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Fabrication of high performance multi-walled carbon nanotubes/polypyrrole counter electrode for dye-sensitized solar cells

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ABSTRACT

In our present study, the composite film of MWCNTs/Ppy (multi-walled carbon nanotubes and polypyrrole) was proposed as CE (counter electrode) catalyst in DSSCs (dye-sensitized solar cells) to speed up the reduction of triiodide to iodide. The MWCNTs/Ppy composite film was synthesized and fabricated it on rigid fluorine-doped tin oxide substrates by using a facile electrochemical polymerization route, and served as CE in DSSCs. The unique structural characteristics including rough surface consisted of the numerous MWCNTs coated on Ppy nanoparticles guaranteed fast mass transport for the electrolyte, and enabled the MWCNTs/Ppy CE to speed up the reduction of triiodide to iodide. The electrochemical analyses came from cyclic voltammetry and electrochemical impedance spectroscopy revealed that the MWCNTs/Ppy CE possessed more excellent electrocatalytic activity, electrochemical stability and lower charge transfer resistance of 2.82 Ω cm^2 in comparison with a sputtered-Pt CE. The DSSC assembled with the novel MWCNTs/Ppy CE exhibited a high light-electric conversion efficiency of 7.42% under the illumination of 100 mW cm^{-2}, comparable to that of the DSSC based on sputtered-Pt electrode (6.85%). Therefore, the MWCNTs/Ppy composite film can be considered as a promising alternative CE for DSSC due to its high electrocatalytic performance and excellent electrochemical stability.

1. Introduction

DSSC (dye-sensitized solar cell) has been demonstrated to be a feasible, low-cost method of producing solar electricity by using of one dye-sensitized TiO_2 photoanode, one redox mediator of iodide/triiodide (I^-/I_3^-) and Pt (platinum) CE (counter electrode) to complete the redox reaction [1]. To date, the highest performing DSSC of this type has achieved power conversion efficiencies of over 15% [2]. This is attained by depositing Pt on a transparent conductive oxide substrate. There exists a drawback with Pt in any low cost application for its scarcity as a precious metal. Thus, it has resulted in efforts to explore Pt-free CE in DSSC with low-cost materials, including the carbon materials [3–5], conducting polymers [6,7], sulfides [8–10], nitrides [11] and as well as carbides [12]. It is notable that these materials are abundant and economic; importantly, they can show high corrosion resistance performance as well as Pt. Among of them, CNTs (carbon nanotubes) have been widely used as the material for catalyst support due to their good properties such as large surface area, high electrical conductivity, excellent mechanical strength, perfect chemical stability and electrocatalytic activity for I_3^- reduction to a certain extent [13,14]. Furthermore, CNTs can be tailored through surface fictionalization to conduct the decoration of CNTs with electrocatalytically active materials. Very recently, Lee et al. [15], reported the successful application of MWCNTs (multi-wall carbon nanotubes) as a catalyst for triiodide reduction in DSSC. Velten et al. [16], demonstrated the replacement of the Pt catalyst normally used in the CE of DSSC by a nanocomposite of dry spun MWNT sheets with graphene flakes. Li et al. [17], pointed that DSSC with the composite CE composed of TiN nanoparticles and MWCNTs presented an improved photovoltaic performance.

Currently, conductive polymers have attracted much attention as CE materials in DSSC, and demonstrated feasible and high performance among Pt-free CEs for their advantages, e.g., low cost-availability, large electrochemical surface area, good film-forming ability and electrocatalytic activity for I_3^- reduction [18]. Compared with the most studied polyaniline and poly(3,4-ethylenedioxythiophene) CEs, there are only a few reports on the

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List of symbols

DSSC	dye-sensitized solar cell
MWCNT	multi-walled carbon nanotube
PCE	power conversion efficiency
Zw	finite layer Nernst diffusion impedance
R_{ct}	charge-transfer resistance
SEM	scanning electron microscopy
FTIR	Fourier transform infrared spectroscopy
EIS	electrochemical impedance spectroscopy
J_{sc}	short-circuit current density
J–V	photocurrent–photovoltage
J_0	exchange current density
J_{lim}	limiting current density
J_{max}	maximum current density
TBP	4-tertpbutylpyridine
CV	cyclic voltammetry
V_{oc}	open-circuit voltage
P_{in}	incident light power
Rs	series resistance
V_{max}	maximum voltage
XRD	X-ray diffraction
Ppy	polypyrrole
Pt	platinum
I^-/I_3^-	iodide/triiodide
CE	counter electrode
FTO	fluorine-doped tin oxide

application of Ppy (polypyrrole) as CE materials in DSSCs, although Ppy has been demonstrated one of the most promising candidates in the application of optical and electrical devices and sensors due to its high conductivity, environmental stability, and the virtue of easy preparation in a high yield [19–21]. In our previous reported [10], a composite CE composed of MWCNTs decorated with tungsten sulfide particles showed an improved photovoltaic performance in DSSC. Yue et al. [22], further demonstrated an enhanced performance of DSSC based on a molybdenum disulfide/carbon nanotubes composite catalytic composite film prepared with glucose aided. In these works, the electrocatalytic activity of sulfide was remarkably promoted due to the fast electron-transport network provided by CNTs in these composites.

At present, it is envisaged that the composite film of Ppy with well-distributed MWCNTs can possibly provide enhanced conductivity as well as reasonable electrocatalytic activity for I_3^- reduction. In this work, the MWCNTs/Ppy composite film was prepared based on Ppy system using electrochemical polymerization method and served as CE in DSSCs. The influence upon electrocatalytic activity for I_3^- reduction was analyzed by electrochemical impedance spectroscopy and cyclic voltammetry. It is expected that photoelectric performances of the DSSC with MWCNTs/Ppy CE can be improved.

2. Experimental

2.1. Materials

The lithium perchlorate ($LiClO_4$), oxalic acid ($C_2H_2O_4$), titanium tetrachloride ($TiCl_4$) and pyrrole were purchased from Shanghai Chemical Agent Ltd., China. The organometallic compound sensitized dye N-719 cis-di(isothiocyanato)-bis-(2,2′-bipyridyl-4,4′-dicarboxylato) ruthenium(II) bis-tetrabutylammonium was obtained from Solaronix SA (Switzerland). MWCNTs were purchased from the Chengdu Organic Chemicals Co., Ltd., Chinese Academy of Sciences. Pyrrole monomer was distilled prior to use. All reagents are of analytical reagent grade. The FTO (fluorine-doped tin oxide) glass substrates (8 Ω cm^{-2}, Hartford Glass Co., USA) were cut into pieces with size of 1 × 2 cm^2 carefully and ultrasonically cleaned sequentially in detergent, acetone and distilled water for 10 min, respectively, which later stored in isopropyl alcohol.

2.2. Preparation of MWCNTs/Ppy counter electrode

In brief, the preparation of the MWCNTs/Ppy CE using an electrodeposition method outlined below. The electrodeposition was carried out with an electrochemical analyzer system (CHI660D, Shanghai Chenhua Device Company, China). All experiments were implemented in a three-electrode cell, including one Pt foil as CE, one Ag/AgCl electrode as a reference electrode and FTO glass with an exposed area of 0.64 cm^2 as the working electrode. The base electrodeposition solution of MWCNTs/Ppy CE was carried out in the aqueous solution consisted of 0.1 M of pyrrole, 0.1 M of $LiClO_4$, 0.1 M of oxalic acid and acid-treated MWCNTs. Of the above finally obtained base plating solution was sonicated for 30 min and then refluxed for 2 h. A constant current density of 10 mA cm^{-2} was served for electrodeposition (the synthesis route and structure diagram shown in Scheme 1). The FTO glass covered with MWCNTs/Ppy composite film was put into an oven at 100 °C for 12 h, and then the MWCNTs/Ppy CE was obtained.

2.3. Fabrication of dye-sensitized solar cell

The TiO_2 anode was prepared as described previously [23–25]. In brief, the dye was loaded by immersing the TiO_2 anode in the 0.3 mM of dye N719 ethanol solution for 12 h. Thus the dye-sensitized TiO_2 anode with thickness of 8–10 μm was obtained. The DSSC was fabricated by injecting the liquid electrolyte (0.05 M of I_2, 0.1 M of LiI, 0.6 M of tetrabutylammonium iodide and 0.5 M of TBP (4-tertpbutylpyridine) in acetonitrile) into the aperture between the dye-sensitized TiO_2 electrode and the CE. The two electrodes were clipped together and wrapped with thermoplastic hot-melt Surlyn.

2.4. Characterization and measurement

The surface morphology of the sample was observed by using JSM-7600F field emission scanning electron microscope (SEM). The composition of sample was studied by Raman spectroscopy (RENISHAW in Via). The crystal structure was explored by using glancing incident X-ray diffraction (GIXRD, Rigaku-TTRAXIII) analysis. FTIR (Fourier transforms infrared) spectroscopy measurement was carried out using a Nicolet Impact 410 FTIR spectrometer. CV (cyclic voltammetry), EIS (electrochemical impendence spectroscopy) and Tafel polarization curves were conducted by using a computer-controlled electrochemical analyzer (CHI 660D, CH Instrument). The electrolyte used in the DSSC test was also injected into the symmetric dummy cells for both EIS and Tafel measurements. EIS was carried out under the simulating open-circuit conditions at ambient atmosphere, sealing with thermoplastic hot-melt Surlyn and leaving an exposed area of 0.64 cm^2. The frequency of applied sinusoidal AC voltage signal was varied from