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Supporting Information

Adjustable Antiperovskite Cobalt-Based Nitrides as Efficient Electrocatalysts for Overall Water Splitting

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**Text S1. Experimental section**

Preparation of CuNCo$_3$/NF and Co$_{0.73}$Co$_3$/NF: In processing, 1 mmol Cu(NO$_3$)$_2$·3H$_2$O (99.0%, Sinopharm Chemical Reagent Co., Ltd), 3 mmol Co(NO$_3$)$_2$·6H$_2$O (98.5% Sinopharm Chemical Reagent Co., Ltd) and 14 mmol Co(NH$_2$)$_2$ (99.0% Sinopharm Chemical Reagent Co., Ltd) were dissolved into 60 mL deionized water and stirred. Then, the prepared aqueous solution and a NF substrate (XRD pattern and SEM images of bare NF were displayed in Fig. S1) were transferred into a 100 mL stainless-steel autoclave and reacted at 120°C for 10h. After the reaction, the sample was washed with deionized water and alcohol, and dried in an oven at 60°C. The obtained hydrothermal precursor was Cu-Co bimetallic hydroxide/NF. Then, the hydrothermal precursor of Cu-Co bimetallic hydroxide/NF was annealed at 420 °C under the flowing NH$_3$ atmosphere for 2h (as depicted in Scheme 1). The obtained product was CuNCo$_3$/NF. The catalyst loading mass of CuNCo$_3$/NF is ~4 mg cm$^{-2}$. Similar processing was carried out to prepare the Co$_{0.73}$Co$_3$/NF, in which 4 mmol Co(NO$_3$)$_2$·6H$_2$O was used to prepare the aqueous solution without addition of Cu(NO$_3$)$_2$·3H$_2$O. The obtained product was CuNCo$_3$/NF. The catalyst loading mass of
CuNCo$_3$/NF is $\sim$4 mg cm$^{-2}$.

Preparation of Pt/C electrode and RuO$_2$ electrode: The 20 wt% Pt/C and RuO$_2$ were used as the reference samples for HER and OER, respectively. 10 mg catalyst was dispersed into the solution with 950 $\mu$L isopropanol and 50 $\mu$L 5 wt% Nafion, and ultrasonically stirred for more than 40 minutes until the dispersed ink was obtained. Then, 400 $\mu$L of the dispersed ink was loaded onto NF with the size of 1$\times$1 cm$^2$ (loading mass of 4 mg cm$^{-2}$). Finally, the as-prepared electrode was dried at room temperature for electrochemical measurements.

**Text S2. Material characterizations**


**Text S3. Electrochemical measurements and evaluations**

The conventional three-electrode system equipped with N$_2$ gas flow system was utilized for electrochemical measurements at room temperature in 1 M KOH electrolyte on a CHI660E workstation. Hg/HgO and graphite rod were used as the reference electrode and counter electrode, respectively. The prepared samples were used as the working electrodes. All the potentials were calibrated to reversible hydrogen electrode (RHE) according to the equation $E$(vs. RHE) = $E$(vs. Hg/HgO) + $E^\circ_{\text{Hg/HgO}} + 0.0591$ pH ($E^\circ_{\text{Hg/HgO}}$: 0.098V, pH: 14). LSV was measured at a scan rate of 2 mV s$^{-1}$. A series of
CV measurements were performed at different scan rates within 20 - 100 mV s⁻¹ in the range of 1.025 - 1.125 V (vs. RHE) in order to calculate the ECSA. The ECSA was calculated as $\text{ECSA} = C_{\text{dl}} / C_s$. $C_{\text{dl}}$ is double-layer capacitance and $C_s$ represents 40 $\mu$F cm⁻² in 1 M KOH. The $C_{\text{dl}}$ was obtained by fitting the half slope of current density and scanning rate at the average potential range of CV. EIS was obtained at overpotential of 300 mV and -200 mV (vs. RHE) for OER and HER respectively in the frequency range of 0.1 - $10^5$ Hz with 5 mV amplitude. The stability of the catalyst was tested by chronoamperometry. All data were calibrated by 90 % iR compensation.

**Fig. S1** (a) XRD pattern and (b) SEM image of bare nickel foam (NF).
Fig. S2 XRD patterns of CoN$_{0.73}$Co$_3$.

Fig. S3 XPS spectra of CoN$_{0.73}$Co$_3$, (a) survey scan, (b) Co 2p, (c) N 1s.
Fig. S4  (a, b) SEM images of Cu-Co bimetallic hydroxide/NF (precursor of CuNCo$_3$/NF). (c) XRD patterns of Cu-Co bimetallic hydroxide/NF. (d, e) SEM images of Co hydroxide/NF (precursor of CoN$_{0.73}$Co$_3$/NF). (f) XRD patterns of Co hydroxide/NF.

In Fig. S4c, XRD patterns of as-prepared Cu-Co bimetallic hydroxide/NF (precursor of CuNCo$_3$/NF) presents the coexistence of Cu(OH)$_2$ (JPCDS No.035-0505), Co(OH)$_2$ (JPCDS No. 002-0214) and NF (JPCDS No. 210-0644) phases. The peaks at 24.02°, 33.83° and 35.52°can be indexed to the (021), (002) and (111) plane of Cu(OH)$_2$, and additional peaks at 17.56°, 34.62° and 36.27° can be assigned to the Co(OH)$_2$.

In Fig. S4f, XRD patterns of as-prepared Co hydroxide/NF (precursor of CoN$_{0.73}$Co$_3$/NF) shows the coexistence of Co(OH)$_2$ (JPCDS No. 002-0214) and NF (JPCDS No. 210-0644) phases. The peaks at about 17.73°, 34.21° and 35.95° can be indexed to the Co(OH)$_2$.

Fig. S5  Electrocatlytical OER testing in 1.0 M KOH. (a) LSV curves for precursors of CuNCo$_3$/NF, CoN$_{0.73}$Co$_3$/NF, RuO$_2$ and NF. (b) Tafel plots. (c) Nyquist plots and equivalent circuit.
**Fig. S6** CV curves of OER testing for (a) CuNCo$_3$/NF and (b) CoN$_{0.73}$Co$_3$/NF with 20, 40, 60, 80 and 100 mV s$^{-1}$ in non-Faradaic potential range.

**Fig. S7** CV curves of OER testing for precursors of (a) CuNCo$_3$/NF and (b) CoN$_{0.73}$Co$_3$/NF with 20, 40, 60, 80 and 100 mV s$^{-1}$ in non-Faradaic potential range.

**Fig. S8** Electrocatalytical HER testing results in 1 M KOH. (a) LSV curves for precursors of CuNCo$_3$/NF and CoN$_{0.73}$Co$_3$/NF, RuO$_2$ and NF. (b) Tafel plots. (c)
Nyquist plots and equivalent circuit.

**Fig. S9** (a) LSV curves and (b) Tafel plots with the mass activity of RuO$_2$, CuNCo$_3$/NF and CoN$_{0.73}$Co$_3$/NF for OER. (c) LSV curves and (d) Tafel plots with the mass activity of 20 wt% Pt/C, CoN$_{0.73}$Co$_3$/NF and CuNCo$_3$/NF for HER.
Fig. S10 (a) LSV curves and (b) Tafel plots with the mass activity for RuO$_2$, precursors of CuNCo$_3$/NF and CoN$_{0.73}$Co$_3$/NF for OER. (c) LSV curves and (d) Tafel plots with the mass activity for 20 wt% Pt/C, precursors of CoN$_{0.73}$Co$_3$/NF and CuNCo$_3$/NF for HER.

Fig. S11 Polarization curves of (a) OER, (b) HER and (c) two-electrode system for overall water splitting with maximum current density of 400 mA cm$^{-2}$. 
Fig. S12 (a) LSV curves of two-electrode electrolyzers (CuNCo$_3$/NF || CoN$_{0.73}$Co$_3$/NF and RuO$_2$/NF || 20 wt% Pt/C/NF). (b) Stability test of two-electrode electrolyzer (RuO$_2$/NF || 20 wt% Pt/C/NF).

Fig. S13 The long-term durability test of CuNCo$_3$/NF || CoN$_{0.73}$Co$_3$/NF at a current density of 100 mA cm$^{-2}$. 
**Fig. S14** Stability tests for (a) OER of CuNCo$_3$/NF and (b) HER of CoN$_{0.73}$Co$_3$/NF.

**Fig. S15** XRD patterns of (a) CuNCo$_3$/NF, (b) CoN$_{0.73}$Co$_3$/NF electrodes after stability test (48 h).
Fig. S16 The high-resolution XPS results for Co 2$p$, Cu 2$p$, N 1$s$ and O 1$s$ of CuNCo$_3$/NF electrode with initial and after stability test (48 h).

Fig. S17 The high-resolution XPS results for Co 2$p$ and N 1$s$ of CoN$_{0.73}$Co$_3$/NF electrode with initial and after stability test (48 h).
The calculation of electrochemical surface area:

The electrochemical surface area (ECSA) of each catalyst can be calculated according to: \[ A_{ECSA} = \frac{C_{dl}}{C_s \text{ per ESCA } cm^2} \]

\( C_s \) is the specific capacitance of atomically smooth planar surface in respective electrolytic medium.\(^1\) In this work, \( C_s \) was 40 μF cm\(^{-2}\) for 1.0 M KOH.\(^2\)
Table S1. The comparison of various electrocatalysts for overall water splitting.

<table>
<thead>
<tr>
<th>Electrocatalysts</th>
<th>Morphology</th>
<th>iR compensation</th>
<th>Voltage at 10 mA cm(^{-2}) (V)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuNCo(_3)</td>
<td></td>
<td>CoN(_{0.73})Co(_3)</td>
<td>Nanosheets and Nanowires</td>
<td>With iR compensation</td>
</tr>
<tr>
<td>FeNi(_{3})N</td>
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<td>FeNi(_{3})N</td>
<td>Nanoparticles</td>
<td>With iR compensation</td>
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<tr>
<td>V-FeNi(_{3})N/ Ni(_3)N</td>
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<td>V-FeNi(_{3})N/ Ni(_3)N</td>
<td>Nanoparticles</td>
<td>With iR compensation</td>
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<td>TiN@Ni(_3)N</td>
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<td>TiN@Ni(_3)N</td>
<td>Nanowires</td>
<td>With iR compensation</td>
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<tr>
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<td></td>
<td>Ni(_3)FeN</td>
<td>Nanosheets</td>
<td>With iR compensation</td>
</tr>
<tr>
<td>Co(_3)FeN(_x)</td>
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<td>Co(_3)FeN(_x)</td>
<td>Nanowires</td>
<td>With iR compensation</td>
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<tr>
<td>NiCoP/rGO</td>
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<td>NiCoP/rGO</td>
<td>Nanocrystals</td>
<td>Without iR compensation</td>
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<td>InNNi(_3)/ InNi (oxy)hydroxide</td>
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<td>InNNi(_3)/ InNi (oxy)hydroxide</td>
<td>Core-shell structure</td>
<td>Without iR compensation</td>
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<td>CoMo(_x)</td>
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<td>CoMo(_x)</td>
<td>Nanosheets</td>
<td>With iR compensation</td>
</tr>
<tr>
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<td>Fe(_3)N@Co(_3)N@CoFe</td>
<td>Nanoparticles</td>
<td>With iR compensation</td>
</tr>
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</table>

Table S2. The comparison of OER activity of the CuNCo\(_3\)/NF with that of other reported catalysts at the current density of 10 mA cm\(^{-2}\).

<table>
<thead>
<tr>
<th>Electrocatalysts</th>
<th>(\eta_{10}) (mV vs. RHE)</th>
<th>Tafel slope (mV dec(^{-1}))</th>
<th>Electrolyte</th>
<th>References</th>
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<tr>
<td>CuNCo(_3)</td>
<td>260</td>
<td>87</td>
<td>1.0 M KOH</td>
<td>This work</td>
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Table S3. The comparison of HER activity of the CoN$_{0.73}$Co$_3$/NF with that of other reported catalysts at the current density of 10 mA cm$^{-2}$.

<table>
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<tr>
<th>Electrocatalysts</th>
<th>$\eta_{10}$ (mV vs. RHE)</th>
<th>Tafel slope (mV dec$^{-1}$)</th>
<th>Electrolyte</th>
<th>References</th>
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<tbody>
<tr>
<td>CoN$_{0.73}$Co$_3$/NF</td>
<td>31</td>
<td>82</td>
<td>1.0 M KOH</td>
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<td>Ag/Ag$<em>{0.80}$Ni$</em>{0.20}$NNi$_3$</td>
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<td>~61</td>
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<td>~85</td>
<td>0.5 M H$_2$SO$_4$</td>
<td>28</td>
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</tbody>
</table>
References


21 L. Zhu, B. Yang, Z. Wu, C. Li, H. Li, H. Li, Y. Huang, X. Zhu, X. Zhu and Y. Sun,


