Iron-doped cobalt phosphide nanowires prepared via one-step solvothermal phosphidization of metal-organic frameworks for oxygen evolution reaction

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1. Experimental

Chemicals

Cobalt (II) nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O; Guanghua Chemical Reagent; AR 98.0%), potassium hydroxide (KOH; Kermel Chemical Reagent; AR 85.0%), white phosphorous (P$_4$; Fuchen Chemical Reagent; AR), ethanol (C$_2$H$_5$OH; Rionlon Chemical Reagent; AR 99.7%), benzene (C$_6$H$_6$; Hushi Chemical Reagent; AR 99.5%), methanol (CH$_3$OH; Guanghua Chemical Reagent; AR 99.5%), 1,3,5-benzenetricarboxylic acid (C$_6$H$_3$(CO$_2$H)$_3$; Aladdin Chemical Reagent; AR 98.0%), acetone (C$_3$H$_6$O; Hushi Chemical Reagent; AR 99.5%), hydrochloric acid (HCl; Kelong Chemical Reagent; AR 38%), triethylamine (C$_6$H$_{15}$N; Guanghua Chemical Reagent; AR 99.0%), ferrous sulfate heptahydrate (FeSO$_4$·7H$_2$O; Tianli Chemical Reagent; AR 99.0%), N,N-dimethylformamide (HCON(CH$_3$)$_2$; Fuyu Chemical Reagent; AR 99.5%), potassium nitrate (KNO$_3$; Hengxing Chemical Reagent; AR 99.0%), tetramethylammonium hydroxide pentahydrate (C$_4$H$_{13}$NO·5H$_2$O; Macklin Chemical Reagent; AR 97.0%), Ni foam (thickness 1.6 mm) were used as received unless stated otherwise. Doubly distilled water was used throughout the experiment.
2. Instrumentation

Electrochemical measurements were carried out using potentiostats (CHI660E and ParSTAT MC). The three-electrode setup is composed of the working electrode, the counter electrode (a cleaned graphite rode), and the reference electrode (the saturated calomel electrode (SCE)). The electrolyte is 1 M KOH (pH = 13.9). The geometric area of the working electrode immersed in the electrolyte is controlled to 1 cm$^2$. The Tafel slope ($b$) is calculated using Eq. 1.

$$\eta = b \log j$$  \hspace{1cm} (1)

where $\eta$ is the overpotential, $b$ is the Tafel slope, and $j$ is the current density. AC electrochemical impedance spectroscopy (EIS) was performed with the alternating voltage amplitude at 5 mV in the range of 100 kHz to 0.01 Hz. The solution resistance acquired from the EIS is used for $iR$ compensation, and all the linear sweep voltammetry and galvanostatic measurements are $iR$ compensated. The potentials are reported in reversible hydrogen electrode (RHE) scale unless otherwise stated. The conversion of the potentials from the measured SCE scale to RHE scale is based on Eq. 2.

$$E_{\text{RHE}} = E_{\text{SCE}} + 0.059 \text{pH} + 0.241$$  \hspace{1cm} (2)

where, $E_{\text{RHE}}$ is the potential in RHE scale, and $E_{\text{SCE}}$ is the potential vs. SCE. The $\eta$ for OER is calculated based on Eq. 3.

$$\eta = E_{\text{RHE}} - 1.23$$  \hspace{1cm} (3)

All experiments were repeated at least three times to ensure reproducibility. Other information on instrumentation can be found in the Supporting Information.
X-ray photoelectron spectroscopy (XPS) was carried out using a Kratos Axis Supra spectrometer at room temperature and ultra-high vacuum (UHV) conditions. The instrument was equipped with monochromatic Al Kα source 1486.6 eV (15 mA, 15 kV), and hemispherical analyser with hybrid magnetic and electrostatic lens for enhanced electron collection. Survey and detailed XPS spectra were acquired at normal emission with the fixed pass energy of 160 eV and 40 eV, respectively. All spectra were charge-corrected to the hydrocarbon peak set to 284.6 eV. The Kratos charge neutralizer system was used on all specimens. Data analysis was based on a standard deconvolution method using mixed Gaussian (G) and Lorentzian (L) line shape (G = 70% and L = 30%, Gaussian–Lorentzian product) for each component. Spectra were analyzed using CasaXPS software (version 2.3.16). X-ray diffraction (XRD) was acquired using (D8 ADVANCE, Bruker) diffractometer having Cu Kα (λ=1.54 Å) source. The instrument was operated at 30 mA current voltage and 40 kV. Field emission scanning electron microscope (S-4800, Hitachi, Japan) and transmission electron microscope (FEI-Tecnai G2 F20) were used to observe the morphology of the catalyst. ICP-AES parameters are the following: forward power 1350 W, plasma gas flow rate 12.0 L min−1, nebulizer gas flow rate 1.0 L min−1, auxiliary gas flow rate 1.0 L min−1, sample uptake speed 50 rpm with white/orange Tygon tubing. A concentric nebulizer was used with a cyclonic spray chamber. No internal standard correction was applied for ICP-AES analysis.
3. X-ray photoelectron spectroscopy

**Figure S1.** (a) XPS survey spectra of the Co$_2$P, CoFeP and CoFeP after the long-term galvanostatic test.
4. X-ray diffraction

Figure S2. XRD patterns of Co MOF and the Co MOF after ion-exchange with Fe^{2+} (labelled as CoFe MOF).
Table S1. Contents of the samples

<table>
<thead>
<tr>
<th></th>
<th>Atomic Percentage (%)*</th>
<th>Co</th>
<th>Fe</th>
<th>P</th>
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<td>Co MOF</td>
<td></td>
<td>100</td>
<td>-</td>
<td>-</td>
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<tr>
<td>ICP- AES</td>
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<td>CoFeP after 30h OER</td>
<td>XPS</td>
<td>45.21</td>
<td>53.77</td>
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30h OER
6. Electrochemistry

Figure S3. CV of Ni foam.
Figure S4. The 4th harmonic FT-ACV curves of the Co MOF, Co$_2$P and CoFeP.

The fourth harmonic Fourier transform AC voltammograms (FT-ACV) of Co MOF/NF, Co$_2$P/NF and CoFeP/NF are shown in Fig. S4, where a large amplitude periodic AC waveform is superimposed on the DC ramp [1]. Region I (1.1 ~ 1.3 V$_{\text{RHE}}$) is associated with the redox of Co$^{2+}$/Co$^{3+}$ and Region II (1.3 ~ 1.45 V$_{\text{RHE}}$) is associated with the structural rearrangement of Co$^{3+}$/Co$^{4+}$ active center formation, while Region III (> 1.45 V$_{\text{RHE}}$) is associated with OER [2]. The fourth harmonic FTACV components of the three samples are shown in Fig. 4b. The anodic shift of the peak potential of the three samples in region II is consistent with the CV, which indicates the existence of strong electronic interactions between Fe and Co.
Figure S5. (a-c) CV of Co MOF/NF, Co$_2$P/NF and CoFeP/NF at different scan rates (20, 40, 60, 80, and 100 mV s$^{-1}$) in 0 - 0.2 V in 1 M KOH.
Figure S6. The CV and LSV of the (a, d) Co MOF/NF, (b, e) Co$_2$P/NF and (c, f) CoFeP/NF in different pH solutions ($x$ M KOH + $(1-x)$ M KNO$_3$, pH = 13.84, 13.72, 13.57, 13.35, and 12.9) at scan rate 5 mV s$^{-1}$.
Figure S7. The CV and LSV of the (a, d) Co MOF/NF, (b, e) Co\textsubscript{2}P/NF and (c, f) CoFeP/NF at different temperatures in 1 M KOH at scan rate 5 mV s\textsuperscript{-1}.
Figure S8. (a) Pulse voltammetry protocol between 1.06 V vs. RHE cathodic and 1.46 V to 1.66 V vs. RHE and (b-d) the corresponding time-current curves.
Figure S9. The reduction peak current densities versus the square root of scan rates of (a) Co MOF/NF, (b) Co$_2$P/NF and (c) CoFeP/NF.

Considering that the Co$^{3+/4+}$ redox process follows the semi-infinite linear diffusion, the Randles-Sevick equation to calculate the OH$^-$ diffusion coefficient is applied.

\[ j_p = 268600n^{3/2}AD^{1/2}C^{1/2}v^{1/2} \]

where \( j_p \) is the peak current density, \( n \) is the number of electrons transferred in the redox process, \( D \) is the diffusion coefficient, \( C \) is the OH$^-$ concentration, \( v \) is the scan rate, and \( A \) is the geometric surface area of the electrode. As shown in Figure S9, the current density of the redox peak of the electrode is linearly related to the square root of the scan rate, indicating that the redox process is determined by the semi-infinite diffusion controlled process. The slopes of the Co$^{4+/3+}$ reduction peak currents versus the square root of the scan rate for Co MOF/NF, Co$_2$P/NF and CoFeP/NF are 0.062, 0.081 and 0.133, respectively. Accordingly, the calculated diffusion coefficients obtained were \( 0.09 \times 10^{-12} \) cm$^2$ s$^{-1}$, \( 0.16 \times 10^{-12} \) cm$^2$ s$^{-1}$ and \( 0.44 \times 10^{-12} \) cm$^2$ s$^{-1}$. The highest diffusion coefficient for CoFeP/NF indicates the fastest OH$^-$ diffusion kinetics, which may be due to the accelerated OH$^-$ diffusion by the inhomogeneous electric field induced by the doped Fe.
7. TEM

**Figure S10.** (a) SEM images of Co$_2$P/NF; (b) TEM and (c-e) HRTEM images of CoFeP/NF.
8. Activity comparison

Table S2. OER activity comparison in alkaline solutions

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>$\eta$ at 10 mA cm$^2$ / mV</th>
<th>Tafel slope / mV dec$^{-1}$</th>
<th>References</th>
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<td>This work</td>
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<td>[3]</td>
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<td>Cu-CoP</td>
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<td>IrO$_2$</td>
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<td>79</td>
<td>[13]</td>
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9. DFT

The mechanism of adsorbate evolution mechanism of oxygen evolution reaction (OER) can be summarized in the following four steps:

\[ \ast + OH^- \rightarrow OH\ast + e^- \]
\[ OH\ast + OH^- \rightarrow O\ast + H_2O + e^- \]
\[ O\ast + OH^- \rightarrow OOH\ast + e^- \]
\[ OOH\ast + OH^- \rightarrow O_2 + H_2O + e^- \]

where the \( \ast \) represents the active site.

The change in the Gibbs free energy of each reaction (\( \Delta G_{1-4} \)) were calculated using the computational standard hydrogen electrode model as follows:

\[ \Delta G_1 = E(OH\ast) + \frac{1}{2}E(H_2) - E(\ast) - E(H_2O) + \Delta ZPE - T\Delta S - eU + k_B T \ln 10 \cdot pH \]

(S1)

\[ \Delta G_2 = E(O\ast) + \frac{1}{2}E(H_2) - E(OH\ast) + \Delta ZPE - T\Delta S - eU + k_B T \ln 10 \cdot pH \]

(S2)

\[ \Delta G_3 = E(0OH\ast) + \frac{1}{2}E(H_2) - E(H_2O) - E(O\ast) + \Delta ZPE - T\Delta S - eU + k_B T \ln 10 \cdot pH \]

(S3)

\[ \Delta G_4 = 4.92 - \Delta G_1 - \Delta G_2 - \Delta G_3 \]

(S4)

where \( E(\ast) \), \( E(OH\ast) \), \( E(O\ast) \), and \( E(OOH\ast) \) represented the total energy of the coordinate species adsorbed in the active sites which are calculated by DFT.

For the calculation of LOM mechanism, the first two steps are the same with AEM, with the following elementary steps are considered.

\[ O\ast + O_{lat} + OH^- \rightarrow O_2\ast + OH\ast + e^- \]
\[ OH\ast \rightarrow OH^- + e^- \]

For these steps, the \( \Delta G \) were calculated using the following equations:
\[ \Delta G_5 = E(H) + 4.92 + \frac{3}{2}E(H_2) + E(H_2O) - E(O) + \Delta ZPE - T\Delta S - eU + k_B T \ln 10 \cdot pH \]

\[ \Delta G_6 = E(O) + \frac{1}{2}E(H_2) - E(H) + \Delta ZPE - T\Delta S - eU + k_B T \ln 10 \cdot pH \tag{S5} \]

The \( \Delta ZPE \) and \( \Delta S \) were the change in the zero-point energy (ZPE) and the change in the entropy, respectively. The ZPE was calculated by the summation of all vibrational frequencies,

\[ \Delta ZPE = \sum \frac{\hbar \nu_i}{2} \]

where \( \nu_i \) corresponds to the vibration frequency of each normal mode. It should be noted that \( 1/2E(H_2) \) substituted the energy of \( H^+ + e^- \) under \( pH=0, p=1 \ atm, \) and \( T=298.15 \ K \) conditions.
Table S3. Equilibrium lattice parameters of Co₆P₃ and Co₅Fe₃P₃.

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<thead>
<tr>
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<th>Co₆P₃ (This work)</th>
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<th>Previous calculation data</th>
<th>Co₅FeP₃</th>
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<td>5.72ᵇ</td>
<td>5.744</td>
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<tr>
<td>c</td>
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<td>3.457ᵃ</td>
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</table>

ᵃTaken from ref. [19] ᵇTaken from ref. [20]
Figure S11. Comparison of OH adsorption at different sites of CoOOH@Co₂P, the OH adsorption energy is (a) 0 eV, (b) 0.15 eV, (c) 0.30 eV and (d) 0.38 eV, respectively.
Figure S12. Structural models of (a) CoOOH@Co$_2$P and (b) Co$_{1.67}$Fe$_{0.33}$OOH@Co$_{1.67}$Fe$_{0.33}$P.

Figure S13. Structural models of Co$_{2-x}$Fe$_x$OOH@Co$_{2-x}$Fe$_2$P.
Figure S14. (a) Gibbs free energy diagram of the OER at 0 and 1.23 V on the Co$_{1.67}$Fe$_{0.33}$OOH@Co$_{1.67}$Fe$_{0.33}$P surface and ModFe-Co$_{1.67}$Fe$_{0.33}$OOH@Co$_{1.67}$Fe$_{0.33}$P surface (another surface Co atom replaced by Fe in the Co$_{1.67}$Fe$_{0.33}$OOH@Co$_{1.67}$Fe$_{0.33}$P model (increased Fe surface content)); (b) Gibbs free energy diagram of the OER at 0 and 1.23 V at the Co sites and Fe sites of Co$_{1.67}$Fe$_{0.33}$OOH@Co$_{1.67}$Fe$_{0.33}$P surface.

Figure S15. (a) Scheme of the OER mechanism on the Co$_{1.67}$Fe$_{0.33}$OOH@Co$_{1.67}$Fe$_{0.33}$P surface; (b) Gibbs free energy diagram of the OER at 0 and 1.23 V on the Co$_{1.67}$Fe$_{0.33}$OOH@Co$_{1.67}$Fe$_{0.33}$P surface.
10. References


10(65): 39909-39915.


