Materials Research Bulletin 61 (2015) 326–332

Contents lists available at ScienceDirect

Materials Research Bulletin

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

Effects of thiourea concentration on electrocatalytic performances of nickel sulfide counter electrodes for use in dye-sensitized solar cells

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ARTICLE INFO

Article history:
Received 7 July 2014
Received in revised form 13 October 2014
Accepted 17 October 2014
Available online 18 October 2014

Keywords:
Inorganic compounds
Catalytic properties
Electrochemical techniques
Electrochemical measurements

ABSTRACT

The low-cost nickel sulfide counter electrode (NiS CE) for the dye-sensitized solar cell (DSSC) is electrodeposited onto the fluorinated tin oxide (FTO) glass substrate by using a cyclic voltammetry (CV) approach. The influences on the morphology and electrocatalytic performances of the NiS CE are studied by changing the thiourea concentration and the cycles of the CV electrodeposition. The electrochemical impedances and photoelectric performances of various DSSCs are also investigated. The results show that the preparation conditions for the best electrocatalytic performance of the NiS CE are under 1.00 mol L^{-1} of the thiourea concentration and 10 cycles of the CV electrodeposition, and the DSSC shows a photovoltaic conversion efficiency of 5.75% under full sunlight illumination (100 mW cm^{-2}, AM 1.5 G).

1. Introduction

Since the first report of the dye-sensitized solar cell (DSSC) in 1991, it has attracted extensive attentions due to its simple production process, low cost, and relatively high energy conversion efficiency [1–8]. The DSSC is usually composed of the dye-sensitized photoanode, I^-/I_3^-redox electrolyte, and counter electrode (CE). Typically, the CE applies a transparent F-doped tin oxide (FTO) or indium tin oxide (ITO) glass coated with platinum (Pt) nanoparticles. Pt acts as a good catalyst to speed up the reduction of I_3^- to I^- [1]. In spite of Pt having high electrocatalytic activity, it is not conducive to prepare large-scale of DSSCs due to its high cost and limited resource [6].

Numerous studies have been made with the aim of displacing the noble Pt by new materials in the DSSC, such as, metal catalytic materials [9–11], carbon-based materials [12–14], conducting polymers [15–20], and inorganic compounds [21–26]. Among them, nickel (Ni) has attracted much attentions due to its abundant resource, high electrical conductivity, and excellent electrochemical properties. Joshi et al. [10] incorporated Ni into carbon nanotubes/nanofibers on the FTO glass as the DSSC CE by using a thermal decomposition process. Bajpai et al. [11] prepared a Pt-free CE by coating Ni nanoparticles onto the graphene, the results showed that Ni nanoparticles could enhance the conductivity and catalytic ability of the CE. However, Ni could be reacted in the I^-/I_3^- redox couple electrolyte, which would bring about a negative effect on the long-term stability of the DSSC. The metal sulfide (MS, M=Ni, Co, Cu, Mo, W, etc.) is a class of effective catalytic material for the I_3^- reduction reaction in DSSCs, and the main methods for the MS preparation include electrochemical deposition [23], chemical bath deposition [27], and electrostatic self-assembly methods [28,29]. Guai et al. [30] electrophoretic deposited S-doped nickel oxide CEs, and obtained a DSSC efficiency of 5.04%. Dou et al. [31] reported a nickel phosphide-embedded graphene CE prepared by the hydrothermal reaction, and received 5.70% of the DSSC efficiency. Sun et al. [23] employed nickel sulfide (NiS) as the DSSC CE by a potential reversal technique, and the achieved DSSC efficiency of 6.83% was very close to that of the Pt CE (7%). Ku et al. [32] used NiS as the CE for the thiolate/disulfide mediated DSSC by a facile periodic potential reversal technique, gained an efficiency of 6.25% against that of 3.98% based on a Pt CE.

In this paper, we electrodeposited NiS CE onto the FTO glass by using a cyclic voltammetry (CV) approach, and investigated the influences of the thiourea concentration and the cycles of the CV electrodeposition on the morphology and electrocatalytic performances of the NiS CE. Under the optimum conditions, the DSSC obtained a photovoltaic conversion efficiency of 5.75% under full sunlight illumination (100 mW cm^{-2}, AM 1.5 G).

2. Experimental

2.1. Materials

Nickel chloride, thiourea, ethanol, iodine, lithium iodide, lithium pechlorate, tetrabutyl ammonium iodide, 4-*tert*-butyl-pyridine, and

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http://dx.doi.org/10.1016/j.materresbull.2014.10.052
0025-5408/

acetonitrile were purchased from Shanghai Chemical Agent Ltd., China (analysis purity grade). Sensitized-dye N719 [*cis*-di(thiocyanato)-*N*,*N*′-bis(2,2′-bipyridyl-4-carboxylic acid-4-tetrabutylammonium carboxylate)ruthenium(II)] was purchased from Dyesol, Australia. The above agents were used without further purification. Fluorinated tin oxide (FTO) glass substrates were purchased from NSG, Japan ($8\,\Omega\,sq^{-1}$).

2.2. *Electrodeposition of NiS CEs*

Prior to the electrodeposition, FTO glass substrates (1.5 cm × 2 cm) were cleaned with deionized water and ethanol in sequence. Three kinds of different electrodeposition solutions were prepared by containing same concentration of nickel chloride ($0.05\,mol\,L^{-1}$) and adding different concentrations of thiourea ($0.75\,mol\,L^{-1}$, $1.0\,mol\,L^{-1}$, and $1.25\,mol\,L^{-1}$, respectively). The CV electro deposition of NiS thin film onto FTO glass substrates were carried out using a computer-controlled Autolab potentiostat (Type III) from an aforementioned electrodeposition solution in a three compartment cell at ambient atmosphere. A cleaned FTO glass substrate, a saturated silver/silver chloride (Ag/AgCl), and a Pt wire were used as the working electrode, the reference electrode, and the counter electrode, respectively. The parameters for NiS CEs were set under the potential interval ranging from −0.9 V to 0.7 V at a scan rate of $0.05\,V\,s^{-1}$ for 5, 10, and 15 cycles, respectively. The achieved NiS CEs were washed in distilled water and dried under a cool air flow. The parameters and sample names for the NiS CEs were listed in Table 1. For comparison, a thermal decomposition Pt CE was employed.

2.3. Assembly of DSSCs

The TiO_2 photoanodes were prepared according to our previous reports [2,5]. The resultant TiO_2 photoanodes were further sensitized by immersing them into a $0.25\,mmol\,L^{-1}$ ethanolic solution of N719 dye for 24 h, followed by air drying. After dye adsorption, the TiO_2 photoanodes were assembled with various CEs. Then the electrolyte was injected into the cell. The redox electrolyte, composed of $0.60\,mol\,L^{-1}$ tetrabutyl ammonium iodide, $0.10\,mol\,L^{-1}$ lithium iodide, $0.10\,mol\,L^{-1}$ iodine, and $0.50\,mol\,L^{-1}$ 4-*tert*-butyl-pyridine in acetonitrile, was employed in photovoltaic conversion measurements.

2.4. Characterizations and measurements

The surface features of the NiS CEs were observed using a scanning electron microscopy (SEM, JEOL-JSM-6701F) operating at 10 kV. The phase identification of the NiS CE was conducted with powder X-ray diffraction (XRD, BRUKER D8-ADVANCE). CVs for I^-/I_3^- system were measured in an acetonitrile solution consisting of $0.05\,mol\,L^{-1}$ lithium iodide, $0.01\,mol\,L^{-1}$ iodine, and $0.05\,mol\,L^{-1}$ lithium pechlorate, the potential window was −0.8 V to 1.2 V (vs. Pt) with different scan rates (50, 75, 100, and $125\,mV\,s^{-1}$) using a computer-controlled potentiostat (Autolab Type III) in a three-electrode electro-chemical cell at a constant temperature of 15 °C, the resultant CEs acted as the working electrode, a Pt-foil as counter electrode and a Pt-wire as reference electrode. The electrochemical impedance spectroscopy (EIS) measurements for the DSSCs were conducted by using an electrochemical work station system (CHI660D, Shanghai Chenhua Device Company, China) at a constant temperature of 15 °C in ambient atmosphere under a dark condition, and the impedance data covered a frequency range of $1–10^5$ Hz with 5 mV of amplitude and 0.8 V bias potential. The resultant impedance spectra were analyzed by means of the Z-view software. The photocurrent density–voltage characteristic of the DSSC was carried out using a computer-controlled CHI660D under illumination by a solar simulator (CEL-S500, Beijing Ceaulight Science and Technology Ltd., China) in ambient atmosphere. The active cell area and the incident light intensity were $0.30\,cm^2$ and $100\,mW\,cm^{-2}$ (AM 1.5 G), respectively. The photoelectronic performances [i.e., fill factor (FF) and overall energy conversion efficiency (η)] were calculated by the following equations [33]:

$$FF = \frac{V_{max} \times J_{max}}{V_{oc} \times J_{sc}} \quad (1)$$

$$\eta(\%) = \frac{V_{max} \times J_{max}}{P_{in}} \times 100\% = \frac{V_{oc} \times J_{sc} \times FF}{P_{in}} \times 100\% \quad (2)$$

where J_{SC} is the short-circuit current density ($mA\,cm^{-2}$), V_{OC} is the open-circuit voltage (V), P_{in} is the incident light power, J_{max} ($mA\,cm^{-2}$), and V_{max} (V) are the current density and voltage in the *J*–*V* curves at the point of maximum power output, respectively.

Table 1
The preparation parameters of various NiS CEs.

CE	Thiourea concentration ($mol\,L^{-1}$)	CV cycles
NiS-a	0.75	10
NiS-b	1.00	10
NiS-c	1.25	10
NiS-d	1.00	5
NiS-e	1.00	15

3. Results and discussion

3.1. Composition of the NiS CE

XRD pattern was employed to investigate the composition of the NiS attached on the FTO glass substrate. In Fig. 1, the crystalline phase of NiS-b can be observed at 30.2, 34.8, 46.0, 53.7, and 73.0°, which are identified to be the (1 0 0), (1 0 1), (1 0 2), (1 1 0), and (2 0 2) diffraction signals, respectively, according to the Joint Committee on Powder Diffraction Standards (JCPDS card No. 75-0613) [34]. And other strong peaks are corresponding to the bare FTO glass. XRD patterns for other NiS CEs are the same as those of the NiS-b, this indicates that the NiS-based CE was successfully electrodeposited onto the FTO glass.

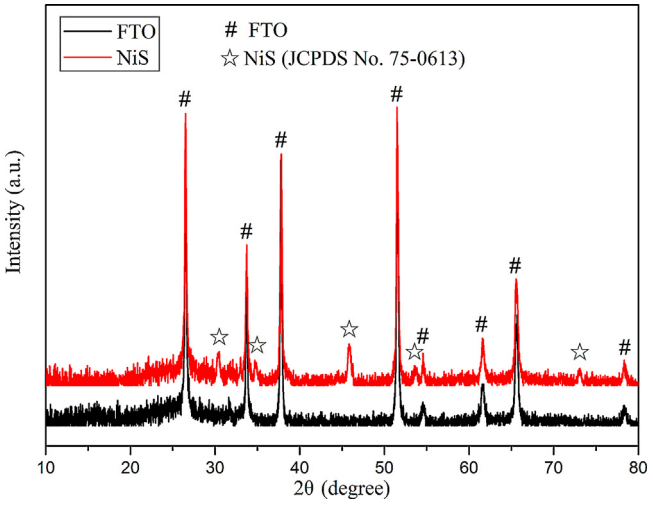

Fig. 1. XRD patterns of the bare FTO and NiS-b CE.