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A transparent and stable polypyrrole counter electrode for dye-sensitized solar cell

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HIGHLIGHTS

- ► A transparent PPy film with electrochemical catalytic activity has been prepared.
- ► A bifacial DSSC based on this PPy film has been reported for the first time.
- ► The DSSC based on this PPy counter electrode shows excellent long-term stability.
- ► The application of this PPy film in DSSC would bring down the production cost.

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ABSTRACT

A novel transparent and stable polypyrrole (PPy) electrode that can properly serve as a counter electrode for the bifacial dye-sensitized solar cell (DSSC) has been prepared by in situ polymerization of pyrrole monomer on FTO glass. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurement show the considerable catalytic activity of PPy counter electrode. The photovoltaic parameters of bifacial DSSCs are strongly dependent on the initial monomer concentration of pyrrole. The optimized PPy counter electrode has been fabricated under the initial monomer concentration of 0.3 M, a bifacial DSSC based on this PPy electrode shows conversion efficiencies of 5.74% and 3.06% corresponding to front- and rear-side illumination, respectively. Compared to the conventional Pt-based DSSCs, the design of bifacial DSSC with transparent PPy counter electrode improves the utilization ratio of incident light. Moreover, the considerable conversion efficiency and the good long-term stability of PPy-based device demonstrated by the stability test highlight the potential large-scale commercial application of this transparent PPy counter electrode.

1. Introduction

As a potential alternative to the traditional silicon-based solar cell, dye-sensitized solar cell (DSSC) has attracted widespread scientific interests due to its low-cost, high conversion efficiency and ease of fabrication [1,2]. A typical DSSC comprises a high surface area dye-sensitized TiO_2 photoanode, a good ion-transporting electrolyte containing a redox couple (I^-/I_3^-) and an efficient counter electrode [3].

Counter electrode (CE) is a critical component of DSSC, which serves as a mediator for collecting electrons from external circuit and reducing I_3^- ions to I^- ions so as to regenerate the redox couple. Platinized counter electrode has been widely used in DSSC so far, due to its high conductivity and catalytic activity for reduction of I_3^- ions. However, platinized CE is restricted by high cost and corrosion of platinum in the presence of I^-/I_3^- redox in electrolyte [4], it is desirable to develop low-cost and more stable materials such as carbon-based materials [5–10] (carbon black, graphite, mesoporous carbon, carbon nanotubes) and conducting polymers including poly(3,4-ethylenedioxythiophene) [11,12] and polyaniline [13,14] as more economic alternatives to platinized CE. As a well known conducting polymer, polypyrrole (PPy) has attracted more and more research interests as a potential candidate for platinized counter electrode because of its facile synthesis, high catalytic activity and considerable environmental stability [15,16].

Recently, the application of spherical PPy as the counter electrode in DSSC had been reported by Jeon et al. [16]. Though a conversion efficiency of 7.7% was obtained, several micrometres thickness of PPy film was required to obtain the desirable catalytic activity and electronic conductivity [6,17]. Therefore, the PPy-based counter electrode they prepared was opaque and unsuitable for

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application in bifacial DSSC. To our knowledge, the bifacial DSSC based on transparent CE that can be operated by introducing light from both sides, has the advantage for higher energy production efficiency [18,19]. Moreover, the mechanical stability of the ex-situ prepared PPy CE could be limited for the poor adhesion between PPy film and FTO substrate. Xia et al. have successfully prepared a thin PPy counter electrode by vapour phase polymerization (VPP) [15]. Unfortunately, the conversion efficiency of device based on this thin PPy CE was very low (3.3%). By now, the preparation of PPy film with both high transparency and sufficient electrochemical catalytic activity still remains a challenge.

In this paper, we report on the use of a transparent PPy film as an efficient counter electrode in bifacial DSSC for the first time (as shown in Fig. 1). The PPy CE is prepared by in situ polymerization of pyrrole monomer on FTO glass and the derived photovoltaic parameters of bifacial DSSCs have been optimized by adjusting the initial pyrrole monomer concentrations. The optoelectrochemical properties of PPy film and the stability of sealed bifacial DSSC based on PPy CE have been investigated. Electrochemical measurements display a low charge transfer resistance of 2.46 Ω cm^2 for the PPy CE, which manifests the sufficient catalytic ability for the reduction of I_3^- ions. The high total (the sum of front-and rear-conversion efficiencies) conversion efficiency (8.8%) and the considerable long-term stability of bifacial DSSCs indicate the potential large-scale commercial application of this transparent PPy counter electrode.

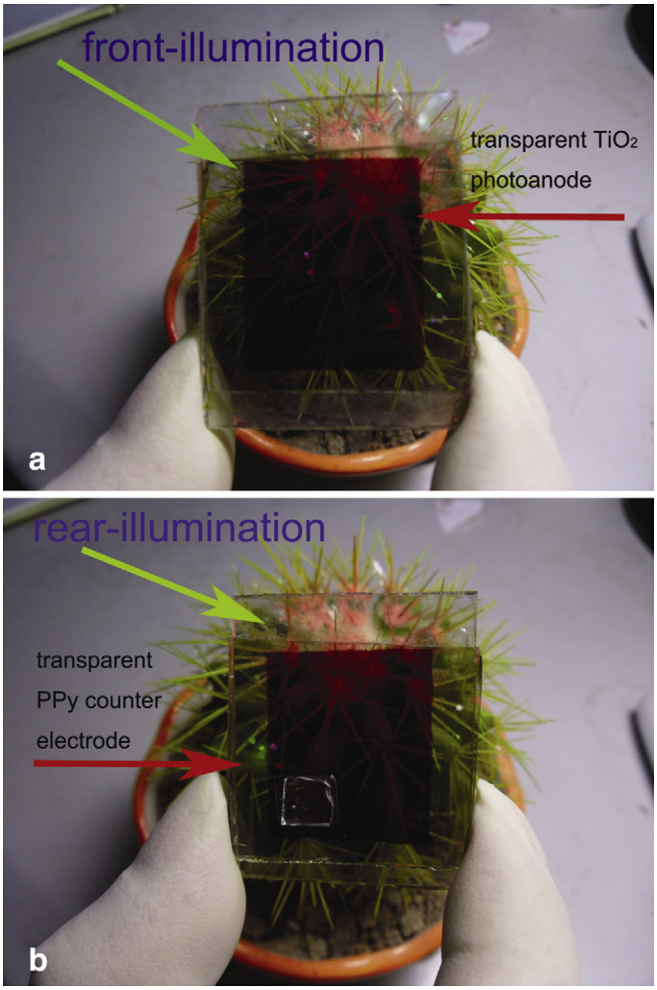

Fig. 1. Digital photographs of the bifacial DSSC employing transparent PPy counter electrode and its operation mode (under front-and rear-illumination).

2. Experimental details

2.1. Preparation of transparent PPy and Pt electrode

In a typical procedure, cetyltrimethylammonium bromide (3.64 g, 10 mM) was first dissolved in 100 mL of 1.0 M HCl solution and then a series of monomer concentrations (0.05 M, 1.0 M, 2.0 M, 3.0 M, 4.0 M) pyrrole were added to the solution with vigorous stirring for 1 h at 0 °C. The resulting viscous mixture was ultrasonicated for 30 min until it became transparent. Then 20 mM ammonium persulfate (APS) was added and the solution turned grey. A piece of well-cleaned FTO glass was immersed in the solution immediately, after being kept at 0 °C for 3 h, the FTO glass was taken out and rinsed with distilled water, the PPy on the nonconductive side was removed. Finally, the PPy/FTO was redoped in 1.0 M HCl for 2 h, and then rinsed and dried at 80 °C for 1 h. The Pt electrode was prepared for comparison by depositing a thin layer of Pt on FTO using magnetron sputtering.

2.2. Assembly of DSSCs

TiO_2 paste was first synthesized by hydrothermal method, then it was doctor-bladed on FTO glass and sintered at 500 °C for 30 min. The procedure was repeated twice. The TiO_2 photoanode was immersed in 50 mM $TiCl_4$ (aqueous) at 70 °C for 30 min and then sintered at 500 °C for 30 min. The resulting TiO_2 photoanode was then immersed in an acetonitrile solution containing 0.5 mM N_3 dye and kept at 60 °C for 12 h. The DSSC was assembled by a sandwiching process: the dye-absorbed TiO_2 photoanode was tightly clipped with PPy or Pt counter electrode, a drop of liquid electrolyte containing 1 M PMII (1-methyl-3-propyl imidazolium iodide), 0.04 M LiI, 0.03 M I_2, 0.1 M GuSN (guanidinium thiocyanate), 0.5 M TBP (4-tert-butylpyridine) in acetonitrile and propylene carbonate ($v/v = 1{:}1$) was added to fill the void between two electrodes by the capillary effect.

2.3. Characterization

UV–visible transmitted spectra of the PPy films were recorded on UV/VIS spectrometer (Lambda 650S Perkin Elmer). The morphologies of the PPy film on FTO glass was observed by scanning electron microscopy (SEM, JEOL, 6700F, Japan) and atomic force microscopy (AFM, SPM9500J3, Shimadzu, Japan). Cyclic voltammetry was performed on CHI 660C (Shanghai, China) electrochemical station with a Pt plate as auxiliary electrode, an Ag/Ag^+ electrode as reference electrode, and a PPy/FTO or a Pt/FTO electrode as working electrode in an acetonitrile solution containing 10 mM LiI, 1 mM I_2 and 0.1 M $LiClO_4$ as supporting electrolyte. Electrochemical impedance spectroscopy (EIS) of the PPy and Pt counter electrodes was also performed on CHI 660C with the frequency from 100 kHz to 0.1 Hz. For the EIS measurement, a symmetric cell configuration with two identical PPy or Pt CEs was assembled with the injection of the same electrolyte for the DSSCs, and the active area of the cells was controlled at 0.25 cm^2 by Surlyn. The photocurrent density–voltage (J–V) characteristics were measured under AM 1.5 simulated illumination with a power density of 80 mW cm^{-2}, the active area was controlled at 0.25 cm^2 by a mask.

3. Results and discussion

Fig. 2 shows the UV–visible transmitted spectra of transparent PPy electrodes prepared under different pyrrole monomer concentrations (Py MC). The thin PPy film on FTO glass shows excellent transparency range from 300 nm to 800 nm. The