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Improving the photovoltaic performance of dye-sensitized solar cell by graphene/titania photoanode

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ABSTRACT

A mixed colloid of graphene and titania is synthesized by a one-step hydrothermal reaction, thus a graphene/titania film photoanode is prepared. The graphene/titania film shows high porosity and large specific surface area, which favors a full adsorption of sensitized dye. On the other hand, the graphene/titania electrode has smaller charge transfer resistance than the pristine titania electrode, which replies that the graphene/titania electrode accelerates electronic transportation and suppresses the charge recombination. Under an optimal condition, the dye-sensitized solar cell based on graphene/titania photoanode achieve a power conversion efficiency of 7.52%, which is increased by 17.7% compared to the cell based on the pristine titania electrode under a simulated solar light irradiation of 100 mW·cm^{-2}.

1. Introduction

On the circumstance of energy crisis, seeking clean and renewable energy resources for supplement or even replacing fossil fuels has motivated the interest in photovoltaic cells. Dye-sensitized solar cell (DSSC), since its prototype was reported in 1991 by O'Regan and Gratzel [1], have been one of the most promising candidate for conventional silicon solar cell because of its low cost, easy preparation, high theoretic efficiency, and less environmental effect [2–4]. A DSSC with power conversion efficiency of 12% has been achieved [5]. However, the efficiency of DSSCs is lower compared to crystalline Si (24.7%) or thin-film CIGS (copper indium gallium selenide, 20.0%) cells, which restricts their potential application [6]; it is still a crucial issue to enhance its efficiency.

A typical DSSC consists of a dye sensitized TiO_2 film photoanode, a redox electrolyte, and a platinized counter electrode [2,3]. As an important component, the photoanode play a role in the separation of photogenerated charge carriers and the transportation of electrons. A composite film electrode consisted of TiO_2 and a high conductive material is favorable for completing photoanode's function. Carbon nanomaterial, such as carbon nanotube (CNT) with TiO_2 as a composite film, has been used to improve charge separation ability [7]. However, this enhancement is limited by poor contact between TiO_2 with CNT. Two-dimensional nanocarbon material, graphene also was introduced to prepare the composite film. Yang et al. [8] introduced graphene into TiO_2 photoanode, thus increased short circuit current density and power conversion efficiency of DSSC by 45% and 39%, respectively. Sun et al. [9] prepared graphene/TiO_2 nanocomposite by heterogeneous coagulation, Tang et al. [10] implanted graphene sheets in TiO_2 nanoparticles film via molecular grafting, Yen et al. [11] incorporated graphene/multi-walled carbon nanotube hybrid in DSSC photoanode, these composite films significantly improved current density and power conversion efficiency of DSSCs due to increase dye adsorption, reduce charge transfer resistance and enhance electron transport rate. Song et al. [12] reported the introduction of reduced graphite oxide in DSSC to enhance the photocurrent density, fill factor and power conversion efficiency due to the formation of rGO-TiO_2 Schottky barrier junction. He et al. [13] used graphene/TiO_2 nanocomposite film as photoanode, which resulted in a great increase in current density and conversion efficiency of DSSC. However the photovoltaic performance of these cells is still lower; and the preparation procedure of graphene/TiO_2 composite film is relative complex.

Herein, we develop a facile one-step hydrothermal method for preparing a mixed colloid consisted of reduced graphene and titania (RGT), and then the photoanode for DSSC. Based on the

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unique structure and properties of graphene, it is expected that the photovoltaic performance of the DSSC with RGT photoanode can be improved effectively.

2. Experimental

2.1. Synthesis of graphite oxide

Flake graphite (average particle diameter: 10 μm) was purchased from Qingdao Tianhe Graphite Co. Ltd., Qingdao, China. Other chemicals were analytical reagent grade, purchased from Sinopharm Chemical Reagent Co., Ltd and were used without further purification. Graphite oxide (GO) was prepared from flake graphite by an improved Hummers' method [14]. Typically, a mixed solution of concentrated H_2SO_4/H_3PO_4 (vol. ratio: 9/1) of 150 ml was prepared, then flake graphite (1 g) and $KMnO_4$ (6 g) was added to the mixed acid solution, which produced a slight heat release and the temperature of the system was raised to 35–40 °C. Under stirring, the system was heated at 50 °C for 12 h. After that, the graphite oxidation was completed, the resultant mixture was cooled in ice bath (~200 ml) with 30% H_2O_2 (10 ml). The mixture was centrifugated (4000 rpm for 15 min), and the obtained solid was washed in succession with 200 ml of 5 wt% H_2SO_4/0.1 wt% H_2O_2 aqueous solution, and 200 ml of 30 wt% HCl aqueous solution. The obtained product was washed several times with abundant deionized water until the pH value of the system equaled to 7. After vacuum-dried at 50 °C overnight, the graphite oxide (GO) thus was obtained.

2.2. Preparation of graphene/TiO_2 colloid

The GO was dispersed into ethylene glycol (EG, 0.5 mg·ml^{-1}) followed by an ultrasonic vibration for 1 h to obtain an even GO/EG solution. In the system, ethylene glycol as a reducing agent can convert graphene oxide to reduced graphene oxide (graphene) [15]. The TiO_2 colloid was prepared by the following procedure [16,17]. Tetrabutyl titanate (10 ml) was added to deionized water (100 ml) under stirring, and a white precipitate was produced immediately. The precipitate was filtered and washed with deionized water. The filter cake was then transferred to a mixed solution (150 ml) contained 1 ml nitric acid and 10 ml acetic acid at 80 °C, under vigorous stirring a light blue TiO_2 colloid was formed. 0.2 g of TiO_2 powder (P-25) was added to 50 ml TiO_2 colloid and a predetermined amount of GO/EG solution was added, followed by an ultrasonic stirring for 30 min. The mixture was hydrothermally treated in an autoclaved at 200 °C for 24 h to form a mixed colloid of reduced GO (graphene) [15] and TiO_2. The resultant slurry was concentrated to 1/5 of its original volume by a thermal evaporation, and then 0.5 g PEG-20000 and a few drops of the Triton X-100 emulsification reagent were added, which produced a even and stable graphene/TiO_2 (RGT) colloid. As a comparison, a pure TiO_2 slurry without rGO was prepared by the same procedure.

2.3. Fabrication of DSSCs

RGT colloid is coated on a cleaned fluorine-doped tin oxide glass (FTO, sheet resistance 8 Ω·cm^{-2}, Hartford Glass Co., USA) by doctor-blade technique, and then calcined at 450 °C for 30 min to form a RGT film. The thickness and active area of the films were controlled at ~10 μm and 0.12 cm^2 by pasting a plastic tape around the edge of the FTO substrate. The film was immerged in a 3.0×10^{-4} M N719 (Solaronix SA, Switzerland) absolute ethanol solution for 24 h to adsorb the dye adequately. Thus a dye-sensitized RGT film photoanode was obtained.

Pt counter electrodes were prepared on the FTO glasses using 0.7 mM H_2PtCl_6 solution, followed by heating at 400 °C for 20 min in air [18,19]. A DSSC was assembled [20] by injecting a redox electrolyte into the aperture between the dye-sensitized RGT film electrode (photoanode) and a platinum-coated counter electrode. The two electrodes were clipped together and a cyanoacrylate adhesive was used as sealant to prevent the electrolyte from leaking. Epoxy resin was used for further sealing the cell. The redox electrolyte was consisted of 0.60 M tetrabutyl ammonium iodide, 0.10 M LiI, 0.06 M I_2, and 0.50 M 4-tert-butyl-pyridine in acetonitrile.

2.4. Characterization

The micro-morphologies of the film electrodes were observed with a transmission electron microscope (H-7650, Hitachi, Japan) and a scanning electron microscope (SEM, S-4800, Hitachi Japan). Raman spectra of samples were measured using a laser light with wavelength of 532 nm with a Renishaw inVia Raman microscope. The XRD patterns of the samples were obtained by using an X'Pert PRO MDP with Cu Kα radiation (λ = 1.5405 Å), 30 mA and 40 kV. The ultraviolet-visible (UV-vis) absorption spectra of samples were measured using a spectrophotometer (UV-2450, Shimadzu, Japan). The specific surface area, pore size and pore volume were measured by the Brunauer-Emmett-Teller (BET) nitrogen adsorption measurement using ASAP 2020 Surface Area and Porosity Analyzer (Micromeritics, Norcross, GA). The current-voltage (I-V) curves of DSSCs were measured [21] with an Electrochemical

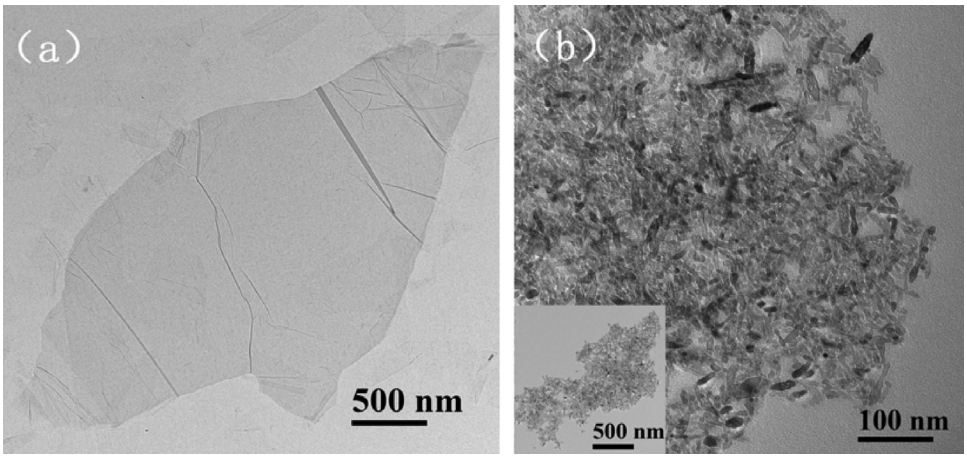

Fig. 1. The TEM images of (a) GO at low magnification and (b) RGT at high magnification. The inset of (b) is the TEM image of RGT at low magnification.