

# Scalable Synthesis of Bifunctional Multi-elements Electrocatalysts with Tailored Morphological and Electronic Properties for Superior Overall Water Splitting

**Xiaomei Wang,<sup>a,b</sup> Weiguang Ma,<sup>a</sup> Zhiqiang Xu,<sup>a,b</sup> Xu Zong,<sup>a,\*</sup> and Can Li<sup>a,\*</sup>**

<sup>a</sup>State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian National Laboratory for Clean Energy, The Collaborative Innovation Center of Chemistry for Energy Materials (iChEM), Dalian, 116023, China

<sup>b</sup> University of Chinese Academy of Sciences, Beijing, 100049, China

\*Corresponding author: E-mail: xzong@dicp.ac.cn, canli@dicp.ac.cn

**Abstract:** Producing hydrogen via electrocatalytic water splitting will benefit from the realization of efficient earth-abundant electrocatalysts and scalable synthetic strategies. Herein, we presented the preparation of bifunctional multi-elements water splitting electrocatalysts consisted of Fe, Co, Ni, S and P with a facile electrodeposition method. We realized tunable modulation on the structural and electronic properties of the catalysts and therefore the electrocatalytic performance by systematically tailoring the non-metal modifiers in the catalysts. Under optimum conditions, the as-prepared catalysts demonstrated excellent performance for both hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), as well as overall water splitting.

**Keywords:** Multi-elements electrocatalysts, Electrodeposition, Overall water splitting.

## 1. Introduction

Developing efficient catalysts based on earth-abundant elements towards HER and OER is important towards the conversion of renewable energy (such as solar energy) via electrocatalytic water splitting. In recent years, constructing multi-elements electrocatalysts has been found to be an effective strategy to obtain efficient electrocatalysts due to the synergetic interplay of different elements on improving the electronic properties of catalysts. However, realizing simultaneous tunable modulation on the electronic and structural properties of multi-elements catalysts with a scalable manner remains challenging.

## 2. Experimental

A series of bifunctional water splitting electrocatalysts were prepared by assembling multi-elements Fe, Co, Ni, S, and P with a scalable electrodeposition method. The amount of P (x M) and S (y M) content were systematically varied during electrodeposition and the resulting samples were denoted as FeCoNiP<sub>x</sub>S<sub>y</sub>.

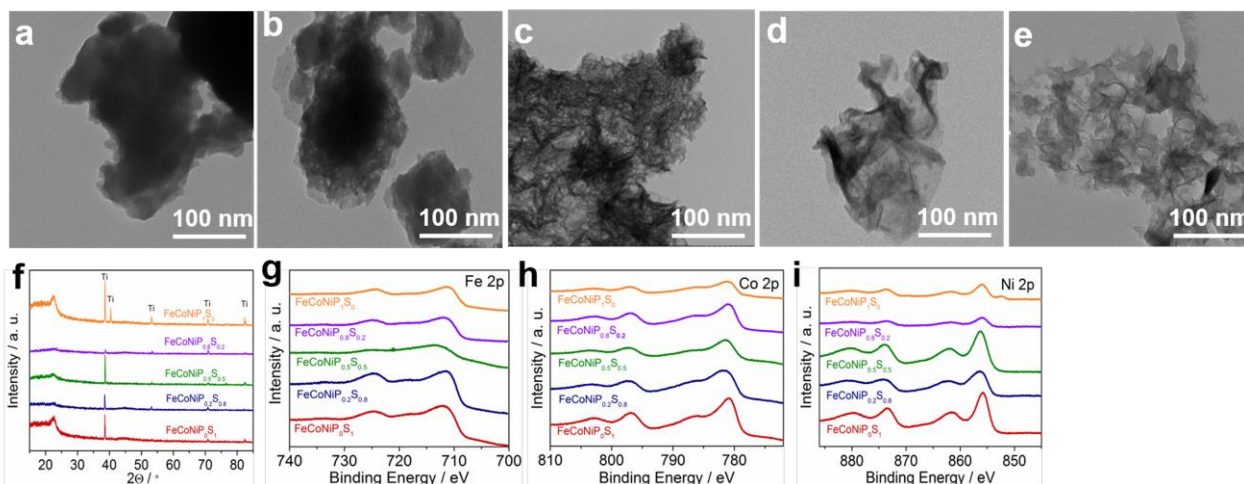
The electrocatalytic performances of FeCoNiP<sub>x</sub>S<sub>y</sub> for HER and OER were evaluated in typical three-electrode configuration. The overall water splitting was carried out in a two-electrode electrolyzer by using the bifunctional electrocatalysts as both the anode and cathode.

## 3. Results and discussion

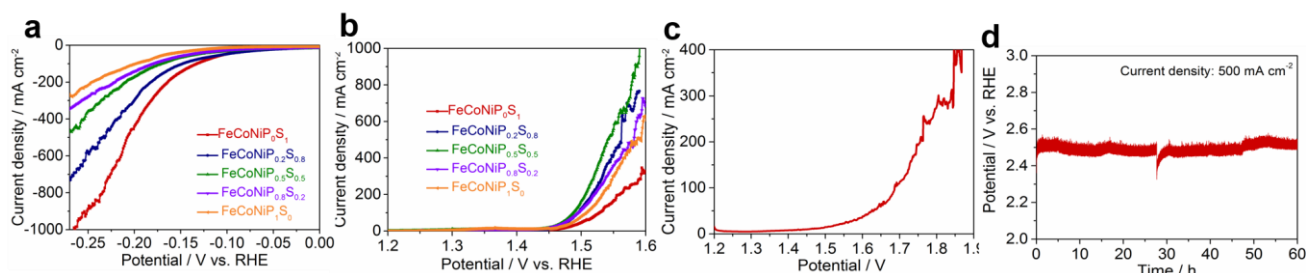
The microstructures of the as-prepared amorphous FeCoNiP<sub>x</sub>S<sub>y</sub> catalysts (Figure 1f) can be modulated by tailoring the amounts of S and P content. As shown in Figure 1a-e, with the increased of S and decreased of P, rippled nanosheets structure was gradually evolved for FeCoNiP<sub>x</sub>S<sub>y</sub>. Moreover, the microelectronic environments of the metals of FeCoNiP<sub>x</sub>S<sub>y</sub> also can be tuned by the non-metal modifiers, which was preliminarily proved by slight shifts of the peak positions for the Fe 2p, Co 2p and Ni 2p spectra with the variation of the S and P contents (Figure 1g-i).

The influence of non-metal modifiers of P and S on the electrocatalytic performances of FeCoNiP<sub>x</sub>S<sub>y</sub> were then investigated in 1 M KOH. HER polarization curves (Figure 2a) show that with increasing the S and decreasing the P contents, a drastic and monotonic increase in the current densities was observed and FeCoNiP<sub>0</sub>S<sub>1</sub> exhibits the highest HER activity with the lowest overpotentials of 43, 135, and 264 mV to achieve current densities of 10, 100 and 1000 mA cm<sup>-2</sup>, respectively. However, the OER activity of FeCoNiP<sub>x</sub>S<sub>y</sub> increase initially with the increase of the S dopant, while further increase in the S content and decrease in the P content led to decreased OER activity (Figure 2b). Among all the FeCoNiP<sub>x</sub>S<sub>y</sub> catalysts,

FeCoNiP<sub>0.5</sub>S<sub>0.5</sub> exhibits the best performance with overpotentials of only 258 and 360 mV to achieve current densities of 100 and 1000 mA cm<sup>-2</sup>, respectively. We found that the increase in the number of active sites rather than the improvement in the intrinsic activity of the active sites for HER is the main reason for the drastically enhanced activities of FeCoNiP<sub>x</sub>S<sub>y</sub> with higher S content. However, the OER activities were influenced by both the modulated apparent activity and intrinsic activity of as-prepared catalysts. When assembled the catalysts as both the anode and cathode for overall water splitting, a current density of 10 mA cm<sup>-2</sup> can be achieved under a low cell voltage of 1.46 V with long-term durability (Figure 2c-d), which is as far as we know the best value reported for bifunctional water splitting electrocatalysts, suggesting the potential for scale-up and sustainable water electrolysis.



**Figure 1.** TEM images of FeCoNiP<sub>1</sub>S<sub>0</sub> (a), FeCoNiP<sub>0.8</sub>S<sub>0.2</sub> (b), FeCoNiP<sub>0.5</sub>S<sub>0.5</sub> (c), FeCoNiP<sub>0.2</sub>S<sub>0.8</sub> (d), FeCoNiP<sub>0.5</sub>S<sub>0.5</sub> (e), and XRD patterns (f), XPS spectra of Fe 2p (g), Co 2p (h) and Ni 2p (i) of the as-prepared catalysts.



**Figure 2.** Linear sweep voltammetry curves for HER (a), OER (b), overall water splitting (c), and long-term durability of overall water splitting at a current density of 500 mA cm<sup>-2</sup> (d).

#### 4. Conclusions

In summary, we assembled multi-elements with a scalable electrodeposition method to obtain a series of bifunctional FeCoNiP<sub>x</sub>S<sub>y</sub> electrocatalysts. Under optimum conditions, the as-prepared catalysts demonstrated excellent performance for overall water splitting (10 mA cm<sup>-2</sup>@1.46 V). This work not only presents a scalable approach for preparing highly efficient and stable bifunctional electrocatalysts based on earth-abundant elements but also highlights the importance of dual electronic and morphological modulation through multi-elements assembly strategy towards HER and OER optimization.

#### References

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