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ScienceDirect

Solar Energy 101 (2014) 176–181

SOLAR ENERGY

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Graphene-compositing optimization of the properties of dye-sensitized solar cells

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Received 7 June 2013; received in revised form 7 October 2013; accepted 3 December 2013
Available online 20 January 2014

Communicated by: Associate Editor Sam-Shajin Sun

Abstract

Graphene-composited TiO_2 photoelectrodes are prepared by hydrothermal method. The influences of different amount of graphene on the structures and properties of the dye-sensitized solar cells (DSSCs) are studied and an optimal graphene-composited DSSC is obtained. Studies indicate that compositing of graphene can effectively enhance the open circuit voltage, short circuit current density, and photoelectric conversion efficiency (η) of the DSSCs. Furthermore, the η of the DSSC with the optimal graphene-composited TiO_2 film is $7.02 \pm 0.06\%$, significantly higher than that of the pure TiO_2 DSSC. These improvements can be attributed to the increased dye absorption due probably to the increase of the photoelectrode films' specific surface area and the good conductivity of graphene.

Keywords: Dye sensitized solar cell; Graphene-compositing; Raman spectra; Dye absorption

1. Introduction

As a potential substitute for the traditional silicon solar cell, dye sensitized solar cells (DSSC) have attracted much attention from researchers in the last two decades for their low cost and simple making processes (O'Gegan and Grätzel, 1991). Generally, a DSSC consists of four parts, namely the photoelectrode, dye, electrolyte and counter electrode. TiO_2, a wide band gap semiconductor material (3.2 eV), is a commonly used photoelectrode material in DSSC for its characteristics such as rich content in the earth, low cost, good chemical stability, non-toxicity, and so on (Hagfeldt et al., 2010). It works as a dye loader, electron acceptor and electron transporter in DSSC (Grätzel, 2003). However, the particle sizes of TiO_2 in photoelectrode films are too small to support any space charge and form inner electric field, and therefore transport of electrons in the TiO_2 porous film is in random and hopping process. The direct effect of this transportation mode is the increase of recombination between the electrons and oxidized states of dye or oxidized particles in electrolyte, which hinder the electrons transportation and thus decrease the photoelectric conversion efficiency (η) of DSSC (Cahen et al., 2000; Benkstein et al., 2003). Therefore, an important aspect in the research of DSSC is to inhibit the charge recombination and increase the charge transportation. Studies indicated that it might be a good way to realize this objective by optimizing the structures of TiO_2 porous films (Wang et al., 2004, 2009; Xu et al., 2011; Martinson et al., 2008; Lee et al., 2011).

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0038-092X/$ - see front matter
http://dx.doi.org/10.1016/j.solener.2013.12.005

To the best of our knowledge, element doping in TiO_2 is an effective way to optimize the structures of TiO_2 porous films (Chandiran et al., 2011; Silveyra et al., 2005). In addition, forming compound or heterojunction photoelectrodes can also make the same effect (Yen et al., 2008). Researches on optimization the performances of TiO_2 DSSCs by forming composite or heterojunction photoelectrodes have been widely reported. For example, Nguyen et al. (2007) prepared TiO_2/SiO_2 nanocomposite materials by electrodeposition method and obtained an increase of 30% of η compared to the bare TiO_2 photoelectrode; Muduli et al. (2012) made a Au–TiO_2 nanocomposite photoelectrode in DSSC and got an η of ~6%; Ahn et al. (2013) reported that incorporation multiwalled carbon nanotubes (CNTs) into TiO_2 nanowires can greatly enhanced the performances of DSSC. Since graphene is a two dimensional material that similar with CNTs, it possesses amazing properties such as high specific surface area (about 2630 $m^2\ g^{-1}$ for a single layer) (Stoller et al., 2008) and good conductivity (about 10,000 $cm^2\ V^{-1}$ - s^{-1} for charge mobility at room temperature) (Geim, 2009). Some works about graphene composited TiO_2 photoelectrode in DSSCs have been reported. For example, by incorporating UV-reduction of graphene oxide into TiO_2, an improved photoconversion efficiency was obtained (Kim et al., 2009). Sun et al. reported that by incorporating graphene into TiO_2 both the dye adsorption and electron lifetime were increased (Sun et al., 2010). Tsai et al. prepared graphene-content TiO_2 by spin coating at room temperature and it applied as working electrodes in dye-sensitized solar cells, and achieved a 15% improvement in the cell efficiency (Tsai et al., 2011). Also, Fan et al. demonstrated that a DSSC using TiO_2 nanosheets/graphene composite film as the photoelectrode can get a photoconversion efficiency of 5.77% (Fan et al., 2012). In our previous work, we reported the incorporation of graphene in the P25 to form compound photoelectrodes by ball-milling method and the improved performance of the DSSCs (Fang et al., 2012). But TiO_2 films made by this way were easy to crack and opaque, therefore, we made graphene-composite TiO_2 films by hydrothermal method, which is a good way to solve the problems resulted by ball-milling method. In this study, we made different amount of graphene composited TiO_2 photoelectrode films by hydrothermal method, and studied the influence of graphene compositing amount on the electric properties of DSSC. The factors and mechanisms of graphene compositing on the improvement of the properties of DSSC were discussed.

2. Experiments

2.1. Preparation of graphene oxide

Preparation of graphene oxide (GO) has been reported before (Fang et al., 2012). The concentration of the GO hydrosol was 5 mg ml^{-1}.

2.2. Preparation of graphene-composited TiO_2 photoelectrodes

TiO_2 slurries with different amount of graphene were prepared by hydrothermal method. 10 ml titanium isopropoxide (Acros Organics, ⩾98%) was slowly hydrolyzed in 50 ml DI-water to obtain a white transparent solution. The solution was diluted with DI-water to 70 ml and put in a 100 ml autoclave for hydrothermal treatment at 220 °C for a period of time. Thus a layered solution was obtained. This solution was then condensed to 1/3 of its original volume by rotary evaporation and mixed with surfactants such as PEG-20000 (polyethylene glycol 20000, Sinopharm Chemical Reagent Co., Ltd., Shanghai) and Triton X-100 (emulsifier; polyethylene glycol tert-octylphenylether; Shanghai) and stirred for 12 h to obtain the final uniform TiO_2 slurry. This slurry was doctor-bladed on FTO glasses, dried, and annealed at 500 °C for 30 min to prepare TiO_2 photoelectrode film with a thickness of about 7 ± 0.05 μm. To study the effects of graphene compositing on the properties of the TiO_2 photoelectrodes and the DSSCs, different amount of 0, 5, 10, 15, 20 and 25 μl GO hydrosol were added into the hydrolytic titanium isopropoxide, and the subsequently obtained photoelectrodes were accordingly numbered as 0, 5, 10, 15, 20, 25, respectively.

2.3. Characterization of graphene-composited TiO_2 photoelectrodes

The graphene-composited TiO_2 photoelectrodes were sensitized by immersing them in N719 (Di-tetrabutylammonium cis-bis(isothiocyanato) bis(2,2′-bipyridyl-4,4′-dicarboxylato) ruthenium(II), Suzhou Chemsolarism Chemical, ⩾99%) solution for 12 h and dried. The DSSC was assembled by sandwiching a electrolyte layer containing 0.05 mM LiI, 0.03 M I_2, 1.0 M PMII (1-methyl-3-propyl imidazolium iodidein) acetonitrile and propylene carbonate (v:v = 1:4) between the graphene-composited TiO_2 photoelectrode and Pt-coated conductive glass counter electrode and clamping with clips. 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 with a mask. Electrochemical impedance analysis (EIS) was conducted on CHI 660C (Shanghai, China) with a frequency range from 100 kHz to 0.1 Hz under the condition of open circuit and 100 mW cm^{-2} irradiation. Raman spectroscopy (Confocal Raman Microspectroscopy, RM1000, Renishaw, England) was employed to confirm the compositing of graphene in the TiO_2 films. And UV–vis spectroscopy (Lambda 650S, Perkin–Elemer, USA) was used to analyze the absorption characteristics of graphene-composited photoelectrode films before and after sensitization.