Reduced Graphene Oxide Modified TiO_2 Nanoparticles Composites for Improved Performance of Dye-sensitized Solar Cells

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Abstract. As a two-dimensional (2D) nanostructure, reduced graphene oxide (rGO) has high specific surface area and excellent conductivity. In this paper, we obtain the TiO_2/rGO (TG) composite via a simple mechanical stirring the mixtures of anatase TiO_2 nanoparticles and graphene oxide (GO) nanosheets followed by a calcination process and apply it as photoanode material in dye-sensitized solar cells (DSSCs). rGO in the TG photoanode can inhibit charge recombination and increase the short-circuit current density (J_{sc}) and thus improve the power conversion efficiency (PCE) of the DSSCs. Moreover, the layered structure rGO increase the dye absorption in the TG-based photoanode and enhance the light harvesting efficiency. As a result, J_{sc} and PCE of DSSCs based on TG photoanode have been considerably increased from 9.75 mA/cm^{-2} to 10.45 mA/cm^{-2}, 3.87 % to 4.16 %, compared with pure TiO_2 photoanode, enhanced by7.2% and 7.5%, respectively.

Introduction

Dye-sensitized solar cells (DSSCs) have attracted extensive attention all over the world because of their relatively high PCE, ease of fabrication, and low production cost [1]. As the major component, TiO_2 photoanode serves as a substrate for dye absorption and a conductor of photogenerated electron from dye to conductive glass. The transmission of photogenerated electrons across the TiO_2 NPs network is one of the major bottlenecks for improving the PCE of DSSCs. A large number of studies have been conducted on DSSCs in which graphene/TiO_2 composites were used as photoanode. Zhao et al. [2] prepared graphene/TiO_2 composite photoanode to promote adsorption of the sensitizing dye because of its high porosity and large specific surface area, and such a DSSC showed a PCE of 7.52 % under a simulated irradiation of 100 mW/cm^2. Lee et al. [3] incorporated monolayer graphene networks with TiO_2 as a photoanode in DSSCs, which yielded a PCE of 5.8 %, and by integrating a 3D tubular-structure graphene path to form a hybrid network, the PCE increased to 6.7%. In this paper, we incorporated rGO nanosheets with anatase TiO_2 nanoparticles to form the TG photoanode, and thus the DSSCs based on TG film show the enhanced PCE which compared with that of pure TiO_2 photoanode. The microstructure of the hybrid composites and the underlying mechanisms for the enhanced photovoltaic performance will be studied in details.

Experiment

Preparation of TG Photoanode

First, the cleaned FTO glass (15Ω/sq, thickness of 2.2 mm) was immersed into 40 mM $TiCl_4$ solution at 70°C for 30 min and then was annealed at 450°C for 30 min. Second, a certain proportion of TiO_2 NPs and the as-prepared GO nanosheets were mixed with deionized water and ultra-sonicated for 30 min. The mixtures were stirred at 65°C in a water bath until the water was evaporated, and then heated at 550°C for 4h with the ramp rate of 2°C/min. The obtained powder was the TiO_2/rGO (TG) composite. Then, 240 mg TG composite, 39mg ethyl cellulose and 390 ml terpineol were incorporated into 8ml ethanol to prepare the TG paste. The paste was made into films on the as-prepared fluorine-doped tin oxide glass by doctor-blade method, followed by a subsequent sintering at 450°C for 30 min [4]. To study the performance of DSSCs based on TG films, pure TiO_2 films were also prepared.

Fabrication of DSSCs

The photoanodes were first immersed into 0.5 mM N719 acetonitrile and tert-butanol (1:1 volume ratio) solution for 24 hours in dark. Then, the photoanodes were washed with ethanol to remove the unanchored dyes. Finally, the dye sensitized photoanodes were sandwiched against Pt counter electrodes in the presence of 60 mm sealing space (Surlyn 1702, DuPont) and I/I_3- liquid electrolyte to assemble solar cells. The liquid electrolyte consisted of 0.1 M lithium iodide (LiI), 0.03 M iodine (I_2), 0.5 M 4-tert-butylpyridine (TBP), 0.6 M 1, 2-dimethyl-3-propylimidazolium iodide (DMPII), and 0.1 M guanidine thiocyanate (GuSCN). The active cell area was typically 0.25 cm^2.

Results and Discussion

Microstructure Characterization

The crystal structure of TG sample, as well as pure TiO_2, GO and rGO, was characterized by XRD patterns. As exhibited in Figure 1, the XRD spectrum of the pure TiO_2 sample is identical to the anatase phase (JCPDS no. 21-1172). The peaks at 25.3°, 37.8°, 48.0°, 53.9°, 55.0° and 62.8° correspond to the (101), (004), (200), (105), (211) and (204) crystal planes of anatase TiO_2. Compared to the XRD pattern of GO, the diffraction peak of rGO powder shifts from 11.2° to 24.3° after the thermal treatment at 450 °C. It reveals the reduction of GO to rGO. In the XRD pattern of TG composite, the diffraction peaks are presented at 25.3°, 37.8°, 48.0°, 53.9°, 55.0° and 62.8°. But it does not show the diffraction peak related to rGO. It is possible that the diffraction peak of rGO at 24.3° with much weaker intensity related to the strong peak of TiO_2 at 25.3°, because of the low amount of rGO in the TG composite.

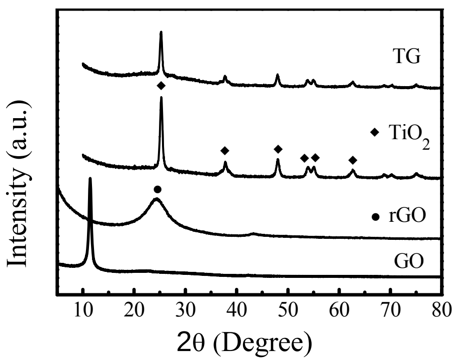

Figure 1. XRD patterns for the GO, rGO, TiO_2 and TG composites.

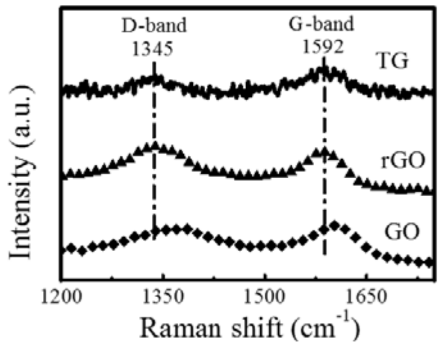

Figure 2. Raman spectra of the GO, rGO and TG composites.

Figure 2. shows the Raman spectra of GO, rGO and TG composites which demonstrate the existence and reduction of graphene materials associated with two typical Raman peaks (G and D bands). The G band is related to the in-plane vibration of ordered sp^2-bonded carbon atoms in a two-dimensional hexagonal lattice, and the D band is assigned to edge or in-plane sp^3 defects and disordered carbon [5]. Compared to GO, the D band shifts from 1363 cm^{-1} to 1345 cm^{-1} and the G band shifts from 1620 cm^{-1} to 1592 cm^{-1} in rGO. The spectrum of TG composite display the same D and G band position as rGO, suggesting the existence of rGO in the composite. At the same time, TG shows a higher intensity ratio of D/G (I_D/I_G = 0.82) in comparison to GO (I_D/I_G = 0.65). The shift of Raman peaks position and the increase of D/G intensity ratio confirm that GO has been reduced into rGO after the thermal treatment.

Photovoltaic Properties of the Solar Cells

In comparison with DSSC based on pure TiO_2, the IPCE of TG DSSC shows a substantial increase during the visible light region, as shown in Figure 3a. This is because of the excellent conductivity of rGO. TiO_2 has a large band gap (about 3.2 eV) which limits its absorption in only UV region and restrains the light harvesting. In Figure 3b, the value of J_{sc} is an integrated result of photocurrent-density in the whole photo-response wavelength. The TG based DSSC exhibits the J_{sc} of 10.45 mA•cm^{-2}, improving 7.2% compared with pure TiO_2 based DSSC (9.75mA•cm^{-2}). The FF of the TG DSSC is increased compared with TiO_2 DSSC which is corresponding to the value of the IPCE and J_{sc}.

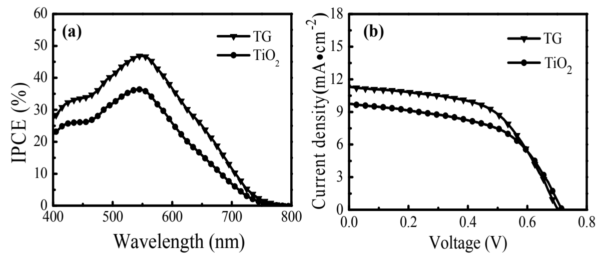

Figure 3. (a) IPCE and (b) photocurrent density-voltage (J-V) curves of DSSCs based on TiO_2 and TG photoanodes.

Generally, the IPCE values expressed as

$$IPCE = (LHE) \times (\eta_{inj}) \times (\eta_{cc}) \quad [6]$$

where the LHE is light harvesting efficiency, η_{inj} is electron injection efficiency and η_{cc} is electron collection efficiency. The LHE is mainly determined by the amount of adsorbed dyes. According to the results in Figure 4, the TG photoanode film shows higher dye-loading than pristine TiO_2 photoanode film because the rGO nanosheets incorporated with TiO_2 increases the internal surface area. This result is consistent with the result of Jsc. In Figure 5, the left semicircle in the high-frequency (R_1) corresponds to the redox reaction of I^-/I_3^- at Pt counter electrode/electrolyte interface, and the middle semicircle in the intermediate frequency (R_2) assigns to the electron-transport at the dye-sensitized metal oxide film/electrolyte interface [7]. It is obvious that the DSSC based on TG composite film (16.19 Ω) has much smaller R_2 value than the TiO_2-based DSSCs (18.93 Ω) (shown in Table 1), indicating much lower electrical transport resistance in the TG composite film which confirms that the rGO can promote the electron transport, restrict the charge recombination and thus to the improve the η_{cc}.

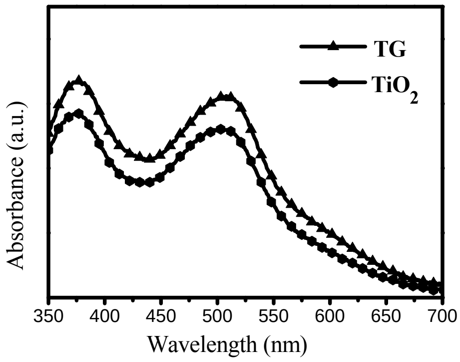

Figure 4. UV-Vis absorption spectra of NaOH solutions containing N719 dye detached from the N719-sensitized TiO_2 and TG photoanodes.

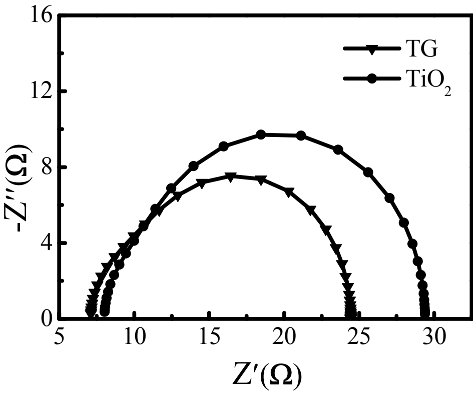

Figure 5. EIS spectra of TiO_2 and TG photoanodes.

Conclusion

In summary, the TiO_2/rGO (TG) photoanode appreciably improves the photovoltaic performance of solar cells based on N719 dye-sensitized TG. It is found that the DSSCs based on TG film show power conversion efficiency of 4.16% and enhanced by 7.5% compared to that of pristine TiO_2 NPs device. Furthermore, the R_2 fitted EIS curves demonstrates that the inner carrier recombination is obviously suppressed by incorporating rGO, thus improve the performance of DSSC.

Table 1. The photovoltaic characteristics of dsscs based on tio_2 and tg photoanodes

Samples	**J_{sc} (mA•cm^{-2})**	**V_{oc} (V)**	**FF (%)**	**η (%)**	**Dye loading (10^{-8} mol/cm^2)**	**R_2 (Ω)**
TiO_2	9.75	0.718	55.31	3.87	9.16	18.93
TG	10.45	0.668	59.58	4.16	13.49	16.19

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