bull. Korean Chem. Soc. 2012, 33 3355.
16. Yang N, Zhai J, Wang D, Chen Y and Jiang L 2010 AcsNano 4 887.
17. Shu W, Liu Y, Peng Z, Chen K, Zhang C and Chen W 2013 JOURNAL OF ALLOYS AND COMPOUNDS 563 229.
18. Sun S, Gao L and Liu Y 2010 083113 2010.
19. Zhi J, Cui H, Chen A, Xie Y and Huang, F. 2015 Journal of Power Sources 281 404.
20. Liu J, Fu X, Cao D, Mao L, Wang J, Mu D, Mi B, Zhao B and Gao Z 2015 ORGANIC ELECTRONICS 23 158.
21. Chem J M 2012 J. Mater. Chem. 22 17027.
22. Fang X, Li M, Guo K, Zhu Y, Hu Z, Liu X, Chen B and Zhao X, 2012 Electrochimica Acta 65 174.
23. Durantini J, Boix P, Gervaldo M, Morales G M, Otero L, Bisquert J and Barea E M 2012 Journal of Electroanalytical Chemistry 683 43.
24. Peining Z, Nair A S, Shengjie P., Shengyuan Y and Ramakrishna S 2012 ACS Appl. Mater. Interfaces 39 4.
25. Tan L, Ong W, Chai S and Mohamed A R 2013 Nanoscale Research Letters 8 1
26. Williams G, Seger B and Kamat P V 2008 AcsNano 2 1487.
27. Guo C X, Yang H, Bin Sheng Z M, Lu Z S and Song Q L 2010 Angew. Chem. Int. 49 3014.
28. Koh T M, Nonomura K, Mathews N, Hagfeldt A, Grätzel M, Mhaisalkar S G and Grimsdale A C 2013 J. Phys. Chem. C 117 15515.
29. Kim S, Parka J and Kim C. 2015 J. Phys. Chem. C 119 26064.
30. Trancik J E, Barton S C and Hone J 2008 Nano Lett. 8 982.
31. Tsai T, Chiou S and Chen S 2011 Int. J. Electrochem. Sci. 6 3333.