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Counter electrodes from binary ruthenium selenide alloys for dye-sensitized solar cells

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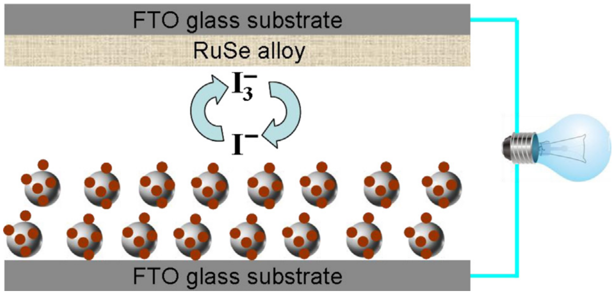
HIGHLIGHTS

- Binary Ru–Se alloy CEs are prepared by a mild hydrothermal reduction method.
- The counter electrode from RuSe alloy CE has superior electrocatalytic activity.
- A power conversion efficiency of 7.15% is recorded from RuSe alloy CE based DSSC.
- The new concept is instructive in designing efficient and cost-effective DSSCs.

GRAPHICAL ABSTRACT



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ABSTRACT

Dye-sensitized solar cell (DSSC) is a promising solution to global energy and environmental problems because of its merits on clean, cost-effectiveness, relatively high efficiency, and easy fabrication. However, the reduction of fabrication cost without sacrifice of power conversion efficiencies of the DSSCs is a golden rule for their commercialization. Here we design a new binary ruthenium selenide (Ru–Se) alloy counter electrodes (CEs) by a low-temperature hydrothermal reduction method. The electrochemical behaviors are evaluated by cyclic voltammogram, electrochemical impedance, and Tafel measurements, giving an optimized Ru/Se molar ratio of 1:1. The DSSC device with RuSe alloy CE achieves a power conversion efficiency of 7.15%, which is higher than 5.79% from Pt-only CE based DSSC. The new concept, easy process along with promising results provide a new approach for reducing cost but enhancing photovoltaic performances of DSSCs.

1. Introduction

Dye-sensitized solar cells (DSSCs) demonstrate advantages over other solar cells due to simple fabrication procedures, environmental friendliness, and relatively high power conversion efficiency [1–3]. As a key component, the counter electrode (CE) plays a role of collecting electrons from external circuit and catalyzing the reduction reaction of redox electrolyte ($I_3^- \rightarrow I^-$) [4–6]. Fluorine-doped tin oxide (FTO) conductive glass supported Pt is an effective CE for DSSC devices, however, the high cost from limited resource has been one of the main restrictions for DSSC commercialization [7]. By addressing this issue, it is a prerequisite to develop alternative CEs with low cost as well as high conduction, electrocatalysis, and readily availability.

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Moreover, the DSSCs assembled from such alternative CEs should have high power conversion efficiencies in comparison with that from Pt CE.

To date, conducting polymers (such as polyaniline and polypyrrole) [8–10], carbon materials (such as graphene and carbon nanotube) [11–13], or their composites have been widely employed as CE candidates due to their good electrocatalytic activity, low cost, simple synthesis, versatile processability, high electrical conductivity, and good environmental stability. Because of the relatively low electron-conduction of conducting polymers and low electrocatalysis of carbon materials, their composites are believed to combine the merits of single components. However, previous researches are focusing on chemical, physical or electrochemical combination [14,15]. The disadvantage of the proposed approaches is relatively high interfacial resistance between conducting polymers and carbon materials, which gives a low charge-transfer kinetics. In our previous reports [16–19], we proposed a reflux synthesis of conducting polymer/carbon material complexes, in which conducting polymers were bonded onto carbon materials via covalent bonding between N atoms (electron donor) and C atoms (electron acceptor). The power conversion efficiencies of the resultant DSSCs were also significantly enhanced in comparison with those using traditional composite CEs. More recently, Ma and coworkers have reported the employment of carbides, nitrides, and oxides as effective CE materials in catalyzing I_3^-/I^-, T_2/T^-, Co^{3+}/Co^{2+} redox couples [20]. Recently, binary alloys from Au–Ag have been employed as counter electrode material in DSSC, demonstrating a conversion efficiency of 7.85% [21]. More recently, we have reported the synthesis of low-Pt alloy CEs by an electrochemical deposition route for efficient DSSC application, giving an impressive efficiency of 10.23% from $CoPt_{0.02}$ alloy CE [22,23]. Also, a series of Pt–Ru alloys were deposited onto conductive glass substrate by a hydrothermal reduction method, showing an efficiency of 6.80% from $PtRu_3$ alloy CE based DSSC [24]. Although the research on binary alloy CEs is in a preliminary state, the impressive photovoltaic performances have demonstrated them to be good alternatives for DSSC application.

In the search for a new class of efficient and cost-effective CEs, we report here the employment of binary ruthenium selenide (Ru–Se) alloys as a way to replace Pt without sacrifice of power conversion efficiencies of the DSSCs. The mild hydrothermal reduction method is believed to be versatile in synthesizing various binary alloy CEs.

2. Experimental

2.1. Preparation of Ru–Se alloy CEs

The feasibility of this strategy was confirmed by following experimental procedures: A mixing aqueous solution consisting of Se powders, $RuCl_3$, and polyvinylpyrrolidone (PVP) was made by agitating Se ultrafine powders (0.001, 0.002, 0.004, 0.006, and 0.01 g), 5 ml of 5 mM $RuCl_3$ aqueous solution, and 1 ml of pure PVP at 60 °C. 2 ml of hydrazine hydrate (85 wt%) was dropped into the above solution, after vigorous agitating for 15 min, the reactant was transferred into a Teflon-lined autoclave and cleaned FTO glass substrate (sheet resistance 12 Ω sq^{-1}, purchased from Hartford Glass Co., USA) with FTO layer downward was immersed in. The total volume of reagent solution was adjusted at 40 ml by adding deionized water. After the reaction at 120 °C for 12 h, the FTO substrate was rinsed by deionized water and vacuum dried at 50 °C.

As references, the Ru-only and Se-only CEs were also prepared according to the above procedures. The Pt CE (300–400 μm in thickness) was purchased from Dalian HepatChroma SolarTech Co., Ltd and used as a standard.

2.2. Assembly of DSSCs

A layer of TiO_2 colloid film with a thickness of 10 μm and area of 0.25 cm^2 was prepared by a sol–hydrothermal method and subsequently calcined at 450 °C for 30 min [25]. The resultant TiO_2 nanocrystalline film was sensitized by immersing into a 0.50 mM ethanol solution of N719 dye (purchased from DYESOL LTD) for 24 h. A DSSC device was fabricated by sandwiching redox electrolyte between a dye-sensitized TiO_2 anode and an FTO supported Ru–Se alloy CE. A redox electrolyte consisted of 100 mM of tetraethylammonium iodide, 100 mM of tetramethylammonium iodide, 100 mM of tetrabutylammonium iodide, 100 mM of NaI, 100 mM of KI, 100 mM of LiI, 50 mM of I_2, and 500 mM of 4-tert-butyl-pyridine in 50 ml acetonitrile.

2.3. Electrochemical characterizations

The electrochemical performances were recorded on a conventional CHI660E setup comprising an Ag/AgCl reference electrode, a CE of platinum sheet, and a working electrode of FTO glass supported RuSe alloy. The cyclic voltammetry (CV) curves were recorded in a supporting electrolyte consisting of 50 mM M LiI, 10 mM I_2, and 500 mM $LiClO_4$ in acetonitrile. Electrochemical impedance spectroscopy (EIS) measurements were carried out in a frequency range of 0.01 Hz–10^6 kHz and at an ac amplitude of 10 mV. Tafel polarization curves were recorded by assembling symmetric cell consisting of binary Ru–Se alloy CE|redox electrolyte|binary Ru–Se alloy CE.

2.4. Photovoltaic measurements

The photocurrent–voltage (*J*–*V*) curves of the DSSCs were recorded on an electrochemical workstation (CHI600E) under irradiation of a simulated solar light from a 100 W xenon arc lamp in ambient atmosphere. The incident light intensity was calibrated using a FZ-A type radiometer from Beijing Normal University Photoelectric Instrument Factory to control it at 100 mW cm^{-2} (AM 1.5). Each DSSC device was measured at least five times to eliminate experimental error and a compromise *J*–*V* curve was employed.

2.5. Other characterizations

The compositions of the binary Ru–Se alloy CEs were detected by inductively coupled plasma-atomic emission spectra (ICP-AES). Prior to ICP measurements, the CEs were immersed in concentration nitric acid to dissolve the FTO glass substrate thoroughly.

3. Results and discussion

The compositions of the binary Ru–Se alloys on FTO glass substrates are determined by ICP-AES equipment. The results display that the atomic ratios of Ru_2Se, RuSe, $RuSe_2$, $RuSe_3$, and $RuSe_5$ are 1.93: 1.00, 1.00: 0.97, 1.00: 1.88, 1.00: 2.86, and 1.00: 4.82, respectively. The measured atomic ratios are close to the stoichiometry of Ru_2Se, RuSe, $RuSe_2$, $RuSe_3$, and $RuSe_5$, therefore, the chemical formulas of the alloy CEs can be expressed according to their stoichiometric ratios.

To investigate the electrocatalytic activity of the synthesized Ru–Se alloy CEs, cyclic voltammetry (CV) is carried out at a scan rate of 50 mV s^{-1}. Fig. 1 shows the typical voltammograms of various CEs for the redox couples (I^-/I_3^-). Two pairs of redox peaks are observed in Pt CE because of the occurrence of two-step reactions between I_3^- and I^- ions [26]. The CV curves of alloy CEs have similar peak positions and shapes to those of Pt-only CE, indicating that the resultant binary Ru–Se alloy CEs have a similar