Coupling electrocatalytic cathodic nitrate reduction with anodic formaldehyde oxidation at ultra-low potential over Cu₂O

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Experimental Procedures

Raw materials

Ammonium persulfate ((NH₄)₂S₂O₈, 98.5%, AR), sodium hydroxide (NaOH, 98%) and potassium hydroxide (KOH, 95%, GR) were purchased from Macklin. Formaldehyde (HCHO, 37 wt%, AR) was purchased from the Xiya Reagent. Formate (HCOOH, 98%, GR), methanol (CH₃OH, 99.5%, AR) and ammonium chloride (NH₄Cl, ≥99.5%) were purchased from Aladdin. All chemicals were used as received without further purification.

Material synthesis

Cu Foam

Commercial Cu foam (1 cm × 1 cm × 0.5 mm) was ultrasonically cleaned in 0.5 M HCl for 15 min to remove surface oxides. The obtained Cu foam was used to synthesise CuO and electrocatalytic NO₃⁻ RR.

CuO

A one-step oxidation method was used to synthesise CuO nanosheets on the Cu foam. Four pieces of Cu foam (1 cm × 1 cm × 0.5 mm) were ultrasonically cleaned in 0.5 M HCl for 15 min to remove surface oxides. Secondly, preparing A and B solutions, where A solution includes 30 ml DI water, 7.2 g NaOH, and the B solution included 30 mL DI water, 2.74 g (NH₄)₂S₂O₈. The A and B solutions were heated to 60 °C and mixed. Four pieces of cleaned Cu foam were completely immersed in the solution for 30 min (flipped every 15 min), and the colour of the Cu foam changed from gold to black. CuO nanosheets were obtained from Cu foam. The obtained CuO was washed three times with water and ethanol and dried at 60 °C overnight. The obtained CuO was used to synthesise Cu₂O and for the electrocatalytic NO₃⁻ RR.

Cu₂O

To synthesise the Cu₂O nanosheets, the obtained CuO was immersed in a solution containing 40 mL 1 M KOH/HCHO for 1 h. The obtained Cu₂O was washed three times with water and ethanol
respectively and dried at 60 °C under vacuum overnight. The obtained Cu$_2$O was used for electrocatalytic HCHO oxidation and NO$_3$-RR.

Characterization

Powder XRD spectra were obtained at steps of 7° min$^{-1}$ in the range 10–80° using a Shimadzu X-ray diffractometer (XRD-6100, Japan) with Cu-Kα radiation ($\lambda = 1.54184$ Å, 30 kV, 40 mA). Field-emission scanning electron microscopy (FE-SEM) images were obtained using a ZEISS Gemini 300 microscope (Germany). TEM characterisation was conducted using an FEI Tecnai G2 F20 S-TWIN instrument (200 kV, USA). The surface structure and chemical bond information were investigated by XPS using a Thermo Escalab 250 Xi instrument with an Al-Kα source (hv = 1486.6 eV). The molecular structure was investigated by Raman spectroscopy using a LabRAMHR800 spectrometer with a 50× objective and 633 nm laser (Horiba Jobin-Yvon, France).

Electrocatalytic experiments

All measurements mentioned in “Ultra-low potential HCHO oxidation via EOD pathway and tandem reaction mechanism” and “Cathodic NO$_3$ reduction to NH$_3$” sections for the OER/HER, FOR/HER, and OER/NO$_3$-RR were performed using a CHI 660E electrochemical work station in an H-type cell separated by an anion exchange membrane at 25 °C.

For the OER/HER systems, the Pt foil, Pt foil, and Hg/HgO (sat. 1 M KOH) were used as the working, counter, and reference electrodes, respectively. Subsequently, 40 mL 1 M KOH was added to both the cathode and anode compartments.

For the FOR/HER systems, Cu$_2$O, Pt foil, and Hg/HgO were used as the working, counter, and reference electrodes, respectively, and 40 mL 1 M KOH and 1 M HCHO/KOH were added to the cathode and anode compartments, respectively.
For the OER/NO$_3^-$RR systems, Cu$_2$O, Pt foil, and Hg/HgO were used as the working, counter, and reference electrodes, respectively. Next, 40 mL 1 M KOH containing 400 ppm NO$_3^-$-N and 40 mL 1 M KOH were added to the cathode and anode compartments, respectively.

All measured potentials were calibrated with respect to the reversible hydrogen electrode (RHE) according to the following equation:

$$E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.059 \ \text{pH} + 0.095.$$

In addition, the measurements described in “Synergistic improvement of electrocatalytic anodic ultra-low potential HCHO oxidation with cathodic NO$_3^-$ reduction” section were obtained using a CHI 660E electrochemical working station in a two-electrode electrolyser H-type cell separated by an anion exchange membrane at room temperature.

For the OER/HER systems, Pt foils were used as both the working and counter electrodes and 40 mL 1 M KOH was added to both the cathode and anode compartments.

For the FOR/HER systems, anodic Cu$_2$O and cathodic Pt foils were used as the working and counter electrodes, respectively, and 40 mL 1 M KOH and 1 M HCHO/KOH were added to the cathode and anode compartments, respectively.

For the OER/NO$_3^-$RR systems, cathodic Cu$_2$O and anodic Pt foils were used as working and counter electrodes, respectively, and 40 mL 1 M KOH containing 100 ppm NO$_3^-$-N and 40 mL 1 M KOH were added to the cathode and anode compartments, respectively.

**Production determination**

**HCOOH determination**

HCOOH was identified and quantified by anion chromatography (SHIMADZU, IC-16i, Shodex IC SI-52 E4). The as-produced HCOOH was determined after diluting the post-test electrolytes to appropriate concentrations to match the calibration curve range.

**NO$_3^-$ and NO$_2^-$ determination**
NO$_3^-$ and NO$_2^-$ were identified and quantified by anion chromatography (SHIMADZU, IC-16i, Shodex IC SI-52 E4). The as-produced NO$_3^-$ and NO$_2^-$ concentrations were determined after diluting the post-test electrolytes to appropriate concentrations to match the calibration curve ranges.

**NH$_3$ determination**

The identification and quantification of NH$_3$ were achieved via cation chromatography (SHIMADZU, IC-16i, CS12A). The as-produced NH$_3$ was determined after diluting the post-test electrolytes to appropriate concentrations to match the calibration curve range.

**H$_2$ determination**

The identification and quantification of H$_2$ were achieved via gas chromatography (GC-2030, Shimadzu). The as-produced H$_2$ was determined after diluting the post-test gas in Ar atmosphere to appropriate concentrations to match the calibration curve range.

**Calculations of average yield rate and Faradaic efficiency**

**HCOOH**

The average yield rate of HCOOH was calculated as follows:

\[
R(\text{HCOOH}) = \frac{(C(\text{HCOOH}) \times V)}{(t \times S \times m(\text{HCOOH}))}
\]

where \(C(\text{HCOOH})\) is the measured HCOOH concentration (mg/L), \(V\) is the total electrolyte volume (L), \(t\) is electrocatalysis time (h), \(S\) is the catalyst area (cm$^2$), and \(m(\text{HCOOH})\) is the molecular mass of HCOOH (46 mg/mmol).

The Faradaic efficiency (FE) for HCOOH electrosynthesis can be calculated using the following formula:

\[
\text{EOD pathway: } \text{FE(EOD pathway)} = \frac{(F \times C(\text{HCOOH}) \times V)}{(46 \times Q)}
\]

\[
\text{Tandem reaction: } \text{FE(tandem reaction)} = \frac{(2F \times C(\text{HCOOH}) \times V)}{(46 \times Q)}
\]

\[
\text{Total reaction: } \text{FE} = \text{FE(EOD pathway)} + \text{FE(tandem reaction)}
\]

where \(F\) is the Faradaic constant (96,485.3 C mol$^{-1}$) and \(Q\) is the total charge passed through the working electrode (C).
NO₂⁻

The average production rate of NO₂⁻ was calculated as follows:

\[ R(\text{NO}_2^-) = \frac{(C(\text{NO}_2^-) \times V)}{(t \times S \times m(\text{NO}_2^-))} \]

where \( C(\text{NO}_2^-) \) is the measured NO₂⁻ concentration (mg/L), \( V \) is the total electrolyte volume (L), \( t \) is the electrocatalysis time (h), \( S \) is the catalyst area (cm²), and \( m(\text{NO}_2^-) \) is the molecular mass of NO₂⁻ (46 mg/mmol).

NH₃

The average production rate of NH₃ was calculated as follows:

\[ R(\text{NH}_3) = \frac{(C(\text{NH}_3) \times V)}{(t \times S \times m(\text{NH}_3))} \]

where \( C(\text{NH}_3) \) is the measured NH₃ concentration (mg/L), \( V \) is the total electrolyte volume (L), \( t \) is the electrocatalysis time (h), \( S \) is the catalyst area (cm²), and \( m(\text{NH}_3) \) is the molecular mass of NH₃ (17 mg/mmol).

The FE for NH₃ electrosynthesis can be calculated using the following formula:

\[ \text{FE} = \frac{(8 \times F \times C(\text{NH}_3) \times V)}{(17 \times Q)} \]

where \( F \) is the Faradaic constant (96,485.3 C mol⁻¹) and \( Q \) is the total charge passed through the working electrode (C).

NO₃⁻ conversion rate

The conversion rate of NO₃⁻ can be calculated using the following formula:

\[ \text{Conversion rate} = \frac{(C_{\text{initial}} - C_{\text{final}})}{C_{\text{initial}}} \times 100 \]

where \( C_{\text{initial}} \) is the initial NO₃⁻ concentration and \( C_{\text{final}} \) is the final NO₃⁻ concentration.

Calculations of the equivalent energy consumption for NH₃ synthesis

Reaction equations

Anode (EOD pathway): 2HCHO + 2OH⁻ - 2e⁻ → 2HCOOH + H₂

\[ \Delta G^0 = -203.152 \text{ kJ/mol} \]

\[ E^0 = -1.05 \text{ V}_{\text{RHE}} \text{ (pH = 14)} \]
\[ \Delta G^0 = -101.58 \text{ kJ/mol} \]

Anode (tandem reaction): \( \text{HCHO} + 2\text{OH}^- - 2e^- \rightarrow \text{HCOOH} + 2\text{H}_2\text{O} \)

\[ \Delta G^0 = -134.847 \text{ kJ/mol} \]

\[ E^0 = -0.699 \text{ V RHE} \ (pH = 14) \]

\[ \Delta G^0 = -134.847 \text{ kJ/mol} \]

In addition, the OER mechanism is summarized as:

Anode: \( 2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + 4e^- + \text{O}_2 \Delta G^0 = 237.129 \text{ kJ/mol} \)

\[ E^0 = 1.23 \text{ V RHE} \]

Cathode: \( \text{NO}_3^- + 6\text{H}_2\text{O} + 8e^- \rightarrow \text{NH}_3 + 9\text{OH}^- \)

\[ E^0 = -0.12 \text{ V RHE} \ (pH = 14) \]

**The equivalent energy consumption for \( \text{NH}_3 \) synthesis**

In the process of synthesizing \( \text{NH}_3 \) based on electrocatalytic \( \text{NO}_3^- \), \( \text{NO}_3^- \) is first converted into an intermediate of \( \text{NO}_2^- \) and then converted into \( \text{NH}_3 \). From the perspective of large-scale industrial synthesis, the electrons used to catalyze the synthesis of \( \text{NO}_2^- \) from \( \text{NO}_3^- \) or directly synthesize \( \text{NH}_3 \) are considered effective electrons, because ultimately \( \text{NO}_2^- \) will also be converted into \( \text{NH}_3 \). Thus, the equivalent Faradaic efficiency (FE) for \( \text{NH}_3 \) electrosynthesis from \( \text{NO}_3^- \) in large-scale industrial can be calculated using the following formula:

\[
\text{FE} (\text{NH}_3+\text{NO}_2^-) = \left(8F \times C(\text{NH}_3) \times V\right)/17 \times Q + \left(2F \times C(\text{NO}_2^-) \times V\right)/46 \times Q
\]

where \( F \) is the Faradaic constant (96,485.3 C mol\(^{-1}\)), \( Q \) is the total charge passed through the working electrode (C) and \( V \) is the volume of electrolyte (40 ml).

Furthermore, the equivalent energy consumption (W) for \( \text{NH}_3 \) synthesis per unit mass is defined as:

\[
E = UQ
\]

\[
m = (\text{FE} \times Q \times M)/(8F)
\]

\[
W = E/m = (U \times Q \times 8F)/(\text{FE} \times Q \times M) = 45.405U/\text{FE} \ (\text{kJ/g}_{\text{NH}_3})
\]
where $U$ is the cell voltage, $F$ is the Faradaic constant ($96,485.3 \text{ C mol}^{-1}$), $Q$ is the total charge passed through the working electrode (C), $E$ is the total energy required to unit mass NH$_3$ synthesis, $M$ is molar mass of NH$_3$ (17 g/mol).
Results and Discussion

1. Supplementary Figures

Fig. S1. SEM images of Cu foam.
Fig. S2. XRD patterns of Cu, CuO and Cu₂O.

Fig. S3. SEM images of obtained Cu₂O at the Cu foam.
**Fig. S4.** Schematic diagram of the synthesis of CuO and Cu$_2$O.

![Schematic diagram of the synthesis of CuO and Cu$_2$O.](image1)

**Fig. S5.** HRTEM images of Cu$_2$O.

![HRTEM images of Cu$_2$O.](image2)

**Fig. S6.** XPS spectra of CuO/CF and Cu$_2$O/CF, showing the presence of Cu$^{II}$ and Cu$^{I}$ species.

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![Fig. S13](image)

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![Fig. S14](image)
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**Fig. S16.** The measured $\text{H}_2$ production rate in anodic HCHO oxidation reaction ranged from the potential 0.1 to 1.1 V$_{\text{RHE}}$. 
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Fig. S30. (a) Ion chromatography calibration curves and (b) the corresponding chromatograms of NO$_2$-N in the concentration range of 20-100 ppm (mg/L) in which the solution environment is 0.5 M KOH.

![Graph showing NO$_2$-N accumulation vs. potential](image)

Fig. S31. the NO$_2$-N yield of cathodic NO$_3$-RR/Cu, NO$_3$-RR/Cu$_2$O, and NO$_3$-RR/CuO in a three-electrode electrolyzer under the condition of the anolyte including 1M KOH, and the catholyte including 1M KOH and 400 ppm NO$_3$-N.

![Graph showing NH$_3$ production rate and Faraday efficiency](image)
**Fig. S32.** The cycling tests of NO$_3^-$RR/Cu$_2$O at -0.5 V$_{RHE}$ for 1h of each cycle in the anolyte including 1M KOH, and the catholyte including 1M KOH and 400 ppm NO$_3^-$.

![Graph showing current density vs. cell voltage for different combinations of Cu$_2$O/HCHO + Cu/NO$_3^-$, Cu$_2$O/HCHO + Cu$_2$O/NO$_3^-$, and Cu$_2$O/HCHO + CuO/NO$_3^-$](image)

**Fig. S33.** LSV curves of the anodic FOR/Cu$_2$O combined cathodic NO$_3^-$RR/Cu, NO$_3^-$RR/Cu$_2$O, and NO$_3^-$RR/CuO in a two-electrode electrolyzer under the condition of the anolyte including 1 M KOH and 1 M HCHO, and the catholyte including 1 M KOH and 100 ppm NO$_3^-$-N.

![Graph showing conversion rate and Faraday efficiency for Cu, Cu$_2$O, and CuO](image)
**Fig. S34.** The NO$_3^-$ conversion rate and Faradaic efficiency of the anodic FOR/Cu$_2$O combined cathodic NO$_3$-RR/Cu, NO$_3$-RR/Cu$_2$O, and NO$_3$-RR/CuO in a two-electrode electrolyzer at the cell voltage of 1.0 V under the condition of the anolyte including 1 M KOH and 1 M HCHO, and the catholyte including 1 M KOH and 100 ppm NO$_3^-$-N.

**Fig. S35.** LSV curves of the anodic FOR/Cu$_2$O (1 M KOH/HCHO) and OER (1 M KOH) combined cathodic NO$_3$-RR/Cu$_2$O in a two-electrode electrolyzer under the catholyte including 1 M KOH and 100 ppm NO$_3^-$-N.
**Fig. S36.** NH$_3$-N and NO$_3^-$-N yield for NO$_3^-$RR/Cu$_2$O matched with FOR/Cu$_2$O after holding various potentials for 2 h by applying cell voltage of 1.0 V in the anolyte including 1M KOH/HCHO and the catholyte including 1M KOH/100, 200 400 ppm NO$_3^-$-N.

**Fig. S37.** Faradaic efficiency of NH$_3$-N and NO$_2^-$-N for NO$_3^-$RR/Cu$_2$O matched with FOR/Cu$_2$O after holding various potentials for 2 h by applying cell voltage of 1.0 V in the anolyte including 1M KOH/HCHO and the catholyte including 1M KOH/100, 200 400 ppm NO$_3^-$-N.
**Fig. S38.** Charge transfer for NO$_3^-$RR/Cu$_2$O matched with FOR/Cu$_2$O after holding various potentials for 2 h by applying cell voltage of 1.0 V in the anolyte including 1M KOH/HCHO and the catholyte including 1 M KOH/100, 200 400 ppm NO$_3^-$-N.

**Fig. S39.** The HCOOH yield in the anode for 2 h of the anodic FOR/Cu$_2$O combined cathodic NO$_3^-$RR/Cu$_2$O in a two-electrode electrolyzer at the cell voltage of 1.0 V under the condition of the anolyte including 1 M KOH and 1 M HCHO, and the catholyte including 1 M KOH and 100 ppm NO$_3^-$-N.
**Fig. S40.** (a) and (b) SEM for anodic Cu$_2$O after test for 20 h (10 times) by applying cell voltage of 1.0 V in the anolyte including 1 M KOH/HCHO and the catholyte including 1 M KOH/100 ppm NO$_3$-N. (c) and (d) SEM for cathodic Cu$_2$O after test for 20 h (10 times) by applying cell voltage of 1.0 V in the anolyte including 1 M KOH/HCHO and the catholyte including 1 M KOH/100 ppm NO$_3$-N.
Fig. S41. XRD for anodic Cu$_2$O before and after test for 20 h (10 times) by applying cell voltage of 1.0 V in the anolyte including 1 M KOH/HCHO and the catholyte including 1 M KOH/100 ppm NO$_3^-$-N.

![XRD image for anodic Cu$_2$O before and after test](image)

Fig. S42. XRD for cathodic Cu$_2$O before and after test for 20 h (10 times) by applying cell voltage of 1.0 V in the anolyte including 1 M KOH/HCHO and the catholyte including 1 M KOH/100 ppm NO$_3^-$-N.

![XRD image for cathodic Cu$_2$O before and after test](image)
**Fig. S43.** NO$_3^-$ conversion rate and Faradaic efficiency for NO$_3^-$RR/Cu$_2$O matched with FOR/Cu$_2$O after holding various potentials for 2 h in the anolyte including 1 M KOH/HCHO and the catholyte including 1 M KOH/100 ppm NO$_3^-$-N ranging the cell voltage of 0.3 V from 1.0 V.

**Fig. S44.** The equivalent energy consumption for NH$_3$ synthesis in a two-electrode electrolyzer.
2. Supplementary Tables

**Table S1** Comparing the potential required for different anodic reactions to reach a current of 10 mA cm$^{-2}$ in a three-electrode set.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Anodic electrolyte</th>
<th>Cathodic reaction</th>
<th>Potential (10 mA cm$^{-2}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_2$O</td>
<td>1 M KOH/ 1 M HCHO</td>
<td>HER</td>
<td>0.026 V$_{RHE}$</td>
<td>This work</td>
</tr>
<tr>
<td>Pt foil</td>
<td>1 M KOH</td>
<td>HER</td>
<td>1.97 V$_{RHE}$</td>
<td>This work</td>
</tr>
<tr>
<td>CuONS/CF</td>
<td>1 M KOH/ 1 M CH$_3$OH</td>
<td>HER</td>
<td>About 1.2 V$_{RHE}$</td>
<td>Angew. Chem. Int. Ed. 2021, 60, 314–3155</td>
</tr>
<tr>
<td>PdAg/NF</td>
<td>0.5 M KOH/ 1 M Ethylene glycol</td>
<td>HER</td>
<td>0.57 V$_{RHE}$</td>
<td>Chem Catal. 2021, 1, 941–955</td>
</tr>
<tr>
<td>CoNiCuMnMo</td>
<td>1 M KOH/ 0.1 M Glycerol</td>
<td>HER</td>
<td>0.55 V$_{RHE}$</td>
<td>J. Am. Chem. Soc. 2022, 144, 16, 7224–7235</td>
</tr>
<tr>
<td>R-NiCuO</td>
<td>1 M KOH/ 0.1 M Glycerol</td>
<td>HER</td>
<td>1.2 V$_{RHE}$</td>
<td>Energy Environ. Sci. 2022, 15, 3004–3014</td>
</tr>
</tbody>
</table>

**Table S2** Comparing the potential required for different anodic reactions to reach a current of 300 mA cm$^{-2}$ in a three-electrode set.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Anodic electrolyte</th>
<th>Cathodic reaction</th>
<th>Potential (300 mA cm$^{-2}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_2$O</td>
<td>1 M KOH/ 1 M HCHO</td>
<td>HER</td>
<td>0.812 V$_{RHE}$</td>
<td>This work</td>
</tr>
<tr>
<td>Pt foil</td>
<td>1 M KOH</td>
<td>HER</td>
<td>2.37 V$_{RHE}$</td>
<td>This work</td>
</tr>
<tr>
<td>CuONS/CF</td>
<td>1 M KOH/ 1 M CH$_3$OH</td>
<td>HER</td>
<td>About 1.7 V$_{RHE}$</td>
<td>Angew. Chem. Int. Ed. 2021, 60, 314–3155</td>
</tr>
<tr>
<td>PdAg/NF</td>
<td>0.5 M KOH/ 1 M Ethylene glycol</td>
<td>HER</td>
<td>Above1.4 V$_{RHE}$</td>
<td>Chem Catal. 2021, 1, 941–955</td>
</tr>
<tr>
<td>CoNiCuMnMo</td>
<td>1 M KOH/ 0.1 M Glycerol</td>
<td>HER</td>
<td>Above 1.4 V$_{RHE}$</td>
<td>J. Am. Chem. Soc. 2022, 144, 16, 7224–7235</td>
</tr>
<tr>
<td>R-NiCuO</td>
<td>1 M KOH/ 0.1 M Glycerol</td>
<td>HER</td>
<td>Above 1.6 V$_{RHE}$</td>
<td>Energy Environ. Sci. 2022, 15, 3004–3014</td>
</tr>
</tbody>
</table>

**Table S3** Comparison of HCOOH production rates from the FOR reaction and other CRR that have been reported.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>HCOOH production rates (μmol cm$^{-2}$ h$^{-1}$)</th>
<th>Potential (V versus RHE)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_2$O</td>
<td>9608</td>
<td>0.9 V$_{RHE}$</td>
<td>This work</td>
</tr>
<tr>
<td>ZnIn$_2$S$_4$</td>
<td>8879</td>
<td>- 1.18 V$_{RHE}$</td>
<td>Nat. Commun. 2021, 12, 5835.</td>
</tr>
<tr>
<td>BiIn alloy NPs</td>
<td>5170</td>
<td>- 0.95 V$_{RHE}$</td>
<td>Appl. Catal. B-Environ. 2022, 311, 121377</td>
</tr>
<tr>
<td>BiSn</td>
<td>4299</td>
<td>- 1.15 V$_{RHE}$</td>
<td>Adv. Sci. 2020, 7, 1902989.</td>
</tr>
<tr>
<td>Bi/CeO$_2$</td>
<td>2600</td>
<td>- 1.3 V$_{RHE}$</td>
<td>Angew. Chem. Int. Ed. 2021, 60, 8798–8802</td>
</tr>
<tr>
<td>MIL-68(In)-NH$_2$</td>
<td>2104</td>
<td>- 1.1 V$_{RHE}$</td>
<td>Angew. Chem. Int. Ed. 2021, 60, 19107–19112</td>
</tr>
<tr>
<td>Bi-BTB</td>
<td>902</td>
<td>- 0.7 V$_{RHE}$</td>
<td>J. Mater. Chem. A 2020, 8, 24486–24492</td>
</tr>
<tr>
<td>GaN:Sn</td>
<td>201</td>
<td>- 0.53 V$_{RHE}$</td>
<td>Energy Environ. Sci. 2019, 12, 2842–2848</td>
</tr>
</tbody>
</table>
Table S4 Comparison of the required potential to achieve 10 mA cm\(^{-2}\) in coupling systems that have been reported.

<table>
<thead>
<tr>
<th>Anodic system (1 M KOH)</th>
<th>Cathodic system</th>
<th>Reactor</th>
<th>Potential (10 mA cm(^{-2}))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 M HCHO/CuO</td>
<td>1 M KOH 100 ppm NO(_3^−)-N/CuO</td>
<td>H-cell</td>
<td>-0.19 V</td>
<td>This work</td>
</tr>
<tr>
<td>1 M CH(_3)OH/CuO</td>
<td>1 M KHCO(_3), CO(_2)/SnO(_2)</td>
<td>H-cell</td>
<td>0.93 V</td>
<td>Angew. Chem. Int. Ed. 2021, 60, 3148–3155.</td>
</tr>
<tr>
<td>0.1 M HMF/Cu foam</td>
<td>1 M KOH/Pt/C</td>
<td>H-cell</td>
<td>Higher than 0 V</td>
<td>Nat. Catal. 2022, 5, 66–73.</td>
</tr>
<tr>
<td>0.2 M furfural/Cu foam</td>
<td>1 M KOH/Pt/C</td>
<td>H-cell</td>
<td>Higher than 0 V</td>
<td>Nat. Catal. 2022, 5, 66–73.</td>
</tr>
<tr>
<td>0.1 M glycerol/NiCo hydroxide</td>
<td>1 M KOH/graphite rod</td>
<td>H-cell</td>
<td>1.33 V</td>
<td>Nat. Commun. 2022, 13, 3777.</td>
</tr>
<tr>
<td>0.1 M glycerol/NiCuO</td>
<td>1 M KOH and 0.1 M KNO(_3)/R-NiCu-OH</td>
<td>flow cell</td>
<td>Near 1.0 V</td>
<td>Energy Environ. Sci., 2022, 15, 3004–3014.</td>
</tr>
</tbody>
</table>