Materials Letters 153 (2015) 114–117

Contents lists available at ScienceDirect

Materials Letters

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

$Co_{0.85}Se$ hollow nanoparticles as Pt-free counter electrode materials for dye-sensitized solar cells

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ARTICLE INFO

Article history:
Received 31 January 2015
Accepted 1 April 2015
Available online 11 April 2015

Keywords:
Solar energy materials
Dye-sensitized solar cells
Counter electrode
Cobalt selenide
Electrocatalytic activity

ABSTRACT

In this paper, $Co_{0.85}Se$ hollow nanoparticles have been successfully synthesized by a one-step solvothermal method. The $Co_{0.85}Se$ counter electrode ($Co_{0.85}Se$ CE) has been fabricated and used for dye-sensitized solar cells (DSSCs). The electrocatalytic activity of CEs has been characterized by cyclic voltammetry, Tafel-polarization curves, and electrochemical impedance spectroscopy. The results indicate that $Co_{0.85}Se$ CE with a large surface area shows the high electrocatalytic activity for the reduction of I_3^-. The power conversion efficiency of the DSSC based on $Co_{0.85}Se$ CE is obtained up to 6.03%, which is slightly lower than that of the DSSC based on Pt CE (6.45%).

1. Introduction

Transition metal chalcogenides especially cobalt selenide have attracted tremendous attention due to their distinctive electrical and magnetic properties [1]. These distinctive properties imply that there are potential applications in many areas such as solar cells, catalysis and ferromagnetism field [2–4]. To date, a wide variety of novel morphologies such as sea urchin-like $Co_{0.85}Se$ [1], graphene-like $Co_{0.85}Se$ [2], tremelliform-like $Co_{0.85}Se$ [3], Co_9Se_8 nanosheets [4], $Co_{0.85}Se$ nanotubes [5] and honeycomb-like CoSe [6] have been synthesized. However, the synthesis of $Co_{0.85}Se$ hollow nanoparticles has rarely been reported.

In solar cell application, DSSCs have become the focus because of their low-cost, simple fabrication process, and higher up scaling [7]. Many electrode materials have been explored [8]. As an important component of DSSCs, the F-doped tin oxide glasses loaded with Pt are normally used as CEs for DSSCs, due to its high electrocatalytic activity and excellent conductivity [7]. However, the high cost and diminishing supply of Pt limit the large-scale application of DSSCs. Among the alternative materials to Pt, most of metal chalcogenides exhibit a good electrocatalytic activity [2,6,9–12]. For example, DSSC based on graphene-like $Co_{0.85}Se$ CE yields a remarkable power conversion efficiency (η) because of the large surface area of graphene-like structure [2]. The large surface area may have contributed to enhance electrocatalytic activity. Therefore, hollow nanoparticles with the large surface area maybe possess the better electrocatalytic activity. Herein, $Co_{0.85}Se$ film composed of $Co_{0.85}Se$ hollow nanoparticles is fabricated and used as CE of DSSCs. The $Co_{0.85}Se$ CE shows the better electrocatalytic activity for the reduction of I_3^-. The η of DSSC based on $Co_{0.85}Se$ CE is slightly smaller than that of DSSC based on Pt CE.

2. Experimental methods

The $Co_{0.85}Se$ hollow nanoparticles were synthesized by a one-step solvothermal method, and dispersed into mixture of n-hexane and ethanol by ultrasonication. The $Co_{0.85}Se$ film was fabricated by a low-temperature spray deposition, and directly used as CE of DSSCs. TiO_2 film was fabricated by a doctor-blade method, and sensitized by N719 dye. The typical DSSCs were assembled in a sandwich structure by an open cell. The photoactive area of DSSCs was 0.2 cm^2. The detailed experimental procedures are described in Supporting information.

3. Results and discussion

The crystallographic structure of $Co_{0.85}Se$ nanoparticles is characterized by X-ray diffraction (XRD) as shown in Fig. 1(a). From XRD pattern, all of the characteristic peaks can be well indexed to the hexagonal $Co_{0.85}Se$ (JCPDS no. 052-1008). The chemical bonding states of each element from $Co_{0.85}Se$ nanoparticles are evidenced by X-ray photoelectron spectroscopy (XPS) as shown in Fig. 1(b)–(d). In the Co 2p spectra, Co $2p_{1/2}$, Co $2p_{3/2}$, and two satellite peaks (marked as “Sat.”) are observed. These peaks can be best fitted with two spin-orbit doublets characteristic of Co^{2+} and Co^{3+} by a Gaussian fitting method. The binding energies of Co^{2+} $2p_{1/2}$, Co^{3+} $2p_{1/2}$, Co^{2+} $2p_{3/2}$, and Co^{3+} $2p_{1/2}$ are 797.3,

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http://dx.doi.org/10.1016/j.matlet.2015.04.008
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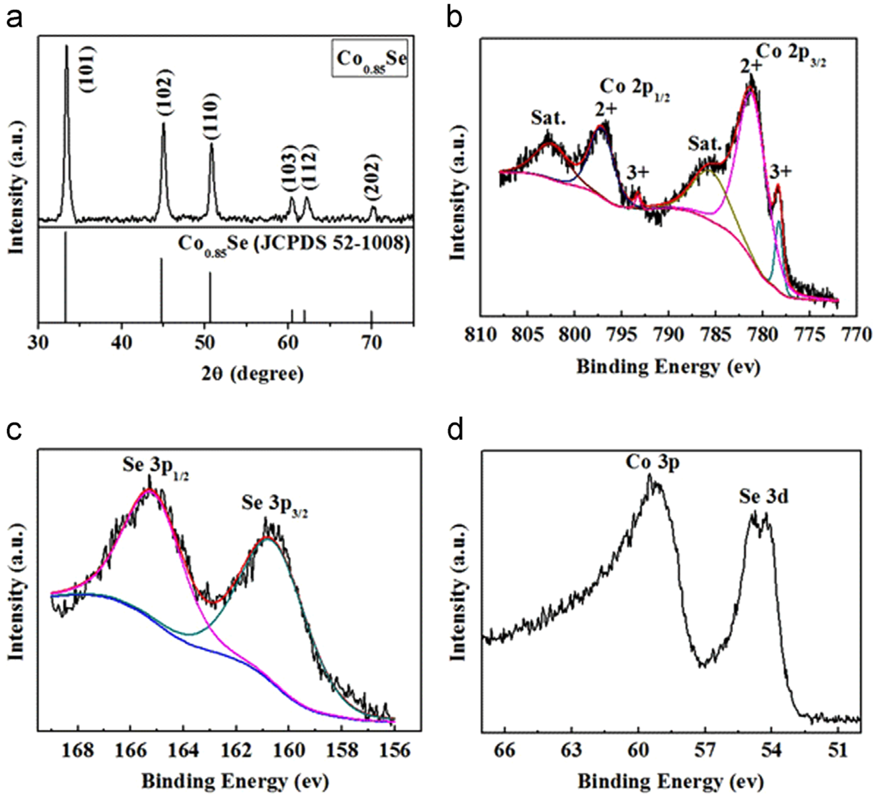

Fig. 1. (a) XRD pattern and XPS spectra of (b) the Co 2p, (c) Se 3p, (d) Co 3p and Se 3d for $Co_{0.85}Se$ nanoparticles.

793.3, 781.1, and 778.4 eV, respectively, which agree very well with the reported values [5,6]. In the Se 3p spectra, Se $3p_{1/2}$ and Se $3p_{3/2}$ peaks are observed at 165.3 and 160.8 eV, respectively. In the Co 3p and Se 3d spectra, the peak at 59.4 eV is consistent with Co 3p and the peak at 54.6 eV is assigned to Se 3d. All the binding energies are in good agreement with the reported values [5,6]. The results of XRD pattern and XPS spectra demonstrate that the sample is constituted by $Co_{0.85}Se$.

Transmission electron microscopy (TEM) images of $Co_{0.85}Se$ nanoparticles is shown in Fig. 2(a). The hollow structure of $Co_{0.85}Se$ nanoparticles is proved by a deep contrast along the nanoparticle edges [9]. Fig. 2(b) shows high-resolution transmission electron microscopy (HRTEM) image of $Co_{0.85}Se$ hollow nanoparticles. HRTEM image demonstrates that hollow nanoparticles have good crystallinity, due to there are many lattice fringes [2]. The lattice distance of about 0.268 nm matches very well with that of the hexagonal $Co_{0.85}Se$ (101) planes (0.269 nm). Therefore, $Co_{0.85}Se$ hollow nanoparticles with a large surface area have been successfully synthesized. $Co_{0.85}Se$ film composed of $Co_{0.85}Se$ hollow nanoparticles is fabricated by a low-temperature spray deposition and sintered under an Ar atmosphere. SEM images of $Co_{0.85}Se$ film are shown in Fig. 2(c) and (d). From SEM images, there is no obvious crack defect and the whole film is dense and homogenous. Most of $Co_{0.85}Se$ hollow nanoparticles exhibit the nearly spherical shape ranging from 100 to 400 nm.

$Co_{0.85}Se$ film is directly used as $Co_{0.85}Se$ CE. In order to investigate the electrocatalytic activity of CEs in the I^-/I_3^- system, cyclic voltammetry (CV) is carried out in a three-electrode system as shown in Fig. 3(a). It is obvious that each CV curve exhibits two pairs of redox peaks. The left pair of redox peaks corresponds to the redox reaction as shown in Eq. (1), while the right pair corresponds to the redox reaction as shown in Eq. (2) [10]:

$$I_3^- + 2e^- \rightleftharpoons 3I^- \tag{1}$$

$$3I_2 + 2e^- \rightleftharpoons 2I_3^- \tag{2}$$

The reduction peak current density (J_{rpcd}) and peak-to-peak separation (E_{pp}) between oxidation and reduction peaks in the left pair of redox peaks are two important parameters to compare electrocatalytic activity of CEs [11]. The larger J_{rpcd} and lower E_{pp} indicate that the CE exhibits the higher electrocatalytic activity. The J_{rpcd} of $Co_{0.85}Se$ CE is similar to that of Pt CE. The E_{pp} of $Co_{0.85}Se$ CE is slightly larger than that of Pt CE (as shown in Table 1). The results show that the CEs have the similar electrocatalytic activity for I_3^- reduction.

To further evaluate electrocatalytic activity of CEs, electrochemical impedance spectroscopy (EIS) is carried out by symmetrical dummy cells under I^-/I_3^- system. The Nyquist plots of EIS and the equivalent circuit model are shown in Fig. 3(b). The simulated values of EIS spectra are summarized in Table 1. The series resistance (R_s) of $Co_{0.85}Se$ CE is larger than that of Pt CE, because of its low electrical conductivity. The charge-transfer resistance (R_{ct}) at the CE/electrolyte interface is inversely proportional to electrocatalytic activity. From Table 1, the results indicate that $Co_{0.85}Se$ CE has the high electrocatalytic activity. Generally, the CE with a large surface area can increase its electrocatalytic activity by increasing the number of active sites per unit area. As a result of hollow structure with a large surface area, the electrocatalytic activity can be enhanced by increasing the number of active sites. In addition, the Nernst diffusion impedance (Z_N) is also inversely proportional to the diffusion coefficient (D) of $I_3{}^-$ [2]. Therefore, the D of $Co_{0.85}Se$ CE is slightly smaller than that of Pt CE.

The electrocatalytic activity of CEs is also investigated by Tafel polarization curves by using symmetrical dummy cells under I^-/I_3^- system as can be seen in Fig. 3(c). In the diffusion zone, the limiting diffusion current density (J_{lim}) of $Co_{0.85}Se$ CE is slightly smaller than that of Pt CE. The value of J_{lim} can also be calculated by Eq. (3).

$$J_{lim} = 2nFDC/l \tag{3}$$