Enhancing the photovoltaic performance of dye-sensitized solar cells by modifying TiO₂ photoanodes with exfoliated graphene sheets

Hui Ding, a Sam Zhang, b* Pi-Chun Juan, c Ting-Yu Liu, c Zhao-Fu Du a and Dong-Liang Zhao a

Exfoliated graphene sheets (EGS) are obtained using simple liquid phase sonication and then mixed with TiO₂ nanoparticles in a dye sensitized solar cell photoanode to achieve higher electrical conductivity and faster electron transfer due to much fewer defects as compared to conventional reduced graphene oxide (RGO): J_{sc}/J_{0} of 0.256 in EGS as compared with that of 1.128 in RGO. The EGS–TiO₂ photoanode yields a conversion efficiency of 8.24%, over a 19% increase compared with that of the RGO–TiO₂ photoanode, and a 43% increase over that of TiO₂ alone under the same conditions.

1. Introduction

Dye-sensitized solar cells (DSSCs), since their pioneering work was reported in 1991, 1 have attracted extensive interests all over the world because of their relatively low cost in fabrication. 2–4 Although the conversion efficiency of DSSCs has achieved 13%, 5 this is still lower compared to crystalline Si (25.0%) 6 or thin-film CIGS (Copper Indium Gallium Selenide, 20.5%) 7 cells.

A typical DSSC comprises a dye sensitized TiO₂ film photoanode, a platinized counter electrode, and a redox electrolyte between the electrodes. As the main component, the photoanode is usually prepared by coating a layer of semiconductor (TiO₂) on conductive glass. 8 The semiconductors act not only as carriers to adsorb dyes but also as the electron transport materials. 9,10 Photogenerated electrons are injected from the dye into the TiO₂ film where they diffuse to the electrode for collection. 8 The major bottleneck in achieving a high power conversion efficiency (PCE) is the transport process of photo electrons across the TiO₂ nanoparticles network, 11,12 which competes with the charge recombination. 13,14 To suppress the recombination and enhance the transport, materials of high conductivity are introduced into the photoanode to channel the photoelectrons out to improve the charge-collection efficiency. 15–18

Graphene, a novel two-dimensional (2D) material with sp²-hybridized honeycomb lattice structure, 19–21 is a planar monolayer of carbon atoms arranged with a carbon–carbon bond length of 0.142 nm. 22 In graphene, 3 of carbon atom’s 4 outer orbital electrons from 3 sigma bonds with its three neighbors in the same plane, leaving the 4th electron out of the plane and free to move. 23,24 Therefore, electrons in the plane behave like massless relativistic particles without crystal lattices’ restrictions leading to an extremely high electron mobility in two dimensions at room temperature (250 000 cm²/V·s), 25 which makes graphene an ideal carrier material in DSSCs photoanodes. To date, there are a few reports on the enhancement of DSSCs based on graphene, 13,26–31 In those studies, graphene materials hold an advantage of high conductivity to transport photoelectrons from the conduct band of TiO₂ to the current collector, giving rise to improvement of PCE in the device. For examples, Yang et al. introduced graphene with TiO₂ in the photoanode through reduction of graphene oxide by hydrazine. 13 Due to the unique advantages of graphene, including its high conductivity, suitable work function (4.4 eV) and good interfacial contact with TiO₂ nanoparticles, graphene flakes can act as bridge to shuttle electrons to the current collector and lower recombination. The short-circuit current density (J_{sc}) and PCE of DSSCs with graphene flakes in photoanode could significantly increase by 43% and 39%, respectively, compared to pure TiO₂ photoanode without graphene. Shu et al. prepared RGO–TiO₂ composites via a solvothermal method and reached a conversion efficiency of 5.5% through reducing the intrinsic resistance and prolong the life-time of the electron transfer in DSSCs. 32 Xiang et al. reported an improving of PCE of DSSCs by modifying TiO₂ photoanodes with nitrogen reduced graphene oxide. 33 Liu et al. developed a few layered graphene/TiO₂ composite using 10,10’-dibromo-9,9’-bianthryl [C₂₈H₁₆Br₂] as precursor to improve interfacial contact between graphene and TiO₂, which in turn increased the life-time of the photo-induced electron. 34 Liu et al. reported
a series of TiO$_2$–graphene stacked photoanodes fabricated by electrospray deposition and found an over 23.6% improvement in PCE.$^{29}$ In our previous work, RGO reduced with vitamin C in TiO$_2$ resulted in an enhancement on photovoltaic performance of DSSCs by lower recombination and improves electron lifetime in photoanode.$^{31}$ Typically, graphene–TiO$_2$ composite electrode is prepared by mixing graphene oxide (GO) and titanium dioxide, and then reducing GO to obtain graphene (RGO) via chemistry reducing agent$^{33,34}$ or hydrothermal reduction.$^{35,36,37}$ Those studies report the primary cause for improvement is that graphene with a high conductivity can increase the conductivity of TiO$_2$. In other words, improving the conductivity of graphene that used in photoanode could further enhance the conversion efficiency of DSSCs. However, the reduction of GO to produce graphene cannot remove all structural defects introduced by the oxidation process and results in lots of basal-plane defects which seriously reduce its conductivity, thus limit the improvement in conversion efficiency. High quality graphene sheets can be obtained by numerous method, such as chemical vapor growth,$^{38}$ reduction of silicon carbide,$^{39}$ micromechanical cleavage$^{40}$ and so on. However, those methods are unsuitable for scalable production of graphene because of the requirements of high throughput and low cost, and what’s more, those methods are difficult to prepare uniform graphene–TiO$_2$ composite which is required in the photoanode of DSSCs. Therefore, it is of prime importance to explore an effective and commercially available technique to produce high quality graphene and uniform graphene–TiO$_2$ composite that can be used as the photoanode of DSSCs.

Recent researches show that the highly conductive graphene can be obtained by liquid-phase exfoliation of graphite flakes.$^{41,42}$ The liquid-phase exfoliation was demonstrated by the strategy of tailoring Hansen solubility parameters in various solvent systems.$^{29}$ Ultrasoundication was used to exfoliate the graphite flakes into exfoliated graphene sheets (EGS) in solvent. High quality graphene can be obtained with appropriate ultrasonic power and operation time.$^{43}$ Without the oxidation and reduction process, there are no added basal-plane defects therefore higher conductivity is expected than conventional RGO.$^{44,45}$ Furthermore, because of the solvent system, the liquid-phase exfoliation can easily get a uniform graphene suspension which is suitable for producing uniform graphene–TiO$_2$ composite for the photoanode of DSSCs. Herein, we explore this facile approach of making high quality graphene and directly mix it with TiO$_2$ in DSSC photoanode for better energy conversion. Graphite flakes are sonicated to EGS in water/acetone with appropriate proportion through simple stirring and centrifugation to form high quality graphene based TiO$_2$ photoanode in DSSCs. Without using special chemical reagents, we rely on the application of physical pressure to make the graphene connecting with TiO$_2$. With EGS–TiO$_2$ photoanode, over 19% and 43% increase in efficiency is achieved respectively over that with RGO–TiO$_2$ and TiO$_2$ photoanode. To the best of our knowledge, this is the first attempt in using liquid-phase exfoliated graphene sheets into TiO$_2$ photoanode to enhance the photovoltaic performance of DSSC and achieves exciting results.

2. Experimental procedures

Fig. 1a shows a schematic representation of the exfoliation process using acetone–water sonication to exfoliate graphene sheets directly from graphite. The exfoliation process of graphene sheets and fabrication of EGS–TiO$_2$ photoanode was described in Fig. 1b. Graphene Oxide (GO) powders with diameter of 500 nm to 3 μm and 99% of 1 monolayers in thickness was purchased from Nanjing XFNANO Materials Tech Co., Ltd. Dye N-719 was purchased from Solaronix Co., Ltd., Switzerland.

2.1 Preparation of graphene suspensions

Graphite flakes (cat # 332461, ~150 μm) was purchased from Sigma-Aldrich. The graphene suspensions were prepared by ultrasonicating graphite flakes (600 mg) in 200 mL DI water/acetone mixtures in a steel vessel using common ultrasonic cleaner (DELTAL, D150H) operating at 150 W and 20 kHZ for 4 hours at room temperature. Then, centrifugation was followed with a speed of 1000 rpm to remove the maintain graphite and keep the exfoliated graphene in the solution. Finally, the initial concentration of the graphene suspension was 0.2 mg mL$^{-1}$.

2.2 Preparation of the EGS–TiO$_2$ composite

Exfoliated graphene–TiO$_2$ composites were prepared using 3.0 g of commercial TiO$_2$ nanoparticles (P25) in each sample. During preparation, 30 mL exfoliated graphene suspension was added and stirred for 3 hours in an ultrasonic horn for a homogeneous suspension. Then, centrifugation was carried out several times with water and ethanol. Finally, the remains were dried in a vacuum dryer at 65 ℃. The concentration of the EGS suspension was 0.2 mg mL$^{-1}$, thus there was 0.20 wt% of EGS in the sample. As such, EGS–TiO$_2$ composite with 0.20 wt% EGS was prepared and is referred to as EGS02. EGS–TiO$_2$ composites with 0.40, 0.60, 0.80, 1.00 wt% of EGS were also prepared in the same manner and are hereby designated as EGS02, EGS06, EGS08, and EGS10, respectively.

2.3 Fabrication of DSSCs

The EGS–TiO$_2$ pastes were synthesized following the Grätzel method.$^{46}$ The prepared pastes were spread on Fluorinated Tin Oxide (FTO) glass using the doctor blade method, and dried at 120 ℃ for 5 min under a pressure of 250 kPa. The film was then annealed for 30 min at 450 ℃ in air at a heating rate of 5 ℃ min$^{-1}$, followed by a treatment in 40 mM TiCl$_4$ aqueous solution at 70 ℃ for 30 min and then annealing again under the same condition. The film was then assembled into DSSC device, as described previously.$^{41}$ In our previously work,$^{41}$ RGO–TiO$_2$ incorporated with 0.60 wt% RGO (or 0.75 wt% GO before reduction) showed the best photovoltaic performance. Therefore, a RGO–TiO$_2$ photoanode with 0.60 wt% RGO and a TiO$_2$ photoanode were also prepared for comparison.
2.4 Characterization

The crystal structures of the EGS, the RGO and EGS–TiO2 were characterized by X-ray diffraction (XRD, PANalytical-X’Pert PRO MPD) with Cu Kα radiation (λ = 1.5405 Å), 30 mA and 40 kV. The morphology and structure of the EGS were investigated by a transmission electron microscopy (TEM, JEOL JEM-2100) and an atomic force microscopy (AFM, Bruker Dimension Edge). Raman spectra of samples were measured using a confocal Raman microscope with a 514 nm laser. The electrical conductivity of EGS and RGO was carried out by a sheet resistance measurement (Napson RG-7B) and the thickness of the films was measured by an Alpha step (KOSAKA-ET3000). The ultraviolet-visible (UV-vis) absorption spectra were obtained by a spectrophotometer (Jasco v670). The electrical conductivity of EGS and RGO was carried out by a sheet resistance measurement (Napson RG-7B) and the thickness of the films was measured by an Alpha step (KOSAKA-ET3000). The ultraviolet-visible (UV-vis) absorption spectra were obtained by a spectrophotometer (Jasco v670). The current density-voltage (J-V) curves of DSSCs were measured by the Keithley 4200 semiconductor characterization system under AM 1.5 simulated illumination at room temperature. Incident photon-to-electron conversion efficiency (IPCE) spectra were obtained using a 300 W Xe light and a monochromator provided by a QE-mini Quantum Efficiency Measurement System (Enlitech). Electrochemical impedance spectroscopy (EIS) measurements of DSSCs were measured by using a Metrohm Autolab potentiostats (PGSTAT 302N), with frequency range from 0.1 Hz to 100 kHz in the condition of 10 mV AC amplitude under 100 mW cm⁻² irradiation. Ultraviolet photoemission spectroscopy (UPS) was performed by on a ULVAC-PHI PHI 5000 VersaProbe II with a He I (21.22 eV) source.

3. Results and discussion

Fig. 2a is the TEM image of the exfoliated graphene sheets (EGS), showing the flakes being less than 3 layers and several micrometers in lateral size. The number of the layers can also be determined by analysis of the electron diffraction pattern. The diffraction spots on the inner circle are obviously brighter than the outer ring in Fig. 2b, implying I(0110)/I(2110) > 1 which indicates the EGS mostly consist of monolayer. Fig. 3a display a typical atomic force microscopy (AFM) image of EGS on a mica substrate, showing that the EGS has a lateral size of 1.5 μm. The corresponding height cross-sectional profile from the AFM image reveal that the EGS has heights about ~0.82 nm. Furthermore, based on the analysis of the AFM image for 150 sheets and Gaussian fit, it is very clear from the histogram (Fig. 3b and c) that the maximum population of EGS has a lateral size about 753 nm and a height about 0.77 nm.

Fig. 4a plots XRD spectra of the original graphite flakes, the RGO and the EGS. The peak position in EGS at around 25° 2θ corresponding to the (002) plane is almost identical to those in the original graphite flakes, indicating that the graphite lattice
parameters remain and the crystal structure is not destroyed. In EGS, no (004) peak at around 55° 2θ is observed, thus the sub-
lattices are almost devoid of long-range order (greater than four
layers).39,47 Fig. 4b plots XRD patterns of EGS–TiO2 mix with
varying amount of EGS, RGO–TiO2 and pure TiO2 films. The
peaks are originated from the anatase and rutile TiO2 phases,
matching well with that of original TiO2 nanoparticle (P25).
Meanwhile, after decoration with RGO or EGS, there is no
obvious peak change at various contents of graphene–TiO2
composites, which is related to that the EGS/RGO content is too
low to be detected by XRD observation.

Raman spectrum could be used to characterize the ‘quality’
of graphene. As shown in Fig. 4c, the Raman spectra of EGS
includes a G peak at ~1583 cm⁻¹ corresponding to the first-
order scattering of the E₂g vibration mode, a D peak at
1350 cm⁻¹ due to a breathing mode of the k-point phonons of
A₁g symmetry first-order zone boundary phonons, and a 2D
peak at ~2700 cm⁻¹ caused by second-order zone boundary
phonons, respectively.48–50 Typically, the defect content can be
characterized by the intensity of the D band relative to the G
band, I_D/I_G.39,50 From Fig. 4c, we note that the I_D/I_G in the EGS is
~0.256 which is significantly lower than that of the RGO
~1.128), indicating that the EGS contain much fewer defects
than RGO. These defects in graphene can be divided into two
main types: basal plane defects and edge defects. The edge
defects usually depend on the size of the graphene flakes,48,51,52
because of the smaller flakes have more edges per unit mass.
Basal plane defects generally result in broadening of G bands,49
which is obvious in the RGO in Fig. 4c (bottom).

To test the electrical conductivity, we measured the sheet
resistance of the EGS and RGO film. The films were obtained by
dying the 10 mL suspension on glass slide at 60 °C for 30 min.
Three different sites of the sample were chosen to measure. The
films thickness was measured by Alpha step as 225 ± 3 nm for
EGS sample and 262 ± 4 nm for RGO sample. The average sheet
resistance of the EGS film was measured to be 3.85 ± 0.05 kΩ
and the RGO was 6.30 ± 0.03 kΩ, or average conductivity of 1150
± 30 S m⁻¹ for EGS, almost twice as high as that of the RGO
(606 ± 12 S m⁻¹).

To investigate the effect of the EGS on the performance of
DSSCs, the photoanodes of EGS–TiO2 and RGO–TiO2 and TiO2
alone were fabricated under strict identical conditions. The
energy conversion efficiency was determined using photocur-
cent density–voltage (J–V) curves (Fig. 5a). EGS02 through EGS10
represents respectively 30, 60, 90, 120, and 150 mL of exfoliated
graphene suspension mixed with the same amount (3.0 grams)
of TiO2 particles, thus indicating increasing amount of EGS in
the photoanode. The relative photovoltaic parameters of the
dSSCs are summarized in Table 1. Fig. 5b shows the incident
photon-to-electron conversion efficiency (IPCE) curves of DSSCs
with different amount of EGS/RGO. The J_SC can be theoretically
calculated by integrating the product of IPCE (λ) and incident
light intensity P_in(λ) of the device over the wavelength (λ) of
the incident light,

\[
J_{SC} = q \int \frac{d\lambda}{\hbar c} \times \text{IPCE}(\lambda) \times P_{in}(\lambda)
\]

where q is the electron charge. Therefore, we could compare the
J_SC experimentally obtained from the J–V curves vs. J_SC calcu-
lated from the spectral IPCE spectra. As shown in Table 1, the
mismatch factor between J_SC (IPCE) and J_SC from J–V curves was
around 0.94, which is within measurement error possibly
occurring in ambient conditions. As shown in Table 1, the
energy conversion efficiency of RGO–TiO2 was 6.91%, that of
TiO2 is 5.77% and the best is 8.24% (EGS06), an increase of
19.2% over the RGO case and 42.8% over the pure TiO2 case.
Various cell parameters also peak at EGS06 as shown in Fig. 5
with increasing EGS content.

The overall efficiency η was evaluated by the short-current
density (J_SC), the open-circuit photovoltage (V_OC), the fill factor
of the cell (FF), and the incident light power density (P_in),
namely,53,54

\[
\eta = \frac{J_{SC} \times V_{OC}}{P_{in}} \times FF
\]

It should be noted that the overall conversion efficiency of
DSSCs is affected significantly by the open-circuit voltage (V_OC),
the short-circuit current density (J_SC), and the fill factor (FF).
The V_OC value of the cells shows a decrease trends with
increasing amount of EGS in photoanodes as shown in Table 1
and Fig. 5. For DSSCs, the V_OC values are mainly obtained as the
difference between the electron’s Fermi level in the TiO$_2$ ($\varepsilon_{\text{CB}}$) and the Nernst potential of the redox couple ($\varepsilon_{\text{redox}}$) in the electrolyte and can be described as,$^{55}$

$$V_{\text{OC}} = \varepsilon_{\text{redox}} - \varepsilon_{\text{CB}} - \frac{\gamma k_B T}{e} \ln \left( \frac{N_e}{n} \right)$$  \hspace{1cm} (3)

where $N_e$ is the effective density of states at the TiO$_2$ conduction band (CB) edge, $\gamma$ is the characteristic constant of TiO$_2$ tailing states, $k_B$ is the Boltzmann constant, $e$ is the elementary charge, $n$ is the electron density in TiO$_2$, and $T$ is the temperature. In principle, $V_{\text{OC}}$ is determined by the energy difference between the quasi-Fermi level of TiO$_2$ under illumination and the chemical potential of redox couples in the electrolyte, which is
closely related to charge recombination process at the TiO2/dye/electrolyte interface.55,56 After decorating with EGS, the charge could get into the external circuit more easily with less charge recombination, and it would cause less electron density (n) in TiO2 CB, leading to a decrease in $V_{OC}$.

The short-circuit photocurrent is another parameter that is fundamental to the efficiency of DSSCs. A good $J_{SC}$ is based on three parameters: good charge injection efficiency from the exited dye to TiO2, a large amount of dye loading onto the TiO2 surface, and the excellent charge collection/extraction efficiency in the photoanode. First of all, for dye N-719 used here, it has been proved in many papers57–59 that the injection from the exited dye molecule to the semiconductor's CB is fast enough to compete with other processes. The UV-vis spectroscopy was used to assess the impact of EGS–TiO2 film on dye absorption (i.e., loading).60 After preparing the photoelectrodes, N-719 dye was adsorbed for 24 hours and desorbed with 1 mM KOH solution for UV-vis analysis. As shown in Fig. 5, the amount of dye adsorbed onto the surfaces of photoanodes decreased in the order: EGS06 > EGS04 > EGS08 > EGS02 > TiO2 > EGS10. The EGS06 adsorbed the highest amount of dye among the tested photoanodes, because the EGS formed sheets between the TiO2 particles to increase the specific surface area resulted in an increase in dye loading.13,30 However, the addition of excess EGS resulted in the formation of graphene sheets shielding TiO2 particles, which decreased the dye loading amount. Therefore, the amount of dye adsorbed is related to the current density and show a good agreement with the trends of $J_{SC}$, as shown in Fig. 5. With appropriated amount, the addition of EGS increased the dye absorption and enhanced the energy conversion efficiency of DSSCs. However, for RGO–TiO2 and EGS06, it does not show any clear difference of the dye loading amount on the Fig. 5. Therefore, the charge collection and transportation efficiency of the injected electrons is critical to the photocurrent of the cell based on EGS and RGO. A good conductor with high electrical transport property is widely accepted that it could act as a high-way to capture and transport electrons from the conductor band of TiO2 to electron collector.13,30,31 After decorating with EGS, the photo electrons in the TiO2 CB could get into the external circuit more easily, and this will be proved by the electrochemical impedance spectrum (EIS) data.

EIS was carried out to give evidence of the graphene effect on boosting the charge transport and reducing the recombination. As shown in Fig. 5, the Nyquist plot contains two main semicircles in the high and medium-frequency regions, where the semicircles in low-frequency region corresponding to redox couple diffusion in the electrolyte are absent. The large semicircle in the medium frequency region relates to the electron transport in the TiO2 film and the back transfer at the TiO2/electrolyte interface.17,53,61 According to the previous study,17,62 the radius of arc in the medium-frequency region reflects resistance to charge transfer at the aforementioned interface. In Fig. 5, it is clearly showed that the semicircle size for the EGS–TiO2 photoanode in the medium-frequency region exhibits significant reduction with increasing amount of EGS than that for the pure TiO2 photoanode, indicating faster electron
transfer process through the graphene bridge. This gives rise to reduced $V_{OC}$ values as increasing EGS content, as shown in Table 1.

A transmission line model, as shown in Fig. 5, is used to characterize the measured EIS of TiO$_2$ and graphene–TiO$_2$ based DSSCs, aimed at simultaneously estimating the charge recombination and transport resistance in the photoanode.\textsuperscript{63-65} This model can be expressed as following formula without considering the effects of the Pt counter electrode or the diffusion in the electrolyte.\textsuperscript{17}
Table 1  Photoelectric parameters of photoanodes containing varying amounts of EGS/RGO

<table>
<thead>
<tr>
<th>Name of cells</th>
<th>Anode with wt% EGS</th>
<th>V_{oc} (V)</th>
<th>J_{sc} (mA cm^{-2})</th>
<th>FF (%)</th>
<th>η (%)</th>
<th>J_{sc} (IPCE) (mA cm^{-2})</th>
<th>J_{sc} (IPCE)/J_{sc}</th>
<th>R_{cr} (Ω)</th>
<th>R_{T} (Ω)</th>
<th>C_{m} (μF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>0</td>
<td>0.704</td>
<td>12.59</td>
<td>65.07</td>
<td>5.77</td>
<td>11.91</td>
<td>0.945</td>
<td>31.21</td>
<td>25.34</td>
<td>107.33</td>
</tr>
<tr>
<td>EGS02</td>
<td>0.20</td>
<td>0.694</td>
<td>13.70</td>
<td>68.81</td>
<td>6.35</td>
<td>12.94</td>
<td>0.944</td>
<td>30.46</td>
<td>17.02</td>
<td>115.24</td>
</tr>
<tr>
<td>EGS04</td>
<td>0.40</td>
<td>0.692</td>
<td>15.46</td>
<td>67.84</td>
<td>7.26</td>
<td>14.73</td>
<td>0.952</td>
<td>29.20</td>
<td>11.11</td>
<td>122.92</td>
</tr>
<tr>
<td>EGS06</td>
<td>0.60</td>
<td>0.690</td>
<td>17.31</td>
<td>69.04</td>
<td>8.24</td>
<td>16.15</td>
<td>0.932</td>
<td>28.65</td>
<td>7.63</td>
<td>168.73</td>
</tr>
<tr>
<td>EGS08</td>
<td>0.80</td>
<td>0.683</td>
<td>14.90</td>
<td>62.25</td>
<td>6.34</td>
<td>14.02</td>
<td>0.941</td>
<td>25.60</td>
<td>6.28</td>
<td>108.24</td>
</tr>
<tr>
<td>EGS10</td>
<td>1.00</td>
<td>0.665</td>
<td>11.37</td>
<td>56.55</td>
<td>4.28</td>
<td>10.82</td>
<td>0.952</td>
<td>14.12</td>
<td>5.56</td>
<td>101.10</td>
</tr>
<tr>
<td>RGO–TiO₂</td>
<td>0.60 wt% RGO</td>
<td>0.697</td>
<td>14.52</td>
<td>68.22</td>
<td>6.91</td>
<td>13.74</td>
<td>0.945</td>
<td>30.57</td>
<td>11.34</td>
<td>165.87</td>
</tr>
</tbody>
</table>

Values are listed for open-circuit voltage (V_{oc}), short-circuit current (J_{sc}), fill factor (FF), energy conversion efficiency (η), calculated J_{sc} from spectral IPCE spectra (J_{sc} (IPCE)) and EIS fitting parameters (R_{cr}, R_{T}, C_{m}). EGS02 through EGS10 represents 0.20, 0.40, 0.60, 0.80, and 1.00 wt% EGS mixed with TiO₂ particles, respectively, thus indicating increasing amount of EGS in the photoanode.

The result can be used to explain the difference of the short-circuit current between the EGS06 and RGO–TiO₂. The high conductive EGS can facilitate charge transport in photoanodes more easily than RGO to improve the photo current even with the same dye loading amount.

In order to explain the influence of electronic structure of EGS in DSSCs, the UPS spectra was measured. Fig. 6a shows the UPS spectra around the secondary electrons threshold region of the EGS sample and the inset shows the full UPS spectrum. The work function (Φ) is determined from the secondary electron threshold as Φ = hν - E_{th}, where hν and E_{th} are the photon energy of excitation light (He I discharge lamp, 21.22 eV) and the secondary electron threshold energy, respectively. The secondary electron threshold was determined by extrapolating two solid lines from the background and straight onset in the secondary electron threshold region of the UPS spectra.

Taking into account of the electron transfer at Pt/electrolyte interface and the diffusion process in electrolyte, a full equivalent circuit model of DSSCs is presented in Fig. 5 (inset in Fig. 5) to explain the transfer and recombination process of the photo-excited electrons in the cells. Corresponding to the transmission line model, the starting point in the circuit (R_{S}) is the series resistance, including the sheet resistance of the FTO glass, the contact resistance of the cell, respectively. R_{pt} and C_{pt} are the charge transfer resistance and the double-layer capacitance at the counter electrode I_{ct} at the electrolyte/Pt/FTO glass interface, DX_{1} is complicated element in the equivalent circuit model (DX type TL-Open), and W1(Ws) represents Warburg impedance (short), respectively. Therefore, the parameters including R_{cr}, R_{T} and C_{m} could be obtained by fitting Nyquist plot and are summarized in Table 1. Obviously, for photoanode decorating with EGS, the charge transport resistance (R_{ct}) is significantly reduced to a low level, compared with that of the pure TiO₂ photoanode (25.34 Ω). However, with too much EGS, the charge recombination resistance (R_{cr}) is also reduced, indicating higher charge recombination and lower V_{oc} of DSSCs, which, in turn, eliminate the benefit of low R_{T} of EGS. Meanwhile, EGS06 achieve the highest C_{m} (168.73 μF) among those cells with or without EGS, indicating the largest amount of dye adsorption, which is in agreement with the UV-vis spectroscopy as discussed above. Moreover, the charge transport resistance of EGS06 is 7.63 Ω, just 67.2% of the RGO–TiO₂ (11.34 Ω), without significantly change the R_{cr} and C_{m}. This obstruction. The electrons can rapidly transport to the EGS without any recombination and low charge recombination at TiO₂/electrolyte interface, and a higher chemical capacitance indicates increased dye adsorption, with those three parameters give a higher η.

(4)  

\[ Z = \left( \frac{R_T R_{cr}}{1 + i \omega \tau_{dx}} \right)^{1/2} \coth \left( \frac{\omega \tau_{dx}}{\tau_{dx}} \right)^{1/2} \]
the excessive graphene can act as a kind of recombination center accelerating recombination of electrons to the dye or back reaction to the electrolyte. Therefore, the fill factor exceeded to the highest value 69.04% with the optimal amount of EGS.

4. Conclusions

For the first time, direct sonication of graphite produced exfoliated graphene sheets (EGS) were mixed with nanosized TiO₂ particles in preparation of photoanode in dye-sensitized solar cells. Energy conversion measurements indicate that the mixed EGS–TiO₂ photoanode results in as much as over 19% and 43% better than RGO–TiO₂ and TiO₂-only counterparts under strict identical preparation conditions. The increase is believed to come from the increased conductivity of EGS owing to fewer basal plane defects as there is no chemical reduction process in comparison with the case of RGO, and to the much better connectivity to the case of TiO₂-only photoanode.

Acknowledgements

The authors gratefully acknowledge funding from the National Nature Science Foundation of China (No. 51301041), the Ministry of Science and Technology (MOST) of Taiwan (104-2221-E-131-011), and Ming Chi University of Technology for financial and research support.

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