



Electro-polymerization of polypyrrole/multi-wall carbon nanotube counter electrodes for use in platinum-free dye-sensitized solar cells



Wenjing Hou^{a,b}, Yaoming Xiao^{a,b,*}, Gaoyi Han^{a,b,*}, Haihan Zhou^{a,b}

^a Institute of Molecular Science, Innovation Center of Chemistry and Molecular Science, Shanxi University, Taiyuan 030006, PR China

^b Key Laboratory of Materials for Energy Conversion and Storage of Shanxi Province, Taiyuan 030006, PR China

ARTICLE INFO

Article history:

Received 14 July 2015

Received in revised form 1 January 2016

Accepted 2 January 2016

Available online 9 January 2016

Keywords:

dye-sensitized solar cell
counter electrode
polypyrrole
multi-wall carbon nanotube
electrocatalytic activity

ABSTRACT

In the development of the dye-sensitized solar cell (DSSC), it is critically important, but remains challenging to discover new counter electrode (CE) materials to replace the expensive and precious platinum (Pt). Herein we electro-polymerize the polypyrrole (PPy) on the multi-wall carbon nanotube (MWCNT)-coated F-doped tin oxide substrate by a facile cyclic voltammetry method to obtain the PPy/MWCNT composite CE. The resultant composite CE shows that the MWCNT is wrapped with 15 nm thickness of PPy nanoparticles, which takes advantage of the high surface area and good conductivity of the MWCNT and good catalytic activity of the PPy for the reduction of triiodide to iodide, providing the fast electron transport and diffusion channels and plenty of interfacial catalytic active sites. The DSSC based on the PPy/MWCNT composite CE shows an excellent photoelectric conversion efficiency of 7.15% under full sunlight illumination (100 mW cm⁻², AM 1.5 G), which is much higher than that of the MWCNT (1.72%) and PPy (5.72%) based DSSCs, and 92.14% that of the Pt-based DSSC (7.76%).

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

The dye-sensitized solar cell (DSSC) has been regarded as a promising candidate for the next-generation solar cell due to its low cost, relatively high energy conversion efficiency, and environmentally friendly fabrication process, since its first prototype in 1991 by O'Regan and Grätzel [1–5]. In general, a DSSC consists of a dye-sensitized porous nanocrystalline TiO₂ anode, an electrolyte containing the iodide/triiodide (I⁻/I₃⁻) redox couple, and a platinized counter electrode (CE). As the most common CE of the DSSC, platinum (Pt) has high conductivity, stability and catalytic activity for the reduction of triiodide (I₃⁻) to iodide (I⁻) [6]. However, the noble metal Pt is one of the most expensive components in the DSSC [6,7], which directly limit the widely commercial application of DSSCs especially for the large-area solar cells [4,8,9]. Meanwhile, the PtL₄ will be produced, due to Pt could be dissolved in the I⁻/I₃⁻ redox couple electrolyte, which will resort to a negative effect on the long term stability of the DSSC [10]. Based on above defects, various CE materials have been explored as promising low-cost alternatives to the Pt catalyst, such as carbon materials [11–13], transition-metal compounds [14–20],

conducting polymers [21–25], and metal alloys [7,26,27]. The universalities of these candidates are comparable electrocatalytic performances for the triiodide reduction and high electron-transfer ability.

Among them, on the one hand, carbon nanotubes reveal some of the most potential for use as an alternative CE due to their features of very high accessible surface area, superior electronic conductivity and excellent mechanical strength [28]. However, the conversion efficiency of the DSSC based on the carbon nanotube CE is relatively low due to the poor catalytic activity for I₃⁻ reduction [11]. On the other hand, the polypyrrole (PPy) nanostructures, on account of easy to fabricate, high catalytic activity for the I₃⁻ reduction and considerable environmental stability, have been considered as one of the most promising CE materials [21–23]. To further improve the catalytic activity, the PPy/multi-wall carbon nanotube (MWCNT) composite CE, combining the good conductivity and the high surface area of MWCNTs with the high catalytic activity of PPy for I₃⁻ reduction, has improved the photoelectric conversion efficiency of the DSSC [29–32]. Early works in fabricating PPy/MWCNT composites are focusing on chemical [29–31] and electrochemical copolymerization approaches [32]. Peng and coworkers prepared PPy/MWCNT composite CE by the chemical polymerization and drop-casting method and employed in the flexible DSSC [29], giving a conversion efficiency of 4.04%. The lower conversion efficiency might contribute to the poor contact between the PPy and MWCNT when prepared by the

* Corresponding author. Tel.: +86 351 7010699; fax: +86 351 7016358
E-mail addresses: [ymxiao@sxu.edu.cn](mailto:yxmiao@sxu.edu.cn) (Y. Xiao), han_gaoyis@sxu.edu.cn (G. Han).

chemical polymerization method. The electrochemical copolymerization approach is also not convenient to prepare the PPy film around the MWCNT [32].

Herein, we fabricated the PPy/MWCNT CE by a facile cyclic voltammetry method to electro-polymerize the PPy nanoparticles on the MWCNT-coated F-doped tin oxide (FTO) substrate. The resultant composite CE showed that the MWCNT was wrapped with 15 nm thickness of PPy nanoparticles. Furthermore, the contact among the PPy, MWCNT, and FTO substrate was enhanced. Due to the high active surface and facile electron transport from the MWCNT and intrinsically excellent electrocatalytic activity from the PPy, a high energy conversion efficiency of 7.15% was achieved for the DSSC based on the PPy/MWCNT CE, which was much higher than that of MWCNT (1.72%) and PPy (5.72%) based DSSCs under full sunlight illumination (100 mW cm^{-2} , AM 1.5 G).

2. Experiment

2.1. Materials

Pyrrole (Py, Sigma–Aldrich), MWCNTs (Purity: >99.5%; Average diameter: 40–60 nm; Length: >10 μm ; Golden Innovation Business Co.), tetrabutyl titanate, acetic acid, nitric acid, sodium dodecyl-sulfate (SDS), polyvinylpyrrolidone K-30 (PVP), triton X-100, iodine, lithium iodide, lithium perchlorate (LiClO_4), tetrabutyl ammonium iodide, 4-tert-butylpyridine, guanidine thiocyanate, acetonitrile, acetone, and ethanol were purchased from Shanghai Chemical Agent Ltd., China (Analysis purity grade). Dye N719 [cis-di(thiocyanato)-N,N-bis(2,2-bipyridyl-4-carboxylic acid-4-tetra-butyl ammoniumcarboxylate) ruthenium (II)] was purchased from Dyesol, Australia. The above agents were used without further purification. F-doped tin oxide (FTO) glass substrates were purchased from NSG, Japan ($12 \Omega \text{ sq}^{-1}$).

2.2. Electro-polymerization of PPy/MWCNT CEs

Raw MWCNTs were refluxed in a 3:1 mixture of H_2SO_4 (98%) and HNO_3 (78%) at 120°C for 15 min to oxidize the graphitic sp^2 carbon into a $-\text{COOH}$ functional group on the side walls of the MWCNTs. The oxidized MWCNTs were further filtered by suction filtration, washed thoroughly with deionized water, and suspended in a 1:1 mixture of acetone and ethanol by ultrasonication for 2 h. The MWCNT suspension with a concentration of 0.5 mg

mL^{-1} was spin-coated on the FTO glass substrate, and dried at 60°C in a drying oven (Suzhou Jiangdong Precision Instrument Co., Ltd., China) to obtain the MWCNT CE.

The PPy was electrodeposited on the MWCNT CE by the cyclic voltammetry (CV) measurement from an aqueous solution containing 10 mM Py, 20 mM SDS, and 20 mM LiClO_4 , which was sonicated for 15 min prior to the experiment. A three-electrode cell with an Electrochemical Workstation (CHI660D, Shanghai Chenhua Device Company, China) was used, and the MWCNT CE and Pt sheet (2 cm^2) were used as the working electrode and counter electrode, respectively. The CV electro-polymerization of the PPy on the MWCNT CE was carried out at a potential window of -0.4 V to 0.8 V for 12 cycles vs. Ag/AgCl at a scan rate of 0.05 V s^{-1} , in which the CV parameters were optimized in advance. The resultant PPy/MWCNT CE was rinsed in distilled water and dried at 60°C . For comparison, the PPy CE based on same CV parameters were also manufactured, and a thermal decomposition Pt CE was employed.

2.3. Fabrication of mesoporous dye-sensitized TiO_2 anodes

FTO glass substrates with the settled size of $2 \text{ cm} \times 1.5 \text{ cm}$ were thoroughly rinsed in the order by deionized water and anhydrous ethanol. The TiO_2 colloid and mesoporous TiO_2 anodes were prepared according to our previous reports [4,7,24]. The thickness of the TiO_2 film was controlled by the thickness of the adhesive type around the edge of the FTO substrate. After drying at room temperature, the TiO_2 anodes were sintered in a muffle furnace at 450°C for 30 min. The resultant mesoporous TiO_2 anodes were immersed in a $2.5 \times 10^{-4} \text{ M}$ solution of dye N719 in absolute ethanol solution for 24 h to adsorb the dye adequately, followed by cool air drying.

2.4. Assembly of DSSCs

The DSSC was fabricated by sandwiching redox electrolyte between a dye-sensitized TiO_2 anode and a CE under an open system without any sealing. The redox electrolyte composed of 0.60 M tetrabutyl ammonium iodide, 0.10 M lithium iodide, 0.10 M iodine, 0.10 M guanidine thiocyanate, and 0.50 M 4-tert-butylpyridine in acetonitrile. The redox electrolyte was also employed in the electrochemical impedance spectroscopy (EIS) and Tafel polarization measurements.

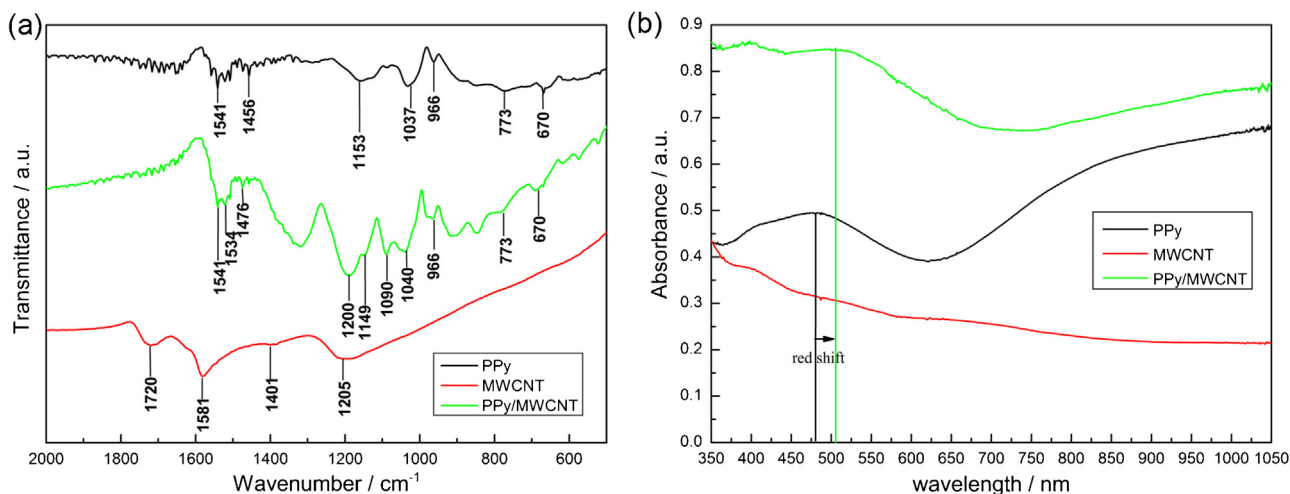


Fig. 1. (a) FTIR and (b) UV-vis absorption spectra of the PPy, MWCNT and PPy/MWCNT.

Download English Version:

<https://daneshyari.com/en/article/6609586>

Download Persian Version:

<https://daneshyari.com/article/6609586>

[Daneshyari.com](https://daneshyari.com)