

Polythiophene/graphene composite as a highly efficient platinum-free counter electrode in dye-sensitized solar cells



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ABSTRACT

Herein we have reported preparation of polythiophene (PTh)/graphene (GR) composite by interfacial polymerization and its use as a counter electrode (CE) for dye-sensitized solar cells (DSSCs). The composite electrode showed excellent catalytic activity for reduction of triiodide. Both the short-circuit photocurrent density and fill factor values of the composite increased on incorporation of GR sheets. The PTh/GR composite CE based DSSCs showed an energy conversion efficiency of 4.8% which is comparable to that of conventional Pt electrode. Thus PTh/GR composite material has proven to be an effective substitute to the expensive Pt electrode for application as next generation counter electrode in DSSCs.

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1. Introduction

Dye-sensitized solar cells (DSSCs) are considered as one of the most attractive low cost photovoltaic (PV) devices since their discovery by O'Regan and Gratzel in 1991 [1–3]. DSSCs are widely investigated recently for their low cost, easy fabrication and high energy conversion efficiency which makes it a promising alternative to conventional silicon solar cells. Usually, a DSSC consists of a dye-sensitized TiO_2 as a photoanode, a iodide/triiodide redox electrolyte and a counter electrode [4]. The counter electrode (CE) plays a crucial role in DSSCs which is mainly responsible for the fill factor characteristics of the photovoltaic device [5]. CE is used to carry electron from the external circuit to the electrolyte and catalyzes the cathodic reduction of I_3^- ions in electrolyte [6]. In general, a platinum (Pt) coated conductive substrate is used as a CE in typical DSSCs due to its high conductivity, high catalytic activity and stability [7,8]. However, Pt is a costly and less abundant metal which causes difficulties in commercialization of DSSCs. Another drawback of Pt is that it dissolves in the electrolyte solution creating by-products like PtI_4 and H_2PtI_6 [9]. Therefore replacement of this expensive material by other cost effective materials is necessary to reduce production cost of DSSCs.

Several researchers have focused on developing new substitutes to replace platinum as CE by using various carbon based materials [10–14]. Among them, graphene (GR) has attracted

huge attention as a promising alternative to Pt in solar cell applications due to its low cost, excellent electrical conductivity, high specific surface area and high mechanical strength [15–18]. However, GR has few numbers of active sites for I_3^-/I^- catalysis reaction which limits its application as a counter electrode in DSSCs [19]. To overcome this problem, conducting polymers, such as polypyrrole (PPy), polyaniline (PANI), poly(3,4-ethylenedioxythiophene) (PEDOT) have been introduced into GR as counter electrodes for their unique features, such as inexpensiveness, good electrochemical stability and high catalytic activity for I_3^- reduction [20–26]. Wang et al. [27] reported the preparation of PANI/GR hybrids by in situ polymerization. The resulting hybrid material was used as a counter electrode in DSSCs which showed a conversion efficiency of 6.09%. The value was comparable to that of Pt CE. Gong et al. [28] reported fabrication of RGO/PPy composite and used it as a counter electrode for DSSCs. The incorporation of RGO sheets improved short-circuit current density from 14.27 to 15.81 $\text{mA}\cdot\text{cm}^{-2}$ and conversion efficiency from 7.11% to 8.14%. Lee et al. [29] developed a CE based on PEDOT–GR composite material which showed an efficiency of 6.26%, due to the high electronic charge transfer and electrochemical activity of the composite. PEDOT: PSS/GR composite was used as a CE in DSSCs by Hong et al. [30] which exhibited an efficiency of 4.5%. Among the conducting polymers, polythiophene (PTh) and its derivatives have gained special appeal because of their easy synthesis, good electrical conductivity, good electrochemical behavior and good environmental stability [31–33]. The incorporation of GR in PTh may enhance the conductivity in the polymer and thereby improving the

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photovoltaic performance. To the best of our knowledge, no works have been reported based on PTh/GR as a CE for DSSCs till now.

In this report we have demonstrated the preparation of PTh/GR composite by liquid/liquid interfacial polymerization and its application as CE in DSSC. Interfacial polymerization is a simple, easy and controllable approach for preparation of bulk quantities of polymers compared to other conventional polymerization system. The PTh/GR composite holds good potential for application as a CE material with advantages of both the component. The properties of composite and its photovoltaic performances were investigated by using various spectroscopic and analytical techniques. DSSCs based on PTh/GR composite shows energy conversion efficiency up to 4.8%, which is comparable to that of Pt electrode.

2. Experimental section

2.1. Materials and method

All chemicals such as graphite flakes, sodium nitrate, sulfuric acid, potassium permanganate, hydrogen peroxide, hydrazine monohydrate, ferric chloride, thiophene monomer and Cis88 bis (isothiocyanato) bis (2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium (II) bis89 tetrabutylammonium (N-719) were purchased from Sigma Aldrich and used directly without further purification. First, graphene oxide (GO) was prepared from natural graphite by modified Hummers method [34] using KMnO_4 and H_2SO_4 as oxidizing agents. The as synthesized GO dispersion is then reduced to GR by adding hydrazine monohydrate as reducing agent. The reaction mixture was heated at 95°C for 16 h and then filtered, followed by washing with deionized water for several times. PTh/GR composite with 3 wt.% of GR loading (with respect to thiophene) was prepared by liquid/liquid interfacial polymerization following our previously reported method for the synthesis of PTh/GO composite [35]. 0.02 g GR was dispersed in 20 mL of CH_3NO_2 by ultrasonication for 1 h. 2.44 g FeCl_3 was added to the dispersion and stirred for 1 h. Then this mixture was added dropwise into 0.4 mL thiophene solution in 10 mL of n-hexane and was constantly stirred for 24 h at room temperature (298 K). For purification, the composite was washed with ethanol and then dried at 60°C for 24 h.

2.2. Fabrication of PTh/GR CEs

Firstly the FTO glass substrates (Sigma-Aldrich, sheet resistance: $15\ \Omega/\text{sq}$) were first cleaned with deionized water followed by anhydrous ethanol and then dried under N_2 atmosphere. The PTh/GR composite paste was prepared by adding 0.20 g of the powdered composite to 4 mL of 0.5 wt% nafion–isopropylalcohol solution and stirred for 12 h. The paste was deposited on FTO-glass by the doctor-blade method. After that the electrode was dried at 80°C for 1 h. For comparison, Pt electrode was prepared by coating a thin layer of Pt on FTO by vacuum coating.

2.3. Assembly of DSSCs

Nanocrystalline TiO_2 paste was deposited on FTO glass plate by doctor blade technique. The resulted electrode is sintered at 500°C for 30 min and gradually cooled to room temperature (298 K). Then the TiO_2 electrode was immersed into 0.3 mM N719 dye in a mixture of acetonitrile-ethanol (1:1 volume ratio) and kept overnight at room temperature. After that the electrode was rinsed with ethanol and dried in air. The electrolyte was prepared by mixing 0.1 M lithium iodide (LiI), 0.6 M I_2 , 0.5 M tertbutylpyridine (TBP) and 0.05 M 1-propyl-3-methyl-imidazolium iodide (MPI) in a mixed solvent of N-methyl-2-pyrrolidone (NMP) and

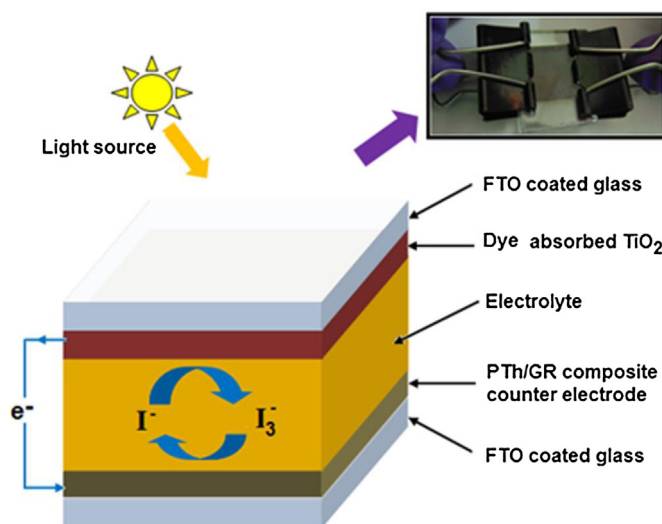


Fig. 1. Schematic diagram for assembly of DSSCs based on PTh/GR composite.

acetonitrile (ratio 1:4). The electrolyte is dropped on the dye-adsorbed TiO_2 film and then the counter electrode is clipped on the TiO_2 photoanode tightly using two clamps. Thus a sandwich-type DSSC was assembled with an active area of $1\ \text{cm}^2$ as shown in the Fig. 1.

3. Characterization and measurements

FTIR spectra of the samples were recorded using a Nicolet Impact-410 IR spectrometer on KBr pellet in the frequency range of range of $500\text{--}4000\ \text{cm}^{-1}$ at room temperature (298 K). X-ray diffraction (XRD) study was done using a Rigaku X-ray diffractometer with $\text{Cu-K}\alpha$ radiation at 30 kV and 15 mA with a scan rate of $0.05^\circ/\text{s}$ in the 2θ range of $5\text{--}70^\circ$. Scanning electron microscopy (SEM) analysis of the prepared samples was performed with a JSM-6390LV instrument (JEOL, Japan). The surface of samples was coated with platinum for SEM analysis. Transmission electron microscopy (TEM) analysis was done with a Philips CM 200 TEM microscope. A small amount of sample was dispersed in ethanol and then the suspension was dropped on 300 mesh copper TEM grids covered with thin carbon films. Cyclic voltammetry (CV) study was performed on a Bio-Logic SP-150 potentiostat with a three electrode system where Pt, Ag/AgCl and PTh/GR/FTO electrode were used as auxiliary, reference and working electrodes respectively, at a scan rate of $100\ \text{mV s}^{-1}$. Acetonitrile solution containing 10 mM LiI, 1 mM I_2 , and 0.1 M LiClO_4 was used as the supporting electrolyte. Electrochemical impedance spectroscopy (EIS) measurements were also performed on Bio-Logic SP-150 potentiostat in the frequency range from $10^5\ \text{Hz}$ to $0.1\ \text{Hz}$ under illumination of a simulated Xenon arc lamp with a power density of $100\ \text{mW cm}^{-2}$ at the open-circuit voltage.

The photocurrent voltage (J-V) characteristic curves of the DSSC (active area, $1\ \text{cm}^2$) were measured applying an external potential bias to a Keithley 2400 device under illumination with a Xenon lamp ($100\ \text{mW cm}^{-2}$) in ambient atmosphere. The fill factor (FF) and photon-to-current conversion efficiency (η) were calculated from the J-V curve using the following equations [36]:

$$\text{FF} = \frac{J_{\text{max}} \times V_{\text{max}}}{J_{\text{sc}} \times V_{\text{oc}}} \quad (1)$$

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