Coupling FeSe\textsubscript{2} with CoSe: an effective strategy to create stable and efficient electrocatalyst for water oxidation

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Experimental section

Chemicals

Ni foam (NF) with a thickness of 1.6 mm and a pore density of 110 ppi was purchased from Changsha Keliyuan. Cobalt (II) chloride hexahydrate (CoCl\textsubscript{2}·6H\textsubscript{2}O), ferric (III) chloride hexahydrate (FeCl\textsubscript{3}·6H\textsubscript{2}O), Se powders, sodium borohydride (NaBH\textsubscript{4}) were purchased from Alfa Aesar. Potassium hydroxide (KOH), hydrochloric acid (HCl), acetone and ethanol were all analytic grade (AR) and purchased from Sinopharm Chemical Reagent. All these chemical reagents were used as received without any further purification. Iridium oxide (IrO\textsubscript{2}), ethanol (99.9\%) and Nafion (5\% in a mixture of lower aliphatic alcohols and water) were purchased from Alfa Aesar.

Synthesis of CoSe/FeSe\textsubscript{2} hybrids

In a typical procedure, Se powders (0.158 g, 2 mmol) were added into deionized water (30 mL) containing NaBH\textsubscript{4} (0.152 g). After ultrasonic dissolution for 10
minutes, a clear NaHSe solution was obtained. Then, 0.2 mmol FeCl$_3$·6H$_2$O and 0.6 mmol CoCl$_2$·6H$_2$O were added to the above solution with continuous stirring for 20 min. Thereafter, the resulting solution was transferred into a Teflon-lined stainless-steel autoclave, which was subsequently heated at 200 °C for 18 h. After cooling to room temperature, the black powders were collected and washed with distilled water and absolute ethanol for several times and dried at 60 °C.

Other Co$_x$Fe$_{1-x}$-Se (x = 0.93, 0.85, 0.69, 0.51) catalysts were prepared using the similar method except that the feeding ratio of metal precursors was varied and the total amount of metal precursors (Co + Fe) was kept constant at 0.8 mmol. Specifically, the feeding ratio of Co/Fe was 11:1 for Co$_{0.93}$Fe$_{0.07}$-Se, 5:1 for Co$_{0.82}$Fe$_{0.15}$-Se, 2:1 for Co$_{0.69}$Fe$_{0.31}$-Se and 1:1 for Co$_{0.51}$Fe$_{0.49}$-Se. The final ratio of metals in Co$_x$Fe$_{1-x}$-Se was determined by the average results of inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis, which were similar with the feeding ratio. The preparing process of CoSe and FeSe$_2$ was the same as that of Co$_x$Fe$_{1-x}$-Se in the absence of FeCl$_3$ or CoCl$_2$.

**Material Characterization**

Powder X-ray diffraction (XRD) patterns of all the samples were obtained by a Rigaku D/M ax-2400 at a scanning rate of 10° min$^{-1}$ over a 2θ range of 20-80°. Transmission electron microscopy (TEM) and energy-dispersive X-ray (EDX) characterization were performed on a Tecnai™ G2 F30 transmission electron microscope equipped with an EDX detector at an acceleration voltage of 200 kV. X-ray photoelectron spectrocope (XPS) data were collected through a VGESCALAB
MKII X-ray photo-electron spectrometer with a Mg-Kα excitation source (1253.6 eV). The molar ratio of Co/Fe in CoSe/FeSe₂ composites was measured by the PQ 9000 inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

**Electrode preparation and electrochemical measurements**

All electrochemical measurements were conducted using a computer-controlled Autolab PGSTAT302N under room temperature. Platinum plate and Hg/HgO electrode were used as counter and reference electrodes, respectively. Typically, the initial 4.0 mg catalysts and 30 μL Nafion solution (5 wt%) were dispersed into 1 mL water-ethanol solution with volume ratio of 1:1 by sonicating for at least 0.5 h to form a homogeneous ink. Then, dropwise, the above dispersion was loaded onto the surface of NF (1 × 1 cm²). Finally, the electrode was dried for 10 h under ambient condition. After weighing and calculating by differential method, the final loading mass of the catalysts was 2.9 mg. For comparison, the electrocatalytic activity of benchmark IrO₂ was also investigated under the same condition.

Linear sweep voltammetry (LSV) was carried out at a scan rate of 5 mV s⁻¹ in 1.0 M KOH. All the polarization curves have been iR-corrected. Unless otherwise stated, the potentials reported in our work were converted to the reversible hydrogen electrode (RHE), where in 1 M KOH, \( E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.924 \text{ V} \). The overpotential (\( \eta \)) of OER at 10 mA cm⁻² was calculated according to the equation: \( \eta_{10} = E_{\text{RHE}} - 1.23 \), considering \( O_2/H_2O \) equilibrium at 1.23 V. The Tafel slope was obtained according to the Tafel equation. Electrochemical impedance spectra (EIS) were collected over a frequency range of 100 kHz to 10 mHz at a direct-current bias.
potential of 1.51 V at room temperature. The electrochemical active surface areas were estimated from the double-layer charging curves using cyclic voltammograms (CVs) at different scan rates of 100-200 mV s\(^{-1}\) in a non-Faradaic region (0.924-0.974 V vs. RHE). The stability was tested by means of chronopotentiometry (CP) measurement under a constant current density of 10 mA cm\(^{-2}\) and chronoamperometry (CA) measurement at a constant potential of 1.51 V. The durability test was performed by cycling the electrode potential (1.20-1.60 vs. RHE) at 200 mV s\(^{-1}\) for 1000 cycles.

The turnover frequency (TOF) value is calculated according to the following equation:

\[
\text{TOF} = \frac{(J \times A)}{(4 \times F \times n)}
\]

where \(J\) is the current density at a given overpotential, \(A\) is the geometric area of the electrode (1 cm\(^2\)), 4 represents 4 electrons/mol of O\(_2\), \(F\) is the Faraday constant (96485.3 C mol\(^{-1}\)), and \(n\) is the mole number of metal ions in the as-prepared samples. In this work, all metal ions in Co\(_x\)Fe\(_{1-x}\)-Se were assumed to be catalytically active no matter whether they are accessible to the electrolyte or not. Therefore, the calculated TOF value represents the lowest limit (J. Am. Chem. Soc., 2014, 136, 15670-15675). For example, at \(\eta = 300\) mV, the Co\(_{0.75}\)Fe\(_{0.25}\)-Se electrode generates a current density of 141.4 mA cm\(^{-2}\). The TOF of Co\(_{0.75}\)Fe\(_{0.25}\)-Se electrodes at \(\eta = 300\) mV can be calculated as follows:

\[
\text{TOF} = \frac{(0.1414 \text{ A cm}^{-2} \times 1 \text{ cm}^{-2})}{(4 \times 96485.3 \text{ C mol}^{-1} \times 2.9 \times 10^{-3} \text{ g} \div 137.89 \text{ g mol}^{-1})} = 1.7 \times 10^{-2} \text{ s}^{-1}
\]
For the rotating ring-disk electrode (RRDE) measurements, the as-synthesized \( \text{Co}_{0.75}\text{Fe}_{0.25}\text{-Se} \) hybrids were coated onto RRDE with Nafion as the binder, which consists of a glassy carbon disk electrode and a Pt ring electrode. A scan rate of 5 mV s\(^{-1}\) and a rotation rate of 1500 rpm were applied for RRDE test. Firstly, in order to determine electron transfer number \((N)\) for OER by detecting the \( \text{HO}_2^- \) formation, the ring potential was constantly held at 1.50 V versus RHE in \( \text{O}_2 \)-saturated 1 M KOH solution. On the other hand, the Faradaic efficiency \((\text{FE})\) was determined by collecting the ring current when fixing the disk current at 100 \( \mu \text{A} \) and ring potential at 0.4 V versus RHE in \( \text{N}_2 \)-saturated 1 M KOH solution. The FE was calculated as follows:

\[
\text{FE} = \frac{I_{\text{ring}}}{(C_e \times I_{\text{disk}})}
\]

Where \( I_d \) is the disk current, \( I_r \) is the ring current, and \( C_e \) is the current collection efficiency (0.21 in this study), which was determined using the same configuration with an \( \text{IrO}_2 \) thin-film electrode. The electron transfer number \((N)\) can be calculated from the disk current \((I_d)\) and ring current \((I_r)\) of RRDE.

\[
N = 4 \times \frac{I_d}{(I_d + I_r)} \times \frac{1}{C_e}
\]

The OER mechanism under alkaline conditions \((\text{Chem. Soc. Rev., 2017, 46, 337-365})\)

\[
\text{M} + \text{OH}^- \rightarrow \text{M-OH} + \text{e}^- \quad (1)
\]

\[
\text{M-OH} + \text{OH}^- \rightarrow \text{M-O} + \text{H}_2\text{O}(\text{g}) + \text{e}^- \quad (2)
\]

\[
\text{M-O} + \text{OH}^- \rightarrow \text{M-OOH} + \text{e}^- \quad (3)
\]

\[
\text{M-OOH} + \text{OH}^- \rightarrow \text{M} + \text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) + \text{e}^- \quad (4)
\]
M is the catalytic active site. Under alkaline conditions, OER starts with the adsorption and discharge of OH\(^-\) anion on the surface of catalysts to form adsorbed OH species, followed by the reaction of OH\(^-\) with the adsorbed OH species to produce H\(_2\)O and adsorbed atomic O. The next step involves the reaction of OH\(^-\) with the adsorbed atomic O to form adsorbed OOH species, which then react with additional OH\(^-\) to form adsorbed O\(_2\) and H\(_2\)O. At last, the adsorbed O\(_2\) desorbs from the catalyst surface (eqn (1)-(4)). Generally, the forming reaction of adsorbed OOH species is identified as the rate-limiting step in OER (J. Am. Chem. Soc., 2011, 133, 5587). The OER activities of transition metal-based materials can be enhanced by modulating their electronic structure due to the significant effect of the interaction of adsorbed OOH species and 3d orbital of transition metal. (J. Am. Chem. Soc., 2017, 139, 8320. Nat. Commun., 2013, 4, 2439.)

**Fig. S1** Schematic illustration of CoSe/FeSe\(_2\) hybrids for preparation (a) and its application in OER (b).
**Fig. S2** (a) TEM images of CoSe. (b) HRTEM image of CoSe.

**Fig. S3** (a) TEM image of FeSe$_2$. (b) HRTEM image of FeSe$_2$.

**Fig. S4** EDX spectrum of Co$_{0.75}$Fe$_{0.25}$-Se hybrid.
Fig. S5 (a) Overpotentials required at $J = 10$ mA cm$^{-2}$. (b) TOFs calculated from the currents at $\eta = 300$ mV. (c) Mass activities at $\eta = 300$ mV. (d) The double layer capacity $C_{dl}$.

Fig. S6 Nyquist plots.
Fig. S7 CV curves of CoSe (a), Co$_{0.03}$Fe$_{0.07}$-Se (b), Co$_{0.85}$Fe$_{0.15}$-Se (c), Co$_{0.75}$Fe$_{0.25}$-Se (d), Co$_{0.69}$Fe$_{0.31}$-Se (e), Co$_{0.51}$Fe$_{0.49}$-Se (f), FeSe$_2$ (g) with different scan rates from 100 mV s$^{-1}$ to 200 mV s$^{-1}$ in 1 M KOH.

Fig. S8 (a) Ring current of Co$_{0.75}$Fe$_{0.25}$-Se hybrids on a RRDE (1500 rpm) in O$_2$-saturated 1.0 M KOH with the ring potential of 1.50 V. (b) Ring current of Co$_{0.75}$Fe$_{0.25}$-Se hybrids on a RRDE.
(1500 rpm) in N₂-saturated 1.0 M KOH solution with the ring potential of 0.40 V. The inset presents the FE testing mechanism of the RRDE, the black columns on the sides are Pt ring electrodes. The Pt ring electrode and glassy-carbon electrode are separated by a non-conductive PTFE barrier (white columns).

Fig. S9 XPS spectra of Co 2p (a), Fe 2p (b), Se 3d (c) and O 1s (d) for Co₀.₇₅Fe₀.₂₅-Se catalysts after OER stability test.

Table S1 The molar ratio of Co/Fe in different catalysts

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursor ratio</td>
<td>11:1</td>
<td>5:1</td>
<td>3:1</td>
<td>2:1</td>
<td>1:1</td>
</tr>
<tr>
<td>ICP result</td>
<td>0.93:0.07</td>
<td>0.85:0.15</td>
<td>0.75:0.25</td>
<td>0.69:0.31</td>
<td>0.51:0.49</td>
</tr>
</tbody>
</table>

Table S2 Comparison of OER catalytic performance with the reported metal selenides

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>Substrate</th>
<th>Overpotential at 10 mA cm² (mV)</th>
<th>Tafel slope (mV/dec)</th>
<th>Reference</th>
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</thead>
<tbody>
<tr>
<td>Co₀.₇₅Fe₀.₂₅-Se</td>
<td>1 M</td>
<td>NF</td>
<td>246</td>
<td>41.4</td>
<td>This</td>
</tr>
<tr>
<td>Nanocomposite</td>
<td>KOH</td>
<td>Work</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------------------------------------</td>
<td>------</td>
<td>------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ultrathin CoSe$_2$ nanosheet</td>
<td>0.1 M</td>
<td>GC</td>
<td>320</td>
<td>44</td>
<td>1</td>
</tr>
<tr>
<td>Mn$_3$O$_7$/CoSe$_2$</td>
<td>0.1 M</td>
<td>GC</td>
<td>450</td>
<td>49</td>
<td>2</td>
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<tr>
<td>(Ni, Co)$_{0.33}$Se$_2$ nanotube</td>
<td>1 M</td>
<td>carbon fabric collector</td>
<td>255</td>
<td>79</td>
<td>3</td>
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<tr>
<td>a-CoSe</td>
<td>1 M</td>
<td>Ti</td>
<td>292</td>
<td>69</td>
<td>4</td>
</tr>
<tr>
<td>FeSe$_2$</td>
<td>1 KOH</td>
<td>NF</td>
<td>245</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>FeSe$_2$ nanoplatelet</td>
<td>1 M</td>
<td>Ni piece</td>
<td>330</td>
<td>48.1</td>
<td>6</td>
</tr>
<tr>
<td>CeO$_2$/CoSe$_2$</td>
<td>0.1 M</td>
<td>GC</td>
<td>288</td>
<td>44</td>
<td>7</td>
</tr>
<tr>
<td>NiCo$_2$Se$_4$ holey nanosheet</td>
<td>1 M</td>
<td>GC</td>
<td>300</td>
<td>53</td>
<td>8</td>
</tr>
<tr>
<td>NiSe-Ni$<em>{0.83}$Se$</em>{0.17}$ hybrid</td>
<td>1 M</td>
<td>carbon paper</td>
<td>300</td>
<td>98</td>
<td>9</td>
</tr>
<tr>
<td>Coral-like CoSe</td>
<td>1 M</td>
<td>GC</td>
<td>295</td>
<td>40</td>
<td>10</td>
</tr>
<tr>
<td>NiSe nanowire</td>
<td>1 M</td>
<td>NF</td>
<td>~320</td>
<td>54</td>
<td>11</td>
</tr>
<tr>
<td>NiSe/NiO$_x$</td>
<td>1 M</td>
<td>NF</td>
<td>243</td>
<td>128.8</td>
<td>12</td>
</tr>
<tr>
<td>CoSe$_2$ microsphere</td>
<td>1 M</td>
<td>GC</td>
<td>330</td>
<td>79</td>
<td>13</td>
</tr>
<tr>
<td>Au-CoSe$_2$ nanobelt</td>
<td>0.1 M</td>
<td>GC</td>
<td>303</td>
<td>42</td>
<td>14</td>
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<tr>
<td>Co$_{0.85}$Se@NC</td>
<td>1 M</td>
<td>GC</td>
<td>260</td>
<td>75</td>
<td>15</td>
</tr>
</tbody>
</table>

**Reference**


**Table S3** Comparison of OER catalytic performance with the reported Ni-Fe oxides.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>Current Density (mA/cm²)</th>
<th>Overpotential (mV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co0.75Fe0.25-Se nanohybrids</td>
<td>1 M KOH</td>
<td>10</td>
<td>246</td>
<td>This work</td>
</tr>
<tr>
<td>NiFe oxide</td>
<td>1 M NaOH</td>
<td>0.5</td>
<td>280</td>
<td>1</td>
</tr>
<tr>
<td>Ni_{0.69}Fe_{0.31}O_{x}/C</td>
<td>1 M KOH</td>
<td>10</td>
<td>280</td>
<td>2</td>
</tr>
<tr>
<td>Fe-Ni-Ox NPs</td>
<td>1 M KOH</td>
<td>10</td>
<td>286</td>
<td>3</td>
</tr>
<tr>
<td>Ni-Fe oxide film</td>
<td>0.1 M KOH</td>
<td>2</td>
<td>329</td>
<td>4</td>
</tr>
<tr>
<td>Fe_{6}Ni_{10}O_{x}</td>
<td>1 M KOH</td>
<td>10</td>
<td>286</td>
<td>5</td>
</tr>
<tr>
<td>Ni_{0.5}Fe_{0.1}O_{x}</td>
<td>1 M KOH</td>
<td>10</td>
<td>336</td>
<td>6</td>
</tr>
<tr>
<td>Fe_{40}Ni_{60}O_{x} film</td>
<td>0.1 M KOH</td>
<td>1</td>
<td>250 ± 30</td>
<td>7</td>
</tr>
<tr>
<td>Ni_{1-x}Fe_{x}O_{y} nanorods</td>
<td>1 M KOH</td>
<td>10</td>
<td>302</td>
<td>8</td>
</tr>
<tr>
<td>Fe_{11%}-NiO/NF</td>
<td>1 M KOH</td>
<td>10</td>
<td>206</td>
<td>9</td>
</tr>
<tr>
<td>Ni-Fe-O composite</td>
<td>1 M KOH</td>
<td>10</td>
<td>244</td>
<td>10</td>
</tr>
</tbody>
</table>

**Reference**


