Supplementary Information

Constructing CoO-CuO$_x$ heterostructure for efficient electrochemical reduction of nitrate to ammonia

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Experimental section

Determination of nitrogen-containing substances

Firstly, UV-Vis absorbance spectrophotometry was used to measure the standard curves for the absorbance change of each nitrogen-containing substance on a concentration gradient of different concentrations. Secondly, the nitrogenous substances in the electrolyte after the reaction were diluted to the concentration range corresponding to the calibration curve, and the ionic concentration of the nitrogenous substances in the mother liquor was measured and calculated. The steps are as follows:

Determination of NH_3:

The amount of NH_3 in solution was determined by the indophenol blue method.[1] The indophenol blue method requires the usage of three reagents, which are made up as follows:

1. Preparation of a mixed solution of sodium citrate, salicylic acid, and sodium hydroxide: 5 g of salicylic acid ($C_7H_6O_3$) and 5 g of sodium citrate ($C_6H_5Na_3O_7$) were co-dissolved in 100 mL of deionized water, then 4 g of sodium hydroxide was added and the mixture was kept stirring to ensure them completely dissolved;

2. Preparation of sodium nitroferrocyanide solution: 1 g of sodium nitroferrocyanide ($Na_2[Fe(CN)_5NO]·2H_2O$) was dissolved in 100 mL water;

3. Preparation of the sodium hypochlorite solution: 8.3 g of sodium hypochlorite solution was dissolved in 100 mL of deionized water.

Take 1.8 mL of the diluted reaction solution, then add 200 μL of sodium nitrosoferricyanide solution, 2 mL of sodium hydroxide-sodium citrate mixed solution and 1 mL of sodium hypochlorite solution, and the solution was kept still for 40 mins. The absorbance at 655 nm using a 10 mm cuvette with water as reference was measured. A standard curve has been constructed using a series of standard ammonium chloride solutions.

Determination of NO_2^-:

The NO_2^- concentration was analyzed using the Griess test.[2] The Grice's reagent was prepared by dissolving P-aminobenzenesulfonamide (4 g), N-(1-naphthalenyl)-ethylenediamine dihydrochloride (0.2 g), and phosphoric acid (10 mL, 1.70 g/mL) in 50 mL of ultrapure water to make a color developing reagent. The corresponding reaction solution was made up to 5 mL to ensure that it was within the detection range. The color development reagent (100 μL) was mixed with the above diluted electrolyte and allowed to stand for 30 mins and the absorbance was recorded at 540 nm. The standard curve is established by a series of standard nitrite solutions with different concentration gradients using the same method.

Determination of NO_3^-:

A quantity of the reacted electrolyte was taken and diluted to 5 mL to ensure that it was within the detection range. Then 100 μL of 1 M HCl, 10 μL of 0.8 wt.% sulfamic acid was added and kept still for 30 mins. Absorption spectra were measured using UV-Vis absorbance spectrophotometer. The absorbance at 220 nm and 275 nm was recorded. The final absorbance was obtained according

to the formula A = A_{220} - $2A_{275}$ (220, 275 is the wavelength, unit: nm). Its standard curve was established by a series of standard concentrations of nitrite solution with the same test method.

Calculation of NH_3 yield, NO_3^- conversion, NH_3 and NO_2^- selectivity, and NH_3 Faradaic efficiency:

For NtrRR, NH_3 yield was calculated by Eq. 1:

$$Yield_{NH3} = (c_{NH3} \times V) / (M_{NH3} \times t \times S) \ (1)$$

The NO_3^- conversion rate was calculated according to Eq. 2:

$$Conversion = \Delta c_{NO3^-} / c_0 \times 100\% \ (2)$$

The NH_3 and NO_2^- selectivity was calculated by Eq. 3:

$$Selectivity = c / \Delta c_{NO3^-} \times 100\% \ (3)$$

The Faradaic efficiency was defined from the electric charge consumed for synthesizing ammonia and total charge passed through the electrode according to Eq. 4:

$$Faradaic\ efficiency = (8F \times c_{NH3} \times V) / (M_{NH3} \times Q) \ (4)$$

Where c_{NH3} is the mass concentration of NH_3 (aq), V is the volume of electrolyte in the cathode compartment (50 mL), M_{NH3} is the molar mass of NH_3, t is the electrolysis time, S is the geometric area of the working electrode (1 cm^2), Δc_{NO3^-} is the concentration difference of NO_3^- before and after electrolysis, c_0 is the initial concentration of NO_3^-, c is the generated concentration of ammonia or nitrite, F is the Faradaic constant (96485 C mol^{-1}), Q is the total charge passing the electrode.

The half-cell energy efficiency (EE) was calculated according to the theoretical energy of the NH_3 product and the consumed electrical power in the three-electrode system, assuming no overpotential for the anodic oxygen evolution reaction. It follows the equation:[3]

$$EE\ (NH_3) = \frac{(E_{O_2/H_2O} - E_{NH_3/NO_3^-}) \times FE_{NH_3}}{E_{O_2/H_2O} - E_{app}}$$

Where $E_{NH3/NO3^-}$ is 0.69 V vs. RHE, the thermodynamic equilibrium potential of NtrRR to NH_3; $E_{O2/H2O}$ is 1.23 V vs. RHE, the equilibrium potential of water oxidation; FE_{NH3} represents the Faradaic efficiency for NH_3, and E_{app} is the applied potential vs. RHE.

The partial current density of NH_3 (i_{NH3}) is calculated using the following equation[4]:

$$Q = it$$

$$i_{NH3} = i \times FE_{NH3}$$

Where i is the total current (A), t is the total reaction time (s), and Q is the total charge passing the electrode.

Isotope labeling tests

Calibration curves for ^{1}H NMR (400 MHz) measurements were conducted using standard solutions of [15]NH_4Cl (>99 at.% [15]N, ≥98.5% purity) at concentrations of 50, 100, 150, 200, and 250 ppm, respectively. The method was described as follows: 60 μL of the standard solution was mixed with 60 μL of 15 mM maleic acid in DMSO-D_6 (99.9 atom% D), 40 μL of 2 M H_2SO_4 in

DMSO-D$_6$, and 500 μL of DMSO-D$_6$. Na^{15}NO$_3$ (>99 atom% ^{15}N, ≥98.5% purity) was used instead of Na^{14}NO$_3$ as the ammonia source in a nitrate reduction isotope labeling test. The test was designed to trace the source of ammonia and determine its concentration. A 0.5 M Na$_2$SO$_4$ solution containing Na^{15}NO$_3$-^{15}N (200 ppm) was added into the cathode tank of the NtrRR. Electrolysis was stopped when the accumulated charge reached 550 C at -0.5 V vs. RHE and ^{1}H NMR was used to detect the concentration of ^{15}NH$_4^+$ in the electrolyte.
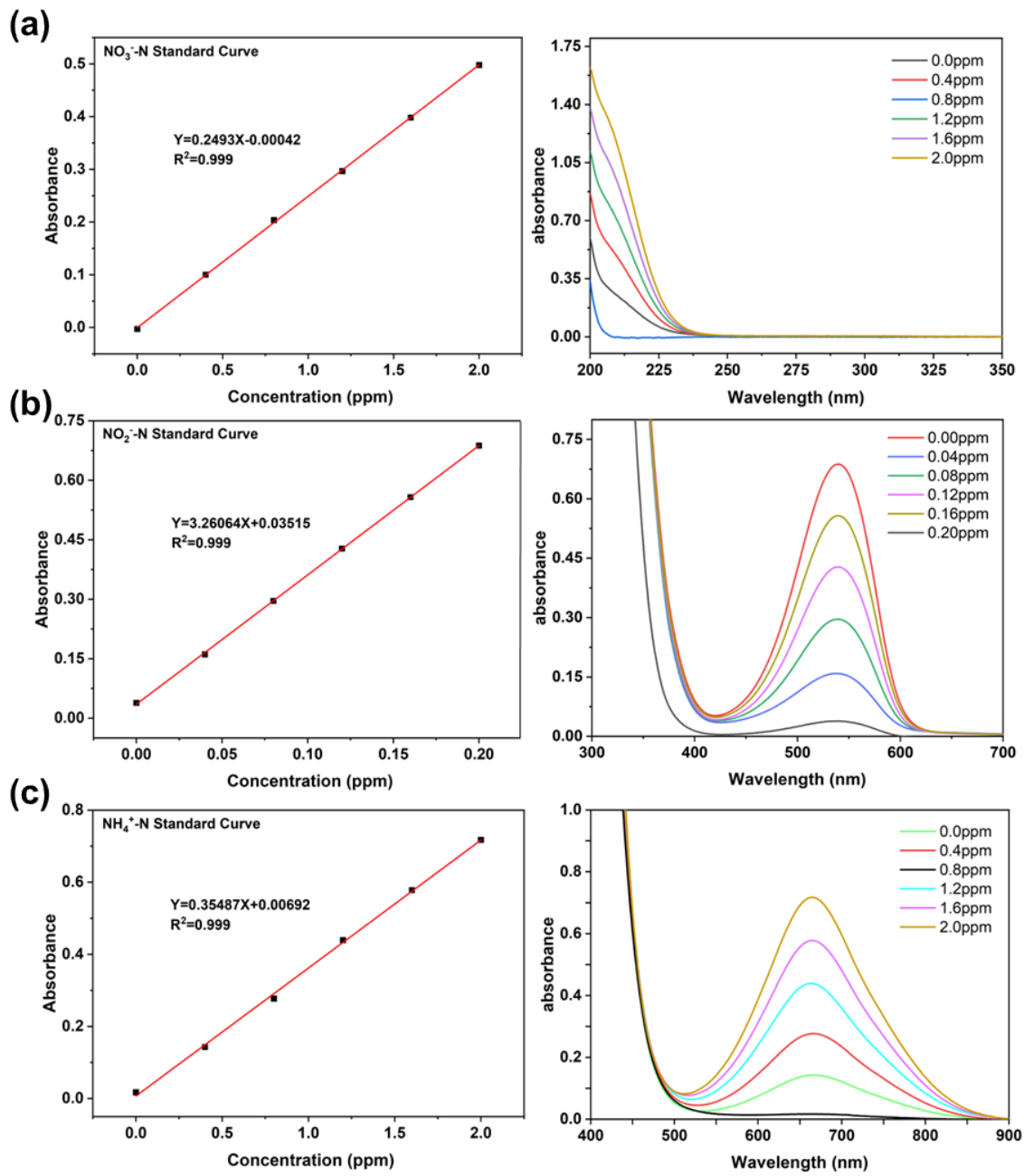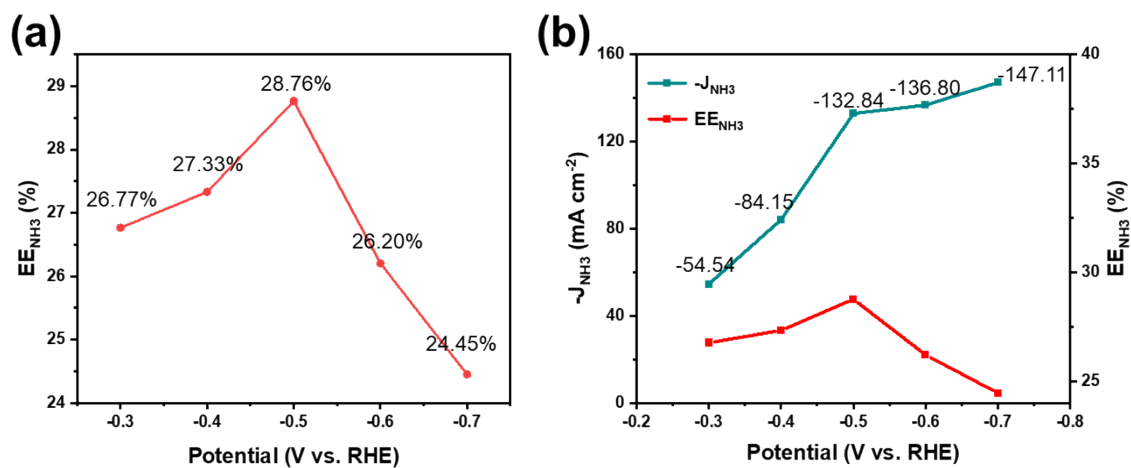
Supplementary Figures
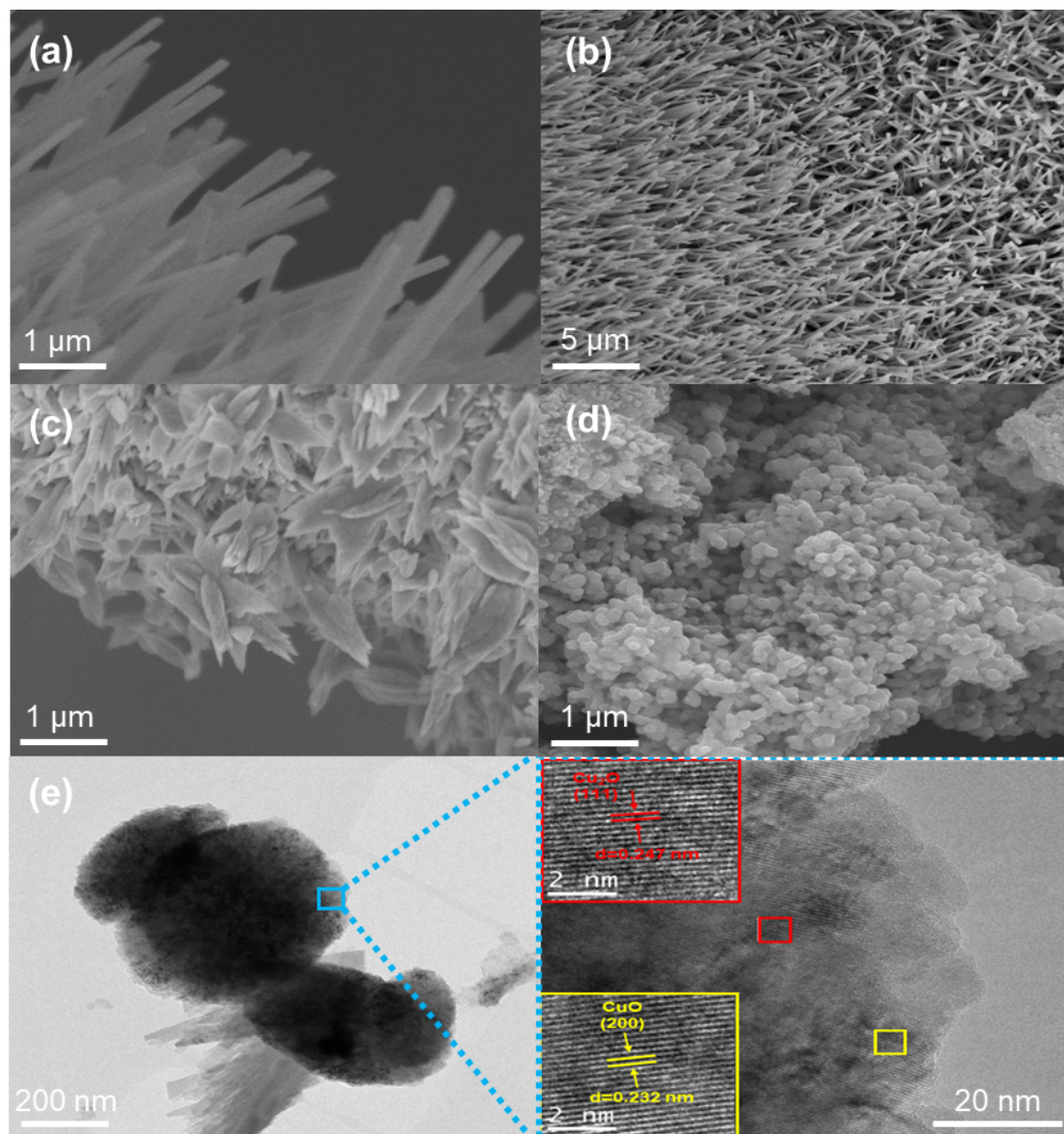
Fig. S1 Representative SEM images of (a), (b) $Cu(OH)_2$, (c) CuO_x/CF, (d) CoO/CF. Representative HR-TEM images of (e) CuO_x/CF.
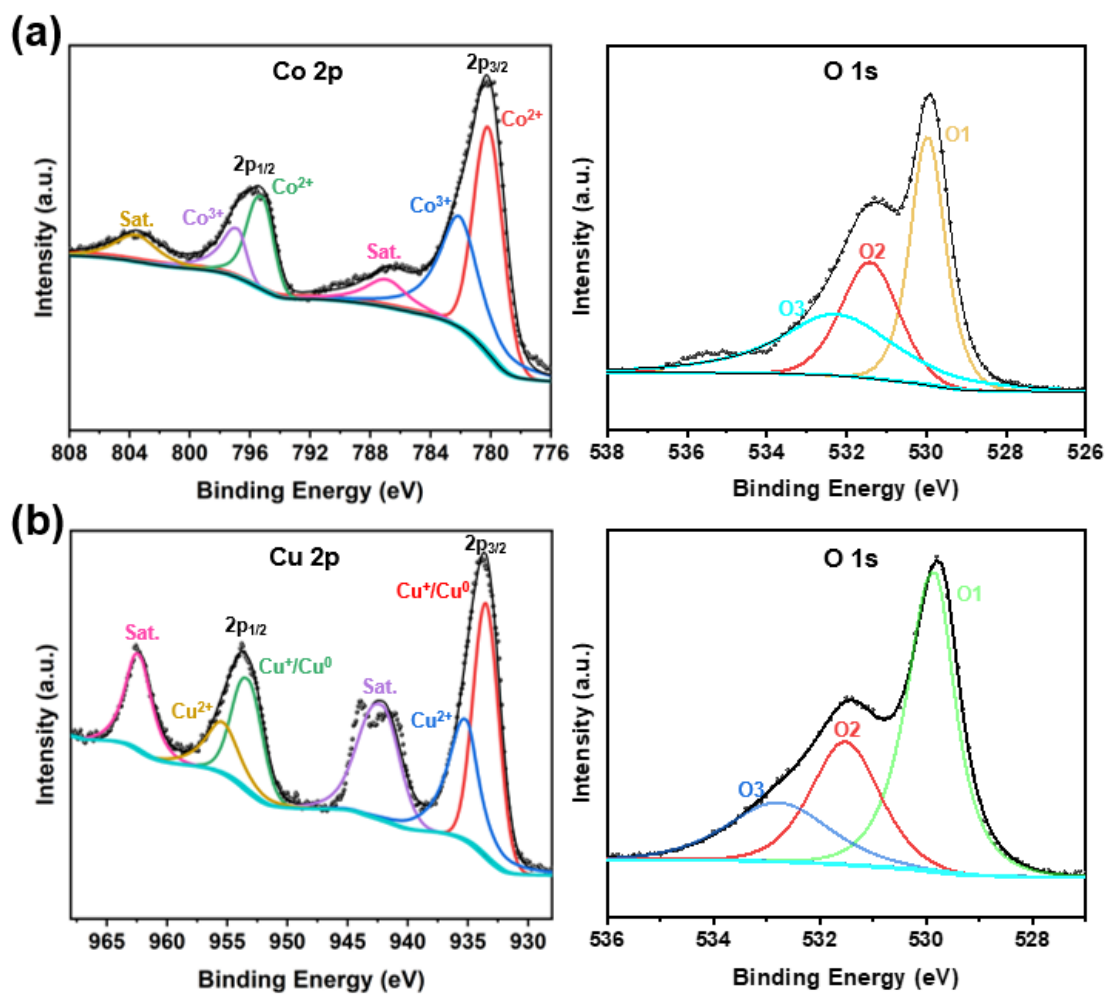
Fig. S2 (a) High resolution XPS spectra of Co 2p (left) and O 1s (right) for CuO_x/CF. (b) High resolution XPS spectra of Cu 2p (left) and O 1s (right) for CoO/CF.
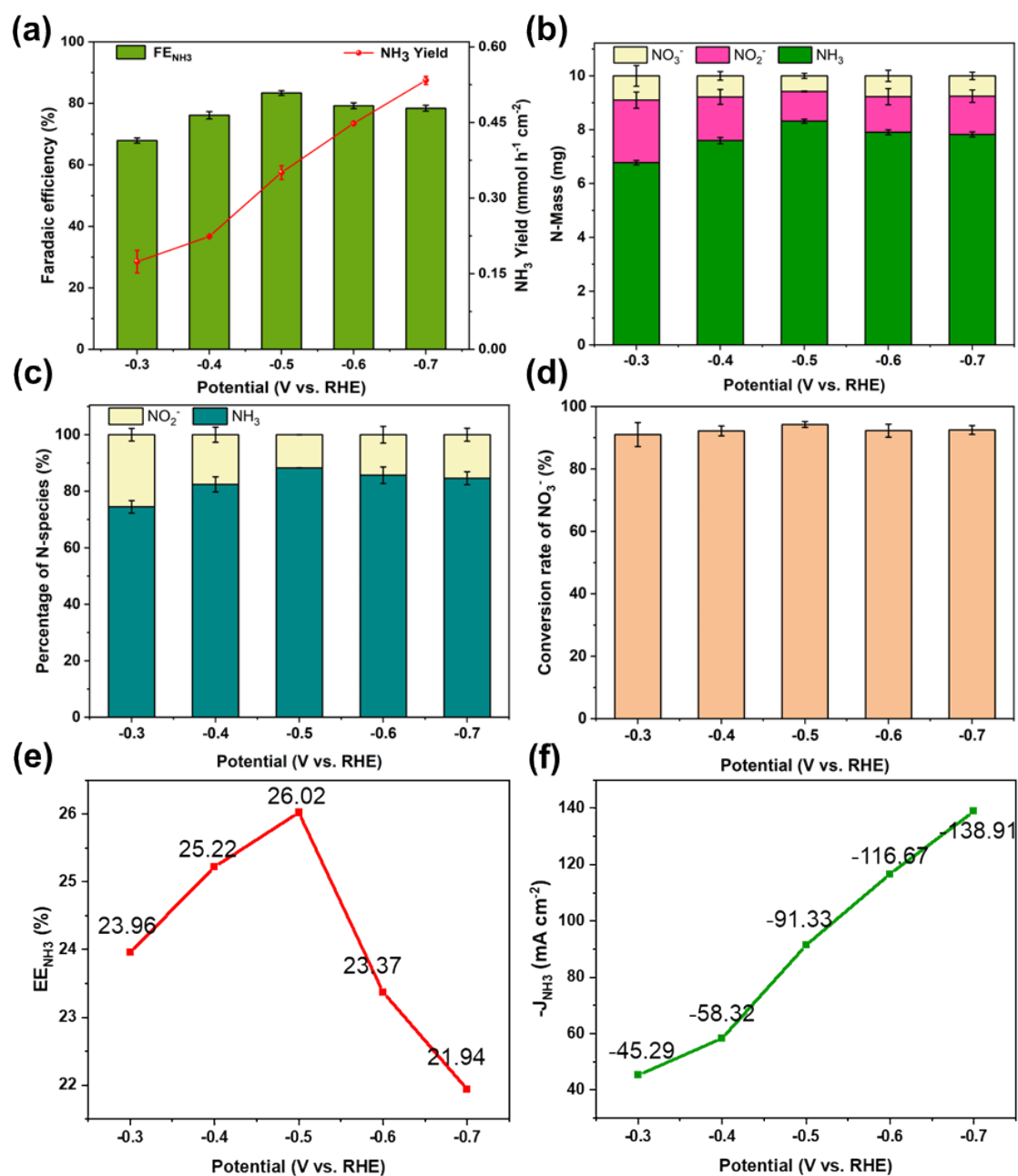
Fig. S3 The absorbance standard curve of (a) NO_3^-, (b) NO_2^-, and (c) NH_3.
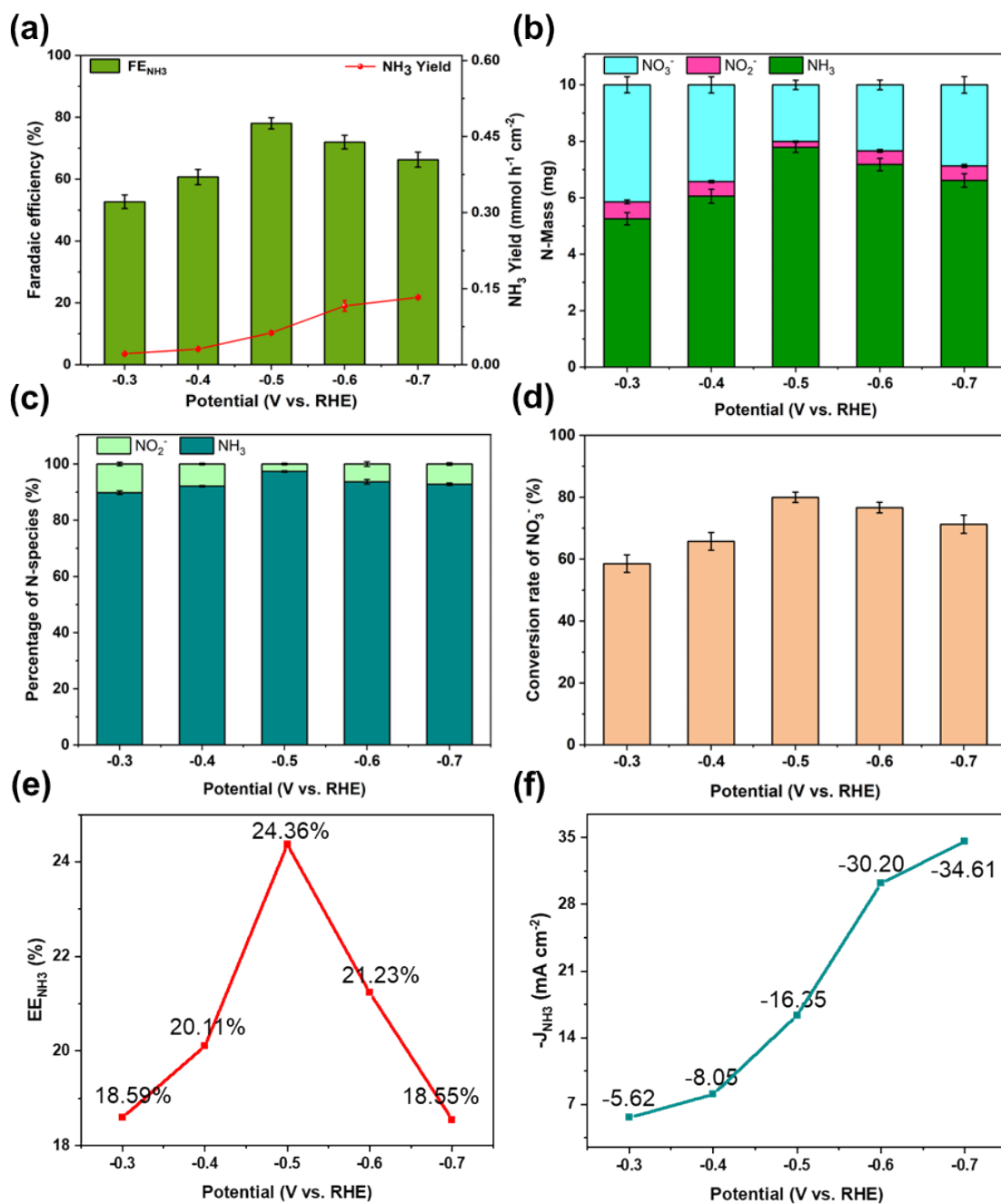
Fig. S4 The NtrRR performance of CoO-CuO$_x$/CF. (a) Half-cell energy efficiencies of NH$_3$. (b) Half-cell energy efficiencies and partial current densities of NH$_3$.

Fig. S5 The NtrRR performance of CuO$_x$/CF. (a) FE$_{NH_3}$ and NH$_3$ yield; (b) Mass ratio of NO$_3^-$, NO$_2^-$, and NH$_3$; (c) Selectivity of NH$_3$ and NO$_2^-$; and (d) NO$_3^-$ conversion rate. (e) Half-cell energy efficiencies of NH$_3$. (f) Partial current densities of NH$_3$.
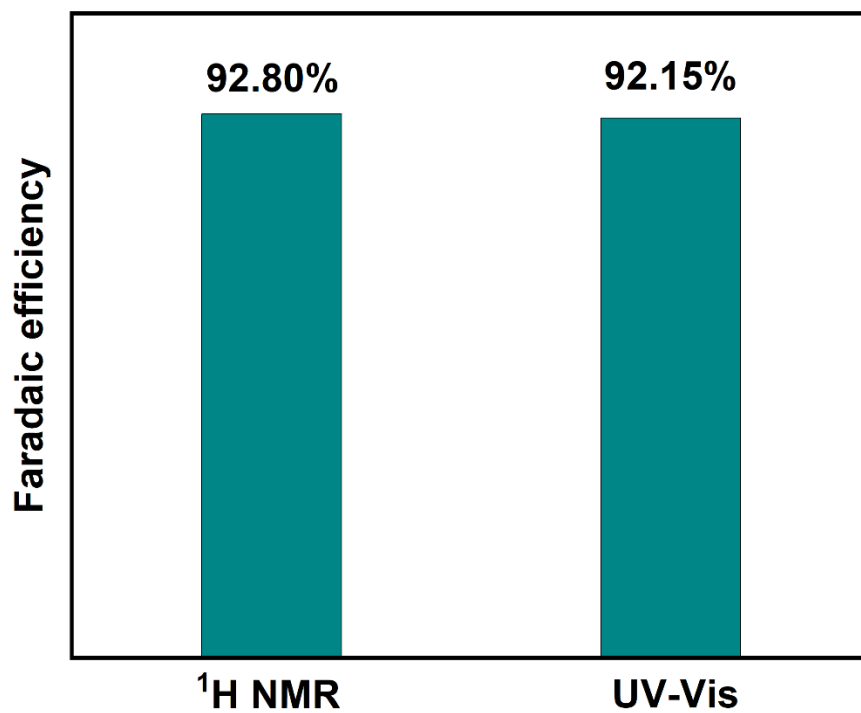
Fig. S6 The NtrRR performance of CoO/CF. (a) FE_{NH3} and NH_3 yield; (b) Mass ratio of NO_3^-, NO_2^-, and NH_3; (c) Selectivity of NH_3 and NO_2^-; and (d) NO_3^- conversion rate. (e) Half-cell energy efficiencies of NH_3. (f) Partial current densities of NH_3.

Fig. S7 The comparison of FE_{NH3} for CoO-CuO$_x$/CF between the UV-Vis absorbance and ^{1}H NMR measurement.

Supplementary Table

Table S1. The NtrRR electrocatalytic activity comparison between CoO-CuO$_x$/CF and other recently reported top-level electrocatalysts with similar structure or architecture.

Electrocatalysts	Electrolytes	Performance	Ref.
CoO-CuO$_x$/CF	200 ppm NO$_3^-$-N + 0.5 M Na$_2$SO$_4$	FE$_{NH3}$: 92.15% NH$_3$ Selectivity: 94.29% NO$_3^-$ conversion rate: 97.48%	This work
Cu@MOFs	70 ppm NO$_3^-$-N + 0.05 M Na$_2$SO$_4$	FE$_{NH3}$: 80.97% NH$_3$ Selectivity: 61.64%	5
Mn$_3$O$_4$/CuO$_x$/CF	200 ppm NO$_3^-$-N + 0.5 M Na$_2$SO$_4$	FE$_{NH3}$: 87.56%	6
Co/NC-800	100 ppm NO$_3^-$-N + 0.1 M Na$_2$SO$_4$	FE$_{NH3}$: 81.2%	7
Cu/TNTA	100 ppm NO$_3^-$-N + 0.1 M Na$_2$SO$_4$	NO$_3^-$ conversion rate: 84.3%	8
oxide-derived Cu	100 ppm NO$_3^-$-N + 0.5 M Na$_2$SO$_4$	FE$_{NH3}$: 80% NH$_3$ Selectivity: 94% NO$_3^-$ conversion rate: 93%	9
Cu/Fe@NCNFs	100 ppm NO$_3^-$-N + 0.1 M Na$_2$SO$_4$ + 0.02 M NaCl	NO$_3^-$ conversion rate: 76%	10
Cu-N-C	50 ppm NO$_3^-$-N + 0.5 M Na$_2$SO$_4$ + 2.0 g L^{-1} NaCl	NH$_3$ Selectivity: 94%	11
Cu@C	1 mM KNO$_3$ + 1 M KOH	FE$_{NH3}$: 72.0%	12

References

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