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Ternary nickel iron phosphide supported on nickel foam as a high-efficiency electrocatalyst for overall water splitting

Chi Zhang, Yunchao Xie, Heng Deng, Cheng Zhang, Jheng-Wun Su, Yuan Dong, Jian Lin*

Department of Mechanical & Aerospace Engineering, University of Missouri, Columbia, MO 65211, United States

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ABSTRACT

Electrochemical water splitting is a promising technology for mass hydrogen production. Efficient, stable, and cheap electrocatalysts are keys to realizing this strategy. However, high price and preciousness of commonly used noble metal based catalysts severely hinder this realization. Herein, we report nickel iron phosphide (Ni-Fe_xP) bifunctional electrocatalyst via the in-situ growth of Ni-Fe(OH)_x on nickel foam (Ni-Fe(OH)_x/NF) followed by low-temperature phosphidation. As a hydrogen evolution reaction (HER) catalyst, the Ni-Fe_xP/NF only needs an overpotential of 119 mV to drive a current density of -10 mA/cm² in a base media. It also shows excellent activity toward oxygen evolution reaction (OER) with low overpotentials of 254 mV, 267 mV, and 282 mV at 50, 100 and 200 mA/cm², respectively. Moreover, when this bifunctional catalyst is used for overall water splitting, a low cell voltage of 1.62 V is needed to deliver a current density of 10 mA/cm², which is superior to commercial electrolyzer and it also shows remarkable stability.

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Introduction

Due to continuous growth of global energy demand and environmental concerns, in the past decades, great efforts have been devoted to explore clean and renewable energy sources to replace fossil fuel [1]. Hydrogen has been widely regarded as a suitable candidate because of its high density, high energy conversion efficiency, and environmental friendliness [2]. Electrochemical water splitting ($2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$) is a promising way to realize a mass production of pure molecular hydrogen without carbon emission [3,4]. At present, RuO₂ and Pt/C are benchmark catalysts for oxygen evolution reaction (OER) and hydrogen evolution reaction (HER), respectively. However, the high price, poor stability,

and scarcity severely restrict their potentials [5,6]. Therefore, it is highly desirable and imperative to develop earth-abundant and efficient OER and HER catalysts.

In recent years, transitional metal sulfides, selenides, carbides, nitrides, phosphides, and phosphates have been widely surveyed as water splitting electrocatalysts [7–16]. Among them, transitional metal phosphides have attracted great attention because of their high catalytic activity and earth abundance [17–19]. Since Sun's group reported the topotactic fabrication of free-standing CoP nanowire arrays on carbon paper with excellent HER activity in acid, neutral, and basic electrolytes [20], much exciting progress toward various metal phosphides such as Ni₂P [21,22], MoP [23], and WP [24] have been achieved. Very recently, experimental and theoretical studies have confirmed that the existence of P atom can

* Corresponding author.

E-mail address: linjian@missouri.edu (J. Lin).

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significantly reduce the absolute value of Gibbs free energy of hydrogen adsorption ($\Delta G^{\circ}_{\text{H}}$), which is thought to be beneficial to enhance the catalytic performance toward HER [25]. Moreover, easily formed P-defects can balance binding intensity between intermediates ($^*\text{OOH}$ and $^*\text{O}$) and catalytic sites to decrease the free-energy barrier [26], thus enhancing the OER activity.

On the other hand, many studies have proved that bimetallic based compounds with certain metal ratios usually exhibit better catalytic performance than their corresponding monometallic counterparts [27–30]. For instance, Husam's group reported NiCoP as a superior bifunctional catalyst towards HER and OER in alkaline media [10]. The experimental and theoretical results suggest that the electronic structure of the monometallic phosphide was altered by introducing extrinsic metals to dramatically enhance the catalytic activity. Among different metal configurations, the synergistic effect between Ni and Fe has drawn extensive attention because researchers find out that even a trace amount of Fe incorporation can greatly improve the turn over frequency of nickel based compounds and then dramatically enhance their OER performance [31]. Although the exact mechanism of this synergistic effect is still under debate, the strategy has been widely deployed in different material systems [32–35]. For instance, Yang' group demonstrated that by the introduction of Fe, the HER catalytic activity and stability of iron-nickel sulfide are greatly improved in acidic solution [27]. Recent work shows that Fe doped Ni_2P as an OER catalyst is superior than pure Ni_2P . It results in an overpotential of 215 mV when current density is 50 mA/cm^2 [36]. Very recently, Ahn and Mathiram adopted a post-MOF conversion strategy to synthesize amorphous carbon incorporated porous Ni–Fe phosphide nanorod on nickel foam (porous Ni–Fe–P@C/NF) through several synthesis steps [37]. However, the MOF treatment is necessary to obtain porous structure and boost the catalytic performance. Despite these progress, to the best of our knowledge, there is little report on Ni incorporated Fe_2P dominated bimetallic compounds as a single-functional electrocatalyst let alone demonstrating their bifunctional HER and OER activities. In this paper, we reported bimetallic Ni–Fe phosphide ($\text{Ni-Fe}_x\text{P}$) directly synthesized on a nickel foam via *in situ* growth of Ni–Fe(OH) $_x$ on nickel foam by co-precipitation and followed by a low temperature phosphidation. The synthesized $\text{Ni-Fe}_x\text{P}$ acts as a highly efficient bifunctional catalyst towards HER and OER in alkaline solution. It affords an overpotential of 176 mV at 50 mA/cm^2 for HER and an overpotential of 254 mV at 50 mA/cm^2 for OER, respectively. Finally, a typical two-electrode full-cell alkaline water electrolyzer based on this bifunctional electrocatalyst was demonstrated. It shows an overpotential of 1.62 V at a current density of 10 mA/cm^2 and an extraordinary stability of more than 140 h at a constant current density of 10 mA/cm^2 .

Experimental

Fabrication of Ni-Fe $_x$ P/NF

All chemicals were used as received without any further purification. The Ni–Fe(OH) $_x$ /NF was prepared via a previously

reported wet chemistry method with a minor modification [12]. In a typical synthesis, 0.022 g trisodium citrate and 0.3336 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were added into a 250 mL flask containing 120 mL deionized water. After vigorously stirring, a clear light green solution was formed. A piece of nickel foam ($2 \text{ cm} \times 1 \text{ cm}$) was washed with 3 M HCl, ethanol, and deionized water several times. Then the pre-cleaned nickel foam was immersed into the prepared solution and heated at $90 \text{ }^\circ\text{C}$ for 2 h in an oil bath with a slow stirring. After cooling down to the room temperature naturally, the precursor was taken out and washed with deionized water and ethanol.

To prepare Ni-Fe $_x$ P/NF, a well known low-temperature phosphidation method was adopted [20,28,38]. To be specific, the obtained Ni–Fe(OH) $_x$ /NF and 0.4 g NaH_2PO_2 were placed at two positions of a porcelain boat with a distance of $\sim 5 \text{ cm}$ in between and then heated at $300 \text{ }^\circ\text{C}$ for 2 h under a static argon atmosphere. After cooling down to room temperature naturally, the Ni-Fe $_x$ P/NF was taken out and ready for test. The mass loading is around 8 mg/cm^2 based on the mass change and the elements ratio. As a comparison, iron foam supported iron phosphide ($\text{Fe}_x\text{P}/\text{IF}$) was prepared through the same procedure. It affords an overpotential of 213 mV at 50 mA/cm^2 for HER and an overpotential of 360 mV at 50 mA/cm^2 for OER, respectively (Figs. 2–3). The results further demonstrated that the increase of catalytic activity was caused by the introduction of nickel.

Characterization

X-ray diffraction (XRD) patterns were carried out on a Rigaku X-ray diffractometer with a Cu K α radiation ($\lambda = 0.15406 \text{ nm}$) to explore crystalline property. The surface morphology was observed with Hitachi S-4800 field emission scanning electron microscopy (SEM). Energy dispersive X-ray spectroscopy (EDS) and EDS elemental mapping were performed with an EDS detector equipped in the Hitachi S-4800 FESEM. High-

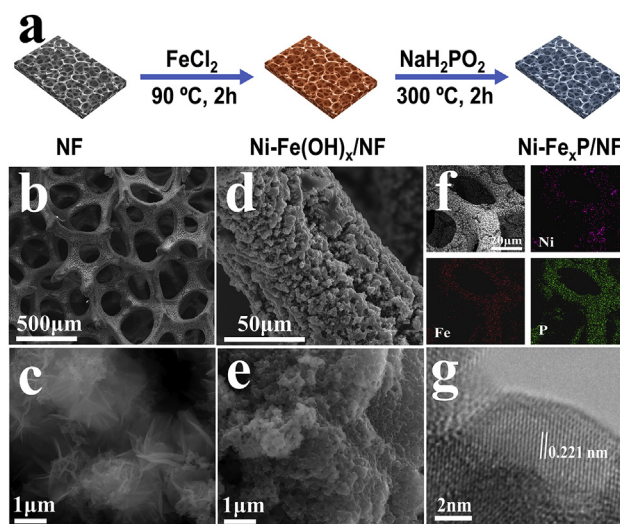


Fig. 1 – (a) Schematic illustration of Ni-Fe $_x$ P/NF. (b) SEM images of (b, c) Ni–Fe(OH) $_x$ /NF and (d, e) Ni-Fe $_x$ P/NF (f) EDS elemental mappings of Fe, Ni, and P in Ni-Fe $_x$ P/NF. (g) High-resolution TEM image of Ni-Fe $_x$ P/NF.

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