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9.07%-Efficiency dye-sensitized solar cell from Pt-free RuCoSe ternary alloy counter electrode

Yuanyuan Zhao, Jialong Duan, Yanyan Duan, Haiwen Yuan, Qunwei Tang *

School of Materials Science and Engineering, Ocean University of China, Qingdao 266100, PR China

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Dye-sensitized solar cell (DSSC) is a promising solution to relieve global energy crisis and environmental issues because of its superiority in low cost, easy fabrication procedures and relatively high efficiency. The decrease of fabrication cost without sacrifice of power conversion efficiency of the DSSCs can doubtlessly contribute to its commercial application. Here we report a new Pt-free RuCoSe ternary alloy counter electrode (CE) by electrodepositing. The DSSC device with RuCoSe ternary alloy CE achieves a power conversion efficiency of 9.07%, which is higher than 7.03% from Pt-only CE based DSSC. The easy preparation method and promising results provide a new method for decreasing cost but enhancing photovoltaic performance of DSSCs.

1. Introduction

Dye-sensitized solar cells (DSSCs) show superiority in relieving energy crisis and environmental issues over other solar cells owing to low cost, relatively high power conversion efficiency, simple fabrication process and environmental friendliness [1–2]. Traditional dye-sensitized solar cells consist of photoanode, electrolyte and counter electrode (CE). As an important constituent part of DSSCs, CEs collect electrons from external circuit and catalyze the reduction reaction of redox electrolyte from I_3^- to I^- [3–4]. Fluorine-doped tin oxide (FTO) conductive glass supported Pt is the state-of-the-art CEs for DSSC devices, however, the high cost and limited reserves have retarded the commercialization of DSSCs [5]. In order to solve this issue, it is essential to develop alternative CEs with low cost, sufficient reserves, high electrocatalytic activity and high conductivity. At the same time, DSSCs with such alternative CEs should show high power conversion efficiency compared with that from Pt CE.

In order to enhance the electrocatalytic activity of CE and the photovoltaic performance of corresponding DSSCs, we developed Pt-free RuCoSe ternary alloy CE by electrodepositing method. The DSSC device with RuCoSe ternary alloy CE achieves a power conversion efficiency of 9.07%, which is higher than 7.03% from Pt-only CE based DSSC. The easy preparation method and promising results provide a new method for decreasing cost but elevating photovoltaic performance of DSSCs.

2. Experimental section

2.1. Preparation of RuSe and RuCoSe CEs

The RuSe and RuCoSe CEs were made by electrodepositing Se, Ru and Co species on cleaned FTO (F-doped tin oxide) glass substrates using a galvanostatic method. In details, a homogeneous solution containing 2 mM SeO_2, 2 mM $RuCl_3$, 1 mM $CoSO_4$, and 100 mM LiCl was made by dissolving corresponding compounds in deionized water. The deposition procedures were performed in a three-electrode cell equipped with CE of a Pt plate, working electrode of an FTO substrate, and reference electrode of an Ag/AgCl (3 M KCl). The current density was controlled at 0.25 mA cm^{-2} at air and the deposition time was 600 s. Finally, the CEs were thoroughly rinsed by deionized water and vacuum dried at 60 °C.

2.2. Preparation of TiO_2 photoanodes

A TiO_2 colloid was synthesized by a sol-hydrothermal method [6]. Briefly, 100 mL of deionized water was mixed with 10 mL of titanium tetrabutanolate under vigorous agitation at room temperature. After hydrolysis for 30 min, the above-mentioned mixture was pump-filtrated to obtain dehydrated filter powders. Subsequently, 10 mL of acetic acid and 0.8 mL of nitric acid were added into the above filter powders dropwise in a flask. Upon agitation

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* Corresponding author.
E-mail address: tangqunwei@ouc.edu.cn (Q. Tang).

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for 15 min at 80 °C, the total volume of the mixture was adjusted to 170 mL by adding deionized water. The reactant was further agitated at 80 °C for 15 min in a sealed atmosphere. Subsequently, the resultant colloid was transferred into a Teflon-lined autoclave and heated at 200 °C for 12 h. A homogeneous mixture consisting of 65 mL of white colloid and 0.4 g of commercial P25 was made under ultrasonic irradiation for 30 min and then transferred to another Teflon-lined autoclave, which was subsequently heated at 200 °C for 12 h. After removing the supernatant liquid, the colloid was mixed with 0.8 g of poly(ethylene glycol) (M_w = 20,000) and 1 mL of OP emulsifier, which was concentrated at 80 °C to obtain TiO_2 colloid. A layer of TiO_2 film with an average thickness of 10 μm and active area of 0.25 cm^2 was made by coating TiO_2 colloid on an FTO glass substrate. Finally, the TiO_2 film was calcined at 450 °C for 30 min and sensitized by 0.25 mmol dm^{-3} N719 ([*cis*-di(thiocyanato)-N,N'-bis(2,2′-bipyridyl-4-carboxylic acid)-4-tetrabutylammonium carboxylate], purchased from DYESOL LTD, Australia) ethanol solution for 24 h to obtain N719 dye-sensitized TiO_2 photoanode.

2.3 Assembly of dye sensitized solar cells

Each dye-sensitized solar cell device was assembled by sandwiching a liquid electrolyte having I^-/I_3^- couples between a dye-sensitized TiO_2 photoanode and a counter electrode to form an architecture of FTO| TiO_2/N719|liquid electrolyte|Pt(RuSe or RuCoSe). The redox electrolyte consisted of 100 mM tetrabutylammonium iodide, 100 mM tetraethylammonium iodide, 100 mM tetramethylammonium iodide, 100 mM NaI, 100 mM KI, 100 mM LiI, 50 mM I_2, and 500 mM 4-*tert*-butyl-pyridine in 50 mL acetonitrile.

2.4 Properties tests

All the photocurrent-voltage (*J-V*) curves of dye sensitized solar cells were performed using an electrochemical workstation (CHI660E, Shanghai Chenhua Device Company, China) under simulated solar light irradiation (a 100 W xenon arc lamp, XQ-500 W, 100 mW cm^{-2}) in an ambient atmosphere.

2.5 Electrochemical characterizations

The cycle voltammetry (CV) curves and electrochemical impedance spectroscopy (EIS) plots were achieved by scanning a symmetric dummy cell. The CV curves were recorded by scanning from 0 to + 0.6 V and back to 0 V at a scan rate of 20 mV s^{-1}, while the EIS plots were measured in a frequency ranging from 0.1 to 1 × 10^6 Hz with an ac amplitude of 5 mV.

3. Results and discussion

Fig. 1a shows the schematic diagram of the dye sensitized solar cell, it is made of a mesoscopic TiO_2/N719 photoanode, a redox electrolyte having I^-/I_3^- couple and a CE from Pt, RuSe or RuCoSe. The solar-to-electric processes are driven by obeying photoelectric conversion principle [7], as shown in Fig. 1b. In details, photosensitive N719 dyes absorb photons from incident light and release photogenerated electrons to mesoscopic TiO_2, which transfer to FTO layer along percolating TiO_2 pathways and finally to CE through external circuit. I^- ions in redox electrolyte reduce oxidized dye molecules and convert into I_3^- ions, which diffuse to CE surface and are reduced back to I^- species catalyzed by CE. In this fashion, the energy source is incident solar light and the final electricity output only dependents on light absorption and conversion.

The photovoltaic performances of dye sensitized solar cells are evaluated by comparing their photovoltaic parameters. Fig. 2A shows the characteristic *J-V* curves recorded under simulated sunlight illumination and the parameters are summarized in Table 1, yielding a η of 7.03% for Pt tailored device. The high cost of preferred Pt CE has been an economic burden for commercialization of mesoscopic-structured photovoltaics, therefore a crucial issue is to develop Pt-free but robust CE candidates [8–11]. By replacing Pt with Pt-free CoSe, RuSe and RuCoSe CEs, the resultant solar cells generate increased efficiencies of 7.53%, 7.81% and 9.07%, respectively, benefiting from increased catalytic activity of metal selenide alloy CEs. Electrochemical characterizations including CV and EIS are used to evaluate electrodic reaction processes. Two pairs of redox peaks are recorded for all CV curves (Fig. 2B), indicating a two-electron reaction in $I_3^- \leftrightarrow I^-$ interconversion. $I_3^- + 2e^- = 3I^-$ is the major process at CE surface, therefore J_{Red1}, E_{pp} and τ are crucial parameters in controlling total catalytic reaction kinetics. In comparison with expensive Pt CE, an increased J_{Red1} and reduced E_{pp} suggest that more electrons participate in the I_3^- reduction process with less energy requirement.

Top-view SEM image in Fig. 3A demonstrate a high surface coverage of porous RuCoSe nanostructure. The loose structure provides large alloy/electrolyte interface and much more channels for I_3^- reduction reaction. The nanostructure of RuCoSe alloy CE was investigated by X-ray diffraction (XRD) in Fig. 3B. The peaks at 2θ = 27.0°, 54.6° and 61.6° match well with (1 1 3), (0 3 1) and (1 0 3) facets of Se (#24-1202, #47-1515, #27-0601) respectively. The narrow and sharp peak at 2θ = 33.5° match well with (2 1 0) facet of $RuSe_2$ (#03-1198). The peak at 2θ = 37.6° match well with (2 1 1) facet of $CoSe_2$ (#09-0234). And the peak at 2θ = 51.5° match well with (2 0 0) facet of Co (#15-0806). The compositions of the as-synthesized metal selenide alloys were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES), showing atomic ratios of 0.995:1.000 (CoSe), 0.998:1.000 (RuSe), and 0.993:0.997:1.000 (RuCoSe). The final atomic ratios are close

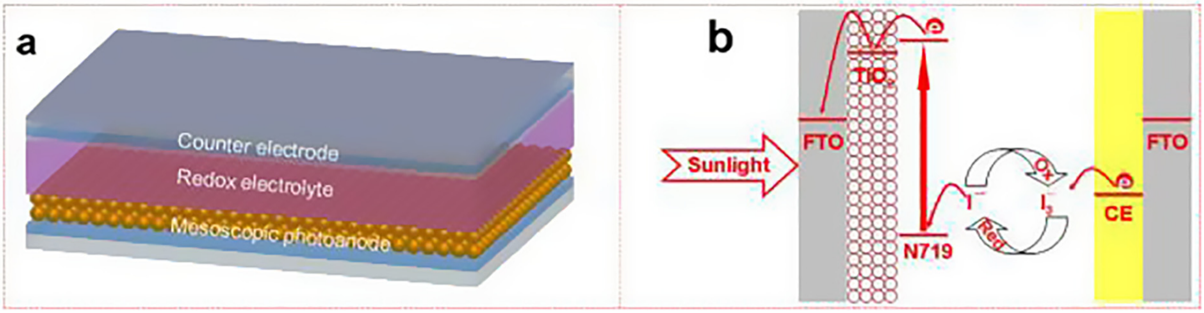

Fig. 1. (a) Schematic diagram and (b) photoelectric conversion processes for the dye sensitized solar cell.