

# Regulation of Microstructure and Composition of Cobalt Selenide Counter Electrode by Electrochemical Atomic Layer Deposition for High Performance Dye-Sensitized Solar Cells



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## ARTICLE INFO

### Article history:

Received 24 July 2016

Received in revised form 22 September 2016

Accepted 16 October 2016

Available online 17 October 2016

### Keywords:

Cobalt Selenide

Counter Electrode

Underpotential deposition

Electrochemical atomic layer deposition

Photoconversion efficiency

## ABSTRACT

By means of electrochemical atomic layer deposition (ECALD), cobalt selenide counter electrodes have been successfully prepared on FTO substrate for the first time. The as-grown films presented amorphous structure and their composition and microstructure could be regulated effectively by adjusting the depositing potential of Se via the route of ECALD. Cycle voltammograms and Tafel polarization measurements revealed that the cobalt selenide counter electrode exhibited an excellent catalytic activity and stability in the  $I^-/I_3^-$  system. Due to the more active catalytic sites and less charge-transfer resistance, the  $Co_{1.2}Se$  counter electrode yielded faster and more complete reduction of  $I_3^-$  to  $I^-$  than the Pt and other compositions of cobalt selenide. As a result, the dye-sensitized solar cell based on the  $Co_{1.2}Se$  counter electrode yielded a photoconversion efficiency of 9.28%, which improved by 136% than that of the DSSC based on the Pt electrode (6.84%). Taking the facility and cost efficiency into consideration, ECALD has great potential in preparing high efficient counter electrode for high performance DSSCs.

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## 1. Introduction

Dye sensitized solar cells (DSSCs) have emerged as a credible alternative to p-n photovoltaic solar cells in recent years in virtue of the high photovoltaic conversion efficiency, environmentally benign preparation process and resource-abundant raw materials [1]. In a typical DSSC, Pt is commonly employed as the counter electrode to collect electrons from external circuit and catalyze the regeneration of  $I^-$  from  $I_3^-$  [2]. However, the scarcity and high cost of noble metal Pt limit its wide application. What's more, the stability of Pt is also a concern because it suffers from serious corrosion by iodine electrolyte and forms the compounds of  $PtI_4$  and  $H_2PtI_6$  [3]. Tang and co-workers tried to alloy Pt with transition metals to prevent the Pt counter electrode from dissolving due to the competitive reactions with the iodide species [4], and many effort have been made to develop more cost-effective Pt-free

counter electrodes such as carbon materials [5] and conductive polymers [6].

Metal chalcogenides are considered to be perfect alternatives to Pt counter electrode because of their favorable catalytic activity and high chemical stability. Several metal sulfides (e.g.  $CoS$ ,  $Co_9S_8$ ,  $WS_2$  and  $CuInS_2$ ) [7–10] have been employed as effective counter electrodes and yielded considerable efficiency comparable to Pt. Recently, metal selenides have attracted much attention owing to their distinctive electronic properties, interesting chemical behaviors and a wide variety of potential applications [11]. As reported by Gong et al. [12], metal selenides presented more superior catalytic activity in the reduction of  $I_3^-$  than metal sulfides.

Nowadays, metal selenide films are mainly fabricated by the methods like hydrothermal method, solvent-thermal method, molecular beam epitaxy (MBE), metal organic chemical vapor deposition (MOCVD), successive ionic layer absorption and reaction (SILAR). Gong et al. fabricated  $Co_{0.85}Se$  and  $Ni_{0.85}Se$  counter electrodes by hydrothermal approach and achieved a remarkable conversion efficiency of 9.40% in the DSSC with the  $Co_{0.85}Se$  counter electrode [12]. Generally, the hydrothermal and solvent-thermal methods require harsh experiment conditions, such as high pressure, high temperature and long reaction time in

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various kinds of organic solvent. As for the MBE and MOCVD methods, they both need expensive apparatus and require high vacuum and air tightness. Moreover, the reactants used in MOCVD are usually inflammable, explosive and toxic. Ji et al. fabricated various metal selenides ( $\text{NiSe}_2$ ,  $\text{CoSe}_2$ ,  $\text{MoSe}_2$ ) on FTO substrates by the method of SILAR [13]. During the preparation, SILAR involves sequential immersion and rinse and appears quite troublesome with repetitive manual manipulation. In this sense, it is of great significance to develop a facile method to grow high-quality and low cost selenide film with high photovoltaic performance.

Electrochemical atomic layer deposition (ECALD) proposed by Stickney et al. [14], is the electrochemical analog of atomic layer deposition. As the basis of ECALD, underpotential deposition (UPD) is a thermodynamics phenomenon that an atomic layer of one element deposits on a second at a potential prior to that needed to deposit the element on itself [15]. By varying the deposition potential and time, the composition of deposits can be easily controlled. At present, ECALD is widely used for prepare II–VI and V–VI semiconductor compound on noble metal substrate [16–18]. In our group, various kinds of semiconductor quantum dots such as CdS, CdTe and  $\text{Ag}_2\text{S}$  have been deposited on  $\text{TiO}_2$  semiconductor substrate by ECALD [19–21]. Besides, we also tried to employ this technique to fabricate  $\text{Cu}_2\text{S}$  counter electrode on FTO [21]. However, to the best of our knowledge, there is no related work about preparing cobalt selenide counter electrode via the method of ECALD yet. In the present paper, cobalt selenide counter electrodes were deposited on FTO successfully by ECALD for the first time. By varying the depositing potential of Se and keeping the potential of Co constant, cobalt selenides with different morphology and compositions have been fabricated. The deposits without further annealing showed an amorphous feature, and the amorphous cobalt selenide electrodes exhibited superior catalytic activity and higher chemical stability towards the iodine electrolyte in compared with Pt electrode. The DSSCs assembled with the  $\text{Co}_{1.2}\text{Se}$  counter electrode yielded a maximum photoconversion efficiency of 9.28%, which increased by 136% in comparison with that of the Pt-based DSSCs under the same conditions.

## 2. Experimental

### 2.1. Preparation of cobalt selenide and Pt counter electrodes

All chemicals used were analytical grade. Se solution consists of 2 mM  $\text{SeO}_2$ , buffered with 50 mM  $\text{CH}_3\text{COONa}$  and 50 mM  $\text{NaNO}_3$ , and the pH value was adjusted to 5 with  $\text{HNO}_3$ . For Co source, the solution contained 2 mM  $\text{C}_4\text{H}_6\text{CoO}_4 \cdot 4\text{H}_2\text{O}$ , 50 mM  $\text{CH}_3\text{COONa}$  and 50 mM  $\text{NaNO}_3$ , and a solution of 50 mM  $\text{NaNO}_3$  with pH = 5 was used as the blank solution. The substrates were ultrasonically cleaned FTO glass (fluorine doped  $\text{SnO}_2$ ,  $14 \Omega/\text{sq}$ , Asahi). Cyclic voltammetry experiments (CV) were conducted on a CHI604D electrochemical workstation to study the electrochemical properties of Se and Co. ECALD process was carried out on an automated electrochemical deposition system [22]. Deposition potential and time of Se and Co were controlled by a constant potential square-wave method. A complete cycle to deposit cobalt selenide was as follows: firstly, Se solution was flowed into the thin-layer flow deposition cell for 20 s at the chosen potential for Se deposition, and held quiescent for 20 s; blank solution was then flushed into the cell for 10 s to rinse out the excessive  $\text{SeO}_2$ ; Secondary, Co solution was pumped into the cell for 15 s and held quiescent at a chosen potential for Co deposition for 15 s followed by rinsing with blank solution for 10 s. By varying the potential of Se while remaining the potential of Co constant, the composition of deposits could be adjusted to different ratios of Co and Se. All of the samples were deposited for 60 cycles without further annealing. For comparison, Pt counter electrode was prepared by drop-casting a

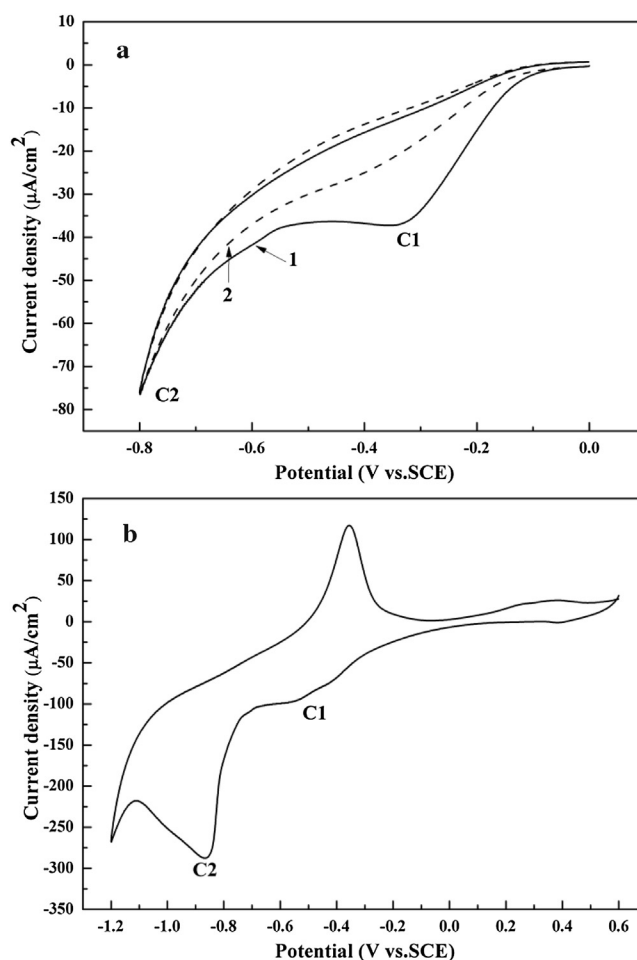
5 mM  $\text{H}_2\text{PtCl}_6$  isopropanol solution on FTO glass, followed by heat treatment at  $450^\circ\text{C}$  for 0.5 h.

### 2.2. Fabrication of DSSCs

$\text{TiO}_2$  nanocrystalline film sensitized with dye N719 was used as the photoanode. The  $\text{TiO}_2$  film prepared by doctor blade method was annealed at  $500^\circ\text{C}$  for 15 min and then immersed in a 0.17 mM N719 dye solution in acetonitrile and tertiary butyl alcohol (volume ratio = 1:1) for 24 h after cooling down to  $80^\circ\text{C}$ . The dye sensitized  $\text{TiO}_2$  films, Surlyn film spacer, different compositions of cobalt selenide counter electrodes, and Pt counter electrodes were assembled as a sandwich structure, respectively. The redox electrolyte was composed of 0.1 M LiI, 0.12 M  $\text{I}_2$ , 1.0 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII) and 0.5 M 4-tert-butylpyridine (4-TBP) and injected into the aperture between two electrodes.

### 2.3. Characterization and measurements

X-ray diffraction (XRD) profiles of the samples were obtained by a Philip X'pert X-ray diffractometer equipped with  $\text{Cu K}\alpha$  irradiation ( $\lambda = 1.5406 \text{ \AA}$ ). The microstructure of the samples was characterized by a Nova NanoSEM 450 field emission scanning electron microscope (FE-SEM). The compositions of deposit were measured with energy dispersive X-ray spectrophotometer (EDX). X-ray photoelectron spectroscopy (XPS) was acquired with an



**Fig. 1.** (a) Cyclic voltammograms of the FTO electrode in a 2 mM  $\text{SeO}_2$  solution, pH = 5. (b) Cyclic voltammogram of the Se-covered FTO electrode in a 2 mM  $\text{C}_4\text{H}_6\text{CoO}_4 \cdot 4\text{H}_2\text{O}$  solution. The scan rate is 20 mV/s.

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