



# Selenium phosphorus co-doped cobalt oxide nanosheets anchored on Co foil: A self-supported and stable bifunctional electrode for efficient electrochemical water splitting

Yi-Fan Jiang, Cheng-Zong Yuan, Xiao Zhou, Ya-Nan Liu, Zhi-Wei Zhao, Sheng-Jie Zhao, An-Wu Xu\*

Division of Nanomaterials and Chemistry, Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Hefei 230026, PR China

## ARTICLE INFO

### Article history:

Received 15 May 2018

Received in revised form

31 August 2018

Accepted 24 September 2018

Available online 25 September 2018

### Keywords:

Selenium phosphorus co-doped cobalt oxide

In-situ growth

Self-supported bifunctional electrode

Strong interaction

Overall water splitting

## ABSTRACT

The design of inexpensive, efficient, durable and self-supported bifunctional electrodes for simultaneously catalyzing the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) in the same electrolyte is essential for renewable energy conversion processes and future sustainable development, however, it still remains a challenging issue. Reported herein is the first example of selenium phosphorus co-doped cobalt oxide nanosheets on highly conductive Co foil collector (CoOSeP@Co foil), fabricated by successively selenylation and phosphorization of a pre-oxidized Co foil, as a novel bifunctional electrode for water electrolysis. Due to the improved intrinsic catalytic activity of cobalt oxide derived from doping and the strong interaction between active CoOSeP nanosheets and highly conductive Co foil collector, the designed CoOSeP@Co foil integrated electrode displays favorable catalytic activities towards both HER and OER in strongly alkaline media, achieving an electrocatalytic current density of  $10 \text{ mA cm}^{-2}$  at a low overpotential of 155 mV for HER and 347 mV for OER, respectively. Beyond that, the electrode could keep working and maintain its catalytic activity for at least 30 h. Furthermore, an alkaline electrolyzer constructed by employing CoOSeP@Co foil as an integrated bifunctional electrode in both the cathode and anode can generate  $10 \text{ mA cm}^{-2}$  at a cell voltage of 1.74 V and shows good long-term stability of more than 30 h. This work not only opens a new avenue to improve the intrinsic catalytic activity of materials by co-doping with heteroatoms, but also brings us a new idea for designing other cost-effective, self-supported, efficient and robust overall water splitting electrodes.

© 2018 Elsevier Ltd. All rights reserved.

## 1. Introduction

Electrochemical water splitting is considered to be an environment-friendly, secure and sustainable technology, which can, to some extent, resolve the growing global energy consumption and consequent environmental crisis [1,2]. However, the commercial electrolyzers usually perform electrochemical water splitting reaction at a cell voltage of 1.8–2.0 V, much higher than the theoretical minimum value of 1.23 V because of the sluggish kinetics and multiple electrons transfer involved in water splitting [3,4]. The water splitting reaction consists of two half-reactions:

anodic oxygen evolution reaction (OER) and cathodic hydrogen evolution reaction (HER), both of which are momentous for the overall efficiency of water splitting [5,6]. Therefore, highly active catalysts for both HER and OER are urgently needed to lower the overpotentials, speed up the reaction rates as well as improve the reaction efficiency [7,8]. Presently, precious metal Pt-based compounds and Ir/Ru-based materials have been identified to be the most state-of-the-art electrocatalysts for HER and OER, respectively [9]. Nevertheless, the high cost, low natural abundance and unsatisfactory durability of noble metals severely restrict their scale-up applications in renewable energy technologies. These limitations have motivated significant research efforts to explore nonprecious-metal, high-efficiency and durable water-splitting electrocatalysts, and, indeed, significant progress has been achieved in the past years. Especially, there have been plentiful

\* Corresponding author.

E-mail address: [anwuxu@ustc.edu.cn](mailto:anwuxu@ustc.edu.cn) (A.-W. Xu).

investigations on transition metal-based catalysts, including chalcogenides [10,11], carbides [12,13], and phosphides [14,15] for the HER, and metal phosphates [16,17], oxides [18–20], hydroxides [21,22] for the OER.

To simplify the system, minimize the cost, improve the water electrolysis efficiency and eventually increase the feasibility of practical application, the electrocatalytic overall water splitting should be conducted in the same alkaline electrolyte using a bifunctional OER and HER catalyst [23]. Unfortunately, most of the investigated HER catalysts work well in acidic media, but underperform in alkaline conditions. Many electrocatalysts can achieve remarkable catalytic behaviors in HER or OER, while few of them can function well toward both HER and OER in the same electrolyzer because of their unstable or inactive property in unfavorable pH environment [24]. Therefore, it is urgently necessary to explore highly efficient, durable and bifunctional electrocatalysts to catalyze the HER and OER simultaneously. Cobalt oxides, an important class of compounds with loosely bonded d electrons [25], have been extensively studied for the application as catalysts [26–28]. As previous reports suggested, Co has been calculated to have a low energy barrier for H adsorption [29], indicating that Co-based composites may be promising candidates for HER, meanwhile, cobalt oxides are also inherently active toward the OER [30]. Accordingly, it is possible to employ cobalt oxides as bifunctional electrocatalysts. However, the easy accumulation and poor electronic conductivity of pure cobalt oxides decrease the active sites and hinder the transport of electrons or protons during the reaction process [18,25].

Doping transition metal compounds with heteroatoms could modify the electronic structure, boost electrical conductivity, optimize the hydrogen adsorption energy as well as increase the number of active sites [31,32], which is verified to be a significant and effective approach to improve the intrinsic activity of catalysts. For instance,  $\text{MoS}_2(1-x)\text{Se}_{2x}$  was reported to exhibit superior HER catalytic performance than pure  $\text{MoS}_2$  and  $\text{MoSe}_2$  [33]. Similar phenomena was also observed for  $\text{WS}_2(1-x)\text{Se}_{2x}$  [34]. Specially, doping with nonmetal elements from different groups is expected to result in significant tuning of the electronic structures [32]. Such as the substitution of sulfur with phosphorus could improve the material stability and HER catalytic durability of ternary cobalt phosphosulfide ( $\text{CoSIP}$ ) anchored on carbon nanotubes [35]. Of particular interest, co-doping with two heteroatoms was confirmed to further improve the electrocatalytic performance by a synergic effect with respect to single heteroatom-doped counter-part [36]. However, the designed synthesis of selenium phosphorus co-doped cobalt oxide ( $\text{CoOSeP}$ ) that can efficiently catalyze hydrogen evolution or oxygen evolution in alkaline solution has not been reported so far. It would be very meaningful if  $\text{CoOSeP}$  can be used as efficient bifunctional electrocatalysts for overall water splitting.

Moreover, most of the established catalysts have to be immobilized on electrode surfaces with the help of a polymer binder (Nafion or PTFE), which may inevitably increase the series resistance, partially cover active sites, inhibit diffusion as well as increase the risk of falling off from electrode surface, thus leading to decreased catalytic activity and stability. Accordingly, developing in situ growth method to construct self-supported electrodes, where the active phases are directly grown on current collectors, may have undeniable practical significance. Specifically, self-supported two-dimensional (2D) nanosheets on current collectors is particularly attractive, because nanosheet could provide a high specific surface area to expose more surface active sites as well as large-area and intimate contact with both electrolyte and electrode for rapid interfacial charge transfer [37].

Herein, for the first time we demonstrate the in-situ growth of selenium phosphorus co-doped cobalt oxide nanosheets on highly

conductive Co foil collector (termed as  $\text{CoOSeP@Co}$  foil) by successively selenylation and phosphorization of a pre-oxidized Co foil. The obtained  $\text{CoOSeP@Co}$  foil self-supported electrode could be directly employed as highly efficient bifunctional electrode to catalyze the HER and OER simultaneously in the same alkaline electrolyte. As a result of in-situ growth method, the intimate contact and strong interaction between catalysts and collector endow the  $\text{CoOSeP@Co}$  foil integrated electrode with high charge transfer efficiency, significantly contributing to its catalytic performance. In addition, the introduction of selenium and phosphorus, which may modify the electronic structure and have synergic effect on improving the intrinsic catalytic activity of catalysts. Accordingly, the  $\text{CoOSeP@Co}$  foil integrated electrode has exhibited good electrocatalytic activity and durability, requiring low overpotentials of 155 mV for the HER, 347 mV for the OER, and 510 mV for the overall water splitting to achieve a  $10 \text{ mA cm}^{-2}$  current density in strongly alkaline media.

## 2. Experimental section

### 2.1. Materials

Co foils were purchased from Shanxi Shengyuan metal material Co. Ltd. All received chemicals were used as obtained without further purification. Potassium hydroxide (KOH), acetone, hydrochloric acid and absolute ethanol were obtained from Sinopharm Chemical Reagent. Selenium (Se) powders and sodium hypophosphite ( $\text{NaH}_2\text{PO}_2$ ) were bought from Aladdin Ltd. (Shanghai, China). The deionized water purified using ion exchange (MilliQ, Millipore) was used throughout all experiments.

### 2.2. Preparation of $\text{CoOSeP@Co}$ foil

Typically, Co foils pieces of  $0.5 \times 4 \text{ cm}^2$  with 0.2 mm thickness and 99.9% purity were ultrasonically cleaned by 3 M HCl, acetone, absolute ethanol and deionized water in sequence before use. To obtain  $\text{CoO}_x\text{@Co}$  foil, a piece of Co foil was calcined in air at 350 °C, 450 °C and 550 °C for 2 h in a muffle furnace with a heating rate of 5 °C  $\text{min}^{-1}$ . Then, Se doped  $\text{CoO}_x$  on Co foil ( $\text{CoOSe@Co}$  foil) was directly synthesized through thermal selenization process using sublimated selenium powders. We positioned 0.1 g selenium powders upstream and  $\text{CoO}_x\text{@Co}$  foil in the center of the furnace. Using a heating ramp of 22 °C/min, the system was heated to the reaction temperature of ca. 450 °C for 2 h. Se sources started evaporating and reacting with  $\text{CoO}_x\text{@Co}$  foil. These experiments were performed in an inert environment facilitated by a steady flow of  $\text{N}_2$ . Subsequently, the obtained  $\text{CoOSe@Co}$  foil together with 55 mg  $\text{NaH}_2\text{PO}_2$  was then calcined at 300 °C for 2 h in a tube furnace under nitrogen atmosphere with a heating rate of 5 °C  $\text{min}^{-1}$ . Finally, the Se, P co-doped CoO on Co foil ( $\text{CoOSeP@Co}$  foil) was produced. The product was denoted as  $\text{CoOSeP@Co}$  foil-350 and  $\text{CoOSeP@Co}$  foil-550, where 350 represents the oxidation temperature of Co foil.  $\text{CoOSeP}$  was also peeled off from Co foil surface for further characterization.

### 2.3. Characterization

The crystal structure and phase composition analyses of the products were performed by X-ray diffraction (XRD) (Philips X'Pert Pro Super X-ray diffractometer equipped with Cu K $\alpha$  irradiation,  $\lambda = 1.5418 \text{ \AA}$ ). The morphology of these samples was examined on a field emission scanning electron microscope (FE-SEM, JEOL JSM-6700F) and transmission electron microscope (TEM, JEM-2100F, 200 kV). The chemical composition and chemical binding energy of samples were measured using energy dispersive X-ray

Download English Version:

<https://daneshyari.com/en/article/10656886>

Download Persian Version:

<https://daneshyari.com/article/10656886>

[Daneshyari.com](https://daneshyari.com)