Chapter 2
Two-Dimensional Graphene Bridges Enhanced Photoinduced Charge Transport in Dye-Sensitized Solar Cells

2.1 Introduction

Graphene, the 2D carbon nanomaterial has drawn much attention nowadays. It is a zero band gap material [1], and electrons in it are just like massless relativistic particles, so it has an excellent electrical conduction in two dimensions [2–6], even at temperatures close to absolute zero and the Dirac point [1]. Based on its astonishing advantages in electrics, graphene has been used in conductive glasses [7] organic photovoltaic cells [8, 9], field effect transistors devices [10], and ultrasensitive sensors [11, 12].

Dye-sensitized solar cells (DSSCs) have attracted considerable interests because of their relatively low cost and high efficiency for the photoelectrical conversion of solar cells, since Grätzel’s group introduced nanostructured TiO₂ film into anode electrodes [13]. Although ~11 % conversion efficiency was obtained [14, 15], further improvements are still necessary. The major bottleneck is the transport of photogenerated electrons across the TiO₂ nanoparticle network, which competes with the charge recombination. To suppress the recombination and improve the transport, there are several strategies including (1) using composite metal oxides as the semiconductor with different band gaps [16]; (2) preparing the porous structure whose direction is perpendicular to the conducting substrate [17–22]; and (3) introducing charge carriers (1D nanomaterials) to direct photogenerated electron [23–25].

Considering their special charge transfer properties, the 1D nanomaterials, such as the carbon nanotubes (CNTs), were introduced into the electrodes [23–25]. However, the efficiency was increased limitedly because of the point contact between nanosphere TiO₂ and columniform 1D nanomaterials (as shown in Scheme 2.1a). On the contrary, the 2D graphene may benefit the charge separation not only due to its excellent conductivity but also good contact with TiO₂ nanoparticles. Graphene is a 2D soft single molecular layered structure, and there are intermolecular forces such as physisorption, electrostatic binding, or charge transfer interactions between
graphene and TiO$_2$ [26], so the nanocrystalline TiO$_2$ can anchor on the graphene flake compactly (Scheme 2.1b) to form graphene bridges, which will decrease the TiO$_2$–TiO$_2$ contacts. Due to its excellent electrical conduction, the bridged graphene behaves as an electron transfer medium to enhance the electron transport from the conduction band (CB) of TiO$_2$ at the anchor position quickly (Scheme 2.1d), and the recombination is reduced as a result.

Herein, we incorporate the 2D graphene into TiO$_2$ nanostructure photoanode to form graphene bridges in DSSCs, and find that graphene can enhance the charge transport rate so as to prevent the charge recombination and increase the light-collection efficiency as well, so the photoelectrical conversion efficiency is improved.

2.2 Results and Discussion

2.2.1 The Characterization of GO and Graphene

GO was synthesized from flake graphite by a modified Hummers method, and graphene was produced by chemical reducing and annealing (see detailed methods) [27]. The image of GO was analyzed through atomic force microscopy (AFM) on new cleaved mica surface (Fig. 2.1). It can be seen that the lateral dimensions of graphene are in the range of 0.2–2 μm and about 1 μm on average. Analysis of the AFM images in Fig. 2.1b revealed the GO sheets with heights in about 1 nm from the cross-sectional view in Fig. 2.1c, which is somewhat larger than the interlayer
spacing of GO (0.73 nm) measured by X-ray powder diffraction (XRD) (Fig. 2.2), however, the similar results can also be observed in other results [28–32]. In addition, the X-ray photoelectron spectroscopy (XPS) (Fig. 2.3a) and Fourier transform IR (FT-IR) (Fig. 2.3c, d) measurements also confirm that the graphite was well exfoliated into small pieces during the strong oxidation process, and the graphene was synthesized [33].

Figure 2.4a, b are XPS survey spectra of photoanodes with and without graphene. The C 1s peak of the electrode with graphene bridges is stronger than that without graphene, confirming that the graphene was successfully introduced into the photoanode.

### 2.2.2 Photocurrent–Voltage (I–V) Characteristics of Different Electrodes

In order to study the effect of 2D graphene bridges in photovoltaic devices, a series of DSSCs were fabricated with different content of graphene in photoanode (see detailed methods). The traditional nanocrystalline electrode (Electrode 1) was also fabricated to comparison. The thickness of all the different electrodes is the same (7 μm), and the results are based on the average one among many electrodes for each ratio.

The parameters and I–V characteristics for solar cells based on the different electrodes were exhibited in Table 2.1 and Fig. 2.5. The results indicate that the efficiency
will not be improved with the increase of the content of graphene all the while, and 0.6 wt% GO composite has got the optimization (we name this electrode as Electrode 2). Considering that the GO will lose weight after the reduction, 0.4 % graphene will be left in the final electrode (about 70 % remaining, Tables 2.2 and 2.3). Moreover, to compare the differences between the 1D and 2D composite, the CNT composite photoanode was fabricated in the same way (Electrode CNT), and the content of CNT is 0.4 %. Hence, Electrode 1, Electrode 2, and Electrode CNT were used in the following experiments to discuss the effects of graphene.

As shown in Fig. 2.5a, a short-circuit current density ($I_{sc}$) of 16.29 mA cm$^{-2}$, an open-circuit voltage ($V_{oc}$) of 0.69 V, and the conversion efficiency ($\eta$) of 6.97 % for Electrode 2 were obtained. As compared, $I_{sc}$, $V_{oc}$, and $\eta$ were 11.26 mA cm$^{-2}$, 0.69 V, and 5.01 %, respectively, for Electrode 1. There are about 45 % increases in $I_{sc}$ and 39 % in $\eta$ for Electrode 2, while nearly the same $V_{oc}$ compared with Electrode 1. In this case, we improve the $I_{sc}$ significantly without sacrificing the $V_{oc}$, indicating that graphene is better than CNTs for DSSCs with the same technique [23–25]. The Fermi level of CNT is between its CB and valence band, which means it is more negative than its CB. Also, the CB of CNT is more negative ($-4.5$ eV vs. vacuum) than the CB of TiO$_2$ ($-4.0$ eV vs. vacuum). All these make the apparent Fermi level decrease
in the CNT composite cell, and the $V_{\text{oc}}$ is sacrificed as a result [24]. However, graphene is a zero band material, [1] and its calculated work function is a little more positive ($-4.42$ eV vs. vacuum) than that of CNT, which is close to work function of FTO ($-4.4$ eV vs. vacuum) [7]. Hence, the apparent Fermi level may not be decreased in the graphene-bridged cell, and the $V_{\text{oc}}$ is not affected. By the way, the introduced 2D graphene bridges increase the charge transport, and suppress the electrons in TiO$_2$ to recombine with the dye and redox species, and hence the $V_{\text{oc}}$ will not be decreased.

Fig. 2.3 The C 1s XPS spectrum of a GO and b Electrode 2. The C 1s XPS spectrum of GO indicates the presence of four types of carbon bonds: C–C (284.8 eV), C–O (286.8 eV), C=O (287.5 eV), and O–C=O (289.0 eV). Although Electrode 2 has the same C 1s species, the intensities of oxide species are much weaker. Besides, there is an additional peak at 288.5 eV, corresponding to the C in the C=N bonds of hydrazone, and FT-IR Spectrum of c GO and d graphene. The characteristic vibrations are the broad O–H stretching peak at 3411 cm$^{-1}$, the strong C=O peak at 1730 cm$^{-1}$, the $\delta$-C–OH peak at 1460 cm$^{-1}$, the O–H deformation peak at 1390 cm$^{-1}$, the C–OH stretching peak at 1240 cm$^{-1}$, the C–O stretching peak at 1060 cm$^{-1}$. The peak at 1622 cm$^{-1}$ is due to the skeletal vibrations of unoxidized graphitic domains. The spectrum of graphene confirms the reduction of GO. The O–H peaks, the C–O peaks, and the C=O peak have been decreased. And a new absorption band at 1550 cm$^{-1}$ may be attributed to the skeletal vibration of the graphene sheets.
In addition, the improved $I_{sc}$ is also reflected in the increased IPCE performance (Fig. 2.6). Comparing with Electrode 1, the IPCE response at all wavelengths is enhanced by a factor of 1.56, while the maximum IPCE ($\text{IPCE}_{\text{max}}$) was 83% at the wavelength of 481 nm for Electrode 2. This increase in IPCE may be due to two factors: (1) as graphene is a 2D nanomaterial, the TiO$_2$ particles can anchor in it very well, so the photoinduced electrons can be captured by the graphene easily. Because graphene is an excellent electron carrier, the rapid photoinduced electron transport is produced, and the recombination and back electron transfer are suppressed as a result; (2) more porous structure of the anode has been formed due to the contributions of graphene, which increase the light scattering as shown in the SEM (Fig. 2.7), nitrogen adsorption experiments (Fig. 2.8a) and UV-vis spectra (Fig. 2.8b), respectively. Furthermore, there is a blue shift to the $\text{IPCE}_{\text{max}}$. The $\text{IPCE}_{\text{max}}$ shift is common in the former reports, but the reason is not very clear [34–36]. We presume that it
may be due to the introduction of many pores in the composite electrode (Fig. 2.7b). And these pores extended the pore distribution to 500 nm (Fig. 2.8a), which includes the wavelength around 480 nm, and the scattering is much easier happened. And there is more reflectance effect around 480 nm (Fig. 2.8b), hence the effect in IPCE is more remarkable, then the blue shift can take place. And it needs further analysis.

Figure 2.7 shows the SEM images of the electrodes after the reduction and annealing, and there are more pores in Electrode 2 (Fig. 2.7b) than in Electrode 1 (Fig. 2.7a) and Electrode CNT (Fig. 2.7c). These pores are in the micrometer scale.

Table 2.2 The XPS data of GO

<table>
<thead>
<tr>
<th>Name</th>
<th>Start BE (eV)</th>
<th>End BE (eV)</th>
<th>Height (counts)</th>
<th>FWHM (eV)</th>
<th>Area (P) CPS. (eV)</th>
<th>At.%</th>
<th>SF</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 1s</td>
<td>292.48</td>
<td>281.04</td>
<td>12417.87</td>
<td>2.1</td>
<td>54207.59</td>
<td>67.84</td>
<td>1</td>
</tr>
<tr>
<td>O 1s</td>
<td>537.73</td>
<td>527.05</td>
<td>24492.12</td>
<td>2.19</td>
<td>60343.76</td>
<td>31.59</td>
<td>2.85</td>
</tr>
<tr>
<td>N 1s</td>
<td>410.51</td>
<td>394.85</td>
<td>221.41</td>
<td>0.25</td>
<td>755.03</td>
<td>0.57</td>
<td>1.77</td>
</tr>
</tbody>
</table>

Table 2.3 The XPS data of graphene

<table>
<thead>
<tr>
<th>Name</th>
<th>Start BE (eV)</th>
<th>End BE (eV)</th>
<th>Height (counts)</th>
<th>FWHM (eV)</th>
<th>Area (P) CPS. (eV)</th>
<th>At.%</th>
<th>SF</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 1s</td>
<td>294.2</td>
<td>281.05</td>
<td>46997.54</td>
<td>1.52</td>
<td>108204.5</td>
<td>87.05</td>
<td>1</td>
</tr>
<tr>
<td>O 1s</td>
<td>538.91</td>
<td>526.54</td>
<td>6680.79</td>
<td>3.46</td>
<td>27021.26</td>
<td>8.53</td>
<td>2.93</td>
</tr>
<tr>
<td>N 1s</td>
<td>407.49</td>
<td>395.2</td>
<td>2627.7</td>
<td>3.13</td>
<td>9327.07</td>
<td>4.43</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Note The XPS data shows that the content of oxygen was decreased after the reduction. The weight loss is oxygen in majority, and the weight losing is about 25% (keep the content of C as a constant). Also, the graphene will lose another 7% weight after calcining at 450 °C in air. So after the treatment, the GO will have about 70% left (30% lose)

Fig. 2.5 a Photocurrent–voltage characteristics of different electrodes. The sensitizer was N₃ (ruthenium dye). The cell active area was 0.20 cm² and the light intensity was 100 mW cm⁻²; b The back current of different electrodes (the insert of the figure is the enlarge plot of back current)
isotherms (Fig. 2.8a). The pore size distribution was calculated by the Barrett–Joyner–Halenda (BJH) analysis from N\textsubscript{2} desorption isotherms. The distribution shows that Electrode \textit{2} has large pores in the mesoporous (20–500 Å) and macroporous (>500 Å) regions. Also, the pore size was extended to the micrometer scale for the graphene composite electrode, which was formed when the H\textsubscript{2}O and N\textsubscript{2}H\textsubscript{4} were released from the anode after the reduction and annealing [37]. This means that the incorporating of graphene will introduce a hierarchical structure and increase the roughness factor. But the introduced roughness did not increase the surface area. The surface areas for Electrode \textit{1} and Electrode \textit{2} are 52.23 and 51.67 m\textsuperscript{2} g\textsuperscript{−1}, respectively, calculated by the multipoint Brunauer–Emmett–Teller (BET) method, which are nearly the same, indicating that the graphene composite electrode will not improve the dye absorption, but the light scattering was increased based on the UV-vis measurement (Fig. 2.8b). The diffuse spectrum shows that the introduced pore performs as a light capture center, and the light scattering was increased by 7 % at all wavelengths comparing with the traditional electrode. The increased light scattering will improve the photo-to-current conversion efficiency. But because the increased light diffuse cannot transform to the photoexcited electrons absolutely, the efficiency increased by light scattering must be less than 7 %. However, the IPCE measurement shows that the efficiency was increased by 56 %. That means the major improvement is not attributed to the light scattering.

With the higher graphene loading, there will be light-harvesting competition between N3 dye and graphene, and the dye adsorption was reduced because the TiO\textsubscript{2} is surrounded by graphene. At the same time, the excessive graphene can act as a kind of recombination center instead of providing electron pathway, and the short circuit will happen easily. All these lead to the decrease of the total efficiencies.
2.2 Results and Discussion

Fig. 2.7 SEM micrographs of (a) Electrode 1, (b) Electrode 2 and (c, d) Electrode CNT. The graphene composite electrode is more porous comparing with other electrodes. Figure (d) is the enlargement of figure (c). Figure (d) indicated that the CNT cannot connect to the TiO$_2$ particle well, and it is the point of contact. The CNT also cannot disperse in the anode well, which may also restrict the efficiency.

Fig. 2.8 a BJH pore size distributions calculated from N$_2$ desorption isotherms, and b Measured diffuse reflectance of sensitized anodes.
2.2.4 Electrochemical Impedance Spectra (EIS) Measurement of Different Electrodes

To confirm the effect of 2D nanomaterial in transporting the electrons and restraining the recombination in the nanostructure, EIS, a powerful tool to clarify the electronic and ionic transport processes in DSSCs [38, 39] was measured under the illumination of one sun at open-circuit potential (Fig. 2.9). In the Nyquist plots (Fig. 2.9a), the biggest semicircle at medium frequencies is attributed to photoinjected electrons in the TiO₂ or back reaction from the injected electrons in TiO₂ to the electrolyte (ca. 1–100 Hz), which is the most important in the device. As shown, the semi-cycle at intermediate frequency regions were decreased for Electrode 2 indicating the fast redox activity of the electrolyte in the working electrode interface. The equivalent circuit of the devices (Fig. 2.9c) has been reported [40–42]. Using Z View software and fitting the semicircle of medium frequencies gives $R_3$ (resistance of charge transfer) and $C_1$ (capacity). Compared with Electrode 1, Electrode 2 has a smaller $R_3$ (21.66 Ω vs. 29.86 Ω), but a bigger $C_1$ (1655 μF vs. 965 μF), showing that the charge recombination in Electrode 2 has been reduced. These results were also supported by the Bode plots (Fig. 2.9b). The medium frequency peak of Electrode 2 is shifted to lower frequency (from ~10.1 to ~6.9 Hz), comparing with Electrode 1. Therefore, incorporating graphene into the TiO₂ nanocrystalline anode will increase the electron transport rate restraining the charge recombination.

In addition, some 1D nanomaterials are also good electron carriers, to prove the outstanding properties of the 2D nanomaterial, the CNT composite electrodes were also fabricated in the same route, and the surface area of electrode CNT was almost the same with other electrodes (53.08 m² g⁻¹). As shown in the former figures (electrode CNT), this electrode had a low efficiency (0.58 %), and the IPCE was low too. The reasons were observed by the EIS measurement. The electrode CNT has the largest $R_3$ (140 Ω) and smallest $C_1$ (28 μF), also the medium frequency peak is at

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Fig. 2.9 a Nyquist and b Bode diagrams of the electrochemical impedance spectra of different electrodes. c Is the equivalent circuit of the device. The spectra were measured under the illumination of one sun at open-circuit potential

2.2.4 Electrochemical Impedance Spectra (EIS) Measurement of Different Electrodes
107 Hz (the highest). These results indicate the CNT is not an ideal charge carrier in this system. The low dark current proves that CNT is a good electron capture [25] (Fig. 2.5b), and it is a good conductor indubitably. But its performance in DSSCs is not so good. That may be due to two factors: (1) CNT is a 1D nanomaterial. The columniform structure cannot attach the TiO₂ particles well, and it is isolated in the anode (Fig. 2.7d). It will not perform as the electron capturer and carrier well; (2) the CNT is not coherent, and the captured electrons cannot transport to the FTO (due to the CNT is not coherent) or TiO₂ (due to the energy level reason), the resistance is high \( R_3 \) as a result. Also, many electrons are captured by CNT without transporting; hence the electrons are superfluous, and the recombination is easy to happen, so the capacity \( C_1 \) is low and the frequency is high. Also, in the CNT composite cell, the light scattering is the lowest, but the transmittance is the highest (Fig. 2.10), and the efficiency decreased to some extent.

2.2.5 Operational Principle of Device

Due to its excellent electrical conduction, the 2D graphene bridges behave as an electron transfer channel, which can transport the photo-induce electron quickly [23]. And the energy level of graphene is between the CB of TiO₂ and FTO [43]. Scheme 2.2a shows the operational principle. Under illumination, the CB of semiconductor TiO₂ receives the electrons from photoexcited dye. Because the TiO₂ is anchored with 2D graphene, and the graphene is homogeneous in the system, the excited electrons are captured by the graphene without any obstruction. The collected electrons can transport from TiO₂ to the conductive substrate quickly and effectively through graphene bridges (Scheme 2.2b), and hence the adverse reactions (recombination and back reaction) are suppressed.
2.3 Conclusions

In summary, 2D graphene is a rising star in material science, and we introduced it into the nanocrystalline anode of DSSC successfully. The short-circuit current density was increased by 45 %, and the conversion efficiency was increased by 39 %. This may be due to a lower recombination and a faster electron transport with the introduction of graphene chiefly. Also the higher light scattering is benefit to a certain extent. This study proved that the 2D charge carriers have more advantages than the 1D material such as the compactly anchor and the homogenous dispersion. The incorporation of 2D nanomaterial with 0D nanoparticles can also be extended to other electronic devices, especially using graphene as an electron accepter and charge transfer medium.

2.4 Postscript

At the beginning of this work, we were not exactly sure that graphene is suitable or not for DSSC, so a lot of attempts were taken by introducing graphene to each part of the cell. Here, I think it is interesting to write the results, which is benefit to understanding the interaction between graphene and TiO₂.

We have tried to introduce graphene into the counter electrode and also the electrolyte, but with the further understanding of graphene, we think the energy level is not match for this approach. Also, there are some difficulties in the film formation for graphene on FTO, otherwise, one can try fabricating of TiO₂-graphene heterojunction, and more promising data may come out.

Please note, in this work, we did not introduce a compact TiO₂ layer in DSSC, neither we did not introduce hierarchical structure into the photoanode by the post-treatment with TiCl₄. For the former, based on the result we obtained, we have tried to build a compact TiO₂ film, but as discussed in the text, for energy level reasons,
the graphene captured electrons are difficult to transfer to the conduction band of TiO₂. Hence, the compact TiO₂ film will affect the electron transport, thus reducing the efficiency of the battery. Herein, it is another proof that proves that the electron transfer direction is from TiO₂ to graphene. The reason for abandoning treatment with TiCl₄ is because it requires annealing for second time. While graphene will be removed to some extent during each annealing circle, it is not easy to precisely control the amount of graphene. Then the experiment is difficult to repeat.

Meanwhile, we have noticed some papers give a hypothesis that the charge is transferred from graphene to TiO₂. Based on my knowledge, we need a further proof to give such a conclusion. At least, based on our experiment result, it is more reasonable to speculate that the electrons transfer direction is from TiO₂ to graphene. Also, we have tried using graphene as dye (in the absent of N3) to excite photoelectrons, but no obvious photocurrent is observed. That means no electrons are injected to the conduction band of TiO₂ from graphene, or the recombination is very fast. On the other hand, even if the electrons can be transferred from graphene to TiO₂, the main body of the charge transport should still be TiO₂. Considering that the bottle neck of DSSC is the charge transport efficiency, there would be no great benefit to introduce graphene into the cell.

However, a possible way is to design graphene quantum dots or chemically modify graphene, which will adjust the energy level of carbon material. One may get a proper size for the charge transport, but the position of valance band should be also considered, which needs to match the energy level of electrolyte.

I have to say, what we used is not exactly graphene, but reduced graphene oxide instead, which presents defects. These defects make it not a true zero band gap but a semimetallic material. I tend to consider it as a semiconductor, then it should form a heterojunction structure with TiO₂, which would produce a certain bending at the band edge. Hence, in the experiment, we can observe that with the addition of graphene, the Voc is decreased to a certain extent. It may due to a reduction of the apparent Fermi level, which is more clear in a dark voltage spectrum.

There are still a lot of mechanisms that are not clear enough in this work. Hence, further modification and improvement are quite necessary. For example: (1) Because it is not possible to add the compact layer, the graphene is easy to cause a short circuit to some extent. How to choose a compact layer with suitable energy level may be the key to further improve efficiency. (2) The real situation of charge transport is not very clear. It still needs a deeper study to reveal whether graphene really possesses advantages comparing with other carbon materials. Some more advanced testing tools or methods can be introduced to explore the mechanism.

2.5 Detailed Methods

Synthesis of GO: GO was synthesized from flake graphite (average particle diameter of 4 μm, Qingdao Tianhe Graphite Co. Ltd., Qingdao, China) by a modified Hummers method [27]. All of the other chemicals were of analytical reagent grade,
and used without further purification. Briefly, graphite powder (5 g) and NaNO₃ (3.75 g) were placed in a flask. Then, concentrated H₂SO₄ (375 mL) was added slowly while stirring in an ice water bath. KMnO₄ (22.5 g) was added gradually under stirring over 1 h, and stirred for another 2 h. After stirring vigorously for 5 days at room temperature, the mixture was stirred at 35 °C for 2 h, and then diluted with 5 wt% H₂SO₄ aqueous solution (700 mL) over 1 h. With stirring at 98 °C for 2 h, when the temperature was reduced to 60 °C, 30 wt% H₂O₂ (30 mL) was added, and the mixture was stirred for 2 h at room temperature. The mixture was centrifuged and washed with aqueous solution of 3 wt% H₂SO₄/0.5 wt% H₂O₂ (2 L) for 15 times. Then the bottom solid was washed with 3 wt% HCl (2 L) aqueous solution with a similar procedure, and one time using H₂O (2 L). After adding another 2 L deionized water and dispersing the solid using vigorous stirring and bath ultrasonication for 30 min, the final water solution was treated with a weak basic ion-exchange resin to remove the remaining HCl acid. The final solution was concentrated to 7.5 mg/mL.

**Preparation of different DSSCs:** To prepare graphene composite electrode, 3 g poly-vinylalcohol (PVA, MW 22,000) water solution (30 %) was dissolved with the mixed solvent containing 9 ml H₂O and 12.5 ml ethanol. Then, 1.62 g P-25 TiO₂ was added to make the suspension of TiO₂. After the suspension was dispersed, Electrode 1 was prepared by doctor blade technique on fluorine-doped tin oxide (FTO) glass for comparison. As to the preparation of graphene composite electrodes, 1.25 ml GO aqueous solution (7.5 mg/ml) was added into the suspension (0.6 wt%). After that, it was stirred and dispersed in ultrasonic cleaner for about 30 min, respectively, so as to let GO get dispersed in the suspension well, and it can anchor TiO₂ perfectly, and then Electrode 2 was prepared. Also the electrodes with 2.5 wt% and 8.5 wt% content of GO were prepared (Electrode 3 and 4) in the same way. In addition, the CNT composite electrode (0.4 wt%) was fabricated as 1.62 g P-25 TiO₂, 3 g PVA water solution (30 %), 9 ml H₂O, 12.5 ml ethanol and 6.5 mg CNT (Shenzhen Nanotech Port Co. Ltd., the diameter is 20–40 nm, and the purity is >95 %), and the fabricated route is the same. And the thickness of all the different films is about 7 μm. At last, the electrodes were treated under hydrazine vapor at 40 °C for 24 h to reduce GO. After the films were rinsed with deionized water and dried by heating to 40 °C in vacuum for 3 h, the electrodes were annealing at 400 °C under Argon flow for 3 h, and the GO was transformed to graphene totally. Then, they were calcined at 450 °C for 1 h in air. The as-prepared films were sensitized by soaking in ethanol solution containing 3 × 10⁻⁴ M the ruthenium dye, Ru(dcbpy)₂(NCS)₂ (N₃) (dcbpy = 2,2′-bipyridine-4,4′-dicarboxylic acid) for 24 h. The DSSCs were composed of a sensitized photoanode, a platinum counter electrode, and an electrolyte. The electrolyte was composed of 0.5 M LiI, 0.05 M I₂, 0.5 M tert-butylpyridine, and 0.6 M 1-propyl-3-methylimidazolium iodide in 3-methoxypropionitrile.

**Characterization:** The AFM images were measured with SPA400 (Seiko Instruments Inc.) on new cleaved mica surface in tapping mode in air. The XRD patterns were obtained by using an X’Pert PRO MDP with CuKα radiation (λ = 1.5405 Å) with 30 mA and 40 kV. XPS data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W AlKα radiation. The FT-IR spectrum was recorded by Bruker Equinox 55 FTIR spectrometer. The I–V characteristics of
the cell were measured by an electrochemical analyser (CHI630A, Chenhua Instruments Co., Shanghai) under solar simulator illumination (CMH-250, Aodite Photonic-electronic Technology Ltd, Beijing) at room temperature. The IPCE was measured by illumination with monochromatic light, which was obtained by a series of light filters with different wavelengths. SEM images were obtained using a JEOL JSM-6700F scanning electron microscope at 3.0 kV. UV-vis spectra were recorded on a Hitachi Model U-4100 Spectrophotometer. The nitrogen adsorption and desorption isotherms at the temperature of liquid nitrogen (77 K) were measured on a Quantachrome Autosorb-1 sorption analyzer with prior degassing under vacuum at 200 °C overnight. Total pore volumes were determined using the adsorbed volume at a relative pressure of 0.99. Multipoint BET surface area was estimated from the relative pressure range from 0.05 to 0.2. The pore size distribution of the electrodes was analyzed using the BJH algorithm. The EIS was carried out on a Zahner IM6e impedance analyzer (Germany) in the frequency range 0.02 Hz–100 kHz with illumination of 100 mW/cm².

References

The Preparation of Nano Composites and Their Applications in Solar Energy Conversion
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