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Graphene quantum dots optimization of dye-sensitized solar cells

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ABSTRACT

Graphene quantum dots (GQDs) optimized TiO_2 photoanodes and their dye-sensitized solar cells (DSSCs) were successfully demonstrated in this study for the first time. The characteristics of GQDs were confirmed by Raman and TEM measurements. Study indicated that the amount of dye-adsorption decreased firstly and then increased as the increase of the GQDs in the photoanodes, while that the J_{sc}, V_{oc} and η of the corresponding DSSCs increased firstly and then decreased. Of all the DSSCs, the DSSC with an optimal amount of GQDs showed the best performance with a minimum dye-adsorption while the maximum J_{sc} of 14.07 ± 0.02 mA cm^{-2} and η of 6.10 ± 0.01%, higher than those of the conventional DSSC (without GQDs) by 30.9% and 19.6%, respectively. The minimum dye-adsorption while the maximum J_{sc} and η obtained in the optimal DSSC are mainly attributed to the unique photoexcitation response of GQDs and the hot electrons injection from GQDs into TiO_2. This study indicates that not only the properties of DSSCs can be improved by GQDs, but more importantly, the reduced use of dye by using GQDs is of significant importance for the low cost and environment-friendly DSSCs.

1. Introduction

Dye-sensitized solar cells (DSSCs), first reported by O'Regan and Grätzel in 1991, have been proved to be the potential substitute for the traditional silicon-based solar cells for their low cost and simple making processes [1,2]. However, even though the theoretical photoelectric conversion efficiency (η) of DSSCs is high up to 33%, the maximum η of DSSCs made in laboratory by a sequential deposition method is 15% [3]. Many factors can influence the η of DSSCs, among them the photoelectrode play important roles. The photoelectrode can load dyes, accept electrons from the dye and transport the electrons to the conductive base [4] in DSSCs. Therefore, it is an effective approach for the enhancement of η of DSSCs by improving the properties of the photoelectrode.

Studies involved in the modification of photoelectrodes have been widely reported, such as elements doping to tune the energy band structure of TiO_2, growing compact layers between TiO_2 layer and the FTO substrate, introducing some noble metal nanoparticles in the TiO_2 film to make use of the surface plasma resonance effect, fabricating the up-conversion layer on the TiO_2 films, forming composite photoelectrodes in DSSCs and so on [5–9], which have improved and optimized the properties of DSSCs to some extent.

In addition, we have reported the composite photoelectrode of graphene-P25 prepared by ball-milling method [10] and that of graphene-TiO_2 by hydrothermal method [11], respectively, and the photoelectric conversion efficiencies of these DSSCs were apparently improved. These studies suggest that graphene is a good material for improving the properties of the DSSCs. Because of the amazing properties such as good conductivity, high specific surface area, and so on, graphene and its derivants have been one of the research focuses for the researchers worldwide in recent years. These include graphene-encapsulated metal oxide [12], graphene nanoballs [13] and graphene quantum dots (GQDs) [14] etc. The GQDs are the graphene sheets with lateral size less than 100 nm [15]. Due to the quantum confinement and edge effects, GQDs hold several fascinating properties such as the strong photoluminescent activity, chemical stability, no toxicity, high optical absorptivity and so on [16,17]

Therefore, to make use of the excellent properties of GQDs, we introduced them into the photoelectrodes in DSSCs, which is highly expected to improve the properties of the photoelectrodes and enhance the η of DSSCs. In this study, we have successfully prepared the GQDs modified TiO_2 photoelectrodes and studied the influences and mechanisms of the GQDs on the properties of TiO_2 photoelectrodes and the DSSCs.

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2. Experiments

2.1. Preparation of GQDs solution

GQDs were prepared via a one-pot hydrothermal method [18]. A certain amount of GO (prepared by Hummers method) [19] was added in 40 mL nitric solution of 2.6 M for 24 h under refluxing at 70 °C. This solution was then cooled naturally to room temperature, and its pH was tuned to 7 with NaOH. Then the solution was ultrasonicated for 60 min and filtered through two 0.22 mm microporous membrane, which followed by adding 0.2 g PEG 10000 and diluting to 50 mL. Then, the mixture was subjected to a hydrothermal process in a 100 mL Teflon-lined stainless-steel autoclave at 200 °C for 24 h to get the GQDs solution. To study the effects of the concentrations of GQDs on the properties of DSSCs and obtain the optimum concentration, different amount of GO of 0.025 g, 0.05 g, 0.075 g, and 0.1 g were used during the GQDs preparation. Correspondingly, these GQDs solutions were labeled as GQDs1, GQDs2, GQDs3 and GQDs4, respectively.

2.2. Preparation of photoanodes and DSSCs

Firstly, the TiO_2 films made by traditional method were immersed in the GQDs solution at 60 °C for 24 h. Then the films were washed with DI-water to remove excess GQDs which were physically absorbed on the TiO_2 films, dried and sensitized by immersing them in ethanol solution of N719 dye at 60 °C for 12 h. After that, the films were washed with ethanol to remove excess dye on the surface and dried to get the sensitized photoelectrodes. To assemble the DSSC, the electrolyte containing 0.05 mM LiI, 0.03 M I_2, 1.0 M PMII (1-methyl-3-propyl imidazolium iodide) acetonitrile and propylene carbonate was dropped into the space between the sensitized photoelectrode and Pt counter electrode which were clamped with a clip to form a sandwich structure.

The DSSCs fabricated are schematically shown as Scheme 1. To sort the TiO_2 photoelectrodes processed by different GQDs solutions (GQDs processed TiO_2 photoelectrode: GTP), the photoelectrodes were labeled as GTP-1, GTP-2, GTP-3,GTP-4, and the photoelectrode without that processing was labeled as TP.

2.3. Characterization

The structure details of the GQDs were obtained by high-resolution transmission electron microscope (HRTEM, JEM-2010FEF). Raman spectra was obtained by a confocal Raman Microspectrocopy (Confocal Raman Microspectroscopy, RM1000, Renishaw, England) to confirm the existence of GQDs in the TiO_2 films. The sensitized photoelectrodes were analyzed by UV-vis spectroscopy (Lambda 650S, PerkinElemer, USA) to determine their ability of light absorption and dye-loadings. The current density-voltage (J-V) characteristics of the DSSCs were measured under AM 1.5 simulated illumination (Newport, 91192) with a power density of 100 mW cm^{-2} and an irradiating area of 0.25 cm^2 by a mask.

3. Results and Discussion

3.1. TEM

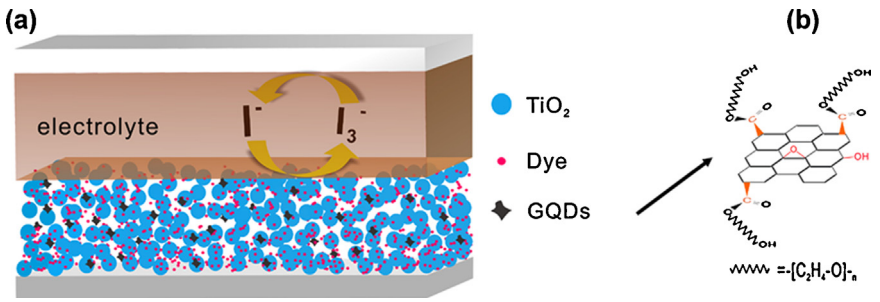
Fig. 1 shows the high resolution transmission electron microscope images of the GQDs. As shown in Fig. 1(a), the small black GQDs were uniformly dispersed with the average size of about 50 nm. Fig. 1(b) gives the structure details of the GQDs. It can be clearly seen in the figure that GQDs were wrapped by a thin layer of PEG which work as a surface-passivating agent to overcome the attraction between graphene sheets [18]. In addition, the layered structure of the GQDs can be clearly observed, showing an interlayer distance of about 0.278 nm, which is similar to the results reported [20–22].

3.2. Raman Spectra

Fig. 2 exhibits the Raman spectra of the photoelectrodes. According to Fig. 2(a), the Raman characteristic peaks locating at about 143 cm^{-1}, 409 cm^{-1}, 515 cm^{-1} and 633 cm^{-1} correspond to the Eg, B_{1g}, A_{1g}/B_{1g} and Eg bands of TiO_2, respectively [23,24]. To exploit the existence of the GQDs in the photoelectrodes, the samples were subjected to detailed detection, as shown in Fig. 2(b). The Raman shifts at 1355 cm^{-1} and 1580 cm^{-1} referred, respectively, to the D-band and G-band of graphene [25], suggesting the existence of the GQDs. In addition, because the GQDs were coated by PEG, as shown in Fig. 1, their Raman feature was similar to that of the functional graphene [26], with the characteristic peak of D-band weaker than that of G-band.

3.3. UV-vis absorption spectra

Fig. 3 depicts the light absorption of the dye sensitized TP and GTPs ranging from 350-800 nm. It can be easily found that the light absorption intensities of the GTPs were weaker than that of the TP, and as the increase of the content of GQDs, the light absorption intensities of the GTPs decreased first and then increased and showed a minimum value for the GTP-2. To determine the dye-loading differences among these films, the 1 cm^2 dye-sensitized TP and GTPs were subjected to dye desorption process by immersing them in 0.1 M NaOH solution. The dye-adsorbed changing with the GQDs contents are shown in Fig. 3(b), in which the dye-adsorbed in all the GTPs are lower than that in the TP and the dye-adsorbed decrease first and then increase with the increase of the GQDs content. The change of the dye-adsorbed is consistent with that of the light absorption intensity of the photoelectrode films. Possible reasons for this phenomenon are proposed as follows: First, the GQDs made in this study contain the groups of carboxyl (-COOH) and hydroxyl (-OH), as shown in Scheme 1(b). Similar to the dye



Scheme 1. (a) Configuration of GQDs modified DSSCs; (b) structure of the GQDs with surface-passivated by PEG.