Electrochimica Acta 168 (2015) 69–75

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Cobalt selenide nanorods used as a high efficient counter electrode for dye-sensitized solar cells

Jia Dong, Jihuai Wu *, Jinbiao Jia, Shaoyun Wu, Pei Zhou, Yongguang Tu, Zhang Lan

Eng Res. Center of Environment-Friendly Functional Materials, Ministry of Education, Institute of Materials Physical Chemistry, Huaqiao University, Quanzhou, 362021, China

ARTICLE INFO

Article history:
Received 30 December 2014
Received in revised form 12 March 2015
Accepted 31 March 2015
Available online 2 April 2015

Keywords:
Dye-sensitized solar cell
counter electrode
cobalt selenide

ABSTRACT

Cobalt selenide ($CoSe_2$) nanorods are prepared by hydrothermal method and used as an efficient Pt-free counter electrode (CE) for dye-sensitized solar cells (DSSCs). Field emission scanning electron microscopy observes that $CoSe_2$ mostly exhibits a nanorod morphology, which facilitates change carrier transfer from their surface to redox electrolyte. Cyclic voltammogram measurement indicates that $CoSe_2$ electrode has larger current density than Pt electrode. Electrochemical impedance spectroscopy shows that the $CoSe_2$ electrode with optimal condition has low series resistance of 8.034 $\Omega \times cm^2$ and has low charge-transfer resistance of 0.097 $\Omega \cdot cm^2$. Under simulated solar light irradiation with intensity of 100 $mW \cdot cm^{-2}$ (AM 1.5), the DSSC based on the $CoSe_2$ CE achieves a power conversion efficiency of 8.38 %, which is higher than the solar cell based on Pt CE (7.83%).

1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted considerable interest since it was reported by O'Regan and Gratzel in 1991 [1]. As a new kind of solar cell, DSSC displays many virtues such as low cost, easy preparation, good photovoltaic performance and environmental benignity compared with traditional photovoltaic devices [2]. A typical DSSC is consist of a TiO_2 nanocrystalline film sensitized with dye molecules, a redox electrolyte containing the iodide/triiodide (I^-/I_3^-) redox couple and a counter electrode (CE) whose main role is to collect the electrons from the external circuit and catalyze the reduction of I_3^- to I^- at the CE/electrolyte interface [3]. Usually, the counter electrodes of DSSCs are fabricated by loading platinum (Pt) on fluorine-doped tin oxide (FTO) glass. The conductive glass loaded by Pt has high conductivity, outstanding electrocatalytic activity and good chemical stability, allowing the charge on the electrode/electrolyte interface to move quickly and efficiently. However, the highly effective Pt CE of the DSSC is produced by a high-temperature hydrolysis or sputtering process. Besides, as a noble metal, Pt is expensive. So it is important to develop alternative counter electrodes with low cost, high conductivity and electrocatalytic activity for the resuction of triiodide. For this reason, much effort has been made to exploit competent substitutes for Pt CEs. The substitutes reported so far include carbon materials [4–7], conducting polymers [8–12] and inorganic compounds such as nitride [13–15], carbide [16,17], etc.

Metal chalcogenide is a prospective CE material in DSSCs owing to their high conductivity and excellent catalytic activity for the reduction of I_3^- [3]. Among them, the metal sulfides are the most researched CE materials [3,18–24]. Recently, Hsu et al. synthesized CoS nanoparticles by CTAB-assisted preparation of a metal organic framework, ZIF-67, and subsequent oxidation and sulfide conversion to CoS [18]. The generated CoS nanoparticles was used as CE for DSSCs, leading to an improved efficiency of 8.1%. Metal oxides also are used as CE materials in DSSCs [25,26], using WO_2 as a CE, the DSSC obtained power conversion efficiency of 7.25% [25], which can match the performance of the DSSC based on a Pt CE. Metal selenides are fewer reported as CE materials [27–29], although they possess good electrochemical properties. Recently, Sun et al. prepared single-crystal cobalt selenide ($CoSe_2$) nanorods by one-step hydrothermal reaction, using the $CoSe_2$ as CE, the DSSC exhibited a power conversion efficiency of 10.20% versus 8.17% for the Pt CE [27].

Here, we present another mild hydrothermal reduction method for preparing cobalt selenide ($CoSe_2$) nanorods. The DSSC based on as-prepared $CoSe_2$ CE produces a power conversion efficiency of

* Corresponding author. Tel.: +86 595 22693899; fax.: +86 595 22692229
E-mail address: jhwu@hqu.edu.cn (J. Wu).

http://dx.doi.org/10.1016/j.electacta.2015.03.226
0013-4686/

8.38% versus 7.83% for the DSSC based on Pt CE under simulated solar light irradiation with intensity of 100 mW·cm^{-2} (AM 1.5).

2. Experimental

2.1. Materials

Unless noted otherwise, all chemicals were of AR grade quality and were used as received. Sodium hydroxide, oleic acid, absolute ethyl alcohol, hydrazine hydrate (80 wt%), cyclonexane, tetra-n-butyl titanate, toluene, nitric acid, glacial acetic acid, poly (ethylene glycol) (molecule weight, 20000), Triton X-100, acetonitrile, tetramethyl ammonium iodide, tetraethyl ammonium iodide, tetrabutyl ammonium iodide, potassium iodide, iodine, were purchased from Sinopharm Chemical Reagent Co., Ltd China. Selenium powder, cobalt chloride hexahydrate, titanium tetrachloride sodium iodide, 4-tert-butyl-pyridine, lithium iodide, and lithium perchlorate were purchased from Aladding. Conducting glass plates (FTO glass, Fluorine doped tin oxide over-layer, sheet resistance 15 Ω·cm^{-1}) were purchased from Nippon Glass Co. JP. Sensitizing dye N719 {cis-[(dcbH$_2$)$_2$ Ru(SCN)$_2$]$^{2-}$, 2(n-C$_4$H$_9$)$_4$N$^+$(dcbH$_2$ = 2, 2′-bipyridine-4, 4′-dicarboxylic acid)} was purchased from Dye sol.

2.2. Synthesis of cobalt selenide nanorods CEs

The $CoSe_2$ nanorods were synthesized via a one-step hydrothermal reaction similar to the method by Wang et al. [30]. Briefly, a mixture containing 1.0 g sodium hydroxide, 0.2 g selenium powder, 0.3 g cobalt chloride hexahydrate, 8 ml oleic acid, 32 ml absolute ethyl alcohol, 10 ml hydrazine hydrate (80 wt%) and 14 ml of deionized water was added to a 100 ml autoclave and reacted at a certain temperature for 12 h. After cooled down to room temperature, the black precipitate at the bottom of the autoclave was collected, centrifuged and washed with absolute ethyl alcohol for several cycles. Then, the products were re-dispersed in hexamethylene with concentration of 0.0625 g·ml^{-1} to form cobalt selenide nanorods ink. Cobalt selenide counter electrodes (CEs) were fabricated by directly drop-casting the ink on the cleaned FTO glass and dry at room temperature. According to the reference [30] the hydrothermal reaction temperature was chosen at 140 °C, 160 °C, and 180 °C, and the corresponding products are designated as $CoSe_2$-140, $CoSe_2$-160, and $CoSe_2$-180, respectively.

2.3. Fabrication of DSSCs

To reduce the recombination of the electrons on the conductive glass with the holes, a underlayer of TiO_2 compact film was prepared by spin-casting the toluene solution of TiO_2 QDs [31] on the conductive glass once and subsequently sintered at 450 °C for 30 min in air. Then a layer of TiO_2 nanocrystal with size about 10–20 nm anode film was also prepared according to the reference [31]. After sintered at 450 °C for 30 min, the above TiO_2 anode was immersed in $TiCl_4$ aqueous solution (0.05 M) at 70 °C for 30 min to form a scattering layer, and then sintered again on the same condition. The resultant TiO_2 photoanodes were soaked in an ethanol solution of N719 dye (2.5×10^{-4} mol·l^{-1}) for 24 h to obtain dye-sensitized TiO_2 photoanode. The dye-adsorbed TiO_2 photoanode and the $CoSe_2$ counter electrode or Pt counter electrode was clipped together. One drop of liquid electrolyte was injected into the interspace between the two electrodes, and a dye-sensitized solar cell thus was fabricated. The liquid electrolyte contained 0.10 M tetramethyl ammonium iodide, 0.1 M tetraethyl ammonium iodide, 0.1 M tetrabutyl ammonium iodide, 0.1 M sodium iodide, 0.1 M potassium iodide, 0.1 M lithium iodide, 0.05 M iodine and 0.50 M 4-tert-butyl-pyridine in acetonitrile.

2.4. Measurements

The morphologies of $CoSe_2$ samples were observed by a field emission scanning electron microscopy (FESEM) (SU8000, HITACHI) and a field emission transmission electron microscopy (FETEM) (Tecnai F30). The crystal structures were analyzed by X-ray diffraction (XRD, Cu Kα radiation, SmartLab 3 kW, Rigaku, Japan). Photovoltaic tests were carried out by measuring the Current-Voltage (J-V) characteristic curves on a Keithley 2400 source meter under the illumination of AM1.5G simulated solar light coming from an AAA solar simulator (Newport-94043A) equipped with a Xe lamp (450 W) and an AM1.5G filter. The light intensity was adjusted with a reference Si solar cell (Oriel-91150). The cyclic voltammetry (CV) curves were obtained in acetonitrile solution containing 10 mM LiI, 1 mM I_2, and 0.1 M $LiClO_4$, using

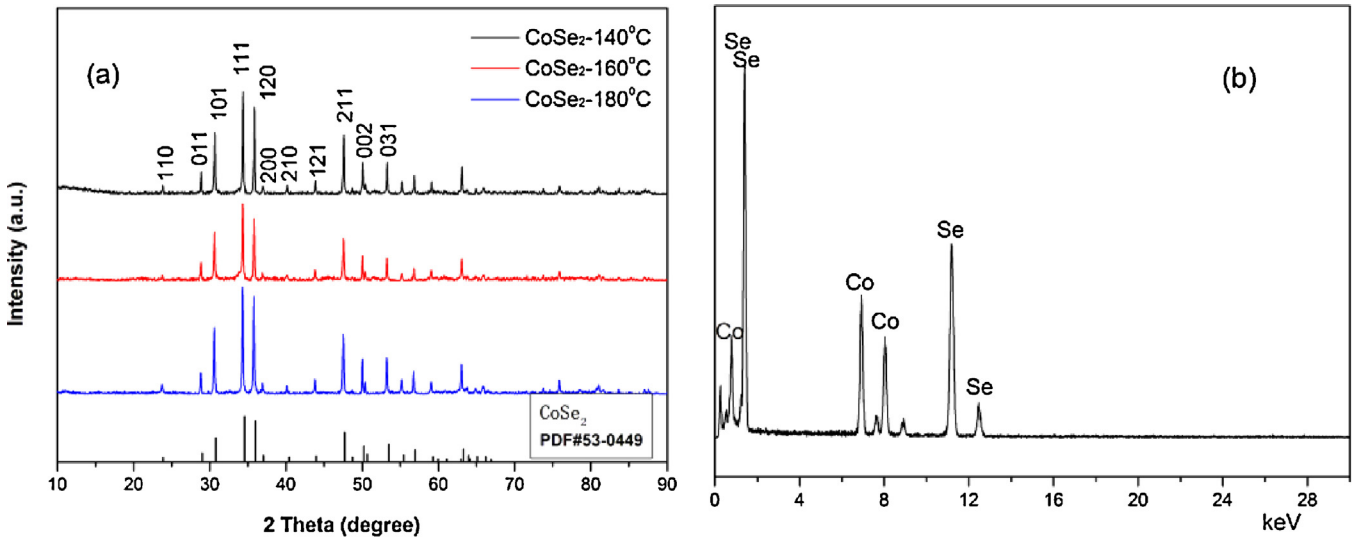

Fig. 1. (a) XRD patterns of $CoSe_2$-140, $CoSe_2$-160, $CoSe_2$-180 powders and standard $CoSe_2$, (b) Energy-dispersive X-ray spectrum of $CoSe_2$-160.