Supporting information of

Enhancing electrocatalytic N₂ reduction to NH₃ by introducing Ni heteroatoms

into NiCuO_x electrocatalyst

Xinxin Han^b[†], Weizhen Zhou^a[†], Xin Huang^a, Haoming Yu^a, Fangqi Yang, Shixia Chen^{a*}, Jun Wang^a

^a School of Chemistry and Chemical Engineering, Nanchang University, Nanchang 330031, People's

Republic of China

^b School of Resources & Environment, Nanchang University, Nanchang 330031, People's Republic

of China

* Corresponding author.

E-mail for S.C.: shixiachen@ncu.edu.cn

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Experimental section

Reagents and chemicals: methanol (CH₄O), 2-MeIM (C₆H₄N₂), ethanol (C₂H₆O), nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O), cobalt nitrate hexahydrate (Cu(NO₃)₂·3H₂O), anhydrous sodium sulfate (Na₂SO₄), sodium hypochlorite (NaClO), ammonium chloride (NH₄Cl), hydrazine chloride (N₂H₄·2HCl), sodium hydroxide (NaOH), sodium salicylate (C₇H₅O₃Na), and carbon paper were bought from Beijing Chemical Corporation. sodium nitroferricyanide (III) dihydrate (Na₂Fe(CN)₅NO·2H₂O), Para-(dimethylamino) benzaldehyde (C₉H₁₁NO), and Nafion were purchased from Aladdin Ltd. (Shanghai, China). Ultra-water used throughout all experiments was purified through a Millipore system.

*Synthesis of NiCu(OH)*_x: All chemical reagents were analytical grade and used without further purification. Initially, 5.452g Ni(NO₃)₂•6H₂O and 4.530g Cu(NO₃)₂•3H₂O were dispersed in 30 mL methanol, the resulting solution named A. 2.463g of 2-MeIM was dispersed in 12mL methanol, the resulting solution named B. Solution A was slowly poured into solution B with gently shaking, and the resultant solution was sonicated in an ultrasonicator for 100min. The precipitate was got after sonication. After centrifugating, washing with methanol for three times and drying, the nattier blue power was got at last.

Synthesis of NiCuO_x: A quartz boat containing NiCu(OH)_x in a tubular furnace under Ar atmosphere which gas flow rate was 100 mL/min. After annealing treatment at 300°C with a heating rate of 5° C/min for 5h, the black powder was obtained at last.

Synthesis of NiCuO_x with different Nickel-copper atomic ratio: With different ingredient proportion (Ni/Cu=0:1, 1:2, 1:1, 2:1, 1:0) of Ni(NO₃)₂•6H₂O and Cu(NO₃)₂•3H₂O, black powders with different atomic proportions were obtained.

Characterizations

Powder X-ray diffraction (XRD) patterns were acquired on a Bruker D8 Advance X-ray diffractometer with a Cu K α radiation (λ =1.5406 Å). X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250Xi.The scanning electron microscopy (SEM) images were obtained in a field emission scanning electron microscopy (ZEISS Sigma 300, Germany). The transmission electron microscopy (TEM) images were collected in a high-resolution TEM (HRTEM, FEI HELIOS NanoLab 600i Titan G2 60-300). The Raman spectra were detected on a Confocal LabRam HR800 spectrometer with 532 nm radiation (HORIBA Jobin Yvon). 1H-NMR measurements were performed on a Bruker Ascend TM 400MHz. UV-Vis was performed by a UV-Vis spectrophotometer (TU-1900, PERSEE).

Electrochemical measurements

The NRR experiment was tested on an electrochemistry workstation (CHI660E), which is utilizing the conventional three-electrode setup. And the three-electrode setup contain a platinum plate (Pt,1 cm \times 1 cm) as the counter electrode, Ag/AgCl (with saturated KCl solution) as the reference electrode and the Ni_xCu_yO as the working electrode (on carbon paper ,1 cm \times 1 cm). All of these electrodes and cell would cleaned by DI water before and after the NRR experiments. The potentials in this experiment were normalized to the reversible hydrogen electrode (RHE) by the formula of E (RHE) = E (Ag/AgCl) + 0.197 + 0.059 pH. Besides, these experiments were conducted in a H-cell, which is separated by a proton-exchange Nafion 212 membrane. Before the NRR test, the new 212 membrane need to pretreated by heating in 0.5 M H₂SO₄ and 3 wt% H₂O₂ solutions at 80 °C for 2 h, respectively. And then put it into ultrapure water at 80 °C for 12 h. The working electrode was prepared by Ultrasonic dispersion method. 2mg NiCuO_x was added into the solution of 100 μ L Nafion solution and 400 μ L ethanol under ultrasonic for 1 h. Then drop 50 μ L of the uniform dispersed ink obtain above on the working electrode. Before the NRR test, ultra-high purity N₂ (99.999%) was pre-purified through 0.05 M H₂SO₄ and 0.05 M NaOH solutions for 30 min, and then flowed into the cathode cell containing to eliminate the effects of NO_x and ammonia.

Determination of ammonia

To identify the NRR products, NH₃ was spectrophotometrically quantified by the indophenol blue method and UV-vis spectrophotometry. The chromogenic agent needed for indophenol blue method needs to be prepared in advance. The chromogenic agent is divided into three parts: Oxidizing agent, Coloring agent and Catalyst agent.

(1) Oxidizing agent: Dissolving 31.25mL NaClO solution (available chlorine \geq 5%) into 0.2M NaOH to form 50mL solution A. And 1.5g NaOH is put into solution A and Uniformly dispersed. The result solution is Oxidizing agent.

(2) Coloring agent: 6.4g sodium salicylate and 1.28g sodium hydroxide are dissolved in 100mL DI water. The result solution is Coloring agent.

(3) Catalyst agent: Dissolving 0.5g sodium nitrite in 50 mL DI water.

50µL Oxidizing agent solution, 500 µL Coloring agent solution and 50µL Catalyst agent

are added into 4mL electrolyte from the cathode cell in order. After each solution is added, the tube needs to be shaken to disperse it respectively. After being placed in darkness at room temperature for

2 h, the solution was determined by a UV-vis spectrophotometer. And the UV-Vis absorption spectrum was measured at a wavelength of 655 nm.

Quantitative measurement of product yield requires the usage of standard curves, The concentrationabsorbance standard curves were calibrated using standard NH₄Cl solution (0.1 M Na₂SO₄ solution as mother solution) with a serious of concentrations (0.0, 0.1, 0.2, 0.3, 0.4, 0.5 μ g mL⁻¹). The standard curve is Y=0.450X+0.0396 (R²=0.999), which shows good linear relation of absorbance value with NH₃ concentration.

Determination of N_2H_4

To identify the by-products, N_2H_4 was spectrophotometrically quantified by the Watt and Chrisp method and UV-vis spectrophotometry. The chromogenic agent needed for Watt and Chrisp method needs to be prepared in advance.

Dissolving 2g $C_9H_{11}NO$ into the mixed solution of 10mL HCl (36%) and 100mL ethanol to form the coloring agent. 5mL coloring agent solution is added into 5mL electrolyte from the cathode cell and then the result solution is placed in darkness at room temperature for 2 h, the solution was determined by a UV-vis spectrophotometer. And the UV-Vis absorption spectrum was measured at a wavelength of 455 nm.

Quantitative measurement of by-product N_2H_4 yield requires the usage of standard curves, The concentration-absorbance standard curves were calibrated using standard N_2H_4 -HCl solution (0.1 M Na_2SO^4 solution as mother solution) with a serious of concentrations (0.0, 0.1, 0.2, 0.3, 0.4, 0.5 µg mL⁻¹). The standard curve is Y=0.7142X+0.0224 (R²=0.999), which shows good linear relation of

absorbance value with N₂H₄ concentration.

Determination of NO_x

Detecting NO_x also need UV-vis spectrophotometry after adding chromogenic agent. 5mg n-(1naphthyl)-ethylenediamine dihydrochloride is added into the mixture of 0.5g sulfanilic acid, 5mL acetic acid and 90 mL DI water, the result solution is chromogenic agent. 4mL coloring agent solution is added into 1mL electrolyte from the cathode cell and then the result solution is placed in darkness at room temperature for 15 min, the solution was determined by a UV-vis spectrophotometer. And the UV-Vis absorption spectrum was measured at a wavelength of 540 nm. The concentration-absorbance standard curves were calibrated using standard sodium nitrite solution (0.1 M Na₂SO₄ solution as mother solution) with a serious of concentrations (0.0, 0.1, 0.2, 0.3, 0.4, 0.5 μ g mL⁻¹). The standard curve is Y=1.0820X+0.0079 (R²=0.999) , which shows good linear relation of absorbance value with NO_x concentration.

*Calculation of NH*₃ yield and Faraday Efficiency

The formula of ammonia yield is as follows:

$$R = \frac{VC}{Mt}$$

The formula of Faraday Efficiency is as follows:

$$FE = \frac{3FCV}{17Q}$$

Where R (mol s⁻¹ cm⁻²) is the NH₃ yield rate, V(50mL) is the volume of electrolyte, C(g mL⁻¹) is the concentration of NH₃ in the electrolyte after NRR, M(g mol⁻¹) is molar mass of NH₃, t(s) is the time

of NRR experiment, F(96485.34 C mol⁻¹) is the Faradaic constant, Q (C) is the quantity of applied electricity during the NRR.

¹⁵N isotopic labelling experiment

¹⁵N isotopic labelling NRR experiment is performed the same as ¹⁴NRR experiment. Before the test, ¹⁵N2 need to be pre-purified by flowing through 0.05 M H₂SO₄ solution and 0.05 M NaOH solution to remove N contamination. All the electrolyte (50 mL) in the cathode chamber is taken out after NRR for 2h, and djusted the PH of which to 3~4 with sulfuric acid. The result solution is then passed through a rotary evaporators to evaporate some of the water to obtain a 2mL concentrated solution. After that, 250 μ L of electrolyte is mixed with 150 μ L of D₂O, 50 μ L of 3.5 mg mL⁻¹ MA solution, and 50 μ L of 0.05 M H₂SO₄. The produced ammonia was quantified using ¹H nuclear magnetic resonance (NMR) measurements. Maleic acid (MA) was used for quantitative analysis.

Computational simulation details

Density functional theory (DFT) calculations were performed in the Vienna ab initio simulation package (5.4.4 VASP)¹. The generalized gradient approximation (GGA) functional PBE², the projector augmented wave (PAW)³ method and the 400eV energy cutoff were adopted. Van der Waals interaction was considered using DFT-D3BJ correction^{4,5}. For geometry optimizations, the convergence tolerance is set as follows: energy= 5.0×10^{-5} eV, force= 5.0×10^{-2} eV Å⁻¹. The Brillourin zone were sampled with Gamma meshes of $3 \times 6 \times 1$, $6 \times 6 \times 2$, and $8 \times 8 \times 1$ for CuNiO, CuO, and NiO, respectively, through all the computational process. A vacuum space of 10 Å was employed to

avoid the interaction between adjacent periodic units.

The free energy changes for different adsorptions were determined as follows:

$$\Delta G = E_{ads} - E_{sur} + \Delta H_{corr} - T\Delta S$$

Here, E_{ads} is the electronic energy for adsorption state; E_{sur} is the electronic energy of unadsorbed surface; while ΔH_{corr} and ΔS are thermal correction to enthalpy change and entropy change, which were obtained through the aid of VASPKIT, version 1.2.5⁶. The visualization of periodic structures and the analysis of electron density difference are performed by VESTA, Version 3.5.5⁷.

Figures



Figure S1. SEM images of (a) Cu(OH)₂, (b) Ni(OH)₂, (c) NiCu(OH)_x, and corresponding (d) CuO, (e) NiO and (f) NiCuO_x.



Figure S2. XPS spectra of O1s in NiCuO_x



Figure S3. Photograph of electrochemical setup for NRR test.



Figure S4. (a) GC and (b) IR spectra of N_2 feeding gas.



Figure S5. (a) UV-vis absorption spectra of indophenol assays with NH_3 concentrations in 0.1 M Na_2SO_4 after incubated for 2 h at room temperature. (b) Calibration curve used for estimation of NH_3 concentration.



Figure S6. (a) UV-Vis absorption spectra of various N_2H_4 concentrations after incubated for 15 min at room temperature. (b) Calibration curve used for estimation of N_2H_4 concentration.



Figure S7. (a) UV-Vis absorption spectra of various NO_x concentrations after standing in darkness for 15 min at room temperature; (b) Calibration curve used for calculation of NO_x concentration.



Figure S8. LSV curves of (a) CuO, (b) NiCuO_x, (c) NiO.



Figure S9. Chronoamperometry results of (a) CuO, (b) $NiCuO_x$, (c) NiO at different applied potentials (-0.1~-0.6 V) in N₂-saturated 0.1 M Na₂SO₄ solution.



Figure S10. UV-Vis absorption spectra of the electrolytes stained with indophenol indicator after NRR electrolysis by (a) CuO, (b) NiCuO_x, (c)NiO at different potentials for 2 h.



Figure S11. NH_3 production rate and Faradaic efficiency for (a) CuO, (b) $NiCuO_x$, (c) NiO at different potentials for 2 h NRR measurement.



Figure S12. UV-vis absorption spectra of the electrolytes that estimated by the Watt and Chrisp method after 2 h reaction on NiCuO_x at different applied potentials (-0.1~-0.6V) in N₂-saturated 0.1 M Na₂SO₄ solution.



Figure S13. Cyclic voltammetry curves of (a) CuO, (b) NiCuO_x, and (c) NiO at various scan rates $(20 \text{ mV s}^{-1} \text{ to } 120 \text{ mV s}^{-1})$ in the region of 0.35 to 0.55 V.



Figure S14. Chronoamperometry results of (a) NiCuO_x-12, (b) NiCuO_x, (c) NiCuO_x-21 at different applied potentials (-0.1 \sim -0.6 V) in N₂-saturated 0.1 M Na₂SO₄ solution.



Figure S15. UV-Vis absorption spectra of the electrolytes stained with indophenol indicator after NRR electrolysis by (a) NiCuO_x-12, (b) NiCuO_x, (c) NiCuO_x-21 at different potentials for 2 h.



Figure S16. NH₃ production rate and faradaic efficiency for (a) NiCuO_x-12, (b) NiCuO_x, (c) NiCuO_x-21 at different potentials for 2 h NRR measurement.



Figure S17. UV-vis absorption spectra of different samples in control experiments to eliminate possible environmental influence.



Figure S18. UV-vis spectrum results of NO_x concentration test on $NiCuO_x$ after 2 h reaction at different applied potentials (-0.1~-0.6V) in N₂-saturated 0.1 M Na₂SO₄ solution.



Figure S19. UV-vis spectrum results of NO_x concentration test on the feed gas before and after H_2SO_4 and NaOH alternating acid-base washing.



Figure S20. UV-vis spectrum results of NH_3 concentration test on the feed gas before and after H_2SO_4 and NaOH alternating acid-base washing.



Figure S21. UV-vis spectrum results of N_2H_4 concentration test by the Watt and Chrisp method on the feed gas before and after H_2SO_4 and NaOH alternating acid-base washing.



Figure S22. (a) The ¹H NMR (400 MHz) spectra of a serious of ¹⁴NH₄⁺ standard solution with known concentration and the NiCuO_x catalyst produced ¹⁴NH₄⁺. Maleic acid (MA) is used as the internal standard; (b) The corresponding calibration curve is used for the calculation of NH_4^+ concentration.



Figure S23. (a) The ¹H NMR (400 MHz) spectra of a serious of ¹⁵NH₄⁺ standard solution with known concentration and the NiCuO_x catalyst produced ¹⁵NH₄⁺. Maleic acid (MA) is used as the internal stand; (b) The corresponding calibration curve is used for the calculation of NH_4^+ concentration.



Figure S24. Chronoamperometry results for the cycling tests on NiCuO_x at -0.2V.



Figure S25. UV-vis absorption spectra of the cycling tests on NiCuO_x at -0.2V.



Figure S26. PXRD pattern of NiCuO_x after long-term NRR test.



Figure S27. SEM image of NiCuO_x after long-term NRR test.



Figure S28. TEM image of NiCuO_x after long-term NRR test.



Figure S29. HRTEM image of $NiCuO_x$ after long-term NRR test.



Figure S30. The XPS spectra of $NiCuO_x$ after long-term NRR test.



Figure S31. Charge density difference image of $*N_2$ adsorbed on (a)NiO surface [isosurface = 0.000239016] and (b)CuO surface [isosurface = 0.0881716]; yellow and blue isosurfaces represent charge accumulation and depletion, respectively.



Figure S32. Key structures of intermediates adsorbed on $NiCuO_x$ of (a) the distal pathway and (b) the alternating pathway (Red: O, brown: Cu, green: Ni, Blue: N, sliver: H).



Figure S33. Key structures of intermediates adsorbed on NiO of the alternating pathway (Red: O, green: Ni, Blue: N, sliver: H).



Figure S34. Key structures of intermediates adsorbed on CuO of the alternating pathway (Red: O, Brown: Cu, Blue: N, sliver: H).

Tables

samples	rate of charge	Atomic content	Metal weight percentage	
	n _{Ni} :n _{Cu}	$n_{\mathrm{N}i}/n_{\mathrm{C}u}$	$M_{Ni}(wt\%)$	M _{Cu} (wt%)
CuO	0:1	0	0	72.41
NiCuO _x -12	1:2	0.016	1.15	80.2
NiCuO _x	1:1	0.048	3.48	78.15
NiCuO _x -21	2:1	0.138	9.32	73.1
NiO	1:0	-	60.88	0

 Table S1. Elemental compositions by ICP-OES.

Catalysts	System	NH ₃ yield rate	FE (%)	Potential (V vs. RHE)	References
NiCuO _x	0.1M Na ₂ SO ₄	11.78 μg h ⁻¹ mg _{cat.} ⁻¹ (0.2 mg)	19.28%	-0.2V	This work
Pt ₃ Fe nanocrystals	0.1M KOH	18.3 μg h ⁻¹ mg _{cat.} ⁻¹ (0.1 mg)	7.3%	-0.05V	8
PdH _{0.43} NRs	0.1M Na ₂ SO ₄	17.53 μg h ⁻¹ mg _{cat.} ⁻¹ (0.1 mg)	18.56%	-0.2V	9
PdNCs@CNFs	0.1M Na ₂ SO ₄	4.4 μg h ⁻¹ mg _{cat.} ⁻¹ (0.1 mg)	14.8%	-0.2V	10
FeCoOOH HNCs	0.1M Na ₂ SO ₄	16.8 μg h ⁻¹ cm _{cat} ⁻¹	14.7%	-0.3V	11
Au ₂₅ @S-G	$0.05M H_2SO_4$	27.5 μg h ⁻¹ mg _{cat.} ⁻¹ (0.1 mg)	2.3%	-0.5V	12
O-CoP/CNT	0.1M Na ₂ SO ₄	39.58 μg h ⁻¹ mg _{cat.} ⁻¹ (0.1 mg)	19.4%	-0.5V	13
Fe(III) grafted MoO ₃	0.1M Na ₂ SO ₄	9.66 μg h ⁻¹ mg _{cat.} ⁻¹ (0.1 mg)	13.1%	-0.6V	14
Li-TiO ₂ (B)	0.5M LiClO ₄	$8.7 \ \mu g \ h^{-1} \ m g_{cat.}^{-1}$	18.2%	-0.4V	15
2.0 %Cu/OV- TiO ₂	0.1M Na ₂ SO ₄	13.6 μg h ⁻¹ mg _{cat.} ⁻¹	17.9%	-0.5V	16
Pt-FeP/C	0.1M KOH	10.95 μg h ⁻¹ mg _{cat.} ⁻¹ (0.2 mg)	15.3%	-0.1V	17

 Table S2. The comparable table of state-of-the-art NRR catalysts.

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