Supporting information for

Enhanced Nitrate-to-Ammonia Activity on CuNi Alloys via Tuning of Intermediate Adsorption

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Materials and methods

Catalyst preparation. All catalysts were prepared via electrodeposition. 0.05 M H₂SO₄ (Sigma-Aldrich) solutions containing 20 mM CuSO₄ + NiSO₄ (Sigma-Aldrich) were used as the deposition baths. The Cu:Ni ratios in the deposited catalysts were controlled by the ratio of CuSO₄ vs. NiSO₄. A three-electrode system was employed for catalyst deposition. A Platinum foil and Ag/AgCl electrode (filled with 3 M KCl) were used as counter and reference electrodes. The electrodeposition was conducted at -1.7 V vs. Ag/AgCl for 400 seconds. Glassy carbon electrodes, 300 nm sputtered Cu on polytetrafluoroethylene (PTFE) membranes (pore size = 400 nm), and Cu foams were used as substrates. The as-made electrodes were rinsed by deionized water (18 MΩ) and dried with N₂.

Material characterization. The crystal structures of the samples were characterized via X-Ray Diffraction with the MiniFlex600 using Cu-K α radiation ($\lambda = 0.15406$ nm) at room temperature. Scanning electron microscopy (Hitachi S-5200) and transmission electron microscopy (Hitachi HF3300) were employed to observe the morphology of the samples. Xray photoelectron spectroscopy (XPS) measurements were carried out on a Thermofisher Scientific K-Alpha spectrometer, using Al K α X-ray radiation (1486.6 eV) for excitation. Operando hard X-ray absorption measurements were performed at the 9BM beamline of the Advanced Photon Source (APS) synchrotron facility located at Argonne National Laboratory (Lemont, IL).

Electrocatalytic measurement of nitrate reduction. The linear voltammetry profiles were obtained on a rotating disk electrode (Pine MSR rotator) using a glassy carbon electrode (GCE, 0.196 cm²) deposited with copper-nickel catalysts as the working electrode. A Platinum wire and an Ag/AgCl electrode (filled with 3 M KCl) were used as counter and reference electrodes, respectively. Other electrocatalytic measurements were performed in a gas-tight flow cell. The

flow cell was connected to an electrochemical workstation (Autolab PGSTAT204). The flow cell consists of three compartments: a gas chamber, a catholyte chamber, and an anolyte chamber. The gas and cathodic compartments are separated by a gas diffusion electrode. Catholyte and anolyte chambers are separated by an anion-exchange membrane (Fumapem FAA-3-PK-130). The nitrate reduction catalyst (on Cu/PTFE or Cu foam), Ag/AgCl electrode (filled with 3 M KCl) and NiFe hydroxides on Ni mesh were employed as working, reference, and counter electrodes, respectively.

Aqueous 1 M KOH (Sigma-Aldrich) solution with different KNO₃ (Sigma-Aldrich) concentration (1, 2, 10, 50 and 100 mM) were used as the both catholytes and anolytes. The flow rate of the Ar gas was fixed at 50 s.c.c.m. Electrolytes were purged with Ar gas to remove dissolved O₂. The single-pass approach was used to measure stability at -0.1 V vs. RHE. 1 M KOH containing 100 mM KNO₃ was pumped into the flow electrolyzer with a flow rate of 0.5 mL min⁻¹. The mass transport limiting current density was calculated according to the following equation:

$$j_{limiting} = \frac{nFD}{\delta}C$$
 (1)

where: $j_{limiting}$ is the mass transport limiting current density; *n* is the number of electron transfers towards the formation of 1 mol of ammonia; *D* represents the effective diffusion coefficient of nitrate, which is 1.4×10^{-5} cm² s⁻¹ for 0.1 M nitrate at 25 °C;¹ δ is the diffusion layer thickness; *C* is the nitrate concentration.

Koutecký–Levich (K-L) analyses were performed according to the K-L equation:

$$\frac{1}{i_m} = \frac{1}{i_K} + \frac{1}{0.2nFD^{2/3}v^{-1/6}C\omega^{1/2}}$$
(2)

where: i_m is the measured current; i_K is the kinetic current from NO₃⁻ electroreduction; n is the

number of electron transfers in the reaction. *F* is Faraday's constant (96485 C mol⁻¹); *D* represents the effective diffusion coefficient of nitrate, which is 1.4×10^{-5} cm² s⁻¹ for 0.1 M nitrate at 25 °C; *v* is the kinematic viscosity of water at 25 °C (1×10^{-6} m² s⁻¹); *C* is the nitrate concentration, and ω represents the electrode's rate of rotation (rpm).

Ammonia detection and efficiency calculations. Produced ammonia was quantified by the indophenol blue method. Electrolytes after catalysis for 1 h were diluted by varying amounts, ensuring the ammonia concentrations in the testing solutions were in the linear range of the indophenol blue method. The coloring agent is composed of 0.36 M salicylic acid, 0.36 M NaOH and 0.18 M potassium sodium tartrate tetrahydrate (all chemicals are from Sigma-Aldrich). 1 mL diluted electrolytes (2-fold dilution for 1 and 2 mM nitrate, 10-fold dilution for 10 mM nitrate, and 100-fold dilution for 50 and 100 mM nitrate) were mixed with 125 μ L coloring agent, 12.5 μ L 0.034 M sodium nitroprusside (Sigma-Aldrich), and 12.5 μ L NaClO (available chlorine 4.00-4.99%, Sigma-Aldrich)/0.75 M NaOH (Sigma-Aldrich) solution. The mixture was allowed to stand for 1 h to ensure a complete coloring reaction. ¹⁵NO₃⁻ measurement was tested by H-nuclear magnetic resonance (H-NMR) technic (Agilent DD2 600).

Ammonia Faradaic efficiency was calculated according to the following equation:

Faradaic efficiency =
$$\frac{n V_{catholyte} c_{NH3} F}{it}$$
 (3)

where *i* is the total current; *n* represents the number of electron transfers towards the formation of 1 mol of ammonia which is 8; $V_{catholyte}$ is the volume of catholyte (mL); c_{NH3} represents the concentration of ammonia (M); *F* is the Faraday constant (96,485 C·mol⁻¹); *t* is the electrolysis time.

The half-cell energy efficiency (EE) was defined as the ratio of fuel energy to applied electrical

power, which was calculated with the following equation:

$$EE_{NH3} = = \frac{(1.23 - E_{NH3}^{0})FE_{NH3}}{1.23 - E}$$
(4)

where E_{NH3}^0 represents the equilibrium potential of nitrate electroreduction to ammonia, which is 0.69 V. FE_{*NH3*} is the Faradaic efficiency for ammonia. 1.23 V is the equilibrium potential of water oxidation (*i.e.* assuming the overpotential of the water oxidation is zero). E is the applied potential vs. RHE after 80% *iR* correction. The full-cell EE was calculated according the following equation:

$$EE_{NH3} = = \frac{(1.23 - E_{NH3}^0)FE_{NH3}}{Applied voltage}$$
(5)

ECSA evaluation. For the ECSA evaluation, the electrochemical double layer capacitance method was employed. All catalysts were reduced at -0.6 V vs. RHE for 2 min, and scanned in 1 M KOH at the sweep rate of 20, 40, 60, 80, and 100 mV s⁻¹. N₂ was purged during the measurement. The potential range was -0.076 to 0.024 V vs. RHE for the Cu₅₀Ni₅₀ alloy, and - 0.175 to 0.025 V vs. RHE for pure Cu. The anodic and cathodic current densities at -0.026 V vs. RHE for the Cu₅₀Ni₅₀ alloy and -0.075 V vs. RHE for pure Cu in the last scan cycle were recorded. The differences in these two current densities (Δj) at different sweep rates were then calculated and plotted against the sweep rates for each catalyst. By doing the linear fitting, we calculated the slopes of the Δj vs. sweep rate curves, which are the double layer capacitances for different catalysts. The double layer capacitance of electropolished Cu foil was obtained from previous report.²

For all the electrochemical tests performed, the applied potentials were converted to the reversible hydrogen electrode (RHE) scale through the following equation:

$$E_{\rm RHE} = E_{\rm Ag/AgCl} (_{3 \rm M \, KCl}) + 0.059 \times pH + 0.205$$
(6)

XAS analysis. An IFEFFIT package was used to analyze the hXAS spectra.^{3, 4} Standard dataprocessing including energy calibration and spectral normalization of the raw spectra was performed using Athena software. To extract the Ni-Cu and Ni-Ni bonding information, a Fourier transform was applied to convert the hXAS spectra from the energy space to the radial distance space. Then, a standard fitting analysis of the first shell between 1 and 3.0 Å was carried out using Artemis software.

Density functional theory calculations In this work, all DFT calculations were carried out with a periodic slab model using the Vienna *ab initio* simulation program (VASP).⁵⁻⁸ The generalized gradient approximation (GGA) was used with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional.⁹ The projector-augmented wave (PAW) method^{10, 11} was utilized to describe the electron-ion interactions, and the cut-off energy for the plane-wave basis set was 450 eV. In all calculations, the atoms at all positions have Hellmann–Feynman forces lower than 0.02 eV Å⁻¹ and the electronic iterations convergence was 10⁻⁵ eV using the Normal algorithm. A 4-layer (4×4) Cu (111) supercell was built to simulate the exposed surface of copper accompanying with a sufficient vacuum gap of 15 Å. Structural optimizations were performed on all modified slab models with a grid of (3 × 3 × 1) k-point.

The NO₃⁻ reduction reaction on different catalysts surfaces were simulated according to the following reactions:

*NO₃⁻ + H₂O + e⁻
$$\rightarrow$$
 *NO₂ + 2OH⁻
*NO₂ + 2H₂O + 2e⁻ \rightarrow *NO + 2OH⁻
*NO + H₂O + 2e⁻ \rightarrow *N + 2OH⁻
*N + H₂O + e⁻ \rightarrow *NH + OH⁻

*NH + H₂O +
$$e^- \rightarrow$$
 *NH₂ + OH⁻
*NH₂ + H₂O + $e^- \rightarrow$ *NH₃ + OH⁻

where the * represent the adsorption site. For each reaction, the free energies were given after gas correction:

$$\Delta G = \Delta E - T\Delta S \tag{7}$$

where ΔE is the reaction energy obtained by the difference between reactant and product molecules absorbed on catalyst surface; ΔS is the change in entropy for each reaction. Entropy values of gaseous molecules are taken from the standard database in the NIST webbook,¹² while the entropies of adsorbate and adsorption site are negligible. Supplementary figures and tables.



Figure S1. SEM images of the Cu₅₀Ni₅₀ (a-c) and pure Cu (d-f) catalysts. The SEM images in Fig. 1 and Figure S1c and f are enlarged images of Fig. S1a, b, d, and e, and were obtained using the same electrode for both Cu and CuNi catalysts. The scale bars are 10 μm in **a** and **d**, 2 μm in **b** and **e**, and 200 nm in c and f. "Feather-like" structures were seen sporadically on electrodes only at 10-, 5-, and 2-μm scale bars due to H₂ evolution during the electrodeposition. At relatively smaller scale bar of 500 and 200 nm, we confirmed that nanodendrites are the predominate catalyst morphologies for both CuNi alloys and pure Cu.



Figure S2. SEM images of the Cu₈₀Ni₂₀ (a, b) and Cu₃₀Ni₇₀ (c, d) catalysts. b and d are the enlarged SEM images of the electrode in a and c. The scale bars are 5 µm in a and c, 500 nm in b and d.



Figure S3. STEM images and EELS mapping analyses of the Cu₅₀Ni₅₀ catalyst. The scale bars in **a-c** and **e-g** are 100 nm.



Figure S4. XRD patterns of carbon-paper-supported Cu₅₀Ni₅₀ and Cu/PTFE-supported

Cu catalysts. The Cu(111) peak of the Cu₅₀Ni₅₀ catalysts is at a higher angle, by 0.4 degrees, compared to pure Cu. In contrast, the actual shifts in Figure 1i are instead 0.1 to 0.2 higher, a fact explainable by the influence of the 300 nm pristine Cu/PTFE substrate.



Figure S5. The Ni2p XPS spectra of catalysts with different Cu-to-Ni ratios. The Ni⁰ $2p_{3/2}$ peak shifts to low binding energies with increasing Ni content. The oxidation of Ni, due to its oxidation in air, is observed in the high intensity of Ni²⁺ 2p peaks.



Figure S6. The Cu2p XPS spectra of the Ni catalysts on Cu/PTFE support. The spectrum of the Ni shows similar Cu2p peak positions but low intensities, consistent with Ni/Ni(OH)₂ coverage compared to that of the bare Cu/PTFE support.



Figure S7. SEM (a) and EDX mapping (b-d) images of the pure Ni catalysts. The scale bars are 10 μm.



Figure S8. *j*-*V* plots of nitrate reduction (80% *iR* corrected) on the pure Ni and Cu RDE. (a) The *j*-*V* plots of nitrate reduction on the pure Ni catalyst in 10 mM nitrate at different rates of rotation. (b) The *j*-*V* plots of nitrate reduction on the Ni catalyst at 400 rpm in electrolytes with different nitrate concentrations. (c) The *j*-*V* plots of nitrate reduction on the pure Cu catalyst in 10 mM nitrate at different rates of rotation. (d) The *j*-*V* plots of nitrate reduction on the Cu catalyst at 400 rpm in electrolytes with different nitrate at 400 rpm in electrolytes with different nitrate reduction on the sweep rates in all tests are 10 mV s⁻¹.



Figure S9. ECSA measurements of the Cu₅₀Ni₅₀ and pure Cu catalysts. (a, b) The cyclic voltammetry profiles obtained on the Cu₅₀Ni₅₀ and pure Cu catalysts at the sweep rates of 20, 40, 60, 80 and 100 mV s⁻¹, respectively. (c) The determination of double layer capacitance for each catalyst. The double layer capacitance of polished Cu foil is 29 μ F cm⁻².¹⁰



Figure S10. Additional *j*-V plots of nitrate reduction (80% *iR* corrected) on the Cu₅₀Ni₅₀ catalysts on RDE. Plots in 10 mM nitrate at different rotating rates. The sweep rates are 10 mV s⁻¹.



Figure S11. *j*-*V* **plots of nitrate reduction (80%** *iR* **corrected) on the different catalysts on RDE in 10 mM nitrate at different rotating rates.** The sweep rates and rates of rotation are 10 mV s⁻¹ and 100 rpm.



Figure S12. Ammonia detection using indophenol blue method. (**a**) The ultraviolet-visible adsorption spectra of different solution with different ammonia concentrations. (**b**) The linear standard curve for the calculation of ammonia production.



Figure S13. ¹**H nuclear magnetic resonance (NMR) analysis for ammonia production.** The 1H NMR spectrum of product obtained by electroreduction of ¹⁴N nitrate (**a**) and ¹⁵N nitrate (**b**).



Figure S14. Nitrate-to-ammonia Faradaic efficiency on the pure Cu/PTFE catalyst in different nitrate concentrations.



Figure S15. SEM images of the Cu₅₀Ni₅₀ (a, b) and pure Cu (c, d) catalysts after 1 h nitrate reduction operation. Scale bars are 500 nm in a and b, 200 nm in c and d.



Figure S16. Comparison of the full-cell EE for NO_3 -to- NH_3 conversion using the $Cu_{50}Ni_{50}/PTFE$ and Cu/PTFE catalysts.



Figure S17. *j*-V plots of nitrate reduction (80% *iR* corrected) on the different catalysts on RDE in 1 mM nitrate. The sweep rates and rates of rotation are 10 mV s⁻¹ and 100 rpm.



Figure S18. NH₃ Faradaic efficiencies different catalysts in 1 mM nitrate electrolyte. The testing potential is -0.06 V vs. RHE.



Figure S19. SEM images of the $Cu_{50}Ni_{50}$ catalyst deposited on Cu foam. Scale bars are 100 μ m in a and 500 nm in b.



Figure S20. *Operando* hXAS spectra of the Cu₅₀Ni₅₀ and pure Cu catalysts at the Cu Kedge. The results indicate pure metallic Cu structures for both catalysts under operating conditions.



Figure S21. Stability test for various CuNi surface models. Ni doped on surface, subsurface of Cu(111) by separate or aggregate distributions: a surface-separate; b surface-aggregate; c surface-subsurface-separate; d surface-subsurface-aggregate; e subsurface-separate; f subsurface-sub-subsurface-separate; g subsurface-aggregate; h subsurface-sub-subsurface-aggregate.



Figure S22. Stable structures of CuNi alloy. 46 possible structures of Cu₈₀Ni₂₀, Cu₅₀Ni₅₀, and Cu₃₀Ni₇₀ alloys.



Figure S23. Intermediate adsorptions on Cu surface. All possible adsorption configurations of $*NO_3^-$, $*NO_2$, $*NO_3^-$, $*NO_2$, $*NH_2$, $*NH_3^-$, $*NH_3^-$ with different adsorption sites and orientations on Cu (111) surfaces.



Figure S24. Stable configurations of the intermediates. The most stable adsorption configurations of *NO₃⁻, *NO₂, *NO, *NH₂, *NH, *N, and *NH₃ on various CuNi surface.

Spot	Cu (%)	Ni (%)
1	52	48
2	57	43
3	54	46

Table S1. A summary of EELS mapping analysis results at different spots on the Cu₅₀Ni₅₀ catalyst.

Table S2. K-L analysis results of NO_3^- reduction on the $Cu_{50}Ni_{50}$ and pure Cu catalysts in 10 mM NO_3^- .

Catalys	Potential	Slope	Interceptio	Number of	Kinetic current
t	(V vs.	(A s ^{0.5})	n (cm ² mA ⁻	electron	density (mA cm ⁻²)
	RHE)		1)	transfer	
Cu ₅₀ Ni ₅₀	-0.25	0.49	0.0045	4.3	222.2
Cu	-0.25	0.43	0.0084	4.8	119.0

Nitrate	Potential	Current	NH ₃ FE
concentration	(V vs. RHE)	density	(%)
(mM)		(mA cm ⁻²)	
	-0.07	1.0	59 ± 1
1	-0.17	1.2	65 ± 3
1	-0.27	1.8	31 ± 3
	-0.35	5.6	9 ± 1
	-0.07	1.5	84 ± 2
2	-0.17	1.8	74 ± 4
Z	-0.26	2.3	45 ± 3
	-0.35	5.5	23 ± 1
	-0.05	6.1	84 ± 1
10	-0.15	6.5	93 ± 2
10	-0.25	6.8	80 ± 2
	-0.34	7.0	48 ± 2
	0.01	19.1	85 ± 1
50	-0.07	26.0	94 ± 2
50	-0.16	27.3	97 ± 2
	-0.25	30.7	94 ± 2
	0.01	21.1	82 ± 2
100	-0.02	36.0	82 ± 3
100	-0.10	40.4	96 ± 2
	-0.15	53.0	00 ± 1

Table S4. A summary of nitrate reduction performance on the $Cu_{50}Ni_{50}/PTFE$ catalyst in different electrolytes.

Nitrate	Potential	Current	NH ₃ FE
concentration	(V vs. RHE)	density	(%)
(mM)		(mA cm ⁻²)	
	-0.07	0.3	32 ± 2
1	-0.16	0.5	42 ± 3
1	-0.26	0.6	35 ± 2
	-0.36	1.7	13 ± 1
	-0.06	0.8	59 ± 3
2	-0.16	1.1	48 ± 2
2	-0.26	1.2	41 ± 1
	-0.35	3.2	17 ± 1
	-0.06	2.0	79 ± 2
10	-0.15	3.4	87 ± 3
10	-0.25	4.0	80 ± 1
	-0.35	4.7	58 ± 1
	-0.03	9.6	64 ± 4
50	-0.10	15.2	83 ± 2
50	-0.19	17.3	87 ± 1
	-0.28	20.0	100 ± 1
	0.01	14.9	62 ± 3
100	-0.10	17.3	60±4
100	-0.12	30.3	90 ± 2
	-0.19	41.6	99 ± 1

 Table S5. A summary of nitrate reduction performance on the pure Cu/PTFE catalyst in different electrolytes.

Potential (V vs. RHE)	CN	R (Å)	$\sigma^2 (10^{-3} \text{\AA}^2)$	ΔE_0 (eV)
-0.15 V	10.8	2.55	8.3	0.32
-0.25 V	11.8	2.54(3)	8.6	-0.32
-0.35 V	11.1	2.55(3)	8.3	0.17

Table S6. The Cu K-edge extend X-ray absorption fine structure (EXAFS) curve-fitting resultsfor $Cu_{50}Ni_{50}$.

Potential (V vs. RHE)	CN	R (Å)	$\sigma^2 (10^{-3} \text{\AA}^2)$	ΔE_0 (eV)
-0.15	11.6	2.48	9.4	-1.6
-0.25	11.7	2.48	8.6	-0.72
-0.35	11.8	2.48	8.4	-0.67

Table S7. The Ni K-edge extended X-ray absorption fine structure (EXAFS) curve-fitting results for Cu₅₀Ni₅₀.

Configuration	Formation energy (eV)
Surface-separate	0.25
Surface-aggregate	0.25
Subsurface-separate	0.24
Subsurface-aggregate	0.24
Surf-sub-separate	0.25
Surf-sub-aggregate	0.25
Sub-sub-separate	0.24
Sub-sub-aggregate	0.24

Table S8. A summary of the stability of different configurations for CuNi systems.

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