Electrochimica Acta 133 (2014) 174–179

Contents lists available at ScienceDirect

Electrochimica Acta

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

Cobalt sulfide thin film as an efficient counter electrode for dye-sensitized solar cells

S. Srinivasa Rao, Chandu. V.V.M. Gopi, Soo-Kyoung Kim, Min-Kyu Son, Myeong-Soo Jeong, A. Dennyson Savariraj, K. Prabakar, Hee-Je Kim*

School of Electrical Engineering, Pusan National University, San 30, Jangjeong-Dong, Gumjeong-Ku, Busan-609 735, South Korea

ARTICLE INFO

Article history:
Received 17 January 2014
Received in revised form 19 March 2014
Accepted 1 April 2014
Available online 15 April 2014

Keywords:
Nano rose petal like structure
Dye sensitized solar cell
Cobalt sulfide
Counter electrode
Charge transfer resistance

ABSTRACT

The power conversion efficiency of dye sensitized solar cells (DSSCs) was improved using a nano rose petal like structured cobalt sulfide (CoS_2) counter electrode (CE) with an iodine triiodide (I^-/I_3^-) electrolyte. The CoS_2 nano rose petals like structure with a mean film thickness of 280 nm prepared using a solution containing 0.1 M cobalt chloride, 0.8 M urea and 0.8 M thioacetamide by inexpensive chemical bath deposition at 80 °C for 3 h resulted in an improved fill factor, short circuit current and open circuit voltage compared to the Pt electrodes. Tafel polarization and electrochemical impedance spectroscopy showed that CoS_2 electrode has smaller charge transfer resistance than Pt electrodes. DSSC fabricated with the CoS_2 CE achieved a power conversion efficiency of 5.32% under 1 sunlight illumination (100 mW cm^{-2}, AM 1.5 G), which surpassed that of the device based on Pt (5.02%).

1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted considerable interest because of their ease of fabrication such as roll-printing technique, low manufacturing cost and environmental friendliness [1,2]. DSSCs are fabricated mainly on titanium dioxide (TiO_2) photoanodes sensitized with N719 dye, a redox electrolyte and platinum (Pt) counter electrode (CE). Recently, DSSC achieved a conversion efficiency of 11.1% using Pt CE [3]. Fluorine-doped tin oxide (FTO) is commonly used as a substrate because of its stability under atmospheric conditions and cost effectiveness compared to indium tin oxide. In DSSCs, the dye plays a key role in increasing the power conversion efficiency and stability. In addition, it increases the electrostatic binding with the TiO_2 surface at lower pH and the dye absorbs sunlight in the visible range. The redox electrolyte, iodide/triiodide (I^-/I_3^-) is a key constituent and an inorganic component in DSSCs, which helps to reduce the power conversion efficiency losses [4]. In DSSCs, the photo electrodes are made from TiO_2 or ZnO because of their high chemical stability. As a result, this kind of photo electrode when exposed to light prevents photo corrosion, resulting in an increased lifetime [5]. Pt plays an important role as a CE in DSSC devices because of its high conductivity and strong chemical stability to increase electron transport towards I_3^- reduction, and has achieved high incident photon to charge carrier efficiency (IPCE) [1,6,7]. Despite these advantages, less abundance and high cost of Pt limits its application towards the commercialization of Pt electrodes in DSSCs [8,9]. For this reason, dynamic research has been focused on the development of cheaper, viable alternatives to Pt without compromising the efficiency using inorganic materials such as metal sulfides, metal nitrides and metal selenides, which have strong electrocatalytic activity as CE materials. Cobalt sulfide (CoS_2) has been proposed as an alternative electrocatalyst to Pt because of its excellent catalytic ability towards I_3^- reduction and inexpensive feedstock [10–14]. Recently, acicular nanorods array-based CoS CE achieved comparable conversion efficiency of Pt CE because of its higher surface area and strong electrocatalytic ability towards the I^-/I_3^- electrolyte [15]. Mingkui Wang et al. [11] synthesized CoS using one-step electrochemical deposition method and reported a photovoltaic conversion efficiency of 6.5%, which is the same as Pt-based DSSC. This suggests that abundant CoS_2 can replace high cost Pt as a CE in DSSC.

In this study, CoS_2 coated on FTO were prepared using an inexpensive chemical bath deposition (CBD) method at different deposition times and concentrations, which resulted in different size distribution of CoS_2. The resulting CoS_2 thin film had a thickness of 280 nm and was used as a counter electrode in DSSCs and achieved highest conversion efficiency of 5.32%.

* Corresponding author. Tel.: +82 51 510 2364; fax: +82 51 513 0212.
E-mail addresses: prabakar@pusan.ac.kr (K. Prabakar), heeje@pusan.ac.kr (H.-J. Kim).

http://dx.doi.org/10.1016/j.electacta.2014.04.010
0013-4686/

2. Experimental

2.1. Preparation of TiO_2 electrode films

The FTO substrate with a sheet resistance of 10Ω/square (Sigma-Aldrich) was used to prepare photoanodes. The substrates were cleaned ultrasonically with acetone, ethanol and deionized water for 10 min each and finally dried with nitrogen gas. The photo electrodes were prepared using a commercially available nanoporous TiO_2 paste with a particle size of 20 nm (Ti-Nanoxide HT/SP Solaronix). TheTiO_2 paste was spread over a FTO substrate using the doctor blade technique followed by annealing at 450 °C for 30 min to remove the organic substances. The TiO_2 paste was applied again and the same procedure was repeated as mentioned above. The thickness of the TiO_2 electrode was found to be 8.3 μm and was used for the fabrication of DSSCs.

2.2. Preparation of CoS_2 counter electrode

All chemicals for the fabrication of the CoS_2 thin films were purchased from Sigma-Aldrich and used without further purification. The CoS_2 thin films were synthesized by a simple chemical bath deposition (CBD) process at different deposition times. Cobalt chloride ($CoCl_2.6H_2O$) and thioacetamide were used as the cobalt and sulfur sources, respectively. Water (H_2O) and urea (CH_4N_2O) were used as the solvent and stabilizing agent, respectively. CoS_2 thin films were deposited on FTO by changing the concentrations of thioacetamide and CH_4N_2O at a deposition times of 1, 2 and 3 h. Ultrasonically-cleaned FTO glass substrates were immersed in a mixture of 0.1 M $CoCl_2.6H_2O$, 0.4 M CH_4N_2O and 0.4 M of thioacetamide, and placed in a hot air oven maintained at 80 °C for 1, 2 and 3 h. After completing the reaction, the thin films were washed with deionized water, ethanol and annealed at 60 °C for 1 h. No CoS_2 thin films were deposited on the FTO glass substrates when the deposition time was less than 1 h. On the other hand, a visible CoS_2 coating was observed on the FTO glass substrate when the deposition time was at least 2 h. The films deposited for 2 and 3 h are denoted as FC2 and FC3, respectively. The concentrations of thioacetamide and urea were changed from 0.4 to 0.8 M to prepare the CoS_2 thin films for the same deposition time of 2 and 3 h and temperature of 80 °C, are named as EC2 and EC3 respectively.

2.3. Materials characterization techniques

X-ray diffraction (XRD, D/Max-2400, Rigaku) was performed to identify the structure and crystallinity of the CoS_2 thin films using a Cu kα source under the following conditions: 40 KV, 30 mA, and 2θrange of 20-80°. The surface features and morphology of the synthesized CoS_2 thin films were observed by field emission scanning electron microscopy (FE-SEM, S-4200, and Hitachi) operated at 15KV. The thickness of the electrode was estimated employing Nanosystems NV-2000 interferometer. The electrocatalytic ability of the CoS_2 thin films were examined by Tafel polarization analysis for the symmetric CoS_2 films deposited on FTO substrates using an electrochemical workstation under dark conditions at a scan rate of 10 mV/s and potential (E) ranging from -1 to +1 V [11,16]. The detailed fabrication of the symmetric cell is reported elsewhere [17]. Electrochemical impedance spectroscopy (EIS) was performed using a Biologic potentiostat/galvanostat/EIS analyzer (SP-150, France) under 1 sun illumination. Impedance analysis software Z view was used to measure the impedance parameters. The photocurrent density-voltage (J-V) characteristics of the DSSCs were examined using an ABET Technologies (USA) solar simulator under 1 sun illumination (100 mW cm^{-2}, AM 1.5G). The optical absorption of the CoS_2 thin films were measured using an OPTIZEN 3220 UV spectrophotometer.

Table 1
Atomic percentage of Cobalt (Co) and Sulfur (S) in various concentrations of urea, thioacetamide and different deposition time (2, 3 h).

CEs	Atomic% of Co	Atomic% of S
FC2	33.06	66.94
FC3	42.43	57.57
EC2	24.27	75.73
EC3	40.67	59.33

3. Results and discussion

Fig. 1 shows high resolution SEM images of FC2, FC3, EC2 and EC3 CEs deposited on a FTO substrate by CBD. The CoS_2 thin films deposited at low urea and thioacetamide concentrations (0.4 M) for 2 and 3 h showed nanorose petals like structure with a different size distribution, as shown in Fig. 1a and b (FC2 and FC3, respectively). The sizes of the nano rose structured films were in the range of 250 to 500 nm. On the other hand, nano rose petals of CoS_2 were formed densely and covered the full surface when the concentration was increased from 0.4 to 0.8 M (EC2 and EC3) and observed a different size distributions and morphology on FTO. The sizes of the nano rose structured films of EC2 and EC3 were in the range of 150 to 450 nm. In addition, the thickness of the EC2 film could be observed to be about 210 nm by non contact 3D surface. The thickness is increased from 210 to 280 nm (EC3) when the deposition time was increased from 2 to 3 h. This observation indicates that the changing deposition time and concentration does not have much effect on the basic morphology of CoS_2 film.

Fig. 2 shows the XRD pattern of the CoS_2 (EC3) thin film, showing only diffraction peaks for FTO and CoS_2 thin films. The resulting XRD peaks located at 27.8°, 39.8°, 46.1°, 49.2°, 54.9°, 67.4°, 69.9°, 72.1°, 74.4°, and 76.8° 2θ were assigned to the crystal planes, [111], [211], [220], [221], [311], [400], [410], [411], [331], and [420], respectively. No impurity peaks were observed in the XRD patterns, suggesting that pure CoS_2 films were deposited on a FTO substrate, and this data matched ICDD file no. 41-1471. XRD studies confirmed that CBD is a convenient method for preparing abundant and highly conducting CoS_2 films directly on FTO.

CoS_2 is a complex metal sulphide because of its non-stoichiometric chemical composition and existence of a large number of phases [18]. Fig. 3 and Table 1 show the elemental composition of CoS_2 thin films, such as FC2, FC3, EC2 and EC3, determined by energy dispersive X-ray spectroscopy (EDX). EDX confirmed the presence of cobalt (Co) and sulfide (S) with an atomic percentage of 33.06 and 66.94, respectively, for the FC2 films. The atomic percentage of Co increased (33.06 to 42.43) and S decreased (66.94 to 57.57), when the deposition time was elevated from 2 to 3 h (FC3). The increased concentration of urea and thioacetamide (0.4 to 0.8 M) in the EC2 samples was attributed to the lower cobalt (24.27) and highest sulfide (75.73) atomic percentages compared to the FC2 and FC3 samples. The atomic percentage of Co increased (24.27 to 40.67) and S decreased (75.73 to 59.33) under the EC3 condition. This suggests that the formation of Co is faster than the S source for 3 h deposition.

The Tafel polarization test is normally performed to analyze the electrocatalytic activity of CEs [11,15]. Fig. 4 shows the Tafel polarization curves of the symmetric dummy cells measured under dark conditions at a scan rate of 10 mVs^{-1}. The Tafel polarization curves showed a logarithmic current density (J_0) as a function of the voltage (V). The anodic and cathodic slopes were in the order of EC3 > Pt > EC2 > FC3 > FC2 CEs. The electrocatalytic ability of the CE is related directly to the exchange current density (J_0). The larger