Journal of Power Sources 369 (2017) 35–41

Contents lists available at ScienceDirect

Journal of Power Sources

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

Cobalt iron selenide/sulfide porous nanocubes as high-performance electrocatalysts for efficient dye-sensitized solar cells

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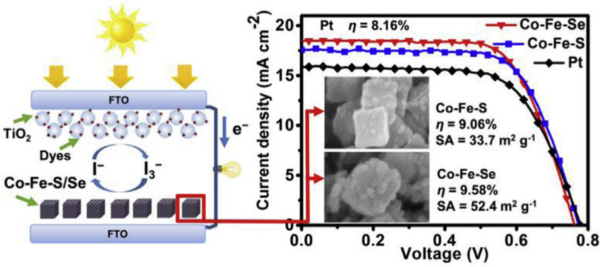
HIGHLIGHTS

- Novel Co-Fe-Se/S porous nanocubes (PNCs) were prepared by a template method.
- The PNCs were applied as efficient CE electrocatalysts for DSSCs.
- The PNCs had large surface area, high catalytic activity and good conductivity.
- The PCEs (9.58% and 9.06%) of the PNCs were higher than that of Pt (8.16%).

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 26 July 2017
Received in revised form
27 August 2017
Accepted 27 September 2017

Keywords:
Cobalt iron selenides
Cobalt iron sulfides
Porous nanocubes
Photovoltaic performances
Counter electrodes
Dye-sensitized solar cells

ABSTRACT

A novel series of ternary compounds, namely cobalt iron selenide/sulfide nanocubes, are successfully synthesized as counter electrode (CE) materials for dye-sensitized solar cells (DSSCs), which deliver excellent performances. Homogeneous cobalt iron Prussian-blue-analog (PBA) nanocubes are prepared as the templates and are subsequently dealt with selenation/sulfidation processes via hydrothermal methods. Owing to their unique morphology, porous structure, high surface area, small charge transfer resistance and high diffusion coefficient, the Co-Fe-Se/S nanocubes possess high catalytic activity and excellent conductivity, which are tested and verified by electrochemical measurements. Meanwhile, cobalt iron selenide/sulfide nanocubes CEs achieve high efficiencies of 9.58% and 9.06%, respectively, which are both higher than that of Pt CE (8.16%). All these prominent merits make them outstanding and promising participants among Pt-free CE materials of DSSCs with lower production costs and higher power conversion efficiency.

1. Introduction

Dye-sensitized solar cells (DSSCs) have been regarded as a kind of promising power conversion devices and have attracted great interest because of their characteristics, such as ease of fabrication, low expenses and high power conversion efficiency (PCE) [1,2]. A typical DSSC device is composed of a counter electrode (CE), a dye-loaded TiO$_2$ electrode and triiodide/iodide redox electrolyte. Each part has been studied to pursue better performance [3–11]. For example, Li et al. synthesized DTP-based dyes, which achieved a power conversion efficiency of 8.14% [6]. Among them, a counter electrode (CE) is viewed as one of the dominant parts of the classical DSSCs, transferring electron from outside circuit to redox electrolyte and reducing I_3^- to I^-. Conventionally, platinum (Pt) was widely applied as common commercial CE material in DSSCs, on account of its favorable and famous conductivity and catalytic

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https://doi.org/10.1016/j.jpowsour.2017.09.080
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activity [12]. However, the abundant commercial application and future development were limited and hindered by its obvious defects, such as low earth-abundance ratio, high price and ease of corrosion [13–15]. In this urgent situation, the further studies on alternatives of Pt are desperately desirable.

To date, in order to seek ideal substitutes, various materials, including transition metal compounds (TMCs) [16–19], carbonaceous materials [20–22], conductive polymers [23,24] and their hybrids [25–27] have been researched. Among them, TMCs stand out because of their low costs, Pt-like catalytic activity and excellent conductivity [1]. Carbide [17], nitrides [16], oxides [19], phosphides [18], sulfides, selenides and their hybrids have been frequently investigated. It is the sulfides and selenides that win most of the attention for not only ease of synthesis via hydrothermal method but also favorable PCEs [14,28–30]. Various alloys, such as Co_3S_4 [31], NiS_2 [26], NiS [32], FeS_2 [33,34], CoS_2 [35], CoS [36], MoS_2 [37–40], $NiSe_2$ [25], $CoSe_2$ [37–39], $FeSe_2$ [41] and so on, have been able to be approached and explored. For example, Cui et al. synthesized CoS_2 embedded carbon nanocages with a high PCE of 8.20% (Pt, 7.88%) [42]. Except the chemical composition, the morphology mainly influences the performance of CE materials in DSSCs. Flower-like [43], nanofilm [25,44–46], nanotube [47], nanocages [42] and other morphologies have been designed and investigated. Thus, the roles that the chemical composition and morphology played could not be ignored in the design of catalyst.

In this work, we chose cobalt iron Prussian-blue-analog (PBA) nanocubes as the precursors, which were hardly out of shape at high temperature but easy to convert, along with relatively high surface area [48,49]. Furthermore, the metal sulfides and selenides had great performance as CE materials in DSSCs with small charge resistance and high diffusion coefficient. For all the above reasons, we designed the synthetic routes that PBA nanocubes were prepared as the templates and subsequently treated with selenation/sulfidation processes via hydrothermal methods. Benefiting from the unique morphology, structure and composition, the devices with Co-Fe selenide and sulfide porous nanocubes delivered PCEs of 9.58% and 9.06%, respectively, which are superior to that of Pt (8.16%). Hence, the results demonstrated the excellent electrocatalytic activity and remarkable conductivity of Co-Fe selenide and sulfide porous nanocubes.

2. Experimental section

2.1. Materials

Potassium hexacyanoferrate (III) ($K_3[Fe(CN)_6]$, Sigma-Aldrich Corporation, ≥ 99.0%), cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, Aladdin Corporation, ≥ 99.0%), sodium citrate nonahydrate ($C_6H_5Na_3O_7 \cdot 9H_2O$, Aladdin Corporation, ≥ 99.0%), selenium powder (Se, Sigma-Aldrich Corporation, ≥ 99.5%), absolute ethanol (C_2H_5OH, Sigma-Aldrich Corporation, ≥ 99.7%), ethylenediamine ($C_2H_8N_2$, Aladdin Corporation, ≥ 99.6%), sodium sulphide (Na_2S, Aladdin Corporation, AR), 4-*tert*-butyl pyridine ($C_9H_{13}N$, Aladdin Corporation, ≥ 98.0%), titanium tetrachloride ($TiCl_4$, Aladdin Corporation, AR), lithium perchlorate ($LiClO_4$, Aladdin Corporation, ≥ 99.9%), iodine (I_2, Aladdin Corporation, ≥ 99.8%), lithium iodide (LiI, Aladdin Corporation, ≥ 99.0%), acetonitrile (CH_3CN, Sinopharm Chemical Reagent, ≥ 99.0%), the **N719** dye (Solaronix Corporation, Switzerland, AR) and 1,2-dimethyl-3-propylimidazolium iodide (DMPII, Aladdin Corporation, ≥ 99.0%) were directly used without any further purification. The FTO glasses were obtained from Nippon Sheet Glass (Japan) with the sheet resistance of 15 $\Omega\ sq^{-1}$.

2.2. Synthesis

2.2.1. Synthesis of Co-Fe prussian-blue-analog (PBA) cubes

In a typical synthesis, 2 mmol of potassium hexacyanoferrate (III) was dissolved in 100 mL of deionized (DI) water to form a uniform clean solution A. 3 mmol of cobalt nitrate and 4.5 mmol sodium citrate were dissolved in 100 mL of DI water to form an orange solution B. Then, the solution A was poured into solution B under vigorously stirring for 10 min. The obtained solution was aged for 2 days at ambient temperature. The black purple Co-Fe PBA nanocubes were precipitated by centrifugation and washed with water and ethanol for several times, and dried at 40 °C for 12 h under vacuum.

2.2.2. Synthesis of Co-Fe-Se nanocubes

80 mg of Se powder was added into an ethanol solution (20 mL) containing 6 mL of ethylenediamine and the mixture was stirred for 0.5 h. Then, 40 mg of the as-prepared Co-Fe PBA cubes was dispersed in absolute ethanol (20 mL) under ultrasonication for 10 min to form a uniform suspension. The suspension was poured into the above solution. The mixture was transformed into a 50 mL teflon-lined stainless-steel autoclave and heated at 160 °C for 6 h. The black sample was dried at 50 °C for 12 h under vacuum after being centrifugated and washed with ethanol. Finally, in order to increase its crystallinity, the production was annealed at 350 °C for 2 h at the heating rate of 1 °C min^{-1} under Ar atmosphere. The production was named as Co-Fe-Se. In comparison, the as-prepared Co-Fe PBA cubes were directly annealed as the same as the sample Co-Fe-Se and the sample named Co-Fe was obtained.

2.2.3. Synthesis of Co-Fe-S nanocubes

40 mg of the as-prepared Co-Fe PBA cubes and 10 mL of Na_2S aqueous solution (4 mg mL^{-1}) were added into an ethanol solution (30 mL), which were dispersed under ultrasonication. The next experimental processes of this black production, named as Co-Fe-S, were the same as that of the sample Co-Fe-Se.

2.3. Fabrications of counter electrodes

FTO glasses were washed with detergent, deionized water, acetone and ethanol in sequence. Typically, 100 mg of the obtained samples were dispersed in 10 mL of ethyl ethanol. After 30 min of sonication and stirring, a uniform ink suspension had been acquired before spinning coating on a piece of already pretreated FTO glass by spin-casting technique at a rotating speed of 500 rpm for 16 s and the covered FTO glass was heated and dried at 120 °C for 5 min. This process was repeated for several times until the coating thickness was suitable. Approximately, the loading capacity of each FTO glass is 0.67 mg cm^{-2}. As a reference, the Pt CE was obtained by thermally depositing a platinum layer (0.02 M hexachloroplatinic acid in isopropanol) on the surface of FTO at 450 °C for 30 min.

2.4. Fabrications of DSSCs

The screen-printing method was utilized to cover the transparent nanocrystalline TiO_2 layer (thickness, ~12 μm) and the scattering TiO_2 layer (thickness, ~4 μm) on the conductive side of the pretreated FTO glass with 20 and 200 nm TiO_2 sols, respectively. After being heated in air at 500 °C for 1 h, the FTO glass was immersed in 0.04 M titanium tetrachloride aqueous solution at 70 °C for 1 h and following sintered in air at 500 °C for 1 h again. Then, the cooled photoanodes were soaked and sensitized in 0.3 mM N719 dye ethanol solution overnight in a dry and dark environment. Finally, to assemble a sandwich structure of DSSCs, the I^-/I_3^- based electrolyte was injected into the vacuum space