### **Supporting Information**

### The Promotion of Nitrite and Nitrate Conversion into Ammonia by

## Improving \*H Utilization via the Construction of Dual Active Centers

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#### **1.** Experimental Procedures

#### Chemicals and materials

Sodium hydroxide (NaOH,  $\geq$ 96.0%), ammonium persulphate ((NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>,  $\geq$ 98.0%), ammonium sulfate-<sup>14</sup>N ((<sup>14</sup>NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, 98.5%), ammonium sulfate-<sup>15</sup>N ((<sup>15</sup>NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>,  $\geq$ 99 at%, 98.5%), sodium nitrate-<sup>14</sup>N (Na<sup>14</sup>NO<sub>3</sub>, 98.5%), sodium nitrate-<sup>15</sup>N (Na<sup>15</sup>NO<sub>3</sub>, <sup>15</sup>N  $\geq$  99 at%, 98.5%), maleic acid (C<sub>4</sub>H<sub>4</sub>O<sub>4</sub>,  $\geq$ 99.0%), deuterium oxide (D<sub>2</sub>O, 99 at% D), Copper acetate monohydrate (C<sub>4</sub>H<sub>6</sub>CuO<sub>4</sub>·H<sub>2</sub>O, 99%), Tungsten chloride (WCl<sub>6</sub>, 99%), Isopropyl Alcohol (C<sub>3</sub>H<sub>8</sub>O, >99%). All chemicals were purchased from Aladdin Co., Ltd and used as received. Carbon paper (CP, the thickness is 0.2mm) was bought from Kunshan Guangjiayuan New Material Co., Ltd. Milli-Q water (18.25 MΩ cm<sup>-1</sup>) was used in all the experiments.

#### Preparation of W<sub>18</sub>O<sub>49</sub> NWs

70 mg of  $WCl_6$  was dissolved in 70 mL of isopropanol, forming a yellow solution after stirring for 30 mins, which was then transferred to a 100 mL hydrothermal reactor and subjected to a reaction at 200°C for 24 hours. The resulting blue solid was collected after centrifugation, being washed three times with ethanol, and being dried at 60°C for subsequent use.

#### **Preparation of W-Cu-L**

70 mg of the obtained  $W_{18}O_{49}$  NWs powder were dispersed in 20 mL of ethanol solution with different concentrations of copper acetate. After being sonicated for 20 minutes, the resulted suspension was transferred to a quartz-capped vial and irradiated with a 15 Hz pulsed laser for 40 minutes. The solid was collected by centrifugation, washed three times with ethanol, then vacuum-dried at 60°C, and labeled as W-Cu-L.

#### **Preparation of W-Cu-C**

The sample preparation process is the same as that of W-Cu-L-6.8%, except that the laser irradiation is replaced by conventional stirring for 40 min.

#### **Preparation of Cu NPs**

The preparation of Cu NPs involved mixing two aqueous solutions of CTAB (0.01 M), the solution of hydrazine (0.08 M) and copper chloride (1 mM). The pH of the copper chloride solution was adjusted to 10 using ammonia solution. After 2 hours of stirring, a turbid solution was formed, which was centrifuged and washed three times with ethanol.<sup>1</sup> The resulted product was then vacuum-dried at 70°C and labeled as Cu NPs.

#### **Materials Characterizations**

Powder X-ray diffraction (XRD) patterns were obtained using a Philips X'Pert PRO SUPER X-ray diffractometer equipped with graphite-monochromated Cu K $\alpha$  radiation ( $\lambda$ = 1.54056 Å). The morphologies and elemental mapping analysis were identified by scanning electron microscopy (SEM Sigma 500, SEISS, Germany) and field emission transmission electron microscope (STEM, JEM-F200, JEOL) equipped with an energy dispersive spectrometer (EDS). X-ray photoelectron spectroscopy (XPS) measurements were carried out with an Escalab 250Xi system using a monochromatic Al Ka source (1,486.6 eV) for the analysis of the surface chemical property. The electron paramagnanetic resonance (EPR) measurements of DMPO-H were carried out at Bruker EMX plus 10/12 (equipped with Oxford ESR910 Liquid Helium cryostat). The ultraviolet-visible (UV-Vis) absorbance spectra were measured on Shimadzu UV-3900 spectrophotometer. The isotope labeling experiments were measured by <sup>1</sup>H NMR measurement (JNM-ECZ600R). The X-ray absorption fine structure (XAFS) measurements were carried out with the table XAFS-500A.

#### The preparation of working electrode

5 mg of the obtained catalysts were dispersed in 1 mL of deionized water, followed by the introduction of 240  $\mu$ L Nafion solution. Subsequently, after being ultrasonicated for about 2 h, well dispersed catalyst inks were obtained. Afterwards, 100  $\mu$ L of catalyst inks were dropped onto the carbon paper with an area of 1.25 cm<sup>2</sup> (0.5 cm × 2.5 cm), followed by being dried at 60 °C overnight.

#### **Electrochemical Measurements**

The electrochemical nitrite reduction reaction were carried out using a standard three-electrode system in a single-chamber electrolytic cell. The catalyst loaded on copper foam, silver chloride reference electrode (Ag/AgCl), and platinum foil were used as working electrode, reference electrode, and counter electrode, respectively.  $0.5 \text{ M} \text{ Na}_2\text{SO}_4$  solution was used as electrolyte, and a certain concentration of NaNO<sub>2</sub> was added to the electrolytic cell as the target reactant. All the electrochemical measurements were performed on electrochemical workstation (CHI 660e, Chenhua, Shanghai). The potential was recorded based on standard hydrogen electrode with the conversion formula of E(RHE)=E(Ag/AgCl)+0.0591pH+0.198. Before the nitrate electroreduction test, polarization curves withsteady state were achieved by linear sweep voltammetry. A constant potential test was carried out at different potentials for 1 hours. For the electrochemical nitrate reduction reaction, the reactant was replaced by NaNO<sub>3</sub> and the reaction time was changed to 1.5 h. All electrochemical data were recorded in CHI 660e electrochemical workstation.

#### N isotope labeling experiments

The N isotopic labeling experiments were carried out using the aforementioned electrochemical nitrate reduction methods in the electrolyte (0.06M NO<sub>3</sub><sup>-</sup>-N) with Na<sup>15</sup>NO<sub>3</sub> and Na<sup>14</sup>NO<sub>3</sub> as N source, respectively.<sup>2</sup> The amount of produced <sup>15</sup>NH<sub>4</sub><sup>+</sup> and <sup>14</sup>NH<sub>4</sub><sup>+</sup> was quantified by the <sup>1</sup>H-Nuclear Magnetic Resonance (NMR) spectroscopy. For quantification, a series of <sup>15</sup>NH<sub>4</sub><sup>+</sup> solutions with known concentration were prepared in 0.5 M Na<sub>2</sub>SO<sub>4</sub> as standards. 50 mL of the <sup>15</sup>NH<sub>4</sub><sup>+</sup> and standard solution with different concentration was mixed with 50 ppm maleic acid. 50 µL deuterium oxide (D<sub>2</sub>O) was added into the above mixed solution of 0.5 mL for NMR test. Calibration was achieved using the peak area ratio between <sup>15</sup>NH<sub>4</sub><sup>+</sup> and maleic acid because the <sup>15</sup>NH<sub>4</sub><sup>+</sup> concentration and the area ratio were positively correlated. Similarly, the amount of <sup>14</sup>NH<sub>4</sub><sup>+</sup> was quantified by this method when Na<sup>14</sup>NO<sub>3</sub> was used as feeding N-source.

#### Ion concentration detection

Colorimetric method was applied to determine the concentration of nitrate, nitrite and ammonium.<sup>[5][5]</sup> Ultraviolet-visible (UV-Vis) spectrophotometer was used to detect the ion concentration of pre- and post-test electrolytes, which were diluted to appropriate concentration and can match the range of calibration curves.<sup>[6][6]</sup> The specific detection methods are as follow:

- 1. Determination of nitrate-N: Nitrate concentrations were measured based on the following standard methods. First, a certain amount of electrolyte was taken out from electrolytic cell and diluted to 5 mL, which fell in the detection range. Then 0.1 mL sulfamic acid solution with concentration of 5 wt% was added to the aforementioned solution. The test of absorption spectrum was carried out using an ultraviolet-visible spectrophotometer and the absorption intensities at wavelength of 220 nm and 275 nm were recorded. The final absorbance value was calculated based on the equation:  $A = A_{220nm} 2A_{275nm}$ . The calibration curve was plotted using a series of concentrations from 0 to 20 mg L<sup>-1</sup>. The sodium nitrate applied for the plotting of calibration curve was pretreated by drying in the oven at 105-110 ° C for 2 h in advance.
- 2. Determination of nitrite-N: The mixture of p-aminobenzenesulfonamide (0.4 g), N-(1-Naphthyl) ethylenediamine dihydrochloride (0.02 g), ultrapure water (5 mL) and phosphoric acid (1 mL, ρ=1.70 g/mL) was used as color reagent. 0.1 mL of color reagent was then introduced in to 5 mL of electrolyte was taken out from the electrolytic cell with stirring for 20 mins. The absorption intensity at wavelength of 540 nm was recorded. The concentration-absorbance curve was calibrated using a series of standard sodium nitrite solutions.
- **3. Detection of ammonium-N:** Indophenol blue spectrometer method was used to quantitatively analyze the ammonia content in the solution. The mixture of NaOH (0.4 g), sodium citrate (1 g), ultrapure water (20 mL) and salicylic acid (1 g) was used and labeled as solution A. The mixture of Sodium Hypochlorite (0.625 mL) and ultrapure water (19.375 mL) was used and labeled as solution B. The mixture of Sodium Nitroprusside (0.1 g) and ultrapure water (10 mL) was used and labeled as solution C. For colorimetric assay, a certain amount of electrolyte was taken out from electrolytic cell and diluted to 2 mL. Then, 2 mL solution A, 0.1 mL solution B and 0.2 mL solution C were added and mixed thoroughly. The absorption intensity at wavelength of 625 nm was recorded after sitting for 120 min. The concentration-absorbance curve was plotted using a series of standard ammonium chloride solutions from 0 to 20 mg L<sup>-1</sup>.

#### H\* detection using DMPO

The experiments of H\* capture for NO<sub>2</sub>RR were conducted in electrolytes with NO<sub>2</sub><sup>-</sup> and without NO<sub>2</sub><sup>-</sup>. In order to ensure the generation of sufficient \*H, the cathode area was set to  $2 \times 2$  cm<sup>2</sup> and the electrolyte was set to 20 mL. After reacting for 20 minutes at reduction potential of – 0.8V vs. RHE, 20 µL of electrolyte was taken out and mixed with 20 µL of DMPO. The mixture was then transferred to a capillary tube for detection. For active hydrogen capture experiment in NO<sub>3</sub>RR, the electrolyte was replaced by NO<sub>3</sub><sup>-</sup> and the reduction potential was changed to – 0.8V vs. RHE.

#### The calculation of the conversion, yield, selectivity, and Faradaic efficiency.

For NO<sub>2</sub>RR, the calculation formula of the evaluation parameters are as follows:

The selectivity of the product can be calculated by: $NH_4^+$  selectivity  $(S_{NH4+}) = C_{NH4+} / \Delta C_{NO2-} \times 100\%$ (1)The yield of  $NH_4^+$  (aq) was calculated using equation:(2)Yield  $NH_4^+ = (C_{NH4+} \times V) / (M_{NH4+} \times t \times m)$ (2)

The Faradaic efficiency was calculated as follows:

Faradaic efficiency =  $(8F \times C_{NH4+} \times V) / (M_{NH4+} \times Q) \times 100\%$  (3) For NO<sub>3</sub>RR, the calculation formula of the evaluation parameters is as follows:

The  $NO_3^-$  conversion rate was calculated as follows:

 $NO_3^- \text{ conversion} = \Delta C_{NO3^-} / C_0 \times 100\%$ <sup>(4)</sup>

The selectivity of the product can be calculated by:

 $NH_4^+ selectivity (S_{NH4+}) = C_{NH4+} / \Delta C_{NO3-} \times 100\%$ The yield of NH<sub>4</sub><sup>+</sup> (aq) was calculated using equation: (5)

The yield of 14114 (aq) was calculated using equation

 $Yield NH_4^+ = (C_{NH4+} \times V) / (M_{NH4+} \times t \times m)$ (6)

The Faradaic efficiency was calculated as follows:

Faradaic efficiency =  $(8F \times C_{NH4+} \times V) / (M_{NH4+} \times Q) \times 100\%$  (7)

where  $C_{NH4+}$  is the concentration of NH<sub>4</sub><sup>+</sup>(aq),  $\Delta C_{NO2-}$  is the concentration difference of NO<sub>2</sub><sup>-</sup> before and after electrolysis,  $\Delta C_{NO3-}$  is the concentration difference of NO<sub>3</sub><sup>-</sup> before and after electrolysis,  $C_0$  is the initial concentration of NO<sub>3</sub><sup>-</sup>, V is the electrolyte volume, t is the electrolysis time, m is the mass of catalyst, F is the Faradaic constant (96485 C mol<sup>-1</sup>), Q is the total charge passing the electrode.

For simultaneous NO<sub>3</sub>RR and NO<sub>2</sub>RR, the FE calculations were conducted under the assumption that nitrite is preferentially reduced.

#### The calculation of the energy efficiency.

Assuming the overpotential of anodic electrode (the water oxidation) is zero, the half-cell energy efficiency (EE) defined as the ratio of chemical energy to applied electrical power was calculated with the following equation:

 $EE_{NH3} = (1.23 - E_{NH3}0) \times FE_{NH3} / (1.23 - E) \times 100\%$  (8) Where  $E_{NH3}0$  is the equilibrium potential (-0.578 V vs. RHE, -0.533 V vs. RHE, pH = 7) of nitrite and nitrate electroreduction to NH<sub>3</sub> in neutral pH, respectively,  $FE_{NH3}$  is the Faradaic Efficiency for NO<sub>2</sub><sup>-</sup> to NH<sub>3</sub> and NO<sub>3</sub><sup>-</sup> to NH<sub>3</sub>, 1.23 V is equilibrium potential of water oxidation (i.e. assuming the overpotential of the water

oxidation is zero), E is the applied potential (vs. RHE) in the experiment.

#### Experimental methods of TBA, mechanism of \*H quenching, and calculation of apparent rate constant

In both NO<sub>2</sub>RR and NO<sub>3</sub>RR processes, 50 mM tert-butyl alcohol (TBA) is added to the electrolyte as a radical scavenger. Electrolyte samples were collected every 10 minutes during electrolysis for analysis. The resulting curves show the relative concentration of the remaining reactants over time, comparing the cases with and without TBA. TBA quenches \*H via the following mechanism:

 $(CH_3)_3COH+*H\rightarrow(CH_3)_3C\cdot+H_2$ 

The apparent rate constant  $(k_{ap})$  was calculated using the equation:

 $\ln c = -k_{ap}t + \ln c_0 \tag{9}$ 

where  $c_0$  is the initial concentration of the reactant, c is the concentration at time t, and t is the reaction time

#### Theoretical calculation model

All the DFT calculation was conducted based on the Vienna Ab initio Simulation Package (VASP).<sup>3, 4</sup> The exchange-correlation potential was described by the Perdew–Burke–Ernzerhof (PBE) generalized gradient approach (GGA).<sup>5</sup> The electron-ion interactions were accounted by the projector augmented wave (PAW).<sup>6</sup> All DFT calculations were performed with a cut-off energy of 400 eV, and the Brillouin zone was

sampled using a  $2 \times 2 \times 1$  k-point grid. The energy and force convergence criteria of the self-consistent iteration were set to  $10^{-4}$  eV and 0.02 eV Å<sup>-1</sup>, respectively. DFT-D3 method was used to describe van der Waals (vdW) interactions.<sup>[6]</sup>

The adsorption energy  $(E_{ads})$  of adsorbate A was defined as

$$E_{ads} = E_{*A} - E_A - E_{sub}$$

where  $E_{*A}$  represents the energy of A molecule adsorbed on the surface.  $E_{sub}$  is the energy of clean surface,  $E_A$  represents the energy of A molecule.

The Gibbs free energy changes ( $\Delta G$ ) were calculated using the following formula:

$$\Delta G = \Delta E + \Delta Z P E - T \Delta S$$

where  $\Delta E$  is the difference of electron energies calculated by DFT;  $\Delta ZPE$  and  $\Delta S$  are the changes of zeropoint energy and entropy, respectively, which are obtained from vibrational frequencies. *T* is the room temperature (298.15 K).

### 2. Supporting Figures



Fig. S1 a)-e) The theoretical models of  $W_{18}O_{49}$  NWs and four representative metal nanoparticles (Ag, Fe, Cu, Co). f) The theoretical models of W-Cu-L-6.8%.



Fig. S2 a-b) TEM images of W-Cu-L-4%; c)-d) TEM images of W-Cu-L-8%.



Fig. S3 a)-b) TEM images of W-Cu-C.



**Fig. S4** a) AFM image and b) corresponding surface potential image of KPFM for W-Cu-L-6.8%. c) The line-scanning surface potential of W-Cu-L-6.8%. d) AFM image and e) corresponding surface potential image of KPFM for  $W_{18}O_{49}$ . f) The line-scanning surface potential of  $W_{18}O_{49}$ .



**Fig. S5** The valence states of W-Cu-L-4%, W-Cu-L-6.8% and W-Cu-L-8%. a) The Cu 2p high-resolution XPS spectra of samples; b) The Cu LMM auger XPS spectra of samples; c) The W 4f high-resolution XPS spectra of samples; d) The O 1s high-resolution XPS spectra of samples.



Fig. S6 EPR spectra of samples.



Fig. S7 TEM characterization of W-Cu-L-6.8% samples synthesized three times in succession.



**Fig. S8** Standard curves of concentration-absorbance of a)  $NO_3^-$ ; b)  $NO_2^-$  and c)  $NH_3^+$  obtained by UV-Vis spectroscopy.



Fig. S9 a-b) SEM images of Cu NPs.



Fig. S10 The chronoamperometry curves of a)  $NO_2RR$  and b)  $NO_3RR$  of W-Cu-L-6.8% at different potentials.



**Fig. S11** a-c) The evaluation parameters of W-Cu-L-6.8%, Cu NPs,  $W_{18}O_{49}$  NWs and W-Cu-C. a) Faradaic efficiency; b) Selectivity of NH<sub>4</sub><sup>+</sup> and c) yield rate of NH<sub>4</sub><sup>+</sup>.



**Fig. S12** The comparison of Faraday efficiency and ammonium yield rate for W-Cu-L-6.8% with reported electrocatalytic NO<sub>2</sub>RR based catalysts.



**Fig. S13** a-d) The evaluation parameters of W-Cu-L-4%, W-Cu-L-6.8%, and W-Cu-L-8%. a)  $NO_3^-$  Conversion; b) Faradaic efficiency; c) Selectivity of  $NH_4^+$ ; d) yield rate of  $NH_4^+$ .



**Fig. S14** a-d) The evaluation parameters of W-Cu-L-6.8%, Cu NPs,  $W_{18}O_{49}$  NWs and W-Cu-C. a)  $NO_3^-$  Conversion; b) Faradaic efficiency; c) Selectivity of  $NH_4^+$ ; d) yield rate of  $NH_4^+$ .



**Fig. S15** The comparison of Faraday efficiency and ammonium yield rate for W-Cu-L-6.8% with reported electrocatalytic NO<sub>3</sub>RR based catalysts.



Fig. S16 Ammonium yield rate of W-Cu-L-6.8% in  $Na_2SO_4$  electrolyte with  $NO_3^-$ , without  $NO_3^-$  and operated at OCP.



**Fig. S17** a) <sup>1</sup>H NMR spectra of various <sup>14</sup>NH<sub>4</sub><sup>+</sup> ion concentration (<sup>14</sup>NH<sub>4</sub><sup>+</sup>-N) using maleic acid as reference (300 ppm); b) Integral area (<sup>14</sup>NH<sub>4</sub><sup>+</sup> / C<sub>4</sub>H<sub>4</sub>O<sub>4</sub>) against <sup>14</sup>NH<sub>4</sub><sup>+</sup> ion concentration (<sup>14</sup>NH<sub>4</sub><sup>+</sup>-N); c) <sup>1</sup>H NMR spectra of the electrolyte after <sup>14</sup>NO<sub>3</sub><sup>-</sup> reduction using W-Cu-L-6.8% at -1.1 V vs. RHE for 1.5 h; d) The <sup>14</sup>NH<sub>4</sub><sup>+</sup> ion concentration (<sup>14</sup>NH<sub>4</sub><sup>+</sup>-N) of the electrolyte quantified by <sup>1</sup>H NMR using maleic acid (300 ppm) as reference.



**Fig. S18** a) <sup>1</sup>H NMR spectra of various <sup>15</sup>NH<sub>4</sub><sup>+</sup> ion concentration (<sup>15</sup>NH<sub>4</sub><sup>+</sup>-N) using maleic acid as reference (300 ppm); b) Integral area (<sup>15</sup>NH<sub>4</sub><sup>+</sup> / C<sub>4</sub>H<sub>4</sub>O<sub>4</sub>) against <sup>15</sup>NH<sub>4</sub><sup>+</sup> ion concentration (<sup>15</sup>NH<sub>4</sub><sup>+</sup>-N); c) <sup>1</sup>H NMR spectra of the electrolyte after <sup>15</sup>NO<sub>3</sub><sup>-</sup> reduction using W-Cu-L-6.8% at -1.1 V vs. RHE for 1.5 h; d) The <sup>15</sup>NH<sub>4</sub><sup>+</sup> ion concentration (<sup>15</sup>NH<sub>4</sub><sup>+</sup>-N) of the electrolyte quantified by <sup>1</sup>H NMR using maleic acid (300 ppm) as reference.



Fig. S19 EE of W-Cu-L-6.8% in NO<sub>2</sub>RR and NO<sub>3</sub>RR processes.



Fig. S20 The performance of the W-Cu-L-6.8% towards the electrolysis of NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> simultaneously.



Fig. S21 Performance of a)  $NO_2RR$  and a)  $NO_3RR$  in 0.2M PB electrolyte compared to 0.5M  $Na_2SO_4$  electrolyte.



Fig. S22 a-b) TEM images of W-Cu-L-6.8% after stability test.



**Fig. S23** The Valence states of W-Cu-L-6.8% before and after stability test. a) The Cu 2p high-resolution XPS spectra before and after test; b) The Cu LMM auger XPS spectra before and after test; c) The W 4f high-resolution XPS spectra before and after test; d) The O 1s high-resolution XPS spectra before and after test.



Fig. S24 FE of different products (NO<sub>2</sub><sup>-</sup>, NH<sub>3</sub>, H<sub>2</sub>, and N<sub>2</sub>) after NO<sub>3</sub>RR electrolysis for W-Cu-L-6.8%.



Fig. S25 NO<sub>3</sub>RR reaction pathway of W-Cu-L-6.8%.



Fig. S26 The NO<sub>3</sub>RR reaction pathway of W<sub>18</sub>O<sub>49</sub> NWs.



Fig. S27 The HER pathway of W-Cu-L-6.8%. a) Cu sites; b) W sites.

# 3. Supporting Tables

Ontion	Summary of element			
	W	Cu	test method / Unit	
W-Cu-L-4%	96.0472	3.9528	ICP-MS / Weight%	
W-Cu-L-6.8%	93.2206	6.7794	ICP-MS / Weight%	
W-Cu-L-8%	92.0153	7.9847	ICP-MS / Weight%	
W-Cu-C	97.1559	2.8441	ICP-MS / Weight%	

 Table. S1 Summary of element percentages obtained by ICP-MS.

Table. S2 Comparison of FE and yield of ammonia by NO<sub>2</sub>RR.

Catalysts	NH <sub>3</sub> FE	NH <sub>3</sub> Yield at the highest FE	Normalized NH <sub>3</sub> Yield	Ref.
W-Cu-L-6.8%	99.5%	1.5 mmol h <sup>-1</sup> mg <sub>cat</sub> <sup>-1</sup>	1.5 mmol h <sup>-1</sup> mg <sub>cat</sub> <sup>-1</sup>	This work
hcp IrNi NBs	98.2%	22.8 mg h <sup>-1</sup> mg <sub>cat</sub> <sup>-1</sup>	1.341 mmol h <sup>-1</sup> mg <sub>cat</sub> <sup>-1</sup>	8
Pd/CuO NOs	91.8%	906.4 µg h <sup>-1</sup> mg <sub>cat</sub> <sup>-1</sup>	$0.053 \text{ mmol } h^{-1} \text{ mg}_{\text{cat}}^{-1}$	9
Cobaloxime	98.1%	19.3 mg h <sup>-1</sup> mg <sub>cat</sub> <sup>-1</sup>	$1.135 \text{ mmol } h^{-1} \text{ mg}_{\text{cat}}^{-1}$	10
CuSb PNs	90.7%	946.1 µg h <sup>-1</sup> mg <sub>cat</sub> <sup>-1</sup>	$0.055 \text{ mmol } h^{-1} \text{ mg}_{\text{cat}}^{-1}$	11
Cu <sub>3</sub> Ni/MXene	95.6%	10.22 mg h <sup>-1</sup> mg <sub>cat</sub> <sup>-1</sup>	$0.601 \text{ mmol } h^{-1} \text{ mg}_{\text{cat}}^{-1}$	12
Ni@JBC-800	83.4%	4117.3 $\mu$ g h <sup>-1</sup> mg <sub>cat</sub> <sup>-1</sup>	$0.242 \text{ mmol } h^{-1} \text{ mg}_{\text{cat}}^{-1}$	13
Ni@HPCF	95.1%	12.04 mg h <sup>-1</sup> mg <sub>cat</sub> <sup>-1</sup>	$0.708 \text{ mmol } h^{-1} \text{ mg}_{\text{cat}}^{-1}$	14
np/ISAA- CuZn	95%	11.8 mg h <sup>-1</sup> mg <sub>cat</sub> <sup>-1</sup>	$0.694 \text{ mmol } \text{h}^{-1} \text{ mg}_{\text{cat}}^{-1}$	15
β-MnPc	92.9%	$16603.4 \ \mu g \ h^{-1} \ m g_{cat}^{-1}$	$1.186 \text{ mmol } h^{-1} \text{ mg}_{cat}^{-1}$	16

Table. S3 Comparison of FE and yield of ammonia by NO<sub>3</sub>RR.

Catalysts	NH <sub>3</sub> FE	NH <sub>3</sub> Yield	Normalized NH <sub>3</sub> Yield	Ref.
W-Cu-L-6.8%	91.4%	0.930 mmol h <sup>-1</sup> mg <sub>cat</sub> <sup>-1</sup>	0.930 mmol h <sup>-1</sup> mg <sub>cat</sub> <sup>-1</sup>	This work
Cu-CA	90.3%	3180 µg h <sup>-1</sup> mg <sub>cat</sub> <sup>-1</sup>	$0.187 \text{ mmol } \text{h}^{-1} \text{ mg}_{\text{cat}}^{-1}$	17

PdCu MSs	85.0%	$3058 \ \mu g \ h^{-1} \ m g_{cat}^{-1}$	0.180 mmol h <sup>-1</sup> mg <sub>cat</sub> <sup>-1</sup>	18
IrNiCu@Cu-20	86.0%	687.3 mmol $h^{-1} g_{cat}^{-1}$	0.687 mmol h <sup>-1</sup> mg <sub>cat</sub> <sup>-1</sup>	19
CuO/CC	90.7%	15.53 mg h <sup>-1</sup> mg <sub>cat</sub> <sup>-1</sup>	0.914 mmol h <sup>-1</sup> mg <sub>cat</sub> <sup>-1</sup>	20
Fe-pyNDI	87%	$14677 \ \mu g \ h^{-1} \ m g_{cat}^{-1}$	0.863 mmol h <sup>-1</sup> mg <sub>cat</sub> <sup>-1</sup>	21
Au-NC/TiO <sub>2</sub>	91%	1923 $\mu g h^{-1} m g_{cat}^{-1}$	0.113 mmol h <sup>-1</sup> mg <sub>cat</sub> <sup>-1</sup>	22
Bi-N-C	88.7%	1.38 mg h <sup>-1</sup> mg <sub>cat</sub> <sup>-1</sup>	0.081 mmol h <sup>-1</sup> mg <sub>cat</sub> <sup>-1</sup>	23
Fe-N/P-C	90.3%	$17980 \ \mu g \ h^{-1} \ mg_{cat}^{-1}$	1.058 mmol h <sup>-1</sup> mg <sub>cat</sub> <sup>-1</sup>	24
Cu <sub>2</sub> O-Ar-40	85.3%	$0.07 \text{ mmol } h^{-1} \text{ mg}_{\text{cat}}^{-1}$	$0.07 \text{ mmol } h^{-1} \text{ mg}_{\text{cat}}^{-1}$	25
Fe-NCS	78.4%	9.47 mg h <sup>-1</sup> mg <sub>cat</sub> <sup>-1</sup>	0.557 mmol h <sup>-1</sup> mg <sub>cat</sub> <sup>-1</sup>	26
Cu <sub>x</sub> O/N-GDY	85.0%	$340 \ \mu mol \ h^{-1} \ mg_{cat}^{-1}$	$0.34 \text{ mmol } h^{-1} \text{ mg}_{\text{cat}}^{-1}$	27
$Ag_{20}Cu_{12}$	84.6%	$0.138 \text{ mmol } h^{-1} \text{ mg}_{\text{cat}}^{-1}$	$0.138 \text{ mmol } h^{-1} \text{ mg}_{cat}^{-1}$	28
Fe/Cu-HNG	92.5%	$1.08 \text{ mmol } h^{-1} \text{ mg}_{\text{cat}}^{-1}$	$1.08 \text{ mmol } \text{h}^{-1} \text{ mg}_{\text{cat}}^{-1}$	29

**Table. S4** Comparison of the quantitative analysis between colorimetric method and <sup>1</sup>H NMR for nitrate electroreduction at the optimal potential (-1.1 V vs. RHE).

Quantitative method	N-sources	Detected ion	Concentration (mmol L <sup>-1</sup> )	Yield rate (mmol h <sup>-1</sup> cm <sup>-2</sup> )
colorimetric method	Na <sup>14</sup> NO <sub>3</sub>	$^{14}NH_{4}^{+}$	46.5	0.930
<sup>1</sup> H NMR	Na <sup>14</sup> NO <sub>3</sub> -	$^{14}\mathrm{NH_4^+}$	48.2	0.964
<sup>1</sup> H NMR	Na <sup>15</sup> NO <sub>3</sub> -	$^{15}NH_{4}^{+}$	48.6	0.972

**Table. S5** FE and YR of  $H_2$  (GC), hydrazine hydrate (UV spectrophotometer) and  $NO_2^-$  (UV

spectrophotometer)	in $NO_2RR$ and	NO <sub>3</sub> RR processes
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	<b>By-products</b>		
Option	H <sub>2</sub> (GC)	Hydrazine ( UV spectrophotometer)	NO₂⁻ (UV spectrophotometer)
NO <sub>2</sub> RR (FE)	0.8%	0	-
NO <sub>2</sub> RR (YR)	0.036 mmol h <sup>-1</sup> mg <sub>cat.</sub> <sup>-1</sup>	0	-
NO <sub>3</sub> RR (FE)	5.1%	2.02%	1.7%
NO <sub>3</sub> RR (YR)	0.213 mmol h <sup>-1</sup> mg <sub>cat.</sub> <sup>-1</sup>	$0.012 \mod{h^{-1}}{mg_{cat.}}^{-1}$	0.07 mmol h <sup>-1</sup> mg <sub>cat.</sub> <sup>-1</sup>

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