Supplementary information

Laser-induced immobilization of amorphous iron-phosphate/Fe$_3$O$_4$ composite on nickel foam for efficient water oxidation

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Experimental section

S1. Chemicals and materials

Iron (III) nitrate nonahydrate (Fe(NO$_3$)$_3$·9H$_2$O, ≥98%), cobalt nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O), ammonium dihydrogen phosphate (NH$_4$H$_2$PO$_4$), and ethanol (EtOH) were purchased from Sinopharm Chemical Reagent Co. Ltd. Nickel nitrate hexahydrate (Ni(NO$_3$)$_2$·6H$_2$O) was purchased from Aladdin. Nickel foam was purchased from Kunshan Jiayisheng Electronics Co., Ltd.

S2. Physical characterizations

Surface morphology was observed using a Gemini SEM 300 field emission scanning electron microscope (FESEM) at an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were obtained by an FEI Tecnai G2 F30 S-Twin type electron microscope operating at 300 kV. Elemental analyses and energy dispersive X-ray (EDX) analyses were performed using an X-max Oxford detector at an accelerating voltage of 15 kV. X-ray photoelectron spectroscopy (XPS) was performed with Al Kα radiation on a scanning X-ray microprobe (Thermo Fisher Scientific Escalab Xi+). Powder X-ray diffractometer (XRD) data were collected with a Smart Lab/3kW using Cu Kα radiation.

S3. Synthesis of L-FePO on NF

30 mg of Fe(NO$_3$)$_3$·9H$_2$O, 40 mg of NH$_4$H$_2$PO$_4$, 0.5 mL of EtOH, and 0.5 mL of DI water were mixed and ultrasonicated for 1 h to prepare the FeHP precursor. 0.2 mL of the above suspension was coated on both sides of a NF substrate with a size of 1 × 2 cm$^2$. The coating area was 1 × 1 cm$^2$. After drying at 60 ℃ for 20 min, the FeHP precursor on NF was laser-irradiated using a laser machine (JL-K6040, Liaocheng Julong Laser Equipment Co., Ltd.) equipped with a focused 10.6 μm CO$_2$ laser. The laser speed and power were set to 10 mm s$^{-1}$ and 8 W, respectively. After the laser-induced irradiation treatment, the L-FePO composite immobilized on NF was successfully obtained. For comparison, the control samples of L-CoPO and L-NiPO on NF were prepared by laser-irradiating Co(NO$_3$)$_2$·6H$_2$O/NH$_4$H$_2$PO$_4$ and
Ni(NO$_3$)$_2$·6H$_2$O/NH$_4$H$_2$PO$_4$ mixture precursors, respectively.

**S4. Electrochemical measurements**

Electrochemical measurements were performed at room temperature using a three-electrode system on an electrochemical workstation (CHI Instruments 660E, China). The L-FePO composite on NF was directly used as a working electrode with a size of 1 × 2 cm$^2$ and a measurement area of 1 × 1 cm$^2$. A Hg/HgO electrode and a graphite rod were used as reference and counter electrodes, respectively. A 1.0 M KOH solution was used as an electrolyte. The OER performance was evaluated by linear scanning voltammetry (LSV) curves at a scan rate of 5 mV s$^{-1}$. Tafel plots were calculated from the corresponding LSV curves. Tafel slope was calculated as follows: $\eta = a + b \log j$, where $\eta$, $a$, $b$, and $j$ refer to overpotential, Tafel constant, Tafel slope, and current density, respectively. Chronopotentiometric (CP) curve was recorded for 100 h at a constant current density of 100 mA cm$^{-2}$. All the LSV and CP curves were used after 90% iR compensation. Cyclic voltammetry (CV) curves were acquired in a potential range of 0-1 V vs. Hg/HgO at different scan rates (10, 20, 40, 60, 80, and 100 mV s$^{-1}$) to evaluate the double layer capacitance ($C_{dl}$) values. Electrochemical impedance spectroscopy (EIS) was measured at an overpotential of 300 mV from 100000 to 0.01 Hz with an amplitude of 10 mV.
**Figure S1.** Photos of (a) NF, (b) FeHP precursor on NF, (c) L-FePO on NF, and (d) L-FePO on NF after the stability test for OER.

**Figure S2.** SEM images of the FeHP precursor loaded on NF prepared by the mixture of Fe(NO$_3$)$_3$·9H$_2$O and NH$_4$H$_2$PO$_4$. 
**Figure S3.** Low and high-magnification SEM images of L-MPO on NF: (a, b) L-CoPO, and (c, d) L-NiPO.

**Figure S4.** Elemental mapping images of corresponding elements of Ni, Fe, P, and O in L-FePO on NF.
Figure S5. EDX spectra of (a) L-CoPO and (b) L-NiPO.

Figure S6. Full XPS spectrum of L-FePO on NF.
Figure S7. (a) LSV curve and (b) Tafel plot of the commercial IrO$_2$ catalyst for OER in an alkaline medium.

Figure S8. LSV curves of L-FePO, the FeHP precursor prepared using Fe(NO$_3$)$_3$/NH$_4$H$_2$PO$_4$ mixture, and L-iron oxide prepared by the direct laser-induced treatment of Fe(NO$_3$)$_3$ coated on NF.
Figure S9. (a) LSV curve and (b) Tafel plot L-FePO on NF measured in 1.0 M PBS.

Figure S10. EIS spectra of L-FePO, L-CoPO, and L-NiPO on NF.
Figure S11. CV curves of (a) L-FePO, (b) L-CoPO, and (c) L-NiPO on NF measured in a non-faradic region of 0-0.1 V vs. Hg/HgO at different scan rates (10-100 mV s\(^{-1}\)).

Figure S12. \(C_{dl}\) plots of L-FePO, L-CoPO, and L-NiPO on NF.
Figure S13. XRD patterns of L-MPO on NF after the stability test for OER

Figure S14. (a, b) SEM, (c) TEM, and (d) HRTEM images of L-FePO after the stability test for OER.
Figure S15. EDX spectra of L-FePO on NF after the stability test for OER in 1.0 M KOH.

Figure S16. Elemental mapping images of L-FePO on NF after the stability test for OER.
Figure S17. High-resolution XPS spectra of (a) Fe 2p, (b) Ni 2p, (c) O 1s, and (d) P 2p.

Figure S18. LSV curve of L-FePO laser-irradiated on Cu foam for OER in 1 M KOH.

The L-FePO composite laser-irradiated on the Cu foam (CF) substrate was applied to investigate the influence of Ni-doping originating from the NF support. The LSV curves show that the $\eta_{100}$ value of L-FePO on CF was 408 mV, which was higher than that of L-FePO on NF, suggesting its poor OER activity. Therefore, the Ni sources doped into L-FePO and the conductive NF support could enhance the electrocatalytic activity to some extent.
### Table S1. OER comparison of L-MPO on NF and recently reported phosphate- and oxide-based electrocatalysts.

<table>
<thead>
<tr>
<th>Electrocatalyst</th>
<th>Support</th>
<th>Electrolyte</th>
<th>Overpotential</th>
<th>Tafel slope (mV dec(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-FePO</td>
<td>Ni foam</td>
<td>1 M KOH</td>
<td>256 mV @ 100 mA cm(^{-2})</td>
<td>71</td>
<td>This work</td>
</tr>
<tr>
<td>P-CoPc@CNT</td>
<td>GCE(^a)</td>
<td>1 M KOH</td>
<td>300 mV @ 10 mA cm(^{-2})</td>
<td>41.7</td>
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<tr>
<td>2D-CoHPi</td>
<td>GCE</td>
<td>1 M KOH</td>
<td>314 mV @ 10 mA cm(^{-2})</td>
<td>31</td>
<td>2</td>
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<tr>
<td>NiCo-LDH/NiCoPi</td>
<td>Ni foam</td>
<td>1 M KOH</td>
<td>300 mV @ 100 mA cm(^{-2})</td>
<td>73</td>
<td>3</td>
</tr>
<tr>
<td>CoFeNiMnMoPi(H EPi)</td>
<td>GCE</td>
<td>1 M KOH</td>
<td>270 mV @ 10 mA cm(^{-2})</td>
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<td>4</td>
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<tr>
<td>Fe(<em>x)Ni(</em>{2-x})P(<em>4)O(</em>{12})/RGO</td>
<td>GCE</td>
<td>1 M KOH</td>
<td>270 mV @ 10 mA cm(^{-2})</td>
<td>43.8</td>
<td>5</td>
</tr>
<tr>
<td>N-NiMoO(_4)/Ni/CNTs</td>
<td>GCE</td>
<td>1 M KOH</td>
<td>330 mV @ 10 mA cm(^{-2})</td>
<td>89.5</td>
<td>6</td>
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<tr>
<td>Fe–Co–O/Co@NC- mNS/NF</td>
<td>Ni foam</td>
<td>1 M KOH</td>
<td>257 mV @ 10 mA cm(^{-2})</td>
<td>41.56</td>
<td>7</td>
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<tr>
<td>Co, S-Fe(_3)O(_4)/IF</td>
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<td>1 M KOH</td>
<td>356 mV @ 10 mA cm(^{-2})</td>
<td>50.9</td>
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<tr>
<td>Co(_2)O(_4) nanomeshes</td>
<td>GCE</td>
<td>1 M KOH</td>
<td>307 mV @ 10 mA cm(^{-2})</td>
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<tr>
<td>NiO(_x)-NiSe(_2)</td>
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<td>1 M KOH</td>
<td>266 mV @ 10 mA cm(^{-2})</td>
<td>53.4</td>
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</table>

Note: a) GCE denotes glassy carbon electrode.

### Reference