



# Self-supported ternary Ni-Fe-P nanosheets derived from metal-organic frameworks as efficient overall water splitting electrocatalysts

Cuijuan Xuan, Zongkai Peng, Kedong Xia, Jie Wang, Weiping Xiao, Wen Lei, Mingxing Gong, Ting Huang, Deli Wang\*

Key Laboratory of Material Chemistry for Energy Conversion and Storage, Ministry of Education, Hubei Key Laboratory of Material Chemistry and Service Failure, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, China

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## ABSTRACT

Developing cost-effective, highly-efficient and stable electrocatalysts is of significance to replace noble metal based materials for overall water electrolysis. In this paper, nickel-iron phosphide nanosheets on nickel foam (Ni-Fe-P/NF) were synthesized through in-situ chemical etching and subsequently phosphating treatment. The Ni foam utilized in this work not only serves as conductive substrate and metal current collector, but also as nickel source for the growth of metal organic frameworks (i.e. Prussian blue analogue pyramids), which were then converted to Ni-Fe-P nanosheets via phosphating. Benefiting from the unique nanostructure, Fe incorporation, and the high conductivity of nickel foam, the resulting Ni-Fe-P/NF could be used as self-supported and binder-free working electrode with superior overall electrochemical water splitting performance. Electrochemical measurement demonstrates that the Ni-Fe-P/NF exhibits excellent electrocatalytic activities with overpotentials of 98 mV for HER and 168 mV for OER to deliver current densities of  $10 \text{ mA cm}^{-2}$  in 1 M KOH solution. Furthermore, the Ni-Fe-P/NF catalyst was also employed as both as anode and cathode for overall water electrolysis, and shows extraordinary activities with low voltage of only 1.486 V to yield  $10 \text{ mA cm}^{-2}$  and outstanding cycling stability with negligible voltage elevation after chronopotentiometry determination for 200 h. This work highlights that direct growth of metal organic frameworks on conductive substrates is an effective method to explore electrocatalysts for multifunctional electrochemical applications.

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## 1. Introduction

Water electrolysis has emerged as a clean and sustainable technology for producing the eco-friendly and renewable hydrogen energy [1]. Electrocatalysts are necessary to reduce the overpotential and enhance the efficiency of energy conversion due to the sluggish kinetics of hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) during the electrochemical water splitting [2]. Currently, platinum-based materials, and iridium- and ruthenium-based substances have been recognized as the most efficient catalysts for HER and OER, respectively [3]. However, the limited reserve and high cost restrict their large-scale applications [3]. Consequently, enormous efforts have been devoted to the exploration of the high-efficient and low-cost catalysts for water electrolysis based on the earth's abundant resources, such as

transition metal-based phosphides [4,5], sulfides [6,7], oxides/hydroxides [8,9], selenides [10,11] and metal-free materials [3,12].

Recently, transition metal phosphides (TMPs) have received far more attention owing to the low electrical resistance and good corrosion tolerance [13]. Various TMPs such as  $\text{Ni}_x\text{P}_y$  [14,15],  $\text{FeP}$  [16,17],  $\text{Fe}_2\text{P}$  [18],  $\text{MoP}$  [19,20], and  $\text{CoP}$  [21,22] have been synthesized and demonstrated as the efficient and stable electrocatalyst for HER and/or OER. Moreover, bimetallic phosphides have particularly received more attention for further enhancement of the catalytic activities [23–25]. Despite significant progress, most of the catalysts only possess HER or OER catalytic activities, or not exhibit excellent catalytic performance for water splitting in the same electrolyte, which would complicate the electrolyzer devices and increase the overall cost for the large-scale commercial production [26]. Additionally, most of these catalysts, generally synthesized in the form of powders, should be loaded onto the current collectors using binder additives (such as Nafion) [27]. These binders employed would block the active sites and lead to

\* Corresponding author.

E-mail address: [wangdl81125@hust.edu.cn](mailto:wangdl81125@hust.edu.cn) (D. Wang).

incomplete contact between the catalysts and the substrates and thus restricting the catalytic properties [28,29]. Furthermore, the catalysts loaded onto the substrate with binder tend to readily detach from the substrate due to the violently evolving gas bubbles during water electrolysis, hence lead to poor long-term stability [27]. In order to address the above issues, bifunctional catalysts could be synthesized by the binder-free pathway to obtain self-supported electrodes for the direct use in water electrolyzers.

Various conductive substrates (e.g. nickel foam [6,10], carbon cloth [30], carbon paper [31,32]) have been employed for the development of the bifunctional electrocatalysts toward water electrocatalysis. Nickel foam (NF) has been reported as the ideal conductive substrate for the synthesis of catalysts due to the low cost, three-dimensional porous structure, high surface area, and good electrical conductivity [27,33]. For example, ternary phosphide (NiCoP) film on NF was prepared via an electrodeposition technique and utilized as efficient catalysts for water electrolysis for delivering  $10 \text{ mA cm}^{-2}$  at required potential of 1.57 V [34]. Ni foam supported iron (Fe)-doped nickel phosphide ( $\text{Ni}_2\text{P}$ ) nanosheet arrays were synthesized by a hydrothermal method and post-phosphidation, which can achieve a current density of  $10 \text{ mA cm}^{-2}$  at 1.61 V during water splitting [35]. The existence of NF could enhance the electric conductivity, and thus promote the reaction kinetics during water splitting [34]. Hu et al. [36] prepared bulk amorphous NiFeP materials by a melting spinning and rapid quenching process, which exhibited excellent OER performance with overpotentials of 219 and 540 mV for yielding a current density of  $10 \text{ mA cm}^{-2}$  in alkaline and acidic electrolyte, respectively. Luo et al. [37] reported a hydrothermal method to synthesize NiFe-layered double hydroxide with the post-phosphidation treatment to obtain the final NiFeP catalysts with excellent OER catalytic activities. Despite the above efforts, developing NF supported bifunctional catalysts for HER and OER in the same electrolyte is still of important significance to further reduce the overpotential and improve the efficiency of the water splitting devices.

Metal-organic frameworks (MOFs) are getting the spotlight to prepare nanostructured materials for energy conversion and storage applications taking advantage of their high porosity, large surface area, as well well-defined structure [38–41]. However, there are limited reports related to direct preparation of MOF-derived catalysts on conductive substrate for full water electrolysis. In this work, the nickel-iron phosphide nanosheet on nickel foam was prepared via a simple two-step method. Prussian blue analogue (PBA) pyramids were obtained through in-situ chemical etching approach, in which the Ni foam serves as nickel precursors formed by acid-etching the substrate and metal current collector. And then PBA pyramids were converted to Ni-Fe-P/NF during phosphating process. The as-prepared Ni-Fe-P/NF exhibits high-efficient bifunctional activities and outstanding stabilities for full water splitting due to the unique nanostructure and the high conductivity of nickel foam.

## 2. Experimental methods

### 2.1. Synthesis of the Ni-Fe-P/NF composite

To remove the surface oxidized layer, a piece of Ni foam ( $1 \text{ cm} \times 3 \text{ cm}$ ) was cleaned through sonication consecutively in 3 M HCl, ethanol, and deionized water (5 min each) before use. 4 mmol of potassium ferricyanide was dissolved in 2 M of hydrochloric acid solution (30 mL) under constant stirring to obtain the clear solution. The pre-treated Ni foam was immersed into the solution and kept at room temperature for 24 h. Then the NiFe-PBA grown on Ni foam was removed from the solution and washed several times

with deionized water and ethanol to remove any unreacted residues, followed by drying at  $50 \text{ }^\circ\text{C}$  overnight in the vacuum oven. After that, the resulting NiFe-PBA/NF was placed in the center of the tube furnace with  $\text{NaH}_2\text{PO}_2$  in the upstream side. After purging nitrogen for 30 min, the furnace was heated to  $350 \text{ }^\circ\text{C}$  at the heating rate of  $3 \text{ }^\circ\text{C min}^{-1}$  for 2 h. And the product denoted as Ni-Fe-P/NF was obtained after the furnace naturally cooling down to room temperature. For comparison, The other Ni-Fe phosphides supported on Ni foam were synthesized through the same method except changing the concentration of hydrochloric acid (0.1 M and 0.3 M) or the molar mass of potassium ferricyanide (0.1 mmol and 0.8 mmol). The Ni-P/NF was also prepared by direct phosphidation of Ni foam.

### 2.2. Material characterization

Powder X-ray diffraction (XRD) patterns of the synthesized catalysts were detected utilizing an X'Pert PRO diffractometer at a scan rate of  $10^\circ \text{ min}^{-1}$ . Field emission scanning electron microscopy (FESEM) were performed by Sirion200. Scanning transmission electron microscopy (S-TEM), Transmission electron microscopy (TEM) and elemental mapping images were obtained on Tecnai G2 F30. Fourier transform infrared spectroscopy (FT-IR) characterization was carried out at ambient temperature with an FT-IR spectrometer (VERTEX 70, BRUKER Inc.). X-ray photoelectron spectroscopy (XPS) data were obtained using an AXIS-ULTRA DLD-600W Instrument.

### 2.3. Electrochemical measurement

Electrochemical determination was all conducted in 1.0 M KOH solution on an Autolab PG302N electrochemical workstation. For the three-electrode setup, the as-prepared Ni-Fe-P/NF or Ni-P/NF served as working electrode with the reverse hydrogen electrode (RHE), and a carbon rod as the reference electrode and the counter electrode, respectively. For comparison, 5 mg of Ir/C or Pt/C catalyst was dispersed in the mixture of Nafion and isopropyl alcohol solution (1 mL), followed by sonication to obtain the homogeneous ink dispersion. Then, 40  $\mu\text{L}$  of the obtained ink was dropped onto Ni foam and dried at room temperature, which is used as the working electrode for comparison. Linear sweep voltammetry (LSV) measurements were performed at the scan rate of  $5 \text{ mV s}^{-1}$  at the potential in the range from 0.2 V to  $-0.5 \text{ V}$  for HER and from 0.8 V to 1.8 V for OER. Electrochemical impedance spectroscopy (EIS) detection was conducted in the frequency range from 100 kHz to 0.01 Hz with an ac perturbation of 5 mV when the potential was  $-0.1 \text{ V}$  for HER and 1.5 V for OER. The durability was tested at the current density of  $10 \text{ mA cm}^{-2}$  or  $20 \text{ mA cm}^{-2}$  for 40 h. Cyclic voltammogram (CV) cycles determination was performed in the potential range from  $-0.3 \text{ V}$  to 0.1 V for HER and 1.4 V–1.8 V for OER at the scan rate of  $100 \text{ mV s}^{-1}$ . For the two-electrode configuration, the identical samples were employed as anode and cathode respectively. LSV curves were collected at the scan rate of  $5 \text{ mV s}^{-1}$  at the potential from 0.8 V to 1.8 V. The stability detection was obtained at the current density of  $10 \text{ mA cm}^{-2}$  for 200 h.

## 3. Results and discussion

The Ni-Fe-P/NF composite is prepared through a two-step method, as shown in Scheme 1. Initially, Ni foam was directly employed as nickel source without adding any nickel salts, and Ni-Fe Prussian blue analogue (NiFe-PBA) nanopyramids were in-situ grown on nickel foam via the chemical etching approach. During the synthesis process, the Ni foam functions as the both supporting scaffolds and nickel source. The Ni ion species dissolved form Ni

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