



# Cobalt sulfide counter electrodes enhanced by a hydro-thermal treatment for use in platinum-free dye-sensitized solar cells



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## ARTICLE INFO

### Article history:

Received 8 October 2014

Received in revised form 15 February 2015

Accepted 5 March 2015

Available online 16 March 2015

### Keywords:

Inorganic compounds

Catalytic properties

Electrochemical techniques

Electrochemical measurements

## ABSTRACT

A small quantity of uncontrollable cobalt (Co) and cobalt hydroxide (Co(OH)<sub>2</sub>), remaining in the cobalt sulfide (CoS) film prepared by the cyclic voltammetry (CV) electrodeposition method, will negatively influence the catalytic activity and stability of the CoS counter electrode (CE). The residual Co and Co(OH)<sub>2</sub> compounds are dissolved after a sodium hydrosulfide (NaHS) hydro-thermal treatment. CV, electrochemical impedance spectroscopy (EIS), and Tafel polarization curves indicate that the treated CoS CE exhibits superior electrocatalytic activity and stability for the I<sub>3</sub><sup>-</sup> reduction. The platinum-free dye-sensitized solar cell (DSSC) using the treated CoS CE obtains an enhanced photovoltaic conversion efficiency of 7.16% compared to that using the untreated CoS CE (5.59%) under full sunlight illumination (100 mW cm<sup>-2</sup>, AM1.5 G).

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## 1. Introduction

The dye-sensitized solar cell (DSSC) has currently attracted extensive attention due to its low cost, easy production and acceptable efficiency compared to conventional inorganic photovoltaic devices [1–5]. In a DSSC, the counter electrode (CE) is usually constructed of an F-doped tin oxide (FTO) glass coated with a platinum (Pt) film to speed up the reduction of I<sub>3</sub><sup>-</sup> to I<sup>-</sup>. It is true that Pt is one of the most effective catalyst material in DSSCs due to its high conductivity and catalytic activity [6]. However, the noble Pt will be dissolved to PtI<sub>4</sub> in the I<sup>-</sup>/I<sub>3</sub><sup>-</sup> redox couple electrolyte, which will result in a negative effect on the long-term stability of the DSSC [7]. For commercialization and large-scale of DSSCs [8,9], a great deal of efforts have been made with the aim of reducing or eliminating the dependence on the noble Pt, such as carbon-based materials [10,11], conducting polymers [12–15], phosphide [16], nitrides [17,18], and sulfides [19–22] have been expected to substitute for the Pt CE.

Among them, the metal sulfide is one of the most perspective catalyst material to replace the expensive Pt as a cost-effective catalyzator for the I<sub>3</sub><sup>-</sup> reduction reaction in DSSCs. Chae et al. [23] prepared a Co<sub>9</sub>S<sub>8</sub> thin film by a solution-processed deposition,

and used it as a promising CE in the DSSC with a photovoltaic conversion efficiency of 2.44%. Rao et al. [24] obtained a CoS<sub>2</sub> CE with nano rose petals like structure by a chemical bath deposition, and the DSSC based on the CoS<sub>2</sub> CE exhibited an efficiency of 5.32%. Kung et al. [25] prepared CoS acicular nanorod arrays (ANRAs) by a two-step approach: Co<sub>3</sub>O<sub>4</sub> ANRAs were firstly synthesized on FTO substrate, and then converted to CoS ANRAs by an ion-exchange reaction; a maximum efficiency of 7.67% was achieved for a DSSC with CoS ANRAs CE. Lin et al. [26] electrodeposited CoS CEs by a facile cyclic voltammetry (CV) technique to supersede the Pt CE in DSSCs, and achieved 6.33% of the DSSC efficiency. Furthermore, Tai et al. [27] firstly electrodeposited Co(OH)<sub>2</sub> nanosheet arrays on the FTO glass by a CV method, and then converted it to CoS by soaking in a chemical bath containing Na<sub>2</sub>S, finally achieved a DSSC efficiency of 6.39%. Recently, we reported that the H<sub>2</sub>S hydro-thermal treatment could enhance the catalytic activity and stability of the NiS CE, which was electrodeposited by a CV method [28].

In our preliminary experiments, we found that a small number of unexpected Co(OH)<sub>2</sub> and Co appeared in the CoS CE by the conventional CV technique, which would bring about negative effects on the electrocatalytic activity and chemical stability of the CoS CE. Here, we used a NaHS hydro-thermal treatment for the CV electrodeposited CoS CE to remove the negative effects of the Co(OH)<sub>2</sub> and Co. The Pt-free DSSC using the treated CoS CE exhibited a superior photovoltaic conversion of 7.16% than that of using the untreated CoS CE (5.59%).

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## 2. Experimental

### 2.1. Materials

Cobalt chloride, thiourea, sodium hydrosulfide, lithium iodide, iodine, lithium perchlorate, tetrabutyl ammonium iodide, ganidine thiocyanate, 4-*tert*-butyl-pyridine, and 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.

### 2.2. Electrodeposition of CoS CEs

Prior to the electrodeposition of CoS CEs, FTO glasses (with size dimension of 1.5 cm × 2 cm) were cleaned thoroughly in deionized water and ethanol for 10 min, respectively. The electrodeposition of CoS thin films onto FTO glass substrates (NSG, 8 sq<sup>-1</sup>) were carried out by a CV technique using a computer-controlled Autolab potentiostat (Type III) from an aqueous solution containing 5.0 mM cobalt chloride and 0.75 M thiourea in a three compartment cell at ambient atmosphere, in which a cleaned FTO substrate served as the working electrode, a Pt wire was used as the counter electrode, and a saturated silver/silver chloride (Ag/AgCl) acted as the reference electrode, respectively. The parameters for all the original CoS CEs were set under the potential interval ranging from -1.0V to 0.4V for 10 cycle at a scan rate of 0.05 V s<sup>-1</sup>. The achieved CoS CE was rinsed with distilled water and dried under a cool air flow, and named as CoS-a CE.

### 2.3. Sodium hydrosulfide hydro-thermal treatment of CoS CEs

The CoS CEs treated by the sodium hydrosulfide (NaHS) were arranged as follows: the original CoS-a CEs were severally placed into three Teflon-lined autoclaves, which filled with 0.01 M NaHS aqueous solution (packing volume <80%) and sealed into three stainless tanks. Then the systems were heated at 80 °C for 1 h, 3 h, and 5 h, respectively. After that, the autoclaves were naturally cooled to room temperature. The obtained samples were rinsed with deionized water for several times and dried under a cool air flow, and named as CoS-b, CoS-c, and CoS-d CEs, respectively. For comparison, the Pt CE was prepared by the thermal decomposition, in which H<sub>2</sub>PtCl<sub>6</sub> isopropanol solution with a concentration of 0.50 wt% was dipped onto the surface of the FTO glass, and followed by being heated at 450 °C for 20 min to obtain the fresh Pt CE.

### 2.4. Characterizations and measurements

The surface feature of the CoS CE was observed using a scanning electron microscopy (SEM, JEOL-JSM-6701F) operating at 10 kV. The phase identification of the CoS CE was conducted with powder X-ray diffraction (XRD, BRUKER D8-ADVANCE). CV for I<sup>-</sup>/I<sub>3</sub><sup>-</sup> system was measured in an acetonitrile solution consisting of 0.05 M lithium iodide, 0.01 M iodine, and 0.05 M lithium perchlorate, the potential window was -0.8 V to 1.2 V (vs. Pt) with different scan rates (50, 75, 100, and 125 mV s<sup>-1</sup>) using the Autolab potentiostat in a three-electrode electrochemical cell at a constant temperature of 25 °C, the resultant CEs acted as the working electrode, a Pt-foil as counter electrode and a Pt-wire as reference electrode. The active area of each CE for the CV test is about 1.50 cm<sup>2</sup>, which is controlled by the real immersing area in the above-mentioned acetonitrile solution and used to calculate the current density. The electrochemical impedance spectroscopy (EIS) measurement for the CoS CE was conducted by using an

electrochemical work station system (CHI660D, Shanghai Chenhua Device Company, China) at a constant temperature of 25 °C in ambient atmosphere under a dark condition, and the impedance data covered a frequency range of 1–10<sup>5</sup> Hz with 5 mV of amplitude and 0V bias potential. The resultant impedance spectra were analyzed by a Z-view software. Tafel polarization curve for the CoS CE was measured using the CHI660D electrochemical work station system from -1.0V to 1.0V at a scan rate of 10 mV s<sup>-1</sup>. The symmetric dummy cell used for Tafel polarization measurement is same as that used in the EIS test, and its active area (0.50 cm<sup>2</sup>) and the distance (30 m) between the two CEs were controlled by the adhesive tape around one piece of CE edge. The redox electrolyte composed of 0.60 M tetrabutyl ammonium iodide, 0.10 M lithium iodide, 0.10 M iodine, 0.10 M ganidine thiocyanate, and 0.50 M 4-*tert*-butyl-pyridine in acetonitrile, was employed in EIS, Tafel polarization, and photovoltaic conversion measurements.

Prior to the cell assembly, TiO<sub>2</sub> photoanodes were prepared according to our previous reports [8,29]. The resultant TiO<sub>2</sub> photoanodes were further sensitized by immersing them into a 0.3 mM ethanolic solution of N719 dye for 24 h, followed by air drying. After dye adsorption, the TiO<sub>2</sub> photoanodes were assembled with various CEs. Then the electrolytes were injected into the cells. The photocurrent density–voltage characteristic of the DSSC was carried out using the 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<sup>2</sup> and 100 mW cm<sup>-2</sup> (AM 1.5), respectively. The photoelectronic performances [i.e., fill factor (FF) and overall energy conversion efficiency (η)] were calculated by the following equations [30]:

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

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

where  $J_{sc}$  is the short-circuit current density (mA cm<sup>-2</sup>),  $V_{oc}$  is the open-circuit voltage (V),  $P_{in}$  is the incident light power,  $J_{\max}$  (mA cm<sup>-2</sup>) and  $V_{\max}$  (V) are the current density and voltage in the  $J$ - $V$  curves at the point of maximum power output, respectively.

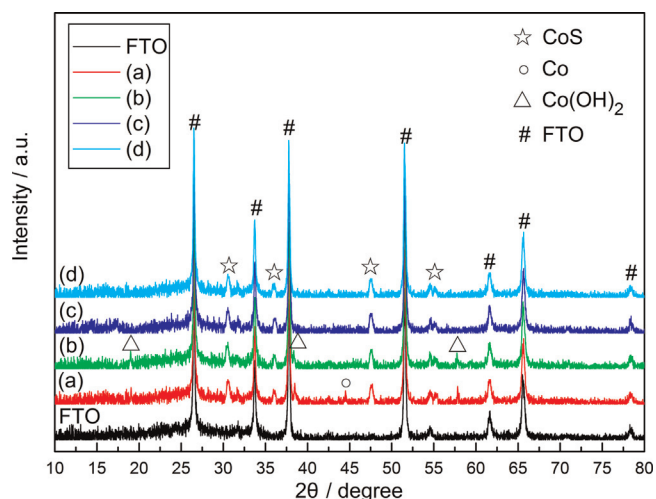


Fig. 1. XRD patterns of the pure FTO glass, (a) CoS-a, (b) CoS-b, (c) CoS-c, and (d) CoS-d, respectively.

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