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In situ preparation of NiS_2/CoS_2 composite electrocatalytic materials on conductive glass substrates with electronic modulation for high-performance counter electrodes of dye-sensitized solar cells

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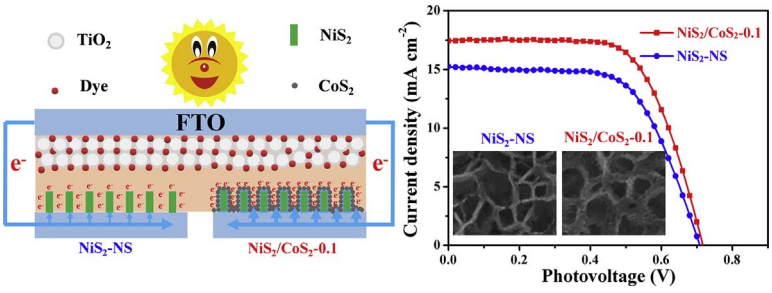
HIGHLIGHTS

- NiS_2/CoS_2/FTO composite CEs were in situ prepared by a CBD and sulfidizing process.
- The formed NiS_2/CoS_2 nanointerface modulates electronic structure of composite CEs.
- CoS_2 nanoparticles covering NiS_2 nanosheets eletrodes reduces Rs and Zw of CEs.
- NiS_2/CoS_2-0.1 CEs show superior electrocatalytic activity.
- NiS_2/CoS_2-0.1 CE shows a better photovoltaic performance than the Pt CE.

GRAPHICAL ABSTRACT



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ABSTRACT

The electrocatalytic composite materials of honeycomb structure NiS_2 nanosheets loaded with metallic CoS_2 nanoparticles are in situ prepared on F doped SnO_2 conductive glass (FTO) substrates used as counter electrodes of DSSCs through chemical bath deposition (CBD) and sulfidizing process. Single crystalline NiS_2 honeycomb structure array lay a foundation for the large surface area of NiS_2/CoS_2 composite CEs. The formed NiS_2/CoS_2 nanointerface modulates electronic structure of composite CEs from the synergetic interactions between CoS_2 nanoparticles and NiS_2 nanosheets, which dramatically improves the electrocatalytic activity of NiS_2/CoS_2 composite CEs; Metallic CoS_2 nanoparticles covering NiS_2 nanosheets electrodes adjusts the electrodes' structure and then reduces the series resistance (Rs) and the Nernst diffusion resistance (Zw) of counter electrodes. The improvement of these areas greatly enhances the electrocatalytic performance of CEs and the short circuit current density (Jsc) and Fill factor (FF) of DSSCs. Impressively, the DSSC based on NiS_2/CoS_2-0.1 CE shows the best photovoltaic performance with photovoltaic conversion efficiency of 8.22%, which is 24.36% higher than that (6.61%) of the DSSC with Pt CE. And the NiS_2/CoS_2-0.1 CE also displays a good stability in the iodine based electrolyte. This work indicates that rational construction of composite electrocatalytic materials paves an avenue for high-performance counter electrodes of DSSCs.

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1. Introduction

Dye-sensitized solar cell (DSSC) is a cheap photochemical cell which has obvious advantages in cost and weak light responsiveness [1–3]. As an important component of DSSC, counter electrode (CE) plays the significant roles of collecting external electrons and electrocatalytic reducing electrolyte from oxidation state to reduction state (such as from I_3^- to I^-) [4–6]. This typical electrocatalytic reduction process requires a combination of multiple primitive steps, including the diffusion, adsorption, catalytic reduction and desorption of electrolyte [7–9]. Among them, the step of electrolyte diffusion demands that electrocatalytic materials have appropriate nanostructures facilitating electrolyte to rapid diffuse. The other three steps need electrocatalytic materials with high conductivity and superior electrocatalytic activity. However, it is difficult for many single-component catalytic material to show excellent performance in all these intermediate catalytic processes [9,10]. Therefore, it is vital for enhancing the performance of the counter electrode and the photoelectric conversion efficiency of DSSCs to rationally design and prepare the multicomponent composite CEs with high conductivity, electrocatalytic activity, and fine microstructure facilitating the rapid diffusion of the electrolyte.

In recent research, a variety of materials have been researched to replace Pt, such as carbonaceous materials [11–14], conducting polymers [15–18], transition-metal sulfides [19–23], selenides [4,5,24,25], nitrides [26], carbides [6,27], etc. Among them, transition-metal sulfides have attracted more attention due to their abundant resource, high electrical conductivity, and decent electrocatalytic activity [23,28–30]. Especially, CoS_2 has metallic conductivity, and it has the same crystal structure, similar lattice constant and matched energy band structure with NiS_2, which provide a superior candidate for composite CEs and is also conducive to the formation of high quality heterointerface of the composite materials [31]. Their matched energy band structure at the interface can effectively drive the transmission of electrons between the two composite components, which usually generate the electronic redistribution and modulation of catalytic performance [10,32]. Therefore, fabrication of the NiS_2/CoS_2 composite electrode is promising for the acquisition of high-performance DSSCs. We know that in situ preparation can effectively increase the electrical conductivity of the electrode for avoiding organic adhesives to increase the resistance of the electrode [1,33]. Furthermore, the two composite components how to in situ construct together on conductive substrates, which will have a significant influence on the microstructure and surface area of the electrode, and then on the kinetics of electronic transport and electrolyte diffusion. However, as far as we know, there are few reports about the effect of the composite form of two materials on electrode's microstructure and electrochemical kinetics.

Herein, we designed and in situ prepared NiS_2/CoS_2 composite electrocatalytic materials on FTO substrates used as counter electrodes of DSSCs via a chemical bath deposition (CBD) and sulfidizing process. Honeycomb structure single crystalline NiS_2 nanosheets array has laid the foundation for the large surface area of NiS_2/CoS_2 composite CEs. Metallic CoS_2 nanoparticles covering NiS_2 nanosheets electrodes not only formed NiS_2/CoS_2 heterointerface but also adjusted the microstructure of NiS_2/CoS_2 composite CE. The formed NiS_2/CoS_2 nanointerface increased conductivity of composite electrocatalytic materials and modulated electronic structure of composite CE from the synergetic interactions between CoS_2 nanoparticles and NiS_2 nanosheets, which dramatically improved the electrocatalytic activity of NiS_2/CoS_2 composite CEs. The series resistance (Rs) and the Nernst diffusion resistance (Zw) of counter electrodes were also reduced for metallic CoS_2 nanoparticles cover layer adjusting the electrodes' structure. Compared with pure NiS_2 and CoS_2 CEs, the NiS_2/CoS_2-0.1 composite CE exhibits excellent the electrocatalytic performance, and corresponding DSSC possessed the best photovoltaic performance with photovoltaic conversion efficiency of 8.22%, which was 24.36% higher than that (6.61%) of the DSSC with Pt CE. Furthermore, the NiS_2/CoS_2-0.1 CE also showed a good electrochemistry stability in the iodine based electrolyte. This work indicated that rational construction of composite electrocatalytic materials paved an avenue for high-performance counter electrodes of DSSCs.

2. Experimental procedure

2.1. Materials

Tetrabutyl titanate (TBT), polyethylene glycol (PEG, MW = 20,000), triton-X100, $Co(NO_3)_2{\cdot}6H_2O$, $K_2S_2O_4$, $NiSO_4{\cdot}6H_2O$, ethanol, Sulfur powder, ammonia, hydrochloric acid, sodium hydroxide, lithium perchlorate, acetic acid, acetonitrile, hydrazine hydrate (85 wt%), sodium borohydride, and propylene propylene carbonate (PC) were obtained from Sinopharm Chemical Reagent Corporation (China). Iodine (I_2, 99.8%) was obtained from Beijing Yili chemicals (China). Lithium iodide (LiI, 99%), 4-tertbutylpyridine (TBP) were purchased from Acros. The Ru dye, cis-diisothiocyanato-bis(2,2′-bipyridyl-4,4′-dicarboxylato) ruthenium (II) bis (tetrabutylammonium) (N719), was purchased from Solaronix. All the reagents used were of analytical purity without further purification. Fluorine-doped stannic anhydride conductive glass (FTO) was used as the substrate for the deposition of mesoporous nanocrystalline titanium dioxide film and counter electrodes.

2.2. Preparation of counter electrodes

The electrocatalytic composite materials of NiS_2 nanosheets loaded with CoS_2 nanoparticles were prepared on FTO substrates through the procedure of chemical bath deposition (CBD) [34], solution soaking and sulfidizing. The schematic illustration of preparing the NiS_2/CoS_2 composite CEs was illustrated in Scheme 1. To deposit nickel-based nanosheets onto FTO, the solution for CBD was firstly prepared through mixing 100 mL of 1 M $NiSO_4{\cdot}6H_2O$, 80 mLof 0.25 M $K_2S_2O_8$ and 100 mL of aqueous ammonia (25–28%). Then the FTO glass substrates were vertically immersed into the solution for 30 min at room temperature. A layer of black precursor deposited on the FTO substrates. The samples were taken out and then were rinsed with deionized water and ethanol for several times. For loading cobalt salt, the dry samples were immersed in 0.1 M or 0.3 M cobalt nitrate solution for 15 min and then were taken out and were dried in a vacuum oven at 50 °C for 1 h. Lastly, the prepared samples were sulfurized at 500 °C for 120 min in a CVD tube furnace with S powder placed at the upstream side and with flowing argon gas to obtain nickel sulfide and cobalt sulfide composites. According to the concentration of cobalt nitrate solution, the composite electrocatalytic samples were named as NiS_2/CoS_2-0.1 and NiS_2/CoS_2-0.3, respectively. For single nickel sulfide nanosheets electrocatalytic sample (named as NiS_2-NS), it was prepared only by above CBD and sulfidizing process. To prepare CoS_2 nanocrystalline sample (named as CoS_2-NP), cobalt nitrate solution was drop-coated on FTO substrates, following by drying and sulfidizing process. As references, Pt CE was prepared according to our previous preparation procedure [20].

2.3. Fabrication of DSSC

Dye sensitized nanocrystalline TiO_2 photoanodes were prepared according to the details in previous reports [35,36]. A sandwich-type DSSC was assembled with the sensitized TiO_2 photoanode, a counter electrode and electrolyte. The electrolyte was composed of 0.05 M LiI, 0.1 M 1,3-dimethy-limidazolium iodide (DMII), 0.1 M Guanidinium thiocyanate (GNCS), 0.03 M I_2, 0.5 M 4-tert-butylpridine (TBP) in mixed solvent of acetonitrile and propylene carbonate (PC) (volume ratio: 1/1).

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