Abstract—Dye-sensitized solar cell (DSSC) is the third generation of solar cells that promises a simple procedure and relatively low-cost materials which can provide electricity by converting light energy into electrical energy. DSSC is a sandwich-like structure consists of conducting electrodes, sensitizer, and electrolyte. In this research, Graphene Quantum Dots (GQDs) is used as an enhancer for DSSC and it will be compared with the conventional DSSC performance. The time adsorption of GQDs is varied to study the improvement in the efficiency of DSSC. GQDs can increase the electron mobility hence increases the efficiency of DSSC. The presence of GQDs and the efficiency of DSSC are examined by using Energy-dispersive X-ray Spectroscopy (EDX) and solar simulator respectively. The result shows that the presence of GQDs have improved the efficiency of DSSC. As time adsorption of GQDs in DSSC increases, the efficiency of DSSC also increases.

Index Terms—Dye sensitized solar cell, Graphene Quantum Dots, power conversion efficiency, time adsorption.

1. INTRODUCTION

Energy in physics is the capacity for doing work. It may exist in potential, kinetic, thermal, electrical, chemical, nuclear, or other various forms. Source of energy can do a transition from one energy to another energy. For example, solar cells use sunlight to convert light energy into electrical energy. There are nine major areas of energy resources. They fall into two categories, which are nonrenewable and renewable. Nonrenewable energy resources, like coal, nuclear, oil, and natural gas, are available in limited supplies. This is usually due to a long time it takes for them to be renew. On the other hand, renewable resources are renewed naturally and over a relatively short period. The five major renewable energy resources are solar, wind, hydro, biomass, and geothermal.

Solar cells categorized as solar energy (renewable energy) are one of the promising photonic devices that are able to convert light energy into electrical energy without producing unwanted byproduct such as carbon dioxide, which leads to global warming. The first generation of solar cells is made up from crystalline silicon. Although the silicon solar cells generation produce high efficiency, but it has to deal with the high cost and complicated fabrication [1], [2]. Then, the second generation has been developed using thin film, but it causes toxicity and still limited by the Shockley-Queisser limit [3]. In 1991, O’Regan and Grätzel reported on a third generation of solar cells, which is dye sensitized solar cells (DSSC) with an efficiency of 7.1% [4]. Since then, many research groups have been working on the DSSC in order to improve the efficiency and stability. DSSC also offers low toxicity and it can produce low-cost energy conversion devices with simple manufacturing procedures [2], [5]-[10].

DSSC is based on the concept of photosensitization of wide band-gap mesoporous oxide semiconductors [5]. It consists of four main layers, which are electrodes (working electrode and counter electrode), photosensitizer (dye), nanostructured wide bandgap semiconductor layer and electrolyte as shows in Fig. 1. The mechanism of DSSC happens when light energy (sunlight) is irradiated into a dye and exciting electrons in the dye. The electrons are injected into Titanium dioxide (TiO$_2$) and it will then diffuse into the electrode. On the counter electrode, electrons are injected into the electrolyte and reduce I$_3^-$ ions to I$^-$ ions. After that, I$^-$ ions diffuse in the solution, reach the dye, give up electrons and become oxidized, forming I$_3^-$ ions [5], [10], [11]. The absorbed dye molecules excited by the sunlight to generate...
Graphene Quantum Dots (GQDs) are varied to observe the differences in efficiency of DSSC compared to conventional preparation of DSSC assembling. Time adsorption of parts, which are the preparation of the electrodes and the fabrication, experimental steps were done in two different and iodolyte is used as an electrolyte. For the DSSC meltonix is used as a spacer to attach both electrodes together platinum solution is used in the counter electrode. Lastly, (Ru) N719 dye is used as a photosensitizer. Meanwhile, the (Sigma-Aldrich) is used as an enhancer while Ruthenium FTO (fluorine tin oxide) coated glass, ethanol, acetone, of GQDs (enhancer). Then the working electrode will working electrode are immersed in different adsorption time GQDs are varied to improve DSSC performance. The TiO₂ absorption spectra showed the optical absorption of the semiconducting layer TiO₂ region as compared with the pure TiO₂ porous [1], [18]. Reza Ghayoor reported when the optical absorption at GQDs increased, the photo generated electrons increased, and it can reduce the use of dye in DSSC and improve the DSSC performance by multi-electron generation [19]. Hence, it shows that GQDs have the properties to help improving the charge transport and poor absorption on visible-region [6], [16], [17].

Besides that, GQDs used to tune the bandgap energy of semiconducting layer TiO₂ due to quantum confinement effect [15]. R. Azimirad et al had proved that the UV visible absorption spectra showed the optical absorption of the GQDs/TiO₂ porous nanocomposite has increased in visible region as compared with the pure TiO₂ porous [1], [18]. Besides that, GQDs used to tune the bandgap energy of semiconducting layer TiO₂ due to quantum confinement effect [15]. R. Azimirad et al had proved that the UV visible absorption spectra showed the optical absorption of the GQDs/TiO₂ porous nanocomposite has increased in visible region as compared with the pure TiO₂ porous [1], [18]. Reza Ghayoor reported when the optical absorption at GQDs increased, the photo generated electrons increased, and it can reduce the use of dye in DSSC and improve the DSSC performance by multi-electron generation [19]. Hence, it shows that GQDs have the properties to help improving the charge transport and performance of DSSC. However, there is less attention on the effect of adsorption time of GQDs as an enhancer in DSSC. Thus, in this study, adsorption time of GQDs are varied to improve DSSC performance. The TiO₂ working electrode are immersed in different adsorption time of GQDs (enhancer). Then the working electrode will be continued with the dye adsorption process. The performance of DSSC containing GQDs are compared with the conventional DSSC.

II. EXPERIMENTAL PROCEDURE
A. Examined Material

Working electrode as in Fig. 1 is fabricated using titanium (IV) oxide anatase (Sigma-Aldrich), de-ionized (DI) water, FTO (fluorine tin oxide) coated glass, ethanol, acetone, isopropanol, and tape. Graphene quantum dots (Sigma-Aldrich) is used as an enhancer while Ruthenium (Ru) N719 dye is used as a photosensitizer. Meanwhile, the platinum solution is used in the counter electrode. Lastly, meltonix is used as a spacer to attach both electrodes together and iodolyte is used as an electrolyte. For the DSSC fabrication, experimental steps were done in two different parts, which are the preparation of the electrodes and the preparation of DSSC assembling. Time adsorption of Graphene Quantum Dots (GQDs) are varied to observe the differences in efficiency of DSSC compared to conventional DSSC.

B. Preparation of Electrode

DSSC consists of two different electrodes that have been sandwiched together, which are working electrode and the counter electrode. At the working electrode, Titanium Dioxide (TiO₂) is used together with GQDs and Ruthenium N719 dye on the conductive side of FTO glass; to absorb the light energy. On the other hand, for the counter electrode, platinum (Pt) is deposited on top of FTO to act as a mirror that will reflect the light back to the circuit and maintain the circulation.

Electrodes are prepared by using two FTO coated glasses (counter electrode and working electrode). FTO coated glasses are cleaned with acetone, ethanol and isopropanol using ultrasonic bath for a few minutes. This method is used as a cleaning method to avoid impurities on the surface of FTO coated glass. After the cleaning process, the FTO glasses are dried using a blower. The conductivity of the glasses is checked using a multimeter to indicate the conductive side of the glasses.

The electrode consists of two parts, which is counter electrode and working electrode. For the counter electrode, the conductive side of the FTO glass is deposited with Pt solution using a spin coater. The micropipette is used to measure 60 ml of Pt solution and then the Pt solution is deposited on the surface of FTO glass inside the spin coater with a speed of 1500 rpm for 60 seconds. After that, the counter electrode is annealed at 450°C for 30 minutes. After the annealing process, the conductivity of the FTO glass is checked to confirm the presence of platinum.

For the working electrode, the conductive side is taped according to the surface area size (1cm²) by using scotch tape. This will help to spread the Titanium (IV) oxide (TiO₂) paste uniformly as shown in Fig. 3. The size of the surface area will determine the active area of the DSSC. After that, a thin layer of TiO₂ paste is applied on the conductive side of FTO glass by using doctor blading methods. Next, it will be dried for several minutes at the room temperature. After the working electrode has dried, the tape is removed carefully, and the working electrode is annealed at 450°C for 30 minutes in the furnace. After the working electrode has cooled down, the process continues with the soaking process. The working electrode is soaked with two different solutions, which are GQDs and Ru N719 dye solution.

Soaking process involves two steps. The first step is to soak working electrode with GQDs in a petri dish for several times (GQDs-12, GQDs-24, GQDs-36, GQDs-48 hours). Petri dish is wrapped with paraffilm and aluminum foil and then it will be stored in the box to prevent from sunlight. This is because TiO₂ and GQDs are photosensitize material. After that, the working electrode is rinsed using DI water and then dried using a dryer. Then, heat treatment is applied to the working electrode before it continues to the second step. The second step is to soak the working electrode with Ru N719 dye solution inside the petri dish. Petri dish is wrapped carefully to avoid the dye from evaporation. After that, the petri dish is stored inside the box for 48 hours. The working
electrode is rinsed with ethanol to remove excessive unattached dye and then it is dried using a dryer. As opposed to the conventional DSSC, the working electrode is soaked with Ru dye solution only without GQDs process.

III. RESULTS AND DISCUSSION

A. Physical Properties of Working Electrode

Fig. 4 shows the photo obtained by using Scanning Electron Microscopy (SEM) with a magnification of 1000 times and 3000 times respectively, concerning the cross-section of the active area (TiO$_2$ area) on the surface of working electrode. Fig. 4(a) shows the thickness of TiO$_2$ layer that adsorbed the GQDs and Ru dye is 40µm. The structure shows that the TiO$_2$ particle has been mixed up with the Ru and GQDs particle forming different particle sizes and colors. In Fig. 4(b), the cross-section of the active area can be seen clearly.

B. Presence of Elements

Fig. 5 shows the graph of Energy-dispersive X-ray spectroscopy (EDX). The graph shows the presence of elements in the sample. From this graph, GQDs are exist in the working electrode. The highest peak is Ti (titanium) which is 48.59%. The second highest peak is Au (gold). Au is used to coat the sample for characterization. Several other elements are also present in the sample such as O (oxide), Si (silicon), Ru (ruthenium), Sn (tin), and C (carbon). Carbon represents the existence of GQDs because graphene is one of the carbon group. GQDs existed at 1.73% from the overall elements. Meanwhile, Ti and O represent the TiO$_2$ paste. On top of that, Si, Sn, and O represent the FTO glass and lastly, Ru, represents the existence of ruthenium N719 dye. TiO$_2$ has the highest percentage of element followed by Ru and GQDs.

C. Performance of DSSC

Table I shows the results of conventional DSSC and GQDs-DSSC. From the results, we are compared the current density (Jsc), voltage open circuit (Voc), fill factor (FF) and efficiency (η). We also observed the differences in the time adsorption of GQDs. The efficiency of the conventional
Conventional DSSC is slightly lower than the GQDs-12 hours efficiency. As the time adsorption of GQDs increases, the efficiency of each sample also increases. GQDs-48 hours have the best Jsc and Voc, which is 9.422 mA/cm² and 0.620 V respectively. This is because GQDs-48 hours adsorbed more GQDs compared to other samples, which has higher electronic mobility that helps to increase the electron transport. Nevertheless, the GQDs-12 hours have the best fill factor, which is 0.582 because of the quality of the sample. Overall, GQDs-48 hours have the best efficiency with 3.084% and GQDs were proven to have increased the performance of DSSC compared to the conventional DSSC. Based on the results, GQDs-48 hours have the best efficiency, followed by GQDs-36 hours, GQDs-24 hours, GQDs-12 hours and conventional DSSC. The current density, Jsc and conversion efficiency, η of GQDs-48 cell generated best performance at 9.422 mA cm⁻² and 3.084% respectively compared to conventional DSSC at 3.115 mA cm⁻² and 1.034%. DSSC with the presence of GQDs as an enhancer has improved the performance of DSSC compared to the conventional DSSC.

IV. CONCLUSION

Dye-Sensitized Solar Cell (DSSC) consists of the electrodes (working electrode and counter electrode), a photosensitizer, nanostructured wide bandgap semiconductor layer, and electrolyte. In this project, GQDs were added in the DSSC as an enhancer to compare the performance with the conventional DSSC. Besides that, the adsorption time for the DSSC was varied too. Fig. 4 shows the SEM image of the cross-section of the active area on the working electrode. The thickness of the active area is 40 μm. On top of that, the elements presence in the working electrode were identified by using EDX. Therefore, the existence of GQDs in the active area were proved. Table I shows the results from the solar simulation calculation and Fig. 6 shows the I-V graph of all samples (Conventional DSSC, GQDs-12, GQDs-24, GQDs-36 and GQDs-48).

| Name               | Jsc (mA/cm²) | Voc (V) | FF   | Efficiency, η (%) |
|--------------------|--------------|---------|------|-------------------|
| Conventional DSSC  | 3.115        | 0.599   | 0.553| 1.034             |
| GQDs-12 hours      | 4.443        | 0.599   | 0.582| 1.553             |
| GQDs-24 hours      | 6.511        | 0.620   | 0.520| 2.099             |
| GQDs-36 hours      | 8.673        | 0.610   | 0.510| 2.698             |
| GQDs-48 hours      | 9.422        | 0.620   | 0.528| 3.084             |

Fig. 6. I-V graph of DSSC with varies adsorption time of GQDs.

ACKNOWLEDGMENT

The research work was sponsored by a University Putra Malaysia grant (GP-IPB/2016/9515402).

REFERENCES

[1] S. Chinnusamy, R. Kaur, A. Bokare, and F. Erogbogbo, “Incorporation of graphene quantum dots to enhance photocatalytic properties of anatase TiO₂,” MRS Communications, vol. 8, pp. 137–144, January 2018.
[2] Z. Xia, “Characterization of dye-sensitized solar cells,” Bachelor thesis, Faculty of Chemistry, Worcester Polytechnic Institute, Worcester, MA, USA.
[3] Y. Xu, T. Gong, and J. N. Munday, “The generalized Shockley-Queisser limit for nanostructured solar cells,” Scientific Reports, vol. 5, 2015.
[4] B. O’Regan and M. Gratzel, “A low-cost, high efficiency solar cell based on dye sensitized colloidal TiO₂ films,” Nature, vol. 353, no. 24, pp. 737-740, 1991.
[5] A. N. Zulkifili, T. Kento, M. Daiki, and A. Fujiki, “The basic research on the Dye-Sensitized Solar Cells (DSSC),” Journal of Clean Energy Technologies, vol. 3, pp. 382-387, September 2015.
[6] N. F. M. Sharif, M. Z. A. A. Kadir, S. Shafie, S. A. Rashid, W. Z. W. Hasan, and S. Shaban, “Charge transport and electron recombination suppression in dye-sensitized solar cells using graphene quantum dots,” Results in Physics, vol. 13, March 2019.
[7] S. Kundu, P. Sarojinijeeva, R. Karthick, G. Anantharaj, G. Saritha, R. Bera, S. Anandand, A. Patra, P. Raguapathy, M. Selvaraj, D. Jayakumar, and K. V. Pillai, “Enhancing the Efficiency of DSSCs the modification of TiO₂ photoanode using N, F and S, co-doped graphene quantum dots,” Electrochimica Acta, vol. 242, pp. 337-343, May 2017.
[8] J. Gong, J. Liang, and K. Sumathy, “Review on dye-sensitized solar cells (DSSCs): Fundamental concepts and novel materials,” Renewable and Sustainable Energy Reviews, vol. 16, no. 8, pp. 5848-5860, October 2012.
[9] J. M. K. W. Kumari, G. K. R. Senadeera, M. A. K. L Dissanayake, and C. A. Thotawatthage, “Dependence of photovoltaic parameters on the size of cations absorbed by TiO₂ photoanode in dye-sensitized solar cells,” Ionics (Kiel), pp. 1-6, 2017.
[10] A. M. Bagher, M. M. A. Vahid, and M. Mobsen, “Types of solar cells and application.” American Journal of Optics and Photonics, vol. 3, pp 94-113, 2015.
[11] R. Nagata and H Murakami, “Development of dye-sensitized solar cell,” Uihac Technical Journal, vol. 70, 2009.
[12] S. Hao and J. Wu, “Natural dyes as photosensitizers for dye sensitized solar cell,” Solar Energy, vol. 80, no. 2, pp. 209-214, 2006.
S. H. Choi, “Unique properties of graphene quantum dots and their applications in photonic/electronic devices,” J. Phys. D: Appl. Phys., vol. 50, pp. 1-10, 2017.

M. Bacon, S. J. Bradley, and T. Nann, “Graphene quantum dots,” Part. Part. Syst. Charact. vol. 31, pp. 415-428, April 2014.

S. Bak, D. Kim, and H. Lee, “Graphene quantum dots and their possible energy applications: A review,” Current Applied Physics, vol. 16, 1192-1201, May 2016.

R. Long, “Understanding the electronic structures of Graphene quantum dot physisorption and chemisorption onto the TiO$_2$ (110) surface: A first-principles calculation,” ChemPhysChem, vol. 14, no. 3, pp. 579-582, 2013.

T. H. Wang, T. W. Huang, Y. C. Tsai, Y. W. Chang, and C. S. Liao, “A photoluminescent layer for improving the performance of dye-sensitized solar cells,” Chem Commun, vol. 51, no. 33, pp. 7253-7256, 2015.

R. Azimirad, S. Safa, M. Ebrahimi, S. Youcefzadeh, and A. Z. Moshfegh, “Photoelectrochemical activity of graphene quantum dots/hierarchical porous TiO$_2$ photoanode,” Journal of Alloys and Compounds, vol. 721, pp. 36-44, 2017.

R. Ghayoor, A. Keshavarz, M. N. S. Rad, and A. Mashreghi, “Enhancement of photovoltaic performance of dye sensitized solar cells based on TiO$_2$ graphene quantum dots photoanode,” Material Research Express, vol. 6, November 2018.

Copyright © 2020 by the authors. This is an open access article distributed under the Creative Commons Attribution License which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited (CC BY 4.0).

Nazalea Yazmin Muhammad was born in 1994 and currently lives in Selangor, Malaysia. She received the bachelor’s degree in engineering (microelectronic engineering) at University of Malaysia Perlis (UniMAP), Arau, Perlis, Malaysia in 2017. She is currently a postgraduate student with the Institute of Advanced Material (ITMA) in University Putra Malaysia.

Mohd Nazim Mohtar received the B. Eng. degree in medical engineering in 2006 and PhD degree in biomedical engineering in 2013 from the University of Surrey, UK. Currently, he is a senior lecturer at the Department of Electrical and Electronic Engineering, University Putra Malaysia. His research interest are sensors, Lab on Chip (LOC) devices and renewable energy.

Muhammad Mahyiddin Ramli received the bachelor of engineering in microelectronic engineering from Kolej Universiti Kejuruteraan Utara Malaysia (KUKUM), Malaysia in 2006. He received the master of engineering science in microelectronic design at University College Cork, Republic of Ireland in 2007. Then, he received his PhD degree from University of Surrey, UK in 2014. Currently, he is a senior lecturer in University of Malaysia Perlis (UniMAP). His current research interest are carbon nanotubes, nano-devices and rubber/polymer nanocomposites.

Suhaidi Shafie received the bachelor of engineering in electrical and electronics from University of Ryukyus, Japan in 2000. From 2000 to 2002, he was with alps electric (m) sdn. bhd. He received the master of engineering in electrical and electronics from University of Agriculture and Technology, Tokyo and the doctor of engineering in nano-vision from Shizuoka university in 2005 and 2008, respectively. He is an associate professor in University Putra Malaysia and the head of functional devices laboratory. He is working in mix signal IC design and solar energy research.