

Electronic Supplementary Information

Experimental

Materials: Copper (II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), sodium nitroferricyanide dihydrate ($\text{C}_5\text{FeN}_6\text{Na}_2\text{O} \cdot 2\text{H}_2\text{O}$), sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$), para-(dimethylamino) benzaldehyde ($p\text{-C}_9\text{H}_{11}\text{NO}$), and salicylic acid ($\text{C}_7\text{H}_6\text{O}_3$) were purchased from Aladdin Ltd, Shanghai, China. Nafion (5 wt%) solution was purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. Hydrochloric acid (HCl), sodium hydroxide (NaOH), Sulfuric acid (H_2SO_4), nitric acid (HNO_3), and ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$) were purchased from Chengdu Kelong Chemical Reagent Factory, China. Hypochlorite solution (NaClO), ammonium chloride (NH_4Cl), hydrazine monohydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$), carbon paper (CP; TGP-H-060), and Zn foil (99.99%) were purchased from Beijing Chemical Corp, China. High-purity N_2 (99.999%) and Ar (99.999%) were purchased from Chengdu Xuyuan Chemical Co., Ltd, China. The ultrapure water used throughout all experiments was purified through a Millipore system. All reagents were analytical reagent grade without further purification.

Synthesis dendritic Cu: The synthesis for dendritic Cu, Zn foil was successively cleaned by acetone, deionized water and ethanol. Then, 600 mM CuSO_4 aqueous solution was prepared. The product was made by immersing Zn foil into the CuSO_4 solution for 8 min, then remove the surplus Zn foil completely, and getting the powder was washed by 0.1 M HCl, deionized water and ethanol, respectively. Finally, vacuum drying for 5 hours under 50°C .

Preparation of Cu/CP: CP was pretreated in 0.05M H_2SO_4 , then was sequentially cleaned in deionized water and ethanol several times by sonication to remove the surface impurities. To prepare the Cu/CP, 10 mg dendritic Cu and 40 μL 5 wt% Nafion solution were dispersed in 960 μL ethanol followed by 30 min sonication to form a homogeneous ink. 10 μL ink was loaded onto a CP ($1 \times 1 \text{ cm}^2$) and dried under ambient condition. (the dendritic Cu loading: 0.1 mg cm^{-2})

Characterizations: X-ray diffraction (XRD) patterns were obtained from a Shimadzu XRD-6100 diffractometer with Cu $\text{K}\alpha$ radiation (40 kV, 30 mA) of wavelength 0.154

nm (Japan). Scanning electron microscopy (SEM) images were collected on a GeminiSEM 300 scanning electron microscope (ZEISS, Germany) at an accelerating voltage of 10 kV. The structures of the samples were determined by Transmission electron microscopy (TEM) images on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) operated at 200 kV. The absorbance data of spectrophotometer were measured on UV-2700 spectrophotometer. The ion chromatography data were collected on Metrohm 940 Professional IC Vario.

Pretreatment before electrochemical measurement: Prior to use, all components of the electrochemical cell were soaked in 0.05 M H₂SO₄ solution for at least 16 h and then washed copiously with deionized water to eliminate any contaminants. Nafion 117 membrane was ultrasonicated in 1 M H₂SO₄, and deionized water at 80 °C for 1 h, respectively. Then it was thoroughly rinsed in deionized water several times. All other labware involved in experiments (vials, containers, needles, pipet, etc.) were also washed with 0.1 M H₂SO₄ and deionized water several times. The N₂ (99.999%) and Ar (99.999%) before entering the cell, they were passed through a saturator filled with 0.05 M H₂SO₄ to remove any possible contaminants. Likewise, gases exiting the cell were passed through another saturator filled with 0.05 M H₂SO₄, which served as an acid trap to capture any generated ammonia. Prior to any electrochemical measurement, we have made sure of the gas tightness of the cells, and saturate the electrolyte and headspace in electrolyser by purging the gas that has been passed through a saturator filled with 0.05 M H₂SO₄ for at least 30 min.

Electrochemical measurement: Electrochemical NRR measurements were performed in a two-compartment cell separated by Nafion 117 membrane using a CHI 660E electrochemical analyzer (CH Instruments, Inc.). The electrochemical experiments were carried out with a three-electrode configuration using graphite rod as the counter electrode and Ag/AgCl/saturated KCl solution as the reference electrode. The working electrode was a CP with catalysis. The potentials reported in this work were converted to reversible hydrogen electrode (RHE) scale via calibration with the following equation: $E(\text{RHE}) = E(\text{Ag}/\text{AgCl}) + 0.059 \times \text{pH} + 0.197 \text{ V}$ and the

presented current density was normalized to the geometric surface area. For electrochemical N₂ reduction, chrono-amperometry tests were conducted in N₂-saturated 0.1 M HCl solution (the HCl electrolyte was purged with N₂ for 30 min before the measurement).

Determination of NH₃: Concentration of produced NH₃ was spectrophotometrically determined by the indophenol blue method.¹ Typically, 2 mL electrolyte was taken from the cathodic chamber, and then 2 mL of 1 M NaOH solution containing 5% salicylic acid and 5% sodium citrate was added into this solution. Subsequently, 1 mL of 0.05 M NaClO and 0.2 mL of 1% C₅FeN₆Na₂O·2H₂O were added into the above solution. After standing at room temperature for 2 h, UV-Vis absorption spectrum was measured at a wavelength of 655 nm. The concentration-absorbance curve was calibrated using the standard NH₄Cl solution with NH₃ concentrations of 0.0, 0.05, 0.10, 0.15, 0.20, 0.25, and 0.30 μg mL⁻¹ in 0.1 M HCl. The fitting curve ($y = 0.356x + 0.051$, $R^2 = 0.999$) shows good linear relation of absorbance value with NH₃ concentration by three times independent calibrations.

Determination of N₂H₄: N₂H₄ presented in the electrolyte was estimated by the method of Watt and Chrisp.² A mixed solution of 5.99 g *p*-C₉H₁₁NO, 30 mL HCl and 300 mL ethanol was used as a color reagent. Calibration curve was plotted as follows: firstly, preparing a series of reference solutions; secondly, adding 5 mL above prepared color reagent and stirring 20 min at room temperature; finally, the absorbance of the resulting solution was measured at 455 nm, and the yields of N₂H₄ were estimated from a standard curve using 5 mL residual electrolyte and 5 mL color reagent. Absolute calibration of this method was achieved using N₂H₄·H₂O solutions of known concentration as standards, and the fitting curve shows good linear relation of absorbance with N₂H₄·H₂O concentration ($y = 0.699x + 0.0436$, $R^2 = 0.999$) by three times independent calibrations.

Calculations of NH₃ yield rate and Faradaic efficiency (FE): The FE for N₂ reduction was defined as the amount of electric charge used for synthesizing NH₃ divided the total charge passed through the electrodes during the electrolysis. The

total amount of NH_3 produced was measured using colorimetric methods. Assuming three electrons were needed to produce one NH_3 molecule, the FE could be calculated as follows:

$$\text{FE} = 3 \times F \times [\text{NH}_3] \times V / (17 \times Q)$$

The rate of NH_3 yield rate (V_{NH_3}) was calculated using the following equation:

$$V_{\text{NH}_3} = [\text{NH}_3] \times V / (m_{\text{cat.}} \times t)$$

The amount of NH_3 was calculated as follows:

$$m_{\text{NH}_3} = [\text{NH}_3] \times V$$

Where F is the Faraday constant (96500 C mol^{-1}); $[\text{NH}_3]$ is the measured NH_3 concentration; V is the volume of the electrolyte in the cathodic chamber (35 ml); Q is the total quantity of applied electricity; $m_{\text{cat.}}$ is the loaded mass of catalyst on carbon paper (0.1 mg) and t is the reduction time (2 h).

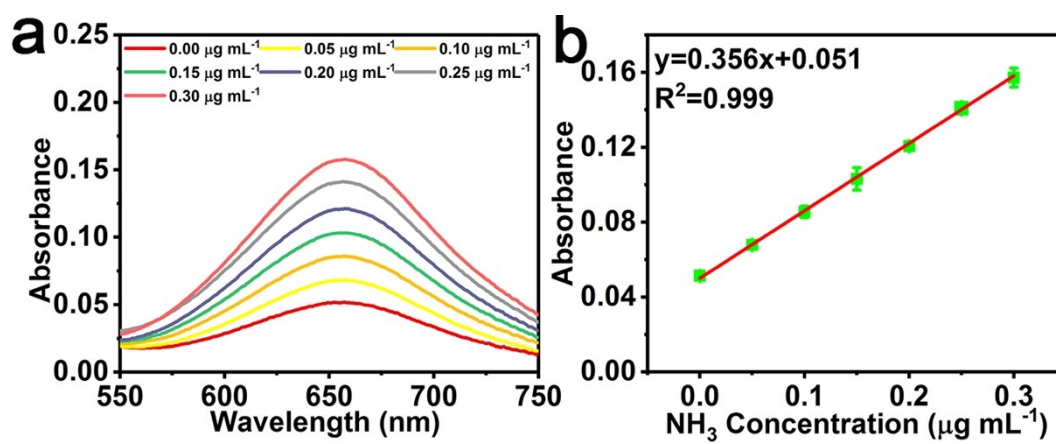


Fig. S1. (a) UV-Vis curves of indophenol assays with NH_3 after incubated for 2 h at room temperature. (b) Calibration curve used for estimation of NH_3 .

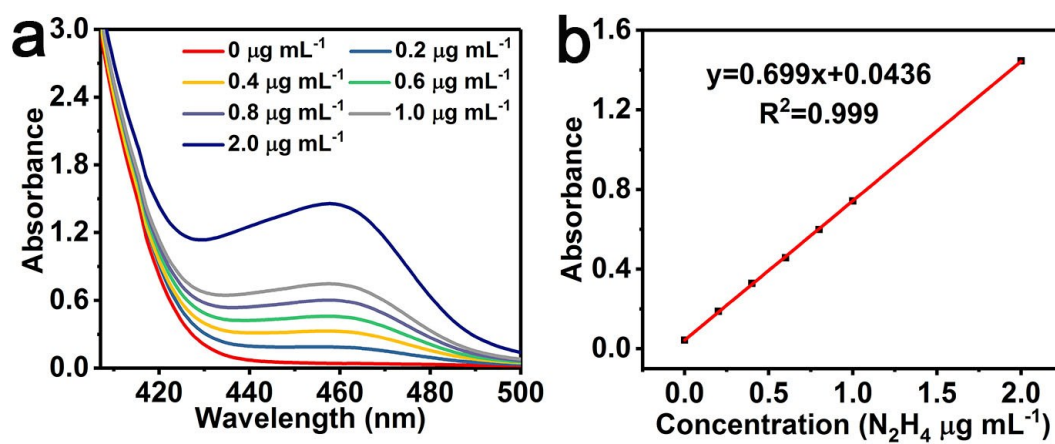


Fig. S2. (a) UV-Vis curves of various N_2H_4 concentrations after adding into chemical indicator by the method of Watt. (b) Calibration curve used for calculation of N_2H_4 concentrations.

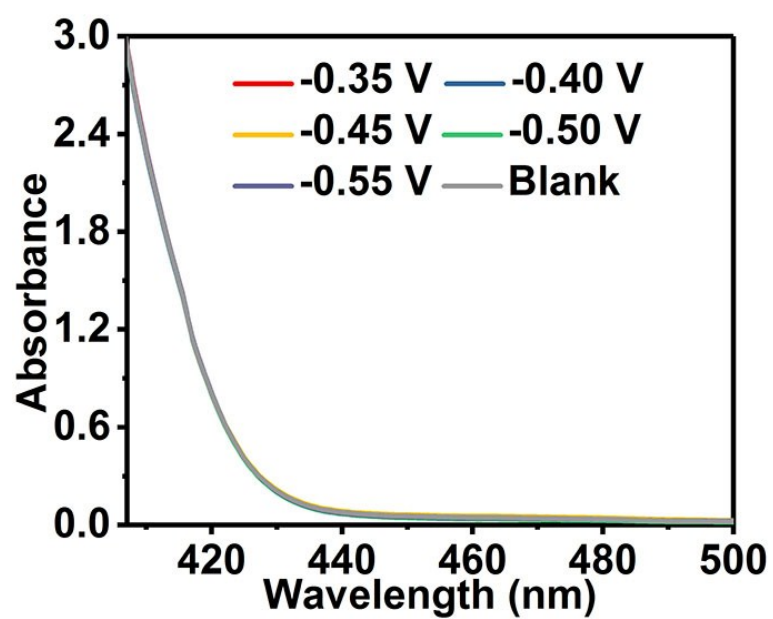


Fig. S3. UV-Vis absorption spectra of the electrolytes treated with the method of Watt and Crisp for 20 min after NRR at a series of potentials

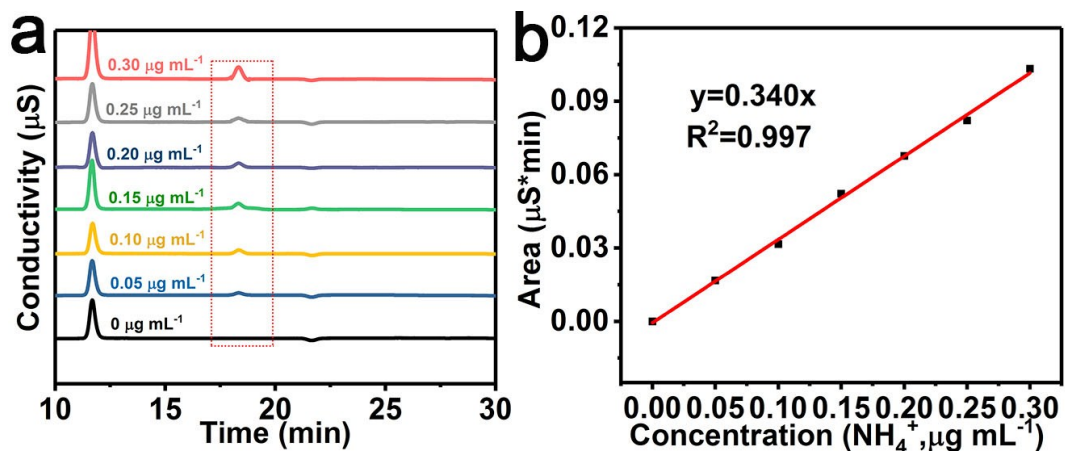


Fig. S4. (a) Ion chromatograms of NH_4^+ with different concentrations in 0.1 M HCl and (b) corresponding standard curve.

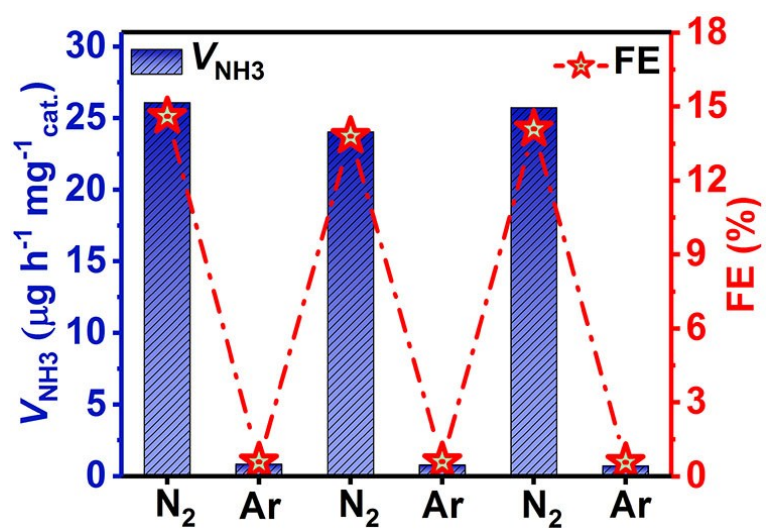


Fig. S5. V_{NH_3} and FEs for Cu/CP with alternating 2 h cycles between N₂- and Ar-saturated electrolytes.

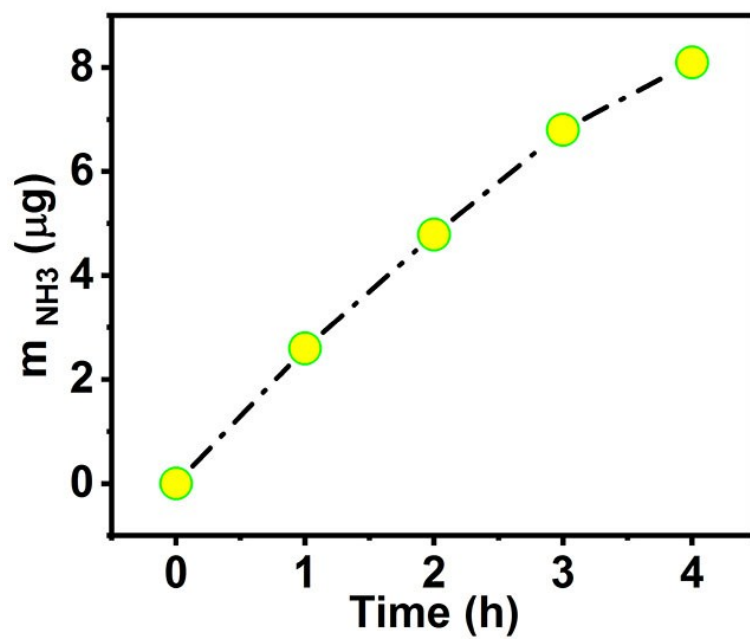


Fig. S6. Amount of NH₃ vs. reaction time at -0.40 V using Cu/CP.

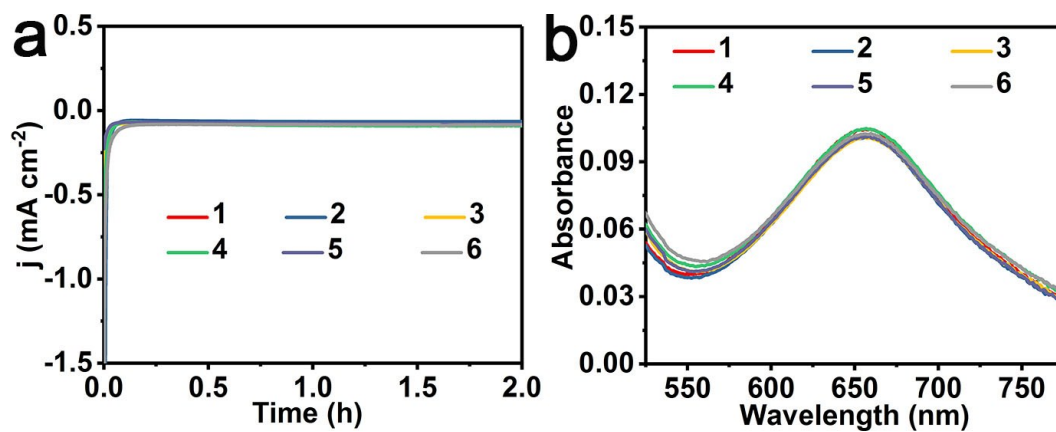


Fig. S7. (a) Time-dependent current density curves of Cu/CP electrode at -0.40 V over 6 cycles. (b) UV-Vis absorption spectra of the electrolytes stained with indophenol indicator after 2 h NRR electrolysis at -0.40 V over 6 cycles.

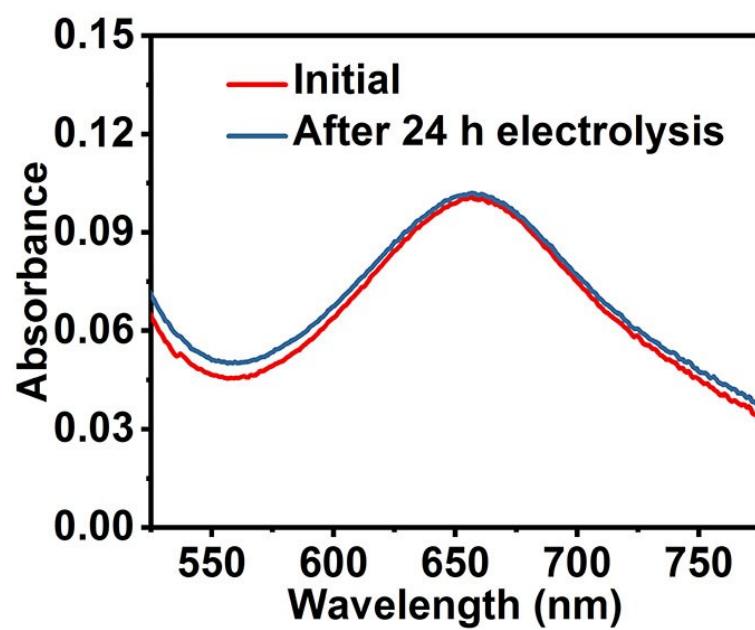


Fig. S8. UV-Vis absorption spectra of the electrolytes stained with indophenol indicator at -0.40 V after electrolysis for 2 h with the initial Cu/CP and the Cu/CP after 24 h electrolysis.

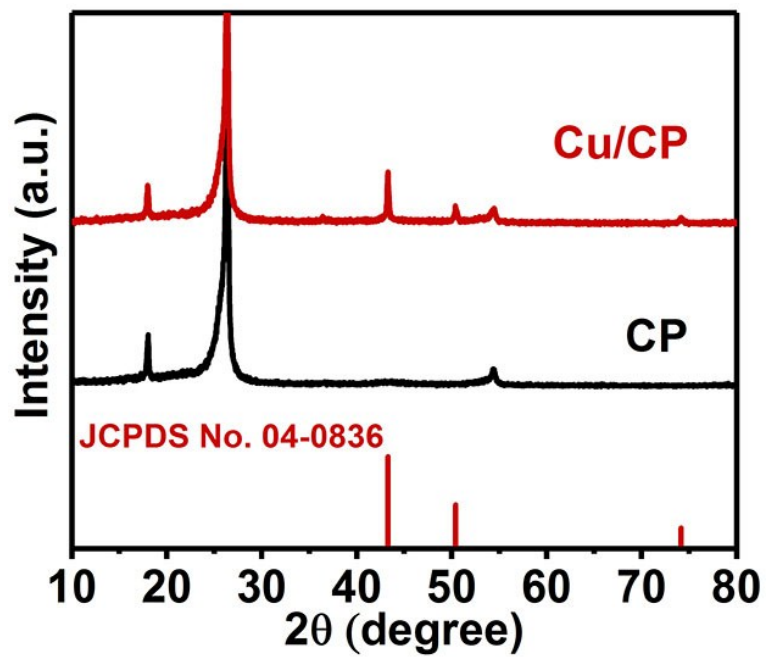


Fig. S9. XRD patterns for Cu/CP and CP after stability test.

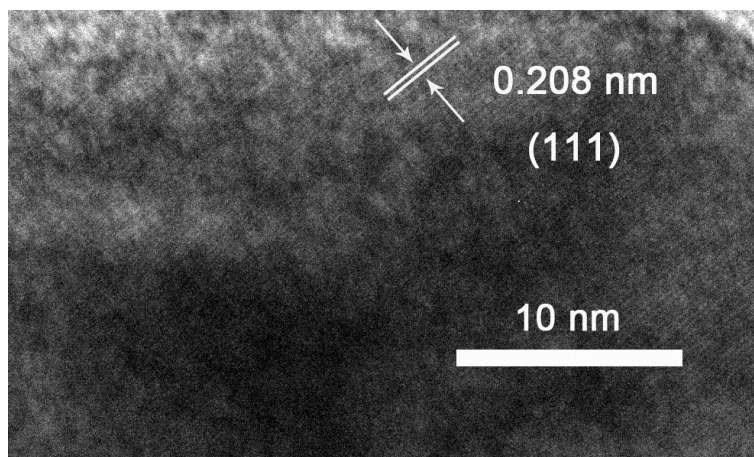


Fig. S10. HRTEM image for dendritic Cu after stability test.

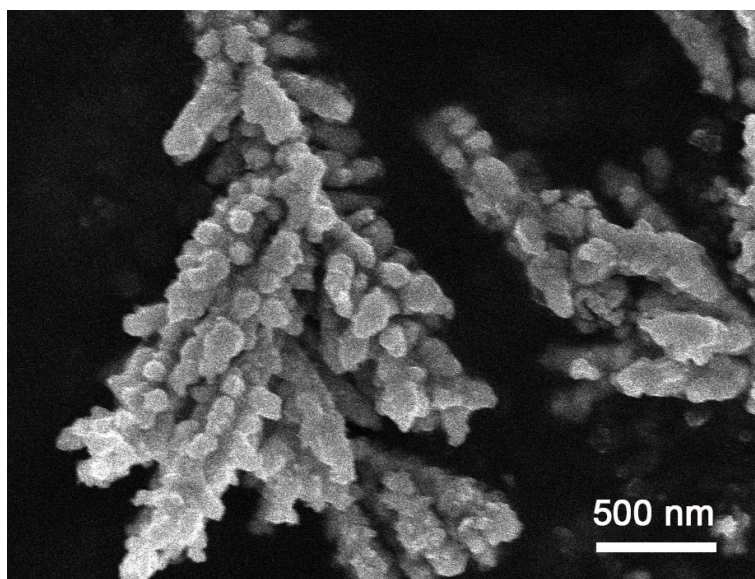


Fig. S11. SEM image for dendritic Cu after stability test.

Table S1. Comparison of the NH₃ yield rate for dendritic Cu with other electrocatalysts under ambient conditions.

Catalyst	Electrolyte	NH ₃ yield rate	Ref.
Dendritic Cu	0.1 M HCl	25.63 $\mu\text{g h}^{-1} \text{mg}^{-1}_{\text{cat.}}$	This work
TiC/C nanofiber	0.1 M HCl	14.1 $\mu\text{g h}^{-1} \text{mg}^{-1}_{\text{cat.}}$	3
LiMn ₂ O ₄ NF/CP	0.1 M HCl	15.83 $\mu\text{g h}^{-1} \text{mg}^{-1}_{\text{cat.}}$	4
PTCA-rGO	0.1 M HCl	24.7 $\mu\text{g h}^{-1} \text{mg}^{-1}_{\text{cat.}}$	5
oxygen-doped graphene	0.1 M HCl	21.3 $\mu\text{g h}^{-1} \text{mg}^{-1}_{\text{cat.}}$	6
La ₂ Ti ₂ O ₇ nanosheet	0.1 M HCl	25.15 $\mu\text{g h}^{-1} \text{mg}^{-1}_{\text{cat.}}$	7
Au flowers	0.1 M HCl	25.57 $\mu\text{g h}^{-1} \text{mg}^{-1}_{\text{cat.}}$	8
N-doped porous carbon	0.1 M HCl	15.7 $\mu\text{g h}^{-1} \text{mg}^{-1}_{\text{cat.}}$	9
Ti ₃ C ₂ T _x nanosheet	0.1 M HCl	20.4 $\mu\text{g h}^{-1} \text{mg}^{-1}_{\text{cat.}}$	10
PCN	0.1 M HCl	8.09 $\mu\text{g h}^{-1} \text{mg}^{-1}_{\text{cat.}}$	11
α -Au/CeO _x -RGO	0.1 M HCl	8.31 $\mu\text{g h}^{-1} \text{mg}^{-1}_{\text{cat.}}$	12
Bi ₄ V ₂ O ₁₁ /CeO ₂	0.1 M HCl	23.21 $\mu\text{g h}^{-1} \text{mg}^{-1}_{\text{cat.}}$	13
NPC	0.1 M HCl	0.97 $\mu\text{g h}^{-1} \text{mg}^{-1}_{\text{cat.}}$	14
Ag nanosheets	0.1 M HCl	2.83 $\mu\text{g h}^{-1} \text{mg}^{-1}_{\text{cat.}}$	15
Au/TiO ₂	0.1 M HCl	21.4 $\mu\text{g h}^{-1} \text{mg}^{-1}_{\text{cat.}}$	16

Table S2. Comparison of the FE for dendritic Cu with other electrocatalysts under ambient conditions.

Catalyst	Electrolyte	FE (%)	Ref.
Dendritic Cu	0.1 M HCl	15.12	This work
TiC/C nanofiber	0.1 M HCl	5.8	3
LiMn ₂ O ₄ NF/CP	0.1 M HCl	7.44	4
PTCA-rGO	0.1 M HCl	6.9	5
oxygen-doped graphene	0.1 M HCl	12.6	6
La ₂ Ti ₂ O ₇ nanosheet	0.1 M HCl	5.87	7
Au flowers	0.1 M HCl	6.05	8
N-doped porous carbon	0.1 M HCl	1.45	9
Ti ₃ C ₂ T _x nanosheet	0.1 M HCl	9.3	10
PCN	0.1 M HCl	11.59	11
α -Au/CeO _x -RGO	0.1 M HCl	10.10	12
Bi ₄ V ₂ O ₁₁ /CeO ₂	0.1 M HCl	10.16	13
NPC	0.1 M HCl	4.2	14
Ag nanosheets	0.1 M HCl	4.8	15
Nb ₂ O ₅ nanofiber	0.1 M HCl	9.26	17
Mo ₂ N nanorod	0.1 M HCl	4.5	18
Fe ₃ S ₄ nanosheets	0.1 M HCl	6.45	19
VN nanosheet array	0.1 M HCl	2.25	20

References

- 1 D. Zhu, L. Zhang, R. E. Ruther and R. J. Hamers, *Nat. Mater.*, 2013, **12**, 836–841.
- 2 G. W. Watt and J. D. Chrisp, *Anal. Chem.*, 1952, **24**, 2006–2008.
- 3 G. Yu, H. Guo, W. Kong, T. Wang, Y. Luo, X. Shi, A. M. Asiri, T. Li and X. Sun, *J. Mater. Chem. A*, 2019, **7**, 19657–19661.
- 4 C. Li, J. Yu, L. Yang, J. Zhao, W. Kong, T. Wang, A. M. Asiri, Q. Li and X. Sun, *Inorg. Chem.*, 2019, **58**, 9597–9601.
- 5 P. Li, J. Wang, H. Chen, X. Sun, J. You, S. Liu, Y. Zhang, M. Liu, X. Niu and Y. Luo, *J. Mater. Chem. A*, 2019, **7**, 12446–12450.
- 6 T. Wang, L. Xia, J. Yang, H. Wang, W. Fang, H. Chen, D. Tang, A. M. Asiri, Y. Luo, G. Cui and X. Sun, *Chem. Commun.*, 2019, **55**, 7502–7505.
- 7 J. Yu, C. Li, B. Li, X. Zhu, R. Zhang, L. Ji, D. Tang, A. M. Asiri, X. Sun, Q. Li, S. Liu and Y. Luo, *Chem. Commun.*, 2019, **55**, 6401–6404.
- 8 Z. Wang, Y. Li, H. Yu, Y. Yu, H. Xue, X. Li, H. Wang and L. Wang, *ChemSusChem*, 2018, **11**, 3480–3485.
- 9 X. Yang, K. Li, D. Cheng, W. Pang, J. Lv, X. Chen, H. Zang, X. Wu, H. Tan, Y. Wang and Y. Li, *J. Mater. Chem. A*, 2018, **6**, 7762–7769.
- 10 J. Zhao, L. Zhang, X. Xie, X. Li, Y. Yong, Q. Liu, W. Fang, X. Shi, G. Cui and X. Sun, *J. Mater. Chem. A*, 2018, **6**, 24031–24035.
- 11 C. Lv, Y. Qian, C. Yan, Y. Ding, Y. Liu, G. Chen and G. Yu, *Angew. Chem. Int. Ed.*, 2018, **57**, 10246–10250.
- 12 S. Li, D. Bao, M. Shi, B. Wulan, J. Yan and Q. Jiang, *Adv. Mater.*, 2017, **29**, 1700001.
- 13 C. Lv, C. Yan, G. Chen, Y. Ding, J. Sun, Y. Zhou and G. Yu, *Angew. Chem., Int. Ed.*, 2018, **57**, 6073–6076.
- 14 P. Song, H. Wang, L. Kang, B. Ran, H. Song and R. Wang, *Chem. Commun.*, 2019, **55**, 687–690.
- 15 H. Huang, L. Xia, X. Shi, A. M. Asiri and X. Sun, *Chem. Commun.*, 2018, **54**, 11427–11430.

- 16 M. Shi, D. Bao, B. R. Wulan, Y. H. Li, Y. F. Zhang, J. M. Yan and Q. Jiang, *Adv. Mater.*, 2017, **29**, 1606550.
- 17 J. Han, Z. Liu, Y. Ma, G. Cui, F. Xie, F. Wang, Y. Wu, S. Gao, Y. Xu and X. Sun, *Nano Energy*, 2018, **52**, 264–270.
- 18 X. Ren, G. Cui, L. Chen, F. Xie, Q. Wei, Z. Tian and X. Sun, *Chem. Commun.*, 2018, **54**, 8474–8477.
- 19 X. Zhao, X. Lan, D. Yu, H. Fu, Z. Liu and T. Mu, *Chem. Commun.*, 2018, **54**, 13010–13013.
- 20 R. Zhang, Y. Zhang, X. Ren, G. Cui, A. M. Asiri, B. Zheng and X. Sun, *ACS Sustainable Chem. Eng.*, 2018, **6**, 9545–9549.