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## Introduction

A large amount of greenhouse gas emissions caused by the burning of fossil energy and by the exhaustion of non-renewable energy have given rise great obstacles to the development of human society.<sup>1</sup> The development of a clean and sustainable energy, such as hydrogen energy, has become crucial.<sup>2,3</sup> In recent years, the external application of voltage to promote the electrolysis of water molecules to produce hydrogen and oxygen is considered to be an ideal method of hydrogen production in the future, which is environmentally friendly and easy to prepare on a large scale. However, the actual hydrogen (oxygen) evolution process requires a potential greater than the theoretical value to overcome the kinetic hindrance, increasing the energy consumption of hydrogen (oxygen) production, particularly the oxygen evolution process that exhibits slower reac-

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The development of hydrogen energy relies to a large extent on the electrocatalysts that are highly efficient and widely sourced. Although transition metal phosphides (TMPs) have made great achievements in reducing the overpotential of hydrogen evolution reaction (HER), improving oxygen evolution reaction (OER) performance that is relatively lagging in view of relatively large overpotentials and high kinetics energy barriers is yet to be achieved. Herein, we propose an extremely convenient and practical approach to prepare iron-doped cobalt phosphide nanoparticles (Fe–Co<sub>x</sub>P NPs) *via* a one-step method by introducing an iron element in the *in situ* synthesis of a metal–organic framework (ZIF-67) and then subjecting to a phosphate treatment. The as-obtained Fe–Co<sub>x</sub>P showed an excellent OER and acceptable HER activities. In particular, for OER, the optimized Fe-doped Co<sub>x</sub>P (Fe<sub>0.27</sub>Co<sub>0.73</sub>P) exhibits an ultra-low overpotential of 251 mV at a current density of 10 mA cm<sup>-2</sup>, a negligible electrocatalytic degradation after 3000 CV cycles, and time over 40 h-reliant current density stability. When employed as cathode and anode electrodes in water splitting, the current density of 10 mA cm<sup>-2</sup> can be achieved at a potential of 1.68 V. Our facile synthetic strategy and innovative ideas are undoubtedly beneficial to the design and construction of advanced water-splitting electrocatalysts.

tion kinetics.<sup>4–7</sup> Therefore, to reduce the high overpotentials of the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER), numerous related studies have been devoted to explore efficient water-splitting electrocatalysts.<sup>8–11</sup> At present, Pt (Ir, Ru)-based electrocatalysts are believed to be the most efficient for HER (OER), while their comprehensive utilization is severely restricted due to their expensive price, rare deposits and unsatisfactory stability during the electrolysis of water reaction.<sup>12–14</sup> Hence, the development of non-precious metal electrocatalysts that significantly reduce the overpotential of OER and HER is an effective approach to alleviate the energy stress.

Transition metal phosphides (TMPs), with strong electrocatalytic activity and extensive resources, tend to exhibit outstanding water-splitting properties in reported non-precious metal electrocatalysts.<sup>15–19</sup> However, it has become difficult to achieve these electrocatalysts due to their complex synthesis procedures. Thus, simplifying the synthetic process and improving the electrocatalytic performance of electrocatalysts are urgent. In addition, OER involving the transport of fourelectrons is more sluggish than HER involving the transport of two-electrons, which makes OER determine the speed of the electrolytic water, thereby resulting in large overpotentials and high kinetic energy barriers.<sup>7</sup> Therefore, reducing the over-

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potential of OER to greatly improve the overall water-splitting efficiency is actually feasible. However, the development of facile synthesis processes to synthesize OER electrocatalysts with a low overpotential is still a great challenge.

In this study, the precursors containing iron and cobalt were synthesized *via* a simple doping strategy using a metalorganic framework (ZIF-67) as the template, and then phosphated to obtain iron-doped cobalt phosphide (Fe–Co<sub>x</sub>P). Altering the ratio of iron salt to cobalt salt could achieve the purpose of adjusting the doping degree of iron. The experimental data showed that the optimal proportion of iron doping could greatly improve the electrocatalytic activity of cobalt phosphide, and the obtained Fe<sub>0.27</sub>Co<sub>0.73</sub>P showed exceedingly good OER performance ( $\eta_{10} = 251$  mV) and recognized HER performance ( $\eta_{10} = 186$  mV). When serving as the cathode and anode electrodes in an electrolytic cell, the Fe<sub>0.27</sub>Co<sub>0.73</sub>P electrodes ( $V_{10} = 1.68$  V) demanded a much less voltage than the CoP electrodes ( $V_{10} = 1.82$  V).

### Experimental

#### Synthesis

The preparation of Fe-doped CoxP: formation of an organicligand solution: 2.649 g of 2-methylimidazole  $(C_4H_6N_2)$  was dispersed in deionized water (40 mL). Formation of a metalsalt solution: iron( $\pi$ ) nitrate nonahydrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) and cobalt chloride hexahydrate (CoCl<sub>2</sub>·6H<sub>2</sub>O) with varying feed ratios of Fe/Co (1:4, 1:3, 2:3) were dispersed in deionized water (20 mL). The total molar amount of metal salts was constant: 4.03 mmol. Under agitation, the metal-salt solution was transferred to the organic-ligand solution at one time. The stirring process was continued for 30 minutes, and then, the mixture was allowed to stand on a 35 °C water bath for 16 h. The product was collected by centrifugation (the cleaning agent used was ethanol), followed by vacuum drying. NaH<sub>2</sub>PO<sub>2</sub> and the FeCo precursor were placed upstream and downstream of the intake port of a tube furnace (the mass ratio of the precursor to phosphorus source was 1:5), respectively. Fe-doped Co<sub>x</sub>P was obtained by phosphating the downstream precursor with PH<sub>3</sub> produced by the thermal decomposition of NaH<sub>2</sub>PO<sub>2</sub>  $(2NaH_2PO_2 = PH_3 + Na_2HPO_4)$ . Using N<sub>2</sub> as the atmosphere, the heating procedure was employed to raise the temperature to 350 °C at a rate of 3 °C min<sup>-1</sup> and kept it warm for 2 h. After cooling by radiation, the solid Fe-Co<sub>x</sub>P was acquired. To investigate the effect of iron doping, CoP was synthesized by the same method but without adding the iron salt.

### **Results and discussion**

#### Structure and composition of Fe-CoxP electrocatalysts

Microscopic images acquired by scanning electron microscopy (SEM) demonstrate that the  $Fe_{0.27}Co_{0.73}$  precursor mainly contains nanosheets (Fig. 1a and S1†). After the phosphorization treatment, the nanosheets basically disappeared to form



Fig. 1 (a) SEM image of  $Fe_{0.27}Co_{0.73}$  precursor. (b) SEM image of  $Fe_{0.27}Co_{0.73}P$ . (c1) XRD pattern of  $Fe_{0.27}Co_{0.73}P$ . (c2) XRD patterns for a slow scan of 1 degree per minute. (d) HRTEM image of  $Fe_{0.27}Co_{0.73}P$ . (e-h) HAADF-STEM image and EDX element mapping images of  $Fe_{0.27}Co_{0.73}P$ .

stacked nanoparticles (Fig. 1b). To investigate the reasons for such substantial changes in the morphology, the precursor was calcined in N2 at the same temperature but without adding phosphorus source (Fig. S2<sup>†</sup>). We could find largesized particle forms, indicating that the change in the morphology was due to the poor thermal stability of the precursors rather than due to the effect of the phosphating processes. The organic ligand in the Fe<sub>0.27</sub>Co<sub>0.73</sub> precursor decomposed easily during the calcination process,<sup>20</sup> and the collapse of the organic skeleton resulted in the final morphology with irregular nanoparticles. Moreover, the XRD patterns of ZIF-67 and the Fe<sub>0.27</sub>Co<sub>0.73</sub> precursor are shown in Fig. S3.<sup>†</sup> The XRD pattern of ZIF-67 is consistent with that of the one previously reported,<sup>21</sup> while the XRD patterns of the Fe<sub>0.27</sub>Co<sub>0.73</sub> precursor and ZIF-67 are basically the same. These indicate that iron enters the lattice of ZIF-67 without destroying it.

Fig. 1(c1) reveals the X-ray diffraction (XRD) pattern of Fe<sub>0.27</sub>Co<sub>0.73</sub>P, which is synthesized by controlling the ratio of iron salt to cobalt salt to 1:3 in the raw material. A sequence of typical diffraction peaks at  $2\theta$  of  $31.6^{\circ}$ ,  $36.3^{\circ}$ ,  $46.2^{\circ}$ ,  $48.1^{\circ}$ , 48.4°, 56.0° and 56.7° are compatible with those of CoP (JCPDS no. 29-0497), and the (011), (111), (112), (211), (202), (020) and (301) crystallographic planes match with these diffraction peaks, respectively. The diffraction peak at 40.8° belongs to Co<sub>2</sub>P (JCPDS no. 54-0413), corresponding to the (111) plane. Due to the low content of  $Co_2P$ , the as-obtained sample with CoP and Co<sub>2</sub>P was denoted as Co<sub>x</sub>P. No extra diffraction peaks of iron-based compounds were observed on analyzing the XRD pattern, indicating that there were a few ironbased compounds, or that most of the iron atoms entered the Co<sub>x</sub>P lattices.<sup>22</sup> Furthermore, the XRD pattern with a slow scan of 1° per minute for a specific peak near 31.7° reveals that the

diffraction peak of Fe<sub>0.27</sub>Co<sub>0.73</sub>P slightly shifts to a large angle compared to the undoped cobalt phosphide (as shown in Fig. 1(c2)), further demonstrating the substitutional doping of Fe ions in the Co<sub>x</sub>P lattices. The inductively coupled plasma atom emission spectrometry (ICP-AES) test demonstrated that the ratio of the two metal atoms (Fe:Co) in Fe-Co<sub>x</sub>P was 0.27:0.73, which was basically in line with the initial Co/Fe feeding ratio. In addition to Fe<sub>0.27</sub>Co<sub>0.73</sub>P, other iron-doped cobalt phosphides with different proportions of iron  $(Fe_{0.22}Co_{0.78}P, Fe_{0.44}Co_{0.56}P, CoP)$  were also investigated (Fig. S4 and S5<sup>†</sup>). The low-resolution TEM image is shown in Fig. S6.<sup>†</sup> It could be seen that Fe<sub>0.27</sub>Co<sub>0.73</sub>P was mainly composed of nanoparticles. The high-resolution transmission electron microscopy (HR-TEM) was used to reveal more information about the crystallographic structure of Fe<sub>0.27</sub>Co<sub>0.73</sub>P. The interplanar spacing between the (200) facets of CoP and the (111) facets of Co<sub>2</sub>P matched the 0.256 and 0.225 nm, as shown in Fig. 1d, respectively. These lattice spacings are slightly larger than that of 0.254 nm and 0.221 nm for undoped CoP and Co<sub>2</sub>P, respectively, which can be attributed to the Fe substitution. Due to the lamellar structure, the Fe<sub>0.27</sub>Co<sub>0.73</sub> precursor had almost no channels.<sup>21</sup> Therefore, as shown in Fig. S7,† Fe<sub>0.27</sub>Co<sub>0.73</sub>P exhibited a small BET surface area (3.40 m<sup>2</sup> g<sup>-1</sup>), indicating no porous structure for it. On the basis of the EDX test, there was an equidistribution of different elements in Fe<sub>0.27</sub>Co<sub>0.73</sub>P nanoparticles (Fig. 1e-h).

The X-ray photoelectron spectroscopy (XPS) test determined the valence state of each element in  $Fe_{0.27}Co_{0.73}P$ . In addition to observing the appearance of the expected elements (Fe, Co and P), other elements (C, N and O) also appear in the whole spectrum of Fig. 2a, which can be derived from the carbonization of organic ligands and the surface oxidation when exposed to air. As shown in Fig. 2b, the peaks (777.6 and 792.4 eV) representing Co  $2p_{3/2}$  and Co  $2p_{1/2}$  that can testify the existence of Co–P bonding are found in the high-resolution spectra of Co 2p.<sup>23–25</sup> In addition, peaks (780.6 and 796.8 eV) of oxidized cobalt generated by air oxidation and satellite peaks



Fig. 2 (a) XPS survey pattern of  $Fe_{0.27}Co_{0.73}P$ . High-resolution XPS spectra of Co 2p (b), Fe 2p (c) and P 2p (d) regions for  $Fe_{0.27}Co_{0.73}P$ .

(785.8 and 801.5 eV) also appeared.<sup>23,24,26</sup> The peaks (708.8, 711.3, 714.1, 722.5 and 724.9 eV) of oxidized iron that majorly appeared due to the exposure to air exist in the Fe 2p spectra (Fig. 2c).<sup>27,28</sup> Moreover, a small peak of Fe 2p at 706.0 eV could be indexed to Fe-P bonding, while the peak at 706.0 eV for Fe<sub>0.22</sub>Co<sub>0.78</sub>P with a lower proportion of iron added to the raw material substantially disappeared (Fig. S8<sup>†</sup>). This could be explained by the fact that after the entry of most of the iron into the crystal lattice of cobalt phosphide, a small amount of iron that failed to enter the crystal lattice was phosphatized.<sup>29</sup> The small amount of iron phosphide formed was advantageous for charge re-distribution, and it synergistically promoted the catalytic performance of the electrocatalyst.<sup>29,30</sup> As shown in Fig. 2d, the peaks (128.2 and 129.2 eV) representing P  $2p_{3/2}$  and P  $2p_{1/2}$  can be indexed to the metal phosphides.<sup>31</sup> In addition, the peak (132.9 eV) of oxidized P species could be assigned to the air exposure.<sup>32</sup> It can be seen that Fe<sub>0.27</sub>Co<sub>0.73</sub>P mainly exists as Co-P bonding and M-O (M is Fe, Co and P) bonding from the XPS analysis result, indicating that iron enters the crystal lattice of cobalt phosphide mainly in the form of doping and thus iron-doped cobalt phosphides were successfully prepared.

#### OER performance of electrocatalysts

The OER performance of the pre-synthesized Fe<sub>0.27</sub>Co<sub>0.73</sub>P coated on a Ni foam (Fe0.27Co0.73P/NF) was first investigated in a 1.0 M KOH solution. As a reference, the electrocatalytic performance of the commercial IrO2 and CoP coated on NF with the same amount of load (3 mg cm<sup>-2</sup>) was also investigated under the same conditions. IR compensation was applied to all of the initial polarization curves. Linear sweep voltammetry (LSV) curves (Fig. 3a) and OER performance histogram (Fig. 3b) show that the  $Fe_{0.27}Co_{0.73}P/NF$  electrode exhibits the minimum overpotential ( $\eta_{10}$  = 251 mV) compared with that of IrO<sub>2</sub>/NF ( $\eta_{10}$  = 293 mV), CoP/NF ( $\eta_{10}$  = 327 mV) and bare Ni foam ( $\eta_{10}$  = 417 mV). In addition, the overpotential of the electrocatalyst at different current densities was also an important indicator for measuring the electrocatalytic performance. The overpotentials required ( $\eta_{10}$  = 251 mV,  $\eta_{20}$  = 269 mV, and  $\eta_{50}$  = 292 mV) for Fe<sub>0.27</sub>Co<sub>0.73</sub>P/NF at different current densities are shown in Fig. 3c. The distinguished OER performance was very competitive with the recently reported transition metal-based electrocatalysts, such as NiCo LDH,<sup>33</sup> ZIF-8/ZIF-67,<sup>34</sup> and Ni<sub>3</sub>N/ NF<sup>35</sup> (Table S1†).

The Tafel curves were fitted in the low voltage region. As shown in Fig. 3d, the Tafel slope values of  $Fe_{0.27}Co_{0.73}P/NF$ ,  $IrO_2/NF$ , CoP/NF and bare Ni foam are 59.1, 71.4, 85.4 and 155.7 mV dec<sup>-1</sup>, respectively. In addition, the multi-step current curve of  $Fe_{0.27}Co_{0.73}P/NF$  shown in Fig. S9† demonstrates that the potential of each section remains almost stable as the current density of the anode increases from 10 to 90 mA cm<sup>-2</sup>. When the current density decreased from 90 to 10 mA cm<sup>-2</sup>, the voltage at 10 mA cm<sup>-2</sup> after a cycle remained basically unchanged, indicating that  $Fe_{0.27}Co_{0.73}P/NF$  possessed splendid mass transport properties and satisfactory mechanical robustness. Moreover, to assess the OER stability



**Fig. 3** (a) OER polarization curves for  $Fe_{0.27}Co_{0.73}P/NF$ , CoP/NF, IrO<sub>2</sub>/NF and NF. (b) Overpotentials at 10 mA cm<sup>-2</sup>. (c) The corresponding overpotentials of  $Fe_{0.27}Co_{0.73}P$  when the current density is 10, 20, 50 mA cm<sup>-2</sup>. (d) Tafel plots. (e) Time-dependent current density curve of  $Fe_{0.27}Co_{0.73}P/NF$ . (f) Polarization curves for  $Fe_{0.27}Co_{0.73}P/NF$  initial and after 3000 CV cycles.

of Fe<sub>0.27</sub>Co<sub>0.73</sub>P/NF, the weak attenuation of current density was acceptable after 40 h in the time-reliant current density stability test (as shown in Fig. 3e), and the degradation of the electrocatalytic activity could be neglected after 3000 CV cycles at a scan rate of 100 mV s<sup>-1</sup> (as shown in Fig. 3f). The above results indicated that Fe<sub>0.27</sub>Co<sub>0.73</sub>P/NF possessed an excellent electrocatalytic stability in alkaline solutions. Besides, the OER activities of Fe<sub>0.22</sub>Co<sub>0.78</sub>P/NF and Fe<sub>0.44</sub>Co<sub>0.56</sub>P/NF were also explored. For various Fe doping proportions, optimized Fe<sub>0.27</sub>Co<sub>0.73</sub>P/NF exhibited the best OER performance and minimum Tafel slope compared with the other two electrocatalysts, as shown in Fig. S10 and S11.†

#### HER performance of electrocatalysts

The same Fe<sub>0.27</sub>Co<sub>0.73</sub>P/NF working electrode was employed to assess the HER electrocatalytic performance by applying the iR-correction in 1.0 M KOH. For comparison, reference materials, such as CoP/NF and Ni foam, were also tested for their HER electrocatalytic performances in the identical condition. As shown in Fig. 4a and b, the Fe<sub>0.27</sub>Co<sub>0.73</sub>P/NF electrode exhibits the minimum overpotential ( $\eta_{10}$  = 186 mV) compared with that of CoP/NF ( $\eta_{10}$  = 252 mV) and bare Ni foam ( $\eta_{10}$  = 291 mV). Fig. 4c presents the Tafel slopes of 60.5, 113.4 and 131.0 mV dec<sup>-1</sup> for Fe<sub>0.27</sub>Co<sub>0.73</sub>P/NF, CoP/NF and Ni foam, respectively. The Fe<sub>0.27</sub>Co<sub>0.73</sub>P/NF electrode also shows the best HER performance and minimum Tafel slope compared with the other two electrocatalysts, as shown in Fig. S12 and S13.<sup>†</sup> To assess the HER stability of Fe<sub>0.27</sub>Co<sub>0.73</sub>P/NF, the decay of current density could be ignored after 40 h in the time-reliant current density stability test (Fig. 4d). Moreover, as shown in



Fig. 4 (a) HER polarization curves of  $Fe_{0.27}Co_{0.73}P/NF$ , CoP/NF and NF. (b) Overpotentials at 10 mA cm<sup>-2</sup>. (c) Tafel plots. (d) Time-dependent current density curve of  $Fe_{0.27}Co_{0.73}P/NF$ .

Fig. S14,† the degradation of the electrocatalytic performance is almost negligible after 3000 CV cycles, revealing the outstanding HER stability of  $Fe_{0.27}Co_{0.73}P$ .

#### Overall water splitting of electrocatalysts

In view of the excellent electrocatalytic activities of  $Fe_{0.27}Co_{0.73}P/NF$  toward OER and HER,  $Fe_{0.27}Co_{0.73}P/NF$  served as cathode and anode simultaneously in the electrolytic cell to test its water-splitting capacity. As shown in Fig. 5a and b,  $Fe_{0.27}Co_{0.73}P/NF||Fe_{0.27}Co_{0.73}P/NF||Fe_{0.27}Co_{0.73}P/NF$  only needs 1.68 V to attain the current density of 10 mA cm<sup>-2</sup>, while CoP/NF||CoP/NF, as benchmark, requires as high as 1.82 V. As shown in Fig. 5c, in comparison with the latter, the former exhibits a lower Tafel slope. Moreover, chronoamperometry was performed to evaluate the stability of  $Fe_{0.27}Co_{0.73}P/NF$ . The  $Fe_{0.27}Co_{0.73}P/NF$  system exhibited a high stability over 35 h, as shown in Fig. 5d.



Fig. 5 (a) Polarization curves of an alkaline electrolyzer using  $Fe_{0.27}Co_{0.73}P/NF \|Fe_{0.27}Co_{0.73}P/NF$  and  $CoP/NF\|CoP/NF$  as the two electrodes. (b) Voltage at 10 mA cm<sup>-2</sup>. (c) Tafel curves. (d) Chronoamperometric electrolysis at a constant voltage of 1.72 V for  $Fe_{0.27}Co_{0.73}P/NF \|Fe_{0.27}Co_{0.73}P/NF$ .



**Fig. 6** (a) Gas collection device of water splitting. (b, c, d, and e) Photographs of hydrogen collected at different times. (f, g, h, and i) Photographs of oxygen collected at different times. (j) Photograph of the electrolytic cell. (k) Photograph of H<sub>2</sub> bubbles attached to Ni foam. (l) Photograph of O<sub>2</sub> bubbles attached to Ni foam. (m) Amount of H<sub>2</sub>/O<sub>2</sub>.

To test the faradaic efficiency of  $Fe_{0.27}Co_{0.73}P$ , hydrogen and oxygen, produced by the electrolysis of water in an electrolytic cell using the  $Fe_{0.27}Co_{0.73}P/NF$  electrodes, were collected *via* a drainage method (Fig. 6a). Fig. 6b–e and f–i display the volume of hydrogen and oxygen produced, respectively, at different times. Fig. 6j shows the electrolytic cell device. Hydrogen and oxygen bubbles attached to the Ni foam are visible, as shown in Fig. 6k and l. According to the volume ratio of hydrogen to oxygen, the calculated faradaic efficiency was as high as 85% (Fig. 6m). The above data demonstrated that  $Fe_{0.27}Co_{0.73}P$  was really an excellent water-splitting electrocatalyst. The process through which the  $Fe_{0.27}Co_{0.73}P/NF$  electrodes electrolyze water to produce hydrogen and oxygen is shown in Video S1.† The process of collecting hydrogen and oxygen by the drainage method is shown in Video S2.†

# Analysis of accelerated electrocatalytic kinetics of electrocatalysts

The OER electrocatalytic performance of  $Fe_{0.27}Co_{0.73}P/NF$  surpassed the performance obtained for commercial IrO<sub>2</sub>/NF and CoP/NF, demonstrating that  $Fe_{0.27}Co_{0.73}P/NF$  possessed a superior OER activity, and the iron doping could greatly enhance the OER activity of CoP. Simultaneously, compared to the different proportions of Fe–Co<sub>x</sub>P/NF (Fe<sub>0.22</sub>Co<sub>0.73</sub>P/NF, Fe<sub>0.27</sub>Co<sub>0.73</sub>P/NF, fe<sub>0.27</sub>Co<sub>0.73</sub>P/N

the surface of the electrocatalyst, the decomposition of OH under ionization, and the formation of active O on the active sites used for oxygen evolution.<sup>36</sup> Accelerating the decomposition process could significantly speed-up the progress of the electrocatalytic reaction. This could be achieved by a reasonable combination of a variety of different electronegative metal elements.<sup>36,37</sup> Owing to the difference in the electronegativities between Fe and Co, it was found that iron-doped cobalt phosphide (Fe-Co<sub>x</sub>P) exhibited a faster decomposition rate for OH<sup>-</sup> and stronger adsorption and ability of bonding to the generated intermediate O than the undoped cobalt phosphide, thereby allowing Fe<sub>0.27</sub>Co<sub>0.73</sub>P to possess a prominent electrocatalytic activity for OER. To provide further insight into the excellent OER performance of Fe<sub>0.27</sub>Co<sub>0.73</sub>P, the product after the OER test was characterized by XPS. The result shows that the Co-P and Fe-P bondings disappear and only the Co-O and Fe-O bondings exist as shown in Fig. S15,† indicating that the surface of Fe<sub>0.27</sub>Co<sub>0.73</sub>P was oxidized in the OER process and then the active intermediates formed, which were beneficial to promote the OER process.

Fe0.27CO0.73P/NF also displayed a preferable HER activity and a Tafel slope smaller than the other ratios of Fe-Co<sub>x</sub>P/NF. The Tafel value of Fe<sub>0.27</sub>Co<sub>0.73</sub>P/NF indicated that the HER process of Fe0.27Co0.73P/NF followed Volmer-Heyrovsky mechanism, which included the adsorption of H<sub>2</sub>O on the surface of the electrocatalyst, the decomposition of H<sub>2</sub>O under ionization, and the active H formed on the active sites that combined with the H<sub>2</sub>O molecule for hydrogen evolution.<sup>38,39</sup> Note that Fe<sub>0.27</sub>Co<sub>0.73</sub>P/NF showed a lower Tafel slope value than that of CoP/NF, indicating that the electrocatalytic kinetics of Fe0.27Co0.73P/NF for HER was faster than that of CoP/NF, and Fe doping was beneficial to improve the HER performance of CoP. This could also be explained by the difference in electronegativities between Fe and Co, which was conducive in accelerating the decomposition rate of H<sub>2</sub>O and enhancing the adsorption and bonding ability to the generated intermediate H for HER. In total, Fe doping could enhance the adsorption and bonding ability of O and H in the process of oxygen evolution and hydrogen evolution and accelerate the decomposition of OH in the OER and the decomposition of H<sub>2</sub>O in the HER, thus greatly promoting the two half reactions for water splitting.

The effect of different iron doping amounts on the active surface area of the electrocatalysis could be judged by the double layer capacitance ( $C_{dl}$ ). Fig. S16 and S17<sup>†</sup> show that the calculated  $C_{dl}$  of Fe<sub>0.27</sub>Co<sub>0.73</sub>P/NF is larger than that of Fe<sub>0.22</sub>Co<sub>0.73</sub>P/NF and Fe<sub>0.44</sub>Co<sub>0.56</sub>P/NF, indicating that Fe<sub>0.27</sub>Co<sub>0.73</sub>P/NF possesses larger active surface area than Fe<sub>0.22</sub>Co<sub>0.78</sub>P/NF and Fe<sub>0.44</sub>Co<sub>0.56</sub>P/NF. Notice that a  $C_{dl}$  of 1.02 mF cm<sup>-2</sup> for Fe<sub>0.27</sub>Co<sub>0.73</sub>P/NF was slightly smaller than  $C_{dl}$  of 1.23 mF cm<sup>-2</sup> for CoP/NF, which could be interpreted by the fact that in the OER process the amount of the active species actually produced determines the real activity of the actual reaction.<sup>40</sup> The electronic transmission capabilities of Fe-Co<sub>x</sub>P/NF could be reflected in the electrochemical impedance spectroscopy (EIS). Fe<sub>0.27</sub>Co<sub>0.73</sub>P/NF displayed

the minimum  $R_{\rm ct}$  compared to the other electrocatalysts (Fig. S18†), indicating that Fe<sub>0.27</sub>Co<sub>0.73</sub>P/NF has faster reaction kinetics and the decrease in charge transfer resistance contribute to the improvement in the electrocatalytic efficiency.

## Conclusions

To sum up, a facile and practical approach was proposed to fabricate iron-doped cobalt phosphide (Fe<sub>0.27</sub>Co<sub>0.73</sub>P) based on a metal-organic framework. With an optimized Fe doping, the obtained electrocatalyst coated on the 3D porous conductive Ni foam substrate (Fe<sub>0.27</sub>Co<sub>0.73</sub>P/NF) required very little overpotentials toward OER ( $\eta_{10}$  = 251 mV) and HER ( $\eta_{10}$  = 186 mV), demonstrating excellent electrocatalytic activities particularly for OER. When Fe<sub>0.27</sub>Co<sub>0.73</sub>P/NF simultaneously served as the cathode and anode in an electrolytic cell containing a 1.0 M KOH alkaline solution, only a 1.68 V potential was required to afford the current density of 10 mA cm<sup>-2</sup>. Moreover, Fe<sub>0.27</sub>Co<sub>0.73</sub>P/NF also showed an excellent long-term electrochemical stability during the OER and HER electrocatalytic processes. Undoubtedly, our strategy for the design and construction of bifunctional electrocatalysts would provide a guidance for the development of multifunctional electrocatalysts with high electrocatalytic activity and stability.

## Conflicts of interest

There are no conflicts of interest to declare.

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## References

- 1 J. H. Kim, D. H. Youn, K. Kawashima, J. Lin, H. Lim and C. B. Mullins, *Appl. Catal.*, *B*, 2018, **225**, 1–7.
- 2 T. Yang, L. Pei, S. Yan, Z. Yu, T. Yu and Z. Zou, *Dalton Trans.*, 2019, **48**, 11927–11933.
- 3 B. S. Kumar, K. Tarafder, A. R. Shetty, A. C. Hegde, V. C. Gudla, R. Ambat, S. K. Kalpathy and S. Anandhan, *Dalton Trans.*, 2019, 48, 12684–12698.
- 4 L. Zhuang, L. Ge, Y. Yang, M. Li, Y. Jia, X. Yao and Z. Zhu, *Adv. Mater.*, 2017, **29**, 1606793.
- 5 X. Wang, L. Dong, M. Qiao, Y. Tang, J. Liu, Y. Li, S. Li, J. Su and Y. Lan, *Angew. Chem., Int. Ed.*, 2018, 57, 9660–9664.
- 6 D. Chen, M. Qiao, Y. Lu, L. Hao, D. Liu, C. Dong, Y. Li and S. Wang, *Angew. Chem., Int. Ed.*, 2018, 57, 8691–8696.
- 7 M. I. Jamesh and X. Sun, J. Power Sources, 2018, 400, 31-68.

- 8 C. Tang, L. Gan, R. Zhang, W. Lu, X. Jiang, A. Asir, X. Sun, J. Wang and L. Chen, *Nano Lett.*, 2016, **16**, 6617–6621.
- 9 C. McCrory, S. Jung, I. Ferrer, S. Chatman, J. Peters and T. Jaramillo, *J. Am. Chem. Soc.*, 2015, **137**, 4347–4357.
- 10 Y. Guo, P. Yuan, J. Zhang, H. Xia, F. Cheng, M. Zhou, J. Li, Y. Qiao, S. Mu and Q. Xu, *Adv. Funct. Mater.*, 2018, 28, 9.
- 11 Z. Pu, C. Zhang, I. Amiinu, W. Li, L. Wu and S. Mu, ACS Appl. Mater. Interfaces, 2017, 9, 16187–16193.
- 12 Y. Yang, L. Dang, M. Shearer, H. Sheng, W. Li, J. Chen, P. Xiao, Y. Zhang, R. Hamers and S. Jin, *Adv. Energy Mater.*, 2018, 8, 9.
- 13 L. Xu, Q. Jiang, Z. Xiao, X. Li, J. Huo, S. Wang and L. Dai, Angew. Chem., Int. Ed., 2016, 55, 5277–5281.
- 14 F. Li, B. Zhang, X. Li, Y. Jiang, L. Chen, Y. Li and L. Sun, Angew. Chem., Int. Ed., 2011, 50, 12276–12279.
- 15 A. Han, S. Jin, H. Chen, H. Ji, Z. Sun and P. Du, J. Mater. Chem. A, 2015, 3, 1941–1946.
- 16 Z. Zhang, B. Lu, J. Hao, W. Yang and J. Tang, Chem. Commun., 2014, 50, 11554–11557.
- 17 Z. Xing, Q. Liu, A. M. Asiri and X. Sun, *Adv. Mater.*, 2014, 26, 5702–5707.
- 18 C. Zhang, Z. Pu, I. Amiinu, Y. Zhao, J. Zhu, Y. Tang and S. Mu, *Nanoscale*, 2018, **10**, 2902–2907.
- 19 Z. Pu, I. Amiinu, C. Zhang, M. Wang, Z. Kou and S. Mu, *Nanoscale*, 2017, **9**, 3555–3560.
- 20 W. T. Koo, S. Yu, S. J. Choi, J. S. Jang, J. Y. Cheong and I. D. Kim, ACS Appl. Mater. Interfaces, 2017, 9, 8201– 8210.
- 21 M. Wang, J. Liu, C. Guo, X. Gao, C. Gong, Y. Wang, B. Liu, X. Li, G. G. Gurzadyan and L. Sun, *J. Mater. Chem. A*, 2018, 6, 4768–4775.
- 22 P. Wang, Z. Pu, Y. Li, L. Wu, Z. Tu, M. Jiang, Z. Kou, I. Arniinu and S. Mu, ACS Appl. Mater. Interfaces, 2017, 9, 26001–26007.
- 23 J. Tian, Q. Liu, A. Asiri and X. Sun, J. Am. Chem. Soc., 2014, 136, 7587–7590.
- 24 Y. Ning, D. Ma, Y. Shen, F. Wang and X. Zhang, *Electrochim. Acta*, 2018, 265, 19–31.
- 25 Y. L. Li, B. M. Jia, B. Y. Chen, Q. L. Liu, M. K. Cai, Z. Q. Xue, Y. N. Fan, H. P. Wang, C. Y. Su and G. Q. Li, *Dalton Trans.*, 2018, 47, 14679–14685.
- 26 Y. L. Li, B. M. Jia, Y. Z. Fan, K. L. Zhu, G. Q. Li and C. Y. Su, Adv. Energy Mater., 2018, 8, 9.
- 27 J. Masud, S. Umapathi, N. Ashokaan and M. Nath, *J. Mater. Chem. A*, 2016, 4, 9750–9754.
- 28 Y. Pei, Y. Ge, H. Chu, W. Smith, P. Dong, P. M. Ajayan,
  M. Ye and J. Shen, *Appl. Catal.*, B, 2019, 244, 583–593.
- 29 F. Li, Y. Bu, Z. Lv, J. Mahmood, G. Han, I. Ahmad, G. Kim, Q. Zhong and J. Baek, *Small*, 2017, 13, 6.
- 30 X. Wang, M. Pi, D. Zhang, H. Li, J. Feng, S. Chen and J. Li, ACS Appl. Mater. Interfaces, 2019, 11, 14059–14065.
- 31 Z. Pu, I. Amiinu, M. Wang, Y. Yang and S. Mu, *Nanoscale*, 2016, 8, 8500–8504.
- 32 Y. Wang, C. Xie, Z. Zhang, D. Liu, R. Chen and S. Wang, *Adv. Funct. Mater.*, 2018, **28**, 1703363.

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- 33 H. Liang, F. Meng, M. Caban-Acevedo, L. Li, A. Forticaux, L. Xiu, Z. Wang and S. Jin, *Nano Lett.*, 2015, 15, 1421–1427.
- 34 S. Liu, Z. Wang, S. Zhou, F. Yu, M. Yu, C. Chiang, W. Zhou, J. Zhao and J. Qiu, *Adv. Mater.*, 2017, 29, 1700874.
- 35 M. Shalom, D. Ressnig, X. Yang, G. Clavel, T. Fellinger and M. Antonietti, *J. Mater. Chem. A*, 2015, **3**, 8171–8177.
- 36 M. Gong, W. Zhou, M. C. Tsai, J. G. Zhou, M. Y. Guan, M. C. Lin, B. Zhang, Y. F. Hu, D. Y. Wang, J. Yang, S. J. Pennycook, B. J. Hwang and H. J. Dai, *Nat. Commun.*, 2014, 5, 4695.
- 37 R. Subbaraman, D. Tripkovic, D. Strmenik, K. C. Chang, M. Uchimura, A. P. Paulikas, V. Stamenkovic and N. M. Markovic, *Science*, 2011, 334, 1256–1260.
- 38 Y. Shi and B. Zhang, Chem. Soc. Rev., 2016, 45, 1529-1541.
- 39 J. Luo, J. Im, M. Mayer, M. Schreier, M. Nazeeruddin, N. Park, S. Tilley, H. Fan and M. Gratzel, *Science*, 2014, 345, 1593–1596.
- 40 Y. M. Liu, Y. Su, X. Quan, X. F. Fan, S. Chen, H. T. Yu, H. M. Zhao, Y. B. Zhang and J. J. Zhao, ACS Catal., 2018, 8, 1186–1191.