



Cobalt-nickel based ternary selenides as high-efficiency counter electrode materials for dye-sensitized solar cells



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ABSTRACT

One important challenge in dye-sensitized solar cells (DSSCs) is to design and construct low-cost counter electrodes (CEs) with good electrocatalytic performance. In this work, a one-step solvothermal method was used to prepare cobalt-nickel (Co-Ni) based ternary selenides with different Co and Ni ratios. Co-Ni based ternary selenide films were fabricated by simple spray deposition for applications as low-cost and high-performance CEs in DSSCs. Electrochemical measurements demonstrate that the Co-Ni based ternary selenide CEs exhibit high electrocatalytic activity and strong charge-transfer ability for the reduction of I_3^- due to the synergistic effect between Co and Ni ions in Co-Ni based ternary selenides. In particular, $Co_{0.42}Ni_{0.58}Se$ CE shows the higher electrocatalytic activity than other Co-Ni based ternary selenide CEs and platinum (Pt) CE. Furthermore, the DSSC with $Co_{0.42}Ni_{0.58}Se$ CE exhibits photoelectrical conversion efficiency (PCE) of 6.15%, which is considerably higher than that of the DSSC with Pt CE (5.53%).

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1. Introduction

With the development of economy and society, renewable and clean energy resources are already being exploited to replace nonrenewable fossil fuels, such as solar, wind, hydrogen, and geothermal energy [1,2]. In order to efficiently use the renewable and clean energy resources, low-cost energy conversion and storage devices with high performances have been explored, for example, solar cells [3], fuel cells [4], light-emitting diodes [5], and supercapacitors [6]. Specially, solar cells have obtained the fast development due to solar energy is very abundant and widely energy resources [1]. Among various solar cells, dye-sensitized solar cells (DSSCs) are considered as one of the most promising alternatives and have attracted intensive attention owing to their simple fabrication procedure, low cost, environmental friendly, and promising photovoltaic performance [7,8].

A typical DSSC consists of TiO_2 film with dye molecules, an electrolyte consisted of I^-/I_3^- redox couple and platinum counter electrode (Pt CE) in a sandwich structure. As one of the key components of DSSCs, CEs play important functions to collect electrons

from the external circuit and to catalyze the reduction of I_3^- ions to I^- ions [9]. As we all known, Pt CE usually has been employed as a standard CE of DSSCs, because of its high catalytic activity and large electrical conductivity [10]. However, the noble metal Pt is very expensive for large-scale applications of DSSCs due to its resource scarcity. In addition, Pt can be easily dissolved into PtI_4 and H_2PtI_6 [9,10]. Therefore, it is necessary to explore low-cost alternative materials with superior performance to replace Pt.

Over the past decade, many alternative materials have been explored and introduced into CEs of DSSCs, such as carbonaceous material [11,12], conductive polymer [13], transition metal nitrides [14], carbides [15], oxides [16], sulfides [17–19], and selenides [20–22], as well as alloy materials [23,24]. Among these alternative materials, Transition metal selenides have been demonstrated to be attractive candidates for CEs of DSSCs. Therefore, DSSCs based on transition metal selenide CEs have exhibited excellent photovoltaic performance [24–28]. In particular, Co-based selenides and Ni-based selenides have been widely investigated owing to its low cost, distinctive electronic properties, chemical stability, comparatively high conductivity and catalytic activity, etc. [22,29,30].

In recent years, a mass of research activities have been focused on the fabrication of Co-/Ni-based selenides with different morphology, structures and phases to enhance the electrocatalytic activity of selenide CEs. In the first instance, the increase of specific surface area is considered as one of efficient methods to enhance

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the electrocatalytic activity of Co-/Ni-based selenides by increasing catalytic active sites [21,22,30,31]. Co-/Ni-based selenides with the special stoichiometric ratio can generate several defects and lattice distortions for I_3^- adsorption, which also result in the more catalytic active sites [24,25]. Then, some unique morphology or compounds of Co-/Ni-based selenides have been designed and constructed to improve the electrocatalytic activity by raising charge-transfer ability [20,29,32,33]. Third, porous structure of Co-/Ni-based selenides have also been designed and constructed to improve the electrocatalytic activity by providing the more diffusion channel for I^-/I_3^- redox couple [24,31,34]. At last, electrocatalytic activity can be improved by controlling work function of Co-/Ni-based selenide CEs [35].

In addition, synergistic effect between Co and Ni ions have been proposed and considered as the effective way to improve the catalytic activity [36–39]. Recent studies have emphasized that Co-Ni based ternary selenides exhibit the higher specific capacity than Co-/Ni-based selenides in the field of supercapacitor, because of synergistic effect in Co-Ni based ternary selenides [38,39]. However, less attention has been paid to the application of Co-Ni based ternary selenides in DSSCs so far. To the best of our knowledge, compared to Co-/Ni-based selenides, Co-Ni based ternary selenides have exhibited high electrocatalytic activity. For example, the nanocomposites of $Co_{0.85}Se/Ni_{0.85}Se$ had been synthesized by a facile co-electrodeposition method [36]. The photoelectrical conversion efficiency (PCE) of the DSSC with $Co_{0.85}Se/Ni_{0.85}Se$ CE was 8.12%, which was little higher than that of the DSSC with Pt CE (8.03%). Ternary metal selenides of $(Ni_{1-x}Co_x)Se_2$ were fabricated by one-step hydrothermal reduction route [37]. However, the content of Ni and Co was lower in $(Ni_{1-x}Co_x)Se_2$, which decreased the catalytic active sites as CE materials. Therefore, the fabrication of Co-Ni based ternary selenides with high content of Co and Ni is still a challenge for further improving the electrocatalytic performance.

Here, we report the fabrication and application of Co-Ni based ternary selenides (described as $Co_xNi_{1-x}Se$, where x value is 0, 0.32, 0.42, 0.52, 0.74, and 1, respectively) with high content of Co and Ni. The morphology, structure and phase of $Co_xNi_{1-x}Se$ can be controlled by tuning the Co and Ni ratio. The electrocatalytic measurements show that $Co_xNi_{1-x}Se$ CEs exhibit high electrocatalytic activity, due to synergistic effect between Co and Ni ions. Specially, $Co_{0.42}Ni_{0.58}Se$ CE exhibits the highest electrocatalytic activity. The DSSC with $Co_{0.42}Ni_{0.58}Se$ CE has achieved the highest PCE of 6.15%, which is larger than that of the DSSC with Pt CE (5.53%).

2. Experimental

2.1. Materials

Selenium oxide (AR), cobalt acetate tetrahydrate (AR), nickel acetate tetrahydrate (AR), benzyl alcohol (AR), n-hexane (AR), acetone (AR) and ethanol (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd of China. Fluorine-doped tin oxide (FTO) glass, TiO_2 paste (TiO_2 nanoparticles with 20 nm in diameter), N719 dye (cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II) bis-tetrabutylammonium) and liquid electrolyte (0.30 M DMPII, 0.05 M I_2 , 0.5 M LiI, 0.5 M 4-TBP in acetonitrile) were purchased from Wuhan Geao Instruments Science & Technology Co., Ltd, China. To eliminate impurities, FTO glasses were cleaned by acetone, deionized water, and ethanol sequentially. Deionized water (resistivity ≥ 18.2 megohm cm) was obtained from Heal Force Easy system. All the chemicals and reagents were used as received without further purification.

2.2. Fabrication of Co-Ni based ternary selenide counter electrodes

Co-Ni based ternary selenides with different Co and Ni ratios were prepared by a one-step solvothermal method. Typically, p mmol of cobalt acetate tetrahydrate and q mmol of nickel acetate tetrahydrate were dissolved into 90 mL of benzyl alcohol. 2.5 mmol of selenium oxide was added into the same solution. Then, the mixture solution was magnetic stirred at 25 °C for an hour. After strongly magnetic stirring, the homogeneous solution was transferred into a Teflon-lined stainless steel autoclave (120 mL). The autoclave was sealed and placed in drying oven. The solvothermal reaction was performed at 180 °C for 15 hours. After the autoclave was cooled down to 25 °C, the precipitate was centrifuged and washed with ethanol for three times. Finally, Co-Ni based ternary selenides were obtained by drying the precipitate at 60 °C under vacuum for 12 hours. To obtain Co-Ni based ternary selenides with different Co and Ni ratios, the p values are 0, 1.0, 1.25, 1.5, 2.0, and 2.5 mmol, respectively. Meanwhile, the q values are 3.5, 2.1, 1.75, 1.4, 0.7, and 0 mmol, respectively. Co-Ni based ternary selenides can be described as $Co_xNi_{1-x}Se$, where x value is 0, 0.32, 0.42, 0.52, 0.74, and 1, respectively.

$Co_xNi_{1-x}Se$ films were fabricated by a spray deposition method. In a typical fabrication procedure, 0.02 g of $Co_xNi_{1-x}Se$ was dispersed into 2 mL of the mixture solution composed of n-hexane and ethanol with the volume ratio of 1:1. $Co_xNi_{1-x}Se$ nanoink (10 mg ml^{-1}) was prepared by ultrasonically dispersing for 1 hour. The $Co_xNi_{1-x}Se$ nanoink was sprayed onto FTO glass to fabricate $Co_xNi_{1-x}Se$ films. Then, the $Co_xNi_{1-x}Se$ films were sintered under an argon atmosphere at 300 °C for 2 hours to obtain $Co_xNi_{1-x}Se$ CE. In addition, Pt CE was used as a reference CE and prepared by pyrolysis of H_2PtCl_6 isopropanol solution at 385 °C for 30 min [18].

2.3. Assembly of dye-sensitized solar cells

A doctor-blade method was applied to fabricate the mesoporous TiO_2 films on FTO glass. The TiO_2 films with the similar thickness were sintered according to the previous reported [7]. After cooling down to 60 °C, the TiO_2 films were immersed in 0.5 mM ethanol solution of N719 dye at 60 °C for 12 hours. Finally, the TiO_2 films were immersed in ethanol for ten minutes and dried to obtain photoanodes. Typical DSSCs with a sandwich structure were fabricated as follows. The photoanode was clamped with one of the as-synthesized CEs on a light blocking mask. The liquid electrolyte was injected into the gap between the photoanode and CE to form an open cell. The photoactive area of DSSCs was 0.20 cm^2 .

2.4. Characterization

The crystalline structure and phase of Co-Ni based ternary selenides were characterized by X-ray powder diffraction (XRD, D8-Discover, Bruker) with Cu $K\alpha$ radiation ($\lambda = 0.154$ nm). The morphology of as-synthesized samples was observed by a field-emission scanning electron microscope (SEM, FEI Nova Nano-SEM 450) equipped with an energy dispersive X-ray spectrometer (EDS) and high resolution transmission electron microscope (TEM, FEI Titan G2 60-300) operating at a voltage of 200 kV. The surface chemical elements and chemical valence state of as-synthesized $Co_{0.42}Ni_{0.58}Se$ were investigated X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra DLD-600W) with a monochromatic Al $K\alpha$ as X-ray source. Cyclic voltammetry (CV) measurements were carried out in a three-electrode system. The mixture solution composed of 1.0 mM I_2 , 10.0 mM LiI, and 0.1 M $LiClO_4$ in anhydrous acetonitrile was used as electrolyte solution. The scan rate is 50 $mV s^{-1}$.

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