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Low cost poly(3,4-ethylenedioxythiophene):polystyrenesulfonate/carbon black counter electrode for dye-sensitized solar cells

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ABSTRACT

A poly(3,4-ethylenedioxythiophene):polystyrenesulfonate/carbon (PEDOT:PSS/C) counter electrode is prepare for using in dye-sensitized solar cells (DSSCs). The PEDOT:PSS/C counter electrode possesses good conductivity of 1.73 S/cm and low charge transfer resistance. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements indicate that the PEDOT:PSS/C electrode has higher catalytic activity than the conventional Pt electrode. Under the optimized conditions, the DSSC with PEDOT:PSS/C counter electrode achieves a high light-to-electric conversion efficiency of 7.01% under a simulated solar light irradiation with an intensity of 100 mW cm^{-2}.

1. Introduction

Harvesting energy directly from sunlight using photovoltaic technology is being increasingly recognized as an essential component of future global energy production. Dye-sensitized solar cells (DSSCs) have been widely recognized as a potential alternative to the conventional silicon solar cell for its low-cost and high conversion efficiency over 12% since Gratzel [1–4] had breakthrough progress on DSSC in 1991.

A standard DSSC consists of a sandwich structure with a dye-sensitized porous nanocrystalline TiO_2 photoanode for absorbing visible light, an iodide/triiodide redox electrolyte, and a counter electrode which serves to collect electrons and catalyze I_2/I^- redox-coupled regeneration reaction in electrolyte. The counter electrode plays a crucial role in DSSC [4–6]. It is typically made of platinized F-doped SnO_2 (FTO) conductive glass. However, platinum is expensive and the two current methods (sputtering and thermal decomposition) for preparing Pt counter electrodes are both high energy-consuming. Therefore, many functional materials have been studied to replace Pt as counter electrodes for more cost-effective DSSCs, such as various carbon-based materials including in carbon black [7], activated carbon [8,9], graphite [9], carbon nanotubes [10,11], graphene [12] and fullerene (C_{60}) [13], and other materials such as tungsten carbide (WC) [14], molybdenum carbide (MoC) [14], tungsten oxide (WO_2)[15], titanium nitride [16], polyaniline (PANI) [17–19], and pyrrole [20]. These materials have low-cost, simple preparation and comparable catalytic activity with Pt for I^-/I_3^-, which have attracted widely interests and researches.

Recently, conducting polymer poly(3,4-ethylenedioxythiophene: polystyrene sulfonate) (PEDOT:PSS) [21,22] attract more attention as promising candidates for a Pt counter electrode due to its excellent catalytic activities, low cost, high transparency, good conductivity, easy preparation and good environmental stability [22].

Here, the conductive polymer PEDOT:PSS is blended with graphite and carbon black to prepare a new of PEDOT:PSS/Carbon (PEDOT:PSS/C) counter electrode for DSSCs. The counter electrode has good conductivity, low cost, facile preparation, and good contact with substrate of FTO glass. It is expected that PEDOT:PSS/C counter electrode can replace the Pt counter electrode used in DSSCs.

2. Experimental

2.1. Materials

Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, surface resistance (Ω/sq) = 1×10^5 to 3×10^5) purchased from Shanghai Chunyuan Phytochemistry Co., Ltd., China. The organometallic sensitized dye N-719 [RuL_2 $(NCS)_2$, L = 4,4′-dicarboxylate-2,2′-bipyridine] was from Solaronix SA (Switzerland). The anhydrous ethanol (ETOH), isopropanol, nitric acid (HNO_3), acetic acid (HAc), dimethyl sulfoxide (DMSO),

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graphite, tetramethylammonium hydroxide (TMAOH), carbon black, polyvinylpyrrolidone (PVP), ethyl cellulose (EC), polyethylene glycols with average molecular weights 20,000 and 400 (PEG-20000 and PEG-400), OP emulsification agent (Triton X-100), tetrabutyltitanate [$Ti(OBu)_4$] and titanium tetrachloride ($TiCl_4$) were analytical purity grade and were purchased from Shanghai Chemical Agent Ltd, China. All reagents were used without further treatment before using.

The conductive glass plate (FTO glass, fluorine doped tin oxide over-layer, sheet resistance of 8 $\Omega\,cm^{-2}$, purchased from Hartford Glass Co., USA) was used as a substrate for precipitation of the TiO_2 porous film and was cut into $1 \times 2\,cm^2$ sheets.

2.2. Preparation of PEDOT:PSS/C electrode

PEDOT and PSS were mixed in an ultrasonic bath at 30 °C for 30 min to form a PEDOT:PSS suspension solution. A polar solvent DMSO was added in the suspension with a PEDOT:PSS/DMSO volume ratio of 2/9 and stirred at room temperature for 6 h to produce an even solution. Then graphite powder, carbon black, PVP, EC, and PEG-400 were added the even solution in sequence at room temperature under stirring to obtain a PEDOT:PSS/C viscous sol. The viscous sol was coated on a FTO conductive glass, after the conductive glass was irradiated and vacuum annealed at 80 °C, a PEDOT:PSS/C counter electrode with thickness of 3–4 μm was obtained.

2.3. Fabrication of dye-sensitized solar cell

A TiO_2 nanoporous film was prepared by the following procedure [23,24]. Tetrabutyltitanate (10 ml) was rapidly added to mixed solution of distilled water (100 ml) and equal volume ETOH, a white precipitate was formed immediately. The precipitate was filtered using a glass frit and washed with distilled water. Under vigorous stirring, the filter cake was added to aqueous solution (150 ml) containing 1 ml HNO_3 and 10 ml HAC at 80 °C, until the slurry became a translucent blue-white liquid. The blue-white liquid was autoclaved at 200 °C for 12 h to form milky white slurry. The resultant slurry was concentrated down to 1/4 of its original volume, then PEG-20000 (10 wt.% slurry) and a few drops of the emulsification agent of Triton X-100 were added to form a TiO_2 colloid.

To increase the reflection of sunlight and enhance light absorption, the large particle (150–250 nm) TiO_2 was prepared using organic alkali TMAOH as peptize and sol-hydrothermal method for 12 h in the solution of pH 13.6. Similar to the TiO_2 nanocrystals preparation, the original volume was concentrated to 1/4, then PEG-20000 (10 wt.% slurry) and a few drops of emulsification regent of Triton X-100 was added to form a TiO_2 colloid.

To reduce the recombination of the electrons on the conductive glass with the electrolyte, a thin TiO_2 blocking layer was deposited on the FTO glass substrate by immersing the glass in 0.15 M $TiCl_4$ isopropanol solution for 12 h, followed by sintering at 450 °C for 30 min [25,26]. Subsequently, two TiO_2 layers with a particle size of 10–20 nm and 150 nm, thickness of 10 μm was coated on the blocking layer by using a "doctor blade method", then sintering at 450 °C for 30 min in air. A dye was loaded by immersing the TiO_2 film in a 0.3 mM dye N719 ethanol solution for 24 h. Thus a dye-sensitized TiO_2 film anode was obtained. A dye-sensitized solar cell was fabricated by injecting a liquid electrolyte (0.05 M I_2, 0.1 M LiI, 0.6 M tetrabutylammonium iodide and 0.5 M TBP in acetonitrile) in the aperture between the dye-sensitized TiO_2 electrode and the PEDOT:PSS/C counter electrode. The two electrodes were clipped together and a cyanoacrylate adhesive was used as sealant. Epoxy resin was used for further sealing the cell. The detailed fabrication procedure for the nanocrystalline TiO_2 photoanodes and the assembly of DSSCs was described by us elsewhere [27,28]. The schematic diagram of the solar cell is showed in Fig. 1.

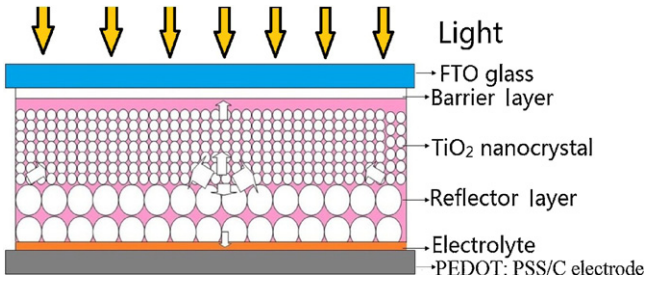

Fig. 1. A schematic diagram of the DSSC with PEDOT:PSS/C counter electrode and reflection layer.

2.4. Measurements

The conductivity of the PEDOT:PSS/C electrode was tested using an RTS-9 model, 4-point probes resistivity measurement system. Cyclic voltammetry (CV) of samples were measured in a three-electrode electrochemical cell with the electrochemical workstation (CHI660D, Shanghai Chenhua Device Company, China) using the PEDOT:PSS/C as the working electrode ($2.2 \times 2.7\,cm^2$), a Pt foil as counter electrode and an Ag/AgCl (the concentration of KCl was 3 M) as reference electrode dipped in an acetonitrile solution of 10 mM LiI, 1 mM I_2, and 0.1 M $LiClO_4$ (scan conditions: 40–200 mV s^{-1}). The electrochemical impedance spectroscopy (EIS) was carried out using a CHI660D electrochemical measurement system at a constant temperature of 20 °C with AC signal amplitude of 20 mV in the frequency range from 0.1 to 10^5 Hz at 0 V DC bias in the dark. A sandwich cell consisting of two identical electrodes (about 6 cm^2), a spacer of 80 μm thick adhesive tape, and an electrolyte consisting of 0.60 M tetrabutyl ammonium iodide, 0.10 M LiI, 0.10 M I_2 and 0.50 M 4-tert-butylpyridine in acetonitrile was used in the EIS measurements.The photovoltaic testing of the DSSCs was carried out by measuring photocurrent–photovoltage (J–V) characteristic curves under white light irradiation of a 100 mW cm^{-2} (AM 1.5) from a solar simulator and (XQ-500 W, Shanghai Photoelectricity Device Company, China) in an ambient atmosphere and using a computer controlled voltage current source-meter of the CHI660D electrochemical measurement system. The incident light intensity and the active cell area were 100 mW cm^{-2} and 0.5 cm^2, respectively. The fill factor (FF) and the overall light-to-electric energy conversion efficiency (η) of the solar cell were calculated according to the following equations [29]:

$$\eta\,(\%) = \frac{V_{max} \times J_{max}}{P_{in}} \times 100\% = \frac{V_{OC} \times J_{SC} \times FF}{P_{in}} \times 100\% \quad (1)$$

$$FF = \frac{V_{max} \times J_{max}}{V_{OC} \times J_{SC}} \quad (2)$$

where J_{SC} is the short-circuit current density (mA/cm^2); V_{OC} is the open-circuit voltage (V), P_{in} is the incident light power and J_{max} (mA/cm^2) and V_{max} (V) are the current density and voltage at the point of maximum power output in the J–V curves, respectively.

3. Results and discussion

3.1. Electrochemical properties of PEDOT:PSS/C electrode

Fig. 2 shows the CVs for the PEDOT:PSS/C and the Pt electrodes in I_2/I^- system ($[I_2]/[I^-] = 1/10$) at a scan rate of 50 mV s^{-1}. The more