

Electronic Supplementary Information

Experimental Section

Product Determination: The ammonia concentration after the NRR test was estimated by the indoxyl blue method.¹ After 2 h of chronopotentiometric measurement, 4 mL of electrolyte was mixed after electrolysis with 0.5 mL of 0.32 M NaOH solution containing 0.4 M sodium salicylate, 50 μ L of 0.05 M NaClO solution containing 0.75 M NaOH, and 50 μ L of 1 wt% C₅FeN₆Na₂O for 1 h. The mixed solution after being left in the dark for 1 h was measured using the ultraviolet–visible (UV–vis) spectrophotometer by a TU-1900 spectrophotometer, and calibrate the produced indoxyl blue by the absorbance at 680 nm wavelength. In order to estimate the ammonia concentration, a series of standard ammonium chloride (NH₄Cl) solutions are used to calibrate the concentration absorbance curve.

The ammonia yield (r_{NH_3}) and Faradaic efficiency (FE) was calculated as follows:

$$r_{\text{NH}_3} = (c_{\text{NH}_3} \times V) / t \times m \quad (1)$$

$$\text{FE} = 3F \times n_{\text{NH}_3} / Q \quad (2)$$

where c_{NH_3} ($\mu\text{g mL}^{-1}$) is the NH₃ concentration, V (mL) is the volume of the electrolyte, t (h) is electrolysis time, m (mg) is the mass catalyst mass, F is the Faraday constant (96485 C mol^{-1}), n_{NH_3} (mol) is the NH₃ concentration and Q (C) is the total electric quantity during each NRR process.

Determination of N₂H₄: Hydrazine was determined by the method of Watt and Chrisp.² In short, 5 mL of electrolyte was mixed with 5 mL of coloring reagent for 20 min. The color reagent was prepared by mixing 5.99 g of *p*-(dimethylamino) benzaldehyde, 300 mL of ethanol, and concentrated 30 mL of HCl. The N₂H₄ produced was measured using an absorbance at 455 nm.

¹⁵N₂ Isotope Labeling Experiments: The ¹⁵N₂ was purchased from WUHAN NEWRADAR

SPECIAL GAS Co., LTD. $^{15}\text{N}_2$ was used as feed gas for isotope labeling experiments to verify the source of ammonia. In this experiment, $^{15}\text{N}_2$ was electrolyzed at -0.2 V for 10 h, the electrolyte solution was concentrated to 3 mL, and then the pH was adjusted to 1~2 by adding 1 M H_2SO_4 . Take out 1 mL of the above electrolyte and mix it with 0.1 mL of D_2O and the NH_3 produced was measured using $^1\text{H-NMR}$.

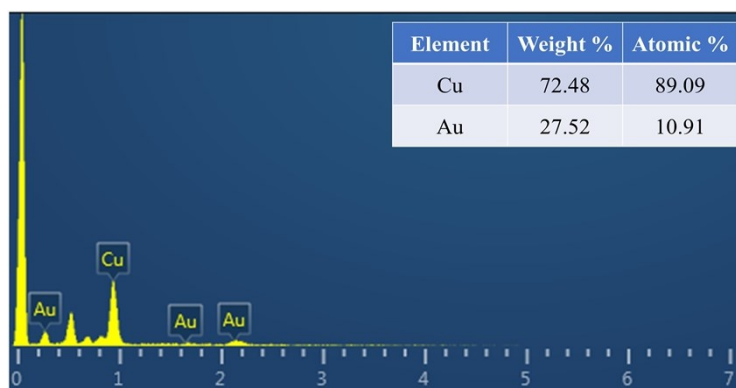


Fig. S1 EDX spectra of the Au₃Cu@Cu nanocages.

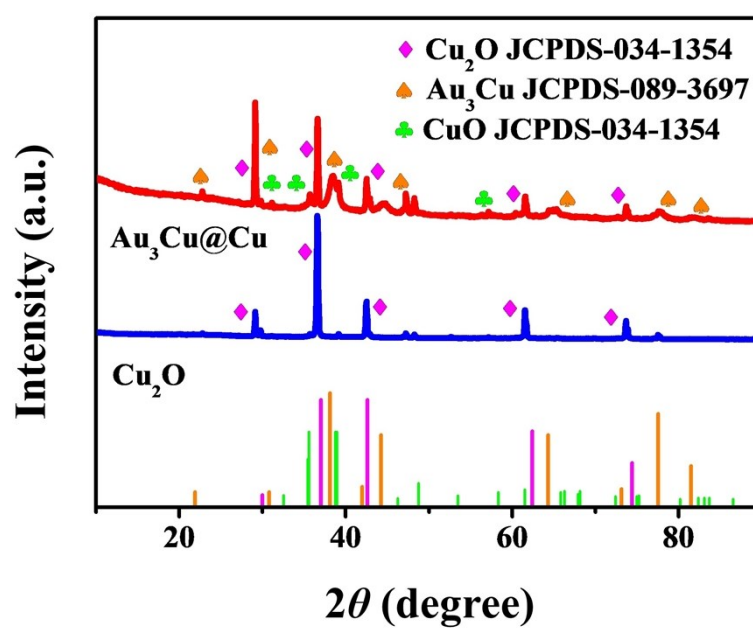


Fig. S2 XRD patterns for the Au₃Cu@Cu nanocages and Cu₂O nanocubes.

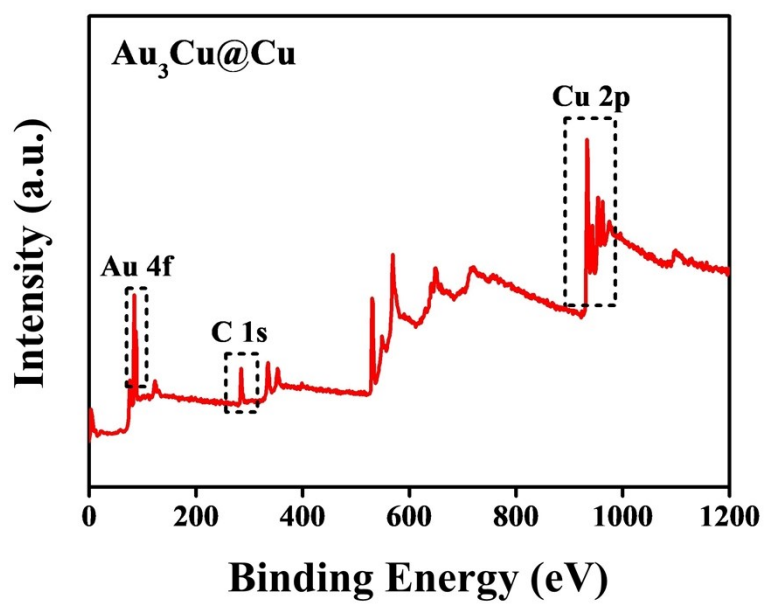


Fig. S3 XPS survey spectrum of the $\text{Au}_3\text{Cu@Cu}$ nanocages.

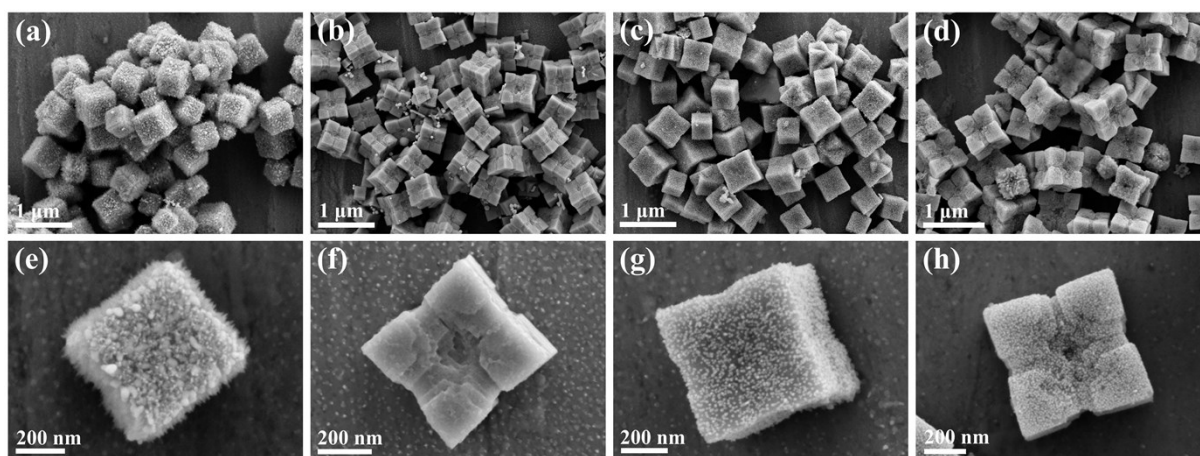


Fig. S4 SEM images of the samples prepared (a and e) without PVP, (b and f) with CTAB, (c and g) with F127 and (d and h) with DM970, respectively, under the typical synthesis.

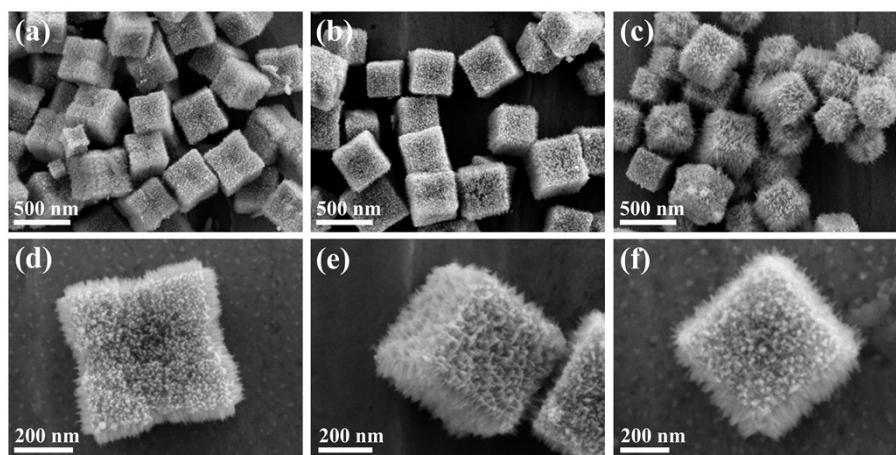


Fig. S5 SEM images of the samples prepared with different amounts of PVP under the typical synthesis: (a and d) 0.05 mg, (b and e) 0.10 mg, (c and f) 0.20 mg.

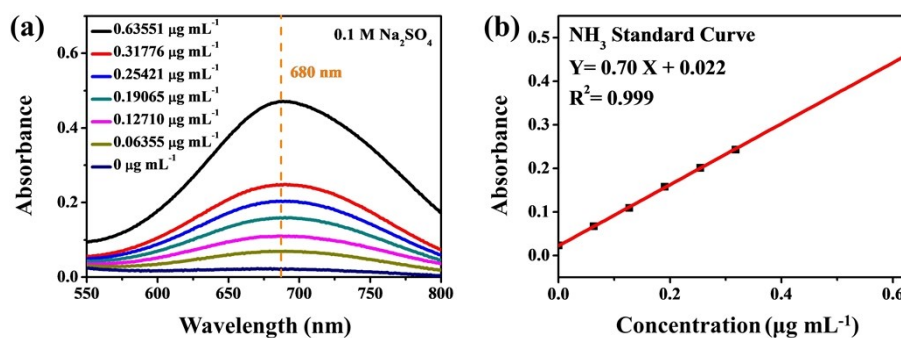


Fig. S6 (a) The UV-Vis absorption spectra and (b) corresponding calibration curves for the colorimetric NH_4^+ assay using the indophenol blue method in 0.1 M Na_2SO_4 .

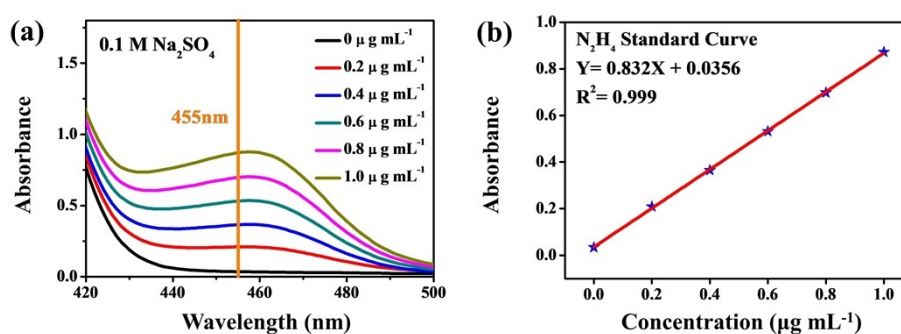


Fig. S7 (a) The UV-Vis absorption spectra and (b) corresponding calibration curve for the colorimetric N_2H_4 assay in 0.1 M Na_2SO_4 .

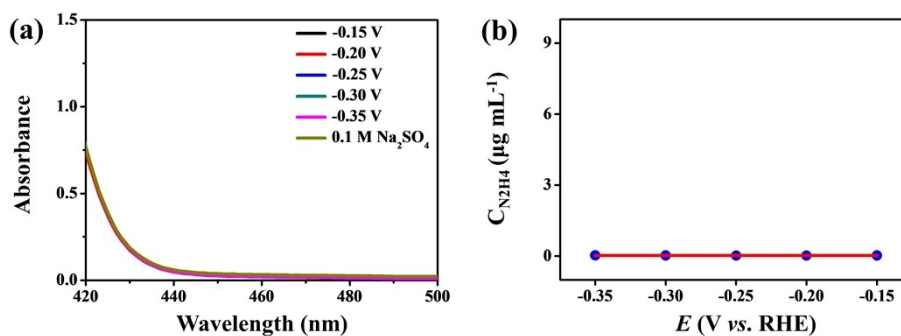


Fig. S8 (a) The UV-Vis absorption spectra and (b) corresponding yield rate of N_2H_4 formation at selected potentials.

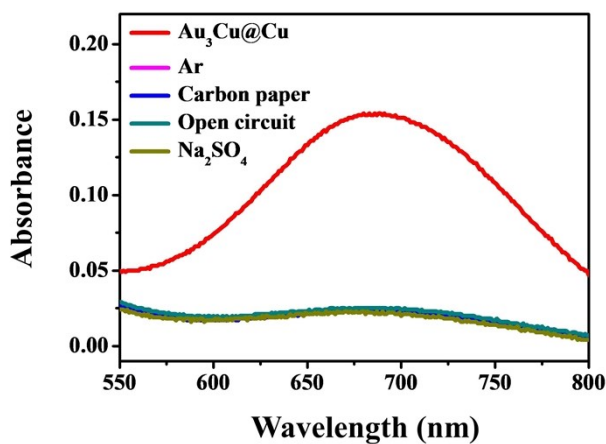


Fig. S9 UV-vis absorption spectra of different solutions after electrolysis for 2 h.

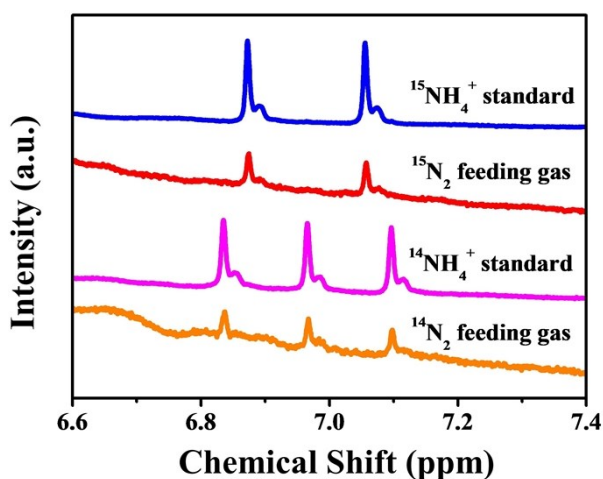


Fig. S10 ^1H NMR spectra of both $^{14}\text{NH}_4^+$ and $^{15}\text{NH}_4^+$ produced from N_2 electrochemical reduction using $^{14}\text{N}_2$ and $^{15}\text{N}_2$ as the feeding gas, respectively.

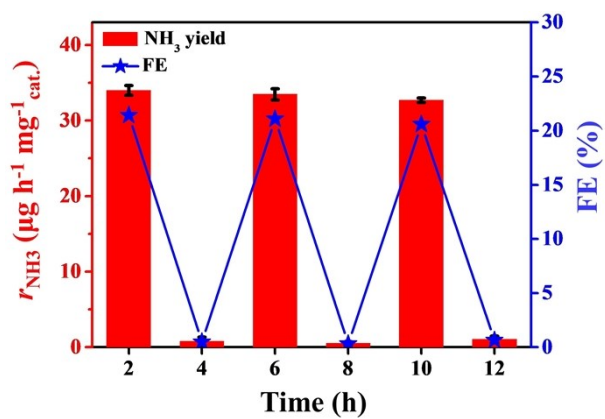


Fig. S11 NH_3 yields and FEs of $\text{Au}_3\text{Cu}@Cu$ nanocages at a potential of -0.2 V with alternating 2 h cycles between N_2 -saturated and Ar-saturated electrolytes with a total of 12 h.

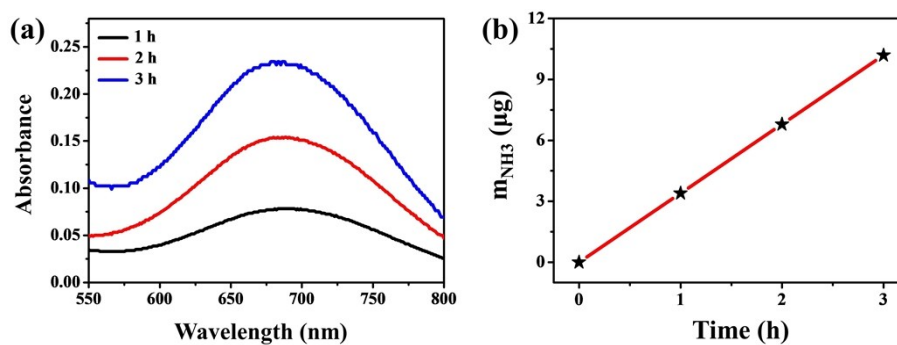


Fig. S12 (a) UV-vis absorption spectra of electrolytic solutions at different reaction times. (b) Curve of NH_3 production vs. reaction time at -0.2 V over $\text{Au}_3\text{Cu}@Cu$ nanocages.

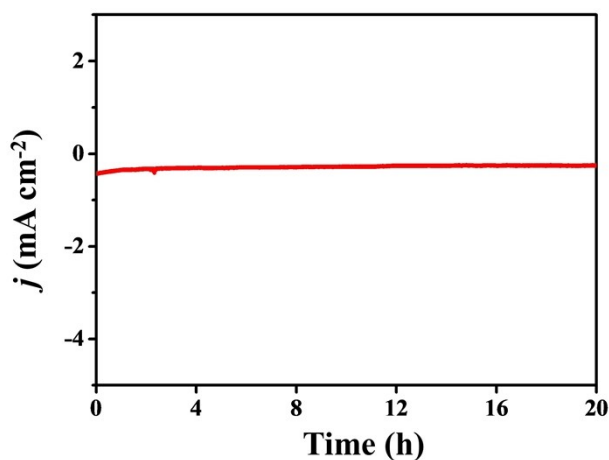


Fig. S13 Time-dependent current density curves of the $\text{Au}_3\text{Cu}@Cu$ nanocages at -0.2 V for 20 h.

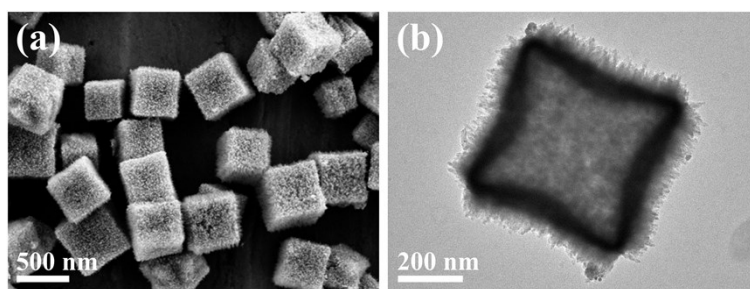


Fig. S14 (a) SEM and (b) TEM images of Au₃Cu@Cu nanocages after electrocatalytic stability testing.

Table S1 Comparisons of the NRR performance of Au₃Cu@Cu nanocages with other reported electrocatalysts.

Catalysts	Electrolyte	NH ₃ yield rate	FE (%)	Ref.
Au₃Cu@Cu Nanocages	0.1 M Na₂SO₄	33.97 μg h⁻¹ mg⁻¹_{cat.}	21.41	This work
Au(111)@Bi ₂ S ₃ Nanorods	0.1 M Na ₂ SO ₄	45.57 μg h ⁻¹ mg ⁻¹ _{cat.}	3.10	3
Au/o-CFP	0.1 M Na ₂ SO ₄	40.60 μg h ⁻¹ mg ⁻¹ _{cat.}	31.30	4
AuPdP NWs	0.1 M Na ₂ SO ₄	18.78 μg h ⁻¹ mg ⁻¹ _{cat.}	15.44	5
AuCu/ZIF-8	0.1 M Na ₂ SO ₄	14.50 μg h ⁻¹ mg ⁻¹ _{cat.}	6.70	6
S/Au NWs	0.1 M Na ₂ SO ₄	21.04 μg h ⁻¹ mg ⁻¹ _{cat.}	15.34	7
Ag ₃ Cu BPNs	0.1 M Na ₂ SO ₄	24.59 μg h ⁻¹ mg ⁻¹ _{cat.}	13.28	8
Boron Nanosheet	0.1 M Na ₂ SO ₄	13.22 μg h ⁻¹ mg ⁻¹ _{cat.}	4.04	9
Fe-doped TiO ₂	0.5 M LiClO ₄	25.47 μg h ⁻¹ mg ⁻¹ _{cat.}	25.60	10

References

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