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PEDOT and derivatives tailored conducting gel electrolytes for high-efficiency quasi-solid-state dye-sensitized solar cells

Qinghua Li*, Haiyang Li, Xiao Jin, Zhongping Chen

Jiangxi Engineering Laboratory for Optoelectronics Testing Technology, Nanchang Hangkong University, Nanchang 330063, PR China

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ABSTRACT

Conducting gel electrolytes are promising in improving long-term durability and power conversion efficiency of quasi-solid-state dye-sensitized solar cell (DSSC). We present here the synthesis of poly (3,4-ethylenedioxythiophene) (PEDOT), PEDOT-graphene complex and PEDOT-graphene/PtCo for robust conducting gel electrolytes. Arising from the enhanced electron concentration of PEDOT derivatives, the final gel electrolytes show superior catalytic activity toward redox I^-/I_3^- couples. Upon illumination by simulated sunlight (air mass 1.5, 100 mW cm^{-2}), the corresponding quasi-solid-state DSSC device yields a power conversion efficiency as high as 8.2% in comparison to 5.5% for PEDOT derivative-free solar cell. Moreover, these PEDOT and derivatives tailored photovoltaics are also featured with good stability over 15 days.

1. Introduction

Electrolytes are prerequisite intermediates for charge transportation, diffusion and conversion processes in energy conversion and storage devices [1–3]. The liquid electrolytes are always featured with high charge transfer and therefore conversion kinetics, however the electrolyte leakage has been a significant burden for long-term stability [4]. Although full solid-state electrolytes markedly enhance durability because of their good chemical or thermal stability in atmosphere environments, the large charge resistance at electrolyte/electrode interface reduces charge extraction and solar cell efficiency [5]. A promising solution to this impasse is to build polymer gel electrolytes having high charge transfer processes and low interfacial resistance [6–8]. Till now, polymer gel electrolytes have been extensively applied in dye-sensitized solar cells (DSSCs) [9–15] by converting solar energy into electricity through complicated photoelectrochemical processes.

In general, the gel electrolytes for quasi-solid-state DSSCs are made by either casting or imbibing method. Early study in this field focuses on casting precursor solutions from liquid I^-/I_3^- electrolytes and linear gelatinizers onto mesoscopic photoanode films [16,17]. This strategy can lead to two disadvantages. The ionic conductivity is mainly attributed to I^-/I_3^- species, but the linear gelatinizers have limited capacity to upload I^-/I_3^- couples. Another problem is the diffusion of flowing gel electrolyte into mesoscopic TiO_2 film, blocking light scattering and absorption by photosensitive dyes. Therefore, the maximized photoelectric conversion efficiency within a range of 4–5% [18,19]. To address this issue, scientists have developed a new revenue of imbibing liquid I^-/I_3^- electrolyte into three-dimensional (3D) gelatinizer frameworks using their extraordinary absorption performances. The imbibed couples diffuse within 3D polymer gel electrolyte according to the principle in liquid state, therefore the ionic conductivity of gel electrolytes is also increased, yielding an optimal solar cell efficiency ranging from 5% to 6% in corresponding photovoltaics [20]. Further enhancement for quasi-solid-state DSSCs has been a challenging problem because of limited liquid electrolyte loading and charge diffusion kinetics. Recently, Tang *et al* have systematically incorporated conducting polymers and carbonaceous materials *etc* electron-conducting species into 3D gel systems [21–25], making conducting gel electrolytes with catalytic activity. It has been previously reported that polyaniline *etc* conducting polymers [26,27] and graphene [28] *etc* carbonaceous materials have catalytic behaviors toward I_3^- reduction reaction, therefore they are regarded as alternative Pt-free counter electrodes (CEs). These incorporated conducting species form interconducting pathways for electron transportation [29], in this fashion, the electrons from external circuit are conducted to

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* Corresponding author.
E-mail address: qhli@hqu.edu.cn (Q. Li).

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conducting gel electrolytes for catalyzing I_3^- reduction reaction. The markedly increased catalytic area has increased the solar cell efficiency from <6% to 7–8% [30]. Although great achievements have been made by building either conducting polymers or carbonaceous materials tailored conducting gel electrolytes, their intrinsic defects drag further enhancements of photovoltaic performances. For example, conducting polymers are usually organic semiconductors with limited electron-conduction ability, while the catalytic activity of carbonaceous materials toward I_3^- reduction cannot meet real requirements. A possible method is to combine conducting polymers with carbonaceous materials by blending or *in-situ* polymerization [31]. However, the physical integration undoubtedly produces large interfacial resistance for charge transfer from carbonaceous materials to conducting polymers.

Graphene is an allotrope of carbon in the form of a two-dimensional, atomic-scale, hexagonal lattice, in which each carbon atom has one σ bond and one π-bond. Therefore, graphene can combine 3,4-ethylenedioxythiophene (EDOT) molecule by a covalent bond because of lone-pair electrons in EDOT [32]. Upon polymerization, the final poly (3,4-ethylenedioxythiophene)-graphene (PEDOT-graphene) complex is featured with high electron concentration and reduced charge-transfer resistance. Moreover, the electron concentration could be further enhanced by incorporating alloyed PtCo species with PEDOT-graphene matrix. Co atom has lower electronegativity (1.88) than Pt atom (2.2), the free electrons from Co atoms deviate to Pt surface during alloying process, which enabled PtCo to have an electron-enriched surface [33]. In the current work, the above-mentioned PEDOT, PEDOT-graphene complex or PEDOT-graphene/PtCo is incorporated into 3D poly (acrylic acid)/poly (ethylene glycol) (PAA/PEG) matrix to form conducting gel electrolyte. Arising from the advantages with catalytic behaviors and markedly shortened charge-diffusion lengths, the photovoltaic properties of these quasi-solid-state DSSCs are promoted in comparison with PEDOT derivate-free device.

2. Experimental

2.1. Synthesis of PEDOT and derivatives

PEDOT, PEDOT-graphene complex and PEDOT-graphene/PtCo were synthesized by a cyclic voltammetry method using an CHI660E Electrochemical Workstation equipped with a conventional three-electrode system. Pt foil, Ag/AgCl and fluorine doped tin oxide (FTO) glass with an active area of $1.5 \times 1.5\ cm^2$ were used as CE, reference electrode and working electrode, respectively. EDOT-graphene complex was prepared through a reflux process using EDOT and graphene as raw materials. In details, 10 mL of EDOT monomer and 0.0799 g of graphene were sealed in a three-necked flask and treated by ultrasonification for 30 min to form a homogeneous solution. After refluxing at 210 °C for 6 h in nitrogen gas atmosphere, the product was preserved in an airtight, dark and cool condition. Finally, a mixture was made by dissolving 0.546 g of the EDOT-graphene complex or EDOT and 0.048 g of cetyl trimethyl ammonium bromide into 100 mL of 1 M HCl aqueous solution. PEDOT and PEDOT-graphene were both electrodeposited under a potential window ranging from −0.2–1 V vs Ag/AgCl for 100 cycles. PEDOT-graphene/PtCo was prepared by electrodepositing PtCo into above-mentioned PEDOT-graphene electrode under a constant potential of −0.6 V for 600 s. 2.63 mL of chloroplatinic acid aqueous solution (1 mM H_2PtCl_6), 0.196 g of cobalt sulfate (7 mM $CoSO_4$) and 0.142 g of sodium sulfate (10 mM Na_2SO_4) was dissolved into 100 mL of deionized water to make a homogeneous solution, which was used as the supporting electrolyte for potentiostatic deposition. PEDOT, PEDOT-graphene complex and PEDOT-graphene/PtCo powers were all collected from their electrodes for further use.

2.2. Synthesis of conducting gel electrolytes

The PAA/PEG membranes were synthesized according to the following procedures. In details, 8 mL of acrylic acid (analytical reagent) and 4.4 g of PEG ($M_w = 20,000$) were mixed in 15 mL of deionized water in a water-bath at 80 °C. Under vigorous agitation, 8 mg of *N,N'*-(methylene)bisacrylamide and 0.225 g of ammonium persulfate were added into above-mentioned mixture. Upon polymerization at a viscosity of around $180\ mPa\ s^{-1}$, the PAA/PEG reagent was transferred into a Petri dish and cooled to room temperature to form hydrous PAA/PEG gel. The PAA/PEG membranes were then molded into φ 2.5 cm die and dried under vacuum at 50 °C. These anhydrous PAA/PEG membranes were immersed in deionized water for 48 h and subsequently freeze-dried under vacuum at −60 °C for 72 h. Finally, the macroporous PAA/PEG membranes were immersed in I^-/I_3^- liquid electrolyte having $1.3\ g\ L^{-1}$ of PEDOT or derivatives for 5 days to reach absorption equilibrium. The liquid electrolyte was made of 100 mM tetraethylammonium lodide, 100 mM tetramethylammonium iodide, 100 mM tetrabutylammonium iodide, 100 mM NaI, 100 mM KI, 100 mM LiI, 50 mM I_2, and 500 mM 4-*tert*-butyl-pyridine in acetonitrile.

2.3. Electrochemical characterizations

The electrochemical performances of conducting gel electrolytes were recorded on a traditional three-electrode conventional CHI660E setup comprising of a reference electrode of Ag/AgCl, a counter electrode of platinum sheet, and a working electrode of conducting gel electrolyte. The cyclic voltammetry (CV) curves were recorded in a supporting electrolyte consisting of 50 mM M LiI, 10 mM I_2, and 500 mM $LiClO_4$ in acetonitrile. Electrochemical impedance spectra (EIS) and Tafel polarization curves were recorded on symmetric dummy cells with architectures of Pt electrode/gel electrolyte/Pt electrode. In details, the EIS plots were carried out on the same electrochemical workstation (CHI660E, Shanghai Chenhua Device Company, PR China) with a frequency range of 0.01 ~ 10^5 Hz and at an ac amplitude of 10 mV. The corresponding EIS plots were fitted by a Z-view software. The Tafel polarization curves were recorded by scanning from −1 to +1 V at a scan rate of 10 mV s^{-1}. All the electrochemical characterizations were performed at room temperature.

2.4. Solar cell assembly and tests

TiO_2 colloid was synthesized by a sol-hydrothermal method according to our previous procedures [34]. A doctor-blading technique was used to prepare a layer of TiO_2 film having a thickness of around 10 μm and active area of $0.09\ cm^2$. After being calcined in air at 450 °C for 30 min, the mesoscopic TiO_2 film was sensitized by a 0.5 mM N719 [purchased from Dyesol LTD, Australia] ethanol solution for 24 h. Each quasi-solid-state DSSC device was made by sandwiching gel electrolyte between a dye-sensitized TiO_2 photoanode and a Pt counter electrode. In details, a photoanode was combined with a CE and hot-sealed by Surlyn film with a thickness of 60 μm. Subsequently, the redox electrolyte was injected into the interspace in vacuum atmosphere.

The photocurrent-voltage (*J-V*) curves of quasi-solid-state DSSCs were recorded on an Electrochemical Workstation (CHI600E) under irradiation of a solar simulator (CHF-XM-500W, Beijing Changtuo Co. Ltd.) from a XQ-200 xenon ($P_{max} = 2000\ mW$) arc lamp in ambient atmosphere. Each efficiency has been measured at least ten times by building different devices to control the standard deviation within ±5%