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PEDOT:PSS and glucose assisted preparation of molybdenum disulfide/single-wall carbon nanotubes counter electrode and served in dye-sensitized solar cells

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ABSTRACT

A flower-like structure complexes of molybdenum disulfide/single-wall carbon nanotubes (MoS_2/SWCNTs) are for the first time synthesized with glucose and poly (3, 4-ethylenedioxythiophene): poly (styrenesulfonate) (PEDOT:PSS) assisted (G-P-A) by the use of an in situ hydrothermal route, and proposed as counter electrode (CE) catalyst for Pt-free dye-sensitized solar cells (DSSCs). The DSSC assembled with the (G-P-A) MoS_2/SWCNTs CE exhibits a high photo-electric conversion efficiency of 8.14% under the illumination of 100 $mW \cdot cm^{-2}$, comparable to that of the DSSC Pt-based (7.78%). Furthermore, the surface morphology of the (G-P-A) MoS_2/SWCNTs complexes with flower-like structure is confirmed by using the scanning and transmission electron microscopes (SEM). The superior structural characteristic along with 3D large interconnected interstitial volume is advantageous fast mass transport for the electrolyte, and enables the (G-P-A) MoS_2/SWCNTs CE to speed up the reduction of triiodide to iodide. The electrochemical performance of the sample is analyzed from cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). It indicates that the (G-P-A) MoS_2/SWCNTs CE possesses excellent electrocatalytic activity in iodide/triiodide electrolyte and lower charge transfer resistance of 1.46 $\Omega \cdot cm^2$ compared to the Pt electrode (2.44 $\Omega \cdot cm^2$). Sum up, the (G-P-A) MoS_2/SWCNTs CE can be considered as a promising alternative CE for Pt-free DSSCs.

1. Introduction

Since the report of dye-sensitized solar cells (DSSCs) in 1991 [1], they have been demonstrated to be a feasible, low cost approach of producing solar electricity by the use of one TiO_2 photoanode adsorbed dye, one redox mediator of iodide/triiodide (I^-/I_3^-) and one platinum (Pt) catalyst to complete the redox reaction. So far, the highest photo-electric conversion efficiencies of DSSCs have achieved over 12% in the past decades [2]. This is obtained by depositing Pt on a transparent conductive oxide substrate. However, Pt as an expensive noble metal provides an excellent performance, but the commercialization of DSSCs is impeded owing to high cost of platinum. Also, the Pt could be decomposed to PtI_4 in I^-/I_3^-redox couple electrolyte, which will affect the long-term stability of the DSSCs. Thus, it has resulted in many efforts to explore Pt-free counter electrode (CE) in DSSCs. The materials include carbon materials [3–5], conducting polymers [6,7], transition metal sulfides [8–10], nitrides [11] and as well as carbides [12].

Among all transition metal sulfides, molybdenum sulfide (MoS_2) as a typical lamellar compound has the similar structure to graphene. The unit cell of MoS_2 consists of three atom layers, e.g., a Mo layer sandwiched between two S layers, and the triple layers are stacked and held together by weak van der Waals interactions [13]. Because of the weak van der Waals interactions between the sheets of sulfide atoms, MoS_2 can be exfoliated into thin pieces. In the view of this, MoS_2 can be prospective used as lubricants [14] hydrogen evolution reactions [15], electrode materials for lithium ion batteries [16] and electrode materials in DSSCs [17]. Furthermore, carbon nanotubes (CNTs) have been widely used as the materials for catalyst support due to their excellent properties, e.g., large surface area, high electrical conductivity, excellent mechanical strength, good chemical stability, superior electrocatalytic activity for I_3^-reduction to a certain extent [18,19]. Additionally, CNTs could be tailored through surface functionallization to prepare

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the decoration of CNTs with electrocatalytically active materials. Currently, increasingly importance has been attached to the composites of MoS_2/CNTs. Tai, et al., [20] reported the nanocomposite of MWCNT (multi-walled carbon nanotubes) @MoS_2 as CE catalyst in Pt-free DSSC to speed up the reduction of triiodide to iodide, and the DSSC assembled based on the MWCNT@MoS_2 CE showed a high power conversion efficiency of 6.45%. Yue, et al., [21] synthesized MoS_2/CNTs composites with glucose aided by hydrothermal method and introduced it in DSSC, which exhibited a high light-to-electric conversion efficiency of 7.92%.

Recently, conductive polymers have attracted much attention as CE materials 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 [22,23].

Thus, taking into account of all these factors, it is envisaged that the MoS_2/SWCNTs composites were synthesized with glucose and poly (3,4-ethylenedioxythiophene): poly (styrenesulfonate) (PEDOT:PSS) assisted (G-P-A) by the use of hydrothermal route, which is prospective resulted in an improvement in the electrical conductivity as well as reasonable electrocatalytic activity for I_3^-reduction. Here, the composite materials of (G-P-A) MoS_2/SWCNTs with flower-like structure are synthesized in the presence of glucose and PEDOT:PSS assisted by using an in situ hydrothermal route, and served as CE for the first time in Pt-free DSSCs. The CE shows excellent electrocatalytic activity and low charge transfer resistance of 1.46 $\Omega\cdot cm^2$, which are demonstrated by the results of cyclic voltammetry (CV) and electrochemical impendence spectroscopy (EIS) measurements. The DSSC assembled with the (G-P-A) MoS_2/SWCNTs CE exhibits a considerably improved performance in photo-electric conversion efficiency of 8.14% under irradiation of 100 $mW\cdot cm^{-2}$ (AM 1.5).

2. Experimental

2.1. Materials

The sodium molybdate ($Na_2MoO_4\cdot 2H_2O$), thiourea, acetonitrile, polyethylene glycol with average molecular weight of 2000 (PEG 2000), glucose, N-methyl-2-pyrrolidinone (NMP), 4-tert-butyl-pyridine (TBP), polyvinyl-difluoride (PVDF), 3, 4-ethylenedioxythiophene (EDOT) and titanium tetrachloride ($TiCl_4$) are purchased from Shanghai Chemical Agent Ltd, China. All reagents are of analytical reagent grade.

The organometallic compound sensitized dye Z-907 *cis*-bis (isothiocyanato) (2, 2‘-bipyridyl-4,4′-dicarboxylato) (2,2′-bipyridyl-4,4′-di-nonyl) ruthenium (II) is obtained from Solaronix SA (Switzerland). Single-wall carbon nanotubes (SWCNT, 90% main range of external diameter < 2 nm, length 2-5 μm, special surface area 500-700 $m^2\cdot g^{-1}$) are purchased from the Chengdu Organic Chemicals Co., Ltd., Chinese Academy of Sciences. The fluorine-doped tin oxide transparent (FTO) glass substrates (8 $\Omega\cdot cm^{-2}$, Hartford Glass Co., USA) are cut into 1×2 cm^2 carefully and ultrasonically cleaned sequentially in detergent, acetone and distilled water for 30 min, respectively; and then stored in isopropyl alcohol.

2.2. Preparation of the (G-P-A) MoS_2/SWCNTs CE

Firstly, raw SWCNTs was refluxed in the 3:1 mixture of 98% H_2SO_4 and 78% HNO_3 at 120 °C to functionalize the graphitic sp^2 carbon into–COOH functional group on the side walls of the SWCNTs. The functionalized SWCNTs were further filtered by suction filtration, washed thoroughly with deionized water, and subjected to drying.

A typical synthesis proceeded of PEDOT:PSS outlines below. 6.95 g PSS (18wt%) aqueous solution was mixed with 75 ml deionic water at room temperature and treated with nitrogen bubbling for 0.5 h. Then 0.5 g EDOT and 0.0077 g $Fe_2\ (SO4)_3\cdot 9H_2O$ were added to initiate the polymerization. The mixture was stirred at room temperature for 2 h, after which a further 0.1673 g $Na_2S_2O_8$ was added. After additional reaction time of 12 h, the mixture was put into a dialytic bag for 48 h to remove the excess reactants. Then the blue solution of PEDOT:PSS was obtained.

In brief, the preparation of the (G-P-A) MoS_2/SWCNTs nanocomposites outlined as following. 4.84 g $Na_2MoO_4\cdot 2H_2O$, 6.12 g thiourea, 1.0 g glucose and 0.5 g PEG 2000 were dissolved in 80 ml PEDOT:PSS solution. After ultrasonication and stirring for 30 min until a homogeneous solution was achieved. After that, 1.5 wt.% of acid-treated SWCNTs was added into the reaction solution. Further sonicated for another 30 min before transferred into Teflon-lined autoclave, and then heated in an oven at 180 °C for 24 h without intentional control of ramping or cooling rate. The black products, as the conductivity active materials, were collected by filter and washed with ethanol and distilled water for 5 times, and then dried in a vacuum oven at 100 °C for 12 h. For comparison, the MoS_2/SWCNTs and (G-A) MoS_2/SWCNTs were also synthesized by using the similar method.

The active materials, e.g., MoS_2/SWCNTs, (G-A) MoS_2/SWCNTs, (G-P-A) MoS_2/SWCNTs powders, were mixed with acetylene black and PVDF in a weight ratio of 8: 1: 1. The paste of the above mentioned mixtures was prepared by the use of NMP as the solvent and kept stirring for 12 h. Subsequently, the as-prepared paste was coated on FTO glass substrate using a doctor blade method with an area of 0.64 cm^2 to form the film with the thickness of ~8 μm. The obtained electrodes were dried at 100 °C for 12 h in a vacuum oven.

2.3. Fabrication of DSSC

A TiO_2 anode was prepared as our previous studies [24,25]. Briefly, a thin TiO_2 blocking layer was spin-coated on FTO substrate at 1500 rpm for 30 s, followed by sintering at 450 °C for 30 min in air. Subsequently, the TiO_2 layer with particle size of 10-20 nm was coated onto the blocking layer by using doctor blade method, and then sintered at 450 °C for 30 min in air. A reflect layer formed by immersing the obtained TiO_2 substrate in 0.15 M $TiCl_4$ solution at 70 °C for 0.5 h and sintering at 450 °C for another 30 min. The dye was loaded by immersing the TiO_2 anode in the 0.3 mM of dye Z907 Tert-butanol/acetonitrile solution for 24 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 in acetonitrile) in 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

The surface morphology of the sample was observed by using JSM-7600F field emission scanning electron microscope (SEM). Field emission transmission electron microscope (TEM, JEOL JEM-2100F, operated at 200 kV with a point-to-point resolution of 0.19 nm) equipped with an energy dispersive spectrometer (EDS) was used to obtain the information of the microstructures and the chemical compositions. The crystal structure was explored by using glancing incident X-ray diffraction (GIXRD, Rigaku-TTRAXIII) analysis. Cyclic voltammetry (CV) measurements of the samples were taken in a three-electrode one-compartment cell with the (G-P-A) MoS_2/SWCNTs CE as working electrode, a Pt foil as counter electrode and Pt wire as reference electrode dipped in an acetonitrile solution of 10 mM LiI, 1 mM I_2, and 0.1 M $LiClO_4$. CV and