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A dye-sensitized solar cell having polyaniline species in each component with 3.1%-efficiency

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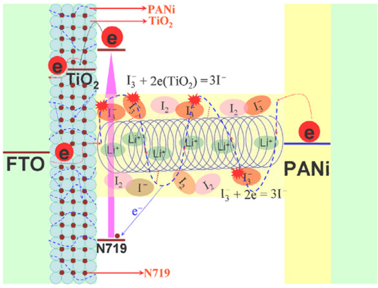
HIGHLIGHTS

- The DSSC having PANi species in each component yield an efficiency of 3.1%.
- The solar cell consists of a PANi/TiO_2 anode, a PANi CE, and a PANi electrolyte.
- The PANi electrolyte can shorten charge diffusion path length.
- The new concept is also applicable to all-carbon solar cells, etc.

GRAPHICAL ABSTRACT



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ABSTRACT

Pursuit of technological implementation with no sacrifice of photovoltaic performances has been a persistent objective for dye-sensitized solar cells (DSSCs). We launch here the experimental realization of a class of DSSCs consisting of polyaniline (PANi) incorporated TiO_2 anodes, PANi counter electrodes (CEs), and iodide doped PANi solid-state electrolytes. The PANi filled in photoanode can inject electrons for dye recovery, whereas the PANi CE fulfills the function of reducing triiodide into iodide ions. In particular, the solid PANi electrolyte has an ability of catalyzing triiodide species, shortening charge diffusion path length, and recovering dye molecules at anode/electrolyte interface. The photovoltaic performances are optimized by adjusting assembly process and lithium iodide dosage, yielding a maximum efficiency as high as 3.1% in the resultant DSSC device accompanied with fast start-up, multiple start/stop cycling, and good stability under persistent irradiation.

1. Introduction

Photovoltaic conversion is a promising solution to the energy requirement for nowaday's low-carbon economy [1–4]. Among excitonic cells, dye-sensitized solar cell (DSSC) [5–9], an electrochemical device converting solar energy into electricity with no emission, has attracted considerable interests because of its

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superiorities on simple fabrication, promising power conversion efficiency, and scalable materials. Since the first prototype created by Grätzel in 1991 [10], an efficiency of 13% has been measured for the cell with Pt counter electrode (CE), dye-sensitized TiO_2 photoanode along with liquid electrolyte containing $I^-/I_3^- I_3^-$ redox couples [11]. However, the bleak commercialization prospect of DSSCs mainly arises from the intrinsic limitations in poor stability resulting from leakage of liquid electrolyte [12–14]. A promising approach of overcoming such an impasse is to design solid-state electrolytes of either enhancing charge transfer ability (I^-, I_3^-) or injecting holes into hole transporting materials (HTMs) [15,16]. Another economic burden for DSSCs is high fabrication cost of Pt Ces [17]. Therefore, many efforts have been made to explore candidates for Pt species, such as conducting polymers [18,19], carbonaceous materials [20,21], metal sulfonates [22], and binary alloys [23,24]. In particular, the DSSC employing either solid-state electrolyte or HTM can not realize the rapid recovery of organic dyes located far from the TiO_2/electrolyte (or HTM) interface, generating an unsatisfactory conversion efficiency [25].

The structure of a solar cell is crucial in determining the functional properties of a photoelectrochemical system. Early works in this area were mainly focused on either replacing TiO_2 by other wide-band-gap oxide semiconductors [26] or using cost-effective CEs [27] or solid-state electrolytes [28,29] for enhanced charge transport and hole injection. To our knowledge, there are no systematic aging studies on efficient DSSCs by combining these three components, particularly using the same species. Here we launch an experimental realization of a class of DSSCs consisting of polyaniline (PANi) incorporated TiO_2 anodes with shortened electron migration length, cost-effective H^+ doped PANi CEs, and I_2 doped PANi solid-state electrolytes having shortened charge diffusion path length along with electrocatalytic and hole-transporting functions. The original intention of this design is to elevate the cell stability, to reduce fabrication cost, and to simplify the preparation techniques. An optimal efficiency as high as 3.1% under air mass 1.5 (AM1.5) global sunlight as well as simple synthesis and scalable components demonstrate the concept to be applicable in enabling the technological implementation of solid DSSCs.

2. Experimental

2.1. Synthesis of I_2 doped PANi

In the dark, 2 g of I_2 was dissolved in 50 mL of ethanol aqueous solution ($V_{water}/V_{ethanol} = 1/1$) to obtain a homogeneous mixture. 3 mL of aniline was dipped in the above mixture within 30 min. The polymerization reaction was carried out at 4 °C. After 48 h, the resultant reactant was air-blowing dried at 50 °C.

2.2. Synthesis of H^+ doped PANi

1.48 mL of aniline was dissolved in 50 mL of 1 M HCl aqueous solution to obtain a homogeneous mixture. A freshly cleaned FTO glass was put at the bottom of the reaction vessel with FTO layer upward. 50 mL of 0.125 M ammonium peroxydisulfate aqueous solution was dipped in the above mixture within 1 h. The polymerization reaction was carried out at 4 °C for 24 h. The H^+ doped PANi CE and resultant reactant were both rinsed by 1 M HCl aqueous solution, filtrated, and finally air-blowing dried at 60 °C for 24 h.

2.3. Preparation of photoanodes

A layer of TiO_2 nanocrystal anode film with a thickness of ~10 μm was prepared by a sol-hydrothermal method. The resultant anodes were further immersed in an N-methyl-2-pyrrolidone solution dissolved H^+ doped PANi solution (0.5 mg mL^{-1}) for 10 min, after being rinsed by anhydrous ethanol and dried by N_2 gas flow, the TiO_2/PANi photoanodes were sensitized by immersing into a 0.25 mM ethanol solution of N719 dye for 24 h.

2.4. DSSC assembly

The DSSC was fabricated by sandwiching solid-state electrolyte between a dye-sensitized TiO_2/PANi anode and a PANi CE. Four strategies were utilized to assemble the solar cell devices: (i) Before the cell assembly, a viscous electrolyte was prepared by dissolving 0.061 g of I_2 doped PANi, 0.11 g of LiI, and 0.25 g of PEO in 50 mL of acetonitrile. After vigorous agitation for 24 h, the reactant was vacuum-dried at 55 °C for 14 h to control the volume at around 5 mL. The viscous electrolyte was dipped on a dye-sensitized anode, after being covered by a PANi CE, the solar cell was air-blowing dried at 60 °C for 15 min and sealed by a Surlyn film (30 μm) through hot-pressing. (ii) The viscous electrolyte was dipped on dye-sensitized anode and then covered by a PANi CE and subsequently sealed by a Surlyn film through hot-pressing. Afterward, the device was air-blowing dried at 60 °C for 30 min (iii) The viscous electrolyte was thoroughly vacuum-dried at 55 °C for 48 h. A slice of the solid electrolyte was sandwiched between a dye-sensitized anode and a PANi CE and then sealed by a Surlyn film through hot-pressing. (iv) The device in approach (ii) was vacuum-dried at 60 °C for 30 min.

2.5. Photovoltaic measurements

The photovoltaic test of the DSSC with an active area of 0.25 cm^2 was carried out by measuring the photocurrent–voltage (*J*–*V*) characteristic curves using a CHI660E Electrochemical Workstation under irradiation of a simulated solar light from a 100 W Xenon arc lamp (XQ-500 W) in ambient atmosphere. The incident light intensity was controlled at 100 mW cm^{-2} (calibrated by a standard silicon solar cell). A black mask with an aperture area of around 0.25 cm^2 was applied on the surface of DSSCs to avoid stray light. Each *J*–*V* curve was repeatedly measured at least five time to control the experimental error within ±5%.

2.6. Electrochemical characterizations

The electrochemical performances were recorded on a conventional CHI660E setup comprising an Ag/AgCl reference electrode, a CE of Pt sheet, and a working electrode of FTO glass supported electrolyte. The 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. Bode phase measurements were carried out in a frequency range of 0.1 Hz ~ 10^5 kHz and an ac amplitude of 10 mV at room temperature. Both Bode plots and Tafel polarization curves were recorded by assembling symmetric dummy cell consisting of PANi CE|solid-state electrolyte|PANi CE.

2.7. Other characterizations

The absorption spectra of resultant anode, electrolyte, and CE were recorded on a UV–vis spectrophotometer at room temperature. The morphologies of the resultant TiO_2/PANi anode and PANi CE were observed with a scanning electron microscope (SEM, S-3500N, Hitachi, Japan). The X–ray diffraction (XRD) data were collected in the 2θ range between 10 and 50° at a scanning speed of 10° min^{-1}. Fourier transform infrared spectrometry (FTIR) spectra were recorded on a PerkinElmer spectrum 1760 FTIR spectrometer. The UV–vis spectra were measured on a UV-3200