

Supporting Information

Crystallographic Orientation of the Substrate Enables Micromole-Level Lithium-Mediated Ammonia Synthesis at 500 mA cm⁻²

Jing Wang ^{a, b}, Yuan Liu ^b, Xingyue Lv ^c, Jingjing Xu ^c, Wanyu Zhao ^b, Xiaoli Zhao ^{c, *}, Tianfu Wang ^b, Xiaowei Yang ^{b, *}

^a College of New Energy and Intelligent Manufacturing, Henan University, Zhengzhou, 450046, China

^b School of Chemistry and Chemical Engineering, State Key Laboratory of Synergistic Chem-Bio Synthesis, Shanghai Jiao Tong University, Shanghai, 200240, China

^c School of Materials Science and Engineering, Tongji University, Shanghai, 201804, China

Corresponding authors:

Xiaoli Zhao (zx136@tongji.edu.cn)

Xiaowei Yang (yangxw@sjtu.edu.cn)

A. Materials and methods

1. Electrolyte preparation

All electrolyte samples were prepared in an Ar-filled glovebox (H₂O < 0.5 ppm, O₂ < 0.5 ppm). Lithium bis(fluorosulfonyl)imide (LiFSI, 99.9%, DoDo) was dried at 80 °C for 12 h in the Ar-filled glovebox prior to use. Tetrahydrofuran (THF, >99.9%, Innochem), Anhydrous ethanol (EtOH ≥99.90%, Greagent) and 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE, ≥99.5%, Adamas) were further dried with molecular sieves for 24 hours prior to use.

2. Electrode preparation:

CuSO₄ used in the electroplating process is purchased from Grate (Shanghai) Technology Co., Ltd. There are mainly four types of electrochemical deposition solutions, which are: 2.5M CuSO₄ + 1M LiFSI solutions、2.5M CuSO₄ + 2M LiFSI solutions、2.5M CuSO₄ + 3.5M LiFSI solutions and 1.5M CuSO₄ + 2.1M LiFSI solutions. Finally, modified copper electrode is prepared by electroplating in 2.5M CuSO₄ + 3.5M LiFSI solutions. The cathode is copper foil, and the anode is copper foil or copper wire. Modified copper electrode is electroplated at 10 mA cm⁻² constant current for 40 minutes by the LAND instrument.

The PtAu/SSC electrodes were prepared by the hydrogen bubble method(1). Prior to use, the SSC was washed with acetone and ethanol three times. The substrate was the 4.5 cm² 316 stainless-steel cloth (McMaster-Carr, 400 mesh, pore size: 30 μm, thickness: 30 μm) which was used as the working electrode (WE). To achieve uniform electrodeposition, the Pt plate (0.25 cm_{geo}², 99.9 %) were electrically connected and used as a split counter electrode, which was placed in the middle of the the working electrode (SSC) during electrodeposition. The 10 mM H₂PtCl₆·6H₂O (Sigma Aldrich, ACS reagent) with 10 mM HAuCl₄·3H₂O (Sigma Aldrich, 99%) in 3 M H₂SO₄ (Sigma Aldrich, 99.999%) solution was used as an electrolyte for electrodeposition PtAu/SSC. A current density of -2.25 A/cm² was applied for 2 min in which rigorous hydrogen evolution and metal deposition took place at the same time, leading to high surface area structures of PtAu on the SSC. After the electrodeposition, the electrodes were rinsed in EtOH and ultra-pure water several times to remove all residual electrolytes.

B. Experiments:

1. Half-cell tests

The half-cell cycling performance was evaluated using a standard battery tester (NewareCT4008) in 2025-type coin cell configurations, with 60 μL of electrolyte per cell and polypropylene (PP) separators. Electrochemical impedance spectroscopy (EIS) measurements were performed using a Bio-Logic VMP3 in the frequency range of 100 kHz to 0.1 Hz with an amplitude of 5 mV. Chronopotentiometry (CP) tests were conducted using the same Bio-Logic VMP3 electrochemical workstation.

2. Nitrogen Reduction Experiments

A three-electrode single-compartment autoclave (Gaossunion Optoelectronic Technology Co., Ltd) was used for all Li-NRR tests. The working electrode (Cu wire, Φ 0.8 mm), counter electrode (Pt plate, 0.25 cm_{geo}² ; PtAu/SSC, 0.45 cm_{geo}²) and reference electrode (Ag wire) were first polished by water proof abrasive paper. Then the Cu wire was immersed in 0.1 M HCl solution to remove contaminants. Following this, the electrodes and the polytetrafluoroethylene cell were thoroughly rinsed with deionized water and anhydrous ethanol at least three times and subsequently dried overnight at 60 °C in air. The WE and CE were placed parallel with a distance of 0.5 cm, and RE was placed next to WE. To minimize the effect of humidity, 15 mL of electrolyte, containing 1 vol% EtOH, was added to the cell inside the Ar-filled glovebox. The reactor was locked tightly to avoid leaking and air exposure, then transferred to the fume hood and the system was flushed with a mixture of N₂ and H₂ (N₂ : H₂ = 90% : 10%) for three times to remove any contaminants. Then, the reactor was pressurized with the mixture of N₂ and H₂ (20 bar, N₂ : H₂ = 90% : 10%) for the Li-NRR test. Chronopotentiometry (CP) was performed under a current density of -4 mA cm⁻² using a potentiostat (Iviumstat). The electrochemical impedance spectroscopy (EIS) was performed at 0V vs. OCV from 100 kHz to 0.01 Hz. The cyclic voltammetry (CV) was measured between -3.5 V/OCV and -1.0V/OCV

at scan rate of 10 mV s⁻¹. ECSA were measured in the non-Faradaic potential region following Li-NRRs(2). The setup was an equilibration time of at least 20 min at open circuit voltage was set. After a stable OCV was obtained CVs were performed at 200 mV to -200 mV vs OCV at scan rates between 10 – 80 mV/s.

C. Quantification of ammonia

To achieve more accurate quantitative analysis, cross-validation was conducted using the well-known ammonia quantification methods: the colorimetric method.

1. Colorimetric method

This method involves adding a color agent to solutions of known concentrations to establish the calibration curve which shows the relationship between absorbance and concentration(3). Then, to determine the concentration of an unknown solution, the color agent is added to it, and absorbance is measured. By substituting this absorbance value into the established relationship equation, the concentration of ammonia can be calculated, thus enabling quantitative analysis.

1.1 Sample preparation: The produced NH₃ was quantified using a modified salicylate method. Alkaline solution: 0.35 g of sodium hydroxide (≥ 98%, Greagent) was dissolved in 30 mL of deionized (DI) water to obtain a 0.4 M NaOH solution. An alkaline solution of 1% sodium hypochlorite was prepared by dissolving 3 g of sodium hypochlorite (≥ 7.5%, Adamas) in water. Salicylate solution: 8.05 g of sodium salicylate (≥ 99.5%, Greagent) and 0.003 g of sodium nitroprusside dihydrate (≥ 99%, Adamas) were dissolved in 20 mL of DI water to prepare the salicylate solution. Calibration solutions were prepared by dissolving NH₄Cl (99%, Adamas) to obtain concentrations in a range of 50, 100, 150, 200, and 250 μM. A typical ammonia sample was 1 mL in volume. To this, 140 μL of hypochlorite solution and 140 μL of salicylate solution were sequentially added.

1.2 Absorbance measurement: Then each sample was placed in a dark room at room temperature for 2 hours. Finally, absorbance at 400-800 nm was measured by UV-vis spectroscopy (INESA L6).

D. Mathematical equation

1. NH₃ yield rate

NH₃ yield rate was calculated using an Equation (1), where C is NH₄⁺-N concentration (ppm), V is the volume of the electrolyte, t is the reaction time, A is the area of working electrode.

$$\text{NH}_3 \text{ yield rate, } w \text{ (nmol s}^{-1} \text{ cm}^{-2}) = \frac{C \times V \times 10^3}{14 \times t \times A} \quad \text{Equation (1)}$$

2. Faradaic efficiency

Faradaic efficiency was calculated using an Equation (2). here n is the number of electron transferred, F is Faradaic constant.

Pseudo-energy efficiency n to nitrogen and water.
(Δ Faradaic efficiency [%] = $\frac{n \times F \times C \times V}{M_p \times Q}$ Equation (2)), m is mass of total produced ammonia in electrolyte after reaction, V is the total passed potential, I is the total passed current, here is the total passed power. The Pseudo-ewant, C is concentration of the product, V is the volume of the electrolyte, M_p is molecular mass of the product, and Q is the total charge passed.

3. Pseudo-energy efficiency

Pseudo – energy efficiency [%] = $\frac{E_{out}}{E_{in}} = \frac{\Delta G_R \times m}{\int V(t) \times I(t) dt}$ as calculated using an Equation (3), where ΔG_R is free-energy of reaction of ammonia oxidation energy efficiency was defined by Ib Chorkendorff et al. for the academic approach in industrial perspective.

Due to the high ammonia yield amount and reliable reproducibility of LMNRR that a large amount of literature has proved, isotope labeling experiment was not conducted here.(4-6)

E. Characterizations

The surface morphology and composition of the working electrode after 10 hours of ammonia electrosynthesis were examined using a field emission scanning electron microscope (Apreo 2S) equipped with energy-dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS, ULVAC-PHI, GENESIS 900).

1. XRD

The XRD patterns were acquired within 2θ range of 30° to 100° using a SC-XRD (D8 Venture) with an X-ray energy of 400 kV/200 mA. The electrodes were pre-covered with polyketone tape in the glove box to avoid any air exposure.

2. SEM

The surface morphology and composition of the working electrode after 10 hours of ammonia electrosynthesis were examined using a field emission scanning electron microscope (Apreo 2S) equipped with energy-dispersive X-ray spectroscopy (EDX).

3. XPS

After the Li-NRR, the electrode was taken to the glove box, rinsed with THF solvent for five times, and dried overnight. X-ray photoelectron spectroscopy (XPS) investigations were carried out with ULVAC-PHI, GENESIS 900, and the binding energies were calibrated against the C 1s reference peak.

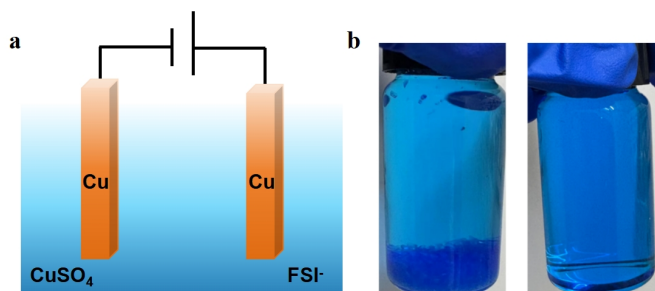


Figure S1. a) Schematic diagram of the electrochemical deposition device. b) The states of electrochemical deposition solutions of different concentrations (3.5 M LiFSI in 2.5 M CuSO₄, 1.0 M LiFSI in 2.5 M CuSO₄).

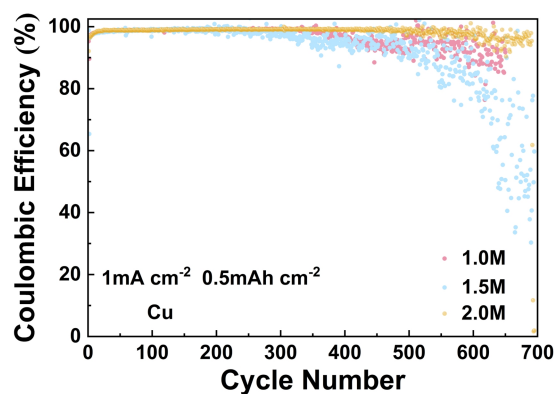


Figure S2. Li plating/stripping Coulombic efficiency on a unmodified Cu working electrode at 1 mA cm⁻² 0.5 mAh cm⁻² in different electrolytes BE.1 (1.0M), BE.2 (1.5M) and BE.3 (2.0M).

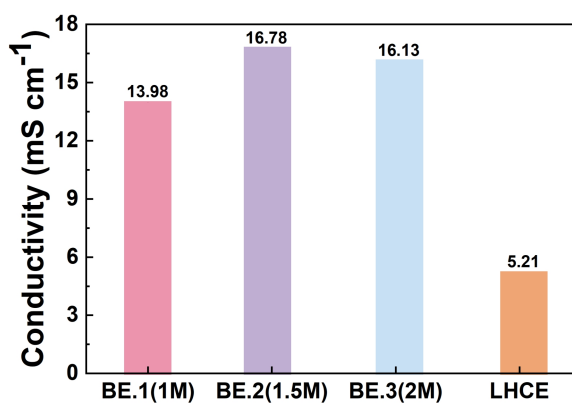


Figure S3. The ionic conductivity of different electrolytes BE.1, BE.2, BE.3 and LHCE.

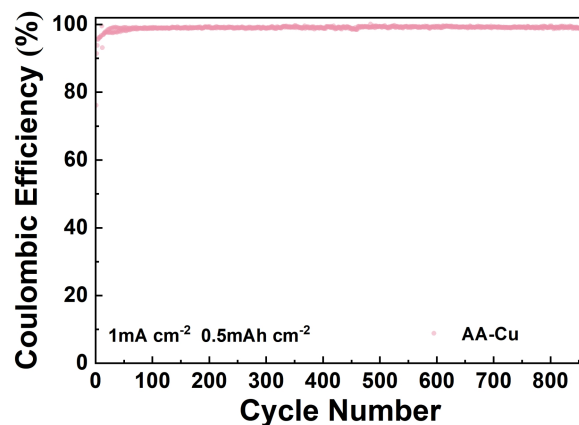


Figure S4. Coulombic efficiency of Li plating/stripping before and after modification of Cu working electrodes at 1 mA cm^{-2} 0.5 mAh cm^{-2} .

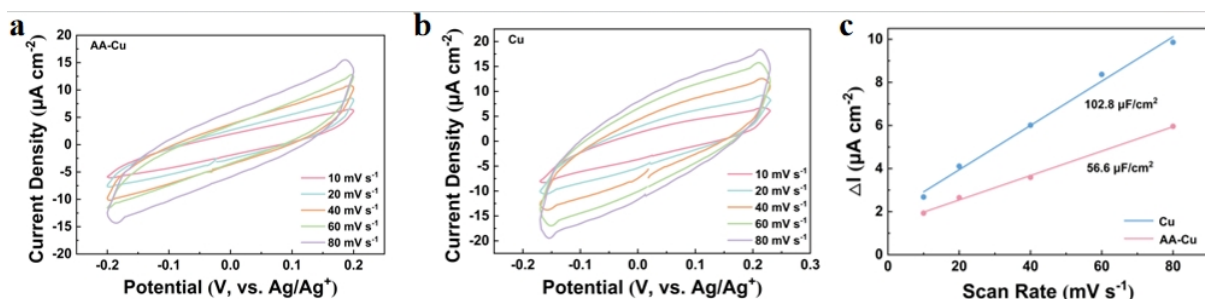


Figure S5. a) Cyclic voltammetry at different scan rates of the copper working electrode after modification from scan rates between $10\text{--}80 \text{ mV s}^{-1}$ in the non-faradaic region. b) Cyclic voltammetry at different scan rates of the copper working electrode before modification from scan rates between $10\text{--}80 \text{ mV s}^{-1}$ in the non-faradaic region. c) The specific capacitance.

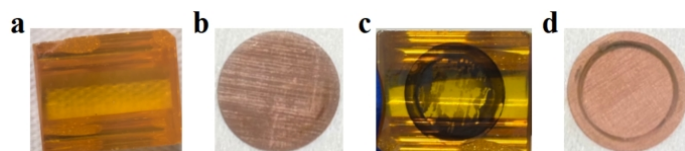


Figure S6. Surface conditions of the in situ cell and the copper mesh for both a, b) the modified Cu experimental group and c, d) the unmodified Cu control group after the in situ FTIR tests.

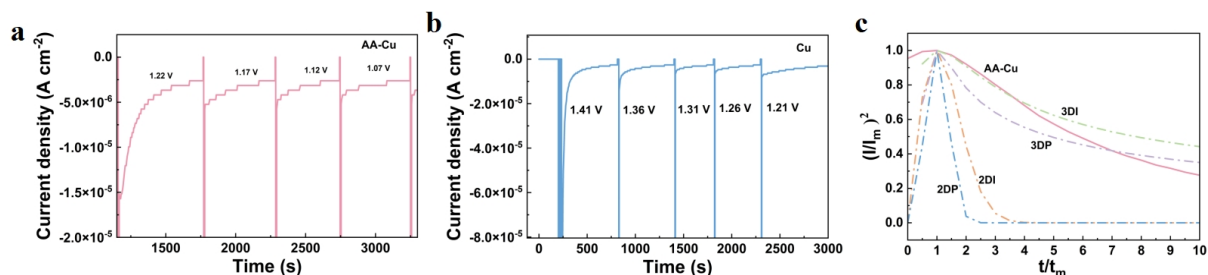


Figure S7. The PITT measurements with the electrolyte (add ethanol). a) The response current with the gradient decreased potential near the reduced potential of AA-Cu b) Cu. c) The t/t_m and $(I/I_m)^2$ plots (solid line) in comparison with theoretical 2D and 3D models.

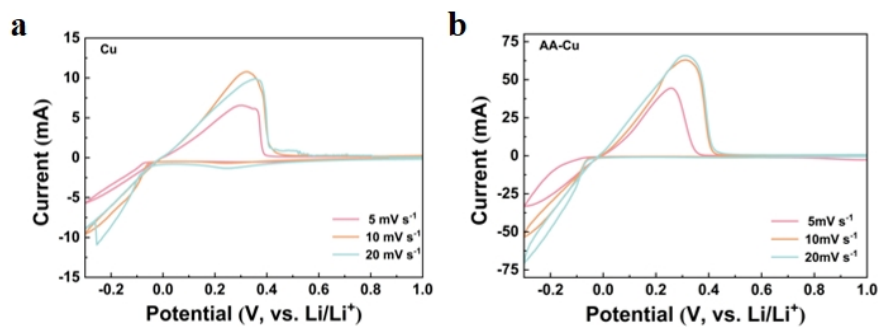


Figure S8. Cyclic voltammetry from -0.3 to 1 V at different scan rates from 5 to 20 mV s^{-1} for a) Cu and b) AA-Cu.

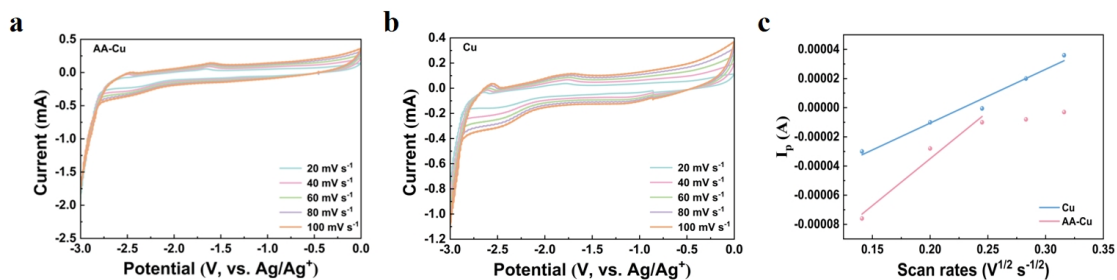


Figure S9. Cyclic voltammetry from -3.0 to 0 V at different scan rates from 20 to 100 mV s^{-1} in the autoclave for a) AA-Cu and b) Cu. c) The corresponding Li^+ diffusion coefficients of the SEIs derived from AA-Cu and Cu.

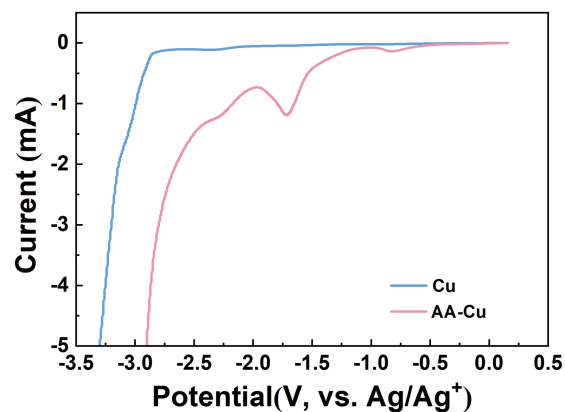


Figure S10. LSV curves of unmodified copper working electrode and modified copper working electrode.

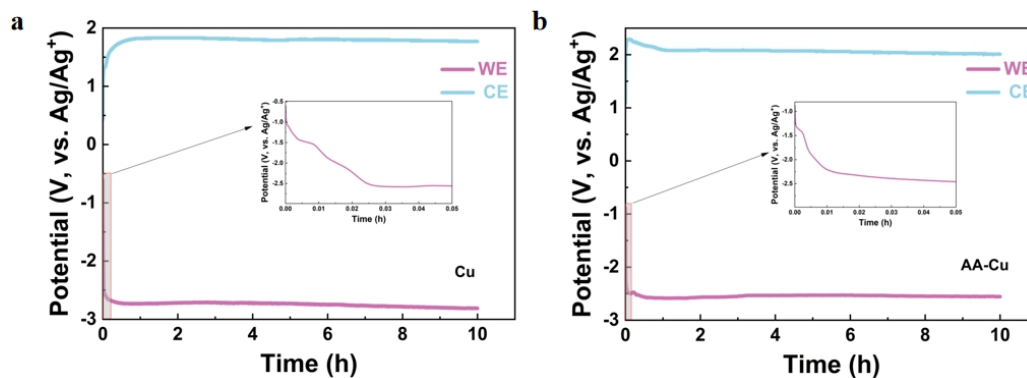


Figure S11. Potential profiles during chronopotentiometric measurement at given current density for the copper working electrodes a) before modification (Cu, Pt) and b) after modification (AA-Cu, Pt).

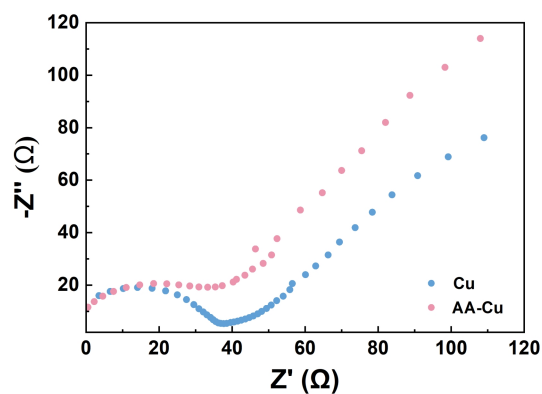


Figure S12. EIS spectra of unmodified copper working electrode and modified copper working electrode.

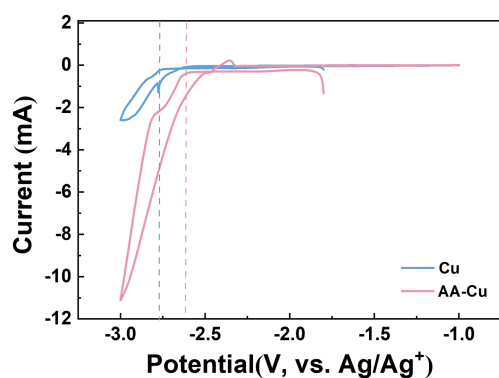


Figure S13. CV curves of unmodified copper working electrode and modified copper working electrode.

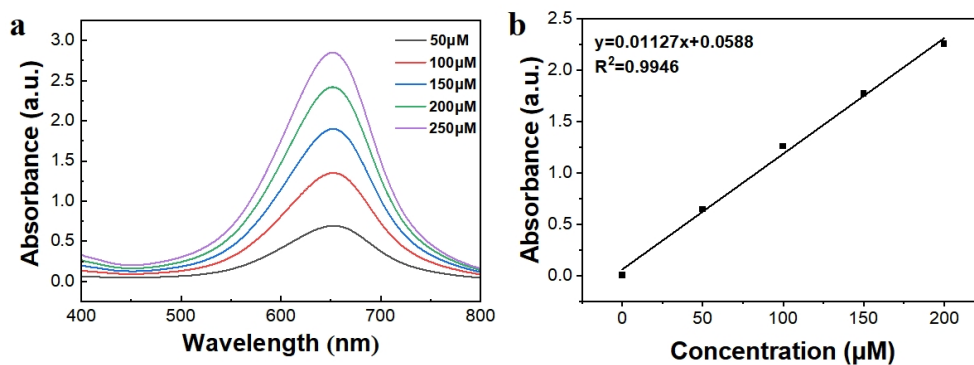


Figure S14. a) Wavelength-Absorbance curves of a series known concentration of NH_4Cl . b) Ammonia Concentration-Absorbance standard curve.

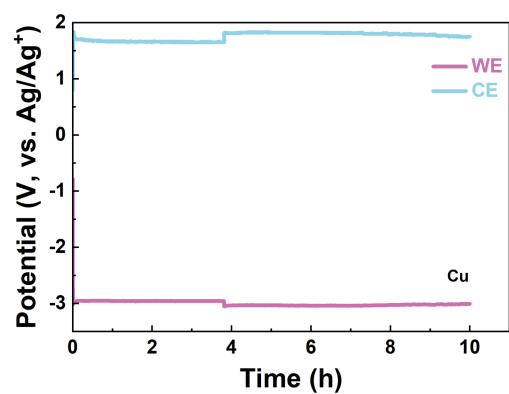


Figure S15. Potential profiles during chronopotentiometric measurement at given current density for the copper working electrodes before modification (Cu (LHCE)).

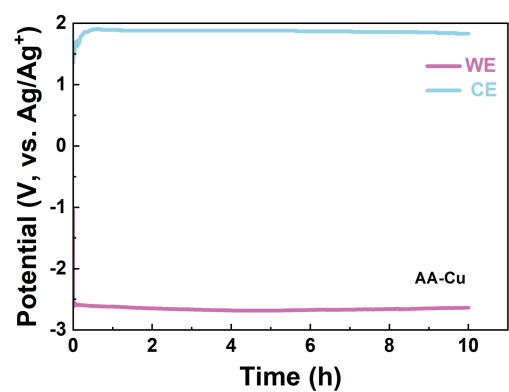


Figure S16. Potential profiles during chronopotentiometric measurement at given current density for the copper working electrodes after modification (AA-Cu (LHCE)).

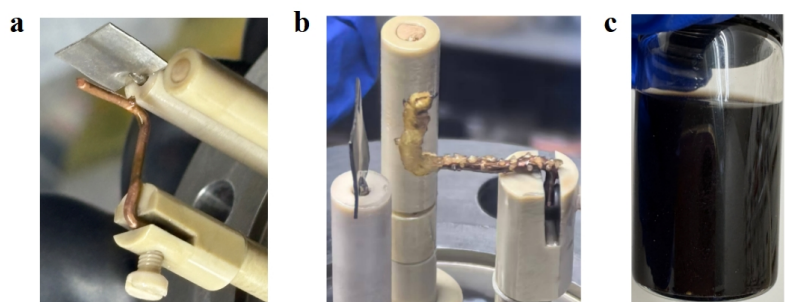


Figure S17. a) The surface condition of the copper wire of the modified copper working electrode (AA-Cu (LHCE)) after 10h CP. b, c) The surface condition of the copper wire and the state of the electrolyte of the unmodified copper working electrode (Cu (LHCE)) after 10h CP.

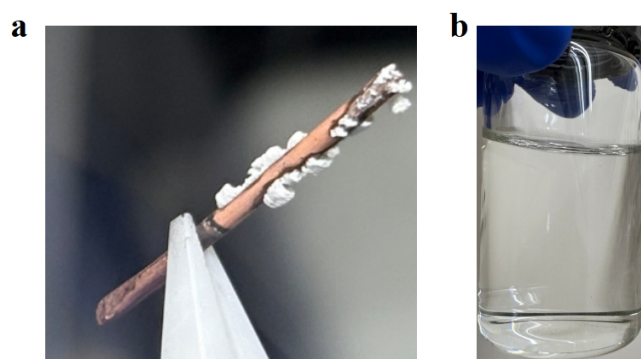


Figure S18. a) The surface condition of the copper wire and b) the state of the electrolyte of the modified copper working electrode (AA-Cu (PtAu)) after 10h CP.

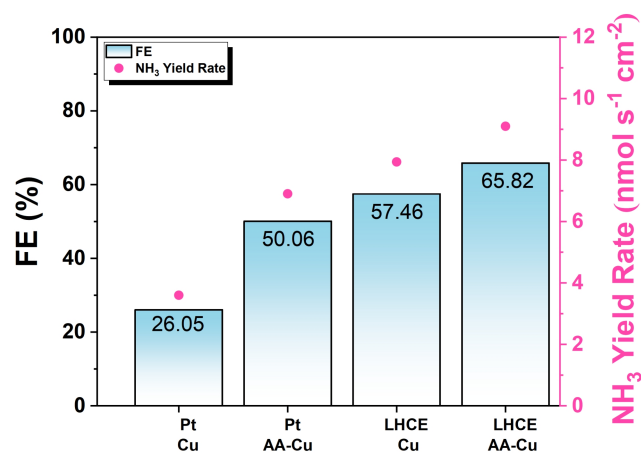


Figure S19. FE and NH₃ yield rate of unmodified copper working electrode (Cu (Pt), Cu (LHCE)) and modified copper working electrode (AA-Cu (Pt), AA-Cu (LHCE)) at a current density of -4 mA/cm² under 20 bar pressure.

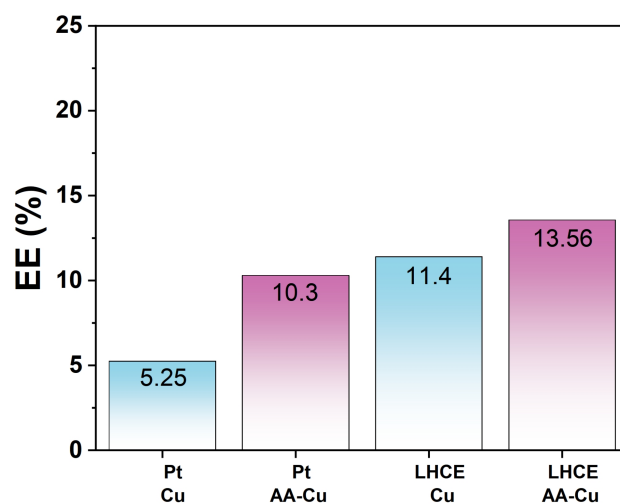


Figure S20. EE of unmodified copper working electrode (Cu (Pt), Cu (LHCE)) and modified copper working electrode (AA-Cu (Pt), AA-Cu (LHCE)).

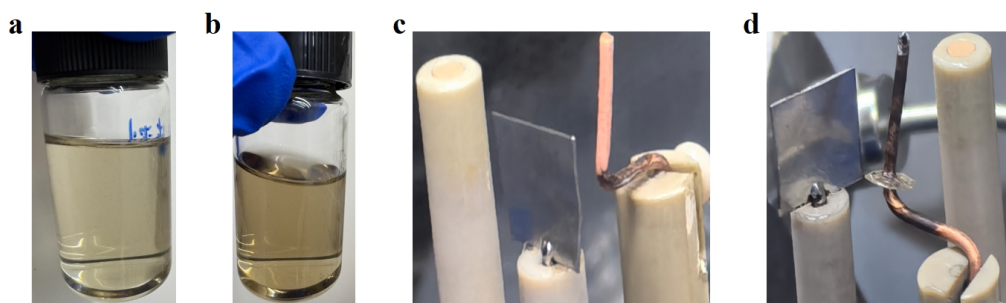


Figure S21. a, c) The state of the electrolyte and the surface condition of the copper wire of the modified copper working electrode after 10h CP. b, d) The state of the electrolyte and the surface condition of the copper wire of the unmodified copper working electrode after 10h CP.

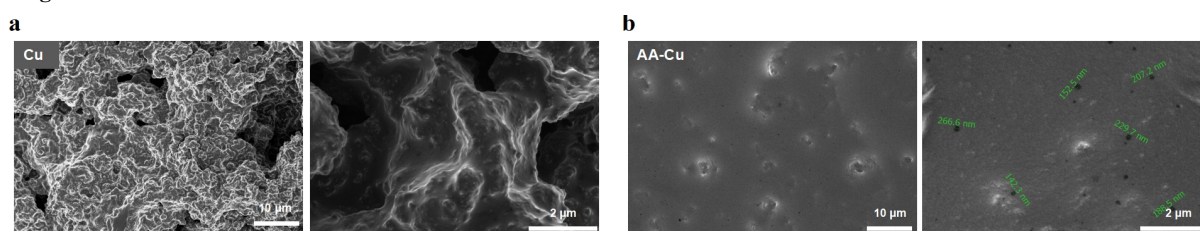


Figure S22. SEM images showing the surface morphology of a) Cu (Pt) and b) AA-Cu (Pt).

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