# Hybrid dye-sensitized solar cells with graphene—A convenient method to seal liquid state devices

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# Hybrid dye-sensitized solar cells with graphene—A convenient method to seal liquid state devices

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Hybrid dye-sensitized solar cells were fabricated with an iodide/triiodide based liquid electrolyte and graphene as the hole transporting material to overcome the leakage problem associated with liquid state devices. Here, a thin layer of the iodide/triiodide based liquid electrolyte was drop cast onto the working electrode which consists of a dye coated mesoporous TiO<sub>2</sub> layer. Then, this thin layer of the liquid electrolyte was sealed with a layer of graphene by the doctor blade method. A platinized transparent conducting oxide glass was used as the counter electrode to complete the device. An overall energy conversion efficiency of  $6.13 \pm 0.10\%$ with a  $V_{\rm OC}$  of 645 ± 20 mV and a  $J_{\rm SC}$  of 14.4 ± 1.2 mA cm<sup>-2</sup> was observed under AM 1.5 irradiation (1000 W m<sup>-2</sup>). These devices exhibit a maximum incident photocurrent conversion efficiency of 51.6% which was observed at a wavelength of 525 nm. Furthermore, electrochemical impedance spectroscopy measurements revealed that the charge transfer resistance at the counter electrode/electrolyte interface was significantly reduced compared to the standard iodide/triiodide redox mediator after applying graphene as the hole transporting material which may promote efficient charge transfer within the device. Published by AIP Publishing. https://doi.org/10.1063/1.5037150

# I. INTRODUCTION

Ever since the construction of high efficient dye-sensitized solar cells (DSCs) by O'Regan and Grätzel, in 1991, these devices have become an attractive route to harvest clean and renewable energy.<sup>1</sup> DSCs comprise a working electrode (WE), a counter electrode (CE), and an electrolyte which rests in between. WE consists of a mesoporous semiconductor layer deposited onto a transparent conducting substrate, typically fluorine doped tin oxide (FTO), which is then coated with a dye. A platinum deposited FTO glass substrate (FTO-Pt) serves as the CE. The electrolytes employed are in the form of liquid, quasi-solid, or solid state. Certified efficiencies as high as  $11.9\%^2$  have been reported for liquid-state DSCs (liquid-DSCs). However, some of the major drawbacks preventing the commercialization of the liquid-DSCs are the leakage of the liquid electrolyte, the degradation of the electrolyte, and the dye that limits the device lifetime.<sup>3</sup> Conversely, solid-state DSCs (solid-DSCs) succeed in surmounting the above barriers faced by liquid-DSCs. For the first time, a solid-DSC with a heterojunction between n-SnO<sub>2</sub> and p-CuSCN was reported by Tennakon et al. in 1988.<sup>4</sup> Substitution of the volatile liquid electrolyte with a solid-state hole transporting material (HTM) is the key feature of solid-DSCs. Cu<sup>5</sup> and CuSCN<sup>6</sup> are extensively used inorganic HTMs, and NiO,<sup>7</sup> a p-type semiconductor, has also been applied as an HTM in solid-DSCs. In addition, spiro-OMeTAD<sup>8,9</sup> and PEDOT<sup>10,11</sup> are organic HTMs that are extensively explored in solid-DSCs. Recent developments in novel photosensitizers have

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revealed that a quinoxaline-based AQ310 organic sensitizer in conjunction with spiro-OMeTAD as the HTM has achieved a photoelectric conversion efficiency (PCE) of 8.0% in solid-DSCs.<sup>12</sup> Moreover, an organic blue-colored dye designated as S5 has shown a record PCE of 7.8%.<sup>13</sup> However, the prevalence of the weak solid-to-solid contacts of these solid-state devices hinders realizing high performances.<sup>14,15</sup>

Recently, an extensive exploration was done on graphene as a CE material and a HTM in photovoltaics due to its remarkable electronic properties.<sup>16</sup> Graphene is the thinnest (thickness of a carbon atom) 2D material and exhibits a high carrier mobility,<sup>17,18</sup> a high specific surface area,<sup>19</sup> and a high optical transparency.<sup>20</sup> Lately, a graphene sandwiched solid-DSC with 3D-ZnO WE and FeS<sub>2</sub> CE has reported a PCE of 7.0%,<sup>21</sup> whereas a PCE of 9.1% has been achieved where graphene is incorporated into a gel polymer electrolyte in quasi-solid-DSCs.<sup>22</sup> Our approach of fabricating a hybrid of a liquid-DSC and a solid-DSC(Fig. 1) offers a pathway to overcome the unfavorable features of both types. A similar study was experimented previously with hybrid-DSCs where an ultra-thin layer of the  $I^-/I_3^-$  redox mediator was sandwiched between the nanocrystalline semiconductor surface and the graphite hole collector to attain a PCE of 3.7%.<sup>3</sup> Herein, we report an improved hybrid-DSC, integrating graphene as the HTM and  $I^-/I_3^-$  as the liquid redox mediator, demonstrating an enhanced PCE of 6.13 ± 0.10% with a  $V_{OC}$  of 645 ± 20 mV, a  $J_{SC}$  of 14.4 ± 1.2 mA cm<sup>-2</sup>, and a *FF* of 0.66 ± 0.04 under simulated one sun irradiation (AM 1.5, 1000 W m<sup>-2</sup> intensity).

# **II. EXPERIMENTAL**

All the reagents were obtained from Sigma Aldrich, Hayman (England), and Merck (Pty) Ltd unless otherwise stated and used as received. Ball milled graphite (particle size  $< 45 \,\mu\text{m}$ , 99%) was obtained from Bogala Graphite mine, Sri Lanka, and conductive FTO glass plates with a resistance of 8  $\Omega/\Box$  and a thickness of 3 mm were purchased from Sigma Aldrich.

#### A. Device fabrication

#### 1. Working electrode (WE)

A dense layer of TiO<sub>2</sub> was spray pyrolyzed on a FTO glass plate at 500 °C, using a solution of 2 mL of titanium tetraisopropoxide and acetylacetone (1:2 v:v) in 18 mL of ethanol. Then, the TiO<sub>2</sub> colloidal suspension was prepared by passing steam through a solution of titanium tetraisopropoxide (10 mL), acetic acid (1.5 mL), and ethanol (15 mL) until it turned to a transparent gel. It was then mixed with distilled water (25 mL) and autoclaved at 150 °C for 3 hours. A mixture of the TiO<sub>2</sub> colloidal suspension (10 mL), acetic acid (2.5 mL), Triton X100 (0.5 mL), and ethanol (10 mL) was ultrasonicated for 10 minutes. Spray pyrolysis was used to deposit a mesoporous TiO<sub>2</sub> layer using the above prepared solution at 150 °C. The fabricated film was then sintered at 500 °C for 30 minutes. The mesoporous TiO<sub>2</sub> film was immersed (~80 °C) in a solution of 0.30 mM N719 in acetonitrile and tert-butanol (1:1 v:v) for 12 hours. Once it was removed from the dye solution, it was rinsed with acetonitrile and then dried under an air flow.



FIG. 1. Schematic diagram of a hybrid-DSC.

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# 2. Electrolyte (lodide/triiodide)

The liquid electrolyte was prepared by dissolving 1-butyl-3-methylimidazolium iodide (0.60 M), iodine (0.03 M), guanidinium thiocyanate (0.10 M), and tert-butylpyridine (0.50 M) in acetonitrile. The iodide/triiodide liquid electrolyte was then added to the dye coated  $TiO_2$  film, and it was allowed to penetrate through the mesoporous layer. After a few minutes, the excess electrolyte was wiped off.

#### 3. Counter electrode (CE)

Graphene was prepared using the modified Hummers method. Potassium permanganate (3 g) was gradually added to the mixture of ball milled graphite (1 g) and sulfuric acid (50 mL) while stirring in an ice bath  $(10 \degree \text{C})$ . Then, the solution was stirred at room temperature for 25 minutes and sonicated in an ultrasonic bath for 5 minutes. Sonication and stirring processes were alternatively repeated 12 times, to which 200 mL of distilled water was added and sonicated for further 2 hours. The mixture was then treated with 1.0 M sodium hydroxide to adjust the pH of the solution to 6, and then, it was sonicated for another hour. Next, a solution containing distilled water (200 mL) and L-ascorbic acid (20 g) was slowly added to the exfoliated graphite oxide suspension at room temperature and heated at 95 °C for one hour. The resulting black precipitate was filtered and washed with 1.0 M hydrochloric acid solution and distilled water. The precipitate was freeze dried to obtain graphene powder. Prepared graphene powder was doctor bladed on top of the working electrode using ethanol. The platinum coated FTO glass substrate was used to complete the device.

#### **B.** Characterization

#### 1. Current-voltage characteristics (J-V)

J-V characteristics of the device were measured under the illumination of 1000 mW cm<sup>-2</sup>, AM 1.5 G simulated sunlight using a computer controlled setup coupled to a Keithley 2400 multimeter and a potentiostat. A 450 W Xenon light source (Oriel, USA) with an AM 1.5 filter was used to obtain the simulated sunlight with the above-mentioned intensity. Prior to the measurements, the solar simulator was calibrated using a reference silicon solar cell.

#### 2. Incident photon to current conversion efficiency (IPCE)

A Keithley 2400 source meter was used for IPCE measurements, and spectra were obtained under short circuit conditions. The light was generated using a Xenon lamp (Oriel, 150 W) and a monochromator (Cornerstone 260). A silicon photodiode (Peccell Technologies, Japan) was utilized to calibrate the output from the light source. The area of the illumination spot was maintained to be slightly smaller than the active area of the test cell.

# 3. Electrochemical Impedance spectroscopy (EIS)

The impedance of the counter electrode was measured using a two electrode system implemented with Auto lab, NOVA 1.11. The electrolyte was inserted between two identical counter electrodes and connected to the instrument. The measurements were obtained separately with graphene, an  $I^{-}/I_{3}^{-}$  liquid electrolyte, and graphene  $I^{-}/I_{3}^{-}$  electrolyte composite systems.

#### 4. Scanning electron microscopy (SEM)

The morphology of the surface of the counter electrode was obtained using an EVO/LS 1.5, Zeiss international scanning electron microscope.

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#### 5. Raman spectroscopy

The Renishaw Invia Reflex Raman Microscope system with a 532 nm laser beam was used. A layer of graphene doctor bladed on the FTO was used.

#### 6. Powder X-ray diffraction (PXRD)

A Siemens D 5000 Powder X-ray diffractometer was used for obtaining PXRD patterns. Cu  $K_{\alpha}$  radiation with a scanning angle (2 $\theta$ ) range from 5° to 40° at the slow scanning rate was employed.

#### **III. RESULTS AND DISCUSSION**

Synthesized graphene was first characterized using PXRD and Raman Spectroscopy. In the PXRD pattern (see Fig. S1), the absence of a sharp peak at 26° clearly indicates the absence of graphite. The broad peak is around 25°, and the  $2\theta$  value with lower intensity shows the absence of a three dimensional crystal structure due to the small size of the layers or a relatively short domain order of the stacked sheet. Peaks are characterized with hexagonal carbon (JCPDS Card No.75–1621), where the peak at 26.5° corresponds to the (002) plane. According to the Debye–Scherrer formula, the average crystal size of graphene powder was calculated to be ~48 nm. Furthermore, the interlayer spacing corresponding to the (002) plane was found to be ~2.27 nm as per Bragg's equation.

In the Raman spectrum of graphene (see Fig. S2), the two bands corresponding to D and G bands appeared at  $1305 \text{ cm}^{-1}$  and  $1584 \text{ cm}^{-1}$ , respectively. The intensity ratio of the D and G bands is a measure of disorder which was calculated to be 1.63. Furthermore, all kinds of  $sp^2$  carbon materials exhibit a strong band in the range of  $2500-2800 \text{ cm}^{-1}$  in the Raman spectrum. This Raman band of graphitic  $sp^2$  materials is called the 2D band. According to the spectrum obtained, the 2D band appears at  $2715 \text{ cm}^{-1}$ . The intensity ratio between the 2D band and the G band gives the idea about the number of graphene layers. For a single layer graphene, this ratio should be 2. Here, the ratio of 2D to G was nearly at 0.5. Thus, this suggests more than one layer (~5) of graphene in the sample.

After the characterization of synthesized graphene, DSCs were fabricated, and the device optimization was focused on the resistance of the  $TiO_2$  dense layer, the thickness of the  $TiO_2$ mesoporous layer, the time allowed for the  $I^{-}/I_{3}^{-}$  based electrolyte to penetrate through the WE, and the thickness of the graphene layer. A dependency of  $J_{SC}$  on the resistance of the  $TiO_2$  dense layer was observed where the maximum  $J_{SC}$  was observed within the resistance range of 500  $\Omega$ -1000  $\Omega$ , and a further increase in the resistance tends to decrease  $J_{SC}$  (Table S1). Although there was no significant dependency demonstrated on the mesoporous  $TiO_2$  layer thickness, 15  $\mu$ m (Table S2) was selected as the optimum thickness as improved V<sub>OC</sub> and FF values were observed. Once the WE was fabricated, the I-/I3- based electrolyte was drop casted, and then, the time allowed for penetration was varied from 2 to 300 minutes (Table S3). The device performance was found to be independent of the time allowed, which implies that the penetration is complete within the first two minutes. Therefore, to avoid solvent evaporation and to reduce fabrication time, 2 minutes was selected as the optimum penetration time. Finally, the thickness of the graphene layer was varied to obtain the thickness ranging from  $1 \,\mu m$  to  $6 \,\mu m$  (Table S4). Increasing the layer thickness of graphene to  $4 \,\mu m$  demonstrated a drastic improvement ( $\sim$ 71%) in J<sub>SC</sub>. Even though there is a slight decrease in V<sub>OC</sub> and FF, the overall device performance was enhanced by 46%. A further increase in the thickness of the graphene layer decreased the device efficiency due to a drop in  $J_{SC}$ . This may be due to short circuiting of the device. When successive graphene layers reside on top of each other, then there is a possibility for electronic conduction not only among the sheets but also along the graphene sheets, leading to short circuiting of the device.

Subsequently, complete optimization of the device led to a maximum PCE of  $6.13 \pm 0.10\%$  with a  $V_{\rm OC}$  of  $645 \pm 20$  mV, a  $J_{\rm SC}$  of  $14.4 \pm 1.2$  mA cm<sup>-2</sup>, and a *FF* of  $0.66 \pm 0.04$  under simulated one sun irradiation (AM 1.5, 1000 W m<sup>-2</sup> intensity). Figure 2 shows the *J*-*V* characteristic



FIG. 2. Characteristic J-V curves at simulated one sun (1000 W m<sup>-2</sup>) of DSCs based on  $I^-/I_3^-$  and  $I^-/I_3^-$  and graphene sensitized with N719. The  $I^-/I_3^-$  electrolyte contained I<sub>2</sub> (0.03 M), tBP (0.50 M), 1-butyl-3-methylimidazolium iodide (0.60 M), and guanidinium thiocyanate (0.10 M) in acetonitrile. The graphene layer thickness is 4  $\mu$ m.

curve for the best performed DSC, and Table I summarizes the average efficiencies observed for devices constructed with the  $I^-/I_3^-$  redox mediator and the hybrid devices constructed with the  $I^-/I_3^-$  based electrolyte and graphene.

The standard devices that consist of an  $I^{-}/I_{3}^{-}$  based electrolyte achieved a maximum PCE of  $9.17 \pm 0.19\%$  with a  $V_{\rm OC}$  of  $711 \pm 37 \,\mathrm{mV}$ , a  $J_{\rm SC}$  of  $16.7 \pm 1.2 \,\mathrm{mA} \,\mathrm{cm}^{-2}$ , and a FF of  $0.79 \pm 0.12$  under simulated one sun irradiation (AM 1.5, 1000 W m<sup>-2</sup> intensity). Significantly lower V<sub>OC</sub> was observed for hybrid-DSCs compared to the standard devices. This could be the result of poor contact between the CE and graphene as a Pt mirror (sputter coated Pt on FTO glass) with a smoother surface was used as the CE in these devices. Lower  $J_{SC}$  observed in hybrid devices may be due to higher interfacial charge recombination reactions or short circuiting of the device as explained above. Furthermore, the scanning electron microscopy image of the surface of the mesoporous  $TiO_2$  layer (Fig. S3) of the hybrid-DSC showed defects on the surface that may have increased the charge recombination losses. Nevertheless, these devices have almost doubled the efficiency reported for the devices based on graphite where the same device architecture was used. The main improvement is the enhancement in  $J_{SC}$ , where more than 14 mA cm<sup>-2</sup> has been generated, while the device based graphite reported only around  $8 \text{ mA cm}^{-2}$ . Higher current generation could be explained as graphene has a higher electrical conductivity than graphite due to the existence of quasiparticles. Electrons that function as if they have no mass are called quasiparticles, and these particles can travel long distances without scattering.

TABLE I. Photovoltaic parameters for DSCs prepared with the  $I^-/I_3^-$  redox mediator (standard DSCs) and the  $I^-/I_3^-$  redox mediator and graphene (hybrid-DSCs), sensitized with the N719 dye measured under simulated one sun (AM 1.5, 1000 W m<sup>-2</sup> intensity) irradiation. The photoanode TiO<sub>2</sub> film thickness is 15  $\mu$ m. Sputter coated Pt on FTO glass was used as the counter electrode. The  $I^-/I_3^-$  electrolyte contained I<sub>2</sub> (0.03 M), tBP (0.50 M), 1-butyl-3-methylimidazolium iodide (0.60 M), and guanidinium thiocyanate (0.10 M) in acetonitrile. The thickness of the graphene layer is 4  $\mu$ m. The average photovoltaic parameters are listed with standard errors derived from 3 different cells.

Electrolyte	$I^{-}/I_{3}^{-}$	$I^-/I_3^-$ and graphene
V <sub>OC</sub> (mV)	711 ± 37	$645 \pm 20$
$J_{\rm SC}$ (mA cm <sup>-2</sup> )	$16.7 \pm 1.2$	$14.4 \pm 1.2$
FF	$0.79 \pm 0.12$	$0.66 \pm 0.04$
η (%)	$9.17\pm0.19$	6.13 ± 0.10



FIG. 3. IPCE measurements under low light conditions (<2% Sun) of DSCs based on  $I^-/I_3^-$  and  $I^-/I_3^-$  and graphene sensitized with N719.

*J-V* characteristics are in good agreement with the incident photon to current conversion efficiency (IPCE) spectra obtained for these two devices (Fig. 3). Even though both spectra have similar shapes, the IPCE spectrum of the hybrid-DSC reached only a maximum IPCE of 51.6% at 525 nm, explaining the lower current density generated within the device, and IPCE observed for the standard device was 59.6% at 535 nm which may have led to the higher current density. The IPCE spectrum of the hybrid-DSC indicates a lower cut off wavelength than the standard devices. Low energy light is absorbed by the bulk of a device, and the low diffusion length will affect collection probability from the bulk. This may reduce the quantum efficiency at higher wavelengths. Therefore, the hybrid-DSC may have a lower cut off wavelength.

Electrochemical impedance spectroscopy (EIS) was carried out on symmetric cells that were fabricated using two identical CEs (sputter coated Pt) and an electrolyte that was sandwiched between them (Fig. 4). The symmetric cells based on  $I^-/I_3^-$  and graphene showed a lower charge transfer resistance at the CE/electrolyte interface (~0.4  $\Omega$ ) when compared to the



FIG. 4. Nyquist plot of electrochemical impedance spectra measured between  $10^5$  and  $10^{-1}$  Hz on counter–counter electrode symmetric cells based on  $I^-/I_3^-$  and  $I^-/I_3^-$  and graphene under dark conditions.

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symmetric cells with the  $I^-/I_3^-$  based electrolyte (~1.4  $\Omega$ ). Even though the contact between the CE and graphene was assumed to be poorer, the charge transfer is favorable in the presence of graphene compared to the liquid electrolyte.

#### **IV. CONCLUSIONS**

In conclusion, an attempt was made to improve the device architecture of the liquid-DSCs by incorporating an ultra-thin layer of an  $I^{-}/I_{3}^{-}$  based liquid electrolyte and sealing it with a layer of HTM, graphene. The presence of graphene after the synthesis was confirmed using PXRD and Raman spectroscopy. Then, the devices that incorporated graphene as the hole transporting material were optimized by focusing on the resistance of the  $TiO_2$  dense layer, the thickness of the TiO<sub>2</sub> mesoporous layer, the time allowed for the  $I^{-}/I_{3}^{-}$  based electrolyte to penetrate through the WE, and the thickness of the graphene layer. An optimized photoelectric conversion efficiency of  $6.13 \pm 0.10\%$  was achieved with a  $V_{\rm OC}$  of  $645 \pm 20 \,\mathrm{mV}$ , a  $J_{\rm SC}$  of  $14.4 \pm 1.2 \text{ mA cm}^{-2}$ , and a FF of  $0.66 \pm 0.04$  under simulated AM 1.5 irradiation and 1000 W m<sup>-2</sup> intensity. Furthermore, they reached a maximum IPCE of 51.6% at 525 nm covering the wavelength range up to 750 nm. The use of graphene as the HTM has reduced the charge transfer resistance at the CE/electrolyte interface of hybrid-DSCs. The lower efficiencies compared to standard DSCs may be due to interfacial charge recombination losses at the WE/electrolyte interface and short circuiting of the device at the graphene layer. Better efficiencies could be achieved by substituting  $I^{-}/I_{3}^{-}$  with an alternative redox mediator with suitable charge transfer kinetics or by introducing a gel polymer electrolyte to suppress these unfavourable reactions. In addition, utilizing a CE with a higher roughness may improve the contact between the CE and graphene, which may enhance the  $V_{\rm OC}$  observed in hybrid-DSCs. Even though the new device architecture demonstrated a lower efficiency compared to that of the state-of-art devices, this study paves the way to fabricate DSCs that combine the properties of both liquid and solid state devices. Furthermore, the reduction of the amount of liquid used within the device may allow the fabrication of stable DSCs.

# SUPPLEMENTARY MATERIAL

See supplementary material for XRD and Raman spectrum of graphene, solar cell optimization data, and SEM of drop cast TiO<sub>2</sub>.

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