Supporting Information

**Metallic and superhydrophilic nickel cobalt diselenides**

**Nanosheets electrodeposited on carbon cloth as bifunctional electrocatalyst**

*Jing Yu,*<sup>a,b</sup> *Yumeng Tian,*<sup>a,b</sup> *Fei Zhou,*<sup>c</sup> *Meiling Zhang,*<sup>a,b</sup> *Rongrong Chen,*<sup>a,b,d</sup> *Qi Liu,*<sup>a,b</sup> *Jingyuan Liu,*<sup>a,b</sup> *Cheng-Yan Xu,*<sup>c</sup>* Jun Wang*<sup>a,b,d</sup>*

**a** Key Laboratory of Superlight Materials and Surface Technology, Ministry of Education, Harbin Engineering University, Harbin 150001, China

**b** College of Materials Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, China

**c** School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China

**d** Institute of Advanced Marine Materials, Harbin Engineering University, Harbin 150001, China
**Fig. S1** Digital photography of the as-deposited NiCoSe$_2$ on the surface of carbon cloth.

**Fig. S2** XRD pattern of the as-deposited NiCoSe$_2$ on carbon cloth
**Fig. S3** SEM images of NiCoSe$_2$ nanosheets with different magnifications.

**Fig. S4** (a) SEM-EDS spectrum of NiCoSe$_2$ nanosheets. (b-e) SEM-EDS mappings of NiCoSe$_2$ nanosheets.
Fig. S5 TEM image of NiCoSe$_2$ nanosheets.
**Fig. S6** SEM images of different samples obtained by electroddeposition. (a) NiCo-OH, (b) NiSe, (c) CoSe, (d) NiCoSe$_2$ obtained at 0.65 V. Inset of (d) is cross-section SEM image.
**Fig. S7** SEM-EDS spectra of Ni-Co-Se samples with different Ni/Co ratios. (a) NiSe, (b) Ni$_{1.5}$Co$_{0.5}$Se$_2$, (c) Ni$_{1.34}$Co$_{0.66}$Se$_2$, (d) Ni$_{0.66}$Co$_{1.34}$Se$_2$, (e) Ni$_{0.5}$Co$_{1.5}$Se$_2$, (f) CoSe.

The Ni/Co ratio in Ni-Co-Se is close to added Ni and Co sources, and the mole ratio of metal and Se is close to 1:1.
Fig. S8 HER polarization curves of NiCoSe$_2$ prepared with different deposition durations.
Fig. S9 SEM images of NiCoSe$_2$ at different electrodeposition durations. (a, b) 100 s, (c, d) 300 s, (e, f) 1200 s, (g, h) 1800 s.

The effect of deposition time on the resultants was investigated to examine the formation process of NiCoSe$_2$ nanosheets. As shown in Figure S8, various of nanoparticles emerged on CC surface and covered CC incompletely with the deposition time of 100 s. Moreover, the nanoparticles exhibited the trend to crimp.
With the increasing time to 300 s, the sample owned the morphology of microflowers comprised of numerous nanosheets. And then these microflowers tended to combine with each other and form interconnected structure. Along with further prolonged deposition time, the sample accumulated densely around CC, which is not favorable to charge diffusion.

Fig. S10 The HER Tafel plots of different samples.
Fig. S11 (a) LSV polarization curves and (b) corresponding Tafel plots toward HER of NiCoSe$_2$ prepared with different deposition potentials of -0.65 V and -0.8 V.

Fig. S12 Electrochemical cyclic voltammetry curves of (a) NiCo-OH, (b) NiSe, (c) CoSe and (d) NiCoSe$_2$ at different scanning rates. The scanning rates are in the ranges from 20 to 200 mV s$^{-1}$ with an interval point of 20 mV s$^{-1}$. 
Electrochemical active surface area (ECSA)

The active surface area of each catalyst was estimated from their electrochemical capacitances according to the following equation:

\[
A(ECSA) = \frac{C_{dl - catalyst} \text{ (mF cm}^{-2}\text{)}}{C_{dl - carbon cloth} \text{ (mF cm}^{-2}\text{) per ECSA cm}^{2}\text{}}
\]

Consequently, the \(A_{ECSA}\) for NiSe, CoSe and NiCoSe\(_2\) were calculated as:

\[
A_{NiSe}^{ECSA} = \frac{2.14 \text{ mF cm}^{-2}}{0.7 \text{ mF cm}^{-2}\text{ per cm}^{2}_{ECSA}} = 3.06 \text{ cm}^{2}_{ECSA}
\]

\[
A_{CoSe}^{ECSA} = \frac{3.01 \text{ mF cm}^{-2}}{0.7 \text{ mF cm}^{-2}\text{ per cm}^{2}_{ECSA}} = 4.3 \text{ cm}^{2}_{ECSA}
\]

\[
A_{NiCoSe_2}^{ECSA} = \frac{10.55 \text{ mF cm}^{-2}}{0.7 \text{ mF cm}^{-2}\text{ per cm}^{2}_{ECSA}} = 15.07 \text{ cm}^{2}_{ECSA}
\]

Turnover frequency (TOF) calculations

The TOF values were eliminated according to:

\[
TOF = \frac{\# \text{total hydrogen (or oxygen) turnovers/ geometric area} \text{(cm}^{2}\text{)}}{\# \text{surface active sites/ geometric area} \text{ (cm}^{2}\text{)}}
\]

The number of the total hydrogen or oxygen turnovers is calculated based on the measured current density by the following equations:

\[
\#H_{2} = \frac{|J| \text{ mA}}{1000 \text{ mA}} \times \frac{1 \text{ C s}^{-1}}{96495.3 \text{ C}} \times \frac{1 \text{ mol e}^{-}}{2 \text{ mol e}^{-}} \times \frac{1 \text{ mol H}_{2}}{1 \text{ mol H}_{2}} \times \frac{6.022 \times 10^{23} \text{ H}_{2} \text{ molecules}}{1 \text{ mol H}_{2}} \times 10^{15} \text{ H}_{2} \text{ s}^{-1} \text{ per mA cm}^{-2}
\]
\[
\# \text{O}_2 = \frac{mA}{cm^2} \times \frac{1 \text{ C s}^{-1}}{1000 \text{ mA}} \times \frac{1 \text{ mol e}^{-}}{96495.3 \text{ C}} \times \frac{1 \text{ mol O}_2}{4 \text{ mol e}^{-}} \times \frac{6.022 \times 10^{23} \text{ O}_2 \text{ mol}}{1 \text{ mol O}_2}
\times 10^{15} \frac{\text{O}_2 \text{s}^{-1}}{\text{cm}^2} \frac{\text{mA}}{\text{cm}^2}
\]

The upper limit of the surface sites can be calculated as following:

\[
\# \text{Surface sites}_{\text{NiSe}} = \left(\frac{4 \text{ atoms per unit cell}}{61.15 \text{ A}^2 \text{ per unit cell}}\right)^2 = 1.62 \times 10^{15} \text{ atoms/cm}^2 \text{ real surf}
\]

\[
\# \text{Surface sites}_{\text{CoSe}} = \left(\frac{4 \text{ atoms per unit cell}}{57.84 \text{ A}^2 \text{ per unit cell}}\right)^2 = 1.68 \times 10^{15} \text{ atoms/cm}^2 \text{ real surf}
\]

\[
\# \text{Surface sites}_{\text{NiCoSe}_2} = \left(\frac{4 \text{ atoms per unit cell}}{59.72 \text{ A}^2 \text{ per unit cell}}\right)^2 = 1.65 \times 10^{15} \text{ atoms/cm}^2 \text{ real surf}
\]

\[
\text{TOF}_{\text{HER}} = \frac{3.12 \times 10^{15} \text{H}_2 \text{s}^{-1}}{\text{per mA}} \times \frac{\text{mA}}{\text{cm}^2} \times \frac{1}{|J|}
\]

\[
\text{TOF}_{\text{OER}} = \frac{1.56 \times 10^{15} \text{O}_2 \text{s}^{-1}}{\text{per mA}} \times \frac{\text{mA}}{\text{cm}^2} \times \frac{1}{|J|}
\]
Fig. S13 Unit cells of NiSe (2 Ni and 2 Se atoms), CoSe (2 Co and 2 Se atoms) and NiCoSe$_2$ (1 Ni, 1 Co and 2 Se atoms), respectively.

Fig. S14 HER polarization curves recorded for NiCoSe$_2$ at initial state, after 2000 CV cycles and 24 h of chronopotentiometric test.
Fig. S15 SEM images of NiCoSe$_2$/CC electrode after HER measurement.

Fig. S16 HER polarization curves of NiCoSe$_2$/CC electrode before and after the continuous bending for 10 times. The LSV curve after 10 times bending is almost overlapping with the initial curve, indicating excellent mechanical stability of NiCoSe$_2$/CC electrode.
Fig. S17 LSV polarization curves toward HER of NiCoSe$_2$ with different Ni/Co ratio.

Fig. S18 (a) LSV polarization curves and (b) corresponding Tafel plots toward OER of NiCoSe$_2$ prepared with different deposition potentials of -0.65 V and -0.8 V.
Fig. S19 LSV polarization curves toward OER of NiCoSe$_2$ with different Ni/Co ratios.

Fig. S20 (a) OER Polarization curves recorded for NiCoSe$_2$ at initial state, after 2000 and 5000 CV cycles. (b) Chronoamperometric curve of NiCoSe$_2$ at a constant current potential of 1.52 V for 200 h of continuous operation.
**Fig. S21** SEM images of NiCoSe$_2$/CC electrode after OER measurement.

**Fig. S22** XPS spectra of NiCoSe$_2$ after OER test. (a) XPS survey spectrum. (b) High-resolution XPS spectra of (b) Ni 2p, (c) Co 2p and (d) Se 3d. The obviously increasing Se oxide species suggest an oxidation on the surface of NiCoSe$_2$ during the OER process.
Table S1. Summary of the electrochemical features and water splitting activities in 1M KOH upon the as-deposited samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>NiCo-OH</th>
<th>NiSe</th>
<th>CoSe</th>
<th>NiCoSe₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>η₁₀ (HER, mV)</td>
<td>393.8</td>
<td>204.8</td>
<td>179.5</td>
<td>112.7</td>
</tr>
<tr>
<td>Tafel slope (HER, mV/dec)</td>
<td>280</td>
<td>150</td>
<td>99</td>
<td>65</td>
</tr>
<tr>
<td>R&lt;sub&gt;a&lt;/sub&gt; (HER, Ω)</td>
<td>124.4</td>
<td>60.3</td>
<td>51.4</td>
<td>44.7</td>
</tr>
<tr>
<td>η₁₀ (OER, mV)</td>
<td>388.1</td>
<td>331.4</td>
<td>313.1</td>
<td>255.8</td>
</tr>
<tr>
<td>Tafel slope (OER, mV/dec)</td>
<td>256</td>
<td>143</td>
<td>92</td>
<td>71</td>
</tr>
<tr>
<td>R&lt;sub&gt;a&lt;/sub&gt; (OER, Ω)</td>
<td>31.8</td>
<td>17.3</td>
<td>14.7</td>
<td>8.0</td>
</tr>
<tr>
<td>η₁₀ (Full water splitting, V)</td>
<td>1.88</td>
<td>1.82</td>
<td>1.68</td>
<td>1.62</td>
</tr>
<tr>
<td>C&lt;sub&gt;dl&lt;/sub&gt; (mF/cm²)</td>
<td>0.94</td>
<td>2.14</td>
<td>3.01</td>
<td>10.55</td>
</tr>
</tbody>
</table>
Fig. S23 Crystal structure of NiSe with (a) top view and (b) side view. Calculated (c) band structures and (d) density of states for NiSe. The Fermi level is set at 0 eV.
Fig. S24 Crystal structure of CoSe with (a) top view and (b) side view. Calculated (c) band structures and (d) density of states for CoSe. The Fermi level is set at 0 eV.
Table S2. Comparison of electrocatalytic performance for NiCoSe$_2$/CC with the state-of-the-art bifunctional electrocatalysts for water splitting in 1M KOH.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>HER $\eta_{10}$ (mV)</th>
<th>OER $\eta_{10}$ (mV)</th>
<th>$E_{10}$ (V)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiCoSe$_2$</td>
<td>112.7</td>
<td>255.8</td>
<td>1.62</td>
<td>This work</td>
</tr>
<tr>
<td>(Ni,Co)$_{0.85}$Se</td>
<td>169</td>
<td>$\eta_{10}$=287</td>
<td>1.65</td>
<td>J. Mater. Chem. A, 2018, 6, 7585-7591</td>
</tr>
<tr>
<td>NiCo$_2$P$_4$</td>
<td>47</td>
<td>284</td>
<td>1.61</td>
<td>J. Mater. Chem. A, 2018, 6, 7420-7427</td>
</tr>
<tr>
<td>Ni$<em>{2.5}$Co$</em>{0.5}$Fe/NF</td>
<td>~150</td>
<td>275</td>
<td>1.62</td>
<td>J. Mater. Chem. A, 2016, 4, 7245-7250.</td>
</tr>
<tr>
<td>Ni$<em>x$Co$</em>{3-x}$O$_4$/NiCo/NiCoO$_x$</td>
<td>155</td>
<td>337</td>
<td>1.75</td>
<td>ACS Appl. Mater. Interfaces, 2016, 8, 3208-3214.</td>
</tr>
</tbody>
</table>

[a] the overall water splitting voltage at the current density of 10 mA cm$^{-2}$.  