Studies on graphene zinc-oxide nanocomposites photoanodes for high-efficient dye-sensitized solar cells

Cite as: AIP Conference Proceedings **1877**, 090005 (2017); https://doi.org/10.1063/1.4999900
Published Online: 11 September 2017

N. A. S. Effendi, N. S. Samsi, S. A. Zawawi, et al.

Studies on Graphene Zinc-Oxide Nanocomposites Photoanodes for High-Efficient Dye-Sensitized Solar Cells

N.A.S. Effendi[1,2,a)], N.S. Samsi[1,2,b)], S.A. Zawawi[3,c)], O.H. Hassan[4,d)], R. Zakaria[1,2,e)], M.Z.A. Yahya[2,5,f)], A.M.M. Ali[1,2,g)]

[1]*Faculty of Applied Sciences, UniversitiTeknologi MARA, 40450 Shah Alam, Selangor, Malaysia*
[2]*Ionics Materials & Devices Research Laboratory (iMADE), Institute of Science, UniversitiTeknologi MARA, 40450 Shah Alam, Selangor, Malaysia*
[3]*Centre of Foundation Studies, UniversitiTeknologi MARA, PuncakAlam Campus, Selangor, Malaysia*
[4]*Faculty of Arts and Design, UniversitiTeknologi MARA, 40450 Shah Alam, Selangor, Malaysia*
[5]*Faculty of Defence Science & Technology, UniversitiPertahananNasional Malaysia, 57000 Kuala Lumpur, Malaysia*

[a)] Corresponding author:naseffendi@gmail.com
[b)]nrsyaf91@gmail.com
[c)]aisyah.zawawi@salam.uitm.edu.my
[d)]oskar@salam.uitm.edu.my
[e)]rosna593@salam.uitm.edu.my
[f)]mzay@upnm.edu.my
[g)] Corresponding author:ammali@salam.uitm.edu.my

Abstract.A dye-sensitized solar cells (DSSCs) using a nanocomposite (NC) semiconductor film, consisting of graphene layer and ZnO nanosheets (Gr-ZnO) is fabricated by electrodeposition process. The DSSCs based on Gr-ZnO NC were determined via electrochemical impedance spectra (EIS), UV–Visible diffused reflectance spectroscopy (UV-Vis), and photovoltaic performances J-V curves to substantiate the explanations. Impedance spectra shows that a smaller charge transport time constant occurs in DSSCs based on Gr-ZnO NC comparing to ZnO. This improved the electron collecting efficiency significantly, resulting in high open circuit voltage. Moreover, Gr-ZnO NC shows an efficient photoinduced charge separation and transportation can be achieved at the interface thus exhibit excellent potential for photocurrent generation compared with sole ZnO. Gr-ZnO NC obtained a maximum photocurrent response for an open-circuit voltage and a power conversion efficiency of 0.96 V and 7.01% respectively, which is doubled from sole ZnO. The fabricated Gr-ZnO NC cells show better performances compared to conventional ZnO structure reference cell.

Keywords: Graphene ZnO, Nanocomposites, Photoanodes, DSSCs

INTRODUCTION

Dye-sensitized solar cells (DSSCs) is one of the emerging area of material science to convert solar energy to electrical energy due to its high efficiency and low cost fabrication [1]. Efforts were made in tailoring various semiconductor material such as TiO_2, ZnO, SnO_2, and other metal oxides on photoanodes but it has disadvantages with its crystallinity and transport of electron within DSSCs [2,3]. Varying the photoanodes with composites-based semiconductor received tremendous interest to enhance its electrical and optical properties for DSSCs [4]. One of the promising candidate is ZnO semiconductor which has been greatly exploited for its unique properties with high electron mobility ca. 200~300 cm^2 Vs^{-1} for bulk material and ~1000 cm^2 Vs^{-1} for single-crystal nanowires. Yet, the photo-conversion efficiency in DSSCs is still low compared to TiO_2>12% [5]. Thus, an implementation of organic conductive materials, particularly graphene that possesses large surface area (~2600 m^2/g) and superior mobility of

4th International Conference on the Advancement of Materials and Nanotechnology (ICAMN IV 2016)
AIP Conf. Proc. 1877, 090005-1–090005-6; doi: 10.1063/1.4999900
Published by AIP Publishing. 978-0-7354-1557-7/$30.00

charge carriers (200,000 cm^2 Vs^{-1}) with ZnO could promote the advantages in Gr-ZnO composites where it can be suitably modified by chemical composition of ZnO and Gr [6].

Modifying the Gr-ZnO composites by chemical composition of ZnO will form a semiconductor nanostructures with good dispersion and highly crystalline on the surface of Gr layer. Consequently, incorporation of Gr with ZnO will lead to a fast charge recombination and transport rate between the conducting electrode and semiconductor nanostructures. The high conductivity of Gr makes it a great material to accept photoinduced charge carriers and to promote the electron transfer rate of the semiconductor nanostructure conduction band to the conducting electrode by trapping the photogenerated electrons thus, improved the conversion efficiency of solar cell devices. So far, many inorganic semiconductors, such as TiO_2, ZnO, CdS and PbO, have been successfully attached onto Gr surface to form unique hybrid materials for photoelectric devices [7,8]. To date, various methods have been used to synthesis and utilize Gr-ZnO composites, such as one-step and multi-step synthesis for several applications. The preparation of ZnO nanostructure, the reduction process of graphene oxide (GO) to Gr and decoration of semiconductor nanostructure into Gr surface with a narrower size distribution and good homogeneity and stability are the three main steps, which can be described as ‘‘one-pot synthesis’’[9].

Therefore, this paper concerned a facile synthesis method of Gr-ZnO NC via an electrodeposition approach using zinc nitrate hexahydrate and hexamethylenetetramine as the starting materials. Graphene was used as a capping agent to enhance the surface area of ZnO nanosheets. The photocurrent properties of the as-synthesized Gr-ZnO NC under visible light irradiation were performed to gain insight into the effect of Gr on the photocurrent properties of ZnO nanosheets.

EXPERIMENTAL

Synthesis of Graphene-Zinc Oxide Nanocomposites with High Crystallinity

The synthesis of highly crystalline graphene-zinc oxide nanocomposites is synthesized from mixture of $Zn(NO_3)_2.6H_2O$ and HMT with graphene platelet nanopowder by electrodeposition process. Firstly, ITO substrates washed ultrasonically with DI water, acetone, and ethanol for 20 min and used as working electrode. Then, ZnO nanoseeds were prepared using an aqueous equimolar reaction mixture method of 0.1 M $Zn(NO_3)_2.6H_2O$ and 0.1 M HMT and left to stir for 30 mins. Graphene with concentration of 5 mg/ml were added to the ZnO nanoseed solutions and continuously stirred for at least 180 minutes at room temperature to obtain homogenous solution forming Gr-ZnO nanoseed. Later, all the samples undergo one-step electrodeposition process where ITO substrates were immersed in the Gr-ZnO nanoseed solution with potentiostatic voltage at 5.0V for 20min until thin film formed. The samples were then washed with DI water and dried at 60 ^oC in the oven for 30mins. For comparison, sole ZnO nanostructure is also electrochemically deposited on the ITO substrates with the deposition bath composed of 0.1 M $Zn(NO_3)_2.6H_2O$ and 0.1 M HMT as controlled sample. Then the samples will undergo hydrothermal growth at 100 ^oC for 2h. Later the samples were annealed at 350 ^oC for 30min and become Gr-ZnO NCs.

Fabrication of CEs and Assembly of DSSCs

A photoelectrochemical cell was fabricated by sandwiching the Gr-ZnO NC coated with N719 dye with graphene onto ITO as counter electrode and clamped in order to optimize the interfacial contact between the cell components. The electrolyte was injected into the cell and filled via a capillary action. Gr-ZnO NC is used as working electrode with graphene coated onto ITO substrates was used as counter electrode of the devices. Gr-ZnO NC is a photovoltaic material and LiI-I_2 is the electrolyte. Finally, the cell was clamped with 15 mm^2 as an illuminated area for photovoltaic reaction.

Characterization

Photovoltaic measurements were carried out on Keithley 2400 source meter under one sun light intensity (100mW/cm^2) simulated by a solar simulator (Oriel, 91193).The optical reflection spectra of the electrodes are determined using a CARY 50 Scab UV-VIS-NIR spectrophotometer. The EIS was performed with a computer-controlled impedance measurement unit (Autotab PGSTAT302N) and carried out by applying sinusoidal perturbations of 10 mV under bias of −0.8 V, and the frequency ranges from 0.05 to 100 kHz.

RESULTS AND DISCUSSION

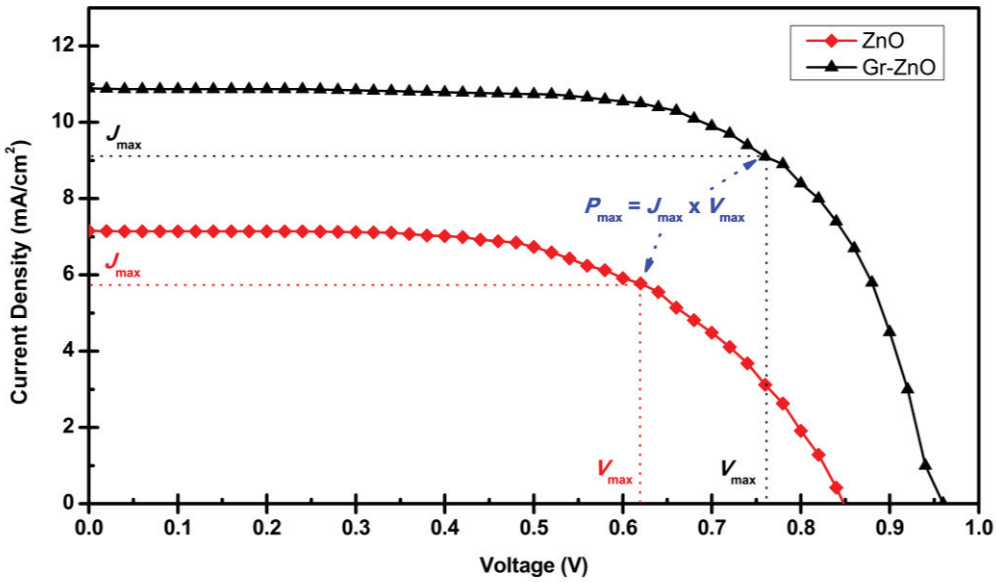

FIGURE 1. Current-voltage (J-V) characteristics of the DSSCs constructed using the ZnO and Gr-ZnO NC photoanode under a simulated illumination with a light intensity of 100 mW/cm^2 (AM 1.5)

The performance of DSSCs of different photoanodes is illustrated in Fig.1. The current density of photoanodes increases up to 10.89 mA/cm^2 with the incorporation of graphene into ZnO. The slight increase in Gr-ZnO NC performances are directly related to light harvesting ability of DSSCs, which, in turn, is influenced by the degree of dye adsorption. Large surface area for dye adsorption thus increases in light harvesting efficiency within the photoanodes. Based on Fig.1, the photovoltaic parameters of DSSCs were calculated and summarized as shown in Table 1. Gr-ZnO NC photoanode achieves higher short circuit current density (J_{SC}) of 10.89 mA/cm^2 with an improvement of 52.09% compared to the sole ZnO photoanode with J_{SC} of 7.16 mA/cm^2. The large J_{SC} in Gr-ZnO NC contributed to an increase of photo-conversion efficiency (PCE) with a high open circuit voltage. This phenomenon might be due to the decreased of Fermi level on the graphene-based photoanode thus injected electrons are forced to drive significant energy gap between lowest unoccupied molecular orbital (LUMO) and conduction band (CB) of dye [10]. Therefore, due to much improved J_{SC}, the Gr-ZnO NC photoanode reached a total PCE of 7.01%, which is nearly 50.36% higher than that of the sole ZnO photoanode (3.48%). Consequently, the slight increment in the FF value is directly proportionally to V_{OC} where electron collection efficiency depends on light harvesting efficiency.

TABLE 1. Photovoltaic Parameters of the DSSCs Based on the ZnO Photoanode and Graphene-ZnO NC

Photoanode	Thickness (μm)	J_{SC} (mA/cm2)	V_{OC} (V)	J_{max} (mA/cm2)	V_{max} (V)	FF (%)	PCE (%)
ZnO	3	7.16	0.85	5.77	0.62	56	3.48
Gr-ZnO	3	10.89	0.91	9.10	0.76	66	7.01

The optical absorbance of solutions containing N719 dyes desorbed from the ZnO and Gr-ZnO NC photoanodes with a known concentration are shown Fig.2. It can be seen ZnO and Gr-ZnO NC exhibit only one prominent absorption peak where ZnO and Gr-ZnO NC is observed at 489nm and 492nm, respectively. The shifting of absorption peak indicates the changing of excitonic state of ZnO nanostructures. Meanwhile, the shifting of peak Gr-ZnO NC indicates a reduced inter-particle spacing due to involvement of graphene which is expected due to stronger electromagnetic coupling within the graphene nanoparticles deposited onto ZnO nanostructures. It was estimated that the amount of dye loading by contrasting the optical absorbance of solutions containing dyes desorbed from the photoanodes (3 μm in thickness) with that of dye solution with a known concentration is $10.30\times10-8$ mol/cm^2 and $10.03\times10-8$ mol/cm^2 for Gr-ZnO NC and ZnO photoanode, respectively. The result shows an increased by 3% in dye loading amount which is incompatible with the 50.36% increase in the J_{SC}. Thus, it can be concluded that the J_{SC} enhancement are affected by the reduced electron recombination facilitated by the incorporation of graphene, rapidly transport the electrons within the photoanodes.

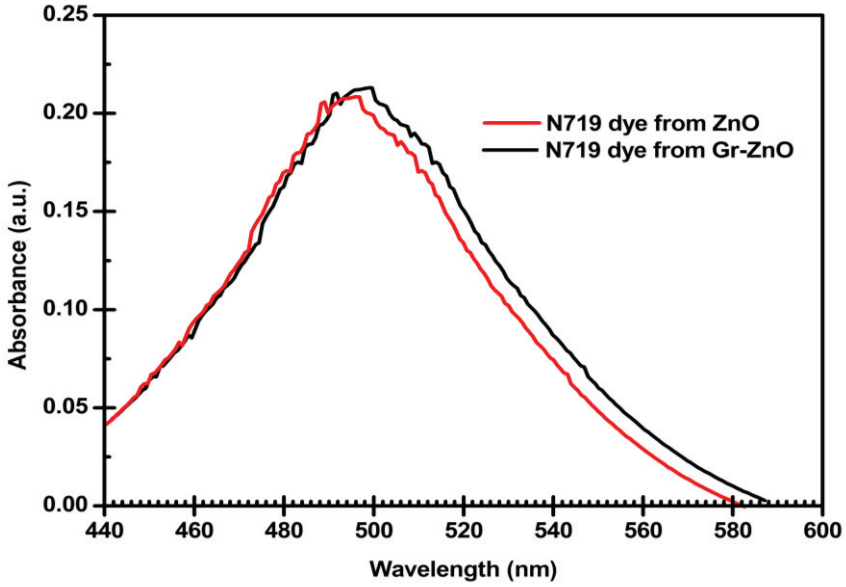

FIGURE 2. Optical absorbance of solutions containing dyes detached from the ZnO and Gr-ZnO NC photoanode

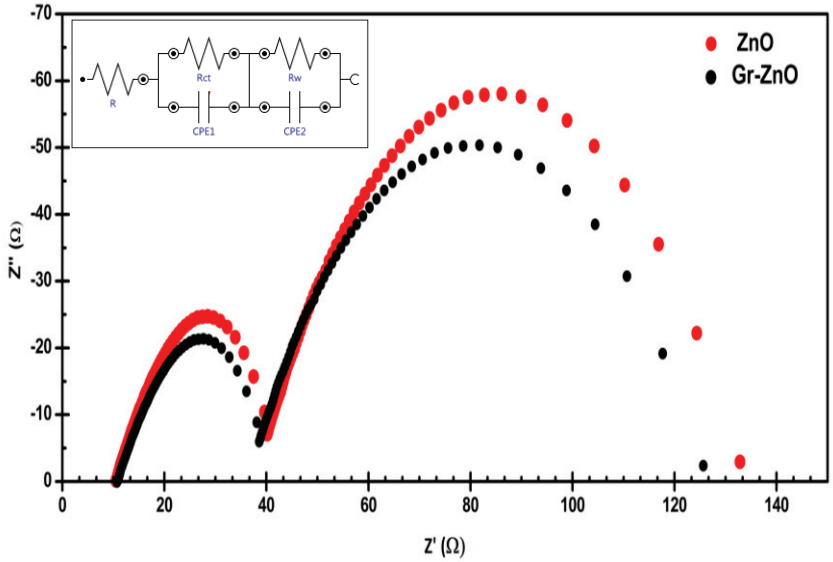

FIGURE 3. Nyquist plots of the electrochemical impedance spectra of the ZnO photoanode and Gr-ZnO NC photoanode. Inset is the equivalent circuit of the device

To further explore the transport of electron and restrain of the back-electron transfer, an electrochemical impedance spectra (EIS) Nyquist plots was performed under illumination of one sun (AM 1.5G, 100 mW/cm^2) at an applied bias of Voc, as shown in Fig.3. Meanwhile, the inset in Fig.3 corresponds as an equivalent circuit of the device It can be seen from Fig.3 that sole ZnO and Gr-ZnO NC exhibit the same characteristics where two semicircles; high frequency region and middle frequency region present in Nyquist plot. The one in the high-frequency region relates to the charge transfer resistance (Rct) at the electrolyte/counter electrode interface, while the other in the middle frequency region corresponds to the charge transfer resistance (Rw) in the photoanode [11]. Based on Nyquist plot there a significant decrease in the semicircle size at middle frequencies by Gr-ZnO NC as compared to sole ZnO, implying acceleration of the electron transfer process due to lower Rw [11], [12]. This results suggesting faster electron transport of charge carries and more effective electron-hole pairs separation achieved over the Gr-ZnO NC as compared to sole ZnO. This result is also supported by the corresponding J-V curves where the current density of the electrodes is related to the electron transfer rate of the electrode materials. The higher current density obtained by Gr-ZnO demonstrates that improved electron transfer is achieved over the DSSCs device.

TABLE 2. Comparison between Previously Published Works and Our Work

Reference	Photoanode	Thickness (μm)	PCE (%)
Our work	Gr-ZnO NC	3	7.01
[13]	ZnO HSN	3.5	2.25
[14]	Iodine-doped ZnO HSN	8	4.5
Our work	ZnO	3	3.48
[10]	ZnO HSN	10	3.51
[15]	ZnO HSN	10	4.4
[16]	ZnO HSN	27	5.34

CONCLUSION

Per the above-mentioned discussions, Gr-ZnO NC photoanode has been successfully prepared and fabricated with high power conversion efficiency (PCE). The determined J-V curves have illustrated by incorporating graphene into the ZnO photoanode can enable the DSSC devices operate more efficiently. The Gr-ZnO NC produce the highest photoelectrical conversion efficiency (η) at 7.01% compared sole ZnO due to its good electrode-electrolyte contact of Gr-ZnO NC [17]. The result is in a good agreement with EIS where graphene acts as catalyst penetrating ZnO for rapidly capturing, transporting, and collecting electrons injected into ZnO before being recombined, and hence the adverse electron transfers (recombination and back transfer) are suppressed in a way, while in the photoanode of the former, photogenerated electrons have to transfer through the ZnO film which is several or even dozens of micrometers thick before reaching the FTO collection electrode. Therefore, the recombination chance for electrons and holes is inevitably increased. Among the DSSCs made from different composite-content WEs from previous published works shown in Table 2, the DSSC fabricated from our composite WE materials is expected to exhibit more attractive prospect in the large-scale production due to its much lower cost.

ACKNOWLEDGMENTS

Authors would like to thank Ministry of Science, Technology and Innovation (MOSTI) Malaysia for funding this research and Ministry of Higher Education (MOHE) for supporting this research under the FRGS grant 600-RMI/FRGS 5/3 (56/2014) and Univesiti Teknologi MARA (UiTM) for the facilities provide in succeeding this research.

REFERENCES

1. P. Optikal et al., “Optical Behavior of Nh 4 I Doped Cellulose Acetate Membrane for Dye Sensitized Solar Cell,” vol. **19**, no. 4, pp. 760–765, 2015.
2. M. Grätzel, “Photoelectrochemical cells.,” Nature, vol. **414**, no. 6861, pp. 338–344, 2001.
3. M. Grätzel, “Dye-sensitized solar cells,” J. Photochem. Photobiol. C Photochem. Rev., vol. **4**, no. 2, pp. 145–153, 2003.
4. J. Maçaira, L. Andrade, and A. Mendes, “Review on nanostructured photoelectrodes for next generation dye-sensitized solar cells,” Renew. Sustain. Energy Rev., vol. **27**, no. 2013, pp. 334–349, Nov. 2013.
5. A. K. Chandiran, M. Abdi-Jalebi, M. K. Nazeeruddin, and M. Grätzel, “Analysis of electron transfer properties of ZnO and TiO2 photoanodes for dye-sensitized solar cells,” ACS Nano, vol. **8**, no. 3, pp. 2261–2268, 2014.
6. C. Hu, T. Lu, F. Chen, and R. Zhang, “A brief review of graphene–metal oxide composites synthesis and applications in photocatalysis,” J. Chinese Adv. Mater. Soc., Apr. 2013.
7. A. H. Castro Neto, N. M. R. Peres, K. S. Novoselov, and A. K. Geim, “The electronic properties of graphene,” Rev. Mod. Phys., vol. **81**, no. 1, pp. 109–162, Jan. 2009.
8. X. Huang et al., “Graphene-based materials: synthesis, characterization, properties, and applications.,” Small, vol. **7**, no. 14, pp. 1876–902, Jul. 2011.
9. Z. Zhang et al., “One-pot electrodeposition synthesis of ZnO/graphene composite and its use as binder-free electrode for supercapacitor,” Ceram. Int., vol. **41**, no. 3, pp. 4374–4380, Dec. 2014.
10. T. P. Chou, Q. Zhang, G. E. Fryxell, and G. Z. Cao, “Hierarchically Structured ZnO Film for Dye-Sensitized Solar Cells with Enhanced Energy Conversion Efficiency,” Adv. Mater., vol. **19**, no. 18, pp. 2588–2592, Sep. 2007.
11. J. Chen et al., “A quantum dot sensitized solar cell based on vertically aligned carbon nanotube templatedZnO arrays,” Electrochem. commun., vol. **12**, no. 10, pp. 1432–1435, Oct. 2010.
12. R. Kern, R. Sastrawan, J. Ferber, R. Stangl, and J. Luther, “Modeling and interpretation of electrical impedance spectra of dye solar cells operated under open-circuit conditions,” Electrochim. Acta, vol. **47**, no. 26, pp. 4213–4225, Oct. 2002.
13. Y. Zhang, L. Wu, Y. Liu, and E. Xie, “Improvements to the hierarchically structured ZnOnanosphere based dye-sensitized solar cells,” J. Phys. D. Appl. Phys., vol. **42**, no. 8, p. 85105, Apr. 2009.
14. Y.-Z. Zheng, X. Tao, Q. Hou, D.-T. Wang, W.-L. Zhou, and J.-F. Chen, “Iodine-Doped ZnONanocrystalline Aggregates for Improved Dye-Sensitized Solar Cells,” Chem. Mater., vol. **23**, no. 1, pp. 3–5, Jan. 2011.
15. Q. Zhang, T. P. Chou, B. Russo, S. a. Jenekhe, and G. Cao, “Polydisperse aggregates of ZnOnanocrystallites: A method for energy-conversion-efficiency enhancement in dye-sensitized solar cells,” Adv. Funct. Mater., vol. **18**, no. 11, pp. 1654–1660, 2008.
16. H.-M. Cheng and W.-F. Hsieh, “High-efficiency metal-free organic-dye-sensitized solar cells with hierarchical ZnO photoelectrode,” Energy Environ. Sci., vol. **3**, no. 4, p. 442, Mar. 2010.
17. X. Wang, L. Zhi, and K. Müllen, “Transparent, conductive graphene electrodes for dye-sensitized solar cells.,” Nano Lett., vol. **8**, no. 1, pp. 323–7, Jan. 2008.