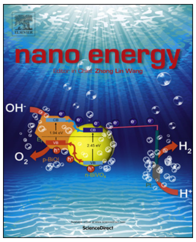
Nano Energy (2015) 18, 1–11

Available online at www.sciencedirect.com

ScienceDirect

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



RAPID COMMUNICATION

Component-controllable synthesis of $Co(S_xSe_{1-x})_2$ nanowires supported by carbon fiber paper as high-performance electrode for hydrogen evolution reaction

Ke Wang[a], Chongjian Zhou[a], Dan Xi[a], Zhongqi Shi[a,*], Cheng He[a,*], Hongyan Xia[a], Guiwu Liu[b,*], Guanjun Qiao[a,b]

[a]*State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, China*
[b]*School of Materials Science and Engineering, Jiangsu University, Zhenjiang 212013, China*

Received 14 August 2015; received in revised form 27 September 2015; accepted 1 October 2015
Available online 9 October 2015

KEYWORDS
Hydrogen evolution reaction;
Nanowire;
Pyrite;
Dopant;
Component controllable synthesis;
Three dimensional

Abstract

The ternary alloyed $Co(S_xSe_{1-x})_2$ nanowires (NWs) supported by carbon fiber paper (CFP) have been successfully synthesized. By adjusting the components of the NWs, it is found that the $Co(S_{0.73}Se_{0.27})_2$ NWs on CFP exhibit the highest electrocatalytic activity towards hydrogen evolution reaction (HER). To drive the current density of 100 mV cm^{-2}, the $Co(S_{0.73}Se_{0.27})_2$ NWs only require a small overpotential of 157 mV in 0.5 M H_2SO_4 solution and the corresponding Tafel slope is only 45.3 mV dec^{-1}. After 20 h continuous electrolysis or cycling for 5000 times in acid electrolyte, the robust catalytic activity is still perfectly preserved. DFT calculation results demonstrate that the high intrinsic activity of $Co(S_{0.73}Se_{0.27})_2$ NWs towards HER is derived from the significant reduction of kinetic energy barrier induced by anion doping. This work presents a new efficient catalyst for HER and the anion doping strategy implemented here could be extended to other earth-abundant electrocatalysts to improve the catalytic performance.

Introduction

Finding a cheap, renewable and clean energy source to replace fossil fuel is still one of the severest challenges we have to face nowadays. Hydrogen as a promising solution to address this issue has drawn extensive interests from

---

*Corresponding authors.
E-mail addresses: zhongqishi@mail.xjtu.edu.cn (Z. Shi), hecheng@mail.xjtu.edu.cn (C. He), gwliu76@mail.ujs.edu.cn (G. Liu).

http://dx.doi.org/10.1016/j.nanoen.2015.10.001

researchers [1-3]. The electrochemical hydrogen evolution has been proved to be a facile and efficient method to produce hydrogen from water [4-6]. However, the high prices and low reserves of commercially available Pt group catalysts have strongly hampered the large-scale production of hydrogen via the electrochemical process. The design and synthesis of earth-abundant catalysts for hydrogen evolution reaction (HER) are still the key to bringing the electrochemical preparation of hydrogen into practical application [7]. Transition metal dichalcogenides with the generalized formula of MX_2, where M represents a transition metal and X represents a chalcogen such as S, Se or Te, have received increasing interests for their prominent performances in electrochemical catalysis for HER and a few examples are NiS_2 [8], CoS_2 [9], $CoSe_2$ [10,11], MoS_2 [12-14], WS_2 [15]. However, the activities of present non-precious electrochemical catalysts towards HER are still far below the expectance of replacing Pt group materials.

To improve the efficiency of electrocatalysts for HER, there are two main methods: (i) increasing the electrochemically accessible area by nanostructuring; (ii) promoting the pristine activity of the catalysts. In terms of the latter, introducing dopants into the crystal lattice of the catalysts has been proven to be an effective way. Although the doping of metal atoms has been extensively investigated, only a few published works focused on bringing in the anions as dopants [4,16-18]. For instance, Xu et al. [19] synthesized the S-doped $MoSe_2$ ultrathin nanosheet showing a much improved catalytic performance; Xu et al. [20] synthesized the $WS_{2(1-x)}Se_{2x}$ nanotubes with CVD method showing a superior catalytic activity than the undoped counterparts; Kibsgaard et al. [21] introduced S to the surface of MoP producing the MoP|S with superb catalytic performance; Gong et al. [22] prepared the ultrathin $MoS_{2(1-x)}Se_{2x}$ alloy nanoflakes and proved that the doping of Se could largely reduce the overpotential needed in HER. Therefore, more researches concentrating on facilitating the catalytic performance by doping anions are required to achieve a better understanding on the mechanism.

Herein we for the first time present the synthesis of component-controllable $Co(S_xSe_{1-x})_2$ nanowires (NWs) supported by carbon fiber paper (CFP) and their excellent performances as electrocatalysts for HER. In our previous work, we reported the necklace-like $CoSe_2$ NWs on CFP as an efficient catalyst towards HER [23]. By replacing part of the Se with S in the synthesis process, the pyrite-type $Co(S_xSe_{1-x})_2$ NWs supported by CFP with controllable components were achieved. Pyrite $CoSe_2$ and CoS_2 have the similar crystal structures that belong to the space group of *Pa3* (T_h^6). The metal atoms octahedrically coordinated with six chalcogens forming a face centered cubic lattice, as shown in Figure 1. By partially replacing Se with S atom, the $Co(S_xSe_{1-x})_2$ is still in the pyrite crystal structure [24] like the $CoSe_2$ and CoS_2 and the catalytic activity could be enhanced simultaneously. Moreover, the $Co(S_xSe_{1-x})_2$ also shows the metallic feature as well as the $CoSe_2$ and CoS_2, which also ensures a high activity towards HER [25]. Besides the improvements in the intrinsic activity, the advanced nanostructure of $Co(S_xSe_{1-x})_2$ NWs also contributes to the superior performance. By arranging the nanocrystals of active materials into NWs that radically align on the mesoporous CFP, the large electrochemically accessible surface area and fast electrolyte diffusion tunnels are formed. The component-controllable synthesis of $Co(S_xSe_{1-x})_2$ NWs ensures us to investigate the influence and mechanism of anion doping strategy on the efficiency in catalysis. The experimental results and density functional theory (DFT) calculations help us draw the conclusion that $Co(S_xSe_{1-x})_2$ NWs are more efficient than either $CoSe_2$ or CoS_2 NWs as electrocatalysts towards HER.

Results and discussion

Figure 2 gives a scheme on the whole preparation process. The synthesis of $Co(S_xSe_{1-x})_2$ NWs on CFP could be divided into two steps: (1) synthesis of $Co(OH)(CO_3)_{0.5}$ NWs on CFP via a hydrothermal method; (2) conversion of $Co(OH)(CO_3)_{0.5}$ NWs to component-controllable $Co(S_xSe_{1-x})_2$ NWs. During the simple hydrothermal process (STEP 1), $Co(OH)(CO_3)_{0.5}$ NWs were successfully grown on CFP and a reliable contact between the NWs and CFP were formed. The XRD pattern and TEM image of $Co(OH)(CO_3)_{0.5}$ NWs are given in Figure S1 and the XRD pattern of $Co(OH)(CO_3)_{0.5}$ NWs perfectly matches the JCPDS PDF48-0058 standard pattern. The chemical reactions between $Co(NO_3)_2 \cdot 6H_2O$, $CO(NH_2)_2$ and NH_4F could be described by the following equations [26]:

$$Co^{2+} + xF^- \rightarrow CoF_x^{(x-2)-} \tag{1}$$

$$H_2NCONH_2 + H_2O \rightarrow 2NH_3 + CO_2. \tag{2}$$

$$CO_2 + H_2O \rightarrow CO_3^{2-} + 2H^+ \tag{3}$$

$$NH_3 \cdot H_2O \rightarrow NH_4^+ + OH^- \tag{4}$$

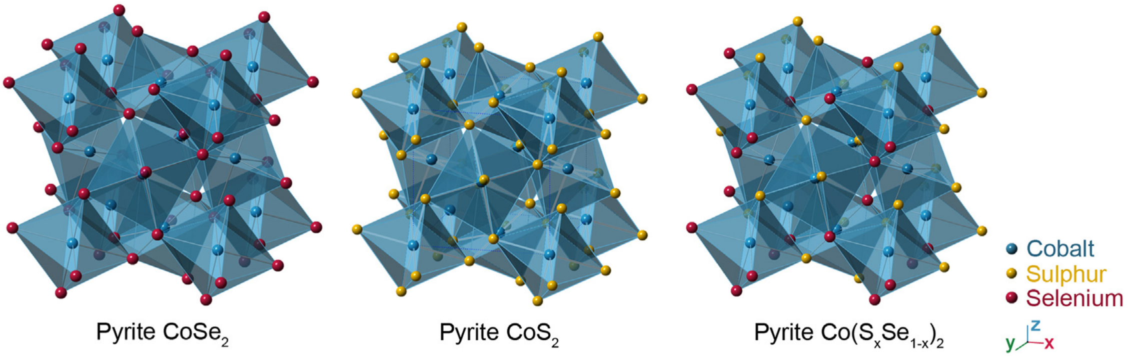


Figure 1 Crystal structures of $CoSe_2$, CoS_2 and $Co(S_xSe_{1-x})_2$ in cubic pyrite-type phase.