In-situ electrochemically deposited polypyrrole nanoparticles incorporated reduced graphene oxide as an efficient counter electrode for platinum-free dye-sensitized solar cells

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This paper reports a rapid and in-situ electrochemical polymerization method for the fabrication of polypyrrole nanoparticles incorporated reduced graphene oxide (rGO@PPy) nanocomposites on a ITO conducting glass and its application as a counter electrode for platinum-free dye-sensitized solar cell (DSSC). The scanning electron microscopic images show the uniform distribution of PPy nanoparticles with diameter ranges between 20 and 30 nm on the rGO sheets. The electrochemical studies reveal that the rGO@PPy has smaller charge transfer resistance and similar electrocatalytic activity as that of the standard Pt counter electrode for the I3⁻/I⁻ redox reaction. The overall solar to electrical energy conversion efficiency of the DSSC with the rGO@PPy counter electrode is 2.21%, which is merely equal to the efficiency of DSSC with sputtered Pt counter electrode (2.19%). The excellent photovoltaic performance, rapid and simple fabrication method and low-cost of the rGO@PPy can be potentially exploited as an alternative counter electrode to the expensive Pt in DSSCs.

In view of the concerns relevant to natural resource depletion and environmental pollution problems and to eradicate the same, dye-sensitized solar cell (DSSC) has appeared to be a promising potential candidate for the production of electricity from solar energy in an efficient and eco-friendly manner. Recently, several efforts have been made to enhance the performance of DSSC, such as introduction of novel photoanodes, electrolytes, dyes and counter electrodes. Among them, counter electrode plays a crucial role in increasing the conversion efficiency of the DSSC as it serves as a mediator for collecting electrons from the external circuit, reduces I3⁻ into I⁻ and moreover it regenerates the oxidized dye after electron injection. The efficient counter electrodes can reduce internal energy loss in DSSCs and thus produce higher current densities and fill factors. So far, the most preferred material for counter electrode in DSSC is platinum (Pt), due to its excellent electrocatalytic activity towards I3⁻ reduction. However, the high-cost and the rarity of Pt significantly hinder its practical application in DSSCs, including mass production and commercialization. This has promoted large research interest in exploring alternative counter electrode materials for Pt-free DSSCs. In the past decades, carbon-based materials, conducting polymers and transition metal based inorganic materials have been used as counter electrode materials and they showed reliable conversion efficiencies in DSSCs like Pt-based counter electrode.

Recently, carbonaceous materials, such as graphite, activated carbon, single-walled carbon nanotubes (SWCNTs), double-walled carbon nanotubes (DWGNTs), multi-walled carbon nanotubes (MWCNTs) and graphene have been employed as potential alternative counter electrode materials, due to their high electronic conductivity, corrosion resistance towards I3 high reactivity for I⁻ reduction and low-cost. Among them, graphene, which is an atomic planar sheet of hexagonally arrayed sp² carbon atoms has been demonstrated to be a promising and efficient counter electrode material for DSSCs, because of its excellent conductivity and high electrocatalytic activity. Even though, some reports revealed that the bare graphene alone does not to be the...
right candidate for a counter electrode in DSSCs, owing to the limited number of active sites for the I$_3$/$I^-$ electrocatalytic reaction. For this reason, further efforts have been undertaken based on the conducting polymers, such as poly(3,4-ethylenedioxythiophene)-poly(styrenesulphonate) (PEDOT:PSS), polypyrrole (PPy) and polyaniline (PANI) incorporated into graphene for DSSC applications because of their merits of both excellent electron conductivity and high catalytic activities. Among the conducting polymers, polypyrrole (PPy) is an excellent and suitable counter electrode material because of its desirable features, including low-cost, environmental stability and large scale processability.

In this work, we report a simple and rapid fabrication method for the preparation of polypyrrole-reduced graphene oxide (rGO@PPy) nanocomposite materials and their application as counter electrode for Pt-free DSSCs. The formation of PPy nanoparticles incorporated reduced graphene oxide nanocomposite film is achieved by a rapid and in-situ electrochemical polymerization method. Previously, Gong et al. reported the chemical polymerization method for the fabrication of PPy incorporated with graphene for counter electrode in the DSSC. However, the fabricated electrode showed agglomeration of PPy that seriously hinder the photovoltaic performance of the DSSC. In this work, we have attempted to fabricate the highly dispersed PPy nanoparticles incorporated rGO counter electrode for DSSCs. To the best of our knowledge, this is the first kind of report that deals about the preparation of highly dispersed PPy nanoparticles incorporated rGO film and its application as a counter electrode for DSSC. The solar to electrical energy conversion efficiency of the rGO@PPy nanocomposite modified counter electrode for DSSC. The solar to electrical energy conversion efficiency of the rGO@PPy nanocomposite modified counter electrode for DSSC. The solar to electrical energy conversion efficiency of the rGO@PPy nanocomposite modified counter electrode for DSSC. The solar to electrical energy conversion efficiency of the rGO@PPy nanocomposite modified counter electrode for DSSC. The solar to electrical energy conversion efficiency of the rGO@PPy nanocomposite modified counter electrode for DSSC.

Results and discussion

Formation of rGO@PPy nanocomposite on ITO substrate. The electrochemical deposition of rGO@PPy on the ITO electrode was carried out by the following fabrication method. The pyrrole monomers were electrochemically oxidized for the polymerization through the initiation step during which the radical cations were formed with the delocalized radical state over the pyrrole ring. The formation of complex was achieved via the electrostatic charge attraction of pyrrole radical cations and pTS anions. The coupling process of pyrrole monomers was taken place by removing two protons since the more preferred location for the radical in the pyrrole ring is α-position. Further growth of polymer chain was continued upon the introduction of freshly obtained radical cations on the existing oligomeric chain. Initially, the pyrrole monomers attracted the pTS anions, owing to the lower molecular density. The introduction of negatively charged GO was also attracted by the pyrrole radical cations at a slower rate, due to the higher molecular density. Concurrently, the GO was reduced to rGO upon the release of free electrons during the formation of pyrrole radical cations. The free electrons were released from the pyrrole monomer during the electrochemical oxidation of pyrrole monomers to pyrrole radical cations, and these free electrons are responsible for the reduction of the graphene oxide. It is known from previous reports that during the formation of pyrrole radical cations, the free electrons that are released and it reduce the GO to rGO. The formation of PPy nanoparticles on the rGO surface was taken place through the π-π stacking and the several other interactions such as Van der Waals force and hydrogen bonding.

The FESEM images of rGO@PPy nanocomposites at the deposition times of 10, 100 and 500 sec on ITO were recorded and are shown in Figure 1. A less distribution of 25–50 nm sized PPy nanoparticles on the surface of rGO sheets at a deposition time of 10 sec is clearly observed from the Figure 1(A and B). Whereas, a uniformly distributed 30 nm sized PPy nanoparticles on the rGO sheets surface is observed for the nanocomposite film deposited at 100 sec (Figure 1(C and D)). When increasing the deposition time to 500 sec, a large amount of PPy nanoparticles with size range between 15 and 30 nm are found to be deposited on the rGO sheets (Figure 1(E and D)). The FESEM images of rGO@PPy nanocomposites suggest that changing the deposition time accelerates the distribution of PPy nanoparticles on rGO sheets during the nanocomposite formation. The difference in the PPy nanoparticles distribution on the rGO surface at different deposition times may significantly influence the electrocatalytic reactions.

Characterization of rGO@PPy nanocomposite. The FT-IR spectra were recorded for GO and rGO@PPy nanocomposite and are shown in Figure 2. The GO have abundant oxygen groups such as –COOH and –OH on its edges. The characteristic FT-IR peaks observed at 1734, 1626, 1404, 1224 and 1058 cm$^{-1}$ due to the stretching vibration of carbonyl (C=O), aromatic (C=C), carboxylic acid (C=O), C–OH and epoxy C–O stretching vibrations, respectively of the GO sample (Figure 2(a)). A broad and intense peak observed at 3355 cm$^{-1}$ is corresponding to –OH peak of GO. The FT-IR spectrum of the rGO@PPy nanocomposite reveals that after the reduction of GO into rGO during the fabrication of rGO@PPy nanocomposite film, the peaks for the oxygen functional groups were significantly reduced/completely vanished for rGO sheets. The existing peaks at 1574 and 1224 cm$^{-1}$ may due to the contribution from the aromatic C=C and residual –OH. The weak peaks were observed for rGO at 1710 and 1385 cm$^{-1}$, because of the red shifted carbonyl (C=O) and carboxylic acid (C=O) stretching vibrations feature obtained from the π-π interaction between rGO sheets and PPy nanoparticles. Moreover, the peaks observed at 1514, 1430, 1119 and 1003 cm$^{-1}$ are corresponding to N–H bending, aromatic ring stretching, C–N stretching and N-H out-of-plane bending of PPy, reveals that successful incorporation of PPy nanoparticles on the surface of rGO in the rGO@PPy nanocomposite film (Figure 2(b)).

Figure 1 | FESEM images of rGO@PPy nanocomposite films at different deposition times of (A and B) 10, (C and D) 100 and (E and F) 500 sec.
X-ray photoelectron spectroscopy (XPS) was used to confirm the functional groups present in the rGO@PPy nanocomposite film. Figure 3 shows the wide scan and de-convoluted C1s core-level spectrum for GO and rGO@PPy nanocomposite. In Figure 3a, the observed peak at 399.6 eV in the entire range of XPS spectrum for rGO@PPy nanocomposite indicates the existence of nitrogen species from the PPy distributed on the surface of rGO sheets28. Meanwhile, the C1s core-level spectrum of the GO could be fitted into five component peaks with binding energies of 284.3, 285.3, 286.6, 287.0 and 288.6 eV, due to the sp2 hybridized carbon, sp3 hybridized carbon, C–O, C=O and COOH species, respectively (Figure 3(b)) 29. Moreover, the C1s core-level spectrum of the rGO@PPy nanocomposite film could be fitted into six component peaks with binding energies of 283.8, 284.5, 285.0, 286.2, 287.7 and 289.0 eV, due to the contribution of sp2 hybridized carbon, sp3 hybridized carbon, C–N, C=O, C=O and COOH, respectively. The oxygenated carbons were also detected in the XPS spectrum of rGO@PPy, however the intensities of these peaks are extremely reduced from those of GO, which indicates the deoxygenation of GO during the deposition process.

The wide-scan XPS results revealed the absence of iron-related compounds in the nanocomposite and the absence of the XPS peak binding energy at 700 eV for FeCl3 and its oxides.

The Raman spectra were recorded for the GO, PPy and rGO@PPy nanocomposite and their results are shown in Figure 4. Two typical peaks in the Raman spectra were observed for the GO and rGO@PPy samples. The peak around 1357 cm\(^{-1}\) (D-band) is related to the defects and disorder in the hexagonal lattice, while the 1595 cm\(^{-1}\) (G-band) is due to the vibration of sp2-bonded carbon atoms in the 2D hexagonal lattice30. Therefore, the D/G intensity ratios (\(I_D/I_G\)) express the atomic ratio of sp\(^3\)/sp\(^2\) carbons in measuring the extent of disordered graphite. The calculated \(I_D/I_G\) ratio for GO is 0.99. For the pure PPy, the characteristic bands observed at 1380 cm\(^{-1}\) and 1577 cm\(^{-1}\) due to the ring stretching mode and the C=C backbone stretching of PPy, respectively31. In addition, the peak at 928 cm\(^{-1}\) and two small peaks at 964 cm\(^{-1}\) and 1060 cm\(^{-1}\) are due to the bipolaron ring deformation and the polaron symmetric C-H in-plane bending vibration, respectively32,33. The calculated \(I_D/I_G\) ratio is 0.88. The Raman spectrum of the rGO@PPy nanocomposite showed the bands for PPy, and proven that the presence of PPy nanoparticles in the nanocomposite. Furthermore, the decrease of the \(I_D/I_G\) value (0.82) of nanocomposite showed that the disordered of graphene is lesser and with the support of peak shift of G-band from 1590 cm\(^{-1}\) to 1570 cm\(^{-1}\) compared to GO confirm the reduction of GO during electrodeposition process34.

Photovoltaic performance of rGO@PPy counter electrode based DSSCs. The photovoltaic performances of the rGO@PPy based counter electrode based DSSCs (Figure 5A) were investigated under a simulated solar irradiation of 100 mW/cm\(^2\) (AM 1.5G). The photocurrent density-photovoltage (J-V) profile is used to examine critical photovoltaic parameters such as open-circuit voltage (\(V_{oc}\)), short-circuit photocurrent density (\(J_{sc}\)), maximum photovoltage (\(V_{max}\)) and maximum photocurrent density (\(J_{max}\)). The fill factor (FF) and power conversion efficiency (\(\eta\)) of the DSSC can be obtained from the Eqns. 1 and 2, respectively35.

\[
\text{FF} = \frac{V_{oc} J_{sc}}{V_{oc} J_{sc} \times FF} \times \frac{V_{oc}}{I_s},
\]

where, \(I_s\) is the intensity of the incident light.

To evaluate the photovoltaic performance of the DSSC, the photocurrent density-photovoltage voltage (J-V) curves were recorded for the rGO@PPy based counter electrode and are shown in Figure 5B and their corresponding photovoltaic parameters are listed in Table 1. The obtained conversion efficiencies DSSCs with rGO@PPy nanocomposite counter electrode prepared at different deposition times of 10, 50, 100, 250 and 500 sec are 0.85, 1.06, 2.21, 1.15 and 0.39%, respectively. In order to obtain an efficient DSSC, optimizing the deposition time of rGO@PPy was varied to obtain the counter electrode with optimum performance in DSSC. The observed results clearly revealed that the conversion efficiency of DSSCs was increased while increasing the deposition time until it
reached a maximum of 100 sec. The increase in the efficiency is due to the increase in the number of PPy nanoparticles on the rGO sheets, which consequently improved the Jsc of the device. This phenomenon can be attributed to the fact that the electrocatalytic activity of rGO@PPy continuously increases with increasing the PPy content in the nanocomposite. Further increase in the deposition time led to decrease in the conversion efficiency (Figure 6a). The decrease in the efficiency for higher deposition time can be ascribed to the distribution of large number of PPy nanoparticles on the rGO sheets that leads to decrease in catalytic activity towards the reduction of I3⁻ into I⁻ ions and to regenerate the oxidized dye after the electron injection process. As a consequence, the overall energy conversion efficiency of DSSC was deteriorated. The Jsc was increased while increasing the deposition time and attained a maximum of 2.21 mA/cm² at the deposition time of 100 sec (Figure 6b). Further increase in the deposition time to 250 sec decreased the Jsc value to ~0.39 mA/cm². It can also be seen that the Voc trends were frustrate within the range of ~0.44 and 0.70 V. The Jmax and Vmax values of the device were also followed the similar trends exhibited by the Jsc and Voc (Figure 6c).

In order to understand the suitability of best rGO@PPy nanocomposite based counter electrode with deposition time of 100 sec, the J-V curve for the sputtered Pt based DSSC was recorded and are shown in Figure 7. When compared to DSSC with Pt counter electrode, the photovoltaic parameters of the rGO@PPy based DSSC were increased (Table 2). The overall solar to electrical energy conversion efficiency of the DSSC with rGO@PPy counter electrode was 2.21%, which was higher than that of the DSSC with sputtered Pt counter electrode (2.19%). The improved photovoltaic performances exhibited by the DSSC with rGO@PPy based counter electrode is due to the highly dispersed PPy nanoparticles on the rGO surface that facilitate high electrocatalytic activity for the I3⁻/I⁻ redox reaction.

Khamsone et al. reported that a DSSC with a polypyrrole film was used as a counter electrode and showed a conversion efficiency of 4.72% which is lower than a platinum counter electrode (7.59%)36. Zhang et al. reported a graphene based counter electrode with an efficiency of 6.81%. However, this was still lower than the platinum sample (7.59%)37. Few works have reported the use of graphene-incorporated polypyrrole as a counter electrode and it’s shown that a conversion efficiency of ~8% has been achieved. However, the obtained efficiency is still lower than that of the Pt-based counter

![Figure 4](image1.png)

Figure 4 | Raman spectra obtained for the (a) GO, (b) PPy and (c) rGO@PPy nanocomposite.

![Figure 5](image2.png)

Figure 5 | (A) Configuration of rGO@PPy counter electrode based DSSC and (B) Photocurrent density-photovoltage (J-V) curves obtained under simulated solar irradiation of AM 1.5 G (100 mW/cm²) for the DSSCs having the TiO₂/N719/Iodolyte configuration integrated with rGO@PPy nanocomposite based counter electrodes prepared at deposition times of (a) 10, (b) 50, (c) 100, (d) 250 and (e) 500 sec.

| Deposition time (s) | Jsc (mA/cm²) | Voc (V) | Jmax (mA/cm²) | Vmax (V) | FF | η (%) |
|---------------------|-------------|--------|---------------|---------|----|------|
| 10                  | 2.49        | 0.68   | 1.83          | 0.47    | 0.51 | 0.85 |
| 50                  | 4.82        | 0.68   | 3.03          | 0.35    | 0.32 | 1.06 |
| 100                 | 7.49        | 0.70   | 5.40          | 0.41    | 0.42 | 2.21 |
| 250                 | 3.78        | 0.66   | 2.34          | 0.49    | 0.46 | 1.15 |
| 500                 | 2.49        | 0.44   | 1.54          | 0.25    | 0.36 | 0.39 |

Table 1 | Photovoltaic parameters of the rGO@PPy counter electrode based DSSCs

Foot note: The DSSCs performance was evaluated under 100 mW cm⁻² simulated AM 1.5G solar light irradiation. Jsc: Short-circuit photocurrent density; Voc: Open-circuit photovoltage; Jmax: Maximum photocurrent density; Vmax: Maximum photovoltage; FF: Fill factor; η: Power conversion efficiency. Area of the cell was 0.5 cm².
Chen et al. reported a graphene-based counter electrode with an efficiency of 5.27%. However, this was lower than that of the platinum (6.02%)\textsuperscript{17}. Gong et al. reported that a DSSC with a poly-pyrrole film was used as a counter electrode, and its showed a lower conversion efficiency (8.14%) than a platinum counter electrode (8.34%)\textsuperscript{22}. Even though the reported DSSC were showed high efficiency but still it is lower when compared to the Pt based DSSC\textsuperscript{17,22,36,37}. In this work, the rGO@PPy counter electrode showed the efficiency of 2.21%, which was higher than that of the DSSC with sputtered Pt counter electrode (2.19%).

**Electrochemical characterizations.** Electrochemical impedance spectroscopic (EIS) measurements were performed to investigate the electrochemical behavior of the rGO@PPy counter electrode. Figure 8 shows Nyquist plots obtained for the rGO@PPy counter electrodes prepared at different deposition times. The Nyquist plots showed semicircles, which are due to the charge-transfer resistance (Rct) that taken place at the rGO@PPy/electrolyte interface. The charge-transfer resistance induces negative impact on the photovoltaic parameters such as FF and overall efficiency. The photovoltaic performances of DSSCs crucially depend on the Rct values which were fabricated with same anodes, dye and electrolyte but rGO@PPy counter electrode with different deposition times. It can be obviously seen that the Rct was decreased while increasing the deposition time from 10 to 500 sec and this can be attributed to the corresponding increase in the PPy nanoparticles on the surface of rGO sheets. When the deposition time was 10 sec, less number of PPy nanoparticles was distributed on the rGO sheets that led to the poor electrical conductivity between redox couple and counter electrode, resulted in larger Rct value and lower photovoltaic performance.

As shown in the Bode phase plots, the frequency angle of the mid-frequency peak (fmid) decreases with an increase in the deposition time during the fabrication of rGO@PPy nanocomposites, which indicated that the electron life time, is elongated in the deposition time range from 50 to 500 sec (Figure 8(B)). However, the rGO@PPy nanocomposite prepared at a deposition time of 100 sec shows a short frequency angle when compared to the rGO@PPy nanocomposite prepared at 500 sec. We believed that a very large number of PPy nanoparticles distributed on the rGO sheets may be responsible for this behavior. The increase in the deposition time induces large charge-transfer resistance to some perturbation for electrolyte diffusion, which greatly influences the impedance behavior in this region. The EIS was recorded for the sputtered Pt electrode and its Nyquist plot along with the rGO@PPy nanocomposite modified electrode is shown in Figure 8(C).

Interestingly, the Rct value of rGO@PPy electrode was found to be 14.8 Ω cm\textsuperscript{2}, which was comparable to that of the sputtered Pt electrode (14.3 Ω cm\textsuperscript{2}), indicating that the identical intrinsic catalytic activities taken place on the surface of rGO@PPy electrode for the reduction of I\textsubscript{3}\textsuperscript{-}. The similar Rct value obtained for rGO@PPy electrode to that of the sputtered Pt electrode suggests that it could be a competitive counter electrode material to the high-cost platinum.

**Conclusions**

The PPy nanoparticles incorporated rGO based counter electrodes were fabricated via an in-situ electrochemical deposition method for...
The rGO@PPy nanocomposite films were deposited at a constant applied potential of 0.8 V by using potentiostat-galvanostat (Elchema model EQCN-502 Faraday cage) at 532 nm. The electrochemical and photocurrent measurements were performed in a computer-controlled Versa STAT 3 electrochemical workstation (Princeton Applied Research, USA).

Fabrication of rGO@PPy counter electrode. The rGO@PPy nanocomposite films were fabricated by a catalyst-assisted in-situ electrochemical polymerization method. Briefly, pyrrole (0.1 M), GO (1 mg/mL), NapTS (0.1 M) and FeCl3 (0.1 M) were mixed in an electrochemical cell and vigorously stirred for 5 min in order to obtain a PPy nanoparticles in the solution. After the formation of PPy nanoparticles, the rGO@PPy nanocomposite films were deposited at a constant applied potential of +0.8 V by using potentiostat-galvanostat (Elchema model EQCN-502 Faraday cage) at room temperature and at different deposition times (10, 50, 100, 250 and 500 sec). After electrodeposition, the films were thoroughly rinsed with high pure de-ionized water five times to remove any impurities related to the iron salts. For the electrodeposition experiments, indium doped tin oxide, graphite and saturated calomel electrode were employed as working, counter and reference electrodes, respectively.

Fabrication of DSSCs and their performance evaluation. The TiO2 photoanodes were fabricated by the following procedure. Initially, 300 mg of P25 was mixed with 5 mL of ethanol which was stirred for 30 min to obtain a homogenous solution. A 0.1 M of TTIP was slowly introduced into the above reaction mixture under ultrasonication. The obtained TiO2 paste was coated on the conducting side of ITO by assembly by capillary action. The DSSC with an active area of 0.5 cm2 was used to measure its performance. Prior to test the photovoltaic parameters, Avaspec-2048 fibre optic spectrophotometer was used to measure the simulated light intensity.

Table 2 | Photovoltaic parameters of the fabricated DSSCs

| Counter Electrode | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (V) | $J_{max}$ (mA/cm$^2$) | $V_{max}$ (V) | FF | η (%) |
|------------------|-------------------|---------|-------------------|---------|---|-----|
| Sputtered Pt     | 5.12              | 0.71    | 4.31              | 0.51    | 0.56 | 2.19 |
| rGO@PPy          | 7.49              | 0.70    | 5.40              | 0.41    | 0.42 | 2.21 |

Foot note: The DSSCs performance was evaluated under 100 mW cm$^{-2}$ simulated AM 1.5G solar light irradiation. $J_{sc}$: Short-circuit photocurrent density; $V_{oc}$: Open-circuit photovoltage; $J_{max}$: Maximum photocurrent density; $V_{max}$: Maximum photovoltage; FF: Fill factor; η: Power conversion efficiency. Area of the cell was 0.5 cm$^2$.

The Pt-free DSSC. The SEM images showed uniform distribution of PPy nanoparticles with diameter in the range of 20–30 nm on the rGO sheets. When increasing the deposition time, large number of PPy nanoparticles was found to be deposited on the rGO surface. The electrochemical studies revealed that the rGO@PPy had smaller charge-transfer resistance and similar electrocatalytic activity for the $I_3^-/I^-$ redox reaction in DSSC. The overall solar to electrical energy conversion efficiency of the DSSC based on the rGO@PPy counter electrode was 2.21%, which was merely equal to that of the DSSC with Pt counter electrode (2.19%). The optimized deposition time for rGO@PPy to obtain higher conversion efficiency in DSSC was 100 sec. The low-cost, excellent performance, rapid and simple fabrication methods of the rGO@PPy modified counter electrode proved to be a potential alternative to the high-cost Pt as counter electrode in DSSC.

Methods

Materials. Titanium dioxide (P25) and pyrrole were purchased from Acros Organics. Graphite flakes were obtained from Ashbury Inc., USA. Common chemicals, such as toluene-4-sulfinic acid sodium salt (NapTS), sulphuric acid (H2SO4, 98%), phosphoric acid (H3PO4, 85%), potassium permanganate (KMnO4, 99.9%), iron (III) chloride (FeCl3) and hydrogen peroxide (H2O2, 30%) were procured from Merck and used as such. Indium doped tin oxide (ITO) coated conducting glass slides (7 Ω/sq) were supplied by Xin Yan Technology Limited, China. N719 (Ruthenizer 535-bisTBA) and Iodolyte Z-100 were received from Solaronix. X-ray photoelectron spectroscopy (XPS) measurement was carried out using Axis Ultra DLD (Kratos analytical Ltd). The surface morphology of the rGO@PPy nanocomposite films were examined by using Hitachi SU 8000 field emission scanning electron microscopy. The FT-IR spectral data were obtained from Perkin-Elmer-1725 FT-IR spectrophotometer. The Raman spectra were recorded using a Renishaw 2000 (mVia) system with an argon ion laser emitting at 532 nm. The electrochemical and photocurrent measurements were performed in a computer-controlled Versa STAT 3 electrochemical workstation (Princeton Applied Research, USA).

Materials characterization techniques. X-ray photoelectron spectroscopy (XPS) was performed using Thermo VG ESCALAB 220i-XL equipped with a monochromatic Al Kα source. The survey spectra were recorded using a pass energy of 160 eV, and high-resolution spectra were obtained using a pass energy of 20 eV. XPS data were analyzed using CasaXPS software.

The fabrication of DSSCs was performed by the following procedure. Initially, 300 mg of P25 was mixed with 3 mL of ethanol. After electrodeposition, the films were thoroughly rinsed with high pure de-ionized water five times to remove any impurities related to the iron salts. For the electrodeposition experiments, indium doped tin oxide, graphite and saturated calomel electrode were employed as working, counter and reference electrodes, respectively.

Fabrication of rGO@PPy nanocomposite films was evaluated under 100 mW cm$^{-2}$ simulated AM 1.5G solar light irradiation. $J_{sc}$: Short-circuit photocurrent density; $V_{oc}$: Open-circuit photovoltage; $J_{max}$: Maximum photocurrent density; $V_{max}$: Maximum photovoltage; FF: Fill factor; η: Power conversion efficiency. Area of the cell was 0.5 cm$^2$.
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Author contributions
S.P.L., Y.S.L. and A.P. designed the experiment and project. S.P.L. prepared the photoanode and Y.S.L. performed the XPS analysis of anodically oxidized glass-like carbon samples. To view a copy of this license, visit http://creativecommons.org/licenses/by-nc-sa/4.0/.

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