Electrochimica Acta 174 (2015) 127–132

Contents lists available at ScienceDirect

Electrochimica Acta

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

Directly hydrothermal growth of antimony sulfide on conductive substrate as efficient counter electrode for dye-sensitized solar cells

Panpan Sun, Fang Yao, Xiaoyao Ban, Niu Huang, Xiaohua Sun*

College of Materials and Chemical Engineering, Hubei Provincial Collaborative Innovation Center for New Energy Microgrid, Collaborative Innovation Center for Energy Equipment of Three Gorges Region, China Three Gorges University, Yichang 443002, China

ARTICLE INFO

Article history:
Received 24 March 2015
Received in revised form 23 May 2015
Accepted 23 May 2015
Available online xxx

Keywords:
dye-sensitized solar cells
counter electrode
Pt
antimony sulfide
electrocatalytic activity

ABSTRACT

Sb_2S_3 film was prepared on conductive substrate FTO via a facile process combining a hydrothermal procedure and post-annealing treatment, which was directly used as counter electrode (CE) for dye-sensitized solar cells (DSSCs). Electrochemical characterizations demonstrate that the as-prepared Sb_2S_3 film exhibits sufficient electrocatalytic activity and stability for catalyzing the oxidation/reduction of triiodide to iodide. When used as CE in DSSCs, device using Sb_2S_3 CE that obtained after 24 h of hydrothermal reaction achieves a maximum power conversion efficiency of 5.37%, equal to that using Pt CE (5.36%). Our study thus provides a highly desirable approach for preparing cheap and highly efficient Pt-free CEs for DSSCs, which has avoided the complicated electrode deposition procedure and large amount of material consumption.

1. Introduction

During the past two decades, dye-sensitized solar cells (DSSCs) have attracted extensive research interest owing to their high energy conversion efficiency, easy fabrication process and low manufacturing cost [1–4]. A typical DSSC is composed of a dye-sensitized nanoparticle-based mesoporous TiO_2 photoanode, a redox couple generally containing triiodied/iodide (I^-/I_3^-) and a counter electrode (CE) [5–6]. Several recent major advances in the design of TiO_2 nanostructures [7–8], dyes [9–10] and electrolytes [11–13] in DSSCs have led to record power conversion efficiencies. The CE, which performs as a catalyst for regeneration of I_3^- to I^- in the electrolyte, and a collector for electrons from the external circuit, is a critical component of DSSCs [14–15]. At present, the best performing DSSC is achieved by using platinum as CE material due to its superior conductivity, good catalytic activity and stability [9,16]. However, the low abundance and high cost of Pt noble metal has restricted the large-scale commercialization of DSSCs. Therefore, considerable efforts have been made on developing low cost Pt-free catalytic materials on the purpose of making DSSCs more competitive for future commercialization and simultaneously maintaining the good performance [17–30].

Recently, inorganic metal compounds based Pt-free catalysts for use in DSSCs developed rapidly, such as carbides [17–23], nitrides [24–26], oxides [27–29], sulfides [30–37] as well as selenides [38–39]. For example, Yang et al. reported low cost Sn_xS CE for DSSCs and demonstrated comparable power conversion efficiency to Pt [40]. Wang et al. reported DSSC with a $NiSe_2$ CE which produced a higher power conversion efficiency (8.69%) than that of DSSC with Pt CE (8.04%) [34]. Despite the high power conversion efficiency achieved from these newly developed CE materials, the complicated electrode deposition procedure on conductive substrate followed by material synthesis and large amount of material consumption render these materials disadvantageous in fabrication process [31]. Therefore, directly growth of these materials on conductive substrate which can be straightforwardly used as CE for DSSCs should be highly desirable. In this regard, Wang et al. reported in-situ growth of $Co_{0.85}Se$ and $Ni_{0.85}Se$ on FTO substrate as high-performance CEs for DSSCs, which exhibited a superior catalytic activity than Pt and generated a promising power conversion efficiency of 9.4% [41]. Huang et al. directly fabricated NiS nanoplatelet arrays on FTO substrate as CE in DSSCs, and achieved a comparable power conversion efficiency to that using Pt CE [42].

Among numerous inorganic metal compounds, antimony sulfide (Sb_2S_3) has emerged as a promising light absorber material in semiconductor-sensitized solar cells [43–45]. Electrocatalytic properties of Sb_2S_3 crystal have seldom been reported, until recently Liu et al. demonstrated the good electrocatalytic activity of Sb_2S_3 crystals with exposed (151) and (211) facets [46]. However, to the best of our knowledge, directly growth of Sb_2S_3 on conductive substrate as CE for use in DSSCs has not been investigated so far. Herein, we report a facile strategy to directly

* Corresponding author.

http://dx.doi.org/10.1016/j.electacta.2015.05.138
0013-4686/

fabricate Sb_2S_3 film on FTO substrate, and use it as CE to assemble DSSC after a post-annealing treatment. Experimental results have demonstrated the electrocatalytic activity of the as-prepared Sb_2S_3 film toward I^-/I_3^- redox couple. When used as CE in DSSCs, Sb_2S_3 film based device exhibits a promising power conversion efficiency of 5.37%, in comparison with that of DSSC based on Pt CE (5.36%), demonstrating its potential use to replace expensive Pt for the fabrication of DSSCs.

2. Experimental Section

2.1. Preparation of the Sb_2S_3 film on FTO substrate

The Sb_2S_3 film was grown on FTO substrate by the reported hydrothermal method with some modification [46]. In a typical preparation, 0.3 g of antimony trichloride ($SbCl_3$), 0.4 g of thiocarbamide and 0.4 g of poly-(binylpyrrolidone) (PVP) were added to 38 mL of ethanol. The mixture was stirred for 20 min to form a light yellow precipitate. Then the precipitate was transferred to 80 mL of deionized water and stirred for another 15 min before transferred to the autoclaves. Afterwards, clean FTO substrates ($2.5 \times 2.5\,cm^2$) were placed upright in the autoclaves with the conducting side facing down. The autoclaves were heated to 150 °C and kept at a constant temperature for 4-24 h. After cooling down to room temperature in air, the FTO substrates were taken out of the autoclaves, rinsed with deionized water, dried in air, and annealed at 450 °C for 30 min under N_2 atmosphere.

2.2. Device fabrication

Nanocrystalline TiO_2 photoanode prepared by the previously reported procedure [11] were immersed overnight in a dry ethanol solution (0.3 mM) of N719 dye at room temperature and subsequently carefully rinsed with ethanol to remove unadsorbed dye. Pt CE was prepared as a reference by chemically depositing platinum from 0.1 M hexachloroplatinic acid in 2-propanol onto FTO substrates. The electrolyte consisted of 0.6 M 1, 3-dimethylimidazolium iodide, 0.1 M guanidinium thiocyanate, 0.05 M LiI, 0.03 M I_2, and 0.5 M 4-tert-butylpyridine in acetonitrile. Sandwich cells were then prepared by clamping together the TiO_2 photoanode with the counter electrode. The electrolyte was then injected into the space between the two electrodes to complete the cell fabrication.

2.3. Characterizations

The morphology of the Sb_2S_3 film was observed with a Hitachi S4800 field emission scanning electron microscope (FESEM). The crystalline phase and structure of the Sb_2S_3 film was characterized by using a Rigaku D/max-2500 X-ray diffractometer. Transmittance spectra of the Sb_2S_3 film were collected on a UV-Vis-NIR spectrophotometer. Photovoltaic performance of DSSCs and electrochemical properties of Sb_2S_3 film were characterized by using an electrochemical workstation (CHI600d). The photocurrent-voltage (J-V) curves were recorded under AM 1.5G simulated solar irradiation from a Solar 3A simulator (Oriel), and the active area of the solar cells was determined to be 0.25 cm^2. Cyclic voltammetry (CV) measurements were conducted in a three-electrode system at a scan rate of 50 mV s^{-1}, using Pt wire as CE, Ag/Ag^+ as reference electrode and the as-prepared Sb_2S_3 film as working electrode. The I^-/I_3^- electrolyte was consisted of 0.1 M $LiClO_4$, 10 mM LiI and 1 mM I_2 in acetonitrile. For electrochemical impedance spectroscopy (EIS) and Tafel polarization measurements, a symmetrical dummy cell was assembled with two identical CEs filled with electrolyte used in DSSCs. In EIS test, the frequency range was from 100 mHz to 0.1 Hz, and the applied bias voltage and ac amplitude were set as 0 V and 10 mV, respectively. Tafel measurements were carried out at a scan rate of 20 mV s^{-1}.

3. Results and discussion

Fig. 1 presents the XRD pattern of the Sb_2S_3 film grown on FTO substrate at 150 °C for 24 h followed by a post-annealing treatment at 450 °C for 30 min. Except for the diffraction peaks attributed to the FTO substrate, the as-prepared Sb_2S_3 displays characteristic patterns associated with stibnite structure (PDF card. 06-0474), which has been presented at the bottom as a reference, indicating that crystalline Sb_2S_3 has been successfully grown on FTO substrate using a simple hydrothermal procedure. After the hydrothermal procedure, FTO substrate remains highly transparent when the growth time is less than 4 h, which exhibits slightly lower optical transmittance than FTO, as shown in Fig. 2. As the growth time increases, optical transmittance of Sb_2S_3 film in the visible light region decreases to 40% after 8 h of growth and finally to $< 20\%$ after 24 h of growth, indicating the increasing loading amount of Sb_2S_3 crystals on FTO substrate.

Fig. 3 shows the SEM images of the as-synthesized Sb_2S_3 films grown at 150 °C for 4 h, 8 h and 24 h, respectively. Typical SEM images in Fig. 3a-b reveal that Sb_2S_3 crystals obtained under 150 °C for 4 h exhibit a sheet structure that covers the surface of FTO substrate. From the clear surface texture of FTO glass, we can conclude that the loading amount of Sb_2S_3 in this case is small, which is not sufficient to cover FTO surface and can explain the high transparency of the film. After 8 h of hydrothermal reaction (see Fig. 3c-d), island structure of micrometers scale forms on the surface of FTO substrate which increases the loading amount of Sb_2S_3. However, the FTO surface coverage is still low. As the growth time is extended to 24 h, the FTO substrate has been fully covered with Sb_2S_3 crystals (Fig. 3e-f). We note that the adhesion of the Sb_2S_3 film on FTO substrate is strong enough in all cases, which ensures that the film is not easy to be scraped off.

To evaluate the electrocatalytic activity of the Sb_2S_3 film for the reduction of triiodide to iodide, the as-prepared Sb_2S_3 films designated as Sb_2S_3-4 h, Sb_2S_3-8 h and Sb_2S_3-24 h were assembled in DSSCs as CEs with Pt CE as a reference. Fig. 4 shows the current density-voltage (J-V) characteristics of DSSCs measured under AM1.5 solar simulator illumination (100mW/cm^2). Detailed photovoltaic parameters are presented in Table 1. It can be seen that DSSC fabricated with Sb_2S_3-4 h CE has an open-circuit voltage (V_{oc}) of 0.66 V, a short-circuit current (J_{sc}) of 13.4 mA/cm^2, a fill factor (FF) of 41.4%, yielding an overall conversion efficiency (η) of 3.66%. These parameters, however, are all enhanced with the extension of growth time for Sb_2S_3 film. Finally, when the growth

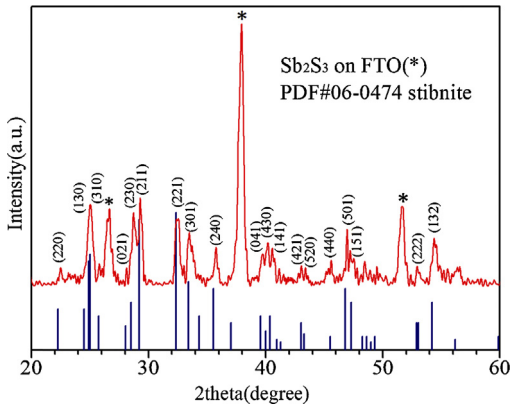

Fig. 1. XRD of Sb_2S_3 film grown at 150 °C for 24 h on FTO substrate and then annealed at 450 °C for 30 min in N_2 atmosphere.