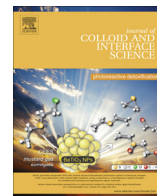




Contents lists available at ScienceDirect

## Journal of Colloid and Interface Science

journal homepage: [www.elsevier.com/locate/jcis](http://www.elsevier.com/locate/jcis)

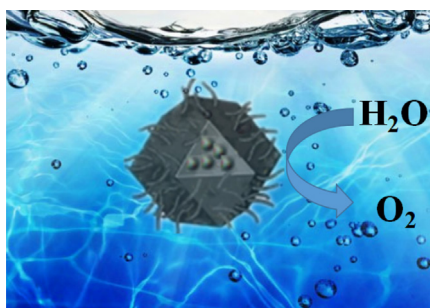
## Regular Article

## Tuning carbon nanotube-grafted core-shell-structured cobalt selenide@carbon hybrids for efficient oxygen evolution reaction

Menglei Yuan<sup>a,b</sup>, Meng Wang<sup>a,b</sup>, Peilong Lu<sup>a,b</sup>, Yu Sun<sup>c</sup>, Sobia Dipazir<sup>a,b</sup>, Jingxian Zhang<sup>a,b</sup>, Shuwei Li<sup>a</sup>, Guangjin Zhang<sup>a,\*</sup><sup>a</sup> CAS Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China<sup>b</sup> University of Chinese Academy of Sciences, Beijing 100190, China<sup>c</sup> School of Science, North University of China, Taiyuan 030051, China

## GRAPHICAL ABSTRACT

In this work, CoSe<sub>2</sub> was rationally designed with carbon nanotube-grafted carbon-coated structure by a convenient hydrothermal-anneal strategy, which leads to the increase of the active sites exposed at the solid-liquid interface and greatly enhances the oxygen evolution reaction performance.



## ARTICLE INFO

## Article history:

Received 1 August 2018

Revised 28 August 2018

Accepted 28 August 2018

Available online 29 August 2018

## Keywords:

CoSe<sub>2</sub>

Zeolite imidazole frameworks

Oxygen evolution reaction

Alkaline medium

## ABSTRACT

The electrochemical oxygen evolution reaction (OER) is sparked extensive interest in efficient energy storage and conversion. Cobalt Selenide (CoSe<sub>2</sub>) is believed to be one of the promising candidates for OER based on Yang Shao-Horn's principle. However, owing to low exposure of active sites and/or low efficiency of electron transfer, the electrocatalytic activity of CoSe<sub>2</sub> is far less than expected. In this work, a novel carbon nanotubes (CNT) grafted 3D core-shell structured CoSe<sub>2</sub>@C-CNT nanohybrid is developed by a general hydrothermal-calcination strategy. Zeolite imidazole frameworks (ZIF) was used as the precursor to synthesis of the materials. It is found that both the calcination temperature and the selenium content can significantly regulate the catalytic performance of the hybrids. The obtained best catalysts requires the overpotential of only 306 mV and 345 mV to reach a current density of 10 mA cm<sup>-2</sup> and 50 mA cm<sup>-2</sup> in 1.0 MKOH medium, respectively. It also exhibits a small Tafel slope of 46 mV dec<sup>-1</sup> and excellent durability, which is superior to most of recently reported CoSe<sub>2</sub>-based and Co-based materials. These superior performances can be ascribed to synergistic effects of the highly active CoSe<sub>2</sub> nanostructure, defect carbon species and the carbon nanotubes exist in the catalyst. Besides, the unique morphology leads to large electrochemical surface area of the catalyst, which is in favor of the exposure of active sites for OER. Due to

\* Corresponding author.

E-mail address: [zhanggj@ipe.ac.cn](mailto:zhanggj@ipe.ac.cn) (G. Zhang).

high efficiency, low cost and excellent durability for OER, the prepared catalysts showed can be potentially used to substitute noble metals utilized in related energy storage and conversion devices.

© 2018 Elsevier Inc. All rights reserved.

## 1. Introduction

Developments in alternative clean energy, energy storage and conversion devices is one of the efficient ways to solve the rapid depletion of fossil fuels and their associated global climate change. Electrochemical water splitting devices can realize the efficient conversion of the electric energy to cost-effective and clean hydrogen [1,2]. Due to kinetically sluggish four-electron process ( $4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$  in alkaline medium), oxygen evolution reaction (OER) is considered as the efficient-limiting step in water splitting [3,4]. Thus, it is critical to design the catalyst that could facilitate multiple electron and proton coupling process under low overpotentials and thus increase the reaction kinetics [5]. So far, noble metal-based ruthenium oxide ( $\text{RuO}_2$ ) and iridium oxide ( $\text{IrO}_2$ ) are still the most efficient OER electrocatalysts [6–8]. However, their commercialization is hampered by high price and limited availability. Consequently, it is very desirable to synthesis novel robust electrocatalysts with high efficiency to substitute the noble metal catalysts. Until now, extensive efforts have been focused on developing transition-metal oxides, [9,10] nitrides, [11,12] phosphides, [13,14] and selenides [15–17]. Benefiting from the relatively low electrical resistivities and high electrochemical activities, many electrocatalysts of transition-metal selenides (TMSs) were prepared and well discussed [18,19]. Among various types of TMSs, cobalt selenides have been confirmed to be one of the promising electrocatalysts for OER due to  $t^6_{2g}e^1_g$  separated from Co 3d electrons has a near-optimum electronic  $e_g$  filling [20]. In addition, when  $e_g$  on the surface of transition-metal cations is odd, it is favorable for obtaining the desired electrocatalyst based on Yang Shao-Horn's principle [21].

It has been reported that geometric structure and electronic regulation are essential to ingenious design of oxygen evolution reaction and hydrogen evolution reaction electrocatalysts [22]. Therefore, tremendous efforts have been devoted to further improve electro-catalytic performance of cobalt selenides by rational design of the structure and regulate chemical component. Xie's group successfully synthesized the ultrathin  $\text{CoSe}_2$  nanosheets with rich  $V_{\text{Co}}$  vacancies, which show an overpotential of 320 mV at 10  $\text{mA cm}^{-2}$  and a Tafel slope of 46  $\text{mV dec}^{-1}$  due to overcoming the insufficient active sites in bulk  $\text{CoSe}_2$  [23]. Fan's group reported that metal organic frameworks-derived  $\text{CoSe}_2$  microsphere with hollow interiors needs an overpotential of 330 mV at 10  $\text{mA cm}^{-2}$  for OER in 1.0 MKOH [24]. On the other hand, great progresses have been made based on the regulation of chemical component. For example, Jin and co-workers synthesized  $\text{Au}_{25}/\text{CoSe}_2$  composite affords a current density of 10  $\text{mA cm}^{-2}$  at a overpotential of ~430 mV, which can be attributed to electronic interactions between  $\text{Au}_{25}$  nanocluster and  $\text{CoSe}_2$  [25]. In addition, Dong's group reported Zn-doped  $\text{CoSe}_2$  nanosheets grown on free-standing carbon fabric collector, which need the potential of 356 mV to reach the current density of 10  $\text{mA cm}^{-2}$  [26]. However, the OER performance of these  $\text{CoSe}_2$  based materials is still much lower than expected. One possible reason is that low electrochemical surface area leads to insufficient exposure of active sites. Thus, preparing  $\text{CoSe}_2$  materials with more exposed active sites and improved charge transfer still remains a huge challenge. Unfortunately, to the best of our knowledge, increasing the electrochemical surface area of the  $\text{CoSe}_2$ -based materials by rationally

designing the morphology to expose more active sites has been rarely explored so far.

Recently, metal organic frameworks (MOFs) have received widespread attention due to their large specific surface area, uniform ordered pores, facile synthesis and regulated pore structure, which is very beneficial for the electrocatalytic process [27,28]. In particular, zeolite imidazole frameworks (ZIFs), as a class of MOFs, have been confirmed to be the ideal precursor to prepared carbon-based nanocomposites through in-situ carbonization to enhance the relevant properties [29].

Herein, we fabricated the carbon nanotubes grafted 3D core-shell  $\text{CoSe}_2@\text{C}$  composites ( $\text{CoSe}_2@\text{C-CNT}$ ) by utilizing simple hydrothermal-calcination strategy. The  $\text{Co}^{2+}$  in the hydrothermally prepared ZIF precursor is first reduced to metallic cobalt during calcination and then reacts with the selenium powder. The resulting unique  $\text{CoSe}_2@\text{C-CNT}$  hybrids possessed large electrochemical surface area (674.7  $\text{cm}^2$  per geometrical area) leads to an excellent electrochemical performance for OER, which needs a low overpotential of 306  $\text{mV}@10 \text{ mA cm}^{-2}$  and 345  $\text{mV}@50 \text{ mA cm}^{-2}$  and a small Tafel slope of 46  $\text{mV dec}^{-1}$ .

## 2. Experimental

### 2.1. Materials

Cobalt nitrate hexahydrate [ $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 99.0%], Zinc nitrate hexahydrate [ $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 99.0%], 2-methylimidazole (98%), Se powder (99.9%) and Iridium dioxide ( $\text{IrO}_2$ , 99.9%) are all purchased from Aladdin Industrial Corporation. Nafion solution (5 wt%) were acquired from Sinopharm Chemical Reagent Co., Ltd. Methanol (99.5%) were purchased from Beijing Chemical Works. All these reagents were used without any further purification.

### 2.2. Synthesis of hollow Zn/Co-ZIF

Hollow Zn/Co-ZIF were synthesized based on a previous literature with minor modifications [30]. In brief, 0.546 g  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 0.558 g  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 0.630 g 2-methylimidazole were dissolved in 7.5 mL methanol, 7.5 mL methanol and 15 mL methanol, respectively under ultrasonication for 3 min at room temperature to form a homogeneous solution. Then, the methanolic solution of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was mixed with 2-methylimidazole solution under ultrasound for 3 min at 40 °C. In the next step,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in methanol solution was stepwise injected into the above-prepared solution by syringe. After magnetic stirring for 1 min, the resulting suspension was transferred into a 50 mL Teflon-lined stainless-steel autoclaves and then hydrothermally treated at 120 °C for 4 h. The products were collected via centrifugation and wash thoroughly with methanol for several times before drying overnight at 80 °C.

### 2.3. Preparation of ZIF-900-0

The as-prepared hollow Zn/Co-ZIF was placed into a quartz boat and transferred into tube furnace and then increased to 900 °C with 5 °C  $\text{min}^{-1}$  and maintained for 2 h under Ar atmosphere, denoted as ZIF-900-0.

Download English Version:

<https://daneshyari.com/en/article/10133182>

Download Persian Version:

<https://daneshyari.com/article/10133182>

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