# Coupling electrocatalytic cathodic nitrate reduction with anodic formaldehyde

# oxidation at ultra-low potential over Cu<sub>2</sub>O

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#### **Experimental Procedures**

#### **Raw materials**

Ammonium persulfate ((NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 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 (CH<sub>3</sub>OH, 99.5%, AR) and ammonium chloride (NH<sub>4</sub>Cl,  $\geq$ 99.5%) were purchased from Aladdin. All chemicals were used as received without further purification.

#### Material synthesis

#### Cu Foam

Commercial Cu foam (1 cm  $\times$  1 cm  $\times$  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 NO<sub>3</sub>-RR.

#### CuO

A one-step oxidation method was used to synthesise CuO nanosheets on the Cu foam. Four pieces of Cu foam (1 cm  $\times$  1 cm  $\times$  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 (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. 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 Cu<sub>2</sub>O and for the electrocatalytic NO<sub>3</sub>-RR.

## Cu<sub>2</sub>O

To synthesise the Cu<sub>2</sub>O nanosheets, the obtained CuO was immersed in a solution containing 40 mL 1 M KOH/HCHO for 1 h. The obtained Cu<sub>2</sub>O was washed three times with water and ethanol respectively and dried at 60 °C under vacuum overnight. The obtained Cu<sub>2</sub>O was used for electrocatalytic HCHO oxidation and NO<sub>3</sub>-RR.

## Characterization

Powder XRD spectra were obtained at steps of 7° min<sup>-1</sup> in the range 10–80° using a Shimadzu Xray diffractometer (XRD-6100, Japan) with Cu-K $\alpha$  radiation ( $\lambda = 1.54184$  Å, 30 kV, 40 mA). Fieldemission 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-K $\alpha$  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<sub>3</sub>**<sup>-</sup> **reduction to NH<sub>3</sub>**" sections for the OER/HER, FOR/HER, and OER/NO<sub>3</sub><sup>-</sup>RR were performed using a CHI 660E electrochemical work station in an Htype 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<sub>2</sub>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<sub>3</sub>-RR systems, Cu<sub>2</sub>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<sub>3</sub>-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:

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

In addition, the measurements described in "**Synergistic improvement of electrocatalytic anodic ultra-low potential HCHO oxidation with cathodic NO**<sub>3</sub><sup>-</sup> **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<sub>2</sub>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<sub>3</sub>-RR systems, cathodic Cu<sub>2</sub>O and anodic Pt foils were used as working and counter electrodes, respectively, and 40 mL 1 M KOH containing 100 ppm NO<sub>3</sub>-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.

## NO3<sup>-</sup> and NO2<sup>-</sup> 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<sub>3</sub> 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<sub>2</sub> 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

## НСООН

The average yield rate of HCOOH was calculated as follows:

R(HCOOH) = (C(HCOOH) \* V)/(t \* S \* m(HCOOH))

where C(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<sup>-2</sup>), and m(HCOOH) is the molecular mass of HCOOH (46 mg/mmol).

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

EOD pathway: FE(EOD pathway) =  $(F \times C(HCOOH) \times V)/(46 \times Q)$ 

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

Total reaction: FE = FE(EOD pathway) + FE(tandem reaction)

where F is the Faradaic constant (96,485.3 C mol<sup>-1</sup>) and Q is the total charge passed through the working electrode (C).

## $NO_2^-$

The average production rate of NO<sub>2</sub><sup>-</sup> was calculated as follows:

 $R(NO_2^{-}) = (C(NO_2^{-}) * V)/(t * S * m(NO_2^{-}))$ 

where  $C(NO_2^{-1})$  is the measured  $NO_2^{-1}$  concentration (mg/L), V is the total electrolyte volume (L), t is the electrocatalysis time (h), S is the catalyst area (cm<sup>-2</sup>), and m(NO<sub>2</sub><sup>-1</sup>) is the molecular mass of NO<sub>2</sub><sup>-1</sup> (46 mg/mmol).

## NH<sub>3</sub>

The average production rate of NH<sub>3</sub> was calculated as follows:

 $R_{(NH_{3})} = (C_{(NH_{3})} * V)/(t * S * m_{(NH_{3})})$ 

where  $C_{(NH_3)}$  is the measured NH<sub>3</sub> concentration (mg/L), V is the total electrolyte volume (L), t is the electrocatalysis time (h), S is the catalyst area (cm<sup>-2</sup>), and m<sub>(NH<sub>3</sub>)</sub> is the molecular mass of NH<sub>3</sub> (17 mg/mmol).

The FE for NH<sub>3</sub> electrosynthesis can be calculated using the following formula:

 $FE = (8 F \times C_{(NH_{3})} \times V) / (17 \times Q)$ 

where F is the Faradaic constant (96,485.3 C mol<sup>-1</sup>) and Q is the total charge passed through the working electrode (C).

#### NO<sub>3</sub><sup>-</sup> conversion rate

The conversion rate of  $NO_3^-$  can be calculated using the following formula:

Conversion rate =  $(C_{initial} - C_{final})/C_{initial}*100$ 

where  $C_{initial}$  is the initial NO<sub>3</sub><sup>-</sup> concentration and  $C_{final}$  is the final NO<sub>3</sub><sup>-</sup> concentration.

#### Calculations of the equivalent energy consumption for NH<sub>3</sub> synthesis

#### **Reaction equations**

Anode (EOD pathway): 2HCHO + 2OH<sup>-</sup> - 2e<sup>-</sup>  $\rightarrow$  2HCOOH + H<sub>2</sub>

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

 $E^0 = -1.05 V_{RHE} (pH = 14)$ 

 $\Delta G^0 = -101.58 \text{ kJ/mol}_{(\text{HCHO})}$ 

Anode (tandem reaction): HCHO + 2OH<sup>-</sup> - 2e<sup>-</sup>  $\rightarrow$  HCOOH + 2H<sub>2</sub>O  $\Delta G^0 = -134.847 \text{ kJ/mol}$   $E^0 = -0.699 \text{ V}_{\text{RHE}} (\text{pH} = 14)$   $\Delta G^0 = -134.847 \text{ kJ/mol}_{(\text{HCHO})}$ In addition, the OER mechanism is summarized as: Anode: 2H<sub>2</sub>O  $\rightarrow$  4H<sup>+</sup> + 4e<sup>-</sup> + O<sub>2</sub>  $\Delta G^0 = 237.129 \text{ kJ/mol}$   $E^0 = 1.23 \text{ V}_{\text{RHE}}$ Cathode: NO<sub>3</sub><sup>-</sup> + 6H<sub>2</sub>O + 8e<sup>-</sup>  $\rightarrow$  NH<sub>3</sub> + 9OH<sup>-</sup>  $E^0 = -0.12 \text{ V}_{\text{RHE}} (\text{pH} = 14)$ 

## The equivalent energy consumption for NH<sub>3</sub> synthesis

In the process of synthesizing NH<sub>3</sub> based on electrocatalytic NO<sub>3</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup> is first converted into an intermediate of NO<sub>2</sub><sup>-</sup> and then converted into NH<sub>3</sub>. From the perspective of large-scale industrial synthesis, the electrons used to catalyze the synthesis of NO<sub>2</sub><sup>-</sup> from NO<sub>3</sub><sup>-</sup> or directly synthesize NH<sub>3</sub> are considered effective electrons, because ultimately NO<sub>2</sub><sup>-</sup> will also be converted into NH<sub>3</sub>. Thus. the equivalent Faradaic efficiency (FE) for NH<sub>3</sub> electrosynthesis from NO<sub>3</sub><sup>-</sup> in large-scale industrial can be calculated using the following formula:

$$FE (NH_3 + NO_2) = (8F \times C(NH_3) \times V) / 17 \times Q) + (2F \times C(NO_2) \times V) / 46 \times Q)$$

where F is the Faradaic constant (96,485.3 C mol<sup>-1</sup>), 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 NH<sub>3</sub> synthesis per unit mass is defined as:

$$E = UQ$$
  
 $m = (FE*Q*M)/(8F)$   
 $W=E/m= (U*Q*8F)/(FE*Q*M) = 45.405U/FE (kJ/g_{NH3})$ 

where U is the cell voltage, F is the Faradaic constant (96,485.3 C mol<sup>-1</sup>), Q is the total charge passed through the working electrode (C), E is the total energy required to unit mass NH<sub>3</sub> synthesis, M is molar mass of NH<sub>3</sub> (17 g/mol).

## **Results and Discussion**

# 1. Supplementary Figures



Fig. S1. SEM images of Cu foam.



**Fig. S2.** XRD patterns of Cu, CuO and Cu<sub>2</sub>O.



Fig. S3. SEM images of obtained  $Cu_2O$  at the Cu foam.



Fig. S4. Schematic diagram of the synthesis of CuO and Cu<sub>2</sub>O.



Fig. S5. HRTEM images of Cu<sub>2</sub>O.



Fig. S6. XPS spectra of Cu 2p for CuO and Cu<sub>2</sub>O.



Fig. S7. XPS survey spectrums of (a) CuO and (b) Cu<sub>2</sub>O



Fig. S8. Raman spectroscopy of CuO and Cu<sub>2</sub>O.



**Fig. S9.** Anodic potentials to achieve varied current densities (10, 100, 200, and 300 mA cm<sup>-2</sup>) by  $Cu_2O$  in 1.0 M KOH with 1.0 M HCHO and Pt foil in 1.0 M KOH without the addition of 1.0 M HCHO.



Fig. S10. LSV curves of (a) 1 M, (b) 0.5 M (c) 0.2 M (d) 0.1 M HCHO oxidation using Cu<sub>2</sub>O foam as the anode and Pt foil as the cathode.



Fig. S11. *Ex-situ* XRD spectra of Cu<sub>2</sub>O after holding at the potential of 0.9  $V_{RHE}$  for 0 s, 200 s, and 400 s ranging from 10-40°.



**Fig. S12.** (a) Ion chromatography calibration curves and (b) the corresponding chromatograms of HCOOH in the concentration range of 1-20 ppm (mg/L) in which the solution environment is 0.01 M KOH.



**Fig. S13.** (a) Ion chromatography calibration curves and (b) the corresponding chromatograms of HCOOH in the concentration range of 20-100 ppm (mg/L) in which the solution environment is 0.01 M KOH.



**Fig. S14.** (a) Ion chromatography calibration curves and (b) the corresponding chromatograms of HCOOH in the concentration range of 100-1000 ppm (mg/L) in which the solution environment is 0.01 M KOH.



Fig. S15. (a) Gas chromatography calibration curves and (b) the corresponding chromatograms of  $H_2$  in the concentration range of 104.4-2002.6 ppm (mg/L) in the Ar atmosphere.



Fig. S16. The measured  $H_2$  production rate in anodic HCHO oxidation reaction ranged from the potential 0.1 to 1.1  $V_{RHE}$ .



Fig. S17. Time-accumulation plots of  $H_2$  over  $Cu_2O$  under low potential in the solution of 1 M KOH/HCHO.



Fig. S18. Time-accumulation plots of  $H_2$  over  $Cu_2O$  under high potential in the solution of 1 M KOH/HCHO.



**Fig. S19.** Time-accumulation plots of HCOOH over Cu<sub>2</sub>O under low potential in the solution of 1 M KOH/HCHO.



Fig. S20. Time-accumulation plots of HCOOH over  $Cu_2O$  under high potential in the solution of 1 M KOH/HCHO.



**Fig. S21.** The Faradaic efficiency of FOR/Cu<sub>2</sub>O at various potentials for 1h in the electrolyte including 1 M KOH/HCHO, matched with HER.



Fig. S22. The cycling tests of FOR/Cu<sub>2</sub>O at 0.9  $V_{RHE}$  for 1h of each cycle in the electrolyte including 1 M KOH/HCHO.



Fig. S23. SEM images of obtained CuO at the Cu foam.



Fig. S24. SEM images of Cu foam which was reduced in 1 M KOH by holding the potential at -0.5  $V_{RHE}$  for 1 h.



Fig. S25. SEM images of CuO foam which was reduced in 1 M KOH by holding the potential at -0.5  $V_{RHE}$  for 1 h.



Fig. S26. The measurement annotation of the nanosheet thickness for SEM for  $Cu_2O$  (a) before and (b) after reduced in 1 M KOH by holding the potential at -0.5  $V_{RHE}$  for 1 h. SEM for CuO (c) before and (d) after reduced in 1 M KOH by holding the potential at -0.5  $V_{RHE}$  for 1 h.



**Fig. S27.** SEM images of  $Cu_2O$  foam which was reduced in 1 M KOH by holding the potential at -0.5





Fig. S28. (a) Ion chromatography calibration curves and (b) the corresponding chromatograms of  $NH_3$  in the concentration range of 20-100 ppm (mg/L) in which the solution environment is 0.5 M KOH.



Fig. S29. (a) Ion chromatography calibration curves and (b) the corresponding chromatograms of  $NH_3$  in the concentration range of 100-200 ppm (mg/L) in which the solution environment is 0.5 M KOH.



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.



**Fig. S31.** the NO<sub>2</sub><sup>-</sup>-N yield of cathodic NO<sub>3</sub><sup>-</sup>RR/Cu, NO<sub>3</sub><sup>-</sup>RR/Cu<sub>2</sub>O, and NO<sub>3</sub><sup>-</sup>RR/CuO in a threeelectrode electrolyzer under the condition of the anolyte including 1M KOH, and the catholyte including 1M KOH and 400 ppm NO<sub>3</sub><sup>-</sup>-N.



Fig. S32. The cycling tests of  $NO_3$ -RR/Cu<sub>2</sub>O at -0.5 V<sub>RHE</sub> for 1h of each cycle in the anolyte including 1M KOH, and the catholyte including 1M KOH and 400 ppm  $NO_3^-$ .



**Fig. S33.** LSV curves of the anodic FOR/Cu<sub>2</sub>O combined cathodic NO<sub>3</sub><sup>-</sup>RR/Cu, NO<sub>3</sub><sup>-</sup>RR/Cu<sub>2</sub>O, and NO<sub>3</sub><sup>-</sup>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<sub>3</sub><sup>-</sup>-N.



**Fig. S34.** The  $NO_3^-$  conversion rate and Faradaic efficiency of the anodic FOR/Cu<sub>2</sub>O combined cathodic  $NO_3^-RR/Cu$ ,  $NO_3^-RR/Cu_2O$ , 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<sub>2</sub>O (1 M KOH/HCHO) and OER (1 M KOH) combined cathodic NO<sub>3</sub>-RR/Cu<sub>2</sub>O in a two-electrode electrolyzer under the catholyte including 1 M KOH and 100 ppm NO<sub>3</sub>-N.



**Fig. S36.**  $NH_3$ -N and  $NO_2^-$ -N yield for  $NO_3^-RR/Cu_2O$  matched with FOR/Cu<sub>2</sub>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<sub>3</sub>-N and NO<sub>2</sub><sup>-</sup>-N for NO<sub>3</sub><sup>-</sup>RR/Cu<sub>2</sub>O matched with FOR/Cu<sub>2</sub>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<sub>3</sub><sup>-</sup>-N.



**Fig. S38.** Charge transfer for NO<sub>3</sub>-RR/Cu<sub>2</sub>O matched with FOR/Cu<sub>2</sub>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<sub>3</sub>-N.



**Fig. S39**. The HCOOH yield in the anode for 2 h of the anodic  $FOR/Cu_2O$  combined cathodic  $NO_3^-$  RR/Cu<sub>2</sub>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<sub>2</sub>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<sub>3</sub><sup>-</sup>-N.
(c) and (d) SEM for cathodic Cu<sub>2</sub>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<sub>3</sub><sup>-</sup>-N.



**Fig. S41.** XRD for anodic  $Cu_2O$  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  $NO_3^--N$ .



Fig. S42. XRD for cathodic  $Cu_2O$  before and after test for 20 h (10 times) by applying cell voltage of 1.0 V in the analyte including 1 M KOH/HCHO and the catholyte including 1 M KOH/100 ppm  $NO_3^{-}$ -N.



**Fig. S43**.  $NO_3^-$  conversion rate and Faradaic efficiency for  $NO_3^-RR/Cu_2O$  matched with FOR/Cu<sub>2</sub>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<sub>3</sub> 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<sup>-2</sup> in a three-electrode set.

Catalysts	Anodic electrolyte	Cathodic reaction	Potential (10 mA cm <sup>-2</sup> )	Ref.
Cu <sub>2</sub> O	1 М КОН/ 1 М НСНО	HER	0.026 V <sub>RHE</sub>	This work
Pt foil	1 M KOH	HER	1.97 V <sub>RHE</sub>	This work
CuONS/CF	1 M KOH/ 1 M CH <sub>3</sub> OH	HER	About 1.2 V <sub>RHE</sub>	Angew. Chem. Int. Ed. 2021, 60, 314 –3155
PdAg/NF	0.5 M KOH/ 1 M Ethylene glycol	HER	0.57 V <sub>RHE</sub>	Chem Catal. 2021, 1, 941–955
CoNiCuMnMo	1 M KOH/0.1 M Glycerol	HER	0.55 V <sub>RHE</sub>	J. Am. Chem. Soc. 2022, 144, 16, 7224–7235
R-NiCuO	1 M KOH/0.1 M Glycerol	HER	1.2 V <sub>RHE</sub>	<i>Energy Environ. Sci.</i> , 2022, 15, 3004–3014

**Table S2** Comparing the potential required for different anodic reactions to reach a current of 300 mAcm<sup>-2</sup> in a three-electrode set.

Catalysts	Anodic electrolyte	Cathodic reaction	Potential (300 mA cm <sup>-2</sup> )	Ref.
Cu <sub>2</sub> O	1 М КОН/ 1 М НСНО	HER	0.812 V <sub>RHE</sub>	This work
Pt foil	1 M KOH	HER	2.37 V <sub>RHE</sub>	This work
CuONS/CF	1 M KOH/ 1 M CH <sub>3</sub> OH	HER	About 1.7 V <sub>RHE</sub>	Angew. Chem. Int. Ed. 2021, 60, 314 –3155
PdAg/NF	0.5 M KOH/ 1 M Ethylene glycol	HER	Above1.4 V <sub>RHE</sub>	<i>Chem Catal.</i> 2021, 1, 941– 955
CoNiCuMnMo	1 M KOH/0.1 M Glycerol	HER	Above 1.4 V <sub>RHE</sub>	J. Am. Chem. Soc. 2022, 144, 16, 7224–7235
R-NiCuO	1 M KOH/0.1 M Glycerol	HER	Above 1.6 V <sub>RHE</sub>	<i>Energy Environ. Sci.</i> 2022, 15, 3004–3014

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

 been reported.

Catalysts	HCOOH production rates (µmol cm <sup>-2</sup> h <sup>-1</sup> )	Potential (V versus RHE)	Ref.
Cu <sub>2</sub> O	9698	0.9 V <sub>RHE</sub>	This work
ZnIn <sub>2</sub> S <sub>4</sub>	8879	- 1.18 V <sub>RHE</sub>	Nat. Commun. 2021, 12, 5835.
BiIn alloy NPs	5170	- 0.95 V <sub>RHE</sub>	Appl. Catal. B-Environ. 2022, 311, 121377.
BiSn	4299	$\sim$ -1.15 V <sub>RHE</sub>	Adv. Sci. 2020, 7, 1902989.
Bi/CeO <sub>2</sub>	2600	- 1.3 V <sub>RHE</sub>	Angew. Chem. Int. Ed. 2021, 60, 8798– 8802.
MIL-68(In)-NH <sub>2</sub>	2104	- 1.1 V <sub>RHE</sub>	Angew. Chem. Int. Ed. 2021, 60, 19107–19112.
Bi-BTB	902	- 0.7 V <sub>RHE</sub>	J. Mater. Chem. A 2020, 8, 24486– 24492.
GaN:Sn	201	- 0.53 V <sub>RHE</sub>	<i>Energy Environ. Sci.</i> 2019, 12, 2842–2848.

**Table S4** Comparison of the required potential to achieve 10 mA cm<sup>-2</sup> in coupling systems that have been reported.

Anodic system (1 M KOH)	Cathodic system	Reactor	Potential (10 mA cm <sup>-2</sup> )	Ref.
1 M	1 M KOH 100 ppm NO <sub>3</sub> -	H-cell	- 0.19 V	This work
HCHO/Cu <sub>2</sub> O	-N/Cu <sub>2</sub> O			
1 M	1 M KHCO <sub>3</sub> , CO <sub>2</sub> /SnO <sub>2</sub>	H-cell	0.93 V	Angew. Chem. Int. Ed.
CH <sub>3</sub> OH/CuO				2021, 60, 3148–3155.
0.1 M HMF/Cu	1 M KOH/Pt/C	H-cell	Higher than 0 V	Nat. Catal. 2022, 5, 66–73.
foam				
0.2 M	1 M KOH/Pt/C	H-cell	Higher than 0 V	Nat. Catal. 2022, 5, 66–73.
furfural/Cu			_	
foam				
0.1 M	1 M KOH/graphite rod	H-cell	1.33 V	Nat. Commun. 2022, 13,
glycerol/NiCo				3777.
hydroxide				
0.1 M	1 M KOH and 0.1 M	flow cell	Near 1.0 V	Energy Environ. Sci., 2022,
glycerol/NiCuO	KNO <sub>3</sub> /R-NiCu-OH			15, 3004–3014.