Supporting Information

Electrochemical Nitrate-to-Ammonia Conversion over a Broad Concentration Range via a Hollow Co_3O_4/CuO Catalyst

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Product analysis methods

The calculation formula for nitrate conversion is as follows:

$$\text{Conversion (\%)} = (C_0 - C_t) / C_0 * 100\% \qquad (1)$$

where C_0 is the initial NO_3^- concentration (mM), and C_t is the NO_3^- concentration at time t (mM).

Energy efficiency (EE) was calculated as the ratio of thermodynamic energy output to electrical energy input:

$$EE_{NH_3} = \frac{\left(E_{OER} - E^{\theta}_{NH_3}\right) * FE_{NH_3}}{E_{OER} - E_{cathode}} * 100\% \qquad (2)$$

where E_{OER} = 1.23 V is the equilibrium potential of the oxygen evolution reaction, $E^{\theta}_{NH_3}$ = 0.29 V is the thermodynamic potential for NO_3^- to NH_3 conversion in neutral solution[1,2], and $E_{cathode}$ is the applied cathodic potential (vs. RHE). For H-Co2Cu1 at -0.8V in 50 mM KNO_3 electrolyte, this yields EE ≈ 43.99%.

Energy consumption per mass of ammonia (kWh kg_{NH3}^{-1}) was calculated using the following equation:

$$Energy\ consumption = \frac{V_{cell} * n * F}{3.6 * M * FE_{NH3}} \qquad (3)$$

Where V_{cell} is the cell voltage (V), n is the number of transferred electrons per mole of NH_3 produced, F is the Faraday constant (C/mol), M = 17 g mol^{-1} is the molar mass of NH_3, FE_{NH3} is faradaic efficiency of ammonia (%).

Supporting Figures and Tables

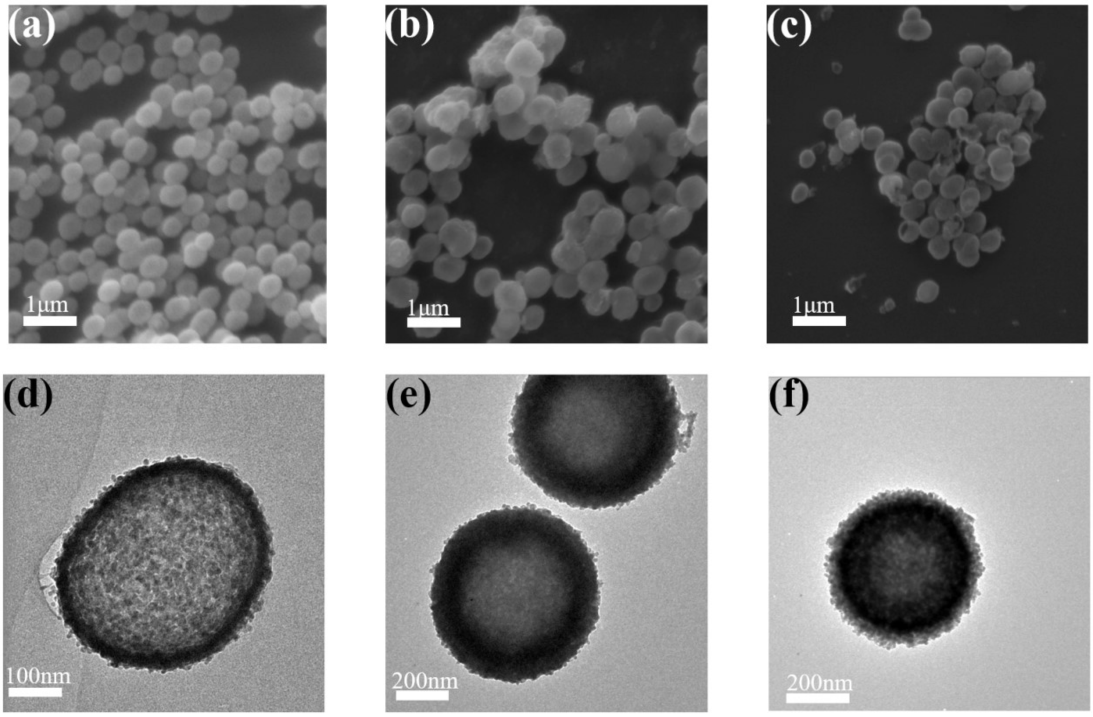

Fig. S1 SEM images of (a) H-Co2Cu1 (b) H-Co1Cu1 (c) H-Co1Cu2 hollow nanoparticles. TEM images of the (d) H-Co2Cu1 (e) H-Co1Cu1 (f) H-Co1Cu2 hollow nanoparticles.

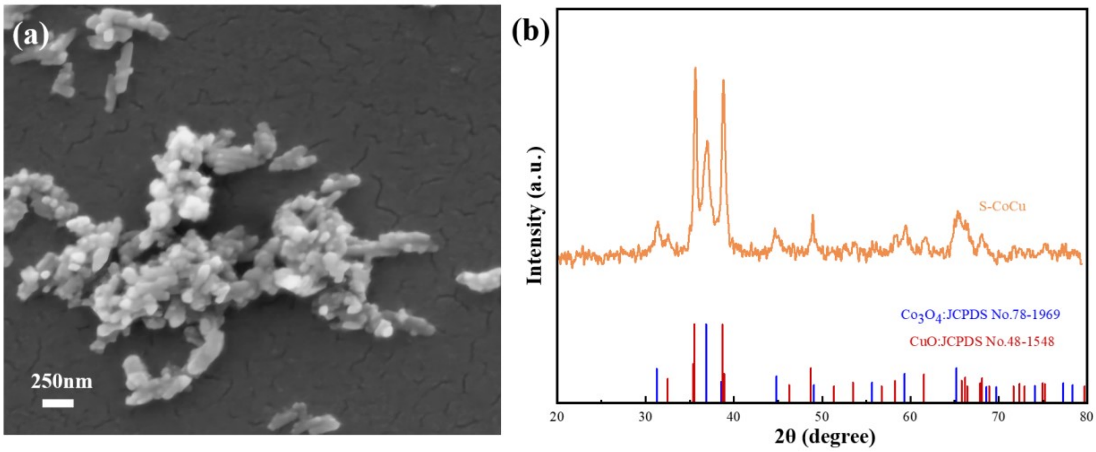

Fig. S2 (a) a representative SEM image and (b) XRD of S-CoCu particles.

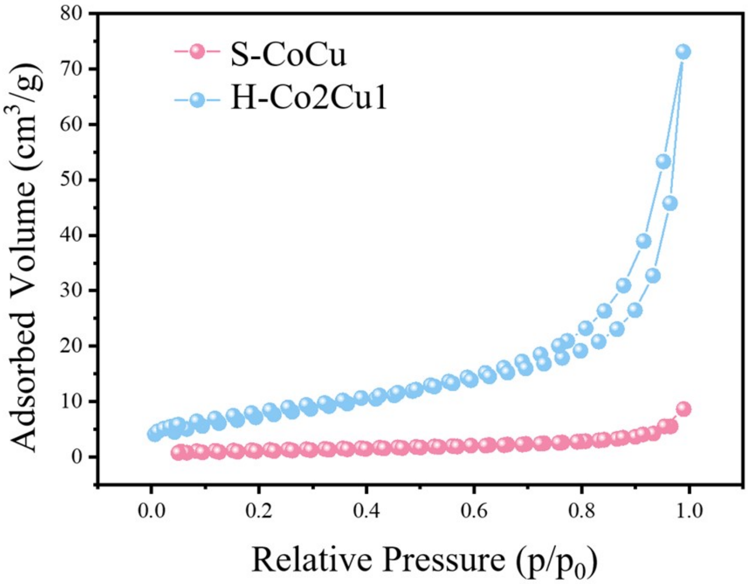

Fig. S3 Specific surface area measurement of H-Co2Cu1 and S-CoCu. BET surface area of H-Co2Cu1 is 30.3 m^2/g, and BET surface area of S-CoCu is 4.5 m^2/g.

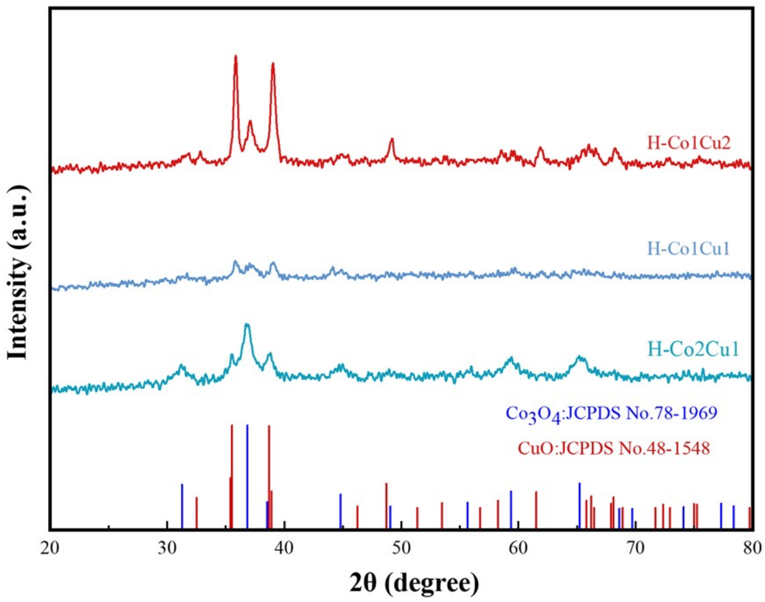

Fig. S4 XRD patterns of H-Co2Cu1, H-Co1Cu1 and H-Co1Cu2 hollow spheres.

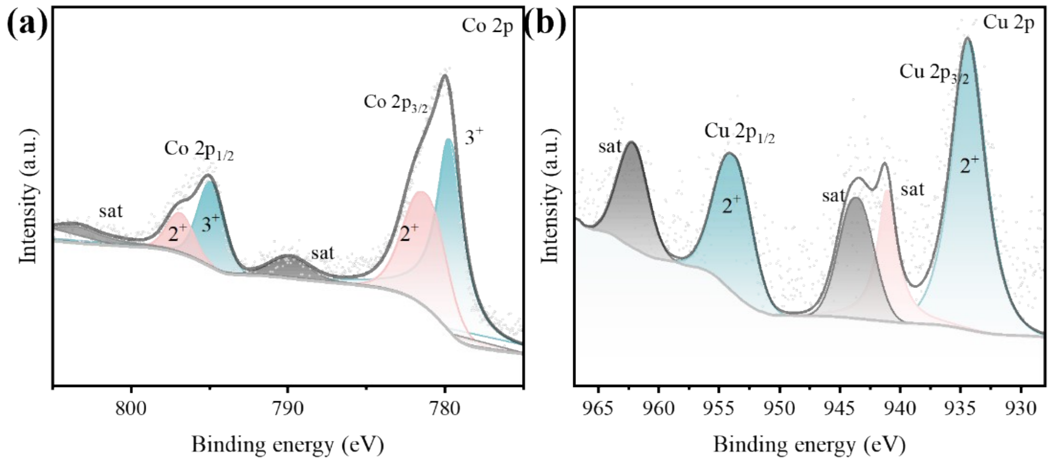

Fig. S5 XPS spectra of (a) Cu 2p for CuO and (b) Co 2p for Co_3O_4.

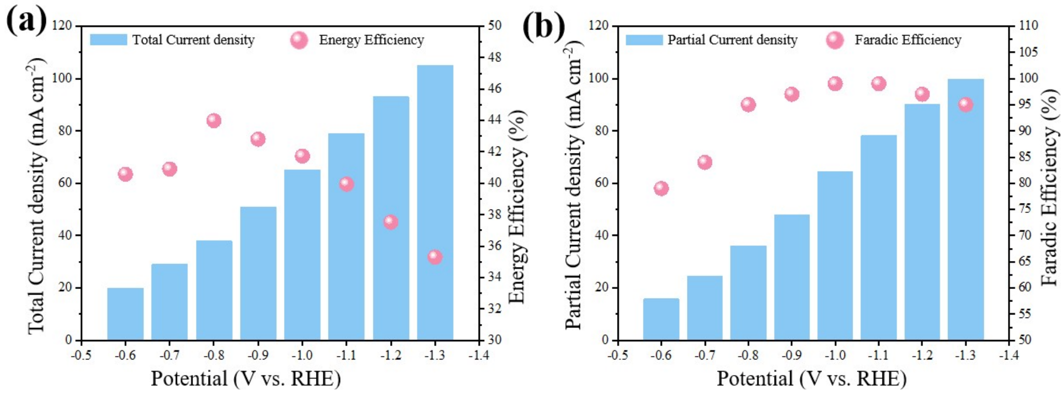

Fig. S6 (a) Potential-dependent activity and energy efficiency at 50 mM nitrate using H-Co2Cu1; (b) Potential-dependent NH_3 selectivity and partial current density at 50 mM nitrate using H-Co2Cu1.

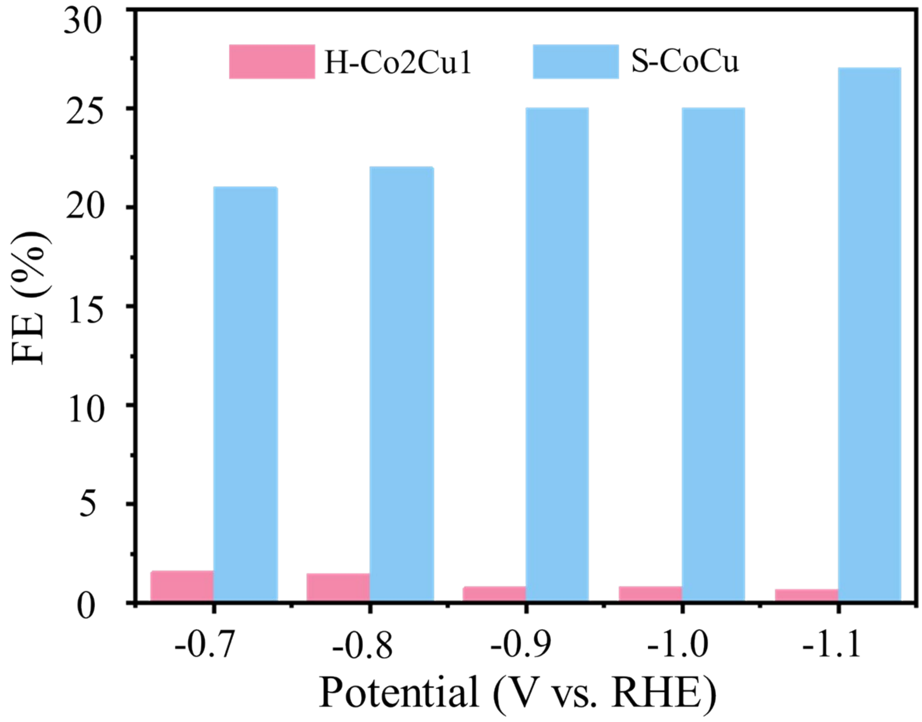

Fig. S7 Faradaic efficiency of NO_2^- for H-Co2Cu1 and S-CoCu in 50 mM KNO_3 electrolyte.

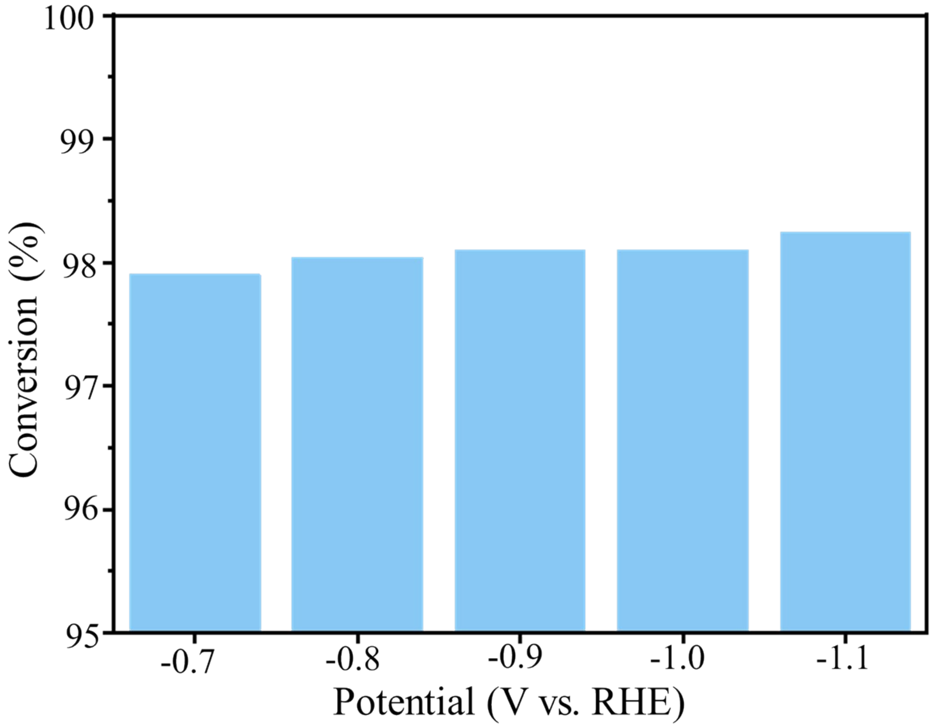

Fig. S8 NO_3^- conversion of H-Co2Cu1 in 0.2 M K_2SO_4 and 50 mM KNO_3 electrolytes.

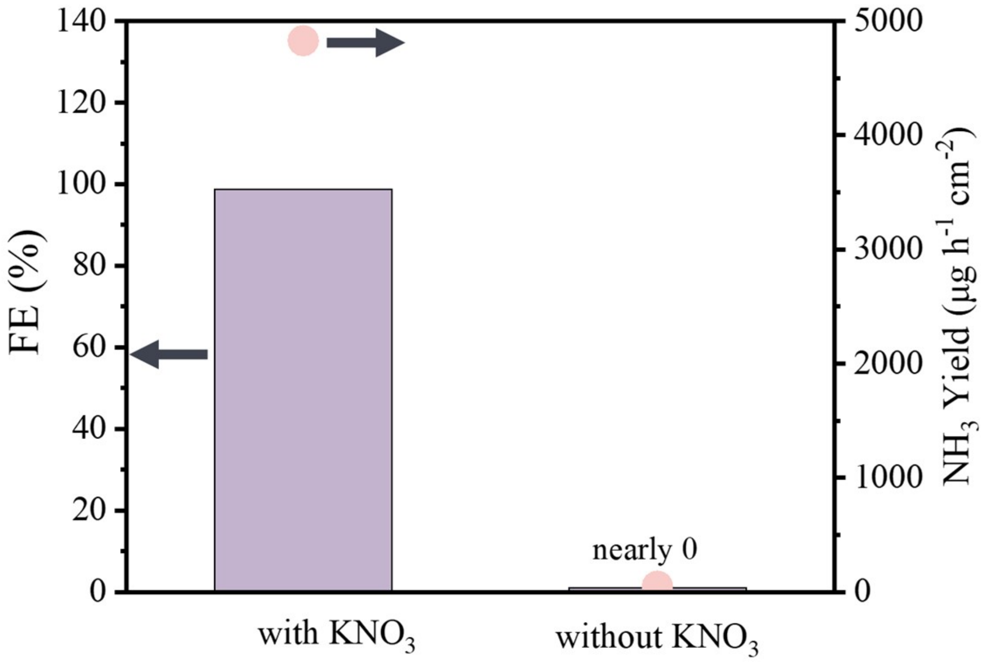

Fig. S9 The NH_3 yield rate and FE of H-Co2Cu1 measured at -1.1 V in 0.2 M K_2SO_4 electrolyte with and without NO_3^- (Bars denote NH_3 FE, and scatter points denote NH_3 yield rate).

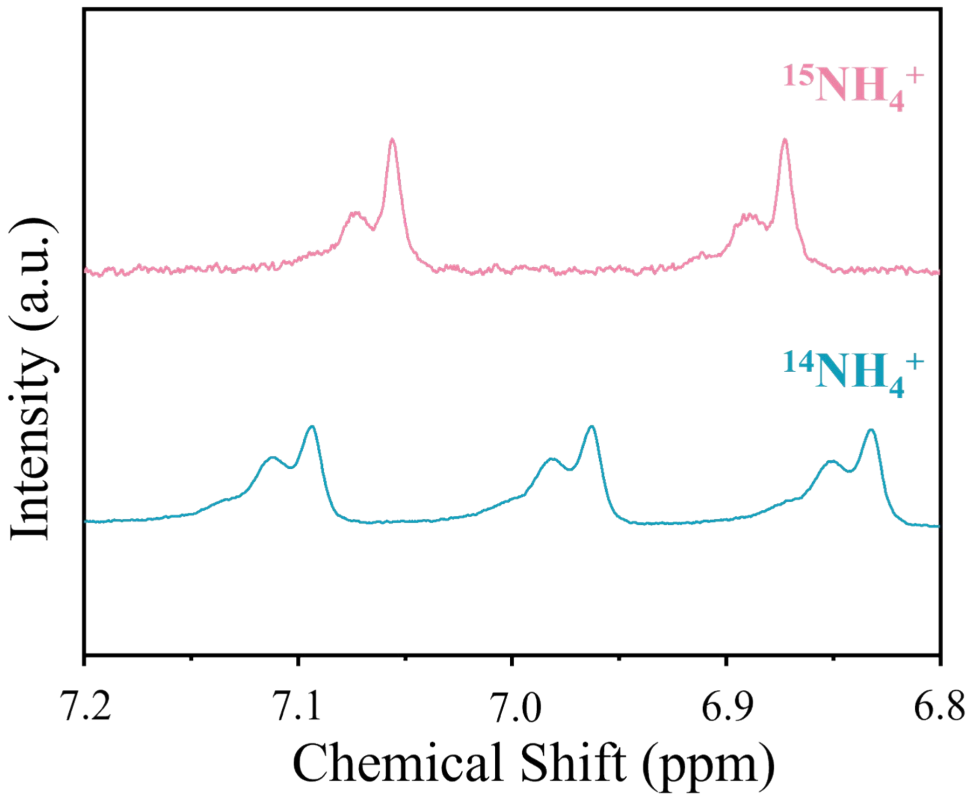

Fig. S10 ^{1}HNMR spectra of the electrolyte after electrocatalytic eNRA reaction using $^{15}NO_3^-$ and $^{14}NO_3^-$ as the nitrogen source.

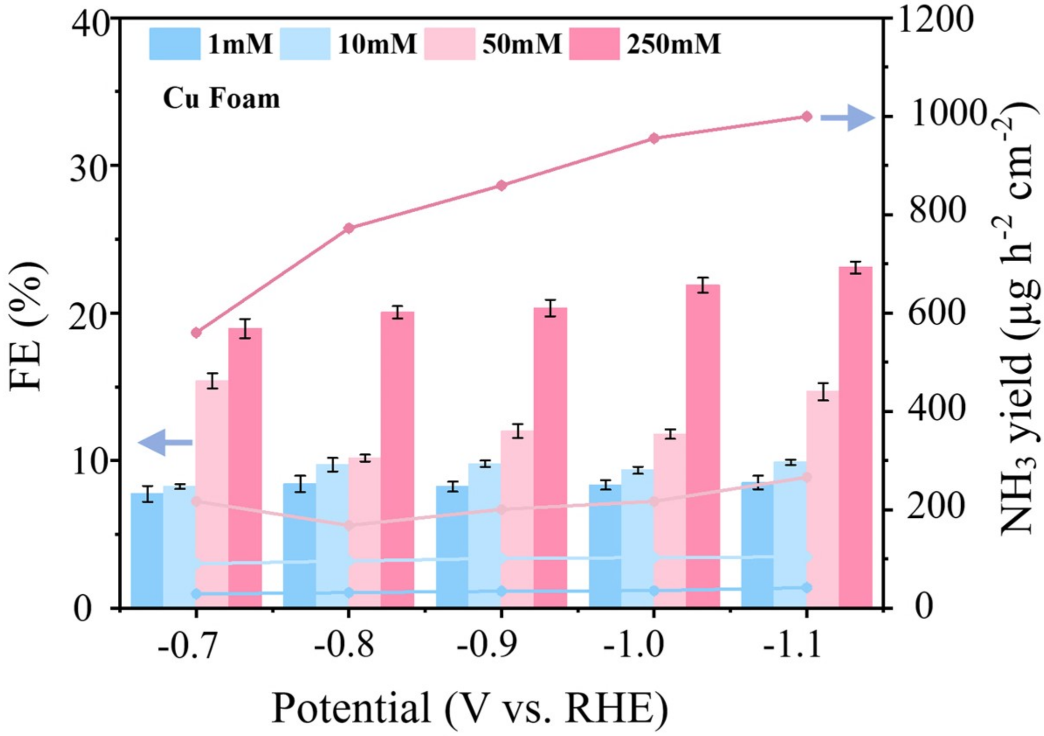

Fig. S11 Faradaic efficiency for NH_3 and NH_3 yield rate of foam copper in different electrolyte concentrations (Bars denote NH_3 FE, and lines denote NH_3 yield rate).

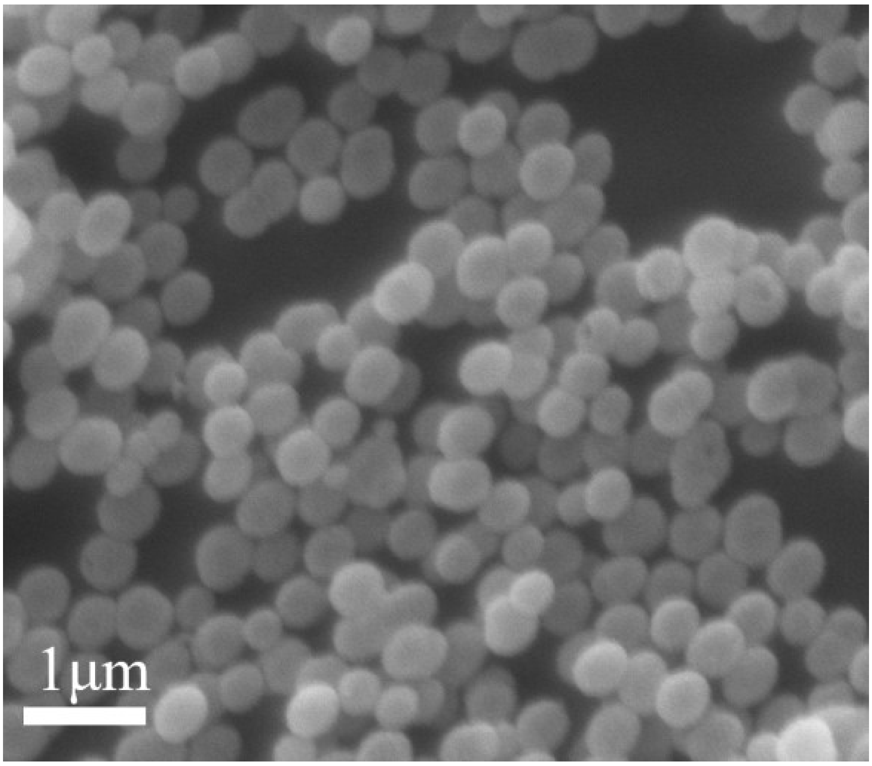

Fig. S12 SEM image of the H-Co2Cu1 hollow spheres after electrolysis.

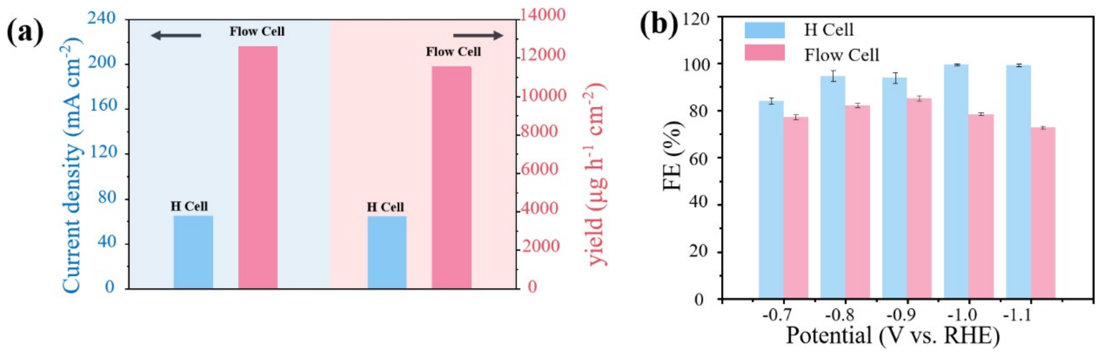

Fig. S13 (a) Comparisons of the measured current densities and NH_3 yield rates measured in H-type cell and flow cell under the same reaction conditions (50 mM KNO_3 electrolyte, −1.0V vs RHE, 1 h reaction time). (b) Faradaic efficiency for NH_3 of H-Co2Cu1 in conventional H-type cell and flow cell within 50 mM KNO_3 electrolyte.

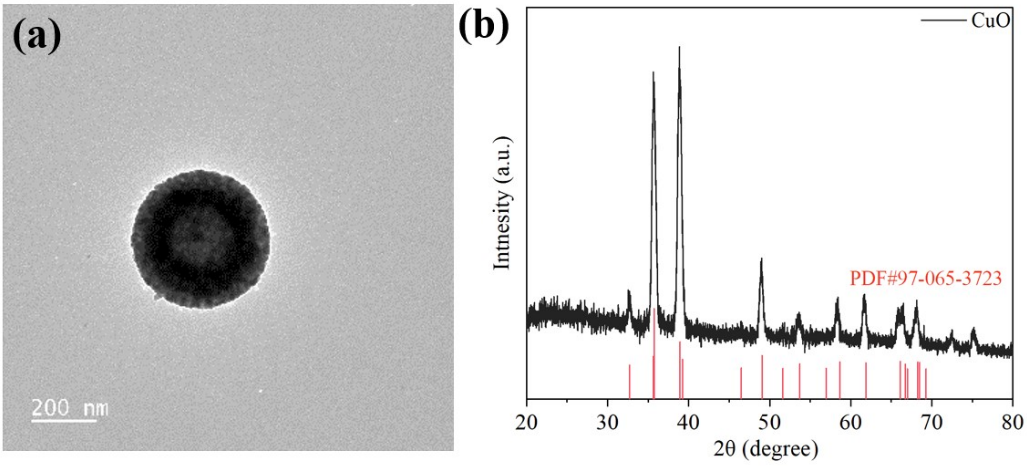

Fig. S14 (a) a representative SEM image and (b) XRD of hollow CuO nanoparticles.

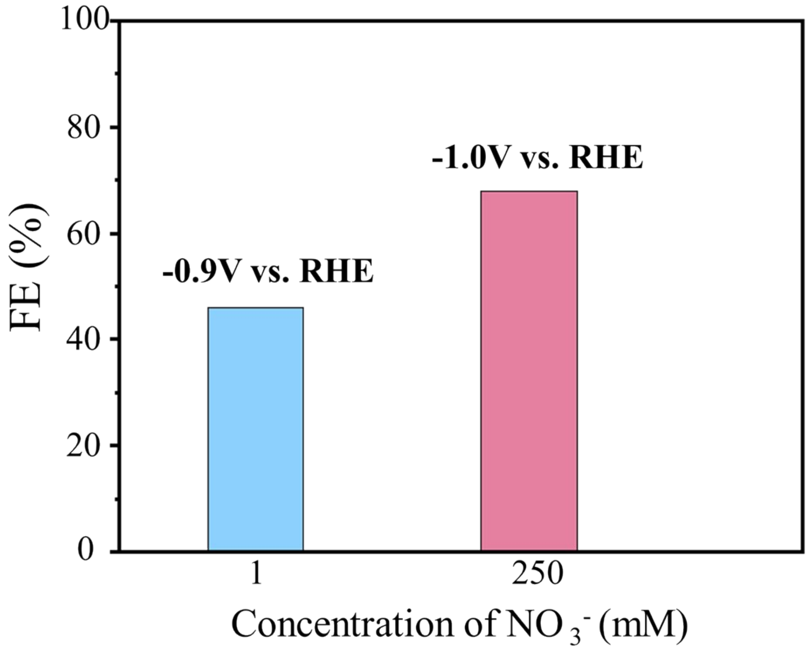

Fig. S15 NH_3 FE of hollow CuO catalysts in 1 mM and 250 mM nitrate concentrations.

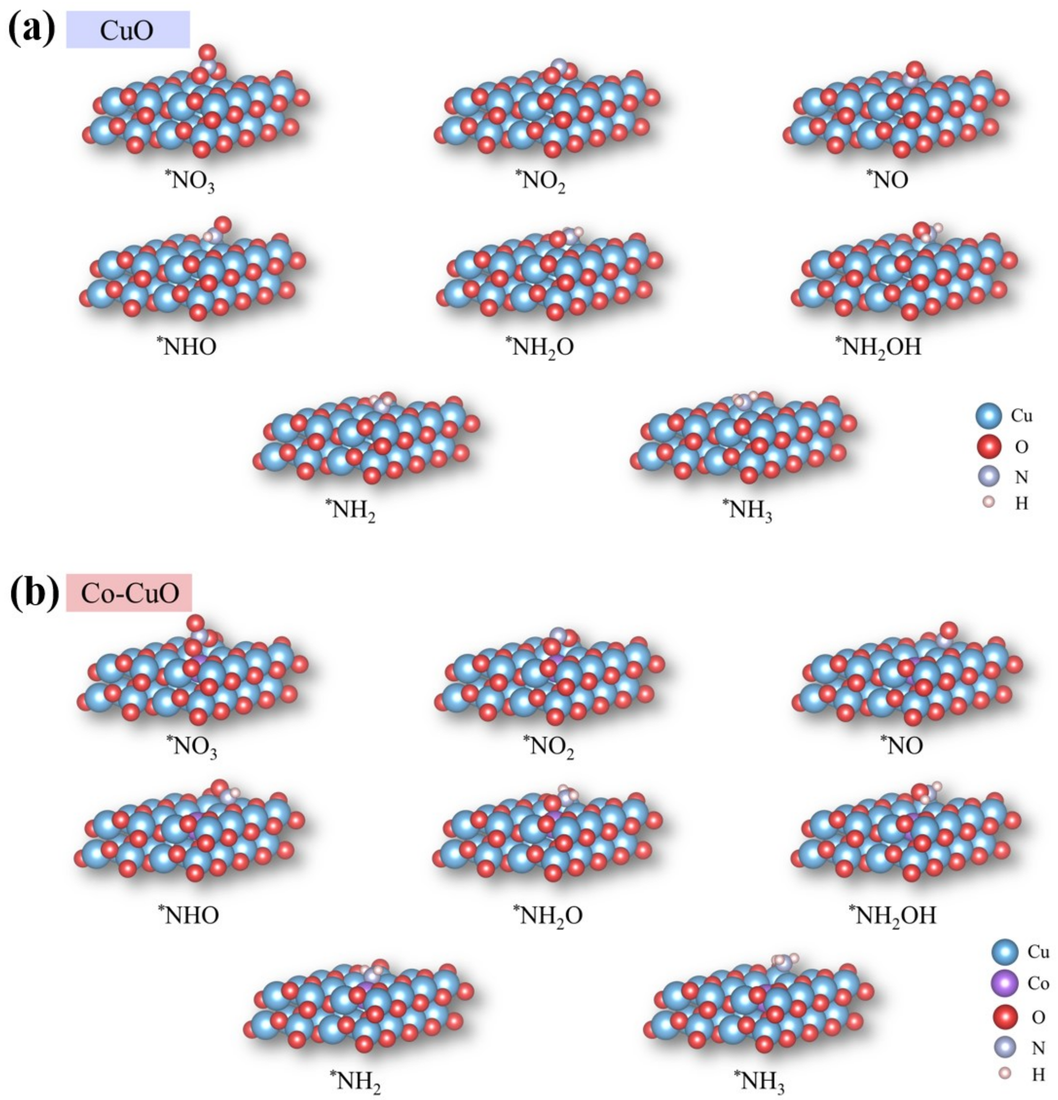

Fig. S16 Corresponding structural models for the reaction pathways on (a) CuO and (b) Co-CuO models.

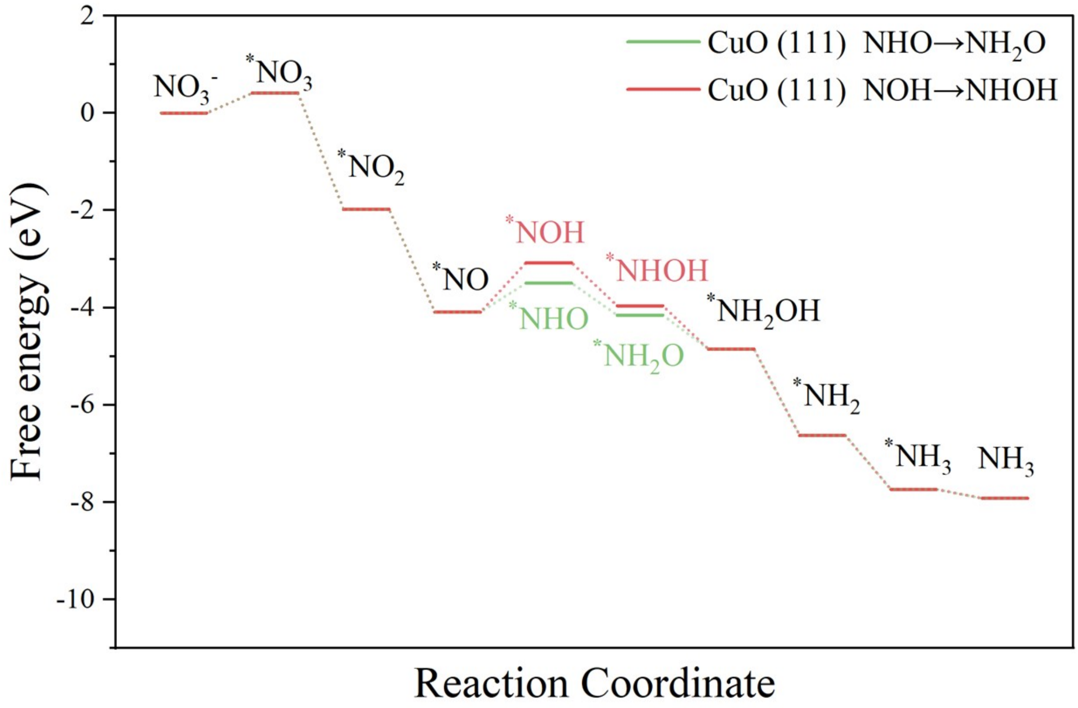

Fig. S17 Calculated free energy profiles for eNRA on the CuO(111) surface. Two competing hydrogenation pathways from *NO are compared: the *NOH → *NHOH route (red) and the *NHO → NH_2O route (green), indicating *NHO/*NH_2O is energetically more favorable on CuO(111), governing the subsequent reduction steps toward NH_3.

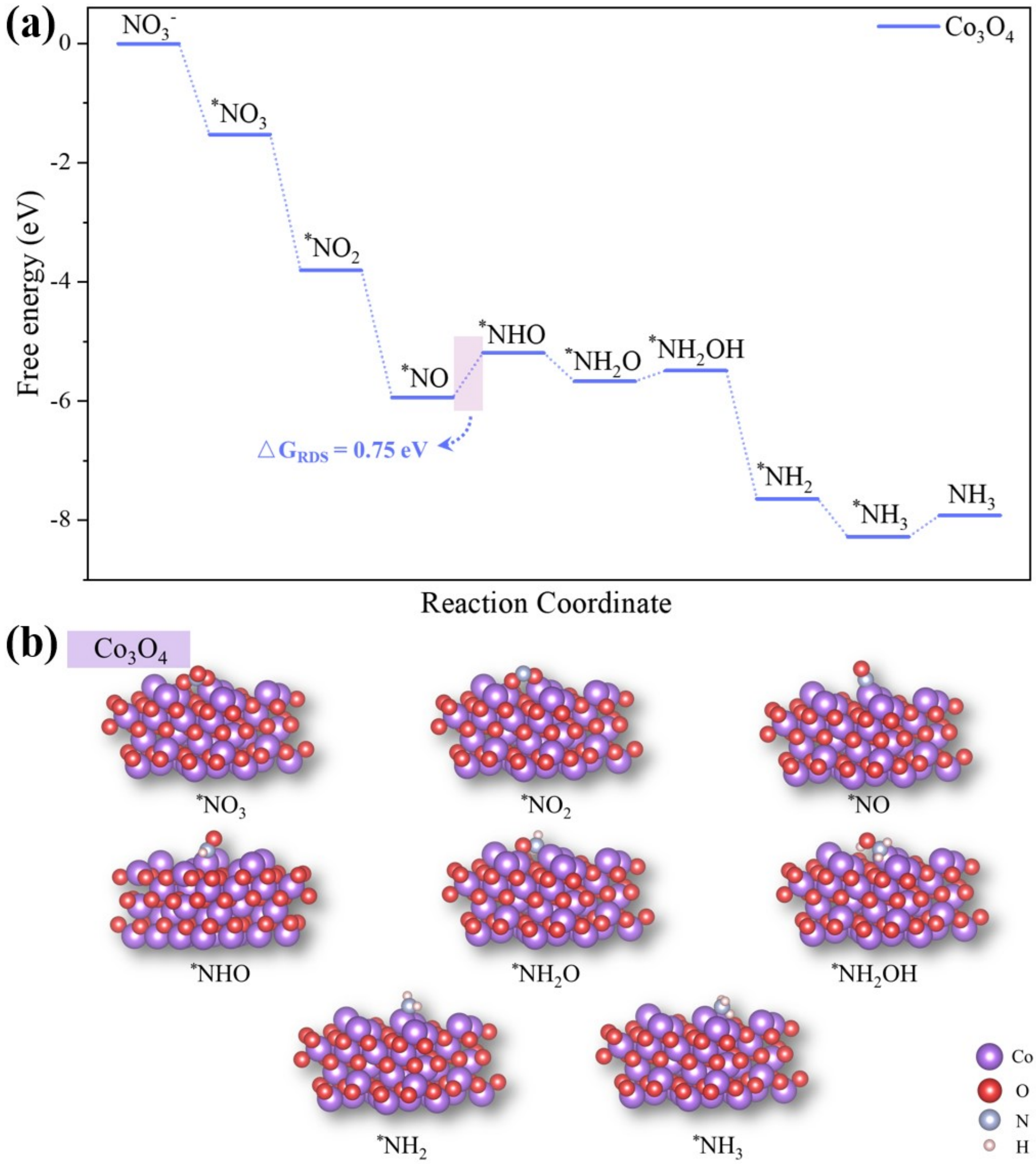

Fig. S18 (a) Calculated free energy profiles for the reaction pathways on Co_3O_4 (111) surface and (b) corresponding structural models.

Table S1. Cu/Co molar ratio of unsupported H-Co2Cu1, H-Co1Cu1 and H-Co1Cu2 measured by ICP-OES.

Catalyst	**Co (mg/L)**	**Cu (mg/L)**	**Co (wt%)**	**Cu (wt%)**	**Co:Cu molar ratio**
H-Co2Cu1	2.25	1.08	45.0	21.6	2.24:1
H-Co1Cu1	1.64	1.80	32.8	36.0	0.98:1
H-Co1Cu2	1.19	2.68	23.8	53.6	0.48:1

Table S2. Comparison of recently reported system energy consumption values.

Energy consumption ($kWh\ kg^{-1}\ NH_3$)	REF
26.95	This work
28.4	3
17.0	4
21.4	5
21.19	6
27.8	7
23.0	8
19.5	9
16.3	10
39.49	11

Table S3. Comparison of eNRA performance of catalysts reported in neutral environment.

Catalyst	NO_3^- Electrolyte (mM)	NH3 yield ($\mu g \cdot h^{-1}\ cm^{-2}$)	FE (%)	REF
H-Co2Cu1	1	74	86	This work
	10	2107	97	
	50	4809	99.8	
	250	8959	250	
CuX	3.6	1340	80	12
Cu_2O/TiO_2-x	3.6	3220	98	13
Cu-CoFe LDH-Ov5	5	1615	95.6	14
Cu_2O/Cu nanosheet	14	2793	93.2	15
r-Cu/Ga_2O_3-SAM20	20	16106	95.48	16
AuRu-Cu_2O/CF	35.7	10810	90.99	17
c-Co@a-Cu	50	4630	99.6	18
TTA-TPH-CuCo	100	13490	92.31	19
Ni-CuO	100	15980	95.26	20
CoTMA	100	4513.5	94.7	21
ZIF-67@HMCS	100	10200	97.6	22
Ca-Cu_2O-OA	100	15020	97.49	23
Cu1Co1 HHTP	100	30200	96.4	24
i$(TCNQ)_2$/NF NTs	200	11286.9	83.7	25
CoCu-NC	200	2450	95.3	26
CuCo-DHTA	500	13490	91.58	27

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