# Supporting information for

# Electronic State Modulation via Electrochemical Reconstruction Enhances Dilute Nitrate-to-Ammonia Reduction Efficiency

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## **1. Experimental Procedures**

### Chemicals

Copper(II) nitrate trihydrate (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O) was purchased from Shanghai Macklin Biochemical Co., Ltd. Zinc(II) nitrate hexahydrat (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) was purchased from Tianjin Fuchen Chemical Reagent Co., Ltd. Sodium carbonate anhydrous  $(Na_2CO_3)$  was purchased from Tianjin Damao Chemical Reagent Co., Ltd. Sodium hydroxide (NaOH), sodium Nitrate (NaNO<sub>3</sub>) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Sodium sulfate  $(Na_2SO_4)$  was purchased from Tianjin Kemio Chemical Reagent Co., Ltd. The water  $(H_2O)$  (18 M $\Omega$  cm<sup>-1</sup>) used in all experiments was prepared by passing through an ultra-pure purification system.

#### **Material Characterization**

TEM images were carried out on JEOL JEM 2100plus. XRD patterns were collected on the D8 Discover. XPS measurements were performed on ESCALAB 250Xi. Fourier transform infrared (FTIR) spectra were measured using a Fourier transform infrared spectrometer (Bruker, TENSOR 27FTIR, Germany). HORIBA in Via Reflex was used to perform the Raman measurements with the laser of 532 nm. ICP-MS was performed on Agilent 5110 to detect mass content of Sn species. <sup>1</sup>H NMR was used to test the isotope labeling experiments on a BRUKER AVANCE 400.

#### Determination of NH<sub>3</sub> by the indophenol blue method

Solution A: 5 g of salicylic acid and 5 g of sodium citrate were dissolved in 100 mL of 1 M NaOH.

Solution B: 3.5 mL of sodium hypochlorite (available chlorine 10-15%) was added into 100 mL of ultra-pure water.

Solution C: 0.2 g of sodium nitroferricyanide was dissolved in 20 mL of ultra-pure water.

The 2 mL of solution A was added to the 2 mL of ammonia containing solution. Then,

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1 mL of solution B and 200  $\mu$ L of solution C were successively added into the above solution. Absorbance measurements were performed after 2 h.

#### Determination of NH<sub>3</sub> by <sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H NMR)

Solution A: 50  $\mu$ L of 0.05M H<sub>2</sub>SO<sub>4</sub> was used to regulate pH of solution;

Solution B: 50  $\mu$ L of DMSO-d<sub>6</sub> was used for a spin-lock field.

Solution C: 50 µL of 1 mM Maleic acid was used for the internal standard.

Solution A, B and C were added into 900  $\mu$ L of ammonia containing solution. After shaking up, 600  $\mu$ L of above mixed solution was added into a NMR tube. Standard Bruker pulse sequence zgesgp was used to suppress the solution water <sup>1</sup>H signal and acquire NMR data. The D1 and NS were set to be 2s and 128, respectively.

#### **Electrochemical measurements**

The electrochemical investigations were carried out with the CHI760E electrochemical workstation. 4 mg of catalyst was ultrasonically stirred for 5 min with a mixture of 475 $\mu$ L ethanol and 475  $\mu$ L water, followed by adding 50  $\mu$ L of Nafion solution with 30 min sonication. The catalyst ink was dropped on carbon paper evenly, and the loading capacity of the catalyst was 0.2 mg·cm<sup>-2</sup>. The H-type electrolytic cell was adopted for electrocatalytic NO<sub>3</sub>RR and was partitioned by the Nafion-117 membrane. The 1 cm<sup>2</sup> carbon paper with catalyst (YLS-25) was applied as the working electrode, platinum wire as the counter electrode, and Hg/HgO as the reference electrode. All measured potentials were converted to the RHE by the followed equation:

 $E(vs. RHE) = E(vs. Hg/HgO) + 0.098V + 0.0591 \times pH$ 

#### The calculation method of Faraday efficiency, conversion rate and yield.

The Faraday efficiency of the NH<sub>3</sub> and NO<sub>2</sub><sup>-</sup> product was calculated as follows.

 $\mathrm{FE}_{\mathrm{NH}_3} {=} \left(8 \times \mathrm{F} \times \mathrm{C}_{\mathrm{NH}_3} {\times} \mathrm{V}\right) {\!/} (\mathrm{M}_{\mathrm{NH}_3} {\times} \mathrm{Q})$ 

 $FE_{NO_2^-} = (2 \times F \times C_{NO_2^-} \times V) / (M_{NO_2^-} \times Q)$ 

The conversion of  $NO_3^-$  was calculated as follows.

NO<sub>3</sub><sup>-</sup> conversion = $\Delta C_{NO_3}$ <sup>-</sup> / C<sub>0</sub> × 100%

The yield of NH<sub>3</sub> was calculated as follows.

 $Yield_{NH_3} = (C_{NH_3} \times V)/(M_{NH_3} \times t \times m)$ 

 $C_{NH_3}$ : Measured NH<sub>3</sub> concentration (mg L<sup>-1</sup>).

 $C_{NO_2}$ : Measured NO<sub>2</sub><sup>-</sup> concentration (mg L<sup>-1</sup>).

 $C_0$ : the onset concentration of  $NO_3^{-}$ .

 $\Delta C_{NO_3}$ : the change in NO<sub>3</sub><sup>-</sup> concentration before and after electrolysis.

 $M_{NH_3}$ : Specific relative molecular mass of ammonia.

V : Volume of electrolyte (30 mL).

F : Faraday standard value (96485 C mol<sup>-1</sup>).

- Q : Gross electric charge (C).
- t : Electrolysis time.
- m : The mass of catalyst.

#### **DFT calculations**

The DFT calculations were performed by Vienna Ab initio Simulation Package (VASP)<sup>1, 2</sup>, employing the projector augmented wave (PAW) method<sup>3</sup>. The generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE)<sup>4</sup> functional was employed in treating the exchange-functional. The energy cutoff for the plane wave

basis expansion was set to 450 eV and the convergence criterion for geometry relaxation was set to a force on each atom less than 0.02 eV/Å. The Brillouin zone integration is treated using  $3\times3\times1$  k-point sampling. The self-consistent calculations adopt a convergence energy threshold of  $10^{-5}$  eV. A  $4\times4\times3$  super cell model of Cu (111) was established. Subsequently, Zn atoms were randomly doped into the Cu (111) model using VASP, and Cu<sub>75</sub>/Zn<sub>25</sub> model was established. To avoid interaction between periodic structures, a vacuum of 20 Å was added along the z direction. We explored the effect of solvation on reaction pathways using an implicit solvation model.

The free energies of the NO<sub>3</sub>RR were calculated by the equation:  $\Delta G = \Delta E_{DFT} + \Delta E_{ZPE} - T\Delta S$ , where  $\Delta E_{DFT}$  represents the DFT electronic energy difference of each steps. The corrections for zero-point energy ( $\Delta E_{ZPE}$ ) and entropy variation ( $\Delta S$ ) were acquired through VASPKIT. The calculations were performed at the temperature of T = 298.15 K.

## 2. Supporting Figures





Figure S1. (a) TEM image of Cu/ZnO and (b) CuZn.



Figure S2. XRD patterns of CuO/ZnO.



Figure S3. XRD patterns of ZnO, Cu<sub>25</sub>/Zn<sub>75</sub>O, Cu<sub>50</sub>/Zn<sub>50</sub>O, Cu<sub>75</sub>/Zn<sub>25</sub>O and Cu.

After calcined in a  $H_2$  atmosphere, the diffraction peaks of CuO of CuO/ZnO disappeared while the ZnO phase remained unchanged.



Figure S4. XRD patterns spectra of  $Cu_{25}Zn_{75}$ ,  $Cu_{50}Zn_{50}$ , and  $Cu_{75}Zn_{25}$ .



Figure S5. Wide-survey XPS spectra of (a)  $Cu_{75}/Zn_{25}O$  and (b)  $Cu_{75}Zn_{25}$ .



Figure S6. Cu 2p XPS spectrum of  $Cu_{75}/Zn_{25}O$  and Cu.



Figure S7. Cu LMM Auger spectra of Cu and Cu<sub>75</sub>Zn<sub>25</sub>.



Figure S8. Zn LMM Auger spectra of Cu/ZnO and Cu<sub>75</sub>Zn<sub>25</sub>.



Figure S9. O 1s XPS spectrum of ZnO.



Figure S10. (a) Ultraviolet absorption and (b) concentration-absorbance calibration

curves of NO<sub>3</sub><sup>-</sup>.



Figure S11. (a) Ultraviolet absorption and (b) concentration-absorbance calibration

curves of NH<sub>3</sub>.



Figure S12. (a) Ultraviolet absorption and (b) concentration-absorbance calibration

curves of NO<sub>2</sub><sup>-</sup>.



Figure S13. I-t curves of NO<sub>3</sub>RR using  $Cu_{75}/Zn_{25}O$  as the working electrode.



Figure S14. FE of H<sub>2</sub>, NO<sub>2</sub> <sup>-</sup> and NH<sub>3</sub> products with (a)  $Cu_{75}Zn_{25}$ ; (b)  $Cu_{50}Zn_{50}$ ; (c)  $Cu_{25}Zn_{75}$ ; and (d) Cu in 0.5 M Na<sub>2</sub>SO<sub>4</sub> and 100 ppm NO<sub>3</sub><sup>-</sup>-N (PH=11.5).



Figure S15. FE, Partial current density and yield rate of NH<sub>3</sub> of CuZn catalyst with

different Cu-Zn ratios.



Figure S16. XRD patterns of Cu<sub>75</sub>Zn<sub>25</sub> before and after 15 cycles.



Figure S17. (a) Cu 2p and (b) Zn 2p XPS spectra of Cu<sub>75</sub>Zn<sub>25</sub> before and after 15

cycles.



Figure S18. <sup>1</sup>H NMR spectra of electrolyte after NO<sub>3</sub>RR for Cu<sub>75</sub>Zn<sub>25</sub> at -0.7 V vs.

RHE for 2 h using  $^{14}\mathrm{NO_3}^-$  and  $^{15}\mathrm{NO_3}^-$  as N-source.



Figure S19. Electrolysis at -0.7 V vs. RHE through successive cycles of NO<sub>3</sub>-

containing and NO<sub>3</sub><sup>-</sup>-free electrolytes.



**Figure S20**. Amounts of produced NH<sub>3</sub> on Cu<sub>75</sub>Zn<sub>25</sub> under different conditions: (1) electrolysis in NO<sub>3</sub><sup>-</sup>-containing solution at -0.7 V *vs*. RHE; (2) electrolysis in NO<sub>3</sub><sup>-</sup>-free solution at -0.7 V *vs*. RHE; (3) electrolysis in NO<sub>3</sub><sup>-</sup>-containing solution at open-

circuit potential (OCP); (4) before electrolysis.



Figure S21. (a) <sup>1</sup>H NMR spectra of electrolyte obtained by electrolysis at -0.7 V vs.

RHE; (b) The ammonia yield rate measured by NMR and UV-vis.



Figure S22. The  $A_{NH2OH}/(A_{NH2OH}+A_{NO2})$  of  $Cu_{75}Zn_{25}$  and Cu at different potentials.



Figure S23. Atomic structure models of adsorbed \*NO<sub>3</sub>, \*NO<sub>2</sub>, \*NH<sub>2</sub>OH, and \*NH<sub>3</sub>

(including side and top views).



Figure S24. The  $A_{NH2OH}/(A_{NO2}+A_{NH2OH})$  of  $Cu_{75}Zn_{25}$  and Cu at different potentials.



Figure S25. HER process over Cu and  $Cu_{75}Zn_{25}$  surfaces.



Figure S26.  $J_{\rm H2}$  of Cu<sub>75</sub>Zn<sub>25</sub> and Cu in 0.5 M Na<sub>2</sub>SO<sub>4</sub> at various potentials.



Figure S27. XPS valence band spectra of  $Cu_{75}Zn_{25}$  and Cu.

## **3. Supporting Tables**

MS.

Element	wt.% Cu <sub>75</sub> /Zn <sub>25</sub> O	wt.% Cu <sub>75</sub> Zn <sub>25</sub>
Cu	70.67	76.07
Zn	23.54	23.93
n(Cu:Zn)	3:1	3.18:1

Table S1. The contents of Cu and Zn in  $Cu_{75}/Zn_{25}O$  before and after NO<sub>3</sub>RR by ICP-

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Table 52. Comparison of 14113 yield fale and FE by NO3KK off various catalysis.							
Catalysts	Electrolyte	Potential (vs. RHE)	NH <sub>3</sub> yield rate (mmol h <sup>-1</sup> g <sub>cat</sub> -1)	FE <sub>NH3</sub> (%)	Conversion rate (%)	Ref.	
Cu <sub>75</sub> /Zn <sub>25</sub> O	100 ppm NO <sub>3</sub> <sup>-</sup> -N, 0.5 M Na <sub>2</sub> SO <sub>4</sub>	-0.7 V	413.9	94.1	97.6	This work	
10Cu/TiO <sub>2-X</sub>	200 ppm NO <sub>3</sub> <sup>-</sup> -N, 0.5 M Na <sub>2</sub> SO <sub>4</sub>	-0.75 V	114.3	81.34	58.3	5	
np- Cu/MnOx	0.1 M NO <sub>3</sub> N, 0.5 M Na <sub>2</sub> SO <sub>4</sub>	-0.75 V	1723.5	86.2	-	6	
TiO <sub>2-x</sub>	50 ppm NO <sub>3</sub> <sup>-</sup> -N, 0.5 M Na <sub>2</sub> SO <sub>4</sub>	-0.74 V	45.0	85.0	95.2	7	
Pd-Cu <sub>2</sub> O CEO	50 ppm NO <sub>3</sub> <sup>-</sup> -N, 0.5 M Na <sub>2</sub> SO <sub>4</sub>	-1.3 V	54.4	96.56	91.3	8	
CuCo/NC	0.2 M NO <sub>3</sub> N, 0.5 M Na <sub>2</sub> SO <sub>4</sub>	-0.79 V	561.1	95.1	-	9	
Cu-Co <sub>3</sub> O <sub>4</sub>	500 ppm NO <sub>3</sub> <sup>-</sup> -N, 0.1 M Na <sub>2</sub> SO <sub>4</sub>	-0.6 V	36.71	86.5	-	10	
CFP-Cu <sub>1</sub> Ni <sub>1</sub>	0.1 M NO <sub>3</sub> N, 0.5 M Na <sub>2</sub> SO <sub>4</sub>	-0.22 V	2550	95.7	-	11	
ZnCr <sub>2</sub> O <sub>4</sub>	0.1 M NO <sub>3</sub> N, 0.1 M PBS	-1.2 V	87.23	90.21	98.3	12	

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