Reduction of graphene oxide at room temperature with vitamin C for RGO–TiO₂ photoanodes in dye-sensitized solar cell

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A B S T R A C T

Graphene has been used to enhance conversion efficiency in dye-sensitized solar cells (DSSC) through increased electronic transportation. Introduction of graphene into DSSC is realized through reduction of graphene oxide (GO) to reduced graphene or RGO in TiO₂ nanoparticles in solution. Chemical and hydrothermal reactions are two commonly used avenues. In the chemical route, toxic hydrazine and its derivatives are the typical reducing agent. Hydrothermal process is not toxic but requires prolonged heating. In this study, we mix flakes of GO with TiO₂ nanoparticles and use vitamin C to realize the reduction at room temperature. The RGO–TiO₂ composite films are then used as photoanode in DSSC. A conversion efficiency of 30% increase (to 7.89%) is obtained as compared to that of the pure TiO₂ photoanode.

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1. Introduction

Dye-sensitized solar cells (DSSCs) have drawn extensive attention because of their relatively low cost and high photoelectrical conversion efficiency potential [1]. Since the pioneer work of O’Regan and Grätzel [2], DSSCs have been intensively studied during the past two decades. Although 13% conversion efficiency was obtained recently [3], further improvements are still necessary. In general, DSSCs are comprised of photoanode (the most frequently used material is anatase TiO₂) decorated by a monolayer of dye molecules (sensitizers), a platinized counter electrode, and an electrolyte solution with a dissolved iodide ion/tri-iodide ion redox couple between the electrodes. The transport progress of photogenerated electrons across the TiO₂ nanoparticle network becomes the major bottleneck of improving the conversion efficiency of DSSCs [4,5]. If the photogenerated electrons couldn’t accomplish the transportation, they will recombine with the holes and get annihilated in the TiO₂ nanoparticle network [6]. To enhance electron transfer ability and suppress the recombination, some charge carriers materials are introduced into photoanode to the direct photo electrons [7–11].

Graphene has attracted a lot of attention because of its unique mechanical, thermal, electrical and optical properties [12–14]. As a 2D material, graphene is a zero band gap material with a single molecular layered structure [14]. In graphene, each carbon atom uses 3 of its 4 outer orbital electrons to form 3 sigma bonds 120° apart with 3 adjacent carbon atoms in the same plane, leaving the 4th electron free to move, therefore, electrons in graphene behave just like massless relativistic particles without crystal lattices’ restrictions [15,16]. As such, graphene possesses excellent electrical conductivities in two dimensions at room temperature (more than 200,000 cm² V⁻¹ s⁻¹) [17]. Since intermolecular forces such as physisorption, electrostatic binding, or charge transfer interactions between graphene and TiO₂ nanoparticles and use vitamin C to realize the reduction at room temperature. The RGO–TiO₂ composite films are then used as photoanode in DSSC. A conversion efficiency of 30% increase (to 7.89%) is obtained as compared to that of the pure TiO₂ photoanode.

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with that reduced using hydrazine or hydrothermal method [24,31]. Herein, we explore this facile approach of making RGO and directly mix it into DSSC for better energy conversion. Flakes of GO are reduced to graphene with VC as a reducing agent in an aqueous solution through simple stirring and centrifugation to form RGO–TiO$_2$ nanocomposite as photoanode in DSSC. Experiments show that the DSSC efficiency is enhanced by 30%.

2. Experimental

The GO reduction and fabrication of RGO–TiO$_2$ DSSC photoanode was described in Fig. 1. Graphene oxide (GO) powders with diameter of 500 nm–3 μm and 99% of 1–3 monolayers in thickness was purchased from Jining LeaderNano Tech LLC., and commercial TiO$_2$ (P25) nanoparticles of diameter of around 21 nm is purchased from Degussa Co., Ltd. in Germany, fluorine-doped tin oxide (FTO) conducting glass with a sheet resistance of 15 Ω cm$^{-2}$ was bought from Nippon Sheet Glass Co., Ltd., Japan, cis-di(thiocyanato)-N,N′-bis(2,2′-bipyridyl-4-carboxylic acid)-4′-tetrabutylammonium carboxylate) ruthenium (II) (N-719) was purchased from Solaronix Co., Ltd., Switzerland. All other chemical reagents used in the experiments were analytical reagents, purchased from Sinopharm Chemical Reagent Beijing Co., Ltd., without additional purification before use.

2.1. Preparation of the RGO–TiO$_2$ nanocomposite

30 mg solid state GO was dissolved in 100 mL deionized water, and sonicated for 2 h until the solution became clear and no precipitate present. Then 3 g of TiO$_2$ powder was added into the GO dispersions and stirred for 1 h in ultrasonic horn for a homogeneous suspension. 500 mg of VC was added to the solution. The as-prepared solution was vigorously stirred for 48 h at room temperature. As the color of the solution turned from yellowish to grayish, GO reduced to graphene. Then, centrifugation was conducted several times with water and ethanol to remove remaining VC and other chemicals from the solution. Finally, the remains were dried in a vacuum dryer at 65 °C. As such, RGO–TiO$_2$ nanocomposite with 1.0 wt.% RGO was prepared. 0.25, 0.5, 0.75, 1.25 wt.% RGO–TiO$_2$ nanocomposites were prepared in the same manner.

2.2. Preparation of the RGO–TiO$_2$ based photoanode

RGO–TiO$_2$ pastes were synthesized following the Grätzel method for preparing TiO$_2$ [32]. Before preparing the photoanode films, FTO...
conducting glass was immersed into a 40 mM TiCl₄ aqueous solution at 70 °C for 30 min, and then a 0.6 × 0.6 cm² film was coated on it by doctor-blading technique. After drying at 125 °C, the RGO–TiO₂ film was heated up at 5 °C per minute to 500 °C and held for 3 h under the nitrogen atmosphere to remove the organic component. The RGO–TiO₂ nanocomposite electrode was prepared after an extended post-treatment using a TiCl₄ aqueous solution followed by a sintering process at 450 °C in air for 30 min. Finally, the resulting electrode was immersed into an N719 ethanol solution for 24 h to form the sensitized photoanode. For comparison, two kinds of electrodes are also prepared: a pure TiO₂ electrode and another made of 0.75 wt.% as-received GO mixed with TiO₂.

2.3. Fabrication of the DSSC

The solar cell was assembled with a Pt counter electrode and the dye sensitized RGO–TiO₂ photoanode. The standard redox electrolyte was a solution of 0.60 M 1-butyl-3-methylimidazolium iodide (BMIIL), 0.03 M iodine (I₂), 0.10 M guanidinium thiocyanate (GSCN) and 0.50 M 4-tert-butylpyridine (TBP) in the mixture of acetonitrile and valeronitrile (volume ratio: 85:15). The solar cell was assembled into a sandwich type cell and sealed by using Surlyn thermoplastic frame.

2.4. Characterization

The crystal structures of the GO, the RGO and the RGO–TiO₂ were characterized by X-ray diffraction (XRD) (D8 Advance, Bruker,
Germany) with Cu Kα radiation (40 kV, 40 mA, λ = 0.0541 nm) at a step size of 0.02° (0.2 s per step). High-resolution transmission electron microscopy (TEM) images were obtained on a JEM-2010 (JEOL Ltd., Japan) at 200 kV. The RGO–TiO2 film’s morphologies and cross section scanning electron microscopy (SEM) images were obtained by a S4800 SEM instrument (HITACHI, Japan) at 15 kV. The reduction effect of VC on GO was obtained on a Raman spectrometer (LabRam HR800, HORIBA Jobin Yvon, France) equipped with a 514 nm laser and Fourier transform infrared spectroscopy (FT-IR) (Nicolet iS10 FT-IR Spectrometer, Thermo Scientific, China). The current density–voltage (J–V) characteristics of cells were measured by the Keithley 4200 semiconductor characterization system (Keithley Instruments, USA) under AM 1.5 simulated illumination (Newport 91160, 300 W xenon lamp, USA). Electrochemical impedance spectrum (EIS) was conducted on Autolab Potentiostat 30 system (Metrohm, Switzerland) with a frequency range from 100 kHz to 0.1 Hz in the condition of 10 mV AC amplitude under 100 mW·cm⁻² irradiation.

3. Results and discussion

3.1. Crystal structure

Fig. 2 shows the XRD patterns of the original GO, the RGO, the TiO2 nanoparticles and the RGO–TiO2 with different contents of RGO. Fig. 2(a) illustrates that the GO had only one peak at around 10° 2θ. After reduction, the peak was widened and moved to around 25° (c.f.,
RGO spectrum). The shift of peak suggested that the GO had been partly reduced to graphene: the GO had smaller interlayer spacing than the GO because the oxygen-containing groups were partially removed [22]. Fig. 2(b) shows that the peaks from the RGO–TiO2 are originated from the anatase and rutile TiO2 phases, and the relative content of anatase and rutile phase is about 4:1, which are in excellent agreement with that of TiO2. There is no obvious peak change at various contents of RGO–TiO2, indicating that the TiO2 nanoparticles maintain their crystal lattice structure of TiO2 after going through the reduction process. The content of RGO is too little to be detected by XRD.

3.2. Morphology of the RGO–TiO2 films

Fig. 3 has TEM images of the graphene oxide before the reduction. Fig. 3(a) shows the lateral size of graphene oxide flakes, which revealed that the graphene oxide’s lateral size was more than 2 μm. Fig. 3(b) is the magnified TEM image of graphene oxide and the layers are clearly seen at the edge of the GO flakes: mostly 3 layers. Fig. 4 is an SEM image of the cross-section of the RGO–TiO2 composite film displaying a film thickness of about 14.5 μm. Fig. 5 is the SEM image of an enlarged view of the top and a cross-section of the RGO–TiO2 photoelectrode film, revealing a good mix between the RGO (flakes) and the TiO2 nanoparticles (round particles). With an increase in amount of RGO in the RGO–TiO2 nanocomposite, the stock of graphene flakes becomes more apparent, as observed from the SEM image in Fig. 6. The graphene flakes may still not be completely covered by TiO2 nanoparticles even when the amount of RGO goes beyond 1 wt.%.

3.3. Removal of oxygen groups

Fig. 7 is the Raman spectra of GO with TiO2 nanoparticles before and after reduction by vitamin C. The Raman spectra exhibit two peaks around 1358 and 1605 cm$^{-1}$ corresponding to the D band and the G band. The D band comes as a breathing mode of k-point phonons of $\Gamma$ symmetry and G band is generally assigned to the $E_{2g}$ phonon of sp$^2$ bonds of carbon atoms [33]. As compared to GO–TiO2, there is an increase in intensity ratio of $I_D/I_G$ in RGO–TiO2. This agrees well with the Raman spectra of the GO reduced by VC [24] or hydrazine [34], indicating that the reduction did take place.

Fig. 8 shows the FT-IR spectra of the TiO2, the GO and the RGO–TiO2 films. The GO peaks at C–O (1060 cm$^{-1}$), C–O–C (1230 cm$^{-1}$), C–OH (1410 cm$^{-1}$), C=O (1720 cm$^{-1}$), and a hump at 3000–3500 cm$^{-1}$ which is attributed to the O–H stretching vibrations of the C–OH groups and water. In RGO–TiO2, the peaks at 1060, 1230, and 1740 cm$^{-1}$ disappeared, indicating that these oxygen-containing functional groups are removed. The RGO–TiO2 composite has a broad absorption at low wavenumbers (below 1000 cm$^{-1}$), that is attributed to the Ti–O–Ti bonds in TiO2. The peak around 1630 cm$^{-1}$ is contributed by the skeletal vibration of the reduced graphene flakes.

3.4. Effect of the RGO–TiO2 photoanode

The effects of the incorporation of RGO were evaluated and listed in Table 1 with regard to short circuit photocurrent density ($J_{SC}$), open-circuit photovoltage ($V_{OC}$), fill factor of the cell (ff) and the overall conversion efficiency ($\eta$). The electrode performance is illustrated by J–V curves under AM 1.5 condition shown in Fig. 9. It is observed from Table 1 that a proper amount of the RGO in the RGO–TiO2 photoanode enhances the energy conversion efficiency of the DSSCs. With 0.75 wt.% RGO, the photoelectric performs the best in this experiment setting with a conversion efficiency of 7.89%, an increase of 30.2% as compared to pure TiO2-based DSSC. The overall conversion efficiency was calculated from $J_{SC}$, $V_{OC}$, ff and the intensity of the incident light ($P_{in}$), [35] namely,

$$\eta = \frac{J_{SC} \times V_{OC} \times ff}{P_{in}}.$$

Consequently, the efficiency of the cell is determined by those three parameters. Fig. 10 shows the trends of $V_{OC}$ and $J_{SC}$ with different contents of RGO in the photoanodes. For DSSCs, the $V_{OC}$ values are obtained as the difference between the electrons’ Fermi level in TiO2 under the illumination and the Nernst potential of the redox couple in the electrolyte [35]. The $V_{OC}$ value of the cells does not show drastic change with different amounts of RGO as shown in Table 1. It means that the Fermi level in TiO2 does not shift much after stirring with VC. Despite the fluctuations, the $V_{OC}$ stay above 0.7 V in those low RGO concentrations (below 1.0 wt.%). When

<table>
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<tr>
<th>Anode with wt. % RGO</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>$V_{OC}$ (V)</th>
<th>ff (%)</th>
<th>$R_s$ (Ω)</th>
<th>$R_{ct}$ (Ω)</th>
<th>$C_{dl}$ (µF)</th>
<th>$\tau$ (ms)</th>
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<tr>
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Table 1

Photovoltaic parameters for DSSCs with anode of TiO2 with varying amount of RGO/GO.

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adding a large number of RGO, graphene layers may be stacked together and not completely covered by TiO$_2$ nanoparticles, as shown in Fig. 6(e-f). Because graphene has the excellent electrical conductivity, there will be a large number of recombination between the interface of graphene and electrolyte. Moreover, more recombination means less electron density, and it would cause a shift of the Fermi level [36], leading to a decrease in $V_{oc}$ (Fig. 10).

The short-circuit current is another fundamental parameter for efficiency of DSSC. A good short-circuit current is based on a good charge injection efficiency from the excited dye to TiO$_2$, the excellent charge transport property and large recombination resistance [28]. For the Ru-complex N-719 used here, the injection from the excited dye molecule to the conduction band (CB) of the TiO$_2$ is fast enough to complete the other processes [37–39]. Therefore, the charge collection and transportation efficiency of the injected electrons becomes a key factor to $J_{sc}$ of the cell. The remarkable electrical transport property of graphene indicates that it is a good conductor, and it is beneficial to capture and transport electrons from the CB of TiO$_2$. That is to say, graphene would act as a high-way to speed up electron transportation and lead to decrease the recombination in the TiO$_2$ electrode. Compared with the pure TiO$_2$ electrode, the $J_{sc}$ of DSSC with 0.75 wt.% RGO is 15.2 mA·cm$^{-2}$, which increased by 24.6%, respectively. The electrical conductivity of GO is billions of times smaller than that in RGO [40, 41]. Without high conductivity, GO can’t capture and transport electrons from the CB of TiO$_2$. Compared with the 0.75 wt.% RGO–TiO$_2$ cell, the $J_{sc}$ of DSSC with 0.75 wt.% as-received GO is 11.6 mA·cm$^{-2}$, which decreased by 28.2%, respectively. As shown in Fig. 10, $J_{sc}$ of RGO–TiO$_2$ anodes first increases to the maximum value and then decreases. The increase can be explained by the remarkable electrical transport property of graphene, which is beneficial to capture and transport charges from TiO$_2$. The electrons transferred from the CB of TiO$_2$ can transport quickly to FTO without recombination or back-transfer reaction, as shown in Fig. 11. Since graphene has a continuous band structure like metal [13,14], electrons transferred from TiO$_2$ into graphene can stay at continuous energy levels near the Fermi level. When graphene contacts with the electrolyte, graphene accelerates the reaction back to tri-iodide [10]. With too much RGO, the flakes over-stack each other, and thus are not able to be fully covered by TiO$_2$ nanoparticles, as such, back transfer reactions at the interface between RGO and electrolyte increase, which, in turn, eliminates the benefit of high conductivity of RGO.

Good fill factor is based on a low total series resistance of the cells. As TiO$_2$ nanoparticles incorporate with RGO and RGO is an excellent conductor, the interior resistance of the cells can be reduced to a lower level to achieve a higher fill factor (Table 1). As shown in Fig. 9 and Table 1, the PCE is decreased by ~10% in the anode incorporated with 0.75 wt.% as-received GO as compared with pure TiO$_2$ anode. In the case of directly using the as-received GO to mix with TiO$_2$ particles, the benefit of high conductivity of RGO does not exist. The electron mobility of GO is about 0.1–10 cm$^2$ V$^{-1}$ s$^{-1}$ [40] that is as slow as the TiO$_2$ nanoparticles [42]. The presence of GO, on the hand, interrupts the connection between TiO$_2$ nanoparticles and increases the number of interfaces therefore increases the interior resistance in the cell, and thus results in a decrease in $f$ (Table 1).

The interfacial electrical properties of DSSCs are characterized by the electrochemical impedance spectrum (EIS). Fig. 12 shows that there are three main semicircles observed in the EIS. The equivalent circuit of the DSSCs shown in Fig. 12 explains the transportation and recombination processes of the photogenerated electrons in the photoanode. The fitted $R_s$ is the series resistance, including the sheet resistance of the FTO glass, the contact resistance of the cell and the transfer resistance of the electrolyte. $R_t$ is the charge transfer resistance of the recombination between the TiO$_2$ nanoparticles and $I_3^-$ in the electrolyte, and $C_I$ is the chemical capacitance of the TiO$_2$ film. $R_{ct}$ and $C_{dl}$ are the charge transfer resistance and the double-layer capacitance at the counter electrode $I_3^-$ at the electrolyte/Pt/FTO glass interface [43,44].

From Table 1, $R_s$ values of the various films are almost the same, which means that the resistance of TiO$_2$/FTO interface has no change despite of different materials with or without RGO. However, the $R_t$ of the films assemble with RGO is smaller comparing with that of the pure TiO$_2$ photoanodes, indicating enhanced electron transportation between the TiO$_2$ nanoparticles and $I_3^-$ in the electrolyte after mixing with RGO. This is a result of the outstanding electrical conduction property of graphene. In DSSCs, electron lifetime ($\tau$) is an important parameter to explain the difference of energy conversion efficiency in different
samples, extractable from the Rg and Cc using $\tau = C_cR_g$ with fitting the EIS curves [35]. Obviously RGO–TiO2 composites have longer electron life-time except at too much RGO (1.25 wt.% RGO). At 0.75 wt.% $\tau = 27.01$ ms, being the longest in Table 1. This result is consistent with the result of short-circuit current and conversion efficiency in Fig. 9.

4. Conclusion

With vitamin C as a reduction agent, direct reduction of graphene oxide (GO) into reduced graphene (RGO) to form RGO–TiO2 nanoparticle photoanode for dye sensitized solar cell (DSSC) takes place at room temperatures with only stirring and centrifugation. Mixing of RGO in the DSSC photoanode improves the energy conversion efficiency. At 0.75 wt.% RGO obtained the conversion efficiency obtained is 7.89%, which is 30.2% increase as compared to its no RGO counterpart (6.06%). This increase is attributed to RGO’s higher conductivity for improved photoelectron transfer and reduced charge recombination.

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