

Supplementary Information

Electrodeposition of 3D dendritic Cu-Sn bimetallic alloy for electrocatalytic nitrate reduction to ammonia

Jinxiu Zhao,^{a,b,*} Jingyi Xu,^c and Liyi Shi^{a,*}

^a *Emerging Industries Institute, Shanghai University, Jiaxing 314050, Zhejiang, China.*

^b *School of Materials Science and Engineering, University of Jinan, Jinan 250022, P. R. China.*

^c *Shandong Genyuan New Materials Co., LTD., Weihai, 264400, Shandong, China.*

*Corresponding author.

E-mail address: shiliyi@shu.edu.cn (L. Shi)

mse_zhaojx@ujn.edu.cn (J. Zhao)

Materials

Sodium nitroprusside ($C_5FeN_6Na_2O_2 \cdot H_2O$), ammonium chloride (NH_4Cl), copper sulfate ($CuSO_4$), potassium hydroxide (KOH), sodium nitrite ($NaNO_2$), sodium nitrate- ^{15}N ($Na^{15}NO_3$), sulfamic acid (NH_2SO_3H), N-(1-naphthyl) ethylenediamine dihydrochloride ($C_{12}H_{14}N_2$), sulfonamide ($H_4N_2O_2S$), phosphoric acid (H_3PO_4) and sodium hypochlorite solution ($NaClO$) were purchased from Maclean. Stannous chloride ($SnCl_2$) and sodium nitrate ($NaNO_3$) were purchased from Sinopharm Chemical Reagent Co., Ltd. Anhydrous sodium sulfate (Na_2SO_4) and sodium salicylate ($C_7H_5NaO_3$) were purchased from Aladdin. Anhydrous ethanol (C_2H_5OH) and hydrazine hydrate ($N_2H_4 \cdot H_2O$) were purchased from Tianjin FuYu Chemical Fine Co., Ltd. Sodium hydroxide ($NaOH$) was purchased from Tianjin Damao Chemical Reagent Factory, and nitric acid (HNO_3), sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) were purchased from Yantai Far East Fine Chemical Co., Ltd.

Characterization

X-ray diffraction (XRD) patterns were acquired by using D8 focus diffractometer (BLumker AXS, Germany). The morphology images were obtained from Gemini 300 field emission SEM (Zeiss, Germany) and JEM-2100 TEM (Zeiss, Germany). Elements species and distribution were obtained by an X-Max^N 50 EDS (Oxford, China). XPS spectra were obtained from an Axis Supra X-ray photoelectron spectrometer (Shimadzu, Japan). The absorbance data of spectrophotometer were measured on TU-1909 spectrophotometer (Beijing Puxi Instrument Co. Ltd, China). The isotope labeling nuclear magnetic resonance (NMR) were measured on AVANCE III HD 600 MHz (Bruker, Swiss Confederation).

Preparation of Cu-Sn alloy

The dendritic Cu-Sn alloy catalysts were synthesized by DHBT electrodeposition technique. Two-step electrodeposition was used to prepare the 3D dendritic Cu-Sn alloy catalyst. Firstly, constant current (0.25 A cm^{-2} for 5 min) electrodeposition was used to form porous structures on the copper foil under acidic conditions (0.5 M

H₂SO₄, SnCl₂, and CuSO₄) using the hydrogen bubble template method to increase the surface area of the catalyst. The 3D dendritic copper-tin bimetallic alloy catalyst was obtained, then washed with ultrapure water and ethanol, and dried at 60 °C for 2 h. The concentration of CuSO₄ and SnCl₂ to synthesize series of Cu-Sn alloy listed in Table S2.

Electrochemical measurements

Electrochemical measurements were performed with a CHI 660E electrochemical analyzer (CHI Instruments, Inc., Shanghai) in a standard three-electrode system using Cu-Sn alloy as working electrode, Ag/AgCl as reference electrode, and graphite rod as counter electrode. For NO₃⁻ reduction experiments, the 0.1 M Na₂SO₄ + 0.01 M NaNO₃ was bubbled with Ar for 30 min before the measurement.

The following formula was utilized to convert the potential reported in this work to RHE scale through calibration: $E(\text{vs RHE}) = E(\text{vs Ag/AgCl}) + 0.197 + 0.059 \times \text{pH}$, and the polarization curve was the steady-state curve after a few cycles. All electrochemical tests were conducted at 25 °C. During NO₃RR tests, two chambers of the H-type electrolytic cell was separated by a Nafion membrane, so that the anode chamber can continuously provide the H⁺ required for the reaction to the cathode chamber for NH₃ formation. Before NO₃RR tests, the Nafion membrane was pre-treated by heating in 5% H₂O₂ solution and ultrapure water at 80 °C for 1 h, respectively. All experiments were carried out at room temperature (25 °C).

Determination of NH₃

The produced ammonia was estimated by indophenol blue method by ultraviolet spectroscopy.¹ In detail, 400 μL electrolyte was diluted to 4 mL for further use, then 4 mL aforementioned solution was removed from the cathodic chamber and added into 50 μL oxidizing solution containing NaClO (ρ_{Cl} = 4 – 4.9) and NaOH (0.75 M), followed by further adding 500 μL coloring solution containing 0.4 M C₇H₅O₃Na and 0.32 M NaOH, and 50 μL catalyst solution (0.1 g Na₂[Fe(CN)₅NO]·H₂O diluted to 10 mL with deionized water) in turn. After standing at 25 °C for 2 h, the UV-Vis absorption spectrum was measured. The concentration of indophenol blue was

determined using the absorbance at a wavelength of 655 nm. In this study, a concentration-absorbance curve was obtained using a standard ammonium chloride solution firstly. The fitted curve ($y = 0.382x + 0.0425$, $R^2=0.999$) indicates a good linear relationship between the absorbance value and the NH_3 concentration.

Calculation of NH_3 yield rate and FE

The NH_3 yield rate and FE were calculated using the following formula:

$$\text{NH}_3 \text{ yield rate} = (c_{\text{NH}_3} \times V) / (17 \times t \times A) \quad (1)$$

$$\text{FE} = [8 \times F \times c_{\text{NH}_3} \times V / 17 \times 10^6 \times Q] \times 100\% \quad (2)$$

Where c_{NH_3} ($\mu\text{g mL}^{-1}$) is the measured NH_3 concentration; V (mL) is the volume of the electrolyte; t (h) is the reduction reaction time; and A (cm^2) is the geometric area of the cathode; F (96485 C mol^{-1}) is the Faraday constant; and Q (C) is the amount of electricity applied.

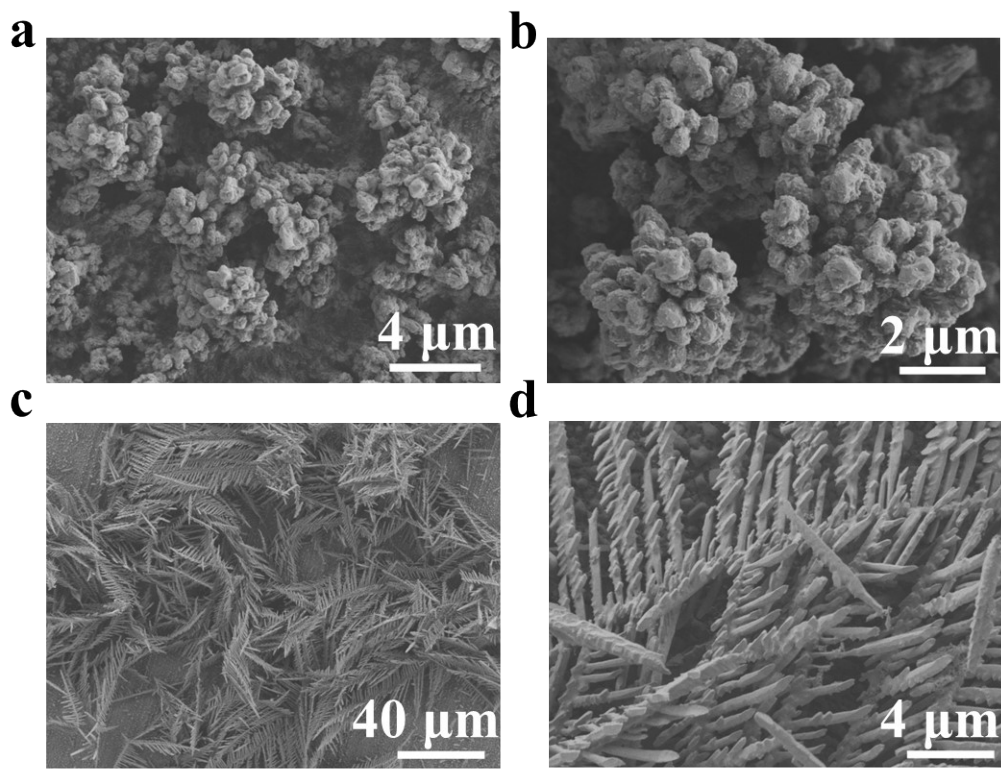


Fig. S1. (a) and (b) SEM images of single Cu. (c) and (d) SEM images of single Sn.

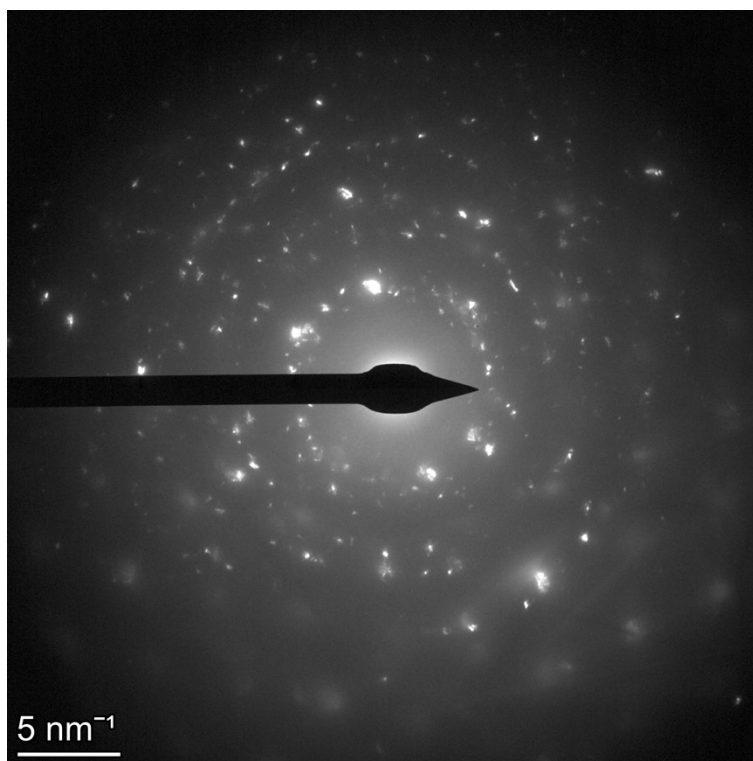


Fig. S2. SAED image taken from Cu-Sn alloy.

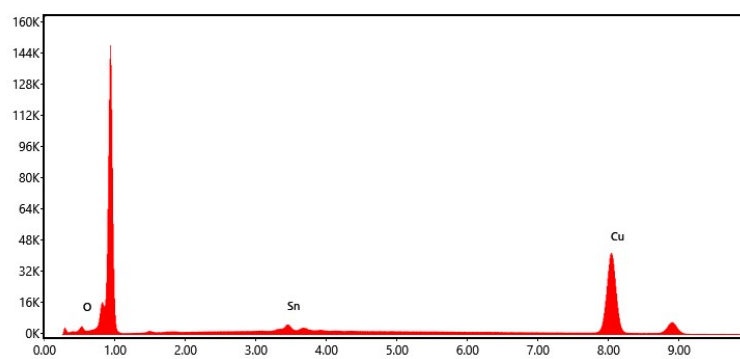


Fig. S3. EDX spectrum of Cu-Sn alloy.

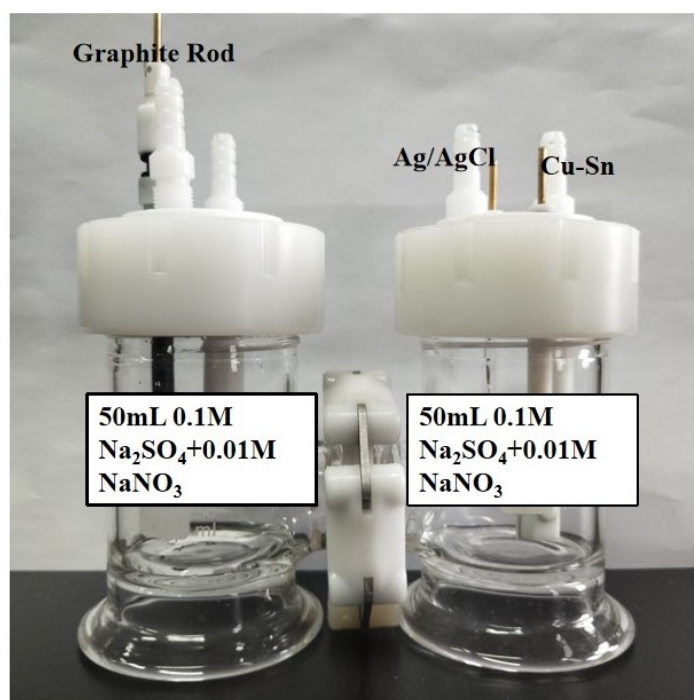


Fig. S4. Optical photograph of the reaction device.

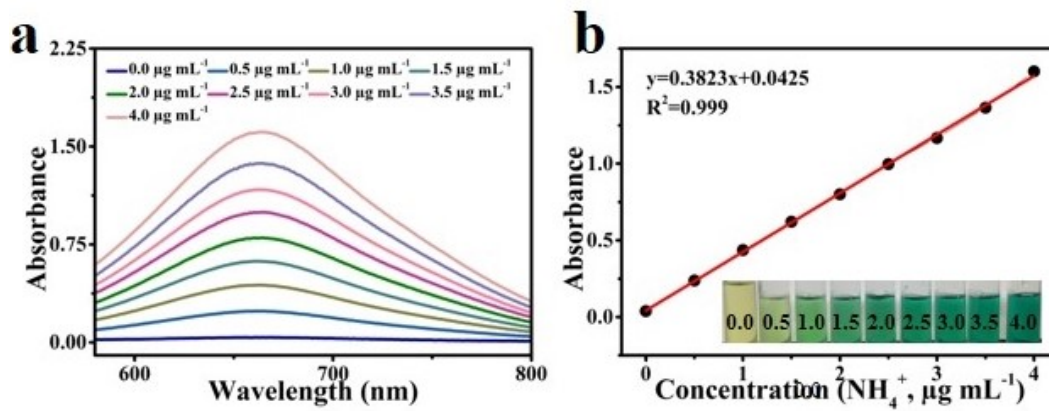


Fig. S5. (a) UV-Vis absorption spectra of various NH_3 concentrations after 1 h of color development at room temperature. (b) Calibration curve used to calculate NH_4^+ concentration.

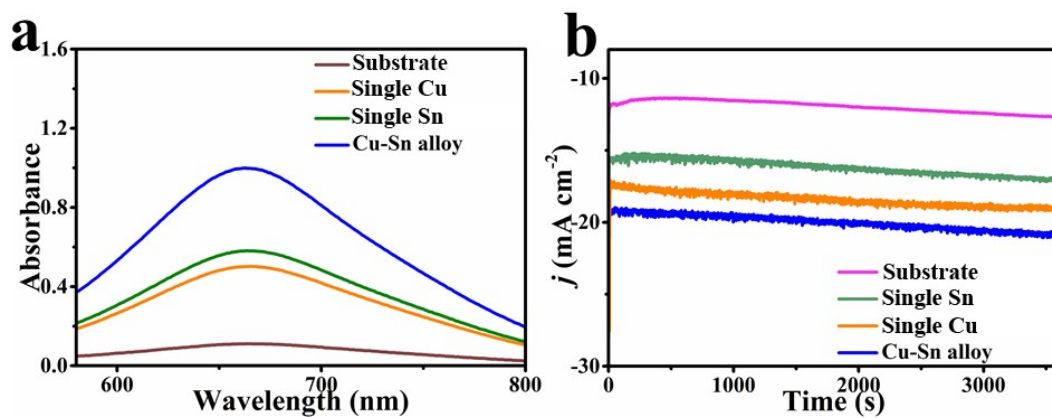


Fig. S6. (a) UV-Vis absorption spectrum of NH_3 concentration and (b) Time-dependent current density curves of substrate, single Sn, single Cu foil, and Cu-Sn alloy for NO_3RR at -1.2 V (RHE).

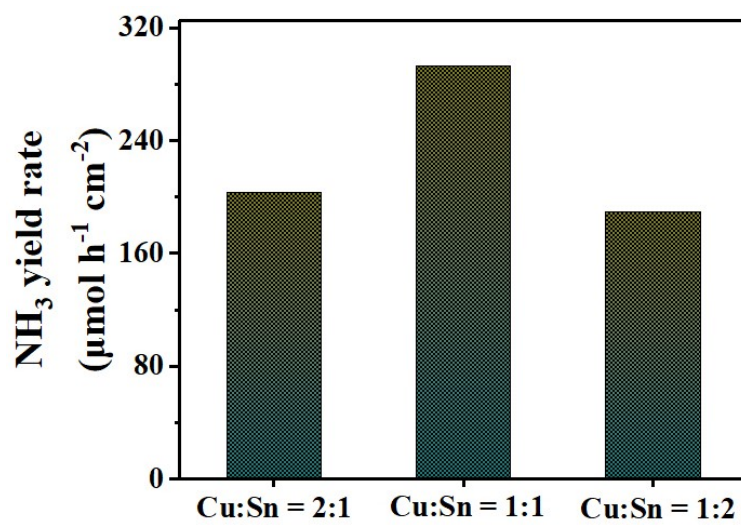


Fig. S7. Average NH₃ yield rates of Cu-Sn alloy with different ratio of Cu and Sn for NO₃RR at -1.2 V vs. RHE.

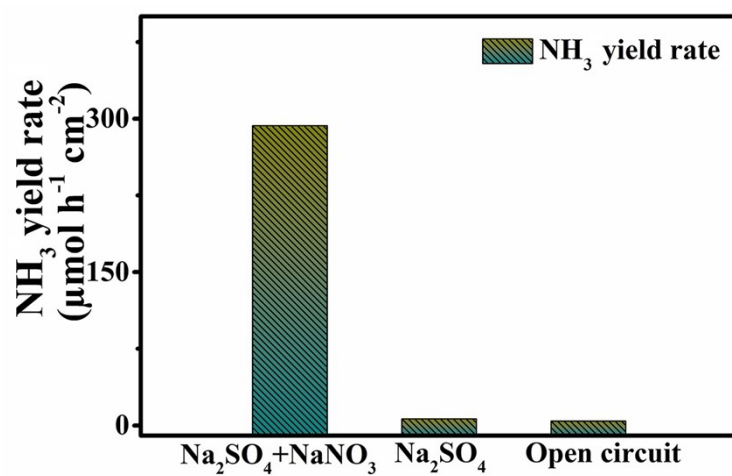


Fig. S8. Average NH₃ yield rates of Cu-Sn alloy in 0.1 M Na₂SO₄ (containing 0.01 M NaNO₃), 0.1 M Na₂SO₄ (without NO₃⁻) and open circuit for NO₃RR at -1.2 V vs. RHE.

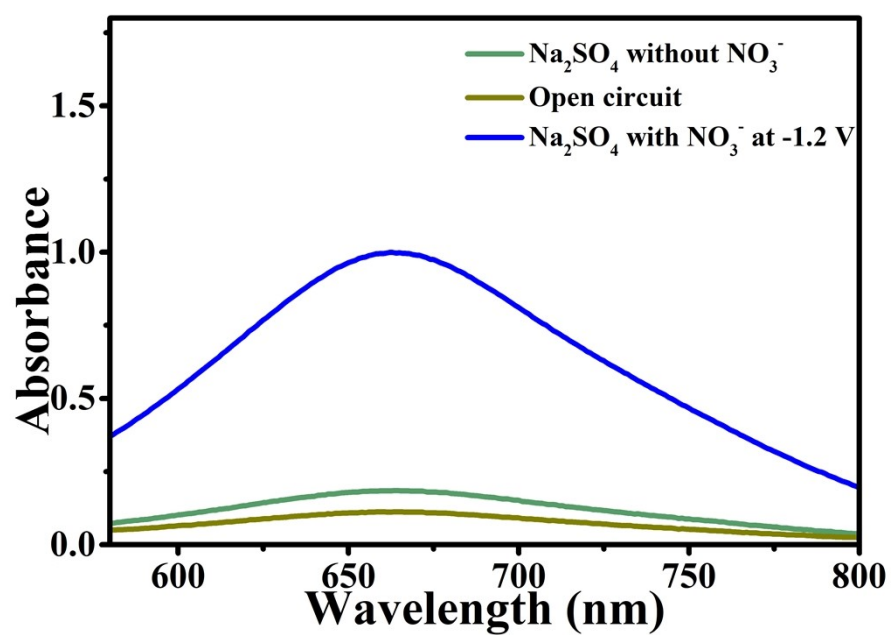


Fig. S9. UV–Vis absorption spectra of the 0.1 M Na₂SO₄ solution and 0.1 M Na₂SO₄ solution (containing 0.01 M NO₃⁻) after charging at -1.2 V vs. RHE for 1 h and at open-circuit potential under ambient conditions for 1 h after incubated with NH₃ color agent.

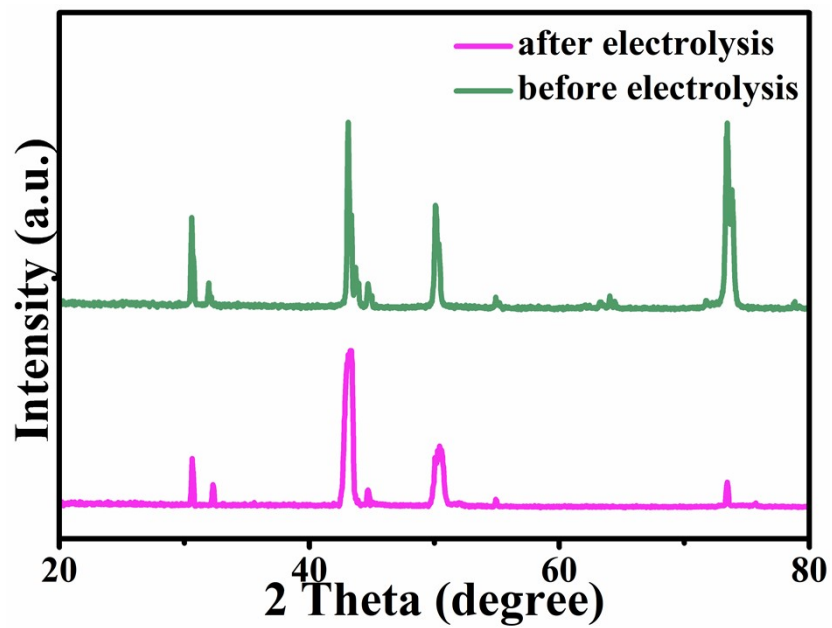


Fig. S10. XRD pattern for Cu-Sn alloy after stability test in 0.1 M Na_2SO_4 (containing 0.01 M NaNO_3).

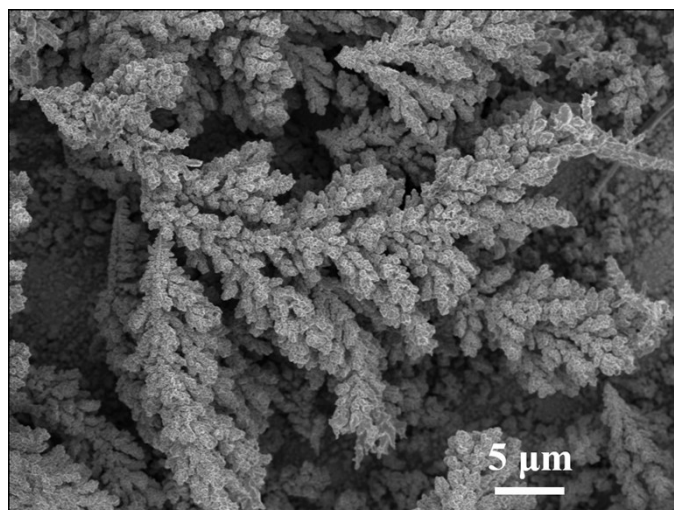


Fig. S11. SEM image of Cu-Sn alloy after stability test in 0.1 M Na_2SO_4 (containing 0.01 M NaNO_3).

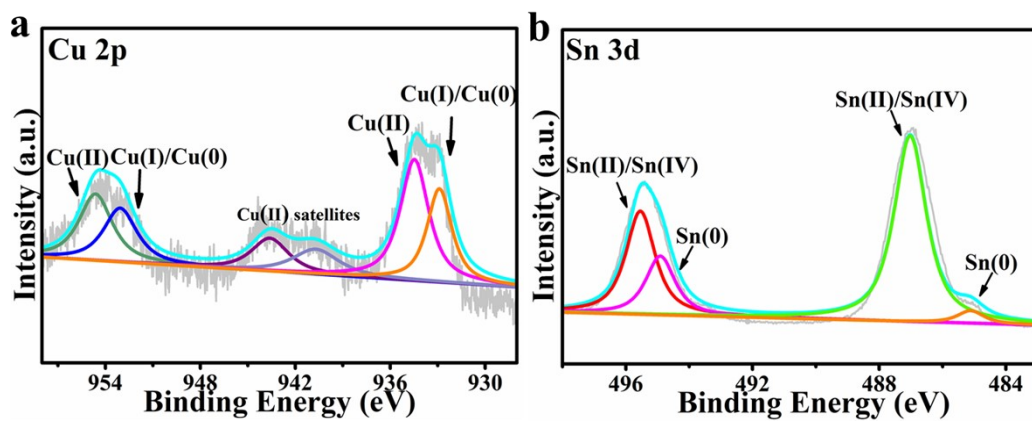


Fig. S12. XPS spectra of Cu-Sn alloy after stability test at -0.8 V (RHE.) in (a) Cu 2p, (b) Sn 3d regions.

Table S1. Comparison of the NH₃ electrosynthesis activity for Cu-Sn alloy in 0.1 M Na₂SO₄ (containing 0.01 M NaNO₃) with other catalysts.

Catalyst	NH ₃ yield rate	FE (%)	Ref.
Cu-Sn alloy	293.12 $\mu\text{mol h}^{-1} \text{cm}^{-2}$	78.57	This work
Cu/Cu ₂ O	0.2449 $\text{mmol h}^{-1} \text{cm}^{-2}$	95.8	2
TiO ₂ -OVs	0.0445 $\text{mmol h}^{-1} \text{cm}^{-2}$	85.0	3
PTCDA	0.030 $\text{mmol h}^{-1} \text{cm}^{-2}$	85.9	4

Table S2. The concentration of CuSO_4 and SnCl_2 to synthesize series of Cu-Sn alloy.

	Cu:Sn = 2:1	Cu:Sn = 1:1	Cu:Sn = 1:2
Concentration of SnCl_2	0.1 M	0.05 M	0.05 M
Concentration of CuSO_4	0.05 M	0.05 M	0.1 M

References

1. D. Zhu, L. Zhang, R. E. Ruther and R. J. Hamers, *Nat. Mater.*, 2013, **12**, 836–841.
2. Y. Wang, W. Zhou, R. Jia, Y. Yu and B. Zhang, *Angew. Chem. Int. Ed.*, 2020, **59**, 5350–5354.
3. R. Jia, Y. Wang, C. Wang, Y. Ling, Y. Yu and B. Zhang, *ACS Catal.*, 2020, **10**, 3533–3540.
4. Y. Wang, A. Xu, Z. Wang, L. Huang, J. Li, F. Li, J. Wicks, M. Luo, D. Nam, C. Tan, Y. Ding, J. Wu, Y. Lum, C. Dinh, D. Sinton, G. Zheng and E. H. Sargent, *J. Am. Chem. Soc.*, 2020, **142**, 5702–5708.