Supplementary Information
for

Optimize the overall water splitting performance of N, S co-doped carbon-supported NiCoMnSx at high current density by the effect of sulfur defects and oxygen vacancies

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Calculation methods of electrochemical related parameters:

**Electrochemically active surface area (ECSAs):** The electrochemically active surface area (ECSA) of the catalysts was determined by the double-layer capacitance measurements in 1 M KOH electrolyte. The doublelayer capacitance \( C_{dl} \) was determined by measuring the non-Faradaic capacitive current charging from the scan-rate dependence of CVs. The potential window of CVs was 0.324 V to 0.524 vs RHE. The \( C_{dl} \) was given by the following equation:

\[
C_{dl} = \frac{d(\Delta j)}{2d\nu_b}
\]

where \( \nu \) is the scan rate, \( j \) is the current density.

The ECSA is calculated from the double layer capacitance according to:

\[
ECSA = \frac{C_{dl}}{C_s}
\]

where \( C_s \) is the specific capacitance of the sample. We use general specific capacitances of \( C_s = 0.04 \text{ mF cm}^{-2} \) based on typical reported values.

**Mass activity:** The Mass activity \( (j_m, \text{ A g}^{-1}) \) is evaluated at the overpotential of \( \eta=400 \text{ mV} \) and the catalyst loading \( m (0.8 \text{ mg cm}_{\text{geo}}^{-2}) \). The current density \( j_{\text{geo}} \) (mA cm\(_{\text{geo}}^{-2}\)) was given by the following equation:

\[
j_m = \frac{j_{\text{geo}}}{m}
\]

**Turnover frequency (TOF):** Assuming that all Co and Mn ions in the catalysts were active and contributed to the catalytic reaction, we obtained molar number of metal atom (\( n \)) by ICP to calculate the lowest TOF. The specific calculation formula was as follows:

\[
\text{TOF} = \frac{jS}{4Fn}
\]

Where \( j \) (A cm\(^{-2}\)) is the current density corresponding to 400 mV; \( S \) is the surface area of electrode, the number 4 is the assumption that all reactions in the paper are four-electron processes; \( F \) is Faraday constant \((96485.3 \text{ C/mol})\), and \( n \) is the metal ions molar number.
Figure S1 (a,f) FESEM images of NCM(OH)x; (b,g) FESEM images of NCM(BDC)x-5; (c,h) FESEM images of NCM(BDC)x-10; (d,i) FESEM images of NCM(BDC)x-15; (e,j) FESEM images of NCM(BDC)x-20; (k) EDS element distribution map of NCMx-10.
Figure S2 (a) XRD patterns of NCM(BDC)x; (b) XPS survey spectra of NCMOx-10 ;(c) XPS survey spectra of NCMSx-10; (d) S 2p spectra of NCMSx-10.
Figure S3 (a,e) Water contact angle of NCMSx-5; (b,f) Water contact angle of NCMSx-10; (c,g) Water contact angle of NCMSx-15; (d,h) Water contact angle of NCMSx-20.
Figure S4 (a) CV curves of NCMOx-5; (b) CV curves of NCMOx-10; (c) CV curves of NCMOx-15; (d) CV curves of NCMOx-20; (e) CV curves of NCMSx-5; (f) CV curves of NCMSx-10; (g) CV curves of NCMSx-15; (h) CV curves of NCMSx-20.
Figure S5 (a) $C_{dl}$ of NCMOx; (b) $C_{dl}$ of NCMSx; (c) ECSA of NCMOx; (d) ECSA of NCMSx.
Figure S6 (a) XRD patterns of NCMSx-10 before and after the reaction; (b) When the excitation wavelength is 530nm, the comparison of the PL curve of NCMSx-10 before and after reaction; (c) When the excitation wavelength is 285nm, the comparison of the PL curve of NCMSx-10 before and after reaction.
Figure S7 (a) Ni 2p patterns of NCMSx before and after the reaction; (b) Co 2p patterns of NCMSx before and after the reaction; (c) Mn 2p patterns of NCMSx before and after the reaction; (d) S 2p patterns of NCMSx before and after the reaction.
Figure S8  (a) SEM image after HER ;(b) SEM image after OER.
**Table S1** Ratios of Co to Mn elements in NCM(BDC)x determined by ICP-OES analysis.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>NCM(BDC)x-5</th>
<th>NCM(BDC)x-10</th>
<th>NCM(BDC)x-15</th>
<th>NCM(BDC)x-20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co:Mn</td>
<td>1:0.88</td>
<td>1:0.99</td>
<td>1:1.01</td>
<td>1:0.82</td>
</tr>
</tbody>
</table>

**Table S2** EIS data fitting results of NCMOx and NCMSx electrodes for HER, respectively.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Rs (Ω)</th>
<th>Rct (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCMOx-5</td>
<td>1.20</td>
<td>168.10</td>
</tr>
<tr>
<td>NCMOx-10</td>
<td>1.10</td>
<td>129.80</td>
</tr>
<tr>
<td>NCMOx-15</td>
<td>1.19</td>
<td>195.80</td>
</tr>
<tr>
<td>NCMOx-20</td>
<td>1.27</td>
<td>222.10</td>
</tr>
<tr>
<td>NCMSx-5</td>
<td>0.98</td>
<td>38.07</td>
</tr>
<tr>
<td>NCMSx-10</td>
<td>1.17</td>
<td>37.37</td>
</tr>
<tr>
<td>NCMSx-15</td>
<td>1.25</td>
<td>99.24</td>
</tr>
<tr>
<td>NCMSx-20</td>
<td>1.29</td>
<td>129.20</td>
</tr>
</tbody>
</table>

**Table S3** EIS data fitting results of NCMOx and NCMSx electrodes for OER, respectively.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Rs (Ω)</th>
<th>Rct (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCMOx-5</td>
<td>0.76</td>
<td>179.11</td>
</tr>
<tr>
<td>NCMOx-10</td>
<td>0.87</td>
<td>142.70</td>
</tr>
<tr>
<td>NCMOx-15</td>
<td>0.87</td>
<td>199.92</td>
</tr>
<tr>
<td>NCMOx-20</td>
<td>0.76</td>
<td>243.84</td>
</tr>
<tr>
<td>NCMSx-5</td>
<td>0.95</td>
<td>123.21</td>
</tr>
<tr>
<td>NCMSx-10</td>
<td>0.94</td>
<td>74.73</td>
</tr>
<tr>
<td>NCMSx-15</td>
<td>0.98</td>
<td>124.22</td>
</tr>
<tr>
<td>NCMSx-20</td>
<td>0.77</td>
<td>127.80</td>
</tr>
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Table S4 The corresponding voltages of NCMOx and NCMSx electrodes at a current density of 10 mA cm$^{-2}$.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>$\eta(\text{j}=10 \text{mA cm}^{-2})$/mV (HER)</th>
<th>$\eta(\text{j}=10 \text{mA cm}^{-2})$/mV (OER)</th>
<th>$\eta(\text{j}=10 \text{mA cm}^{-2})$/V (Overall water splitting)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCMOx-5</td>
<td>-160</td>
<td>321</td>
<td>1.796</td>
</tr>
<tr>
<td>NCMOx-10</td>
<td>-152</td>
<td>334</td>
<td>1.788</td>
</tr>
<tr>
<td>NCMOx-15</td>
<td>-161</td>
<td>356</td>
<td>1.847</td>
</tr>
<tr>
<td>NCMOx-20</td>
<td>-164</td>
<td>375</td>
<td>1.878</td>
</tr>
<tr>
<td>NCMSx-5</td>
<td>-123</td>
<td>234</td>
<td>1.642</td>
</tr>
<tr>
<td>NCMSx-10</td>
<td>-105</td>
<td>226</td>
<td>1.506</td>
</tr>
<tr>
<td>NCMSx-15</td>
<td>-136</td>
<td>228</td>
<td>1.535</td>
</tr>
<tr>
<td>NCMSx-15</td>
<td>-158</td>
<td>245</td>
<td>1.660</td>
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</tbody>
</table>

Table S5 When the current density is 10 mA cm$^{-2}$, the HER and overall water splitting performance of NCMSx-10 are compared with other non-precious electrocatalysts in alkaline electrolytes.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>HER/mV</th>
<th>Overall water splitting /V</th>
<th>Electrolyte</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCMSx-10</td>
<td>105</td>
<td>1.506</td>
<td>1 M KOH</td>
<td>This work</td>
</tr>
<tr>
<td>NiCo$_2$O$_4$</td>
<td>110</td>
<td>1.65</td>
<td>1 M KOH</td>
<td>1</td>
</tr>
<tr>
<td>MoS$_2$-NiS$_2$/N-doped graphene</td>
<td>172</td>
<td>1.64</td>
<td>1 M KOH</td>
<td>2</td>
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<tr>
<td>NiFeOH/CoS$_x$</td>
<td>146</td>
<td>1.563</td>
<td>1 M KOH</td>
<td>3</td>
</tr>
<tr>
<td>NiCoSe/C</td>
<td>143</td>
<td>1.68</td>
<td>1 M KOH</td>
<td>4</td>
</tr>
<tr>
<td>CVN/CC</td>
<td>118</td>
<td>1.64</td>
<td>1 M KOH</td>
<td>5</td>
</tr>
<tr>
<td>Co$<em>{0.9}$S$</em>{0.58}$P$_{0.42}$</td>
<td>139</td>
<td>1.59</td>
<td>1 M KOH</td>
<td>6</td>
</tr>
<tr>
<td>Co$<em>{0.25}$Fe$</em>{0.75}$S$_2$</td>
<td>267</td>
<td>1.60</td>
<td>1 M KOH</td>
<td>7</td>
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</table>
References


