Incorporation of graphene into SnO₂ photoanode for dye-sensitized solar cells

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Abstract

In dye-sensitized solar cell (DSSC) photoanodes, tin dioxide (SnO₂) structures are promising alternative semiconducting oxide to the conventional titania (TiO₂), but they suffer from poor photovoltaic (PV) efficiency caused by insufficient dye adsorption and low energy value of the conduction band. A hybrid structure consisting of SnO₂ and reduced graphene oxide (SnO₂-RGO) was synthesized via a microwave-assisted method and has been employed as a photoanode in DSSCs. Incorporation of RGO into the SnO₂ photoanode enhanced the power conversion efficiency of DSSC device by 91.5%, as compared to the device assembled without RGO. This efficiency improvement can be attributed to increased dye loading, enhanced electron transfer and addition of suitable energy levels in of the photoanode. Finally, the use of RGO addresses the major shortcoming of SnO₂ when employed as a DSSC photoanode, namely poor dye adsorption and slow electron transfer rate.

Keywords

Photovoltaic, dye-sensitized solar cells, photoanodes, tin dioxide, graphene

1. Introduction

One of the mature developments in new energy production approaches is the dye-sensitized solar cell (DSSC) [1]. For a broad perspective of the field, there are several good reviews available [2-4]. A typical DSSC photoanode is made using a transparent conducting oxide (TCO) substrate, wide band gap oxide semiconductor and dye sensitizer. A nanocrystalline TiO_2 semiconductor is mostly used as the semiconductor due to its unique properties [5]. Despite the high power conversion efficiencies (PCEs) achieved by devices fabricated with TiO_2 photoanodes [6-8], the intrinsic low carrier mobility of TiO_2 is a matter of great concern [9, 10]. This issue has led many researchers to probe the development of alternative photoanode materials.

Among many alternative semiconductors, SnO_2 has been the subject of numerous investigations [11-13]. This is partially due to the fact that SnO_2 has a higher electron mobility than TiO_2 [14, 15]. Since the first use of SnO_2 in DSSCs, significant developments have been made in the SnO_2 photoanodes [11, 13]. These developments include morphology control, doping with various species, surface modification, and hybrid structures with other oxide semiconductors [16-18]. Despite the considerable effort to improve SnO_2 based photoanodes, a major challenge for SnO_2 based DSSCs is still their low performance caused by poor dye adsorption capability [19]. Additionally, the SnO_2 photoanode based DSSCs suffer from a low open circuit voltage (V_{oc}) value due to the intrinsically low energy of the conduction band of SnO_2 [20]. Therefore, addressing these issues is of great importance for the development of SnO_2 based photovoltaic (PV) cells. Moreover, although SnO_2 possesses higher electron mobility than TiO_2 , further improvement in the electron transport in SnO_2 photoanode would be of great value to maximize the efficiency.

Due to their excellent conductivity, carbon nanotubes (CNTs) and graphene can act to improve electron transport and reduce the charge recombination which results from sluggish charge transport of semiconducting oxide based photoanodes; thus significantly enhancing the PCE of PV cells [21-26]. Over the past few years, researchers have incorporated graphene derivatives into various TiO_2 structures and shown remarkable efficiency enhancement [27-30]. However, until now, there has been no report on the use of graphene structures in SnO_2 photoanodes for DSSCs. Moreover, the kinetics of dye adsorption and performance enhancement for carbonaceous photoanodes is still unclear, with some studies suggesting contrary results [21, 28, 29, 31, 32]. Therefore, exploring the effect of graphene or reduced graphene oxide (RGO) in SnO_2 photoanode based DSSCs would be valuable.

Herein we report a facile preparation of hybrid structures based on morphologically controllable SnO₂ combined with RGO for use as a photoanode in DSSCs. To the best of our knowledge, this work is the first effort involving the application of a graphene structure in SnO₂ photoanode based DSSCs. We found that the incorporation of RGO into the SnO₂ film not only enhances the electron transfer rate of the photoanode, it also increases the adsorption of dye molecules into the film, thus greatly improving DSSC performance.

2. Experimental

2.1. Materials

All chemicals were purchased from Sigma-Aldrich and used without further purification, unless otherwise stated. Tin (II) chloride dihydrate (SnCl₂·2H₂O) powder (>99% purity, Merck) was used as a starting material. Fluorine-doped tin oxide (FTO) coated glass electrode with a sheet resistance (R_s) of ~12 Ω/□ (TCO30-8), Ruthenizer 535-bisTBA (N719 dye), iodide/tri-iodide electrolyte (Iodolyte Z-50), DuPont Surlyn® (Meltonix 1170-60) and Platinum catalyst (Platisol T) were obtained from Solaronix, Switzerland.

2.2. Preparation of graphene oxide

Graphite oxide was prepared from natural graphite using the approach from Marcano et al. [33]. Briefly, a 9:1 (v:v) mixture of sulfuric acid (95-98% H₂SO₄) and phosphoric acid (85% H₃PO₄) (240:27 mL) was kept in the cold room (3-5°C) until it was added to a mixture of graphite flakes (2 g) and potassium permanganate (99% KMnO₄) (12 g). The oxidation process of graphite was carried out by stirring the mixture at ~50°C for 12 h. Upon completion, the reaction was cooled down to room temperature and poured onto ice (approximately 300 mL) with 30% hydrogen peroxide (H₂O₂) (2 mL). The mixture was then washed with distilled (DI) water, 30% hydrochloric acid (HCl) and ethanol (x 2 times). For each sequential wash, the product was centrifuged at 4400 rpm for 3 h and the supernatant decanted away. The obtained light brown sample was then vacuum-dried overnight at room temperature. Then the as-prepared graphite oxide was exfoliated in water (1 mg mL⁻¹) by bath ultrasonication (Elma, Germany) for 60 min to obtain homogenous graphene oxide (GO) dispersion.

2.3. Synthesis of SnO₂-RGO hybrid

The SnO₂-RGO hybrid was prepared using a facile microwave-assisted method [34]. In a typical process, six glass beakers containing 90 mL DI water and different GO content (0 mg,

2 mg, 4.5 mg, 7 mg, 12 mg and 50 mg) were ultrasonicated for 2h. Meanwhile, 1.5 g of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ powder was added into 200 mL of 0.02M HCl solution. Then the previously prepared GO dispersions were added into the $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ solutions, followed by stirring for 30 min. The as-obtained mixtures were then reacted using a microwave technique (StartSYNTH Microwave Synthesis Labstation, Milestone s.r.l) for 5 min under 600 W power. The temperature was adjusted to 90°C during the microwave treatment. After cooling to room temperature, the obtained precipitates were centrifuged at 2000 rpm for 10 min and washed several times with DI water, followed by drying overnight at 80°C in an oven to obtain SnO_2 -RGO powders. Finally, six samples of different RGO content (0 wt%, 0.2 wt%, 0.45 wt%, 0.7 wt%, 1.2 wt% and 4.75 wt% in the hybrid) were prepared and have been used for DSSC fabrication. It should be noted that the amount of SnO_2 in these samples was not changed. For the calculation of the RGO concentration in the hybrid, it was assumed that the conversion of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ to SnO_2 is 100% based on the lack of Cl peak observed in various hybrid characterizations.

2.4. Device fabrication

Firstly, viscous SnO_2 and SnO_2 -RGO pastes were prepared from the previously prepared six samples according to the established procedures described in the literature [35]. FTO coated glass substrates were cleaned by a detergent (Pyronex), followed by washing with Milli-Q water, acetone and ethanol under ultrasonication for 10 min each and subsequently dried with a nitrogen gas. The cleaned FTO glass substrates were immersed in a 40 mM TiCl_4 aqueous solution at 70°C for 30 min. Then the TiCl_4 treated FTO electrodes were coated with the SnO_2 and SnO_2 -RGO pastes by a doctor blade technique to prepare the photoanodes. All photoanode films were obtained by applying two layers of adhesive scotch tape (*MagicTM Tape*, 3M) on the FTO electrode, which gives a film thickness of ~15 μm [36]. It is well established that the photoanode thickness of 12-16 μm is the optimum condition for achieving high DSSC performance [36-38]. After the deposition of SnO_2 and SnO_2 -RGO pastes onto the FTO substrates, the photoanode films were gradually heated under an air flow at 125°C for 5 min, 325°C for 5 min, at 375°C for 15 min and at 450°C for 30 min, followed by cooling to room temperature. Then the films were again soaked in 40 mM TiCl_4 solution at 70°C for 30 min, followed by sintering at 450°C for 30 min. After cooling to ~50°C, the prepared films were immersed into 0.5 mM N719 dye in an ethanol solution for 20 h at 40°C. Then, the dye adsorbed photoanodes were washed with ethanol to remove non-adsorbed dye from the films.

In the meantime, platinum (Pt) catalyst was coated onto FTO substrates from Pt precursor (Solaronix) by a brush-painting method to prepare the counter electrodes. The dye-adsorbed photoanodes and Pt counter electrodes were assembled into a sealed sandwich-type cell, with a 60 μm thick hot-melt sealing Surlyn between each layer. The electrolyte solution, Iodolyte Z-50 (Solaronix), was introduced into the cell via a vacuum-filling method through an injection hole on the counter electrode side. Finally, the hole was sealed with scotch tape.

2.5.Characterization

Scanning electron microscopy (SEM) images were obtained using an Inspect F50 SEM (FEI) with accelerating voltage of 10 kV. Energy dispersive X-ray spectroscopy (EDX) analysis was completed on the same system with Team EDS Octane Pro (EDAX) attachment. Elemental compositions of the samples were analyzed at binding energy ranging from 0 eV to 1200 eV using a X-ray photoelectron spectroscopy (XPS), Leybold Heraeus LHS-10 with a SPECS XR-50 dual anode source operating at 250W. The Mg-K α source, which has energy of 1253.6 eV, was used for the XPS analysis. X-ray diffraction (XRD) patterns were carried out on a powder X-ray diffractometer at 40 kV and 15 mA in the range of $2\theta = 3\text{--}80^\circ$ using Cu K α radiation (Model Miniflex 600, Rigaku, Japan). Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR) spectra were acquired over a wavenumber range of 4000-500 cm^{-1} in transmission mode using a Frontier FTIR spectrometer (Perkin Elmer, USA) with a germanium crystal. Raman spectroscopy was carried out on LabRAM HR Evolution spectrometer (Horiba Jobin Yvon, Japan). Raman spectra were collected using a 532 nm laser (mpc 3000) as the excitation source. A 50x objective was used with a confocal hole size of 100 μm . Auger spectromicroscopy “PHI 710 scanning auger nanoprobe” operating at base vacuum below 1×10^{-9} Torr was used to analyse the elemental analysis of the samples. Sputtering samples for the analysis was performed using ultra high purity Argon. Data was collected using an electron beam of 10 kV, 10nA.

To determine the adsorbed amount of dye molecules in the SnO_2 and SnO_2 -RGO films, the dye in the films was dissolved in 0.1 M NaOH aqueous solution and then measured by a Varian Cary 50G UV-vis Spectrophotometer at wavelengths ranging from 300 to 1000 nm. Sheet resistivities were performed on the microscope slide substrate coated with SnO_2 -only and/or SnO_2 -RGO hybrid using a four point probe technique (KeithLink Technology Co., Ltd. Taiwan). The photocurrent–voltage (J – V) characteristics were investigated using a Keithley 2400 SMU instrument and recorded using a custom LabView Virtual Instrument program. A standard silicon test cell with NIST-traceable certification was used to calibrate

the power density as 100 mW cm^{-2} at the sample plane of the collimated xenon-arc light source, which was passed through an AM 1.5G filter. The active area of each device was 0.25 cm^2 . The J - V curves were measured in the air through reverse-scan direction from 1 V to -1 V. Incident-photon-to-current conversion efficiency (IPCE) measurements as a function of wavelength ranging from 400 nm to 800 nm were taken by passing chopped light from a Xenon source through a monochromator and onto the devices.

3. Results and discussion

The preparation of SnO_2 -RGO hybrid is shown in Scheme 1. Firstly, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ powder (Fig. S1) was mixed with GO (Fig. 1a) in aqueous hydrochloric acid (HCl, 0.02 M) to form a homogenous solution, which was stirred and reacted using a microwave technique. During this process, GO was reduced and is termed “RGO”. Then, the resulting product was centrifuged and dried to obtain a SnO_2 -RGO hybrid. For comparison, the same process was carried out in the absence of GO to produce only SnO_2 [36].

The SEM image in Fig. 1b shows that the synthesized SnO_2 is a 1 dimensional (1D) microstructure with a rod-like shape. It is worth noting that 1D structures can provide fast electron transport pathway [39]. Fig. 1c depicts the SEM image of the SnO_2 -RGO hybrid, which demonstrates clear differences compared to GO (Fig. 1a) and SnO_2 -only. It can be seen that the SnO_2 micro-rods were well mixed and wrapped in the RGO flakes, as expected, to form the hybrid material. As shown in Fig. 1d and 1e, during the microwave-assisted synthesis, small SnO_2 nanoparticles were also formed on both SnO_2 rods and RGO flakes which are expected to be beneficial for dye adsorption.

Fig. 2a shows the XRD patterns of GO, SnO_2 -only and SnO_2 -RGO hybrid. GO displays an intense peak at around $2\theta = 10.9^\circ$, which corresponds to the (002) reflection of the stacked GO nanosheets [40]. It can be observed that the SnO_2 -only sample shows broad and weak peaks ((110), (101), (200), (211) and (112)), which can be indexed to a tetragonal-structured SnO_2 with poor crystallinity [41]. It is well known that after the reduction process, the diffraction peak of the GO shifts to around $2\theta = 24.5^\circ$. This peak at $2\theta = 24.5^\circ$ cannot be observed in the XRD pattern of the hybrid because this peak will be overlapped with the SnO_2 peak (110). Another noticeable feature in the XRD pattern of SnO_2 -RGO is that the SnO_2 in the hybrid shows narrow and strong peaks, which can be assigned to a tetragonal structure (JCPDS card no. 41-1445), indicating an improved crystallinity of SnO_2 and larger

average crystal size [42]. This improvement in the crystallinity is often observed in nanocarbon-metal oxide materials and is attributed to a heat-sink effect in which the nanocarbon facilitates crystallization via heat transfer [43].

The results of the XRD analysis were further confirmed by characterizing the samples using XPS (Fig. 2b), ATR-FTIR (Fig. 3a) and Raman spectroscopy (Fig. 3b). It can be clearly observed from the Raman spectra of the SnO₂-RGO hybrid (Fig. 3b) that the I_D/I_G ratio of RGO increased compared to that of the GO. This increase in the I_D/I_G ratio can be attributed to the defects caused during reduction of GO [27]. Moreover, it should be noted that in the XPS survey spectra, negligible peaks (Cl 2p) can be found in the SnO₂-based samples, which could be attributed to the unreacted Cl⁻ of SnCl₂·2H₂O. Additionally, Auger and EDX elemental analysis were carried out on selected area of SEM images of the SnO₂-RGO hybrid and reveal small amount of chlorine remaining in the sample (see Fig. S2). These results of Auger and EDX spectroscopies were in good agreement with the XPS and may explain the sample crystallinity.

To study the influence of RGO on the efficiency of PV cells, DSSCs were fabricated using six photoanodes of different RGO content in the hybrid and were evaluated using simulated AM1.5 sunlight with an output power of 100 mW cm⁻². Notably, for the fabrication of DSSCs, the photoanodes were immersed in a TiCl₄ aqueous solution before they were soaked in the dye solution. This process is a commonly followed strategy to deposit a thin layer of TiO₂ over SnO₂ (SnO₂-RGO in our case) which can improve the V_{oc} of the SnO₂-based DSSCs [18, 44-46]. Therefore, the photoanodes were denoted as “TiO₂-SnO₂-RGO (X)”, where the value of X indicates the weight concentration (wt%) of RGO in the hybrid. For example, the photoanode film prepared with 0.2 wt% RGO is denoted “TiO₂-SnO₂-RGO (0.2)”.

The photocurrent density–voltage (J – V) characteristics of the DSSCs assembled with these photoanodes are shown in Fig. 4a and the corresponding PV parameters have been summarized in Table 1. The control DSSC device (TiO₂-SnO₂-RGO (0)) fabricated based on SnO₂ photoanode without RGO showed an average PCE (η) of $1.28 \pm 0.52\%$ with a short-circuit current (J_{sc}) value of 4.78 ± 0.95 mA cm⁻² and V_{oc} of 0.64 ± 0.01 V which are typical values for such cells [12, 18].

It can be seen from Table 1 that from TiO₂-SnO₂-RGO (0) to TiO₂-SnO₂-RGO (0.7) (increasing RGO content), the J_{sc} value increases from 4.78 ± 0.95 to 10.23 ± 0.88 mA cm⁻². We hypothesize that this increase in the J_{sc} is due to the improved dye loading into the film and enhanced electron transfer within the photoanode [22, 27, 28]. In order to confirm our hypothesis, we fabricated SnO₂ films (Fig. S3) with different RGO content and investigated the dye adsorption capability of the films. No treatment with TiCl₄ solution was done to allow the effect of RGO in the SnO₂ film on the extent of dye adsorption to be probed without any interference. As shown in Fig. S3, the films after dye adsorption and also the solutions after subsequent desorption of the dye molecules using NaOH show that the dye adsorption of the SnO₂ films was significantly improved by incorporating RGO. Moreover, UV-vis spectra in Fig. 4b show the absorbance of dye desorbed from the films and shows that dye adsorption increases with increasing RGO concentration in the hybrid. This improvement in the dye adsorption is most likely due to a better matching of the molecular nature of the N719 dye and the chemical nature of the hybrid. N719 has both polar groups and aromatic regions. Since our RGO was derived from GO, some functional groups (-OH, -COOH etc.) would remain on the surface of RGO due to the partial reduction and these would interact with the polar groups on N719. These functional groups may be playing an important role in the dye adsorption [21]. SnO₂ would also interact with these polar groups. The introduction of the RGO provides some aromatic nature to the hybrid and one can speculate that this will create polar and aromatic regions in close proximity and will further enhance dye adsorption. Additionally the high-surface area of RGO may contribute to the adsorption of the dye [28]. Interestingly, the dye adsorption of the film with the highest RGO content (4.75 wt%) is starting to saturate, indicating that adding more RGO into the film would likely not lead to significant further increases in dye adsorption (see Fig. S4).

To determine the mechanism for the improved J_{sc} value, the resistivity (R_s) of the TiCl₄ treated SnO₂ film without and with 0.45 wt% RGO was measured using a four point probe. The same film thickness on a glass substrate was obtained using the doctor blade method (see experimental details). The film without RGO shows a R_s of 4.51×10^6 Ω/□, while the RGO incorporated film exhibits a comparatively low R_s (1.81×10^6 Ω/□) (see Table S1). The decrease in the R_s (nearly 3-fold) of the film with RGO is due to the fact that high conductivity of the RGO in the hybrid reduces the interfacial resistance between SnO₂. In addition, the measured series resistance (R_{series}) of the TiO₂-SnO₂-RGO (0.45) based DSSC was 97.9 Ω, which was ~1.7-fold lower than that of the control cell (Table S1). On the basis

of these results, it is clear that the presence of RGO accelerated electron transport process within the photoanode and suppressed the charge recombination of the cells; thus significantly enhancing the η [21, 22, 28].

However, although TiO₂-SnO₂-RGO (0.7) based cell showed the highest J_{sc} (10.95 mA cm⁻²), the measured average η ($2.08 \pm 0.17\%$) was not the best observed, despite the films having high dye adsorption. When the RGO concentration in the hybrid further increased to 1.2 wt% and 4.75 wt%, a significant drop in the J_{sc} value and V_{oc} was observed for the TiO₂-SnO₂-RGO (1.2) and TiO₂-SnO₂-RGO (4.75) based DSSCs, thus resulting in very poor efficiencies. We attribute this η decrease of the DSSCs with higher RGO loading to (i) opacity of the film (see films before dye adsorption in Fig. S3) reducing light absorption and (ii) high catalytic property of RGO, which has been shown to limit the continuous electron transfer at the photoanode [2, 21, 47].

It is well established that although carbon materials can facilitate electron transport in the DSSC, the catalytic activity of carbon materials toward reduction of the electrolyte causes significant charge recombination at the interface of the photoanode and electrolyte (since this reaction should only occur at the cathode) if too high concentration of carbon is used [2]. Fig. 4c shows the dark J - V characteristics of DSSCs fabricated without and with RGO in the SnO₂ photoanodes. It is known that the magnitude and onset of the dark current indicates the level of charge recombination between the electrons from the dye excitation process and the I₃⁻ ions in the electrolyte [48]. It can be seen that the dark current onset shifted to a lower potential after adding a small amount of RGO into the SnO₂ photoanodes. This is known to be due to the increased charge recombination rate of the DSSCs caused by the reaction between the RGO and electrolyte. Therefore, at a given voltage, the dark current increased when the RGO was added into the SnO₂ photoanode of DSSC. Our finding is in line with similar report of adding carbon powders into TiO₂ photoanodes [48].

Indeed, the highest η (3.16%) with an average η of $2.94 \pm 0.24\%$ was achieved for the device based on TiO₂-SnO₂-RGO (0.45). In the TiO₂-SnO₂-RGO based DSSC, the TiO₂ can act as a barrier layer reducing the contact of RGO with the electrolyte and therefore reducing the likelihood of RGO catalyzing recombination at the photoanode. Taking into account the TiO₂ deposition process (dip coating) which unlikely to achieve 100 % coverage, we speculate that with higher RGO content the net amount of RGO in contact with the electrolyte will increase

accordingly. Moreover, we fabricated SnO_2 and SnO_2 -RGO photoanodes based DSSCs without TiCl_4 treatment and their PV results have been plotted in Fig. S5a. The efficiencies of these DSSCs were ~ 2 -fold lower than those of the devices fabricated with TiCl_4 treatment, confirming that the use of TiCl_4 treatment is a vital method to enhance the cell performance in SnO_2 photoanode DSSCs.

It can be seen from Table 1 that all parameters of DSSC fabricated with SnO_2 photoanodes increased after incorporating 0.45 wt% RGO. The calculated η enhancement of TiO_2 - SnO_2 -RGO (0.45) photoanode based device was impressive (91.5%) as compared to the control cell especially in light of the fact that a very small amount of RGO is required to realise these large improvements in efficiency. This photoanode (TiO_2 - SnO_2 -RGO (0.45)) was chosen for further investigation to fully understand the role of RGO in the DSSC.

IPCE spectra offer important information on the light harvesting efficiency which is mainly determined by the absorption of light by the dye molecules at the photoanode and electron transport processes. The IPCE spectra of the DSSCs with and without RGO in the photoanode are illustrated in Fig. 4d. It should be noted that the IPCE spectra of the DSSCs were characterized after the devices were aged for approximately 10 days. The IPCE of the TiO_2 - SnO_2 -RGO (0.45) photoanode based device is higher than that of the control DSSC over the entire wavelength region. The lack of wavelength dependence indicates that the addition of RGO into the SnO_2 photoanode improves the DSSC performance without altering the internal mechanism, likely by enhancing electron transfer rate and increasing dye adsorption onto the photoanode.

As discussed earlier, RGO in the hybrid ensures rapid electron transport process (Fig. 5a) and significantly enhances the J_{sc} value of the DSSC. Importantly, it can be expected that incorporation of RGO in the SnO_2 photoanode would improve the DSSC performance owing to presence of suitable energy levels. Fig. 5b shows an energy level diagram for the TiCl_4 treated SnO_2 photoanode with RGO. Since a thin TiO_2 layer was deposited on the FTO and on the SnO_2 or SnO_2 -RGO layers by TiCl_4 treatment, it is reasonable to include the energy level of TiO_2 in this diagram. The red arrow in Fig. 5b represents the fact that the electron transfer from the conduction band of SnO_2 to that of TiO_2 is not possible due to their mismatching band energy levels. As the TiO_2 coverage on the FTO is incomplete (not 100%), both SnO_2 and TiO_2 are in contact with the FTO and hence electron transfer from both the

SnO₂ and TiO₂ to the FTO is still feasible. The results from Fig. S6 and S7 show that despite the fact that the TiO₂ on the FTO is very thin, it does make a contribution to the current and voltage of the cell and as such is important to show. Since the energy level of RGO (-4.40 eV) lies between the conduction band of TiO₂ (-4.26 eV) and SnO₂ (-4.56 eV), the electrons can be rapidly transferred stepwise from the TiO₂ to the SnO₂ conduction band (see Fig. 5b) [18, 28]. Here RGO can act as a bridge between TiO₂ and SnO₂. This effective electron transfer would likely reduce the charge recombination of the cell, thus improves the performance.

Finally, the PV parameters of our best-performing cells have been compared with values reported in the literature for other DSSCs with SnO₂ based photoanodes. Table 2 summarizes the PV parameters such as J_{sc} , V_{oc} , FF and η of DSSC devices fabricated with various SnO₂ structures based photoanodes and our best performing cells. It can be observed from Table 2 that the efficiency observed for our DSSC fabricated with SnO₂-RGO photoanode is comparable or higher than those achieved by other 1D and 3D SnO₂ structured photoanode films. Therefore, this indicates that the incorporation of graphene structures into SnO₂ photoanode is an effective strategy to achieve high efficiency DSSCs.

4. Conclusion

In summary, the successful application of RGO structures in 1D SnO₂ micro-rod based photoanodes for DSSCs has been demonstrated. Herein we show that the application of RGO overcomes the major shortcoming of SnO₂ when applied as a DSSC photoanode, namely poor dye adsorption. In addition, owing to its suitable energy levels and excellent conductivity, RGO significantly improved the electron transport rate in the cells. Importantly, PCE (η) of the DSSC was significantly improved to 3.16% by incorporating a very small amount of RGO into the photoanode, demonstrating a ~91.5% enhancement in the efficiency when compared to SnO₂-only photoanode based DSSC (1.65%).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version.

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Figures and Figure captions

Scheme. 1. Synthetic procedure of SnO₂-RGO hybrid structure.

Fig. 1. SEM images of (a) GO, (b) SnO₂ micro-rod and (c) SnO₂-RGO hybrid. High resolution SEM images of (d) SnO₂ micro-rod and (e) RGO sheet in the hybrid showing that small SnO₂ nanoparticles are formed on SnO₂ and RGO surface.

Fig. 2. (a) XRD patterns and (b) XPS survey spectra of the samples.

Fig. 3. (a) ATR-FTIR and (b) Raman spectra of SnO₂-only, GO and SnO₂-RGO hybrid materials. Long dash line in ATR-FTIR spectra proves that “-OH” is different from the “C=C” in the hybrid.

Fig. 4. (a) J - V curves of DSSCs assembled with different RGO content in the TiO₂-SnO₂ photoanode measured under AM 1.5G illumination at 100 mW cm⁻². (b) UV-vis spectra of N719 dye molecules desorbed from SnO₂ films with different amount of RGO using 0.1 M NaOH solution. (c) J - V curves of DSSCs fabricated without and with RGO in the SnO₂ photoanodes measured under the dark state. (d) Normalized IPCE value of DSSCs fabricated based on TiO₂-SnO₂ photoanodes with (0.45 wt%) and without RGO.

Fig. 5. (a) A possible mechanism for the enhanced electron transfer in SnO₂-RGO hybrid. (b) Energy level diagram for the TiCl₄ treated SnO₂ photoanode with RGO.

Table 1. PV parameters of the DSSCs fabricated based on SnO₂ photoanodes with different RGO content. Average values and the standard deviations of the DSSCs are shown based on at least three cells for each device. Parameters of the best cells are highlighted in **bold**.

Device	RGO, wt%	J_{sc} , (mA cm ⁻²)	V_{oc} , (V)	FF	η (%)
TiO ₂ -SnO ₂ -RGO (0)	0	5.735 ; 4.78 ± 0.95	0.64 ; 0.64 ± 0.01	0.45 ; 0.43 ± 0.04	1.65 ; 1.28 ± 0.52
TiO ₂ -SnO ₂ -RGO (0.2)	0.2	8.196 ; 8.20 ± 0.15	0.64 ; 0.63 ± 0.01	0.45 ; 0.44 ± 0.01	2.36 ; 2.27 ± 0.07
TiO ₂ -SnO ₂ -RGO (0.45)	0.45	10.185 ; 9.41 ± 1.00	0.67 ; 0.67 ± 0.01	0.46 ; 0.46 ± 0.01	3.16 ; 2.94 ± 0.24
TiO ₂ -SnO ₂ -RGO (0.7)	0.7	10.954 ; 10.23 ± 0.88	0.52 ; 0.50 ± 0.02	0.39 ; 0.41 ± 0.04	2.15 ; 2.08 ± 0.17
TiO ₂ -SnO ₂ -RGO (1.2)	1.2	2.914 ; 2.91 ± 0.03	0.52 ; 0.51 ± 0.01	0.45 ; 0.44 ± 0.01	0.68 ; 0.66 ± 0.03
TiO ₂ -SnO ₂ -RGO (4.75)	4.75	1.984 ; 1.74 ± 0.26	0.31 ; 0.27 ± 0.05	0.46 ; 0.43 ± 0.04	0.29 ; 0.22 ± 0.08

Table 2. PV parameters of the DSSCs fabricated based on various SnO₂ photoanode structures and our best performing cell (TiO₂-SnO₂-RGO (0.45)).

Structure	Ref.	J_{sc} , (mA cm ⁻²)	V_{oc} , (V)	FF	η (%)
This study	-	10.18	0.67	0.46	3.16
SnO ₂ nanoparticles	[49]	7.63	0.35	0.43	1.14
SnO ₂ nanoparticles	[44]	4.90	0.40	0.51	1.00
SnO ₂ nanoparticles	[50]	7.90	0.47	0.55	2.03
SnO ₂ nanofibers	[51]	7.04	0.51	0.38	1.34
SnO ₂ multiporous NFs	[12]	10.0	0.44	0.45	2.00
SnO ₂ nanoflowers	[52]	7.30	0.70	0.60	3.00
SnO ₂ NWs + NPs	[53]	9.90	0.53	0.49	2.53
SnO ₂ spheres (hierarchical mesoporous)	[54]	12.3	0.52	0.58	3.70

Supplementary Information

Incorporation of Graphene into SnO₂ Photoanode for Dye-Sensitized Solar Cells

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Fig. S1. SEM image and EDX elemental analysis (inset) of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ sample (used as the starting material).

Fig. S2. (a) Auger and (b) EDX elemental analysis on the selected area (highlighted by red rectangle in (a) and circle in (b)) of the corresponding SEM images of SnO_2 -RGO hybrid, as shown in the inset in b).

Fig. S3. Dye adsorption capability of the films (SnO₂-RGO (X)) with different RGO content. In SnO₂-RGO (X), the value of X indicates the weight concentration (wt%) of RGO in the hybrid. For instance, the concentration of RGO in the SnO₂-RGO (0.45) was 0.45 wt%.

Fig. S4. The absorbance of these solutions at a wavelength of 520 nm.

Fig. S5a shows the J–V curves of DSSCs assembled with different RGO in the SnO₂ photoanodes (without any TiCl₄ treatment on the photoanode). The overall trend in the efficiency changes (increased after adding appropriate amount of RGO into the SnO₂ and decreased at too high concentration of RGO in the photoanodes) of DSSCs without and with TiCl₄ treatment was very similar, demonstrating that adding RGO into SnO₂ photoanode can enhance the PV efficiency, regardless of additional TiCl₄ treatment. A possible energy diagram for SnO₂-RGO photoanode based DSSC is shown in Fig. S5b. In this device structure, RGO enhances the electron transport rate and can also act as a bridge between dye and SnO₂. Notably, the efficiency of our SnO₂-only based DSSC was within the range (ranging from 0.6% to 1.0%) of previously reported values [1-3].

Fig. S5. (a) J–V curves of DSSCs fabricated with different RGO content in the SnO₂ photoanode without the TiO₂ blocking layer and (b) an energy level diagram for the SnO₂-RGO photoanode without any TiO₂ blocking layer.

It should be noted that TiO₂ was formed on the FTO by TiCl₄ treatment. However, it is well established that the TiO₂ does not completely cover FTO which makes electron transfer process possible between SnO₂ and FTO [4–7]. In order to prove that the coverage of TiO₂ during from TiCl₄ treatment on FTO is not 100%, DSSCs with a structure FTO/TiO₂/SnO₂/dye/electrolyte/Pt/FTO (without the second TiCl₄ treatment) were fabricated and their J–V characteristics are illustrated in Fig. S6a. It is reasonable to

expect that the DSSC fabricated with such structure cannot work if the TiO_2 completely (100%) covered the FTO because the conduction band of TiO_2 (-4.25 eV) is higher than that of SnO_2 (-4.56 eV) and thus energy transfer from the SnO_2 to the FTO through TiO_2 layer would not be feasible (see Fig. S6b). Interestingly, the fabricated DSSC exhibited a good efficiency (1.17%) with increased V_{oc} value, as compared to SnO_2 photoanode based DSSC without any blocking layer TiCl_4 treatment. Cells with the TiO_2 blocking layer only and SnO_2 -free photoanode give a very poor performance (see Fig. S7). The improvement in efficiency for the cell of Fig. S6 compared to the cell without graphene of Fig. S5 means that while the TiO_2 on the FTO must play a small role in the cell, the SnO_2 must also be in direct contact with the FTO and able to transfer electrons. This clearly show the thin TiO_2 layer does not cover the FTO completely and electron transfer from both oxides must occur. The incomplete coverage and thinness of TiO_2 on the FTO means the majority of the photovoltaic performance is from the SnO_2 layer.

Fig. S6. (a) J–V curves of DSSC device assembled with the photoanode structure of FTO/thin $\text{TiO}_2/\text{SnO}_2/\text{dye}$ (without second TiCl_4 treatment). Inset shows the device structure. (b) A possible energy level diagram for this DSSC photoanode.

In addition, only TiCl_4 treated FTO as a photoanode based DSSC was fabricated and its performance is depicted in Fig. S7. For this experiment, the cleaned FTO was immersed in a 40 mM TiCl_4 aqueous

solution at 70°C for 30 min, followed by drying with N₂ gas and annealing at 450°C for 30 min. After cooling to room temperature, second TiCl₄ treatment was performed in a same manner. Finally the film was sintered at 450°C for 30 min and then exposed the dye solution as before. As a result, the fabricated cell showed high V_{oc} value, but its PCE was very poor (0.13%). This result is reasonable since the V_{oc} parameter is determined by the energy level difference between the conduction band of semiconducting photoanode material (TiO₂ here in this device) and the potential energy of the electrolyte. The very low J_{sc} value of this cell is due to the insufficient dye-loading into the photoanode film as only very thin TiO₂ and low surface area layer is formed on the FTO. A poor fill factor value could also be associated with the incomplete coverage of TiO₂ on the FTO. These results again show that the SnO₂ is the main active element of the these photoanodes.

Fig. S7. J–V curves of DSSC fabricated with thin TiO₂ layers on FTO as a photoanode. Notably, TiO₂ layers were formed on the FTO by 2 times TiCl₄ treatment as was done for the normal device structure.

Inset shows the device structure.

Table S1. Electrical parameters of SnO₂ photoanode without and with RGO and their DSSCs.

Sample	Sheet resistance, R_s ($\Omega/\square$)	Series resistance, R_{series} (Ω)	Shunt resistance, R_{shunt} (Ω)
TiO ₂ -SnO ₂ -RGO (0)	4.51×10^6	167.0	1600
TiO ₂ -SnO ₂ -RGO (0.45)	1.81×10^6	97.9	1920

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