



# Octopus tentacles-like $\text{WO}_3/\text{C}@\text{CoO}$ as high property and long life-time electrocatalyst for hydrogen evolution reaction



Yi Lv, Yongkang Liu, Changmiao Chen, Taihong Wang, Ming Zhang\*

Key Laboratory for Micro/Nano Optoelectronic Devices of Ministry of Education, School of Physics and Electronics, Hunan University, Changsha 410082, China

## ARTICLE INFO

### Article history:

Received 2 February 2018

Received in revised form

29 April 2018

Accepted 22 May 2018

Available online 23 May 2018

### Keywords:

Octopus tentacles-like

$\text{WO}_3/\text{C}@\text{CoO}$

Carbon coating

Synergistic effect

HER

## ABSTRACT

Enlarging the specific surface area and increasing the number of active sites of catalysts have been the key factors to improve the properties of hydrogen evolution reaction (HER) catalysts. Herein, we report a novel remarkable octopus tentacles-like tungsten oxide and carbon coated cobalt oxide ( $\text{WO}_3/\text{C}@\text{CoO}$ ) catalyst on Ni foam (NF) for HER at the first time, which is synthesized via simple hydrothermal process and immersion method. The obtained Ar/ $\text{H}_2$ -treated  $\text{WO}_3/\text{C}@\text{CoO}/\text{NF}$  catalyst exhibits excellent electrocatalytic activity toward HER with an onset potential of 40 mV (vs. RHE) and a Tafel slope of 115 mV  $\text{dec}^{-1}$  in 1 M KOH, which is significantly better than the Ar-treated  $\text{WO}_3/\text{C}@\text{CoO}/\text{NF}$  and the  $\text{CoO}/\text{NF}$  NWs. In addition, the prepared Ar/ $\text{H}_2$ -treated  $\text{WO}_3/\text{C}@\text{CoO}/\text{NF}$  electrode has an outstanding electrocatalytic durability in a long period of stability test for 110 h. Such outstanding property of the Ar/ $\text{H}_2$ -treated  $\text{WO}_3/\text{C}@\text{CoO}/\text{NF}$  electrocatalyst is attributed to its 3D conductive substitute, carbon coating, strong synergistic effect of between  $\text{WO}_3$  and  $\text{CoO}$  and the unique octopus tentacles-like structure making it a very excellent catalyst for hydrogen production. All these experimental results clearly suggest that Ar/ $\text{H}_2$ -treated  $\text{WO}_3/\text{C}@\text{CoO}/\text{NF}$  electrocatalyst can improve HER catalytic activity and thus has potential practical applications in water splitting.

© 2018 Elsevier Ltd. All rights reserved.

## 1. Introduction

The problems of global energy crisis and climate change caused by greenhouse gases become more and more serious, the search for the environmentally friendly, renewable and affordable energy source is vital for national development nowadays [1–4,59]. Among the potential alternative energy resources, hydrogen energy with high mass energy density and zero emission of greenhouse gases is considered as an ideal clean energy source to replace the role of petroleum [5–7]. The production of molecular hydrogen by water-splitting reaction is an important method, but there is a lack of continuable catalysts composed of low-cost and abundant elements on earth that can efficiently catalyze in hydrogen evolution reaction (HER) [8]. The noble metal platinum (Pt) exhibits high activities and stabilities as HER catalysis and can observably enhance the reaction rate with the initial potential of almost close to zero for high efficiency energy conversion [9–11]. However, its high cost and scarcity have hindered the industrialization process

of hydrogen production by water electrolysis technology [3,12–16]. Therefore, comparably efficient, noble-metal-free and durable HER electrocatalysts are being actively pursued [17,18,60]. All along, the preparation of catalysts for efficient HER has been a hot research topic.

Over the past years, earth-abundant, low-cost transition metal oxides (TMOs) have been studied as HER catalysts, such as nickel oxides [19,20], iron oxides [21] and cobalt oxides [22,23]. Cobalt oxides have been proven to be a candidate for efficient hydrogen production, not only because of its relatively low price, but also its superior catalytic activities for electrocatalysis [24–26]. For example, Chen et al. demonstrated excellent activity  $\text{Co}/\text{Co}_3\text{O}_4$  nanosheets for HER with the unique metal/oxide core/shell structure [27]. M. Tour et al. reported porous cobalt-based thin film for efficient hydrogen generation and oxygen generation [28]. Nevertheless, the catalytic activity and stability of these alternative catalysts are still not on par with conventional noble metal catalysts. The catalytic property of these catalysts is very limited due to low conductivity and small number of active sites [22]. Nowadays, three-dimensional (3D) self-supporting electrodes are becoming more and more popular in electrochemical research. Compared

\* Corresponding author.

E-mail address: [zhangming@hnu.edu.cn](mailto:zhangming@hnu.edu.cn) (M. Zhang).

with conventional electrodes coated on two-dimensional (2D) substrate, the properties of 3D self-supporting electrodes are always better than the plane electrodes [29,30]. As we all know, NF has a 3D frame structure which ensures uniform growth of nanomaterials with large surface areas and greater surface roughness, while decreasing the contact resistance and increasing the electrical conductivity [31,32]. Indeed, the superiority of such technology is fully demonstrated by electrocatalyst, such as the  $\text{MoO}_2/\text{NF}$  nanosheets [33] and  $\text{WO}_3\text{-x}/\text{NF}$  nanosheets [34]. On the other hand, the composition of TMOs with other nanomaterials (e.g., metals, conductive materials), because of the synergistic effect of different components, could also provide more active sites and promote fast charge transfer between the external circuit and electrode to enhance the catalytic activity in electrocatalytic HER [35,36]. In addition, as a superior HER catalyst, it not only needs to demonstrate the excellent HER activity, but also long life-time is very important in the alkaline environments found in practical large-scale application [37].

Herein, we for the first time prepared octopus tentacles-like C and  $\text{WO}_3$  coated CoO by hydrothermal process and immersion method. It is based on the CoO nanowires (NWs) which were vertically grown on 3D NF substrate via a facile hydrothermal process. In order to improve the electrical conductivity of electrode, the conductive polymer of polyvinyl alcohol (PVA) was integrated into the nanowire arrays, and PVA has viscosity that could fix the tungsten oxide onto the surface of the nanowires as a thin layer of nanometer size, while maintaining the ordered nanowire-structure unchanged [38]. The unique octopus tentacles-like structure and strong synergetic coupled effect of the Ar/ $\text{H}_2$ -treated  $\text{WO}_3/\text{C}@/\text{CoO}$  NWs provide a large specific surface area, more hydrogen adsorption activity sites and fast electron transfer rate. As a result, Ar/ $\text{H}_2$ -treated  $\text{WO}_3/\text{C}@/\text{CoO}$  NWs are directly used as the electrode for HER in alkaline solution, which proves outstanding properties of onset potential of 40 mV, Tafel slope of 115  $\text{mV dec}^{-1}$ . And it only needs overpotential of about 55 mV to achieve the current density of  $10 \text{ mA cm}^{-2}$ . In addition, it also shows a good stability.

## 2. Experimental section

### 2.1. Synthesis of CoO nanowires on Ni foam

CoO nanowires were grown on Ni foam (NF) by a simple hydrothermal method that the previous literatures have been reported. In detail, Ni foam was cleaned with 3 M HCl for several times. 0.727 g cobalt nitrate hexahydrate and 0.6 g urea were dissolved in 50 mL deionized water, and the obtained homogeneous solution was further transferred into a 100 mL Teflon-lined stainless steel autoclave and the clean nickel foam was placed vertically in the autoclave. Then the autoclave was put into the oven and maintained at 95 °C for 8 h. After the reaction, the Ni foam with CoO NWs precursor was washed with deionized water for several times and dried in vacuum at 60 °C. Finally the Ni foam with CoO NWs precursor was annealed in Ar at 400 °C for 2 h.

### 2.2. Synthesis of $\text{WO}_3/\text{C}@/\text{CoO}$ on Ni foam

0.85 g Polyvinyl Alcohol (PVA) and 0.5 g Ammonium metatungstate ( $(\text{NH}_4)_6\text{H}_2\text{W}_{12}\text{O}_{40}\cdot\text{xH}_2\text{O}$ ) were dissolved in 10 g deionized water, and the mixture was heated in the oven at 60 °C and then stirred to obtain a homogeneous solution by a magnetic stirrer. Next the Ni foam with CoO NWs precursor was soaked in this homogeneous solution for 10 h. After soaking, the Ni foam with precursor was dried in vacuum at 60 °C. Finally the Ni foam with precursor was annealed at 400 °C for 2 h in Ar or Ar/ $\text{H}_2$  to obtain  $\text{WO}_3/\text{C}@/\text{CoO}$  materials.

### 2.3. Characterizations

The characterizations of the samples were carried out by scanning electron microscope (SEM, Hitachi S-4800, 5 kV), transmission electron microscopy (TEM, JEOL JEM-2100F), X-ray photoelectron spectroscopy (XPS, Surface Science Instruments S-probe spectrometer), X-ray diffraction (XRD, Cu  $\text{K}\alpha$  irradiation,  $\lambda = 1.5418 \text{ \AA}$ ) and Inductively coupled plasma atomic emission spectrometry (ICP, Vista Axial).

### 2.4. Electrochemical measurements

All of the HER electrochemical measurements for all materials were carried out by using a typical three-electrode setup. For testing conditions in 1.0 M KOH, the samples were used as a working electrode. Ag/AgCl electrode and graphite rod electrode served as reference electrode and counter electrode, respectively. For comparison, the commercial Pt/C (10 wt %, loaded on the Ni foam at  $8 \text{ mg/cm}^{-2}$ ) catalyst was tested in the same system. Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) measurement were measured in 1 M KOH solution at scan rates of  $50 \text{ mV s}^{-1}$  and  $5 \text{ mV s}^{-1}$ , respectively. All the potentials, measured an Ag/AgCl electrode, were converted into the reversible hydrogen electrode (RHE) on the basis of equation  $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 + 0.059 \text{ pH}$ . CV experiments were conducted at the potential range from 0 to  $-0.1 \text{ V}$  vs. RHE at scan rate of 20, 40, 60, 80, 100  $\text{mV s}^{-1}$ , respectively. The accelerated degradation measurements of the catalysts were evaluated by conducting CV sweeps between 0.1 and  $-0.2 \text{ V}$  vs. RHE at a scan rate of  $200 \text{ mV s}^{-1}$  for 2000 cycles followed by LSV measurement at a scan rate of  $5 \text{ mV s}^{-1}$ . The long-term stability was tested at the current density of  $10 \text{ mA cm}^{-2}$ . All HER property curves were tested without iR correction.

## 3. Results and discussion

The preparation of C and  $\text{WO}_3$  coated CoO nanowires is illustrated in Fig. 1. To be specific, CoO NWs precursor was first grown on the NF via a simple hydrothermal reaction. After being grown with CoO NWs precursor, the color of NF changed from gray to dark purple. And then the NF with CoO NWs precursor was soaked in a homogeneous solution of ammonium metatungstate and PVA for 10 h. Subsequent removing and placing it in a vacuum drying oven. Finally, the precursor was annealed in Ar or Ar/ $\text{H}_2$  atmosphere at 400 °C for 2 h, and it was converted into  $\text{WO}_3/\text{C}@/\text{CoO}$ . In consequence, the color of NF further turned to black (Fig. S1). In the process of synthesis, PVA not only acts as a viscous material to promote a better combination of CoO and  $\text{WO}_3$ , but also leads to the generation of the carbon layer to cover in the surface of the CoO NWs.

The morphology and structural evolution of the as-prepared samples are analyzed by scanning electron microscope (SEM) and transmission electron microscope (TEM). The image of the bare NF

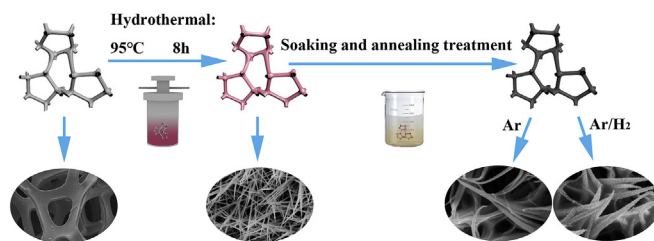


Fig. 1. Scheme illustration of the formation of C and  $\text{WO}_3$  coated CoO nanowires on Ni foam.

Download English Version:

<https://daneshyari.com/en/article/6602301>

Download Persian Version:

<https://daneshyari.com/article/6602301>

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