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Strategic Integration of Graphene into Multilayer Photoanode; Enhancing Efficiency of Quasi-Solid-State Dye-Sensitized Solar Cells Under Ambient and Low Irradiance

T. M. W. J. Bandara

awijendr@yahoo.com

University of Peradeniya

S. M. S. Gunathilake University of Peradeniya

G. G. D. M. G. Gamachchi University of Peradeniya

B. M. K Pemasiri University of Peradeniya

L. Ajith DeSilva University of West Georgia

M. A. K. L. Dissanayake National Institute of Fundamental Studies

G. R. A. Kumara University of West Georgia

Research Article

Keywords: Graphene solar cell, Low light, Efficiency enhancement, Dye solar cells, Graphene, Multilayer Photoanode

Posted Date: May 7th, 2024

DOI: https://doi.org/10.21203/rs.3.rs-4335227/v1

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Additional Declarations: No competing interests reported.

Version of Record: A version of this preprint was published at Journal of Applied Electrochemistry on September 23rd, 2024. See the published version at https://doi.org/10.1007/s10800-024-02204-x.

Abstract

Graphene is a potential candidate material to boost efficiency in solar cells. The performance of multilayer TiO₂ photoanode based quasi-solid-state dye-sensitized solar cells (DSSCs) is improved by strategically integrating graphene into the appropriate layer of the photoanode. For this purpose, graphene was synthesized from vein graphite, received directly from the mine site, providing a costeffective, feasible and new approach to enhance DSSC efficiency. Raman and XRD spectra confirm the successful exfoliation of graphite, forming graphene. Graphene integration into layers was analyzed using SEM images. The cells were constructed using photosensitized spin-coated TiO₂ multilayer photoanode, Pt counter-electrode, and binary salts gel-polymer electrolyte. Appreciable performance improvement was observed when graphene was added to the fourth layer of the photoanode. The guasisolid-state DSSC without graphene demonstrated 5.50% efficiency, 700 mA open circuit voltage, 11.04 mA cm⁻² short circuit current density and 71.2% fill factor under 1000 W m⁻² irradiation. In contrast, the DSSC improved by graphene exhibited 6.8% efficiency, 13.4 mA cm⁻² short circuit current density, 770 mA open circuit voltage and 66.2% fill factor under 1000 Wm⁻² irradiation. Furthermore, the efficiency and fill factor increase were observed when the irradiance decreased. The DSSC exhibited a remarkable efficiency of 9.4% under 67 W m⁻² irradiance. Achieving higher efficiency for guasi-soid state configuration without relying on volatile solvent-based electrolytes is another significance of this study. The study uncovers that the strategic incorporation of graphene, synthesized in an economically viable manner, into specific layers of the photoanode significantly enhances the power conversion efficiency in DSSCs.

1. Introduction

One of the biggest challenges in the 21st century is to replace fossil fuels with renewable and more environmentally friendly energy sources while supplying the ever-increasing energy demand. The development of low-cost and efficient solar cells with emerging technologies is the long-term solution to this energy crisis [^{1,2,3}]. Due to the lower production costs and the relatively high-power conversion efficiency (PCE), dye-sensitized solar cells (DSSCs) have received greater attention from researchers during the last decade [^{4,5,6}]. DSSCs have attained a maximum power conversion efficiency of 15.0% liquid electrolytes under ambient conditions [⁷].

The photoanode in a DSSC plays a key role in absorbing light energy and producing current and voltage through photoexcitation. The photoanode consists of a transparent conductive oxide (TCO) layer coated on a glass substrate. On top of this layer lies the mesoporous nanocrystalline wide-bandgap semiconducting material (TiO₂). The power conversion efficiency of a DSSC is basically governed by the properties of the photoanode. A high-performing photoanode should have a large specific surface area for more dye adsorption, faster electron transport, high resistance to photo-corrosion, high electrical conductivity, and excellent interfacial contact between the dye molecules and the electrolyte [⁸, ⁹]. By integrating highly conductive carbon nanostructures such as graphene, graphene oxide, carbon

nanotubes and fullerene into TiO_2 photoelectrode, DSSC performance can be enhanced due to the improved charge transport properties TiO_2 composite electrode. Among these carbon materials, graphene stands out due to its remarkable properties such as excellent optical transmittance, tunable bandgap, high specific surface area, and high mechanical strength. Further, with the addition of graphene or graphene quantum dots, the PCE of DSSCs can be improved through up-conversion and down-conversion [¹⁰,¹¹,¹²], broadening the spectral absorption of the photoelectrode [¹³] and improving electron mobility.

Fang et al. first [¹⁴] reported graphene quantum dot (GQD) assisted dye sensitized TiO₂ photoelectrodes demonstrating an efficiency of 6.10%, making 19.6% enhancement with GQD inclusion. Fan et al. [¹⁵] reported a TiO₂/graphene nanocomposite-based DSSC with 5.77% efficiency which is a 25% enhancement over graphene-free cell. This efficiency improvement is attributed to reduced electrode-electrolyte interfacial resistance, diminished charge recombination rates, enhanced light scattering, and the enhancement of charge transport resulting from the addition of graphene. Pattarith. K et al. [¹⁶], report higher efficiency of 9.15% for the cell optimized using graphene, benefiting from enhanced dye loading, improved of electronic conductivity, and reduced recombination. For an optimized TiO₂ photoelectrodes with RGO and graphene, Tang. B et al. [¹⁷] achieved a state-of-the-art efficiency of 11.8% for optimized TiO₂ photoelectrodes with reduced light scattering and the increased surface area for dye adsorption. The above efficiencies have been reported using problematic liquid electrolytes and ambient 1000 W m⁻² irradiance.

The performance of a DSSC or any other solar cell mainly depends on the intensity of photon flux /solar irradiation incident to the cell. In nature, sunlight intensity does not remain constant throughout the day or year. Some studies have shown that the efficiency of traditional Si-based solar cells decreases with the decreasing irradiance level [¹⁸, ¹⁹]. Only a few studies have been focused on investigating the performance of quasi-solid state DSSCs as a function of light intensity [²⁰]. In addition, to our knowledge, there are no reported studies focused on investigating the performance of graphene-incorporated photoanode-based quasi-solid state DSSC. Therefore, it is very important to investigate DSSC performance variation with the light intensity in order to estimate the power generation at different times of the day.

In addition to graphene and graphene oxide various other carbon-based materials have also been explored for the improving photoanodes in DSSCs. However, each presents its unique set of advantages and disadvantages. Carbon nanotubes (CNTs) for instance, have gained attention due to exceptional electrical conductivity, high surface area, and tubular structure [^{21,22}]. However, challenges such as CNT aggregation and difficulty of achieving uniform distribution on photoanode may have impacted their effective utilization in DSSCs. Carbon nanofibers (SNFs) are one-dimensional nanostructures similar to CNTs with good electrical conductivity and mechanical strength [²³]. Despite their advantages,

challenges in synthesizing and difficulty in proper alignment within the photoanode are considerable drawbacks. Carbon aerogels, a three-dimensional porous carbon structure offers a large surface area for dye adsorption and electron transport [²⁴].

According to the literature, while relatively higher efficiencies are recorded for graphene added DSSCs compared to control devices, the highest efficiency achieved (15%) by conventional DSSCs has not yet been surpassed. Additionally, the complexity of synthesis and poor stability and scalability issues hindered their application. This field necessitates further research to develop effective strategies for integrating carbon-based materials such as graphene into DSSC photoanodes to address these challenges.

By taking above mentioned key factors into account, the present study focuses on systematically incorporating a small amount of graphene into the multi-layer photoanode. Interestingly, in this study the integration of graphene into the 4th layer of the 6-layer TiO₂ photoanode resulted in enhanced solar cell performance. In addition, one of the challenges of utilizing graphene in solar cells is their high cost. This study presents a low-cost feasible, and novel method for synthesizing graphene using vein graphite received directly from the mine site for incorporation into photoanodes. Another significance of this study is achieving higher efficiency for quasi-soid state configuration without relying on volatile solvent-based electrolytes in the DSSCs.

2. Experimental

2.1 Materials

Transparent and conducting FTO substrates having a sheet resistance of 10 Ω cm⁻² and rutheniumbased 535-bisTBA (N719) dye sensitizer were purchased from Solaronix SA. Titanium dioxide nanopowders of average particle sizes of 21 nm (P25) and 13 nm (P21) were procured from Evonik, Germany. The starting materials for the preparation of the gel polymer electrolyte; iodine (I₂), ethylene carbonate (EC), propylene carbonate (PC), 1-Methyl-3-propylimidazolium iodide (MPII) and 4-tertbutylpyridine (4-TBP) with purity greater than 98%, Tetrahexyl ammonium iodide, lithium iodide and Polyethylene oxide (MW = 4,000,000) were purchased from Sigma Aldrich. Before using, tetrahexyl ammonium iodide, lithium iodide and polyethylene oxide (PEO) were vacuum dried for about 2 h at 50 °C.

2.2 Preparation of graphene

Graphene can be synthesized using various methods for applications [²⁵]. In this study, the electrolyte solution for the exfoliation was prepared by dissolving 26.14 g of K_2SO_4 in 300 mL of deionized water (0.5 M). Shiny slippery fibrous (SSF) natural Sri Lankan vein graphite obtained from the Kahatagaha mine site mining site was used as starting material [²⁶]. Two pieces of vein graphite samples were directly used as the anode and cathode. The separation between the two electrodes was kept at about 3 cm and

electrochemical exfoliation of graphite was conducted by applying a 10 V (DC) between the two graphite electrodes for 2 hours. After that, the layer floating on the top of the exfoliated graphite (EG) suspension was collected and filtered using a PTFE membrane filter (0.2 µm pore size). Then, the EG was washed several times with DI water to remove residual salt and it was placed in the oven at 80 °C for 3 h.

For further exfoliation, 1 g of electrochemically EG was added to 100 ml of DMF and it was sonicated for 3 hours in order to synthesize graphene as already reported [²⁷]. After the sonication, the solution was stirred with the help of a magnetic stirrer for 24 hours in order to further minimize the particle size. The resulting solution was then oven-dried and the precipitate was used for the characterization and solar cell fabrication.

2.3 Preparation of graphene added multilayer photoelectrode

For the preparation of 1st and 2nd layers of TiO₂ photoanode, 0.5 g of TiO₂ nanoparticles with an average particle size of 13 nm (P90 powder) was mixed with 0.1 mol dm⁻³ HNO₃ for about 30 minutes in an agate mortar with a pestle. In order to prevent the coating of TiO₂ in the area needed for FTO contacts, half of the FTO electrode was masked with scotch tape. Then, the TiO₂ slurry was spin-coated on a well-cleaned FTO substrate of 1 cm⁻² 2 cm size at 2300 rpm for 2 minutes. For this purpose, freshly prepared TiO₂ slurry was spread homogeneously on the FTO substrate with the help of a pestle, and spinning commenced immediately after the application of the TiO₂ slurry on the glass substrate, without allowing time for it to dry. Subsequently, the photoelectrode was air dried at ambient conditions for 24 h and then, sintered in air at about 450 °C for 30 minutes. For the preparation of the 3rd layer of the photoelectrode, 0.5 g of TiO₂ nanoparticles of particle size 21 nm (P25) was ground with 0.1 mol dm⁻³ and the resulting slurry was spin-coated at 1000 rpm for 2 minutes and followed by sintering at 450 °C.

The 4th, 5th and 6th TiO₂ layers were prepared following the spin coating and sintering process used for the 3rd layer preparation, except that, 0.1 g of PEO (4,000,000 molar weight) and a few drops of Titron X 100 (surfactant) were added to the TiO₂ slurry and well-grounded before the spin coating is carried out. In order to optimize the test cells with graphene-added electrodes, preliminary studies were conducted to select suitable layers and find appropriate graphene content. Preliminary observations confirmed that the addition of 1% of graphene to slurry used for 4th layer preparation gives solar cells performance enhancement.

The improved (graphene added) 4^{th} layer was prepared following the spin coating and sintering process used for the preparation of the 4^{th} layer. To prepare the graphene added photoanode, 0.005 g of graphene was added to the TiO₂ slurry and well-grounded prior to spin coating. This slurry was used to coat the 4^{th} layer of the photoelectrode. The configuration of the photoanode prepared with 6 successive layers of spin-coated TiO₂ nanoparticle layers is illustrated schematically in Figure 01. The optimized gel polymer electrolyte was prepared as per the stoichiometric composition of $(EO)_{10}(EC)_{40}(PC)_{40}Lil_{(1.2)}(Hex_4NI)_{(0.8)}(4-TBP)_{(0.85)}(MPII)_{0.25}l_{2(0.2)}$ where the abbreviation EO represents one monomer unit of the polymer PEO [²⁸].

As the initial step for the preparation of the electrolyte, appropriate amounts of Hex_4NI , LiI, MPII, and 4-TBP were dissolved in PC and EC co-solvents mixture in a closed vial. Then, after adding the appropriate amount of PEO, the mixture was stirred continuously until a homogenous mixture was obtained. Afterward, the mixture was heated up to 100 °C with constant stirring until it was converted into a transparent slurry. Finally, the mixture was cooled down to 40 °C, and 1_2 (11.5 mg) was added, and the mixture was stirred well. The resulting gel polymer electrolyte from this process was characterized and utilized for solar cell fabrication. The relevant molar ratios and weights for the electrolyte are given in Table 01.

Table 1: The weight composition and molar ratios of polymer (PEO), solvents (EC and PC), performance enhancers (MPII and 4-TBP), and iodide salts in the gel polymer electrolyte

Component	Weight/ mg	Molar ratio
PEO	100.0	10.0
PC	927.0	40.0
EC	800.0	40.0
MPII	15.1	0.25
Hex ₄ NI	87.5	0.80
Lil	36.5	1.20
4-TBP	26.1	0.85
l ₂	11.5	0.20

2.5 Fabrication of the DSSC

Two different DSSCs were assembled by sandwiching the gel polymer electrolyte between a Pt-coated glass counter electrode and a dye-sensitized TiO_2 photoelectrode with 6 spin-coated TiO_2 layers. One DSSC contained the photoelectrode prepared by incorporating graphene into the 4th layer.

3. Characterization3.1 Characterization of the photoelectrode

The X-ray diffraction (XRD) technique was utilized for crystallographic characterization of the photoanode. Cu K-α radiation wavelength 1.5405 Å from the Rigaku Ultima-IV X-Ray Diffractometer

(KYOWAGLAS-XATM, Japan) was used to generate the XRD patterns of the TiO₂ film. In order to get the XRD spectrum, two single-layer electrodes were prepared with and without graphene in the same way the 4th layer was prepared.

The scanning electron microscopic (SEM) images of the TiO_2 film were taken using Zeiss EVO-LS15 SEM. These images of the films were used to investigate the morphology of the TiO_2 films and the thickness of the photoanode.

3.2 Characterization of the DSSC

Finally, the fabricated DSSCs were irradiated with PEC-LO1 solar simulator. By keeping the active area of the cell at 19 mm² and by varying the light intensity, current-voltage (*I-V*) data were measured with a potential scan rate of 10 mV s⁻¹ using Keithley 2400 source meter and Pecell software. The light intensity was varied by changing the distance from the solar simulator to the cells. The obtained data were used to calculate the solar cell performance parameters *J*sc, *V*_{oc}, *ff*, and the PCE of the cell.

The PCE of the cell at variable intensity levels was calculated using;

$$PCE = \frac{P_{max}}{I}$$

1

where P_{max} is the maximum power output of the cell and *I* is the irradiance of the incident light. The fill factor (*FF*) of the cell was determined using;

$$FF = \frac{P_{max}}{V_{OC}J_{SC}}$$

2

Therefore,

$$PCE = \frac{FFV_{OC}J_{SC}}{P_{solar}}$$

3

Equation (3) was used to calculate the intensity-dependent PCE values which are tabulated in Table 2. **3.3 Electrochemical impedance spectroscopy**

Electrochemical impedance spectroscopy (EIS) data of the solar cells and electrolytes were measured by a Potentiostat (Autolab PGSTAT128N) together with a frequency response analyzer (FRA) module. Impedance data were collected with NOVA 1.1 software. During the measurements, the cells were placed in a Faraday cage. The EIS measurements of solar cells were done by applying a bias voltage similar to the V_{oc} of the respective cells. To get EIS data of electrolytes, sample cells were prepared by sandwiching the electrolyte between two stainless steel electrodes. The measurement frequency window was 0.1 Hz – 1000 kHz and scanning was conducted with 80 steps.

4. Results and Discussion

Understanding the variation in electrical conductivity of PEO-based electrolytes with temperature is crucial for optimizing electrolytes for different operating conditions. The ionic conductivities were calculated using the complex impedance data provided in Figure 2 (a). The Arrhenius equation aids in predicting conductivity trends and provides insights into the activation energy of charge carriers. The ionic conductivity obtained using complex impedance measurements is depicted in Figure 2 (b) as a function of 1000/T, where *T* represents the electrolyte temperature. The top axis of the plot in Figure 2 (b) specifies the electrolyte temperature. The electrolyte exhibits an ionic conductivity of 3.37 mS cm⁻¹ at 293.0 K, which increases to 7.31 mS cm⁻¹ at 353.0 K. The data presented in Figure 2 (b) were fitted to the following equation:

$$\sigma = A \exp\left(-\frac{E_a}{K_B T}\right) \tag{4}$$

where σ , *A*, *E*_a, and *K*_B represent the conductivity, the pre-exponential factor, the activation energy respectively and the Boltzmann constant. The obtained values for the *E*a and *A* by linear fitting to Equation 4 are 51.6 meV and 0.48 S cm⁻¹, respectively.

4.2 XRD measurements

The XRD pattern for the 4th layer prepared with TiO₂ and graphene is given in Figure 03. The 2 θ values along with relevant TiO₂ phases and crystal planes are marked. Most of the peaks correspond to the dominant anatase phase of TiO₂ (101, 004, 200) and the presence of several characteristic peaks in the XRD spectra provides evidence for the polycrystalline nature of the TiO₂ films. Peaks (110) and (101) correspond to the rutile phase of TiO₂ and the origin of the peak (110) FTO is due to the diffraction pattern associated with FTO glass. In comparison, (101)A, (111)R, and (200)A peaks have become broader for graphene-free samples, which can be attributed to the smaller size of crystallites or an increase in lattice defects in graphene-free samples. Furthermore, the intensity of reflection from the (004)A plane has diminished in the graphene-free sample since it is not a preferred orientation of the sample.

In Figure 03 (a), the peak related to graphene is clearly seen at (001) crystal plane. However, the intensity of the peak is not as strong as TiO_2 peaks because only 0.005 g (1% w/w) of graphene has been used to fabricate the photoanode. The absence of significant carbon peaks can be due to the dominance of TiO_2 content (99%) in the electrode.

4.3 Raman spectroscopy

Figure 04 shows the Raman spectra of the exfoliated graphene. Two dominant peaks are visible namely the G band and 2D band at intensities 1580 cm⁻¹ and 2730 cm⁻¹, respectively. The occurrence of the G band is due to the stretching vibrational motion of SP² hybridization of carbon-carbon bonds, and the peak position occurs at 2730 cm⁻¹ is a characteristic signature of graphene [26].

The number of layers in exfoliated graphene was calculated using the intensity ratios between 2D and G peaks (I_{2D}/I_G). According to the experimental results, the value obtained for I_{2D}/I_G ratio is 1.43. This data confirmed the successful synthesis of double layered graphene [26]. This exfoliated double layered graphene synthesized directly from vein graphite is used to fabricate the photoanodes of the solar cells investigated in this study.

SEM images of the fabricated photoelectrodes at a magnification of 100,000 are shown in Figure 4. Figure 4(a) shows the top surface morphology of a 4-layer photoelectrode fabricated without graphene in the 4th layer while Figure 4(b) shows the improved photoelectrode by adding graphene to the 4th layer. When comparing the morphologies of these two layers, it can be observed that 4 layered electrodes prepared by adding graphene to the 4th layer (Figure 4(b)) consist of graphene sheets. The presence of graphene in the 4th layer can enhance the conductivity in the photoelectrode and alter the dye adsorption properties as well as influence the photocurrent, PCE, and fill factor of the DSSCs. Also, the presence of graphene may minimize the charge transfer resistances at the interfaces of the TiO₂ layer by faster electron transport which can hinder recombination. In addition, graphene can contribute to efficiency enhancement by improving light scattering as well.

Figures 4(c) and 4(d) show the top surface morphology of the two 6-layer photoelectrodes prepared without and with graphene to the 4th layer, respectively. These images confirm the formation of crack-free, nanocrystalline mesoporous thin films with high porosity that offer a large surface area for dye absorption. As we can see, these two images (Figure 4(c) and 4(d)) both look identical in the surface morphology because the same procedures and steps have been repeated to fabricate the 6th layer electrodes except for the 4th layer. The image in 4(d) confirms there are no graphene sheets visible. Therefore, the graphene in the 4th layer is well covered by the 5th and 6th TiO₂ layers.

4.4 Dependence of Cell Performance on Irradiance Level

Solar cell characteristics were evaluated as a function of intensity by taking *FV* characteristic curves. Both graphene-added and graphene-free cells exhibited typical dye-sensitized solar cell behavior but with variations in their parameters. The plots for current density vs. cell potential (*J-V*) and power density vs. cell potential (*P-V*) are shown in Figure 06. The *J-V* and *P-V* curves of the graphene-added DSSCs at each intensity level are given in Figures 06(a), and 06(b), respectively. The *J-V* and *P-V* curves of the graphene-free control DSSCs at each intensity level are shown in Figures 05 (c) and(d), respectively. The photocurrent density and output power density of both cells decrease with decreasing intensity due to the reduction of photon flux and thus resulting in low photoelectron generation.

The *J*-*V* and *P*-*V* characteristic curves in Figure 06 are used to determine the open-circuit voltage (V_{oc}), the short circuit current density (J_{sc}), the fill factor (*ff*), and the PCE of the fabricated DSSC under different irradiation levels. The values calculated for graphene-free DSSC (control cell) at different intensity levels are given in Table 03 while the respective values for the graphene-added cell (test cell) are given in Table 04.

The cell fabricated without graphene in the 4th layer exhibited significantly low performance compared to that of the graphene-added cell. The fabricated DSSC without graphene achieved 5.39% of efficiency under 1108 W m⁻² irradiance while that in graphene added cell is 6.43%. With the gradual decrease of light irradiance level, the PCE of the cells increases though the net power output drops. This PCE increase observed in both cells with decreasing irradiance is attributed to an increase in fill factor which indicates the decrease in resistive losses (Tables 03 and 04). For example, the PCEs of graphene-free and graphene -added cells increase from 5.05% to 6.82% under one sun illumination (1000 W m⁻²). Consequently, the highest PCE and *ff* are exhibited at the lowest tested irradiance level of 67 W m⁻². The PCEs of graphene-free and graphene-added cells increase to 6.68% and 9.40% under 67 W m⁻² intensity level. With the results obtained from both cells, it is evident that the efficiency and fill factor of the DSSCs increase with the decrease of irradiation. Achieving higher efficiencies in dye-sensitized solar cells under low light intensities agrees with the literature [^{29,30,31}].

Further in both the cells *ff* has increased with decreasing light intensity. It can be due to reduced, recombination kinetics, non-radiative thermalization losses and charge transport losses. At the lower intensities, the generation of electron-hole pairs in the photoelectrode is less. This decreases the probability of carrier recombination before reaching the electrodes. Therefore, cells exhibit higher photocurrent at maximum power output contributing to a higher fill factor. At lower intensities, a smaller number of photons are available to excite electrons. Therefore, along with decreasing carrier generation and associated non-radiative recombination and thermalization of charge carriers decrease contributing to enhancing the fill factor. Since current and number charge carriers at lower light intensities are less, the resistive losses due to diffusion and the resistances are low and hence a higher fill factor can be expected.

Table 2: Calculated values for the V_{OC} , J_{SC} , ff, η , and the maximum power of the cell under different irradiation levels for cells prepared without adding graphene to the 4th layer.

Intensity /	$V_{\rm oc}$ / V	J _{sc} /	V _{opt} / V	J _{opt} /	P _{max} / W	ŋ/%	ff /%
W m ⁻²		mA cm ⁻²		mA cm ⁻²			
1108	0.7	12.3	0.53	11.3	5.98	5.39	69.6
1000	0.7	11.0	0.53	10.38	5.5	5.50	71.2
607	0.7	7.24	0.53	6.80	3.61	5.94	71.2
381	0.69	4.56	0.54	4.25	2.30	6.02	72.9
251	0.68	3.13	0.54	2.92	1.58	6.29	74.1
180	0.67	2.24	0.54	2.11	1.14	6.33	76.1
136	0.66	1.67	0.54	1.60	0.86	6.35	78.2
104	0.65	1.32	0.54	1.25	0.67	6.48	78.7
85	0.64	1.08	0.54	1.04	0.56	6.59	80.9
67	0.63	0.87	0.55	0.81	0.45	6.68	81.5

Table 3: Calculated values for the V_{OC} , J_{SC} , ff, η , and the maximum power of the cell under different irradiation levels for cells prepared by adding graphene into the 4th layer.

Intensity /	V _{oc} / V	J _{sc} /	V _{opt} / V	J _{opt} /	P _{max} / W	ŋ/%	ff /%
W m ⁻²		mA cm ⁻²		mA cm ⁻²			
1108	0.74	17.0	0.47	15.2	7.12	6.43	56.5
1000	0.77	13.4	0.54	12.6	6.82	6.82	66.2
607	0.71	9.69	0.50	8.97	4.49	7.40	65.2
381	0.71	6.34	0.52	5.92	3.08	8.07	68.3
251	0.70	4.20	0.53	3.98	2.11	8.41	71.9
180	0.69	3.02	0.54	2.88	1.55	8.62	74.5
136	0.69	2.27	0.55	2.17	1.20	8.79	76.3
104	0.68	1.73	0.55	1.70	0.94	9.01	79.5
85	0.68	1.42	0.55	1.42	0.78	9.23	81.3
67	0.68	1.11	0.55	1.15	0.63	9.40	83.1

4.5 Incident photon-to-current efficiency (IPCE)

IPCE measurements offer valuable insight into the spectral response and performance of a DSC across the solar spectrum. By varying the wavelength of the incident light, the obtained IPCE spectrums for the two distinct variants of the fabricated solar cells are given in Figure 7. The reference solar cell is composed of a photoanode solely made of TiO_2 nanoparticles which provides a baseline for comparison. During characterization, it exhibits moderate IPCE values with a single narrow absorption peak. This graphene-free cell exhibits a maximum IPCE of 40.65 at 525 nm. The test cell, enhanced with graphene, shows higher IPCE with two distinctive peaks at ~345 nm and ~530 nm along with IPCE of 44.35 and 53.76%. The IPCE value is usually determined by the charge collection at the collecting electrode and dye loading capacity. With added graphene on TiO_2 could capture and shuttle electrons quickly to the collecting electrodes which leads to the improvement of the IPCE value of the graphene-based solar cell over the entire wavelength of the spectrum [³², ³³].

4.6 Electrochemical impedance (EIS) spectroscopy

In order to get further insight into the higher efficiency of the test cell, EIS data is utilized. Figures 8 (a) and 8 (b) represent the Nyquist plots and Bode phase diagrams for the two cells. Using the impedance spectra Bode diagram was plotted and estimated the values of electron transport lifetime $(t_{\rm tr})$, recombination lifetime $(t_{\rm rec})$ and diffusion length $(D_{\rm L})$ are given in Table 5.

The $D_{\rm L}$ is the average distance traveled by a charge carrier within the semiconducting material before it recombines. This length plays a crucial role in determining the efficiency of charge carrier transport and lifetime inside the cell. In this study, $D_{\rm L}$ was calculated by following the equation, along with the impedance data analysis [³⁴, ³⁵, ³⁶].

$$D_L = L \sqrt{\frac{R_{rec}}{R_{tr}}}$$

Where, R_{tr} and R_{rec} represent the charge transfer resistance and recombination resistance. *L* is the layer thickness [³⁷]. Nyquist plots in Figure 8 (a) were used to determine the R_{tr} and R_{rec} for each cell and layer thickness was measured using high-resolution scanning electron microscopy (*L*= 5.2 mm).

Table 4: Recombination lifetimes (t_{rec}), electron transport lifetimes (t_{tr}) and diffusion lengths (D_L) of the prepared DSCs.

Cell	(<i>L</i>)/ mm	<i>t</i> _{rec} / mS	<i>t</i> _{tr} / mS	D _L / mm
DSC with TiO ₂ /Graphene photoelectrode	5.2	3.22	0.34	7.1
DSC with TiO ₂ only photoelectrode	5.2	2.43	0.25	6.2

Interestingly the study shows the DSC fabricated with TiO_2 and graphene has a higher diffusion length value than that of the reference cell. The increased diffusion length enhances the likelihood that the charge carriers will reach the electrodes contributing to enhancing collection efficiency. In a DSC photogenerated electrons and holes are separated at the dye-semiconductor interface. However, a certain number of charge carriers recombine instead of traveling through the external circuit, which could negatively impact the overall performance of the solar cell. By increasing the recombination lifetimes, it is possible to prolong the duration of which these electron-hole pairs remain separated. This prolonged duration allows more charge carriers to reach the electrodes and contribute to the photocurrent. The study shows the fabricated solar cell with TiO_2 and graphene contains higher recombination lifetimes compared to the reference cell. This longer lifetime may have impacted positively to improve cell efficiency.

4.7 Effect of graphene on cell performance

The cell fabricated by adding graphene shows higher V_{OC} , J_{SC} , *ff*, and PCE compared to the cell without graphene. The observed performance enhancement is very likely due to the positive effects imposed by the incorporated graphene. For a better visualization of the behavior PCE and *ff* variations of the cells with light intensity are shown in Figure 9 (a) and (b) respectively.

Graphene has excellent electrical conductivity and optical properties, enabling it to enhance the absorption of light and facilitate efficient charge transport within the solar cell, leading to higher conversion efficiencies and increased power output. The improved performance with added graphene observed in this study can be attributed to the combined effects of the following process.

- Decreased charge transport resistance of the photoelectrode and charge transfer resistance between two interfaces of TiO₂ as a result of increased conductivity [^{38,39}]. The reduction of resistive losses improves the photocurrent of the cell. The decrease of resistive losses with added graphene is inferred by the higher *ff* shown by the graphene-incorporated cell.
- 2. The improved charge transfer between the FTO current collectors indirectly helps to reduce the recombination losses. The behavior is evident by the increase of V_{OC} , and *ff* of the graphene-added cell. This process enables more efficient conversion of light energy to electricity.
- 3. The V_{oc} enhancement can be contributed by faster electron extraction by graphene added interlayer from the excited dye molecules [⁴⁰, ⁴¹]. Graphene's large surface area and high carrier mobility facilitate improved electron injection from the excited dye molecules to the Graphene/TiO₂ layer, thereby enhancing the efficiency of the dye to photoelectron conversion process. This can also reduce energy loss due to non-radiative decay.
- 4. Graphene's large surface area can facilitate the distribution of TiO₂ and thus can enhance the effective surface area available for dye adsorption by the electrode as inferred by analyzing SEM images. This promotes higher dye loading, leading to increased light absorption and improved device performance.

Finally, it can be deduced that the DSSC made with graphene-added photoelectrode- exhibited impressive efficiency enhancement under low irradiation. For instance, the addition of 1% of graphene to the 4^{th} TiO₂ layer of the photoanode improves the efficiency of the cell from 5.50% to 6.82% under one sun illumination (1000 W m⁻²). This is a 24% efficiency improvement. Efficiency enhancements given by the graphene-added DSSC with respect to graphene-free solar cells (control device) are given in Table 6 for different irradiance levels.

Table 5: Efficiency enhancements by the graphene-incorporated photo electrode-based DSSCs with respect to the graphene-free solar cell.

Intensity / W m ⁻²	1108	1000	607	381	251	180	136	104	85	67
Efficiency enhancement /%	19.3	24	24.6	34.1	33.7	36.2	38.4	39.0	40.1	40.7

The present study shows that not only graphene can be used to enhance DSSC performance but also that graphene can be successfully synthesized from natural vein graphite using a scalable and cost-effective method.

4. Conclusions

This study reports efficiency enhancements in graphene-incorporated, quasi-solid-state DSSCs under ambient and low-light conditions. The XRD results and high-resolution SEM images confirmed the presence of anatase TiO_2 nanoparticles in photoelectrodes. The Raman spectroscopy confirmed the successful fabrication of two-layer graphene from the vein graphite. One of the challenges of widely utilizing graphene in solar cells is their high cost. This study presents a cost-effective, feasible, and novel method to exfoliate vein graphite sourced directly from the mine site and a strategic way to integrate them in photoanodes. SEM images confirm the presence of graphene in the most effective layer of the photoanode.

The PCEs of 5.05% graphene-free cells (control cell) increased to 6.82% with the integration of graphene into the photoanode, exhibiting 24% enhancement at ambient irradiation. The V_{oc} , J_{sc} , and ff, values of graphene-incorporated DSSC are 6.82%, 770 mV, 13.4 mA cm⁻², and 66.2% respectively at 1000 W m⁻². Notably, the efficiency and fill factor exhibited an intriguing increase at lower light intensities. The synthesized graphene incorporated DSSC achieved a remarkable efficiency of 9.4% and a fill factor of 83.1% at 67 W m⁻² solar irradiance. The efficiency enhancement for 67 W m⁻² intensity compared to 1000 W m⁻² is ~38%.

The performance of the improved DSSC by integrating the synthesized graphene from vein graphite outperforms the reference cell at all the intensities measured. This improved efficiency is attributed to the higher charge carrier recombination lifetime (3.22 mS) and high diffusion lengths (7.1 μ m) of the improved DSC by integrating graphene into to photoanode.

Declarations

Funding

The authors would like to acknowledge the financial support from the Postgraduate Institute of Science, University of Peradeniya (grant No. PGIS/2020/10), and Peradeniya University Research Grant No. 2023/34/S.

Author Contribution

T.M.W.J. Conceptualization, Methodology, Project administration and Supervision, Writing, Reviewing Editing fund acquisition and Formal analysis.S.M.S.G. Data collection, Formal analysis and measurement, 1st draft preparation. G.G.D.M.G.G: Data collection, Formal analysis and measurement.B.M.K.P., Writing, Reviewing, Editing and Formal analysis. L.A.DeS.,Writing, Reviewing, Editing and Formal analysis. M.A.K.L.D. and G.R.A.K., Writing, Reviewing, Editing and Formal analysis.

Acknowledgement

The authors would like to acknowledge Udara Wadasinghe in University Peradeniya, for the technical support given for this project.

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Figures



Figure 1

A schematic diagram to illustrate the configuration of the multilayer photoelectrodes investigated in this study: (a) without graphene and (b) with graphene in the 4th layer



a) Complex impedance plots of the electrolyte at different temperatures, b) the graph of conductivity (σ) versus 1000/T obtained using complex impedance measurements.



XRD spectra of the 4^{th} layer prepared with (a)TiO₂ and 1% graphene, (b) TiO₂ only



Raman spectra of the exfoliated graphene samples.



(a) The SEM image of the 4th layer of the TiO₂ electrode prepared without adding graphene, (b) SEM image of the 4th layer of the electrode prepared by adding graphene to the 4th layer. SEM images of the 6-layer photoanodes prepared (c) without adding graphene and (d) SEM image of the top (6th) layer of the electrode prepared by adding graphene to the 6th layer.



Figure 6

(a) Current density vs. cell potential curves for the cell prepared without graphene (b) Current density vs. cell potential curves for the cell prepared by adding graphene to the 4th layer (c) Power density vs. cell potential curves for the cell prepared without graphene (d) power density vs. cell potential curves for the cell prepared by adding graphene to the 4th layer.



IPCE spectra of the DSCs with TiO_2 photoelectrode and graphene TiO_2 added photoelectrode.



Figure 8

(a) The Nyquist plots and (b) the Bode phase diagrams for the two prepared DSCs.

The $D_{\rm L}$ is the average distance traveled by a charge carrier within the semiconducting material before it recombines. This length plays a crucial role in determining the efficiency of charge carrier transport and lifetime inside the cell. In this study, $D_{\rm L}$ was calculated by following the equation, along with the impedance data analysis [³⁴, ³⁵, ³⁶].



Figure 9

(a) Efficiency variation of the cells with light intensity, and (b) Variation of the fill factor of the cells with light intensity.