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Lamellar structured $CoSe_2$ nanosheets directly arrayed on Ti plate as an efficient electrochemical catalyst for hydrogen evolution☆

Huaqing Xiao[a], Shutao Wang[a,*], Cong Wang[a], Yanyu Li[a], Hongrong Zhang[a], Zhaojie Wang[a], Yan Zhou[a,*], Changhua An[a], Jun Zhang[b]

[a] *College of Science, China University of Petroleum (East China), 66 Changjiang West Road, Qingdao Economic Development Zone, Qingdao, Shandong 266580, People's Republic of China*
[b] *State Key Laboratory of Heavy Oil Processing, China University of Petroleum (East China), 66 Changjiang West Road, Qingdao Economic Development Zone, Qingdao, Shandong 266580, People's Republic of China*

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ABSTRACT

Splitting water by electrochemical reactions is considered to be the most promising strategy to create hydrogen. Herein, an efficient hydrogen evolution cathode was developed by *in-situ* growth of lamellar structured cobalt diselenide ($CoSe_2$) nanosheets on the surface of commercial titanium (Ti) plate ($CoSe_2$NS@Ti) in the first time. Both SEM images and XRD data confirmed that the Ti plate is homogeneously coated by few stacking layers of lamellar structured $CoSe_2$, which could provide more active sites for hydrogen evolution reaction (HER) with the thickness about 20 nm. This catalytic cathode shows exceptionally high activity for hydrogen evolution with 152 mV overpotential to afford a current density of 10 mA cm^{-2} and a high exchange current density of 5.01×10^{-3} mA cm^{-2}, as well as high cyclic stability with negligible decrease of cathodic current after 500 cycles. Remarkably, the $CoSe_2$NS@Ti catalyst exhibits fast hydrogen evolution kinetics with Tafel slope of 38.5 mV per decade, which approaches the state-of-art Pt catalyst (Pt/C) in 0.5 M H_2SO_4. This $CoSe_2$NS@Ti material is easily prepared with excellent electrocatalytic performance, thus could be a promising earth-abundant electrocatalyst for the HER and other renewable energy applications.

1. Introduction

Hydrogen has been considered to be a progressive energy carrier since few decades ago [1] as a potential alternative energy source to fossil fuels [2]. Splitting water by electrochemical reactions is one of the most promising way to create hydrogen [3]. Electrochemical reduction of water for hydrogen production is an important component of several developing clean-energy technologies. Therefore, an efficient electrocatalyst for hydrogen evolution reaction (HER) is needed for achieving large cathodic current densities at low overpotentials (η). Although the state-or-art noble metal of platinum (Pt) performs excellently in HER catalysis [4,5], its practical application is severely hampered by the high costs and low reserves. Alternatively, many earth-abundant nanomaterials have been successfully synthesized and proven to be efficient HER electrocatalysts [6–8], such as transition-metal chalcogenides [9,10], borides [11], phosphates [12,13], carbides [14,15], nitrides [16,17], and oxides [18]. Furthermore, novel catalysts with improved activities could be constructed when combined with certain conducting substrates. These substrate supported catalyst could serve directly as electrode with enlarged surface area and enhanced electron transfer kinetics, such as porous $NiSe_2$ grow on Ni foam [19], Ni-doped Mo_2C nanowires supported on Ni foam [20], MoS_x/graphene protected Ni foams [21], $CoSe_2$ necklace-like nanowires[20] and $CoSe_2$ nanoparticles [22] grown on carbon fiber paper. Despite the significant progress, fabrication of earth-abundant catalysts for HER with both excellent activity and cyclic stability still remains in challenge.

Recently, $CoSe_2$ has been proven to be one of the most active earth-abundant electrocatalyst for HER [23]. The low-spin configuration of 3d electrons of Co affords metallic property of $CoSe_2$, which can significantly improve the charge transport along the catalyst [22,24]. Generally, $CoSe_2$ exists in crystals of cubic pyrite and orthorhombic marcasite phases. These two types of crystal structures are distinguished by the octahedral sharing of chalcogen atoms [25]. Previous synthetic strategies of $CoSe_2$

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* Corresponding authors.
E-mail addresses: shtwang@upc.edu.cn (S. Wang), yanzhou@upc.edu.cn (Y. Zhou).

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usually includes vapor selenization [22,26,27] and solvothermal methods [24,28,29]. Both the two methods offer facile and efficient synthetic procedures. Among them, the lamellar mesostructured $CoSe_2$ nanobelts (NBs) [30] can readily be applied on substrates in one-step and has showed enhanced catalytic activity in HER [28] and oxygen evolution reactions (OER) [31].

Lamellar structured $CoSe_2$ synthesized with the assistance of diethylenetriamine (DETA) shows promising catalytic activity due to the metallic structure [30] and layer distortion [29], which is believed to be beneficial for electron transfer and enhanced stability, respectively. However, drop casting of catalysts on electrode surface may still affect the catalytic performance since indirect contact between catalysts and electrode surface. The direct growth of $CoSe_2$ on a conducting substrate which act directly as electrode can be beneficial for catalytic performances [32]. Besides, the presence of DETA benefits not only for synthesizing thin and long nanobelts, but also possible for lamellar structured nanosheets. In this work, we perpendicularly grew lamellar structured $CoSe_2$ nanosheets on Ti plate ($CoSe_2$NS@Ti) by tuning reaction conditions and was used directly as cathode in the first time. This high-surface-area three-dimensional (3D) architecture electrode exhibited excellent HER performance with a low overpotential of 106 mV *vs.* RHE, fast electrode kinetics (a Tafel slope of 38.5 mV per decade) and a large exchange current density (5.01×10^{-3} mA cm^{-2}). This new achievement has widened the scope of the two-dimensional (2D) nanosheets array growing on a conductive metal substrate to afford a 3D electrode and believed to have more real-life applications.

2. Experimental

2.1. Reagents

Ti plate (thickness = 0.1 mm) was purchased from Shanxi Rike New Material Technology Co., Ltd., China. DETA and Nafion solution (5%) was obtained from Alfa Aesar. Cobalt acetate ($Co(CH_3COO)_2 \cdot 4H_2O$), sodium selenite ($Na_2SeO_3$) and ethanol ($C_2H_5OH$) were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. All the regents were used as received without further purification. Deionized water (DIW) was obtained from AODLON professional water processing system (Qingdao, China) with resistance greater than 18 $M\Omega$.

2.2. Synthesis of $CoSe_2$NS@Ti

Ti plate was polished to remove surface impurities and then sonicated respectively in 6 M HCl solution, ethanol and water for 10 min prior to further experiments. 0.8 mmol $Co(CH_3COO)_2 \cdot 4H_2O$ and 0.8 mmol Na_2SeO_3 were dissolved into 20 mL DIW and 20 mL DETA (volume ratio of $V_{DETA}:V_{DIW} = 1:1$). After the mixture was further sonicated 1 h, it was transferred to a Teflon-lined autoclave with the capacity of 50 mL. Then, pieces of Ti (2×3 cm^2) were immerged in the solution. After that, the autoclave was sealed and heated at 180 °C for 14 h. When the autoclave was cooled to room temperature naturally, the product was washed with water and alcohol several times. The final sample was collected after being dried in vacuum desiccator.

2.3. Synthesis of $CoSe_2$ NBs

The synthetic procedure of $CoSe_2$ NBs was similar to that of $CoSe_2$NS@Ti hybrid, and the solvothermal process was carried out without Ti plate.

2.4. Characterizations

The crystalline structures of the samples were confirmed with powder X-ray diffraction (XRD) by using a Philips X'Pert diffractometer with Cu Kα radiation (λ = 0.15418 nm). Transmission electron microscopy (TEM) and high resolution transmission electron microscope (HRTEM) analysis were obtained on a JEM-2100UHR transmission microscope (JEOL, Japan) operated at 200 kV. Scanning electron microscopy (SEM) were conducted with a Hitachi S-4800 field emission scanning electronic microscopy (FESEM). X-ray photoelectron spectroscopy (XPS) was performed on a VG ESCALABMK II spectrometer using an Al Kα (1486.6 eV) photon source. Fourier Transform-Infrared (FTIR) spectra were measured by using a Thermo Nicole FTIR spectrometer (NEXUS, USA).

2.5. Electrochemical measurements

Electrochemical measurements were performed on a CHI 660E electrochemical workstation (CH Instruments, Inc., Shanghai) using a standard three-electrode system. $CoSe_2$NS@Ti, bare Ti

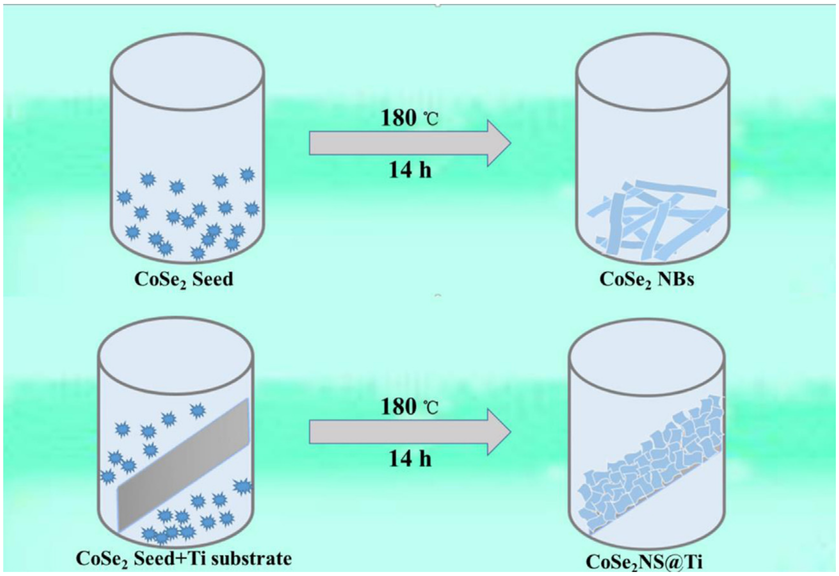

Fig. 1. Schematic illustration for the synthesis of $CoSe_2$ NBs and $CoSe_2$NS@Ti nanocomposites.