Supporting information

Cu/NiO nanorods for efficiently promoting the electrochemical nitrate reduction to ammonia

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Contents

Experimental Section

Electrochemical measurements of nitrate reduction reaction (NO₃RR)

Determination of ion concentration

The ultraviolet-visible (UV-Vis) spectrophotometer was used to detect the ion concentration of pre- and post-tested electrolytes after diluting to appropriate concentration to match the range of calibration curves. The specific test methods are as follows:

Determination of ammonia

Ammonia-N was determined using salicylic acid-potassium sodium tartrate chromogenic reagent as the color reagent. First, a certain amount of electrolyte was taken out from the electrolytic cell and diluted to 2 mL to the detection concentration range. Next, 2 mL salicylic acid-potassium sodium tartrate chromogenic reagent was added into the diluted electrolyte, and mixed thoroughly. Then, 0.05 mL sodium hypochlorite and 0.2 mL sodium nitroprusside solution were put into the above solution. The absorption intensity at a wavelength of 655 nm was recorded. The concentration-absorbance curve was calibrated using a series of standard ammonium chloride solutions and the ammonium chloride crystal was dried at 108°C for 2 h in advance.

Determination of NO₃⁻

Firstly, a certain amount of electrolyte was taken out from the electrolytic cell and diluted to 2 mL. Then, 0.1 mL 1 M HCl and 0.01 mL 0.8 wt% sulfamic acid solution

were added into the aforementioned solution. The absorption spectrum was measured using an UV-Vis spectrophotometer and the absorption intensities at a wavelength of 220 and 275 were recorded. The final absorbance is calculated using the following formula: $A = A_{220nm} - 2A_{275nm}$. The concentration-absorbance curve was calibrated using a series of standard potassium nitrate solutions.

Determination of NO_2^-

Color reagent was a mixture of p-aminobenzenesulfonamide (0.1 g), N-(1-naphthyl) ethylenediamine dihydrochloride (0.01 g), deionized water (5 mL) and phosphoric acid (0.294 mL, $\rho = 1.685$ g mL^{-1}). First, the electrolyte was diluted to the detection concentration range. Subsequently, 1 mL color reagent was added into the diluted electrolyte in a colorimetric cuvette. After shaking and standing for 10 minutes, the absorbance measurements were performed at wavelength of 540 nm. The obtained calibration curve was used to calculate the nitrite concentration.

Determination of N_2H_4

First, a certain amount of electrolyte was taken out from the electrolytic cell and diluted to 2 mL to the detection concentration range. Subsequently, 1 mL color reagent was added into the diluted electrolyte in a colorimetric cuvette. Color reagent was a mixture of anhydrous ethanol (50 ml), HCl (5 ml) and p-$C_9H_{11}NO$ (1 g). The absorption intensity at a wavelength of 455 nm was recorded after standing for 20 min.

Isotope Labeling Experiments

$K^{15}NO_3$ was used as the feeding N-source to perform the isotopic labeling nitrate reduction experiments to verify the source of ammonia. 0.1 M PBS was used as the

electrolyte, and $K^{15}NO_3$ with a concentration of 0.1 M $^{15}NO_3^-$ was added into the cathode compartment as the reactant. After electroreduction, electrolyte with obtained $^{15}NH_4^+$ was taken out and the pH value was adjusted to be weak acidic with 1 M HCl for qualitative analysis by ^1H NMR (600 MHz) with external standards of maleic acid.
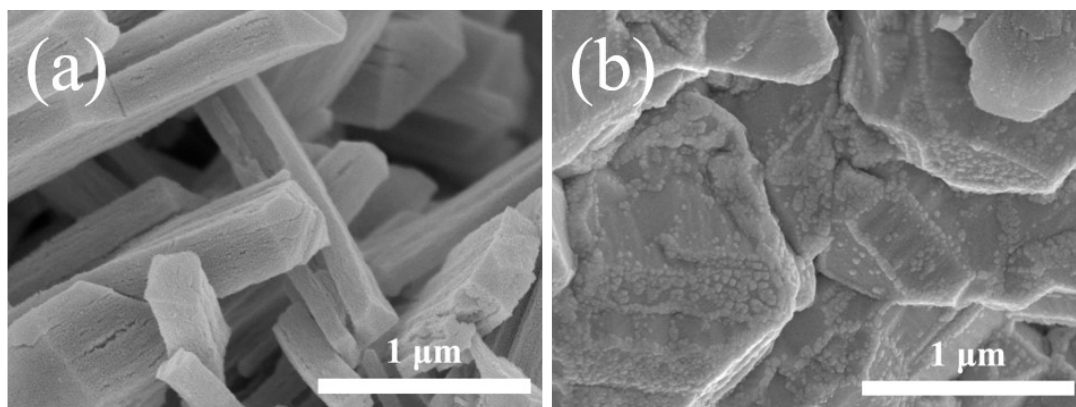
2. Supporting Figures and Table

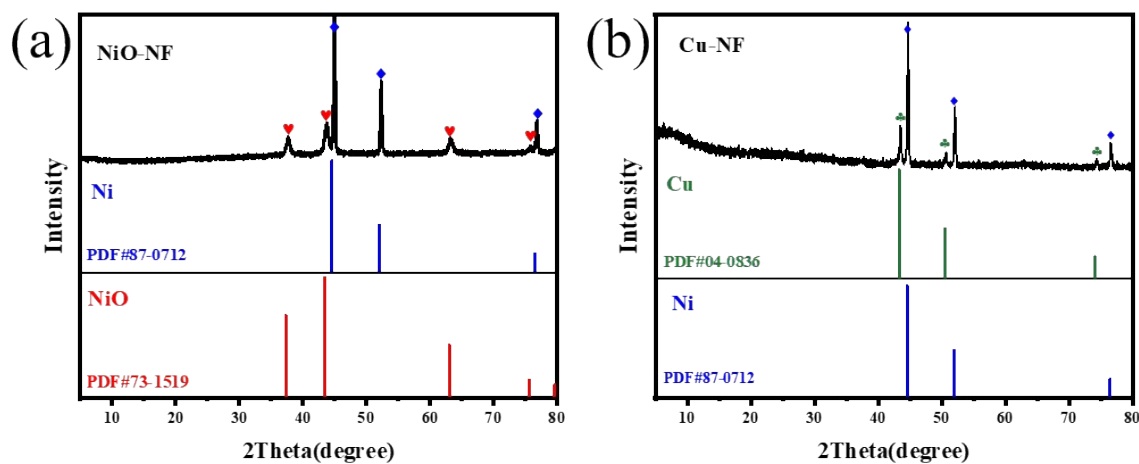**Fig. S1** (a) SEM images of NiO-NF, (b) Cu-NF.

Fig. S2 XRD patterns of (a) NiO-NF, (b) Cu-NF and their standard PDF cards.
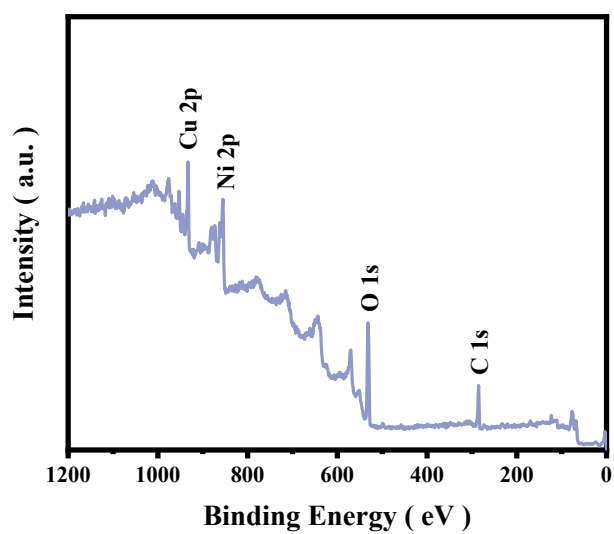
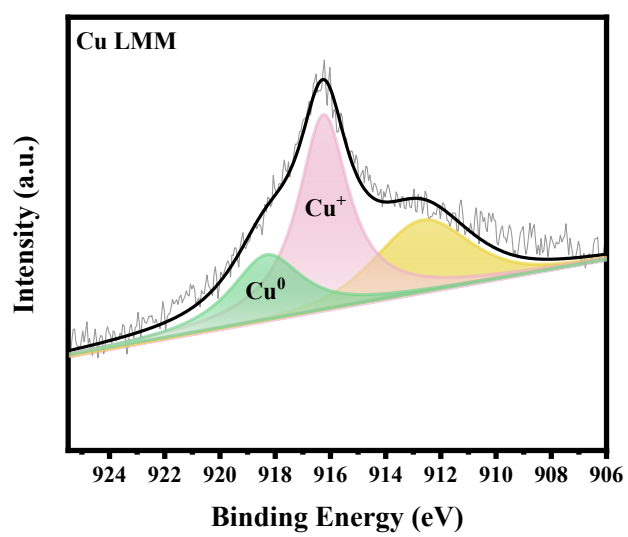**Fig. S3** The XPS survey spectra of Cu/NiO-NF.
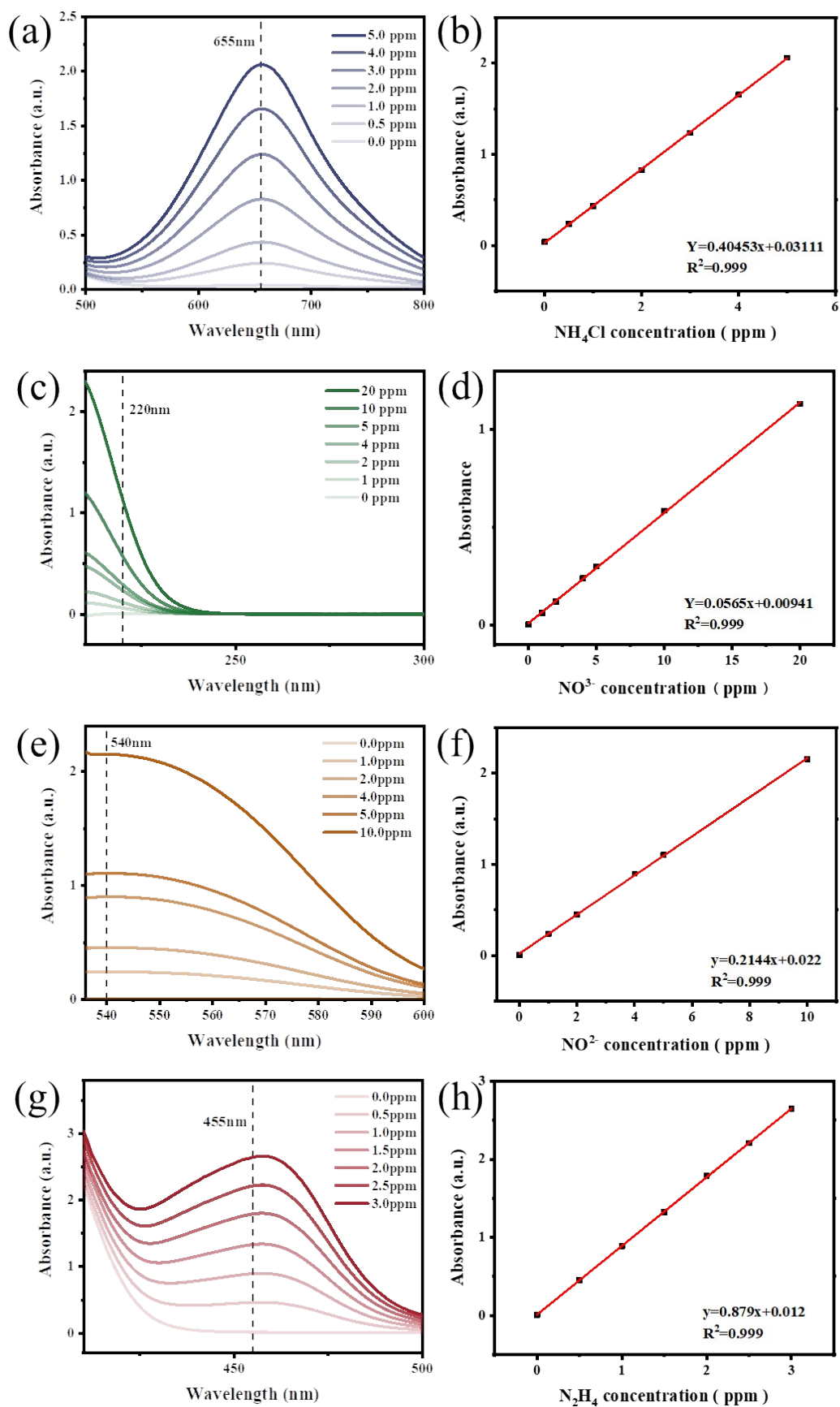

Fig. S4 Cu LMM Auger electron spectra (AES) of Cu/NiO-NF.

Fig. S5 (a) UV-Vis absorption spectra for various concentrations. (b) Calibration curve

used to estimate the concentration of NH$_3$-N. (c) UV-Vis absorption spectra for various concentrations. (d) Calibration curve used to estimate the concentration of NO$_3^-$-N. (e) UV-Vis absorption spectra for various concentrations. (f) Calibration curve used to estimate the concentration of NO$_2^-$-N. (g) UV-Vis absorption spectra for various concentrations. (h) Calibration curve used to estimate the concentration of N$_2$H$_4$.
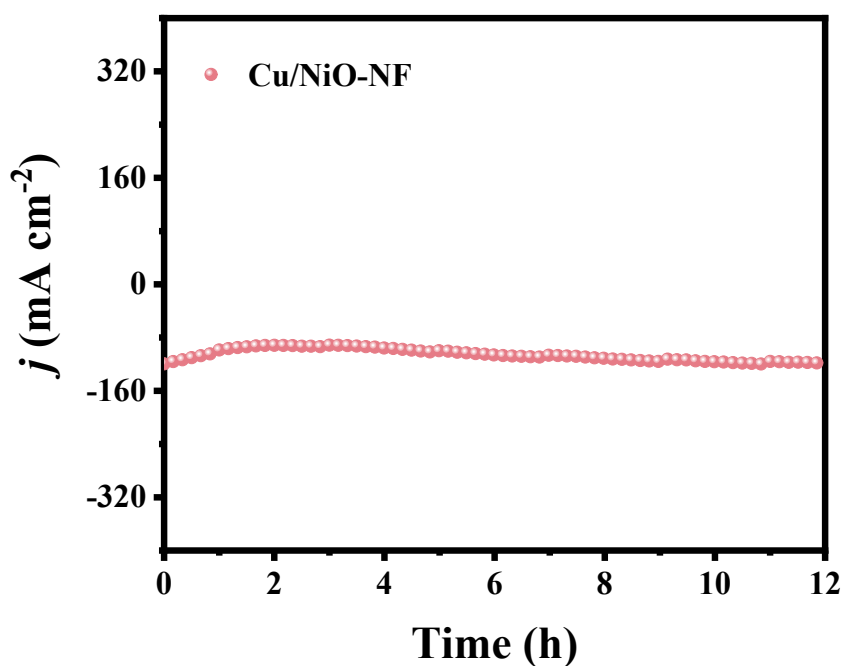

Fig. S6 *i-t* curve of Cu/NiO-NF tested in 0.1M PBS+0.1M NO$_3^-$ for 12 hours at -1.0 V (vs. RHE).

Fig. S7 (a) The CV curves at various scan rates and (b) the capacitive current densities

of the Cu/NiO-NF. (c) The CV curves at various scan rates and (d) the capacitive current

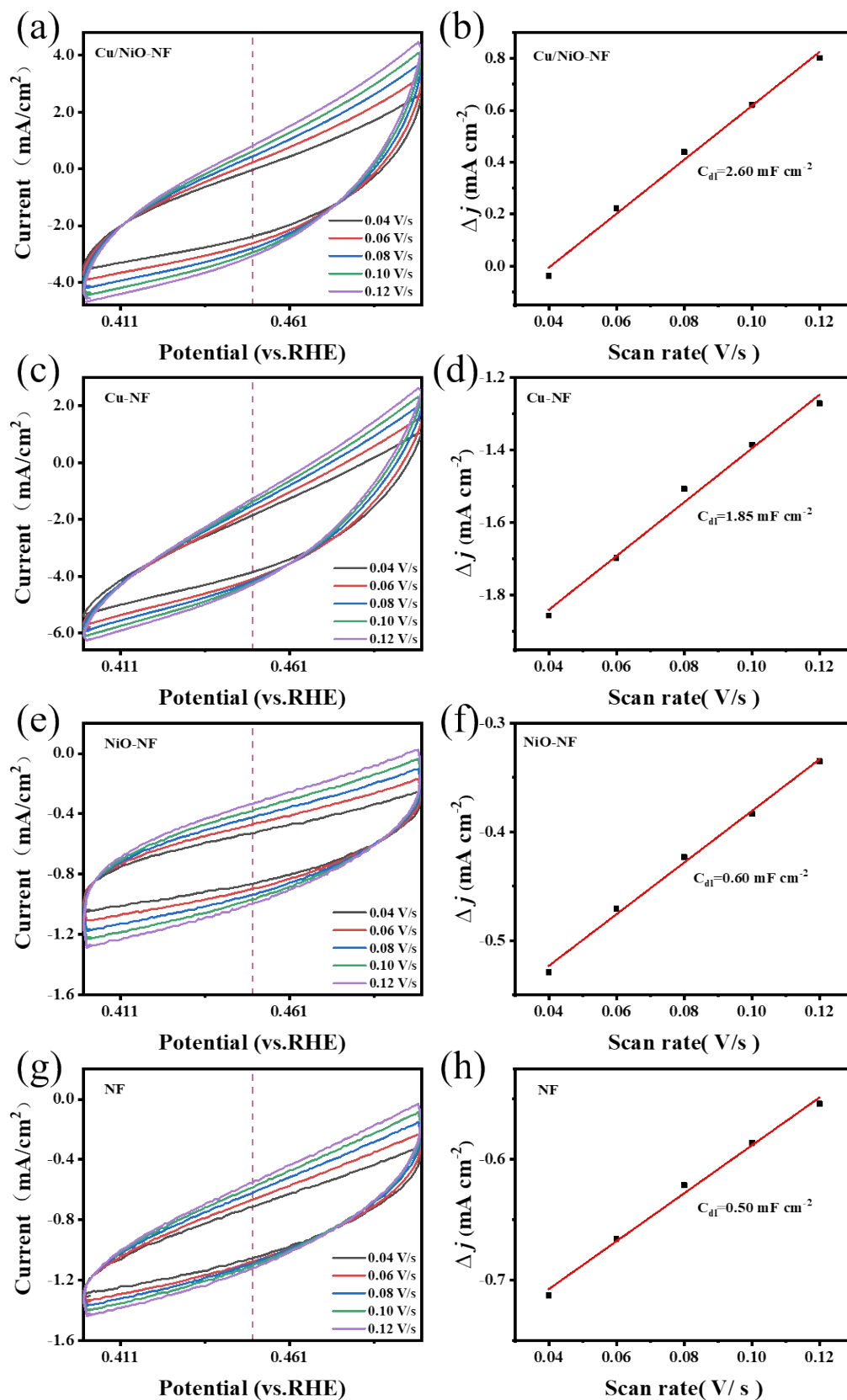densities of the Cu-NF. (e) The CV curves at various scan rates and (f) the capacitive current densities of the NiO-NF. (g) The CV curves at various scan rates and (h) the capacitive current densities of the NF.

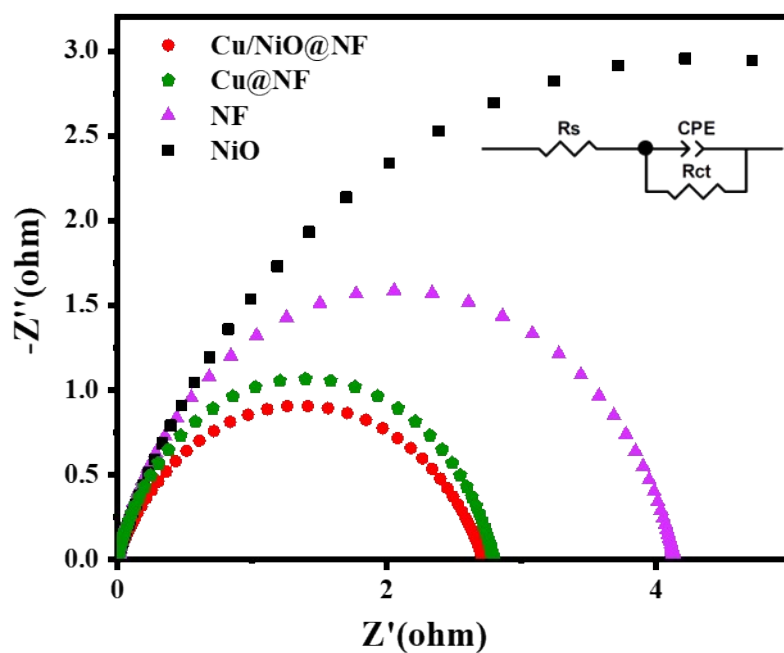**Fig. S8** Nyquist plots of Cu/NiO-NF, Cu-NF, NiO-NF and NF at -1.0 V (vs. RHE) in 0.1 M PBS solution, inset: the equivalent circuit diagram.
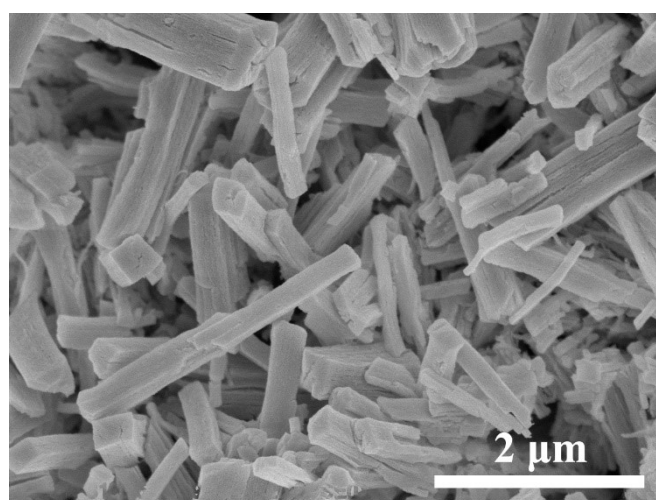

Fig. S9 SEM image of Cu/NiO-NF after performing the long-term *i-t* test of electrochemical NO_3RR.
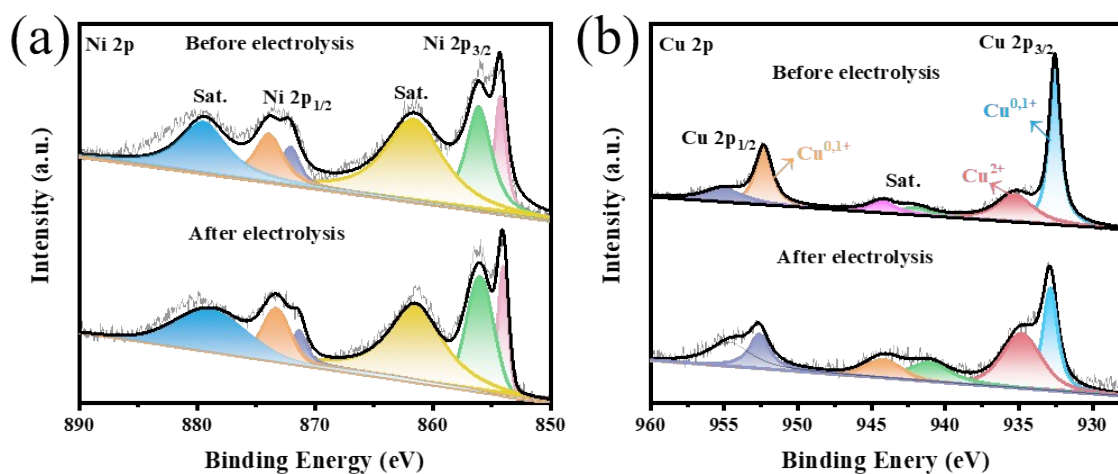
Fig. S10 (a) Ni 2p XPS spectra and (b) Cu 2p XPS spectra of Cu/NiO-NF before and after long-term *i-t* tests for NO$_3$RR.
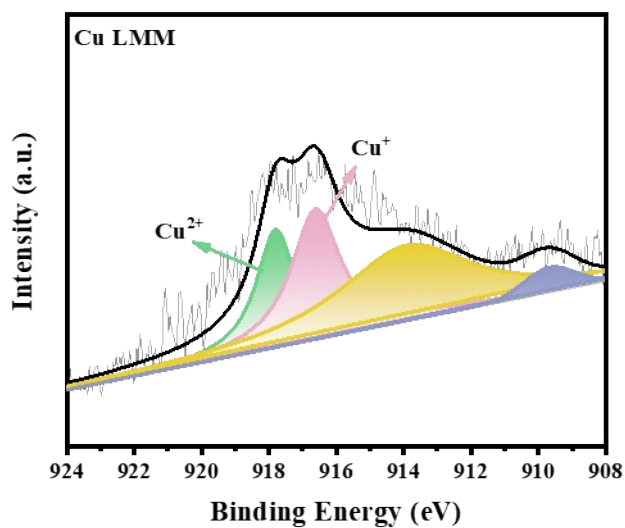

Fig. S11 Cu LMM Auger electron spectra (AES) of Cu/NiO-NF after long-term *i-t* test for NO$_3$RR.

Table S1. The comparison of electrochemical ENO_3RR performance between

Cu/NiO-NF and some other reported electrocatalysts in neutral electrolytes.

Electrocatalysts	Electrolytes	Performance	Ref.
Cu/NiO-NF	0.1 M KNO_3 0.1 M PBS	rNH_3: 0.60 mmol h^{-1} cm^{-2} (10.2 mg h^{-1} cm^{-2}) FE NH_3: 97.81% (-1.0 V vs. RHE)	**This work**
OD-Cu cubes	0.1 M KNO_3 0.1 M PBS	rNH_3: 0.22 mmol h^{-1} cm^{-2} FE NH_3: 93.9% (-0.9 V vs. RHE)	1
Co_2P	0.1 M $NaNO_3$ 0.5 M Na_2SO_4	rNH_3: 0.30 mmol h^{-1} cm^{-2} FE NH_3: 88.6% (-0.6 V vs. RHE)	2
O-Cu-PT-CDA	0.1 M PBS 500 ppm NO_3^-	rNH_3: 0.026 mmol h^{-1} cm^{-2} FE NH_3: 85.9% (-0.4 V vs. RHE)	3
FOSP-Cu-0.1	0.5 M Na_2SO_4 0.1 M KNO_3	rNH_3: 0.10 mmol h^{-1} cm^{-2} FE NH_3: 93.91% (-0.266 V vs. RHE)	4
PdCu/Cu_2O hybrids	0.5 M Na_2SO_4 100 ppm NO_3^-	rNH_3: 0.19 mmol h^{-1} cm^{-2} FE NH_3: 94.32% (-0.8 V vs. RHE)	5
Cu/Cu_2O NWAs	0.5 M Na_2SO_4 200 mgL^{-1} NO_3^-	rNH_3: 0.25 mmol h^{-1} cm^{-2} FE NH_3: 95.8% (-0.85 V vs. RHE)	6
Co_3O_4/Co-h	0.1 M Na_2SO_4 1000 mgL^{-1} NO_3^-	rNH_3: 0.26 mmol h^{-1} cm^{-2} FE NH_3: 88.7%	7

		(-0.8 V vs. RHE)	
Fe SAC	0.1M K_2SO_4 0.5 M KNO_3	rNH$_3$: 0.46 mmol h^{-1} cm^{-2} FE NH$_3$: 74.9% (-0.66 V vs. RHE)	8
Cu/TiO$_{2-x}$	0.5 M Na_2SO_4 200 ppm NO_3^-	rNH$_3$: 0.11 mmol h^{-1} mg^{-1} FE NH$_3$: 81.3% (-0.75 V vs. RHE)	9
Cu-NBs-100	0.1 M PBS 500 ppm NO_3^-	rNH$_3$: 0.13 mmol h^{-1} cm^{-2} (-0.15 V vs. RHE)	10

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