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Porous Structured Ni-Fe-P Nanocubes Derived from Prussian Blue Analogue as Electrocatalyst for Efficient Overall Water Splitting

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ABSTRACT: Exploring non-precious metal electrocatalysts to replace the noble metal based catalysts for full water electrocatalysis is still an ongoing challenge. In this work, porous

structured ternary nickel-iron-phosphides (Ni-Fe-P) nanocubes were synthesized through one-step phosphidation of Ni-Fe based Prussian blue analogue. The Ni-Fe-P nanocubes exhibit rough and loose porous structure on the surface under suitable phosphating temperature, which is favorable for the mass transfer and oxygen diffusion during electrocatalysis process. As a result, Ni-Fe-P obtained at 350 °C with poorer crystallinity offers more unsaturated atoms as active sites to expedite the reactants absorption. Additionally, the introduction of nickel improved the electronic structure and then reduced the charge transfer resistance, which would result in a faster electron transport and the enhancement of the intrinsic electrocatalytic activities. Benefiting from the unique porous nanocubes and the chemical composition, the Ni-Fe-P nanocubes exhibit excellent HER and OER activities in alkaline medium, with low overpotentials of 182 mV and 271 mV for delivering current density of 10 mA cm⁻², respectively. Moreover, the Ni-Fe-P nanocubes show outstanding stability for sustained water splitting in the two-electrode alkaline electrolyzer. This work not only provides a facile approach for designing bifunctional electrocatalysts, but also further extends the application of metal-organic frameworks in overall water splitting.

1. INTRODUCTION

Electrochemical water splitting has been considered as one of the most promising technologies to generate hydrogen as the clean and sustainable substitute for traditional fossil fuels.¹ However, the practical overpotential applied in water electrolysis is generally far larger than the theoretical voltage gap of 1.23 V due to the sluggish kinetics of hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) involved in water splitting^{1, 2}. Developing high-efficient catalysts is necessary to reduce the applied voltage of water splitting and expedite reaction

kinetics. Currently, platinum-based electrocatalysts are reported to possess the highest catalytic activity toward the HER,³ and meanwhile Ir- and Ru-based materials exhibit the most efficient OER activity, but their high expense and rarity demerits limit the widely industrial implementation.⁴ Thus, it is particularly significant to develop high-efficient and low-cost catalysts for HER and OER based on the earth-abundant elements.

Toward this end, considerable efforts have been dedicated to developing non-noble metal nanomaterials including transition metal catalysts (e.g. metal phosphides,^{5, 6} sulfides,^{7, 8} and oxides^{9, 10}) and non-metal catalysts.^{11, 12} Among them, transition metal phosphides, especially MoP,^{13, 14} FeP,^{15, 16} CoP,^{17, 18} Ni₂P,^{19, 20} have been investigated and regarded as the promising alternatives toward HER or OER due to their excellent stability in the electrolyte within a wide pH range.^{21, 22} Previous studies have shown that the electrocatalytic activities of single-metal phosphide toward HER or OER can be further improved through the introduction of other metal.^{3, 23, 24} For example, Brock et al.^{25, 26} reported that the doping of Mn atoms into Co phosphide or Fe phosphide effectively enhanced the OER catalytic activities. The incorporation of Mn atoms could contribute to lowering the energy barrier for the proton-coupled electron transfer processes, promoting the O-O bond generation and oxygen evolution. Liu et al.²⁷ demonstrated that the Fe doped Co₂P/Nitrogen-Doped Carbon Nanotubes (Fe-Co₂P/NCNTs) exhibited improved electrocatalytic activities for HER, which could be attributed to the presence of Fe can expose more catalytic active sites with a large specific area and modulate electronic property. Among the transition metal-based materials, NiFe-based (oxy)hydroxides have been demonstrated as the efficient OER electrocatalysts since the synergism between Ni and Fe could tune the affinity to oxygen on the catalyst surface sites toward the optimal value and facilitate the O-O bond generation as well as the oxygen evolution.²⁸⁻³² Besides, for metal phosphide, the

metal and P could serve as hydride acceptor and proton acceptor, respectively, favorable for the proton-discharging process and evolution of hydrogen.²⁷ Therefore, it is highly desirable to develop NiFe-based phosphides for overall water splitting by combining the advantages of NiFe-based materials for OER and the phosphides for HER. On the other hand, the physical characteristics of the catalysts also play an essential role in enhancing the catalytic activities.^{33, 34} Compared to zero-, one- or two- dimensional structured materials, the catalysts with three-dimensional porous architecture could provide highly desirable advantages including offering the fast channels for mass transfer and ion diffusion, increasing more active sites and thus accelerating the reaction rate.³⁴ However, complex and tedious procedures are usually required to synthesize the multicomponent metal phosphides with three-dimensional porous morphology by using the conventional chemical approaches. Besides, in order to simplify the electrolyzer system and reduce the overall cost, the electrocatalysts are expected to exhibit both HER and OER performances in the same condition, which is challenging for most of the reported catalysts. Thus, it is highly desirable to explore the three-dimensional porous multicomponent metal phosphides as bifunctional electrocatalysts for water electrocatalysis in the same media.

Metal-organic frameworks (MOFs), a family of crystalline material coordinated by metal ions center and organic ligand, have aroused considerable attention due to the superior properties such as high porosity, flexible tunability, and well-defined architecture.³⁵ Benefiting from the unique advantages, MOFs have been used as precursors to synthesize nanomaterials (such as carbon,³⁶⁻³⁸ metal oxide,³⁹ and etc.), showing promising prospects in energy conversion and storage applications. Recently, Prussian blue analogue (PBA) as a typical transition metal organic framework has emerged as the appealing precursors for the synthesis of three-dimensional nanostructured materials for energy storage and conversion.^{35, 40} In this work, Ni-Fe

Prussian blue analogue (NiFe-PBA) was used as the template to synthesize nickel iron phosphide (Ni-Fe-P) nanocubes via one-step phosphidation strategy. The as-prepared Ni-Fe-P materials remain well-defined structure with porous nanocube morphology under the suitable phosphating temperature of 350 °C. Besides, the incorporation of nickel enhanced the electron transport and then decreased the charge transfer resistance. Benefiting from the unique structure and chemical composition, the resulting Ni-Fe-P cubes exhibit excellent HER and OER activities and outstanding long-term stability. Furthermore, when used in the two-electrode alkaline electrolyzer, Ni-Fe-P cubes also possess superior water electrocatalysis performance.

2. Experimental Methods

Synthesis of Ni-Fe-P

NiFe-PBA was synthesized through a co-precipitation approach according to the literature⁴¹ with some modification. Specifically, 0.1426 g of nickel chloride hexahydrate and 0.2647 g of tri-sodium citrate dihydrate were dissolved in deionized water (20 mL), and then mixed with potassium ferricyanide ($K_3[Fe(CN)_6]$, 0.1317 g) dissolved in 20 mL of deionized water. After continuous magnetic stirring for three minutes, the obtained mixed solution was kept at room temperature and aged for 10 h. The precipitates were collected by centrifugation and washed with mixed water/ethanol for several times before drying at 60 °C overnight. The obtained NiFe-PBA and NaH_2PO_2 with the mass ratio of 1:20 was placed in two separate positions in the tube furnace with NaH_2PO_2 at the upstream side. And then the products were heated up to different temperatures with a heating rate of 3 °C min⁻¹ and kept at this temperature for 2 h under N_2 atmosphere. The final products were denoted as Ni-Fe-P-T, where T represents the annealing

temperature. For comparison, pure Fe Prussian blue (Fe-PB) was synthesized according to the literature,⁴² and annealed with the same phosphidation method.

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. Transmission electron microscopy (TEM) images, dark field scanning transmission electron microscopy (DF-STEM) images, and electron energy loss spectroscopy (EELS) data were all collected using a Gatan Tridiem spectrometer. Thermal gravimetric analysis (TGA) was acquired from room temperature to 800°C at a heating rate of $10^{\circ} \text{C min}^{-1}$ on TA Q500 Instrument. 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.

Electrochemical measurement

All the electrochemical tests were conducted on an Autolab PG302N electrochemical workstation with high-speed rotators from Pine Instrument in three electrode configuration or two electrode setup at room temperature.

In the three electrode configurations, a glassy electrode (GCE) or modified GCE served as working electrode, while the reverse hydrogen electrode (RHE), and a carbon rod were used as the reference electrode and the counter electrode, respectively. Homogeneous catalyst ink dispersion was obtained by sonication the samples (5mg) and Nafion/isopropyl alcohol mixed solution (1 mL). The prepared ink ($16.5 \mu\text{L}$) was dropped onto the working electrode followed

by drying at room temperature naturally to obtain the loading amount of about 0.42 mg cm^{-2} . The loading amount of Pt/C and Ir/C was 0.08 mg cm^{-2} . The HER and OER performances were both detected in 1.0 M KOH medium. Linear sweep voltammetry (LSV) was obtained at the potential ranging from 0.2 to -0.5 V vs. RHE for HER and from 0.8 to 1.8 V vs. RHE for OER at a scan rate of 5 mV s^{-1} . The stability test was performed at a current density of 10 mA cm^{-2} for 10 h with a rotation speed of 1600 rpm. EIS determination was conducted in the frequency range from 100 kHz to 0.01 Hz with an ac perturbation of 5 mV at the potential of -0.1 V and 1.5 V for HER and OER, respectively. The overall electrochemical water splitting was detected by LSV measurement at the potential from -0.5 to 1.8 V.

In two electrode setup, two identical catalyst electrodes were utilized as cathode and anode to construct a symmetrical full electrolyzer. 40 μL of the as-obtained ink was loaded onto the Ni-foam before drying naturally at room temperature to obtain a loading amount of 1 mg cm^{-2} . LSV was obtained at the potential from 0.8 to 1.8 V. Chronoamperometry measurement was carried out to assess the long-term durability at the current density of 10 mA cm^{-2} .

3. RESULTS AND DISCUSSION

The Ni-Fe-P nanomaterial was synthesized through co-precipitation approach and the following phosphidation, as depicted in Scheme 1. The synthesis of NiFe-PBA was accomplished by precipitation of nickel chloride and $\text{K}_3[\text{Fe}(\text{CN})_6]$, and the corresponding morphology of the precursor was characterized via Field emission scanning electron microscope (FESEM) and transmission electron microscopy (TEM). Figure 1 a and S1 present that NiFe-PBA exhibits homogenous cube architecture with smooth surface. The diameter of the cube is in the range from 100 to 150 nm. The crystalline structure of NiFe-PBA was initially examined via X-ray

diffraction (XRD, Figure S2), where NiFe-PBA exhibits the characteristic diffractions of face-center-cubic structure (JCPDS card 46-0906) with no other impurities observed, suggesting the formation of pure NiFe-PBA.

Scheme 1 Schematic illustration for the synthesis of Ni-Fe-P catalysts.

The obtained NiFe-PBA precursor was then used as the template for the synthesis of ternary Ni-Fe-P via direct phosphidation under N_2 atmosphere (Scheme 1). During the calcination, sodium hypophosphite would release PH_3 ,⁴³ which served as phosphorus source to react with NiFe-PBA precursor. Thermogravimetric analysis (TGA) of NiFe-PBA was conducted to investigate the details during annealing process (Figure S3). The mass loss below 200 °C corresponds to the coordinated and zeolitic waters in ferricyanides.⁴⁴ With the temperature increase to about 300 °C, formation of ferrocyanide occurred.⁴⁴ And then the observed gradual weight loss with the prolonged heating can be ascribed to the total decomposition of the MOF crystal architecture. Based on TGA results, three different temperatures (i.e. 250, 350 and 450 °C) were selected for the phosphidation of NiFe-PBA. XRD patterns of the obtained Ni-Fe-P at different temperatures (Figure S4a) showed that the characteristic diffraction peaks of NiFe-PBA disappear after phosphidation. Meanwhile, Ni-Fe-P product is composed of a mixture of Ni_2P (JCPDS no. 65-9706) and Fe_2P (JCPDS no. 85-1727) with weak crystalline phase. The broad peak at around 25° could be indexed as (002) plane of graphite-type carbon diffractions. The chemical structures of NiFe-PBA and Ni-Fe-P samples were then characterized by FT-IR

determination. As can be seen in Figure S4b, the peaks located at $\sim 3408\text{ cm}^{-1}$ and $\sim 1611\text{ cm}^{-1}$ correspond to the OH stretching vibration and bending vibration of the water molecules for NiFe-PBA,⁴⁵ while the two peaks at 2158.2 cm^{-1} and 2113.5 cm^{-1} are the characteristic stretching vibration of CN group.⁴⁶ After phosphidation at $350\text{ }^{\circ}\text{C}$ and $450\text{ }^{\circ}\text{C}$, the complete disappearing of characteristic peaks of NiFe-PBA further demonstrating the decomposition of MOFs precursor. Besides, the SEM images (Figure 1) demonstrate that Ni-Fe-P-250 and Ni-Fe-P-350 could remain the cube morphology, relatively better than Ni-Fe-P-450, which suffered from serious aggregation between the particles.

Figure 1 SEM images of NiFe-PBA (a), and the prepared Ni-Fe-P at $250\text{ }^{\circ}\text{C}$ (b), $350\text{ }^{\circ}\text{C}$ (c) and $450\text{ }^{\circ}\text{C}$ (d).

Figure 2 DF-STEM image (a) and TEM image (b) of Ni-Fe-P-350; (c) Enlarged TEM images and HRTEM images (inset) of Ni-Fe-P-350; Enlarged DF-STEM image of Ni-Fe-P-350 (d) and the corresponding EELS elemental mapping of Ni (e), Fe (f), and P (g).

ADF-STEM and TEM characterizations were performed to further examine the morphology of Ni-Fe-P obtained at 350 °C. As depicted in Figure 2a, b and c, the resulting Ni-Fe-P-350 maintained the cube morphology with many granular particles interconnected with each other to generate the porous architecture. Interestingly, it is noted that the surface of Ni-Fe-P became rough with obvious loose and porous feature after phosphidation at 350 °C, which could be ascribed to the easier reaction between the surface of precursor and PH_3 . The unique structure is conducive to providing and exposing more active sites, thus accelerating mass transfer and promoting their enhanced electrocatalytic activity. The inter-planar distance calculated to be 0.22 nm from HRTEM (inset of Figure 2c), ascribed to the (111) plane of Ni-Fe-P-350 phase. The

small and randomly arranged grains of Ni-Fe-P-350 demonstrate the poor crystallinity which is consistent with XRD results. Electron energy loss spectroscopy (EELS) elemental mapping images in Figure 2 illustrate the presence of Ni, Fe, and P, further implying the successful conversion of the NiFe-PBA to Ni-Fe-P nanocube.

Figure 3 (a) XPS survey spectrum of Ni-Fe-P-350; High-resolution spectra of Ni 2p (b), Fe 2p (c), and P 2p (d) for Ni-Fe-P-350, respectively.

The chemical compositions and valence states of the elements on the Ni-Fe-P-350 surface are characterized through X-ray photoelectron spectroscopy (XPS) detection. The survey spectra in Figure 3a manifest the existence of Ni, Fe, as well as P, in agreement with elemental mapping results. The high-resolution Ni 2p spectrum in Figure 3b shows that the peaks around 853.4 and 870.8 eV can be ascribed to $\text{Ni}^{\delta+}$ in Ni-P bond, and the peaks located at 856.7 and 874.6 eV correspond to oxidized Ni species with satellites peaks at 861.6 and 880.3 eV.^{23, 47} Figure 3c

displays the high-resolution Fe 2p spectrum, in which peaks at 707.5 and 720 reflecting Fe-P bonding while the other peaks ascribed to the oxidized state Fe formed on the surface.⁴⁸ The fitting-lined high-resolution P 2p spectrum in Figure 3d deconvoluted into two peaks located at 129.3 and 130.0 eV corresponding to metal phosphides.⁴⁹ And the other peak at 134.2 eV reflects P-O bonding generated on the surface of Ni-Fe-P due to the exposing in air atmosphere.⁵⁰ Notably, the binding energy of P 2p_{3/2} shows negative shift compared with elemental P (130.2 eV), while Ni 2p_{3/2} and Fe 2p_{3/2} exhibit positive shift compared to metal Ni (852.5 eV) as well as metal Fe (706.7 eV),^{51, 52} indicating the cationic state of Ni and Fe atoms and the anionic state of P atom. The mixed valence of Ni, Fe and P atoms could increase electron transfer rate, thus promoting the catalytic process toward HER and OER. Additionally, according to the XPS spectrum, the atomic ratio of P, Fe and Ni was determined to be 19.67:2.79:4.24. Moreover, X-ray Fluorescence (XRF) characterization was conducted to further illustrate atomic ratio of Ni, Fe and P for the Ni-Fe-P-350 catalyst. As shown in Figure S5, the average ratio of P, Fe and Ni based on the three measurements was 66.41: 13.69: 19.90. XPS and XRF results suggested that the atomic ratio of Ni and Fe was about 3:2, which is consistent with the Ni-Fe-PBA precursor. And the proportion of P determined by XPS was slightly higher than that determined by XRF, which would be favorable for the enhancement of catalytic activities on Ni-Fe-P-350. Comparison of the XPS spectra for Ni-Fe-P-350 and Fe-P was then utilized to illustrate the effect of nickel incorporation on the electronic structure of Fe and P. As shown in Figure S6, compared with the counterpart in Fe-P samples, a negative shift was observed in the binding energies of high-resolution Fe 2p_{3/2} spectra for Ni-Fe-P-350 catalysts, realizing the lower Fe valence in Ni-Fe-P-350. Besides, peak in the P 2p_{3/2} spectrum of Ni-Fe-P-350 shifted toward the lower binding energy in comparison with that in Fe-P material, indicating the lower P valence in Ni-Fe-P-350.

The above results demonstrate that the incorporation of nickel is of great importance for modulating the electronic structure of Fe and P. Considering the tight interaction between Ni, Fe and P, Ni-Fe-P-350 with unique properties are expected to possess enhanced catalytic activities toward HER and OER.

The electrochemical determination was carried out on the three-electrode setup with the catalysts modified glassy carbon electrode as the working electrode. The HER performance of the obtained Ni-Fe-P nanomaterials was explored via the linear sweep voltammetry (LSV) curves. Generally, the onset potential for yielding 1 mA cm^{-2} (η_0) and the overpotential for delivering 10 mA cm^{-2} (η_{10}) were employed to illustrate the catalytic activities of the catalysts.⁵³ It can be clearly observed in Figure 4a that Ni-Fe-P-350 presents much lower onset potential of 90 mV than Ni-Fe-P-250 (106 mV), Ni-Fe-P-450 (113 mV). Besides, Figure 4a displays that the overpotentials at 10 mA cm^{-2} for Ni-Fe-P-250, Ni-Fe-P-350, Ni-Fe-P-450 are 246 mV, 182 mV, 230 mV, respectively. Figure 4b further realizes that Ni-Fe-P-350 nanocubes exhibit the lowest η_0 and η_{10} compared with Ni-Fe-P obtained at 250 °C and 450 °C, suggesting the optimal phosphating temperature of 350 °C. The phosphidation temperature of 350 °C could allow the formation of a crystal structure and remain the well-defined nanocube architecture, while lower or higher the temperature would result in unsatisfied poor crystalline structure or aggregated morphology. LSV curves in Figure 4c and Figure S7 display that η_0 and η_{10} of Ni-Fe-P-350 (90 mV and 182 mV) are much lower than Fe-P (131 mV and 224 mV), NiFe-PBA and Fe-PB, illustrating the incorporation of nickel and phosphidation are essential for enhancing the HER activities. To get insight into the catalytic reaction, Tafel plots were utilized to evaluate the catalytic kinetics for HER. The Tafel plots were obtained from LSV curves (Figure 4c) based on the Tafel equation ($\eta = b \log j + a$, where j is the current density and b is the Tafel slope).³ As

shown in Figure 4d, Ni-Fe-P-350 showed much smaller Tafel slope value (85 mV dec⁻¹) than FeP (92 mV dec⁻¹), indicating the improved HER kinetics through the introduction of nickel and a Volmer-Heyrovsky mechanism with the electrochemical desorption as the rate determining step.⁵⁵ Electrochemical impedance spectroscopy (EIS) was examined to further examine the HER kinetics of the as-synthesized catalysts. As depicted in Figure S8, Ni-Fe-P-350 possesses much lower charge transfer resistance than FeP, demonstrating a faster electron transfer rate, which is favorable for the enhancement of the HER kinetics.

Figure 4 (a) LSV curves of the obtained Ni-Fe-P at different temperatures. (b) The HER overpotentials for delivering the current densities of 1 mA cm⁻² (η_0) and 10 mA cm⁻² (η_{10}) of Ni-Fe-P at 250 °C, 350 °C and 450 °C. LSV curves (c) and the corresponding Tafel slopes (d) of Ni-Fe-P-350, Fe-P, Pt/C and Ir/C.

Evaluation of the OER electrocatalytic performance of the samples was performed at the same condition. As shown in Figure 5 and S9, Ni-Fe-P-350 exhibits much lower overpotential

(271 mV) at 10 mA cm^{-2} than the other two NiFe-based phosphides samples, FeP, NiFe-PBA, Fe-PB, even better than Ir/C and Pt/C. The results indicate that the suitable phosphating temperature, the introduction of nickel, and phosphidation are important for the enhancement of OER activity. Additionally, the smaller Tafel slope and lower charge transfer resistance (Figure 5d and S10) further confirmed the conducive role of nickel and phosphidation in Ni-Fe-P-350 for promoting the kinetics of OER and accelerating electron transport.

Figure 5 (a) LSV curves of the obtained Ni-Fe-P annealing at 250 °C, 350 °C, and 450 °C, respectively. (b) The OER overpotentials for delivering the current densities of 10 mA cm^{-2} (η_{10}) of the prepared Ni-Fe-P at 250 °C, 350 °C and 450 °C. Comparison of LSV curves (c) and the corresponding Tafel slopes (d) of Ni-Fe-P-350, Fe-P, Pt/C and Ir/C.

Based on above electrochemical measurements, it comes out that Ni-Fe-P-350 exhibits excellent catalytic activities toward HER and OER in 1 M KOH media. Combined the physical characterization and electrochemical determination, it is concluded that the superior bifunctional activities of Ni-Fe-P-350 could be mainly attributed to the following respects. The unique porous

cube architecture with rough and loose surface could ensure the adequate contact between the catalysts and the electrolyte, and provide and expose much more active sites, thus promote the fast mass transfer and oxygen diffusion.⁵⁶ Besides, the poor crystallinity of Ni-Fe-P-350 due to the small and randomly arranged grains contained could offer more unsaturated atoms as active sites,⁵⁷ facilitating the adsorption of reactants in the active site, thus accelerating the reaction rate. Furthermore, the modification of the electronic structure of Fe and P caused by the incorporation of Ni is beneficial for the proton-discharging process in HER,⁵¹ leading to the improved HER performance. Meanwhile, the changed electronic environment of Fe and P would tune the energy barrier of intermediate toward the optimal value and also promote oxygen evolved from the surface of the catalysts, resulting in the enhancement of OER catalytic activities.⁵⁸ Meanwhile, besides of modifying the electronic structure, the introduction of nickel could reduce the charge transfer resistance, resulting a faster electron transport and the enhancement of the intrinsic electrocatalytic activities toward HER and OER.⁵⁷

Stability is of vital significance to examine the catalyst performance toward HER and OER. Thus, chronopotentiometry was conducted to illustrate the stability of Ni-Fe-P-350 in alkaline media at 10 mA cm⁻² for HER and OER, respectively. Figure S11 clearly depicted that, after a period of 10 h, Ni-Fe-P-350 showed negligible potential loss for HER and OER. The excellent HER as well as OER performance of Ni-Fe-P-350 make it far more promising as a bifunctional catalyst for water electrocatalysis.

Figure 6 (a) Polarization curves of the Ni-Fe-P-350 for overall water splitting performance in the three-electrode setup at the scan rate of 5 mV s⁻¹. (b) Polarization curves of the Ni-Fe-P-350, Ir/C, Pt/C, as well as Ni foam in the two-electrode electrolyzers at the scan rate of 5 mV s⁻¹. (c) Long-term durability test of the Ni-Fe-P-350 electrolyzer at 10 mA cm⁻² and the photograph during the overall water splitting (inset).

To further explicate the bifunctional performance of Ni-Fe-P-350 catalysts, LSV curves were detected in the three-electrode system with the potential window ranging from -0.5 V to 1.8 V at the scan rate of 5 mV s⁻¹. The voltage (ΔE) required for yielding 10 mA cm⁻² for both HER and OER ($\Delta E = E_{\text{OER}, j=10} - E_{\text{HER}, j=10}$) was utilized to assess the performance toward water splitting. And the smaller ΔE value represents the better catalytic activities in the process of water electrolysis. Figure 6a presented that the voltage gap of Ni-Fe-P-350 was about 1.68 V, far less than FeP, NiFe-PBA, Fe-PB, and Pt/C and very closer to Ir/C, demonstrating the exceptional bifunctional activities of Ni-Fe-P-350. Based on the above results, the Ni-Fe-P-350 nanocubes

loaded onto nickel foam served as both cathode and anode to further explore the potential application in water electrolysis devices. LSV detection was carried out in a two-electrode water electrolyzer. Figure 6b depicts that Ni-Fe-P-350 could yield 10 mA cm^{-2} at cell voltages of about 1.67 V, much smaller than Pt/C and nickel foam and close to Ir/C, indicating Ni-Fe-P-350 possesses excellent water splitting activities. Chronopotentiometry test was then performed to assess the long-term durability of Ni-Fe-P-350 at 10 mA cm^{-2} . During the water electrolysis process, both H_2 and O_2 evolve continuously at the cathode and anode, respectively, clearly seen from the inset of Figure 6c. And Figure 6c displayed the negligible decay (about 6 % activity loss) occurred on Ni-Fe-P-350 sample after 40 h continuous water electrocatalysis test. The outstanding activity and extraordinary long-term durability of Ni-Fe-P-350 make it a prospective electrode material for real water electrocatalysis applications.

4. CONCLUSIONS

In summary, ternary Ni-Fe-P nanocubes with porous structure were successfully prepared via the direct phosphidation method with metal-organic frameworks as the precursor. The as-prepared Ni-Fe-P catalysts at 350 °C exhibit distinctive porous nanocube morphology with the rough and loose surface feature. Electrochemical detection demonstrates that the resulting Ni-Fe-P-350 exhibits excellent HER and OER activities and outstanding long-term stability. Furthermore, when used in a two-electrode alkaline electrolyzer, Ni-Fe-P-350 materials also possess superior water electrocatalysis performance. The exceptional bifunctional catalytic performance of Ni-Fe-P-350 for overall water electrolysis could be attributed to (i) the unique porous nanocube structures provide and expose much more active sites and ensure the adequate contact between catalyst and electrolyte, beneficial for the mass transfer and oxygen diffusion; (ii) the weak crystallinity of Ni-Fe-P-350 could offer more unsaturated atoms as active sites facilitating the

adsorption of reactants on the active site; (ii) the introduction of nickel could tune the electron structure of Fe and P, and reduce the charge transfer resistance, leading to the faster electron transport and the accelerated kinetics during the water electrolysis. This work not only proposes high-efficient bifunctional ternary porous nanocubes for water splitting applications but also further highlights the great potential of MOFs for the synthesis of the nanomaterials for energy conversion applications.

ASSOCIATED CONTENT

Supporting Information.

Detailed additional SEM images, electrochemical performance. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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REFERENCES

- (1) Roger, I.; Shipman, M. A.; Symes, M. D. Earth-Abundant Catalysts for Electrochemical and Photoelectrochemical Water Splitting. *Nat. Rev. Chem.* **2017**, *1*, 0003.
- (2) Tee, S. Y.; Win, K. Y.; Teo, W. S.; Koh, L. D.; Liu, S.; Teng, C. P.; Han, M. Y. Recent Progress in Energy-Driven Water Splitting. *Adv. Sci.* **2017**, 1600337.
- (3) Zou, X.; Zhang, Y. Noble Metal-Free Hydrogen Evolution Catalysts for Water Splitting. *Chem. Soc. Rev.* **2015**, *44*, 5148-5180.
- (4) Suen, N.-T.; Hung, S.-F.; Quan, Q.; Zhang, N.; Xu, Y.-J.; Chen, H. M. Electrocatalysis for the Oxygen Evolution Reaction: Recent Development and Future Perspectives. *Chem. Soc. Rev.* **2017**, *46*, 337-365.
- (5) Shi, Y.; Zhang, B. Recent Advances in Transition Metal Phosphide Nanomaterials: Synthesis and Applications in Hydrogen Evolution Reaction. *Chem. Soc. Rev.* **2016**, *45*, 1529-1541.
- (6) Dutta, A.; Pradhan, N. Developments on Metal Phosphides as Efficient OER Pre-catalysts. *J. Phys. Chem. Lett.* **2017**, *8*, 144-152.
- (7) Lu, Q.; Yu, Y.; Ma, Q.; Chen, B.; Zhang, H. 2D Transition-Metal-Dichalcogenide-Nanosheet-Based Composites for Photocatalytic and Electrocatalytic Hydrogen Evolution Reactions. *Adv. Mater.* **2016**, *28*, 1917-1933.
- (8) Jiang, J.; Lu, S.; Gao, H.; Zhang, X.; Yu, H.-Q. Ternary FeNiS₂ Ultrathin Nanosheets as an Electrocatalyst for Both Oxygen Evolution and Reduction Reactions. *Nano Energy* **2016**, *27*, 526-534.
- (9) Osgood, H.; Devaguptapu, S. V.; Xu, H.; Cho, J.; Wu, G. Transition Metal (Fe, Co, Ni, and

- Mn) Oxides for Oxygen Reduction and Evolution Bifunctional Catalysts in Alkaline Media. *Nano Today* **2016**, *11*, 601-625.
- (10) Wang, J.; Wu, Z.; Han, L.; Lin, R.; Xin, H. L.; Wang, D. Hollow-Structured Carbon-Supported Nickel Cobaltite Nanoparticles as an Efficient Bifunctional Electrocatalyst for the Oxygen Reduction and Evolution Reactions. *ChemCatChem* **2016**, *8*, 736-742.
- (11) Hu, C.; Dai, L. Carbon-Based Metal-Free Catalysts for Electrocatalysis beyond the ORR. *Adv. Mater.* **2017**, *29*, 1604942.
- (12) Zhang, J.; Qu, L.; Shi, G.; Liu, J.; Chen, J.; Dai, L. N, P-Codoped Carbon Networks as Efficient Metal-free Bifunctional Catalysts for Oxygen Reduction and Hydrogen Evolution Reactions. *Angew. Chem.* **2016**, *128*, 2270-2274.
- (13) Xiao, P.; Sk, M. A.; Thia, L.; Ge, X.; Lim, R. J.; Wang, J.-Y.; Lim, K. H.; Wang, X. Molybdenum Phosphide as an Efficient Electrocatalyst for the Hydrogen Evolution Reaction. *Energy Environ. Sci.* **2014**, *7*, 2624-2629.
- (14) Wu, Z.; Wang, J.; Liu, R.; Xia, K.; Xuan, C.; Guo, J.; Lei, W.; Wang, D. Facile Preparation of Carbon Sphere Supported Molybdenum Compounds (P, C and S) as Hydrogen Evolution Electrocatalysts in Acid and Alkaline Electrolytes. *Nano Energy* **2017**, *32*, 511-519.
- (15) Jiang, P.; Liu, Q.; Liang, Y.; Tian, J.; Asiri, A. M.; Sun, X. A Cost-Effective 3D Hydrogen Evolution Cathode with High Catalytic Activity: FeP Nanowire Array as the Active Phase. *Angew. Chem. Int. Ed.* **2014**, *53*, 12855-12859.
- (16) Xiong, D.; Wang, X.; Li, W.; Liu, L. Facile Synthesis of Iron Phosphide Nanorods for Efficient and Durable Electrochemical Oxygen Evolution. *Chem. Commun.* **2016**, *52*, 8711-8714.
- (17) Popczun, E. J.; Read, C. G.; Roske, C. W.; Lewis, N. S.; Schaak, R. E. Highly Active

- Electrocatalysis of the Hydrogen Evolution Reaction by Cobalt Phosphide Nanoparticles. *Angew. Chem.* **2014**, *126*, 5531-5534.
- (18) Chang, J.; Xiao, Y.; Xiao, M.; Ge, J.; Liu, C.; Xing, W. Surface Oxidized Cobalt-Phosphide Nanorods as an Advanced Oxygen Evolution Catalyst in Alkaline Solution. *ACS Catal.* **2015**, *5*, 6874-6878.
- (19) Stern, L.-A.; Feng, L.; Song, F.; Hu, X. Ni₂P as a Janus Catalyst for Water Splitting: the Oxygen Evolution Activity of Ni₂P Nanoparticles. *Energy Environ. Sci.* **2015**, *8*, 2347-2351.
- (20) Bai, Y.; Zhang, H.; Li, X.; Liu, L.; Xu, H.; Qiu, H.; Wang, Y. Novel Peapod-Like Ni₂P Nanoparticles with Improved Electrochemical Properties for Hydrogen Evolution and Lithium Storage. *Nanoscale* **2015**, *7*, 1446-1453.
- (21) Kibsgaard, J.; Tsai, C.; Chan, K.; Benck, J. D.; Nørskov, J. K.; Abild-Pedersen, F.; Jaramillo, T. F. Designing an Improved Transition Metal Phosphide Catalyst for Hydrogen Evolution Using Experimental and Theoretical Trends. *Energy Environ. Sci.* **2015**, *8*, 3022-3029.
- (22) Tian, J.; Liu, Q.; Asiri, A. M.; Sun, X. Self-Supported Nanoporous Cobalt Phosphide Nanowire Arrays: an Efficient 3D Hydrogen-Evolving Cathode over the Wide Range of pH 0-14. *J. Am. Chem. Soc.* **2014**, *136*, 7587-7590.
- (23) Li, Y.; Tian, Y.; Yan, Y.; Chang, H.; Ouyang, R.; Miao, Y. NiCoP Nanoparticles as Efficient Electrocatalyst for Oxygen Evolution Reaction in an Alkaline Solution. *Int. J. Electrochem. Sci* **2016**, *11*, 9917-9927.
- (24) Gupta, S.; Patel, N.; Fernandes, R.; Hanchate, S.; Miotello, A.; Kothari, D. Co-Mo-B Nanoparticles as a Non-Precious and Efficient Bifunctional Electrocatalyst for Hydrogen and Oxygen Evolution. *Electrochim. Acta* **2017**, 64-71.
- (25) Li, D.; Baydoun, H.; Verani, C. N.; Brock, S. L. Efficient Water Oxidation Using CoMnP

- Nanoparticles. *J. Am. Chem. Soc.* **2016**, *138*, 4006-4009.
- (26) Li, D.; Baydoun, H.; Kulikowski, B.; Brock, S. L. Boosting the Catalytic Performance of Iron Phosphide Nanorods for the Oxygen Evolution Reaction by Incorporation of Manganese. *Chem. Mater.* **2017**, *29*, 3048-3054.
- (27) Pan, Y.; Liu, Y.; Lin, Y.; Liu, C. Metal Doping Effect of the M-Co₂P/Nitrogen-Doped Carbon Nanotubes (M= Fe, Ni, Cu) Hydrogen Evolution Hybrid Catalysts. *ACS Appl. Mater. Interfaces* **2016**, *8*, 13890-13901.
- (28) Subbaraman, R.; Tripkovic, D.; Chang, K.-C.; Strmcnik, D.; Paulikas, A. P.; Hirunsit, P.; Chan, M.; Greeley, J.; Stamenkovic, V.; Markovic, N. M. Trends in Activity for the Water Electrolyser Reactions on 3d M (Ni, Co, Fe, Mn) Hydr(oxy)oxide Catalysts. *Nat. Mater.* **2012**, *11*, 550-557.
- (29) Anantharaj, S.; Ede, S. R.; Sakthikumar, K.; Karthick, K.; Mishra, S.; Kundu, S. Recent Trends and Perspectives in Electrochemical Water Splitting with an Emphasis on Sulfide, Selenide, and Phosphide Catalysts of Fe, Co, and Ni: a Review. *ACS Catal.* **2016**, *6*, 8069-8097.
- (30) Friebe, D.; Louie, M. W.; Bajdich, M.; Sanwald, K. E.; Cai, Y.; Wise, A. M.; Cheng, M.-J.; Sokaras, D.; Weng, T.-C.; Alonso-Mori, R. Identification of Highly Active Fe Sites in (Ni, Fe)OOH for Electrocatalytic Water Splitting. *J. Am. Chem. Soc.* **2015**, *137*, 1305-1313.
- (31) Dionigi, F.; Strasser, P. NiFe-Based (Oxy)hydroxide Catalysts for Oxygen Evolution Reaction in Non-Acidic Electrolytes. *Adv. Energy Mater.* **2016**, *6*, 1600621.
- (32) Gong, M.; Dai, H. A mini review on NiFe-Based Materials as Highly Active Oxygen Evolution Reaction Electrocatalysts. *Nano Res.* **2015**, *8*, 23-39.
- (33) Xu, M.; Han, L.; Han, Y.; Yu, Y.; Zhai, J.; Dong, S. Porous CoP Concave Polyhedron

- Electrocatalysts Synthesized from Metal-Organic Frameworks with Enhanced Electrochemical Properties for Hydrogen Evolution. *J. Mater. Chem. A* **2015**, 3, 21471-21477.
- (34) Liu, M.; Li, J. Cobalt Phosphide Hollow Polyhedron as Efficient Bifunctional Electrocatalysts for the Evolution Reaction of Hydrogen and Oxygen. *ACS Appl. Mater. Interfaces* **2016**, 8, 2158-2165.
- (35) Mahmood, A.; Guo, W.; Tabassum, H.; Zou, R. Metal-Organic Framework-Based Nanomaterials for Electrocatalysis. *Adv. Energy Mater.* **2016**, 6, 1600423.
- (36) Salunkhe, R. R.; Kaneti, Y. V.; Kim, J.; Kim, J. H.; Yamauchi, Y. Nanoarchitectures for Metal-Organic Framework-Derived Nanoporous Carbons Toward Supercapacitor Applications. *Acc. Chem. Res* **2016**, 49, 2796-2806.
- (37) Salunkhe, R. R.; Kamachi, Y.; Torad, N. L.; Hwang, S. M.; Sun, Z.; Dou, S. X.; Kim, J. H.; Yamauchi, Y. Fabrication of Symmetric Supercapacitors Based on MOF-Derived Nanoporous Carbons. *J. Mater. Chem. A* **2014**, 2, 19848-19854.
- (38) Salunkhe, R. R.; Young, C.; Tang, J.; Takei, T.; Ide, Y.; Kobayashi, N.; Yamauchi, Y. A High-Performance Supercapacitor Cell Based on ZIF-8-Derived Nanoporous Carbon Using an Organic Electrolyte. *Chem. Commun.* **2016**, 52, 4764-4767.
- (39) Tang, J.; Wu, S.; Wang, T.; Gong, H.; Zhang, H.; Alshehri, S. M.; Ahamad, T.; Zhou, H.; Yamauchi, Y. Cage-Type Highly Graphitic Porous Carbon–Co₃O₄ Polyhedron as the Cathode of Lithium-Oxygen Batteries. *ACS Appl. Mater. Interfaces* **2016**, 8, 2796-2804.
- (40) Xia, W.; Mahmood, A.; Zou, R.; Xu, Q. Metal-Organic Frameworks and their Derived Nanostructures for Electrochemical Energy Storage and Conversion. *Energy Environ. Sci.* **2015**, 8, 1837-1866.
- (41) Yu, X. Y.; Yu, L.; Wu, H. B.; Lou, X. W. D. Formation of Nickel Sulfide Nanoframes from

- Metal-Organic Frameworks with Enhanced Pseudocapacitive and Electrocatalytic Properties. *Angew. Chem.* **2015**, *127*, 5421-5425.
- (42) Zhang, L.; Wu, H. B.; Lou, X. W. Metal–Organic-Frameworks-Derived General Formation of Hollow Structures with High Complexity. *J. Am. Chem. Soc.* **2013**, *135*, 10664-10672.
- (43) Xiao, P.; Chen, W.; Wang, X. A Review of Phosphide-Based Materials for Electrocatalytic Hydrogen Evolution. *Adv. Energy Mater.* **2015**, *5*, 1500985.
- (44) Martinez-Garcia, R.; Knobel, M.; Reguera, E. Thermal-Induced Changes in Molecular Magnets Based on Prussian Blue Analogues. *J. Phys. Chem. B* **2006**, *110*, 7296-7303.
- (45) Wang, Q.; Wang, N.; He, S.; Zhao, J.; Fang, J.; Shen, W. Simple Synthesis of Prussian Blue Analogues in Room Temperature Ionic Liquid Solution and Their Catalytic Application in Epoxidation of Styrene. *Dalton Trans.* **2015**, *44*, 12878-12883.
- (46) Pang, H.; Zhang, Y.; Cheng, T.; Lai, W.-Y.; Huang, W. Uniform Manganese Hexacyanoferrate Hydrate Nanocubes Featuring Superior Performance for Low-cost Supercapacitors and Nonenzymatic Electrochemical Sensors. *Nanoscale* **2015**, *7*, 16012-16019.
- (47) Pan, Y.; Liu, Y.; Zhao, J.; Yang, K.; Liang, J.; Liu, D.; Hu, W.; Liu, D.; Liu, Y.; Liu, C. Monodispersed Nickel Phosphide Nanocrystals with Different Phases: Synthesis, Characterization and Electrocatalytic Properties for Hydrogen Evolution. *J. Mater. Chem. A* **2015**, *3*, 1656-1665.
- (48) Yan, Y.; Xia, B. Y.; Ge, X.; Liu, Z.; Fisher, A.; Wang, X. A flexible Electrode Based on Iron Phosphide Nanotubes for Overall Water Splitting. *Chem. Eur. J.* **2015**, *21*, 18062-18067.
- (49) Wang, X.; Tong, R.; Wang, Y.; Tao, H.; Zhang, Z.; Wang, H. Surface Roughening of Nickel Cobalt Phosphide Nanowire Arrays/Ni Foam for Enhanced Hydrogen Evolution Activity.

- ACS Appl. Mater. Interfaces* **2016**, 8, 34270-34279.
- (50) Han, A.; Chen, H.; Sun, Z.; Xu, J.; Du, P. High Catalytic Activity for Water Oxidation Based on Nanostructured Nickel Phosphide Precursors. *Chem. Commun.* **2015**, 51, 11626-11629.
- (51) Hao, J.; Yang, W.; Zhang, Z.; Tang, J. Metal-Organic Frameworks Derived $\text{Co}_x\text{Fe}_{1-x}\text{P}$ Nanocubes for Electrochemical Hydrogen Evolution. *Nanoscale* **2015**, 7, 11055-11062.
- (52) Liang, H.; Gandi, A. N.; Anjum, D. H.; Wang, X.; Schwingenschlögl, U.; Alshareef, H. N. Plasma-Assisted Synthesis of NiCoP for Efficient Overall Water Splitting. *Nano Lett.* **2016**, 16, 7718-7725.
- (53) Wang, X.; Kolen'ko, Y. V.; Bao, X. Q.; Kovnir, K.; Liu, L. One-Step Synthesis of Self-Supported Nickel Phosphide Nanosheet Array Cathodes for Efficient Electrocatalytic Hydrogen Generation. *Angew. Chem. Int. Ed.* **2015**, 54, 8188-8192.
- (54) Long, X.; Li, J.; Xiao, S.; Yan, K.; Wang, Z.; Chen, H.; Yang, S. A Strongly Coupled Graphene and FeNi Double Hydroxide Hybrid as an Excellent Electrocatalyst for the Oxygen Evolution Reaction. *Angew. Chem.* **2014**, 126, 7714-7718.
- (55) Chen, W.-F.; Muckerman, J. T.; Fujita, E. Recent Developments in Transition Metal Carbides and Nitrides as Hydrogen Evolution Electrocatalysts. *Chem. Commun.* **2013**, 49, 8896-8909.
- (56) Wu, Z.; Guo, J.; Wang, J.; Liu, R.; Xiao, W.; Xuan, C.; Xia, K.; Wang, D. Hierarchically Porous Electrocatalyst with Vertically Aligned Defect-Rich CoMoS Nanosheets for HER in Alkaline Medium. *ACS Appl. Mater. Interfaces* **2017**, 9, 5288-5294.
- (57) Li, Y.; Zhao, C. Iron-Doped Nickel Phosphate as Synergistic Electrocatalyst for Water Oxidation. *Chem. Mater.* **2016**, 28, 5659-5666.

- (58) Xiao, X.; He, C.-T.; Zhao, S.; Li, J.; Lin, W.; Yuan, Z.; Zhang, Q.; Wang, S.; Dai, L.; Yu, D.
A General Approach to Cobalt-Based Homobimetallic Phosphide Ultrathin Nanosheets for
Highly Efficient Oxygen Evolution in Alkaline Media. *Energy Environ. Sci.* **2017**, *10*, 893-
899.

Table of contents