Electrochimica Acta 137 (2014) 721–727

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Pulse-reversal electropolymerization of polypyrrole on functionalized carbon nanotubes as composite counter electrodes in dye-sensitized solar cells

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ARTICLE INFO

Article history:
Received 31 March 2014
Received in revised form 2 May 2014
Accepted 4 June 2014
Available online 11 June 2014

Keywords:
Dye-sensitized solar cells
Counter electrode
Carbon nanotube
Polypyrrol
Pulse-reversal electropolymerization

ABSTRACT

In this current work, we proposed a modified two-step method to prepare multiwalled carbon nanotube/polypyrrol (MWCNT/PPy) composite counter electrodes (CEs) toward triiodide reduction in dye-sensitized solar cells (DSCs). MWCNTs were deposited onto the surface of fluorinated tin oxide (FTO) glass substrates by electrophoretic deposition, and then subjected to the PPy electropolymerization by using a pulse-reversal technique. With regard to the electropolymerization of PPy on the MWCNTs-coated FTO substrate by conventional cyclic voltammetry (CV) method (designated as MWCNT/PPy-CV CE), the MWCNT/PPy-PR CE still retrained the mesoporous morphology originating from the MWCNT conductive framework and the PPy thin film was found to be evenly coated on the MWCNT surface. According to the extensive electrochemical analyses, the mesoporous nanostructure of the MWCNT/PPy-PR CE provided increased active surface area for I_3^- reduction and facilitated the electron transport at the interface of CE/electrolyte and the redox electrolyte penetration within the CE. As a result, the DSC assembled with the MWCNT/PPy-PR CE reaches a comparable photovoltaic efficiency of 6.21% to that of the DSC based on the Pt CE (6.66%).

1. Introduction

To meet the increasing demand for low-carbon energy, tremendous research efforts have been made to develop clean and renewable alternative energy sources. In recent years, dye-sensitized solar cells (DSCs) have attracted considerable interest as electrochemical devices converting solar energy to electricity due to the advantages of relatively high power conversion efficiency (PCE) and low manufacturing cost [1]. Typically, a DSC comprises a dye-sensitized TiO_2 nanocrystalline photoanode, an electrolyte containing tri-iodide/iodide (I_3^-/I^-) redox couples, and a counter electrode (CE). In additional to the investigations of the TiO_2 photoanodes and redox electrolytes [2,3], the CE as an indispensable component in DSCs has recently caught increasable attention [4,5]. The role of a CE is generally to transfer electrons from the external circuit back to the I_3^-/I^- -containing redox electrolyte and to speed up the reduction of the I_3^- to I^- for sustaining low overvoltage, which can reduce the charge recombination at the photoanodes and result in an improved PCE [6]. Platinum (Pt) has been considered as the best CE material for I_3^- reduction because of its excellent conductivity, electrocatalytic activity, and stability [7,8]. However, the high price of Pt metal limits its practical application for large-scale DSCs. Therefore, a great deal of efforts has been made to explore Pt-free CE. Several conducting polymers, such as polyaniline [9,10], poly(3,4-alkylenedioxythiophene) [11,12], and polypyrrole (PPy) [13,14], have been implemented into DSCs as promising CEs for catalyzing I_3^- reduction. Among them, PPy has attracted great interest due to its low cost, simple process, considerable environmental stability, and relatively high conductivity [15,16]. Nevertheless, its relatively high charge transfer resistance and hindered electron transport between PPy particles would cause the increased overpotential for catalyzing I_3^- reduction [17,18].

It is well known that carbon nanotube (CNT) possesses the characteristics of highly surface area, fast electron-transport architecture, and excellent mechanical strength [19]. As a result, several studies reported the synergistic effect for catalyzing I_3^- reduction by combining the highly conductive CNTs with the electrocatalytic PPy, and thus resulting improved PCE of DSCs [20–23]. Peng et al. [20] prepared PPy/multi-walled CNT composite on a flexible conducting substrate as a CE via a drop-casting method, and the DSC based on the PPy/multi-walled CNT (MWCNT) CE reached

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http://dx.doi.org/10.1016/j.electacta.2014.06.028
0013-4686/

a conversion efficiency of 4.04%. He et al. [21] further used a simple dip-coating method to fabricate PPy/single-walled CNT CE and reached an impressive PCE of 8.30%. Yue et al. [22] synthesized a PPy/MWCNT CE through a one-pot electropolymerization approach, and therefore demonstrated a PCE of 7.24%. Although all of aforementioned works presented improved electrocatalytic activity of the PPy/CNT composite CEs, the CNTs were incorporated into the PPy matrix. To effectively utilize the high surface area of CNTs, Luo et al. [23] used a two-step preparation method, in which electrophoretic deposition of MWCNT matrix on conducting glass substrate was first performed and followed by electropolymerization of PPy on to the MWCNT surface by a conventional cyclic voltammetry (CV) method. However, the PCE of the DSC with the two-step prepared MWCNT/PPy-CV CE only achieved 3.78%. It is possible due to the unevenly and thoroughly coated PPy on the conductive MWCNT network.

To address this issue, in this study we proposed a modified two-step approach to fabricate PPy evenly coated MWNCT composite. The electrophoretic deposition of MWCNT matrix on fluorine-doped tin oxide (FTO) conducting substrate was first conducted, and followed by electropolymerization of PPy film on to the MWCNT surface via a pulse-revisal potentiostatic (PR) technique. It is worthy noted that the pulse electropolymerization of conducting polymers possessed lots of strengths in terms of controlled particle size and improved uniformity by facilitating the mass diffusion of monomers to the electrode surface from the bulk electrolyte [24,25]. Compared to the MWCNT/PPy-CV CE, the PPy thin film was much uniformly coated on MWCNT surface for the MWCNT/PPy-PR CE, thus particularly improving fill factor from 0.47 to 0.61 and PCE from 4.13% to 6.21%, which is comparable with that of the DSC based on Pt CE.

2. Experimental details

2.1. Preparation of CEs

The functionalized MWCNT was achieved by refluxing MWCNTs (0.5 g) in a 3:1 mixture of H_2SO_4 (98%) and HNO_3 (78%) at 120 °C for 2 h. After the oxidation reaction, the functionalized MWCNT precipitate was filtered off, washed with deionized water, and vacuumly dried at 70 °C for 24 h. The obtained functionalized MWCNT precipitate was subsequently dispersed in a mixture solution of acetone and ethanol with 1:1 in volume ratio. After ultrasonication for 2 h, the functionalized MWCNTs solution in the concentration of 0.5 g L^{-1} was finally prepared for the electrophoretic deposition. A two-electrode system in which a cleaned FTO glass substrate (NSG, 13 Ω sq^{-1}) and a Pt foil (4 cm^2) kept parallel and served as the working and counter electrode, respectively, was used for the electrophoretic deposition. Then, a constant potential of 50 V vs. open-circuit potential was employed for 60 s. The resultant MWCNT film in the thickness of ca. 0.5 μm was obtained and then dried at 60 °C for 10 min, designated as MWCNT CE.

The electropolymerization of PPy thin film onto FTO and MWCNT/FTO glass substrates were conducted at an ambient atmosphere from a simple aqueous solution (50 mL) containing 0.1 M pyrrole, 0.1 M oxalic acid, and 0.1 M $LiClO_4$. A three-compartment cell, with an FTO or MWCNT/FTO glass substrate as the working electrode, a Pt foil as the auxiliary electrode, and an Ag/AgCl electrode filled with saturated KCl in water as the reference electrode, was used for the electropolymerization. Herein, two electropolymerization methods were utilized for preparing the PPy thin film onto FTO or MWCNT/FTO substrates. One was done by the CV method, which was carried out using a computer-controlled electrochemical analyzer (CHI 6081D, CH Instrument) within the potential region between +1.2 and −0.2 V vs. Ag/AgCl at a scan rate of 50 mV s^{-1} for 10 cycles. Another way is the PR potentiostatic electropolymerization method conducted by ZAHNER electrochemical workstation (Zahner-Elektric Gmbh &Co. KG, Germany). The PR parameters were set with the pulse-on potential of +0.7 V vs. Ag/AgCl, the pulse-reversal potential of −0.3 V vs. Ag/AgCl, pulse-on period of 1 s, pulse-reversal period of 0.5 s, and the total duration time of 450 s via ZAHNER THALES software. After the electropolymerization, the various PPy and MWCNT/PPy thin films on FTO glass substrates were rinsed with deionized water and then dried at 80 °C under vacuum for 6 h. For comparison, Pt thermally decomposed on FTO glass substrate was used as a control experiment.

2.2. Preparation of TiO_2 photoanodes

The TiO_2 photoanodes was fabricated by using a facile screen-printing method via a semiautomatic screen printer (ATMA, AT45PA). After that, the photoanodes composed of the 12 μm transparent nanocrystalline TiO_2 layer (ETERDSC Ti-2105A, Eternal Chemical Co.) and 4 μm scattering TiO_2 layer (ETERDSC Ti-2325, Eternal Chemical Co.) coated onto the cleaned FTO glass substrates were obtained. The TiO_2 photoanodes with an area of 0.16 cm^2 were gradually sintered under an air flow at 150 °C for 10 min, 325 °C for 5 min, 375 °C for 5 min, 450 °C for 15 min. When the as-prepared TiO_2 photoanodes were cooled down to 80 °C, they were immersed in 0.3 mM N719 (*cis*-diisothiocyanato-bis(2,2′-bipyridyl-4,4′-dicarboxylato)ruthenium (II)bis (tetrabutylammoni-um), Everlight Chemical Industry Co.) for 12 h at room temperature. The dye-sensitized TiO_2 photoanodes were washed with absolute alcohol, and dried in air.

2.3. Assembly of DSC

DSCs were fabricated with a sandwiches structure by assembling the dye-sensitized TiO_2 photoanodes and CEs. These two electrodes were adhered to thermoplastic hot-melt surlyn and clipped together. Then the redox liquid electrolyte consisting of 1 M 1,3-dimethylimidazolium iodide (Merck), 0.5 M 4-tert-butylpyridine (Aldrich), 0.15 M iodine (J.T. Baker), and 0.1 M guanidine thiocyanate (Aldrich) in 3-methoxypropionitrile (Acros) was injected into the sandwiched cells through the pre-drilled holes on the CEs. Finally, the holes were sealed with Surlyn films covered with thin glass slide by heat pressing.

2.4. Characterizations and photovoltaic measurements

Fourier transform infrared spectra (FTIR) for the CEs were recorded on a Perkin Elmer Spectrum Gx FTIR Spectrometer with KBr as pellets. The surface morphologies of the CEs were examined using a field-emission scanning electron microscopy (FESEM; JSM-7600F). To investigate the electrocatalytic activity and electrochemical kinetic of the CEs, CV and electrochemical impedance spectroscopy (EIS) were performed with the aforementioned CHI 6081D electrochemical analyzer and ZAHNER electrochemical workstation, respectively. CV tests were conducted in a three-electrode electrochemical cell containing a 3-methoxypropionitrile solution of 50 mM LiI, 5 mM I_2, and 0.5 M $LiClO_4$ at a scan rate of 10 mV s^{-1}, using the as-prepared CEs as the working electrode, a Pt foil as an auxiliary electrode, and Pt wire as a reference electrode. The symmetric dummy cells fabricated with the redox electrolyte between two identical CEs were used for impedance studies. The EIS spectra were obtained under open-circuit potential with a frequency region of 0.1-10^6 Hz at ac amplitude of 10 mV under dark conditions. The resultant impedance spectra were further analyzed by using Z-view software. The photocurrent-voltage curves of the DSCs were measured with a computer-controlled Keithly 2400