Journal of Power Sources 263 (2014) 246–251

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Phosphorus-doped reduced graphene oxide as an electrocatalyst counter electrode in dye-sensitized solar cells

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HIGHLIGHTS

- Phosphorus (P)-doped rGO was synthesized with two bonding states of P–C and P–O.
- For the first time, P-doped rGO is employed as the counter electrode (CE) in DSSC.
- P doping can effectively enhance the electrocatalytic activity of rGO.
- P–C structures have higher electrocatalytic activity than P–O ones.
- P-doped rGO shows comparable electrocatalytic activity to Pt as CE.

ARTICLE INFO

Article history:
Received 19 December 2013
Received in revised form
7 February 2014
Accepted 24 March 2014
Available online 24 April 2014

Keywords:
Phosphorus-doped graphene
Counter electrode
Electrocatalytic activity
Dye-sensitized solar cells

ABSTRACT

In this study, phosphorus (P) atoms were doped into reduced graphene oxide (rGO) with two bonding states of P–C and P–O by using annealing treatment. For the first time, the P-doped rGO (PrGO) was employed as the counter electrode (CE) for dye-sensitized solar cell (DSSC). The electrochemical studies reveal that the P doping can effectively enhance the electrocatalytic activity of rGO, and P–C structures have higher electrocatalytic activity than P–O ones for I^-/I_3^- redox reaction. More significantly, PrGO shows comparable electrocatalytic ability to Pt as CEs. It therefore seems promising for PrGO to be widely used in metal-free DSSCs with low cost and high efficiency.

1. Introduction

Due to the low cost, simple fabrication process and reasonable conversion efficiency, dye-sensitized solar cells (DSSCs) have received much attention [1–4]. A typical DSSC consists of three components: a dye-sensitized TiO_2 photoanode, an I^-/I_3^- electrolyte and a counter electrode (CE). Commonly, Pt films on the conductive glass were employed as CE materials, which have high electrical conductivity and electrocatalytic ability for I^-/I_3^- redox reaction [1–4]. However, due to the high cost of Pt, it is significant to develop cheap CE materials for DSSCs with high conversion efficiencies.

So far, various carbonaceous materials, conductive polymers and inorganic compounds have been proposed as cheap CE materials for DSSCs [5–9]. Among them, reduced graphene oxide (rGO), one kind of carbonaceous materials, has attracted considerable attention due to its remarkable electrical, optical, and mechanical properties as well as its extraordinarily high surface area [10–12]. Several groups have reported that the DSSCs employing rGO CEs have high conversion efficiencies [3,4,12,13]. Thus, it is significant to investigate the electrochemical properties of rGO and further enhance its electrocatalytic activity for I^-/I_3^- redox reaction.

Recently, many reports have demonstrated that heteroatom doping can effectively modulate the electron structure and improve the electrochemical properties of rGO. For example, nitrogen (N), boron (B) and sulfur (S) atoms doped into graphene can enhance the electrical conductivity and electrocatalytic activity of rGO, which can be used as electrode materials of supercapacitors [14–16], Li-ions batteries [17,18], fuel cells (oxygen reduction reaction) [19–22] and DSSCs [23–26] with high performances. Most recently, phosphorus-doped rGO (PrGO) was synthesized and further used as electrode materials for supercapacitors [27], fuel cells [28,29] and Li-ions batteries [29]. However, to the best of our knowledge, the application of PrGO as metal-free CEs in DSSCs has not been explored.

In this study, PrGO was synthesized by annealing a mixture of graphene oxide (GO) and triphenylphosphine, which were

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http://dx.doi.org/10.1016/j.jpowsour.2014.03.118
0378-7753/

employed as the carbon and phosphorus (P) sources, respectively. For the first time, the PrGO was used as the CE for DSSC. It shows remarkable catalytic activity, which can be comparable to the Pt CE. We have systematically investigated the electrocatalytic mechanism of PrGO for I^-/I_3^- redox reaction. The studies reveal that P doping can effectively enhance the catalytic activity of rGO, and the P–C structures have higher catalytic activity than P–O ones.

2. Experimental

2.1. Synthesis of PrGO

GO was synthesized from flake graphite (Qingdao Tianhe Graphite Co. Ltd., Qingdao, China) by a modified Hummers method [30]. To synthesize PrGO, 1 g GO and 1 g triphenylphosphine were first ultrasonically dispersed in ethanol for 30 min, and then spread onto an evaporating dish and dried, forming a uniform solid mixture. And then, the mixture was placed into a quartz tube and annealed at 600–1000 °C for 30 min with argon and hydrogen. The flux of argon and hydrogen were both 500 sccm. Finally, the PrGO was obtained by collecting and washing several times. For comparison, the undoped rGO was synthesized by the same procedure except that the triphenylphosphine (P source) was absent. The as-synthesized PrGO and rGO samples are denoted as PrGO*X* and rGO*X*, respectively, where *X* represents the annealing temperature (°C).

2.2. Fabrication of PrGO and rGO CEs

The PrGO (or rGO) CE was fabricated as follows. First, 90 wt% PrGO (or rGO) and 10 wt% polyvinylidene fluoride (PVDF) were dispersed in *N*-Methyl-2-pyrrolidone (NMP) by using an ultrasonic horn, and then a layer of paste was coated on fluorine-doped tin oxide glass plates. The CEs were heated in vacuum at 120 °C overnight. The size of CE was 1 cm^2. For comparison, 100 nm Pt film sputtered on FTO was employed as the Pt CE.

2.3. Fabrication of DSSCs

The DSSC was made of a photoanode, a CE and a DHS-E23 electrolyte solution. The TiO_2 photoanode, N719 and DHS-E23 were purchased from Co. Ltd. Dalian Heptachroma SolarTech. The TiO_2 photoanode was sensitized by immersing into an ethanol solution containing the 0.5 mM N719 dye solution for 12 h. The area of TiO_2 photoanode was 0.36 cm^2.

2.4. Characterization

The transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) images were taken with an FEI Tecnai G2 microscope. XPS was performed on a Kratos XSAM800 using Al Ka radiation (144 W, 12 mA, 12 kV). The photocurrent density–voltage characteristics of DSSCs were measured using a Keithley-2000 and Yokogawa-7651 source meters under the excitation of 100 mW cm^{-2} AM 1.5 white light from a solar simulator (XQ350W, Shanghai Lansheng Electronic Co., Ltd). Cyclic voltammetry (CV) measurements were conducted, in which an as-prepared CE was taken as the working electrode in the two-electrode one-compartment cell and the Pt sheet was simultaneously served as both the reference electrode and counter electrode in an acetonitrile solution with 10 mM LiI, 1 mM I_2, and 0.1 M $LiClO_4$. The electrochemical impedance spectroscopy (EIS) measurements were performed in the frequency range of 0.1 Hz–1 MHz in a two-electrode system on an electrochemical workstation (CHI660D, Chenhua Instruments Co., Shanghai).

3. Results and discussions

Fig. 1(a) shows a typical TEM image of PrGO900. The image reveals transparent graphene sheets with wrinkle and fold features, which may originate from defective structures formed during the P doping and reduction process of GO. The corresponding EDX spectrum (Fig. 1(b)) confirms the presence of P atoms in PrGO900 (The Si peak in Fig. 1(b) originates from the Si (Li) detectors). Fig. 1(c)–(e) represent the STEM elemental mappings of PrGO900. The similar C and P mappings reveal that the doped P atoms are homogenously distributed in the plane of graphene.

In order to further confirm the P doing and investigate the bonding configurations of P atoms in PrGO, the XPS measurements were performed at room temperature. As shown in Fig. 2(a), the P peak appears and the intensity of O peak decreases in the XPS spectrum of PrGO900 compared to GO. It indicates that the P atoms

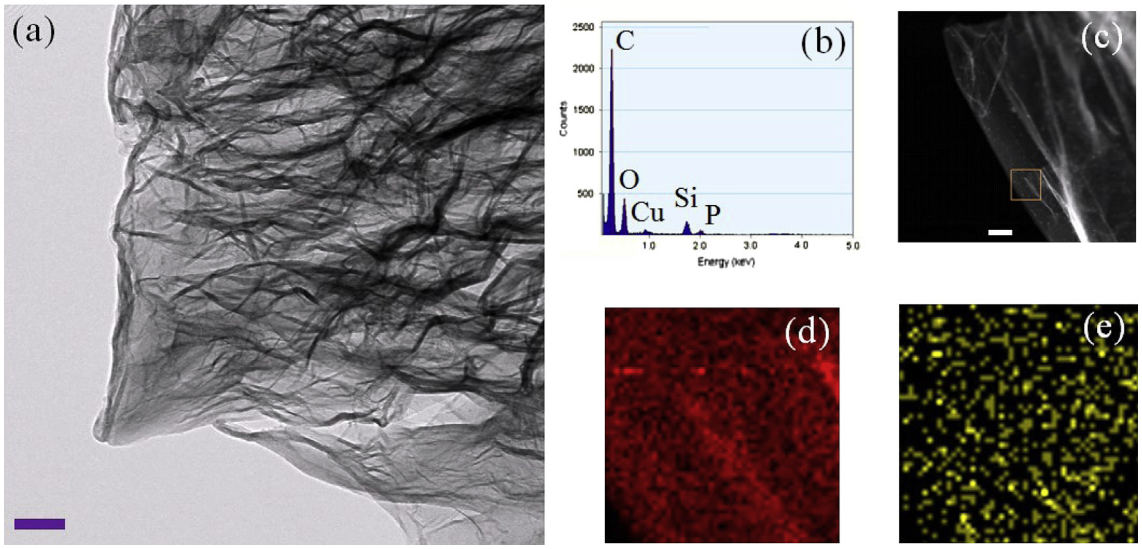

Fig. 1. (a–c) TEM image, EDX spectrum and STEM image of PrGO900, respectively. (d) C- and (e) P-elemental mapping of orange square region in (c). The scale bars in (a) and (c) are both 100 nm.