Electronic Supplementary Information

In-situ reconstructed prism-like CuO on copper foam assisted by fumaric acid for enhanced electrochemical nitrate reduction reaction

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Experimental

Materials and methods

Scanning electron microscopy (SEM) was performed on a Gemini 500 field emission scanning electron microscope to observe the surface of the as-prepared CF catalysts. High-resolution transmission electron microscopy (TEM) was conducted on a FEI Tecnai G2 F30 transmission electron microscope to study surface structural characteristics, and the sample was dispersed in ethanol via ultrasonication and was loaded on the copper grid. Powder X-ray diffraction (XRD) was performed on a MiniFlex600 instrument using Cu Kα radiation source. Fourier transform infrared spectra (FT-IR) data were collected on Thermo Fisher Nicolet iS10 spectrometer over the range of 4000 - 400 cm^{-1} in KBr pellets. Ultraviolet-visible (UV-vis) absorption spectra were determined by a RIGOL Ultra-3600 UV-vis spectrophotometer in quartz cuvettes. ^{1}H NMR spectra were obtained using a Bruker Ascend 400 NMR spectrometer.

Preparation of CuO/CF

Commercial copper foam (CF) was treated in acetone upon ultrasonication for 15 min to remove surface impurities and greasy dirt. After purification and drying, FU-CF was prepared using a solvothermal method. The pretreated CF substrate (2 cm × 1 cm) was immersed in a solution of fumaric acid in *N*,*N*-dimethylformamide (DMF) (5 mL, 0.2 mol L^{-1}). Subsequently, the mixture was heated at 80 °C for 4 h. After cooling to room temperature, the resulting CF was thoroughly washed with deionized water. Electrochemical in situ reconstruction was performed with a three-electrode system in the electrolyte containing 1.0 mol L^{-1} KOH and 0.1 mol L^{-1} KNO$_3$ for 3600 s at a constant potential of -0.1 V vs. RHE. The electrode was washed with deionized water and dried, to obtain CuO/CF.

FDC-CF and BTC-CF were prepared by the same procedures using 2,5-furandicarboxylic acid (H$_2$FDC) and 1,3,5-benzenetricarboxylic acid (H$_3$BTC), respectively. CuO/CF-0.2M, CuO/CF-0.4M and CuO/CF-0.6M were synthesized in various concentration of 0.2, 0.4 and 0.6 mol L^{-1} fumaric acid, respectively. CuO/CF-2h, CuO/CF-4h, CuO/CF-6h and CuO/CF-8h were synthesized in various reaction time of 2, 4, 6 and 8 h, respectively.

Preparation of DMF-CF

DMF-CF was prepared using solvothermal method. CF was heated in 5 mL DMF at 80 ^{o}C for 3 h. After cooling to room temperature naturally, the electrode was washed with deionized water and dried, to obtain DMF-CF.

Electrochemical experiment

The electrochemical nitrate reduction reaction experiments were performed on a CHI660E electrochemical workstation (Shanghai Chenhua). In a standard three-electrode system with a H-type electrolytic cell separated by a Nafion 117 Membrane, the CuO/CF electrode, Hg/HgO (1.0 mol L^{-1} KOH) and a graphite rod were utilized as the working electrode, counter electrode and reference electrode, respectively. 1.0 mol L^{-1} KOH with 0.1 mol L^{-1} KNO_3 aqueous solution was employed as the electrolyte (the catholyte) and 1.0 mol L^{-1} KOH aqueous solution was used as the electrolyte (the anolyte). All the potentials given vs. the Hg/HgO electrode were transformed to the RHE reference scale with the equation of E/V (vs. RHE) = E/V (vs. Hg/HgO) + 0.0591×pH + 0.098. Linear-sweep voltammogram (LSV) curves were measured from +0.4 V to -0.6 V vs. Hg/HgO (1.0 mol L^{-1} KOH) at a scan rate of 10 mV s^{-1} at room temperature and all the polarization curves were performed without *iR*-correction. Electrochemical impedance spectroscopy (EIS) was performed with an amplitude of 10 with frequency ranging from 0.01 to 100 kHz to reveal the surface resistance and diffuse characteristics. Double-layer capacitance values (C_{dl}) were obtained by a series of scan rate of 20, 40, 60, 80 and 100 mV s^{-1} to evaluate the electrochemical active surface are (ECSA). The chronoamperometry measurement and amperometric *i-t* experiments were tested to conduct long-term stability tests at different voltage and time. After catalysis, the resulting CuO/CF was washed with deionized water and dispersed in ethanol under ultrasonication. The upper dispersion was subjected for centrifugation to collect the powder CuO/CF, which was used for further analysis (powder XRD, FT-IR and TEM).

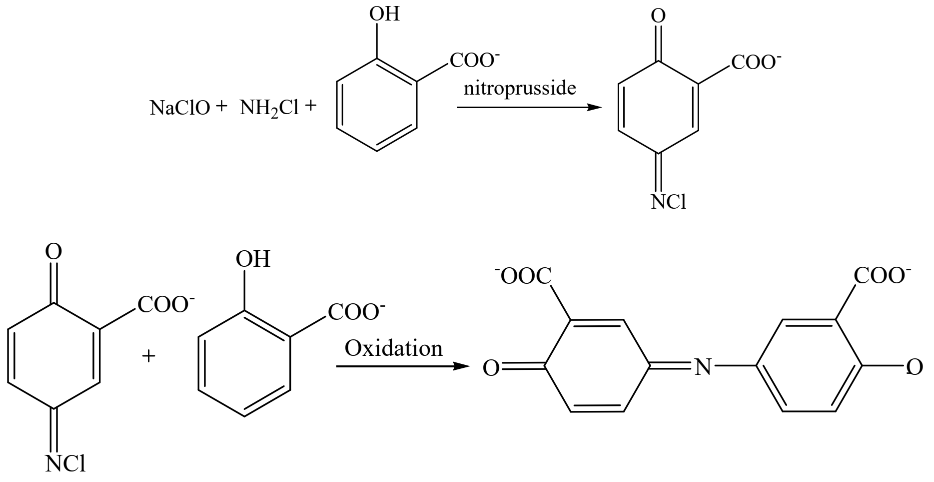
Determination of ammonia-N by ^{1}H NMR

The pH of 1.0 mL electrolyte from the cathode cell was adjusted to 3 - 4 by 4.0 mol L^{-1} H_2SO_4 and maleic acid (about 20 mg) as internal standard was added. Then 0.5 mL of the above solution was mixed with 100 μL D_2O for ^{1}H NMR. The concentration of NH_3 was quantified by compared the integral area of generated NH_3 with the vinylic singlets for maleic acid.

Determination of ammonia-N by UV-vis spectroscopy

First, 1.0 mL electrolyte from the cathode cell was diluted to 2.0 mL to reach the detection range. After the addition of 2.0 mL of 1.0 mol L^{-1} NaOH solution containing 5.0 wt.% salicylic acid and 5.0 wt.% sodium citrate, 1.0 mL of 0.050 mol L^{-1} NaClO and 0.10 mL of 1.0 wt.% sodium nitroprusside solution were added in turn. The Berthelot reaction was applied for colorimetric detection of NH_3, in which NH_3 reacts with Berthelot reagents (salicylate, hypochlorite, and sodium nitroprusside as the catalyst) to generate indophenol blue dye by a three-step reaction under alkaline conditions. After the reaction lasted for approximately 1 h at room temperature, the absorption intensity was verified by the maximum absorbance peak at 655 nm through UV-vis spectroscopy, and the standard concentration-absorbance curve was determined by a series of standard solutions of dried ammonium chloride.

$$NH_3 + NaClO \longrightarrow NH_2Cl + NaOH$$



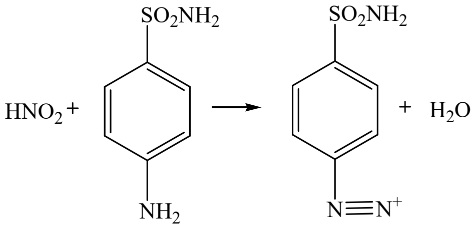
Determination of nitrate-N[53,54]

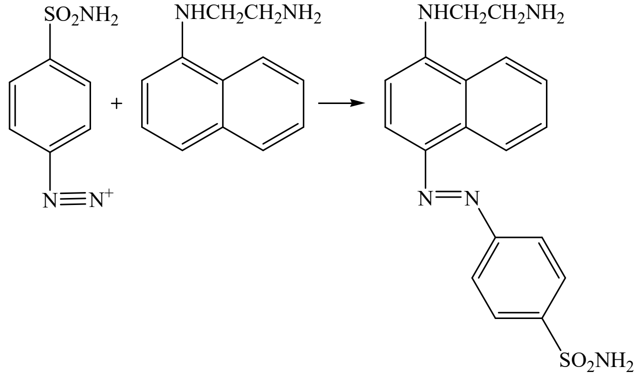
First, 0.05 mL electrolyte from the cathode cell was taken out and diluted to 5.0 mL. Next, 0.10 mL of 1.0 mol L^{-1} HCl and 0.010 mL 0.8 wt.% sulfamic acid solution were successively added in the above electrolyte. Specially, sulfamic acid was used to reduce NO_3^- to innocuous N_2O. After standing for 30 min, the solution mixture was measured using UV–vis spectroscopy at the absorption wavelength of 220 and 270 nm. The final absorbance was quantified according to the equation $A = A_{220\ \mathrm{nm}} - 2A_{275\mathrm{nm}}$. The standard concentration-absorbance curve was determined by a series of standard solutions of dried sodium nitrate.

$$HSO_3NH_2 + HNO_3 \longrightarrow N_2O + H_2SO_4 + H_2O$$

Determination of nitrite-N[56]

p-Aminobenzene sulfonamide (2.0 g) and *N*-(1-Naphthyl) ethylenediamine dihydrochloride (0.10 g) were dissolved in ultrapure water (25.0 mL) and phosphoric acid (5.0 mL, ρ = 1.68 g mL^{-1}) to prepare a color reagent. 0.005 mL electrolyte from cathode cell was taken out and diluted to 5.0 mL to the detection rang. Then, 1.0 mL of 1.0 mol L^{-1} HCl and 0.10 mL of the color reagent were successively added in the above solution. Nitrite was converted to a light-absorbing azo dye by a two-step reaction. After the solution was thoroughly mixed and allowed to stand for 30 min, the absorption intensity was recorded using UV–vis spectroscopy at a wavelength of 540 nm. The standard concentration-absorbance curve was calibrated by a series of standard solutions of dried sodium nitrite.





After experiments, the volume of hydrogen was recorded to calculate the Faradic efficiency according to the followed formula. Moreover, NO_2^- and NH_3 in the post-electrolyte through colorimetric method were qualitatively analyzed by UV-vis spectrophotometry. And then the concentration of NO_2^- and NH_3 was obtained by standard concentration-absorbance curves to further calculate the Faradic efficiency according to the following formula,

$$\mathrm{NH_3\ Faradic\ efficiency} = 8FV_0\Delta c_{\mathrm{N-NH_3}}/Q$$

$$\mathrm{NH_3\ yield} = V\Delta c_{\mathrm{N-NH_3}}/(tS)$$

$$\mathrm{H_2\ Faradic\ efficiency} = 2FV_1\rho/(MQ)$$

$$\mathrm{NO_2^-\ Faradic\ efficiency} = 2FV_0\Delta c_{\mathrm{N-NO_2^-}}/Q$$

where Δc_{N-NH_3} and $\Delta c_{N-NO_2^-}$ are the concentration in N-NH_3 and N-NO_2^-, respectively, after electrolysis, F is the Faradic constant (96485 C mol^{-1}), V_0 is the volume of electrolyte in the cathode compartment (30 mL) and V_1 is the volume of generated hydrogen, ρ is the mass density of hydrogen (0.0899 g dm^{-3}), M is the molecular weight of hydrogen (2.01588 g mol^{-1}), t is the electrolysis time, S is the area of the reaction substrate, and Q is the total electric charge passing the electrode.

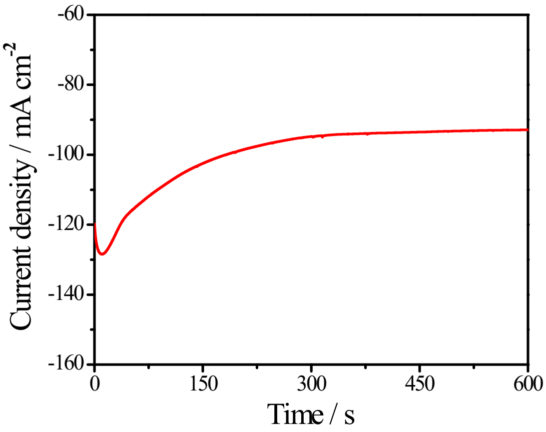


Fig. S1 *I-t* curve of CuO/CF at -0.3 V_{RHE}.

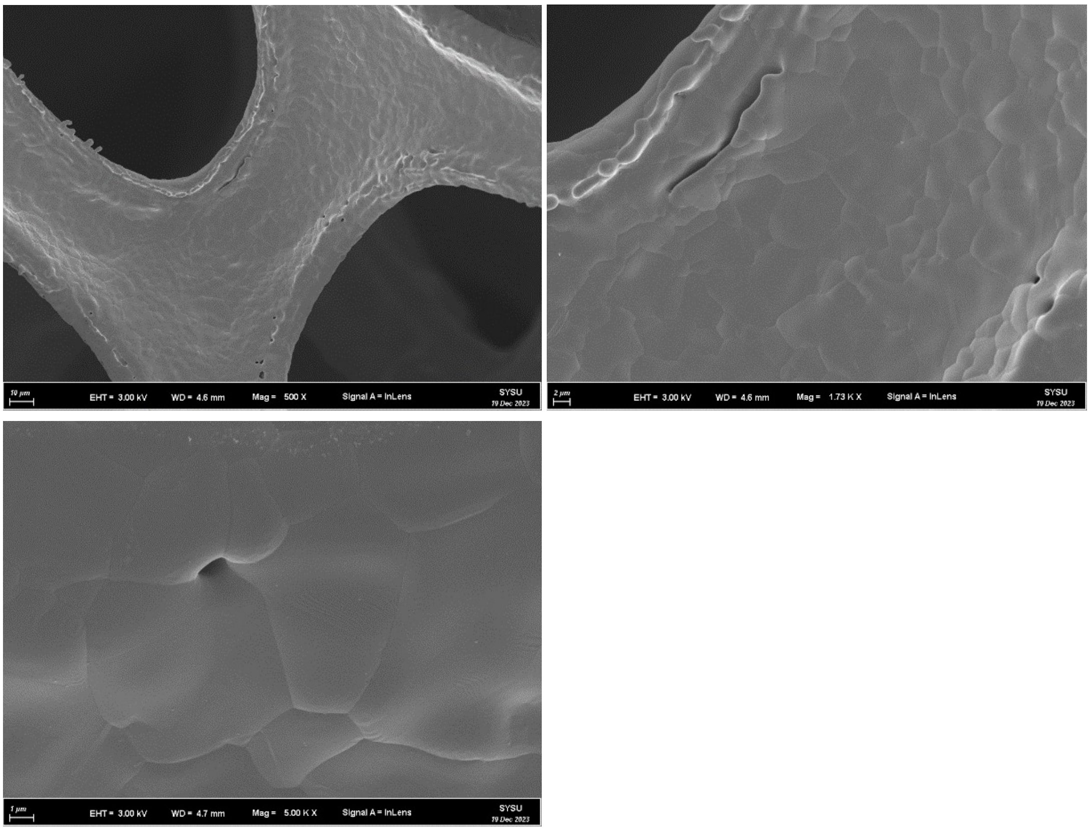


Fig. S2 SEM images of comercial copper foam.

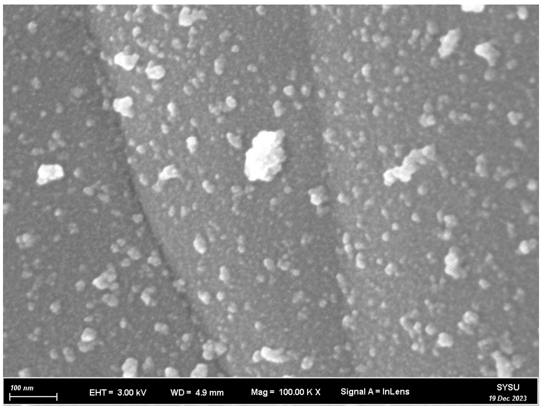


Fig. S3 SEM image of DMF-CF.

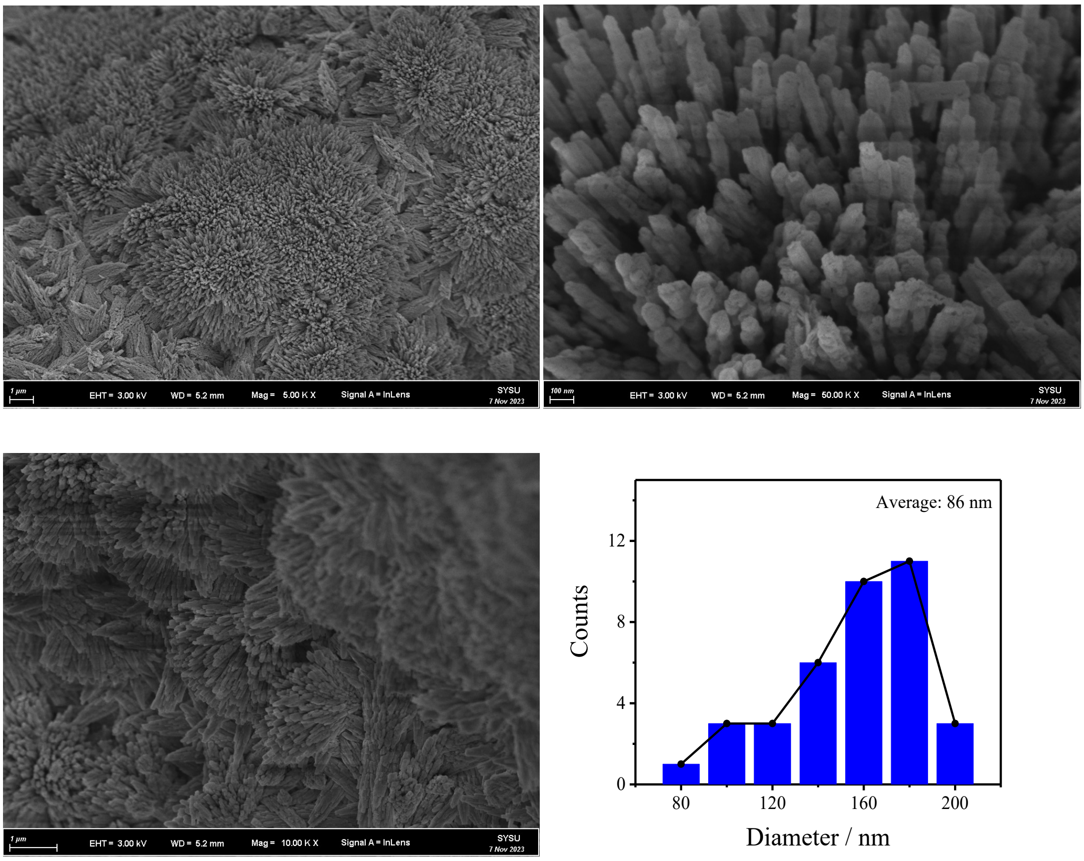


Fig. S4 SEM images and corresponding particle size distribution of FU-CF.

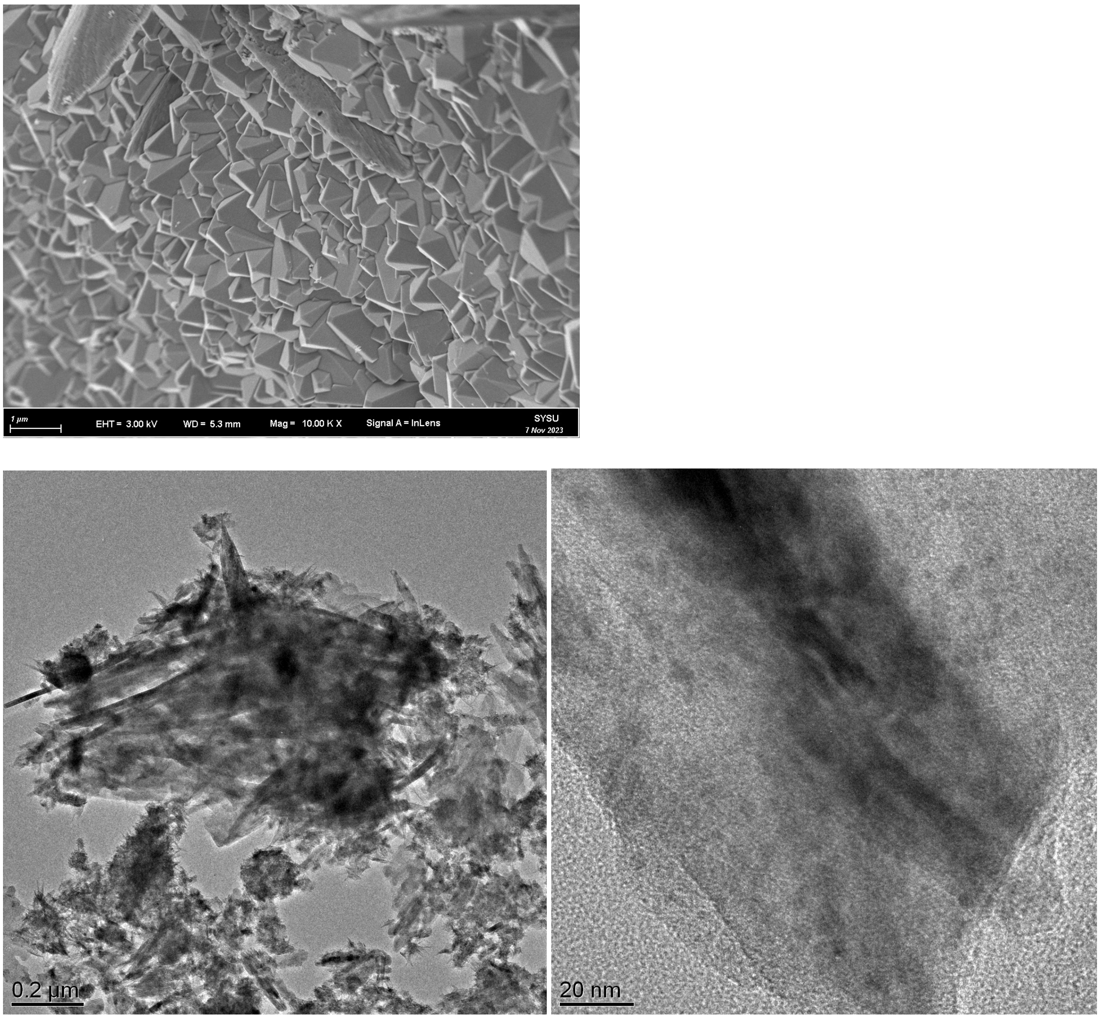


Fig. S5 SEM and TEM images of CuO/CF.

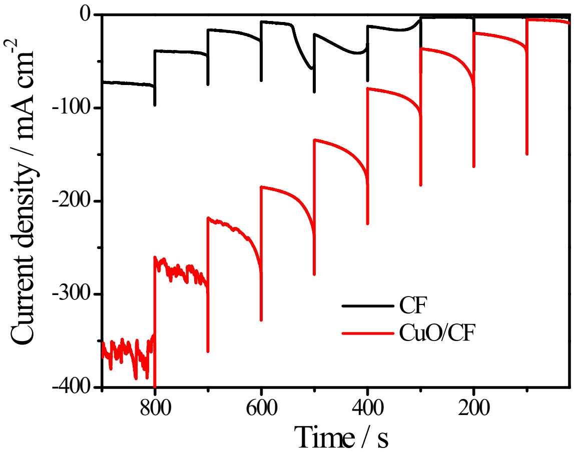


Fig. S6 Multi-potential steps curves of CuO/CF and CF in NO_3RR with and without the presence of 0.1 mol L^{-1} KNO_3.

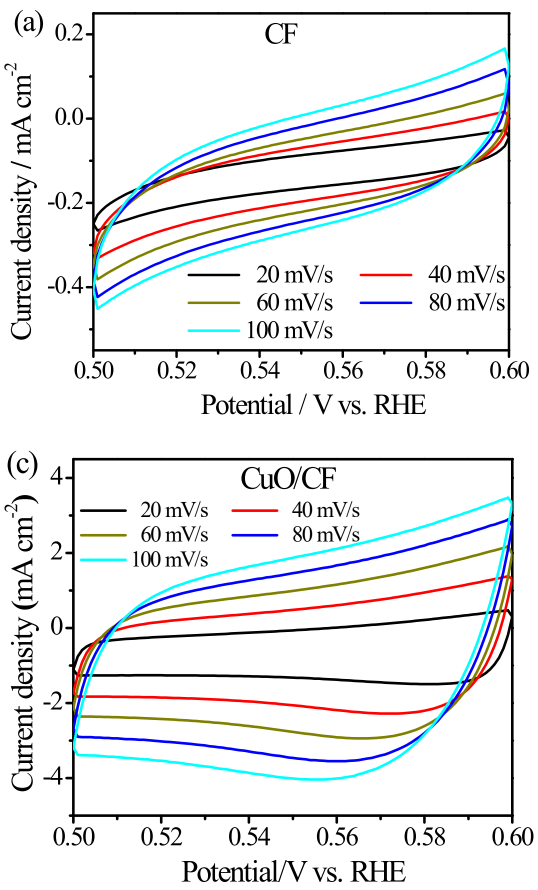


Fig. S7 CV curves at various scan rates increasing from 20 to 100 mV s^{-1} of (a) CF, (b) DMF-CF and (c) CuO/CF at non-faradic reaction region.

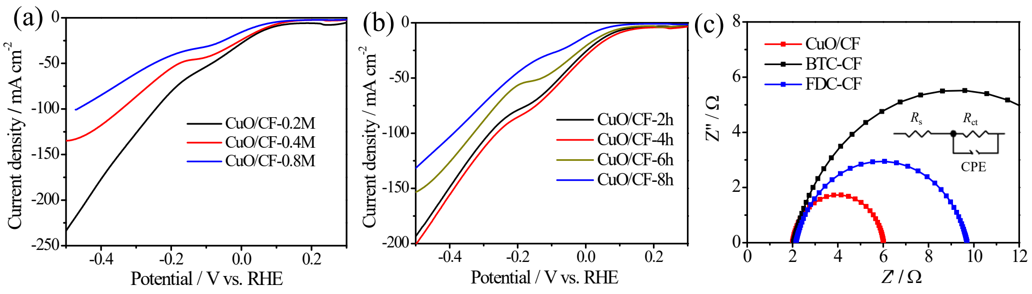


Fig. S8 (a) LSV curves of CuO/CF prepared in various concentrations of fumaric acid. (b) LSV curves of CuO/CF-2h, CuO/CF-4h, CuO/CF-6h and CuO/CF-8h prepared with various time. (c) Electrochemical impedance spectroscopy of CuO/CF, BTC-CF and FDC-CF at -0.3 V_{RHE}.

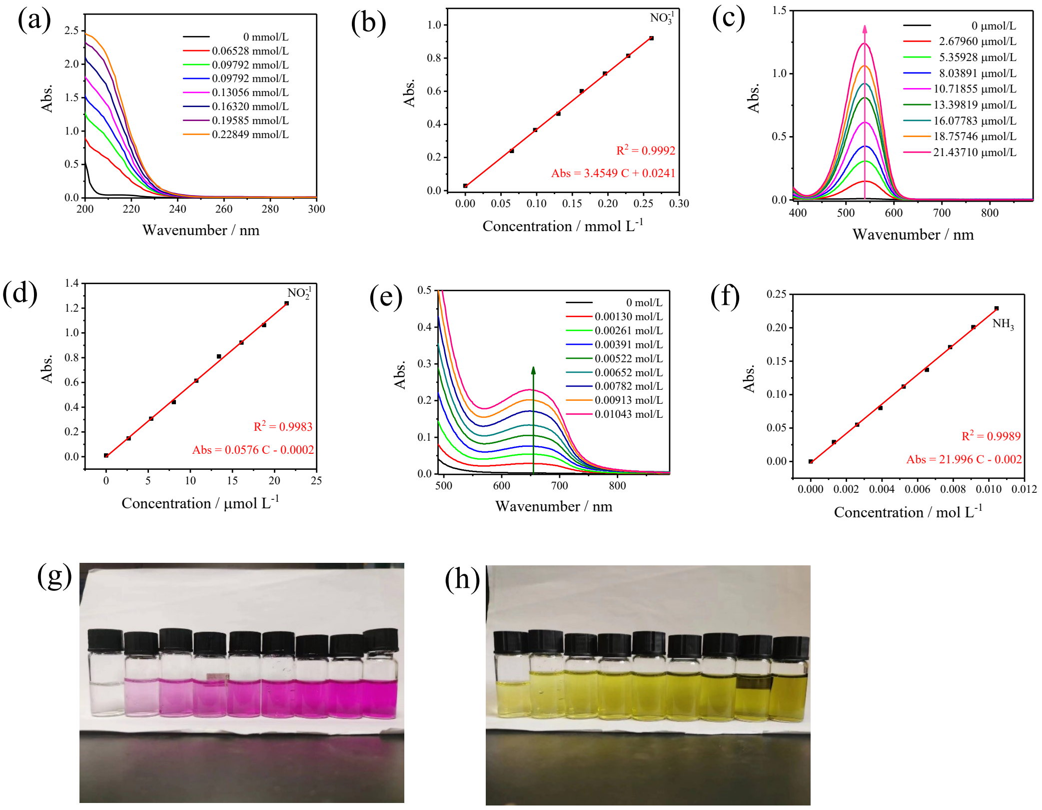


Fig. S9 Standard curves of (a and b) NO_3^-, (a, d and g) NO_2^- and (e, f and h) NH_3 via UV-vis spectroscopy.

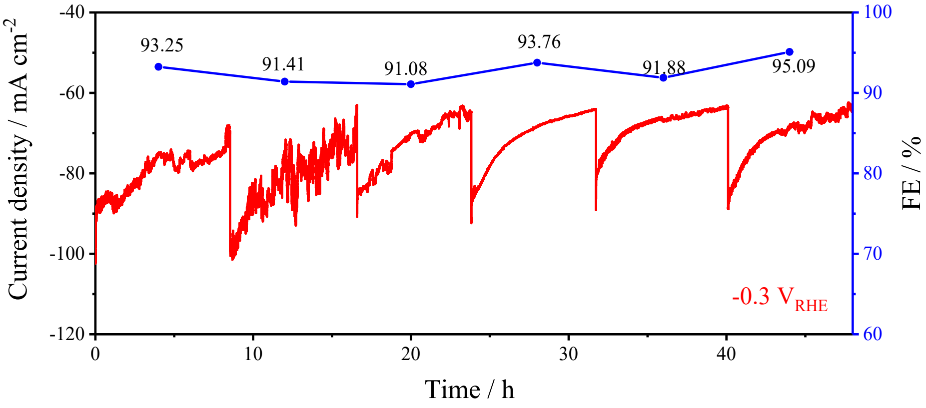


Fig. S10 *I-t* stability tests and Faradic efficiency of at -0.3 V_{RHE} in 6 circles during 48 h.

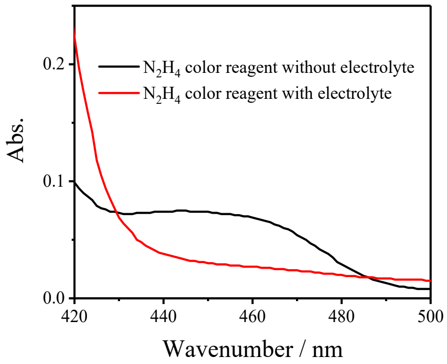


Fig. S11 N_2H_4 colorant reagent with and without the resulting electrolytic solution via UV-vis spectroscopy.

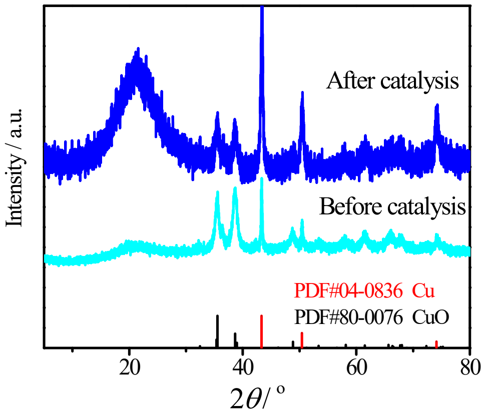


Fig. S12 XRD patterns of powder CuO/CF before and after the *E-t* stability test in 1 mol L^{-1} KOH and 0.1 mol L^{-1} KNO_3.

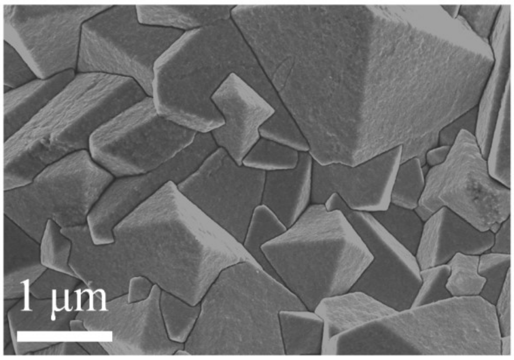


Fig. S13 SEM image of CuO/CF after the *E-t* stability test in 1 mol L^{-1} KOH and 0.1 mol L^{-1} KNO_3.

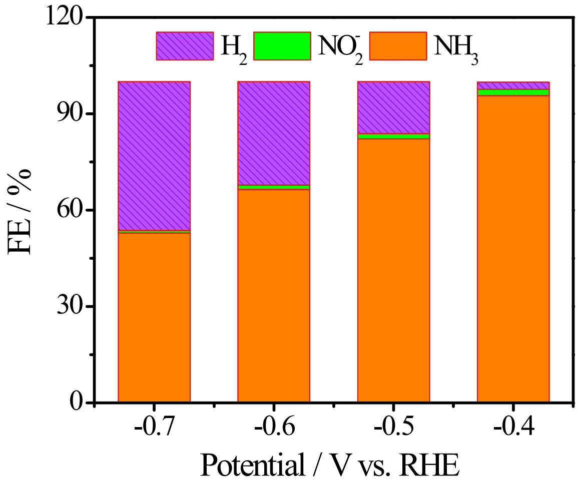


Fig. S14 FE of various products of CuO/CF at various potentials.

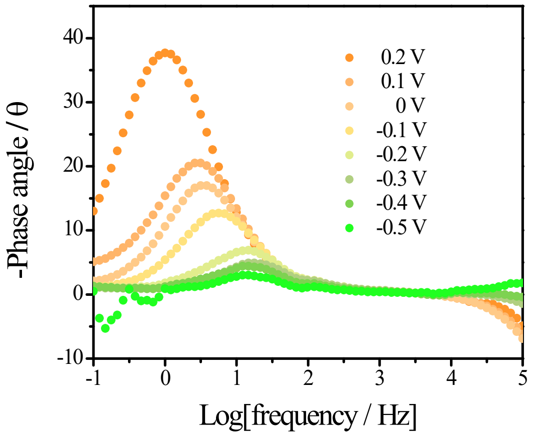


Fig. S15 Bode plots of CuO/CF at various applied potentials.

Table S1 Fitting data of equivalent circuit of the chare transfer resistance (R_{ct}) and the solution resistance (R_{s}) in alkaline and neutral electrolytes.

Electrode	CF (Alkaline)	DMF-CF (Alkaline)	CuO/CF (Alkaline)	BTC-CF (Alkaline)	FDC-CF (Alkaline)	CF (Neutral)	DMF-CF (Neutral)	CuO/CF (Neutral)
R_{ct}/Ω	136.1	15.4	1.6	14.5	7.8	432.6	6.0	4.6
R_{s}/Ω	2.3928	2.4691	2.4032	2.0413	2.1490	3.7649	3.7814	3.6881

Table S2 Summary of electrochemical nitrate reduction to ammonia activity of CuO/CF and reported Cu-based electrocatalysts.

Catalyst	NH_3 selectivity	FE/%	NH_3 yield /(mmol cm^{-2} h^{-1})	Electrolyte	Potential/V (vs. RHE)	Ref
CuFe-P/IF	-	72	～0.6	1 M NaOH + 0.1 M $NaNO_3$	-0.5	31
$Cu_{30\%}$@NHC	-	77.05	～0.213	0.1 M Na_2SO_4 + 0.1 M KNO_3	-0.8	15
Cu SA/NC	100%	100	0.44	0.5 M Na_2SO_4 + 200 ppm $NaNO_3$	-0.7	63
ER-Cu	92.7%	96.0	0.391	1 M KOH + 0.1 M KNO_3	−0.2	64
Ag–Cu–P	-	94.29	0.566	1 M KOH + 0.1 M KNO_3	-0.3	65
CuO_x-H/NSePC	～85%	87.2	0.464	1 M KOH + 0.1 M KNO_3	-0.53	12
Cu(x)-OMS-1	100%	99.7	0.51	0.5 M Na_2SO_4 + 0.05 M KNO_3	-1.2	S1
7% Cu–CeO_2	-	88.15	0.0101	0.5 M Na_2SO_4 + 0.15 M $NaNO_3$	-0.5	20
Co_3O_4@NC/ CuO_x/CF	100%	93.77	～0.529	0.5 M KOH + 0.1 M KNO_3	−0.4	S2
Cu/2D-CuO_x	97.6%	89.53	0.087	1 M KOH + 0.1 M KNO_3	-0.8	64
CuO/CF	96.38%	95.66	0.741	1 M KOH + 0.1 M KNO_3	-0.5	This work
CuCo-TPA-E	100%	99.62	1.12	1 M KOH + 0.1 M KNO_3	-0.326	29
Cu/CoO_x @NFs	100%	95.1	4.11	1 M KOH + 0.1 M KNO_3	-0.15	30

References

S1 S. Li, C. Xiao, R. Chen, M. Wang, Y. Ma, K. Luo, M. Shen, Y. Zhu, Y. Li and C. Li, *Green Chem.*, 2023, **25**, 10549–10555.

S2 J. Yu, Z. Xi, J. Su, L. Li, P. Jing, X. Xu, B. Liu and J. Zhang, *ACS Mater. Lett.*, 2024, **6**, 2591–2598.