Supporting Information

Molybdenum-Iron-Cobalt Oxyhydroxide with Rich Oxygen Vacancies for Oxygen Evolution Reaction

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Experimental Section

All materials were of analytical grade and used without further purification.

Synthesis of MoOxCo(OH)_{2-x}

In a typical synthesis, 2 mmol of Na_{2}MoO_{4}·2H_{2}O and 4 mmol of glucose were dissolved into 50 mL of DI water. The mixture was treated with an intense ultrasonication for a few minutes and then transferred to a 1000 mL Teflon stainless steel autoclave. Afterwards, Co(OH)_{2} nanowires supported was immersed in the reaction solution. The autoclave was sealed and maintained at 150 °C for 6 h and then cooled to room temperature.

Structure Characterizations

A field emission scanning electron microscopy (FESEM; ZEISS-Merlin), a transmission electron microscopy (TEM, JEOL-2010) with energy dispersive X-ray spectroscopy (EDX), and a high-resolution TEM (HRTEM, JEOL-2010) were used to characterize the morphology and composition of samples. (XRD) curves of samples were recorded on Rigaku at 40 kV and 40 mA, and X-ray photoelectron spectroscopy (XPS) curves are obtained on a PHI Quantera SXM (ULVAC-PHI) instrument to determine the compositions and the valence states of the elements in the samples.

Electrochemical measurements.

All electrochemical measurements were performed on a CHI 760E electrochemical work station with a typical three-electrode setting at room temperature. A graphite rod and a Hg/HgO electrode were selected as a counter and reference electrode, respectively. The self-supporting array grown on carbon cloth (1×1 cm, mass loading ~ 2.5 mg/cm²) was directly used as a working electrode. The electrochemical data were collected in an electrolyte of 1.0 M KOH. The measured potentials via the Hg/HgO electrode were converted to those based on a reversible hydrogen electrode (RHE) by the Nernst equation: E(RHE) = E(Hg/HgO) + 0.0591*pH + 0.098. The overpotential (η) was calculated according to the following equation: η = E(RHE)-1.23 V. Linear sweep voltammetry curves for OER were established at a scanning rate of 5 mV/s before 50 cycles of the cyclic voltammetry tests at a scan rate
of 50 mV/s were conducted to obtain stable curves. The Tafel slopes were obtained from the polarization curves by the equation, $\eta = a + b \log (i)$. The chronoamperometry was operated to evaluate the stability under different current densities. Electrochemical impedance spectroscopy (EIS) measurements were performed over a frequency range of 0.1-10^6 Hz by applying an AC amplitude of 50 mV. All data presented were within 90% iR-correction.
Figure S1. (a) XRD patterns of different electrocatalysts.
Figure S2. (a) Raman spectra of MoO₃Co(OH)₂₋ₓ, MoFe₀.₅OₓCo(OH)₂₋ₓ, and Co(OH)₂ electrocatalysts.
Figure S3. (a, b) SEM images of Co(OH)$_2$.

Figure S4. Images of Fourier transform corresponding to Fig 2a and 2c that reveal the lattice spacing of MoFe$_{0.5}$O$_x$Co(OH)$_{2-x}$.

Figure S5. (a, b) SEM images of MoFe$_{0.5}$O$_x$Co(OH)$_{2-x}$.
Figure S6. TEM images of (a) Co(OH)$_2$, (b) MoFeO$_x$Co(OH)$_{2-x}$, (c) MoFeO$_{0.5}$Co(OH)$_{2-x}$.

Figure S7. EPR spectra of MoFeO$_x$Co(OH)$_{2-x}$, MoFeO$_{0.25}$Co(OH)$_{2-x}$, and MoFeO$_{0.5}$Co(OH)$_{2-x}$.

Figure S8. O1s XPS of comparative (a) MoO$_x$Co(OH)$_{2-x}$ and (b) Co(OH)$_2$. 
Figure S9. (a) CV curves of (a) Co(OH)$_2$, (b) MoO$_x$Co(OH)$_{2-x}$, (c) MoFe$_{0.25}$O$_x$Co(OH)$_{2-x}$, (d) MoFe$_{0.5}$O$_x$Co(OH)$_{2-x}$, (e) MoFeO$_x$Co(OH)$_{2-x}$ electrocatalysts at scan rates from 10 to 50 mV s$^{-1}$.

Figure S10. Long-term durability test of Co(OH)$_2$ and MoO$_x$Co(OH)$_{2-x}$ at different potentials for OER.
Figure S11. (a) SEM image and (b) TEM image of MoFe<sub>0.5</sub>O<sub>x</sub>Co(OH)<sub>2</sub>-x after the stability test.

Figure S12. XRD pattern of MoFe<sub>0.5</sub>O<sub>x</sub>Co(OH)<sub>2</sub>-x before and after the stability test.
Table S1. The metallic composition of MoO$_x$Co(OH)$_{2-x}$, MoFe$_{0.5}$O$_x$Co(OH)$_{2-x}$, MoFe$_{0.25}$O$_x$Co(OH)$_{2-x}$, and MoFeO$_x$Co(OH)$_{2-x}$, catalyst by ICP-MS. Regardless of oxygen in this characterization.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Co (at.%)</th>
<th>Mo (at.%)</th>
<th>Fe (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoO$<em>x$Co(OH)$</em>{2-x}$</td>
<td>90.13</td>
<td>9.87</td>
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<tr>
<td>MoFe$_{0.25}$O$<em>x$Co(OH)$</em>{2-x}$</td>
<td>88.46</td>
<td>9.01</td>
<td>2.53</td>
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<td>MoFe$_{0.5}$O$<em>x$Co(OH)$</em>{2-x}$</td>
<td>86.97</td>
<td>7.51</td>
<td>5.52</td>
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<tr>
<td>MoFeO$<em>x$Co(OH)$</em>{2-x}$</td>
<td>83.61</td>
<td>6.21</td>
<td>10.18</td>
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**Table S2.** Comparison of the OER activities of the MoFe_{0.5}O_{x}Co(OH)_{2-x} sample in this work with recently-reported catalysts.

<table>
<thead>
<tr>
<th>catalysts</th>
<th>Overpotential (mV)</th>
<th>j /(mA cm^{-2})</th>
<th>Tafel slope (mV dec^{-1})</th>
<th>Reference</th>
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<tbody>
<tr>
<td>MoFe_{0.5}O_{x}Co(OH)_{2-x}</td>
<td>223</td>
<td>10</td>
<td>43.6</td>
<td>This work</td>
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<tr>
<td>CoFeV-LDH</td>
<td>242</td>
<td>10</td>
<td>57</td>
<td>S1</td>
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<td>CoMoV-LDH</td>
<td>270</td>
<td>10</td>
<td>106</td>
<td>S2</td>
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<tr>
<td>CoMo hydr(oxy)oxide</td>
<td>377</td>
<td>10</td>
<td>41.88</td>
<td>S3</td>
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<tr>
<td>CoFe-LDH</td>
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<td>10</td>
<td>53</td>
<td>S4</td>
</tr>
<tr>
<td>Fe_{x}Co_{1-x}OOH</td>
<td>266</td>
<td>10</td>
<td>30.0</td>
<td>S5</td>
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<td>Ir-doped NiV(OH)_{2}</td>
<td>260</td>
<td>10</td>
<td>55.3</td>
<td>S6</td>
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<tr>
<td>NiCo_{16-x}P_{6}</td>
<td>290</td>
<td>10</td>
<td>66</td>
<td>S7</td>
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<tr>
<td>CoP-CeO_{2}</td>
<td>224</td>
<td>10</td>
<td>90.3</td>
<td>S8</td>
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<tr>
<td>Pt-Cu@Cu_{x}O</td>
<td>250</td>
<td>10</td>
<td>56</td>
<td>S9</td>
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<td>NiCoMo</td>
<td>304</td>
<td>10</td>
<td>56.4</td>
<td>S10</td>
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References: