Electronic Supplementary Information

Robust and Superwetting Island-shaped Phytate Bimetallic Oxyhydroxide Porous Nanoclusters via a Mild Self-assembly—Etching-catching—Electrochemical Oxidization Strategy for Enhanced Oxygen Evolution Reaction

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Experimental Section

Materials

Ni foam (NF) was purchased from Latech Scientific Supply Pte. Ltd. Phytic acid (PA), FeCl$_3$.6H$_2$O, KOH, H$_2$SO$_4$(95-98wt%) and ethyl alcohol were bought from Sigma-Aldrich Chemical Reagent Co.

Preparation of PBMC and PBMO

PBMC was prepared as follows. In a typical synthesis, in order to remove the oil, a piece of NF was immersed in ethyl alcohol at room temperature for 2 min. Then NF was dipped into 5 volume% H$_2$SO$_4$ for 2 min at room temperature to remove the oxide of NF surface. Then NF was immersed into 5g/L phytic acid (PA) solution for 1 h at room temperature. Finally, NF was immersed into 50g/L FeCl$_3$.6H$_2$O solution for 1 h at room temperature. It is noting that NF will be cleaned by deionized water for several times among the above two processes. To obtain PBMO by electrochemical oxidation process, such PBMC was electrochemical oxidized with a scan rate of 5 mV/s at the region from +0 to +0.8 V versus Hg/HgO in 1.0 M KOH electrolyte.

Some reaction equations during the fabrication process are shown in scheme S1.

Characterizations

The morphology of samples was observed by ZEISS SEM Supra 40. Transmission electron microscopy (TEM) of samples was carried out on a JEOL-3010 (300 kV acceleration voltage). XRD patterns were measured by Bruker D8 Advanced
Diffractometer System. The element analysis of samples was determined by X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra DLD). The Fourier transform infrared (FT-IR) spectra and Raman spectra were conducted on a Varian 3100 Excalibur Series FT-IR Spectrophotometer and a Horiba MicroRaman HR Evolution System, respectively.

**Electrochemical measurements**

OER were studied in a typical three-electrode cell connected to a Bio-logic VMP 3 using the PBMO/NF as the working electrode(1×1cm²), Pt as a counter electrode and Hg/HgO as a reference electrode. All the measured potentials were converted to reversible hydrogen electrodes (RHE) according to $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.059\ pH + 0.098\ V$. LSV curves were carried out with the scan rates of 1mV/s. Tafel slopes of the experiments were all derived from LSV curves. EIS was measured under the following conditions: frequency ranges 200 kHz to 100 mHz. All the electrochemical datas were presented with 100% iR compensation.
(1) Self-assembly process

I chelation reaction

\[ \text{Ni} + \text{PA} \rightarrow \text{Ni}^{2+}-\text{Phytate} + \text{H}_2 \]

II absorption reaction

\[ \text{Ni}^{2+}-\text{Phytate} + \text{PA} \rightarrow \text{Ni}^{2+}-\text{Phytate-PA} \]

(2) Etching-Catching process

I etching reaction

\[ \text{Ni} + 2\text{Fe}^{3+} \rightarrow \text{Ni}^{2+} + 2\text{Fe}^{2+} \]

II catching reaction

\[ \text{Ni}^{2+}-\text{Phytate-PA} + \text{Ni}^{2+} + \text{Fe}^{3+} + \text{Fe}^{2+} \rightarrow \text{Ni}^{2+} - \text{Fe}^{3+} - \text{Fe}^{2+} - \text{Phytate} \]

III absorption reaction

\[ \text{Ni}^{2+} - \text{Fe}^{3+} - \text{Fe}^{2+} - \text{Phytate} + \text{pCl} \rightarrow \text{Ni}^{2+} - \text{Fe}^{3+} - \text{Fe}^{2+} - \text{Phytate-Cl}_p \]

PBMC

(3) Electrochemical Oxidization process

electrochemical oxidation reaction

\[ \text{Ni}^{2+} - \text{Fe}^{3+} - \text{Fe}^{2+} - \text{Phytate-Cl}_p + \text{mKOH-ne}^- \rightarrow \text{NiO(OH)-FeO}_x\text{(OH)}_y - \text{Phytate-K}_m\text{Cl}_p \]

PBMO

Note:

\( \text{NiO(OH)-FeO}_x\text{(OH)}_y - \text{Phytate-K}_m\text{Cl}_p \) can also be marked as \( \text{NiO(OH)K}_x\text{Cl}_y - \text{FeO}_x\text{(OH)}_y\text{K}_x\text{Cl}_y - \text{Phytate} \)

Scheme S1 Some reaction equations during the fabrication process
Supplementary Explanation

The explanation of redox reaction of Ni and Fe$^{3+}$

\[
\text{Ni}^{2+} + 2e^- \rightleftharpoons \text{Ni(s)} \quad \varepsilon_{\text{Θ}} = -0.25 \text{V} \quad (1)
\]

\[
\text{Fe}^{3+} + e^- \rightleftharpoons \text{Fe}^{2+} \quad \varepsilon_{\text{Θ}} = 0.77 \text{V} \quad (2)
\]

\[
\Delta G_{\text{Θ}} = -nFE_{\Theta} \quad (3)
\]

\[
\Delta E_{\Theta} = 2 \times 0.77 - (-0.25) = 1.79 > 0.2 \text{V} \quad (4)
\]

\[\Delta E_{\Theta} > 0 \text{ so } \Delta G_{\Theta} < 0\]

According to Rule of experience, when $\Delta E_{\Theta} > 0.2 \text{V}$, Redox reaction can be carried out automatically.

So Ni can react with Fe$^{3+}$ according to the below equation:

\[
\text{Ni} + 2\text{Fe}^{3+} \rightarrow \text{Ni}^{2+} + 2\text{Fe}^{2+} \quad (5)
\]
Figure S1 the digital photos of PBMC(a) and PBMO(b)
Figure S2 EDS test image and test results after self-assembly process
Figure S3 The spectroscopic characterization of nickel foam after self-assembly process (a) FTIR spectra of nickel foam after self-assembly process (b) Raman spectra of nickel foam after self-assembly process (c) XPS spectra of nickel foam after self-assembly process
Figure S4 (a) The XPS spectrum of O element of PBMC (b) The XPS spectrum of O element of PBMO
**Figure S5** The dynamic hydrophilicity and aerophobicity property of as-prepared materials. (a) the water droplet wetting process observation of PBMC. (c) the water droplet wetting process observation of PBMO. (c) the air bubble wetting process observation underwater of PBMC (d) the air bubble wetting process observation underwater of PBMO.

Note: The contact angle instrument use stainless steel as needle and the alkali droplet can not be dropped smoothly owing to “Alkali climbing” phenomenon. Herein, the dynamic wetting process of as-prepared materials in alkali solution (1M KOH) can not be observed. The contact angle data of the alkali droplet (1M KOH) wetting property of different materials were obtained by using manual plastic needle.
Figure S6 The influence of different etching-catching time on the morphology of PBMC (a) 0.5h (b) 1h (c) 1.5h (d) 2h (e) 2.5h
Figure S7 The LSV performance of PBMO under different counter electrode.
Figure S8 EIS(a) and Bode curves(b) of PBMO at 1.48V vs RHE.
Figure S9 FTIR of PBMO and PBMO after OER stability test.
Figure S10 SEM image(a) and magnification SEM image(b) of PBMO after OER stability test
Scheme S2 can interpret the formation process of island-shaped PBMC template

Scheme S2 can interpret the formation process of PBMC. When Ni foam after self-assembly was immersed into FeCl₃ solution, PA molecular in absorption outside layer can chelate Fe³⁺ during etching I period. With the extension of time, the redox corrosion reaction generates more and more metal ion and abundant metal ion is chelated by PA molecular, and the PA layer turns to the complete chelation layer. At the same time, some Cl⁻ penetrate into the gap with PA-metal complex molecular(etching II period). With prolonging the time, more and more pitting corrosion even stress
corrosion crack phenomenon appears. Moreover, Cl\textsuperscript{-} can absorb inside of PBMC by absorption effect. Finally, PBMC template with enriched nanopores and microcrack diffusion tunnels is formed on Ni foam.

\[ \text{Scheme S3} \]

\[ \text{the formation process of PBMO during anodization process.} \]

Scheme S3 can describe the formation process of PBMO. Firstly, the metal site of PBMC is electrochemically oxidized to nanosphere phytate-metal oxyhydroxide. Secondly, K\textsuperscript{+} can be doped into PBMO by electrochemical and chemical oxidation corrosion reaction. At last, PBMO in situ grows on Ni foam.
**Table S1.** ICP test of electrolyte before and after OER stability test (10mA/cm², 10h)

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Ni/ppm</th>
<th>Fe/ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before OER stability test</td>
<td>ND</td>
<td>0.02</td>
</tr>
<tr>
<td>After OER stability test</td>
<td>ND</td>
<td>&lt;0.01</td>
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</table>

Note: ND means “Not Detected”.
Supplementary METHODS

Calculation of $ECAS$ (electrochemically active surface area)

The electrochemical double-layer capacitance $C_{dl}$ is calculated as the below equation:

$$C_{dl} = J_c \div \nu$$  \hspace{1cm} (1)

The charge current $J_c$ was measured from CV curves where no apparent Faradaic process happened. $\nu$ is the scan rate as shown in Fig 4j.

As shown in Fig 4k, the electrochemical double-layer capacitance $C_{dl}$ value of PBMO is 9.54 mF.

The electrochemically active surface area $ECAS$ is calculated as the below equation according to the previous reports:

$$ECAS = C_{dl} \div C_s$$  \hspace{1cm} (2)

The specific capacitance value of the sample $C_s$ is 0.040 mF/cm$^2$ according to the literatures, so the $ECAS$ of PBMO/NF electrode is 238.5 cm$^2$.

Calculation of $RF$ (roughness factor)

The roughness factor $RF$ of as-prepared PBMO/NF electrode is 238.5 as determined by the below equation 3:

$$RF = ECAS \div GSA$$  \hspace{1cm} (3)

The geometric surface area (GSA) of the PBMO/NF electrode is 1 cm$^2$.

Table S2. Summary of the electrocatalytic OER activity of the previously reported NiFe-based catalysts in 1M KOH electrolyte
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$j$ [mA/cm$^2$]</th>
<th>Overpotential [mV] @ $j$</th>
<th>Tafel slope (mV/dec)</th>
<th>Substrate</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBMO</td>
<td>10</td>
<td>243</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>256</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Ni-MOF@Fe-MOF</td>
<td>10</td>
<td>265</td>
<td>82</td>
<td>GCE</td>
<td>Adv. Funct. Mater., 2018, 1801554</td>
</tr>
<tr>
<td>Fe-Ni@NC-CNTs</td>
<td>10</td>
<td>274</td>
<td>45.47</td>
<td>GCE</td>
<td>Angew. Chem. Int. Ed., 2018, 57, 8921</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>322</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni$<em>{0.75}$Fe$</em>{0.25}$Se$_2$ hollow nanochains</td>
<td>10</td>
<td>267</td>
<td>67</td>
<td>GCE</td>
<td>Nano Energy, 2018, 47, 275.</td>
</tr>
<tr>
<td>FeNi-LDH/Ti$_3$C$_2$-MXene</td>
<td>20</td>
<td>258</td>
<td>48</td>
<td>NF</td>
<td>Nano Energy, 2018, 44, 181.</td>
</tr>
<tr>
<td>Ni$<em>{1.3}$Fe$</em>{1.3}$ LDH nanosheets</td>
<td>10</td>
<td>310</td>
<td>76</td>
<td>GCE</td>
<td>ACS Nano, 2015, 9, 1977.</td>
</tr>
<tr>
<td>Ni$<em>{1.3}$Fe$</em>{0.5}$P</td>
<td>10</td>
<td>264</td>
<td>55</td>
<td>GCE</td>
<td>Nano Energy, 2017, 34, 472.</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>280</td>
<td>55</td>
<td>GCE</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>293</td>
<td>114</td>
<td>CF</td>
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</tr>
</tbody>
</table>
Table S3. Summary of the electrocatalytic OER activity of as-reported organic metal-based and organic metal-derived catalysts in 1M KOH electrolyte

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$j$ [mA/cm$^2$]</th>
<th>Overpotential [mV @ $j$]</th>
<th>Tafel slope (mV/dec)</th>
<th>Substrate</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBMO</td>
<td>10</td>
<td>243</td>
<td>100</td>
<td>290</td>
<td>44 NF</td>
</tr>
<tr>
<td>Ni-MOF@Fe-MOF</td>
<td>10</td>
<td>265</td>
<td>82</td>
<td>GCE</td>
<td>Adv. Funct. Mater., 2018, 1801554</td>
</tr>
<tr>
<td>MAF-X27-OH/Cu foil</td>
<td>10</td>
<td>338</td>
<td>82</td>
<td>Cu Foil</td>
<td></td>
</tr>
<tr>
<td>P-doped-Co@NC-3/1</td>
<td>10</td>
<td>340</td>
<td>85</td>
<td>GCE</td>
<td>Adv. Energy Mater., 2018, 8, 1702048</td>
</tr>
<tr>
<td>NiCo@NiCoO$_2$/C PMRAs</td>
<td>20</td>
<td>366</td>
<td>83.97</td>
<td>carbon fabric</td>
<td>Adv. Mater., 2018, 30, 1705442</td>
</tr>
<tr>
<td>Co3Ni3(bdc)4(OH)4</td>
<td>10</td>
<td>189</td>
<td>-</td>
<td>CF</td>
<td>Nat Energy, 2016, 1, 16184</td>
</tr>
<tr>
<td>Hierarchically structured Co3O4@CoP</td>
<td>10</td>
<td>238</td>
<td>51.4</td>
<td>Ni foil</td>
<td>Adv. Energy Mater., 2017, 7, 1602643</td>
</tr>
<tr>
<td>Fe-Ni@NC-CNTs</td>
<td>10</td>
<td>274</td>
<td>45.47</td>
<td>GCE</td>
<td>Angew. Chem. Int. Ed., 2018, 57, 8921</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>322</td>
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</tr>
</tbody>
</table>

GCE: glassy carbon electrode,
NF: nickel foam
CF: copper foam
Au-RDE: Au rotating disk electrode,
HOPG: highly-ordered pyrolytic graphite,
SS: stainless steel

REFERENCES


