Electronic Supplementary Information

Experimental Section

Chemicals and materials

Cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), urea (CH_4N_2O), ammonium chloride (NH_4Cl), ammonium fluoride (NH_4F), yttrium chloridehexahydrate ($YCl_3 \cdot 6H_2O$), ammoniumchloride-^{15}N ($^{15}NH_4Cl$-^{15}N), potassium nitrate-^{15}N ($K^{15}NO_3$-^{15}N), potassium sulfate (K_2SO_4), sulfamic acid, phosphoric acid, p-aminobenzenesulfonamide, N-(1-Naphthyl) ethylenediamine dihydrochloride, potassium sodium tartrate, $NaNO_2$ and Nessler's reagent and potassium nitrate (KNO_3) were purchased from Aladdin (Shanghai, China). Hydrochloric acid and ethanol (C_2H_5OH) were purchased from Beijing Chemical Works.

Synthesis of Y-Co(OH)F/CF and Co(OH)F/CF

A one-step hydrothermal method with some modifications was applied to prepare Y-Co(OH)F/CF catalysts. First, the cleaned Cu foam (2×4 cm^2) was submerged in an aqueous solution with 30 mL of the following: 5 mmol $Co(NO_3)_2 \cdot 6H_2O$, 5 mmol urea, 400 mg NH_4F and 0.05 mmol $YCl_3 \cdot 6H_2O$. After being transferred into a 50 mL Teflon autoclave, the solution was heated at 120 °C for 12 hours. In the end, deionized water was used to clean up the generated Y-Co(OH)F/CF sample, and then dried at 50 °C in the oven. With the exception of adding 0.05 mmol $YCl_3 \cdot 6H_2O$, the Co(OH)F/CF counterpart was synthesized similarly to Y-Co(OH)F/CF.

Materials Characterization

The morphology of Y-Co(OH)F/CF was investigated with a Zeiss Gemini 500 scanning electron microscope. Images from transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and high-angle annular dark-field scanning transmission electron

microscopy (HAADF-STEM) were recorded on a TalosS-FEG. Using a PANalytical X'Pert-PRO X-ray diffractometer with Cu K radiation, the powder X-ray diffraction(XRD) patterns of Y-Co(OH)F/CF were examined. The X-ray photoelectron spectrometer (XPS) manufactured by Kratos Analytical was used for studying the chemical valence states and elemental makeup of Y-Co(OH)F/CF. On a Bruker Avance NEO 600 NMR spectrometer, the spectra of ^{1}H NMR were analyzed.

Electrochemical NO_3RR measurements

A three-electrode setup was used for the electrochemical technique, and the CHI 660 electrochemical workstation was used for all electrochemical tests. A Pt foil, Y-Co(OH)F/CF (1×1 cm^2), and SCE were used in the three-electrode setup as the counter electrode, working electrode and reference electrode, respectively. 35 mL of 0.5 M K_2SO_4 was placed separately to the H-cell's anode and cathode chambers for the nitrate reduction tests. From −0.7 to −1.5 V (vs. SCE), linear sweep voltammetry (LSV) curves were captured at a scan rate of 10 mV s^{-1}. After the LSV curves had stabilized, the 35 ml of 0.5 M K_2SO_4 was swapped out for 0.5 M K_2SO_4 with 200 mg L^{-1} KNO_3-N. Pass argon gas through the electrolyte for 30 minutes, and two hours of chronoamperometry (i-t) investigates were conducted at various potentials with a 500 rpm mixing rate. Nitrate and ammonia concentrations were determined by UV-VIS spectroscopy. Electrochemical impedance spectroscopy (EIS) measurements were performed in a 0.5 M K_2SO_4 aqueous solution with 200 mg L^{-1} of NO_3^--N at -1.3 V (vs. SCE) with frequency from 0.1 Hz to 100 kHz and an amplitude of 5 mV.

Determination of NO_3^--N

First, the electrolyte was withdrawn and diluted to 5 ml according to the measurement range after

the two hours of testing. Than 0.1 mL of HCl solution (1 M) and 0.01 mL of 0.8 wt% sulfamic acid solutionare then added to the electrolyte in sequence. After a thorough shake, the color was produced in drak for ten minutes. The absorbance was measured by UV-Vis spectrophotometry in the wavelength range of 200 nm and 300 nm. The final absorbance of NO_3^--N was calculated by the following formula: A = A220nm-2A275nm. The calibration curve is created by measuring the absorbance corresponding to the reference concentration of KNO_3 solution.

Determination of NO_2^--N

First, 5 mL of deionized water was used to dissolve 0.02 g of N-(1-naphthyl) ethylenediamine dihydrochloride and 0.4 g of p-aminobenzene sulfonamide. Add 1 mL of phosphoric acid (= 1.70 g mL^{-1}) next to act as a color developing agent. For 20 minutes, 5 mL of diluted electrolyte was combined with 0.1 mL of color developing agent. UV-Vis spectrophotometry was used to get the peak absorption spectrum at a wavelength of 540 nm. By using $NaNO_2$ standard solution, the calibration curve was produced.

Determination of NH_3-N

The diluted electrolyte was added Potassium sodium tartrate solution (0.1 mL, ρ=500 g/L) and as-prepared Nessler's reagent (0.1 mL). After shaking well, the color was developed for 20 min in drak. UV-Vis spectrophotometry was used to detect the absorbance between the wavelengths of 380 nm and 530 nm. The absorbance at 420 nm is the absorbance of NH_4^+-N. The calibration curve is created by measuring the absorbance corresponding to the reference concentration of NH_4Cl solution.

^{15}N Isotope Labeling Experiments

Isotope labelling experiments using $K^{15}NO_3$ as the raw nitrogen source. Before the NO_3RR test, a

0.5 M K_2SO_4 electrolyte solution containing 200 mg L^{-1} $K^{15}NO_3$-^{15}N was added to the cathode chamber as the reactant. The pH of the tested electrolyte was adjusted to 1-2 with 4 M H_2SO_4 solution. In order to further quantify the NH_4^+–N concentration, a standard curve of $^{15}NH_4^+$–^{15}N concentration versus integrated area ($^{15}NH_4^+$–^{15}N/$C_4H_4O_4$) was obtained using ^1H NMR with maleic acid ($C_4H_4O_4$) as the external standard. First, different concentrations of $^{15}NH_4^+$-^{15}N (50, 100, 150, 200 and 250 mg L^{-1}) were dissolved in 0.5 M K_2SO_4, using 120 mg L^{-1} $C_4H_4O_4$ as a standard solution. Next, 0.05 mL of deuterium oxide (D_2O) was mixed with 0.5 mL of the acidified electrolyte or standard solution and the ^1H NMR spectrum was further obtained by nuclear magnetic resonance detection.

Calculation equations of conversion ratio of NO_3^-, the selectivity of product, the yield rate of NH_4^+ and the Faradaic efficiency (FE):

$$\text{Conversion}_{(NO3-)} = \Delta c_{NO3-}/c0 \times 100\% \quad (1)$$

$$\text{Selectivity}_{(NH4+)} = c_{NH4+}/\Delta c_{NO3-} \times 100\% \quad (2)$$

$$\text{Yield}_{(NH4+)} = (c_{NH4+} \times V)/(M_{NH3} \times t \times S) \quad (3)$$

$$\text{FE} = (8F \times c_{NH4+} \times V)/(M_{NH4+} \times Q) \quad (4)$$

where Δc_{NO3-} is the concentration difference of NO_3^- before and after reduction, c_0 is the initial concentration of NO_3^-, c_{NH4+} is the measured NH_4^+ concentration, V is the electrolyte volume in the cathode chamber (35 mL), t is the electrolysis time (2 h), M_{NH3} is the molar mass of NH_3, S is the geometric area of working electrode (1 cm^2), F is the Faraday constant (96485 C mol^{-1}), and Q is the total charge during electrolysis.

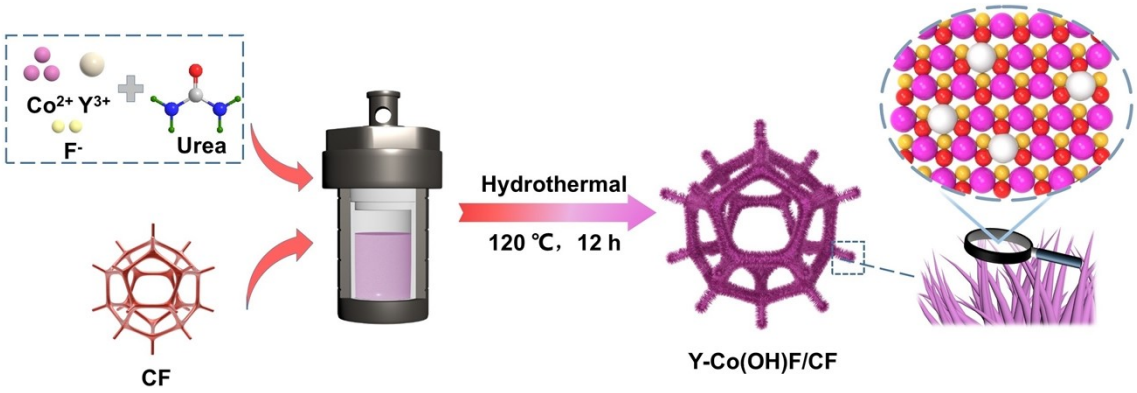

Fig. S1 Schematic illustration of the synthesis procedures for the Y-Co(OH)F/CF.

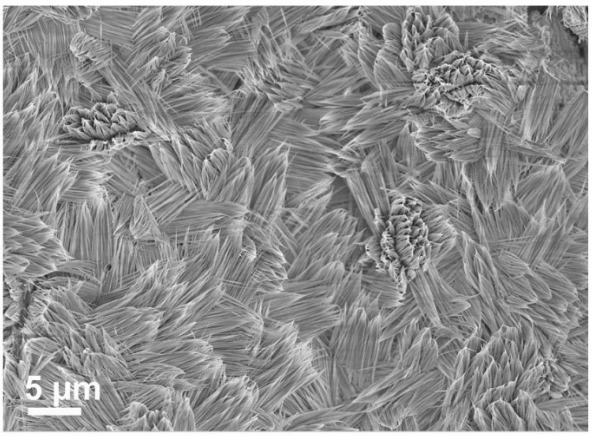

Fig. S2 SEM image of Co(OH)F/CF.

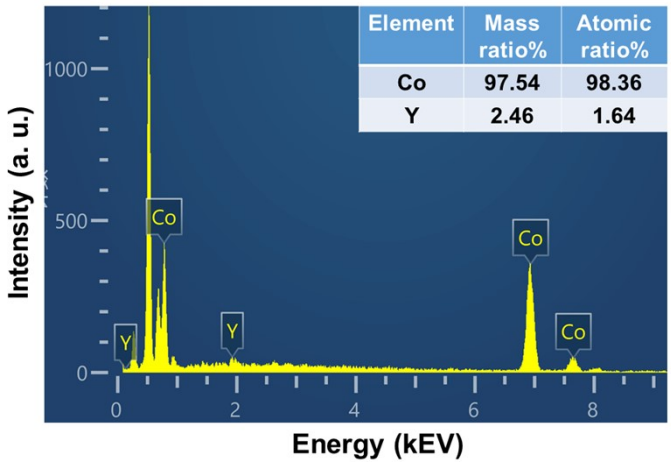

Fig. S3 EDS spectrum of the Y-Co(OH)F/CF.

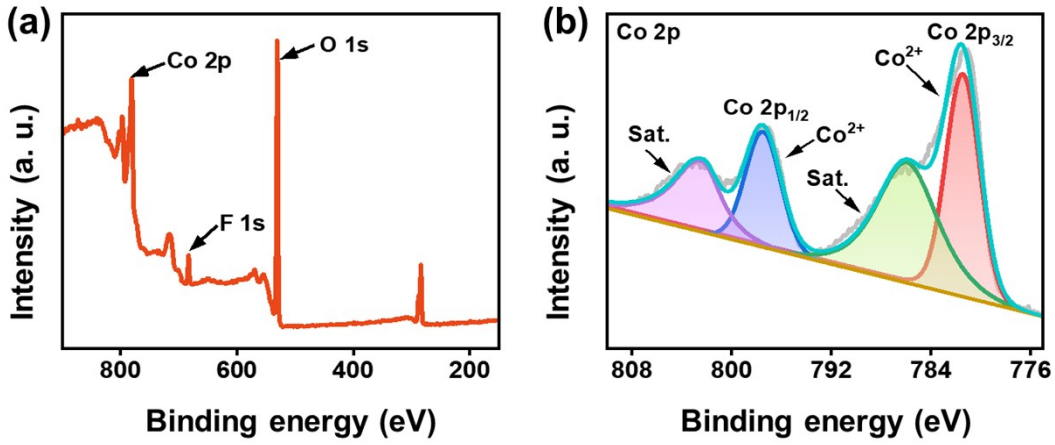

Fig. S4 (a) Full XPS spectrum and (b) high-resolution Co 2p XPS spectrum for Co(OH)F.

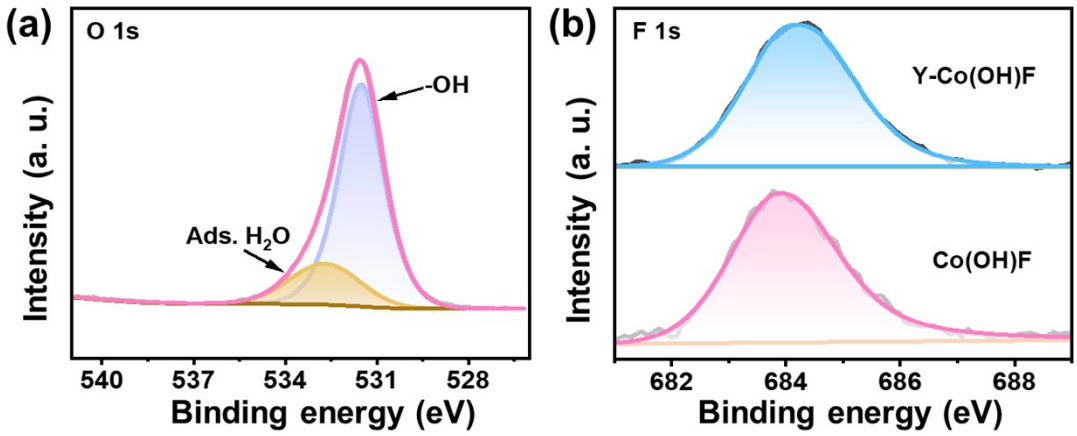

Fig. S5 (a) High-resolution O 1s XPS spectrum for Y-Co(OH)F; (b) High-resolution F 1s XPS spectra for different samples.

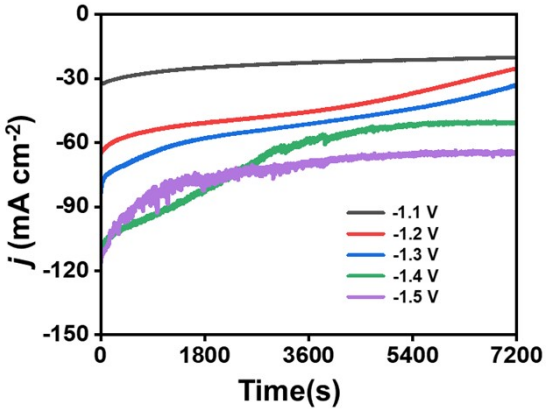

Fig. S6 The i-t curves of the Y-Co(OH)F/CF in 0.5 M K_2SO_4 with 200 mg L^{-1} KNO_3-N at different potentials.

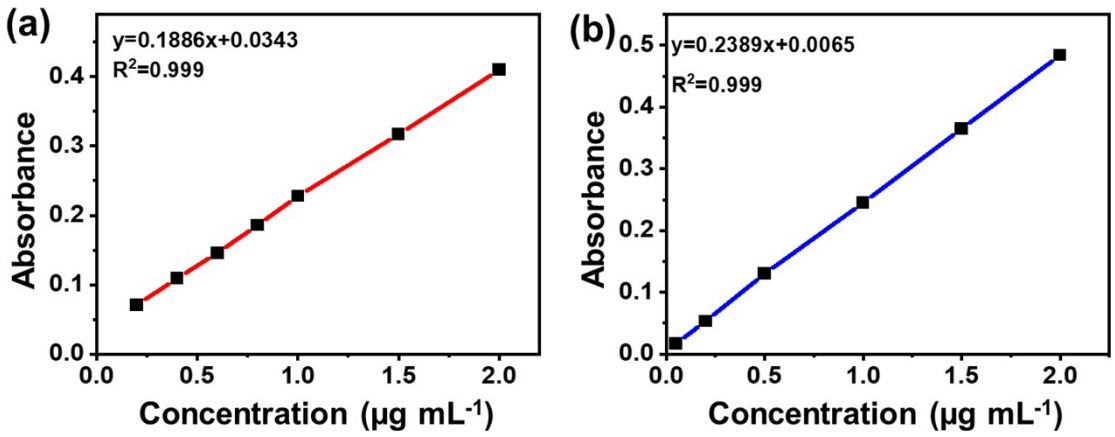

Fig. S7 (a) Corresponding calibration curve for calculating the concentration of NH_4^+–N. (b) Corresponding calibration curve for calculating the concentration of NO_3^-–N.

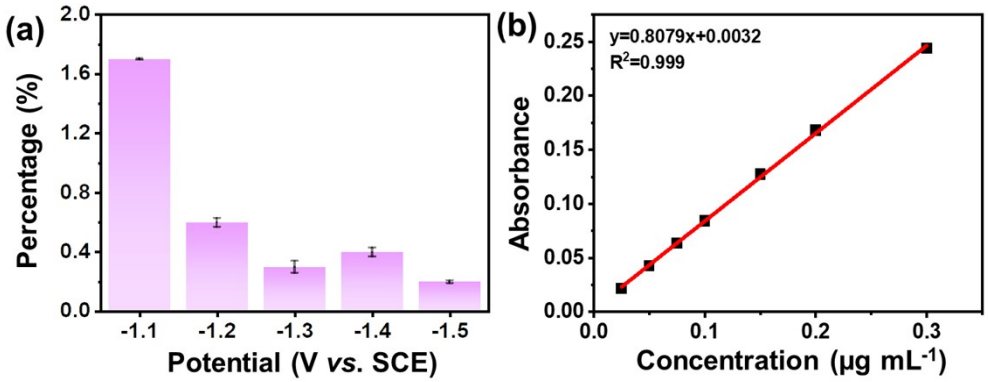

Fig. S8 (a) Selectivity of NO_2^--N over the Y-Co(OH)F/CF at different potentials. (b) Calibration curve used to estimate the concentrations NO_2^--N.

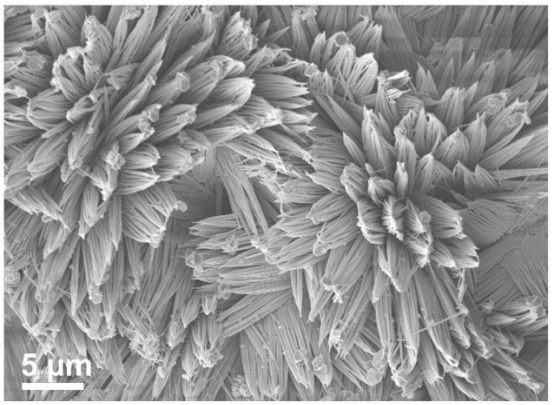

Fig. S9 SEM image of Y-Co(OH)F/CF after NO_3RR testing.

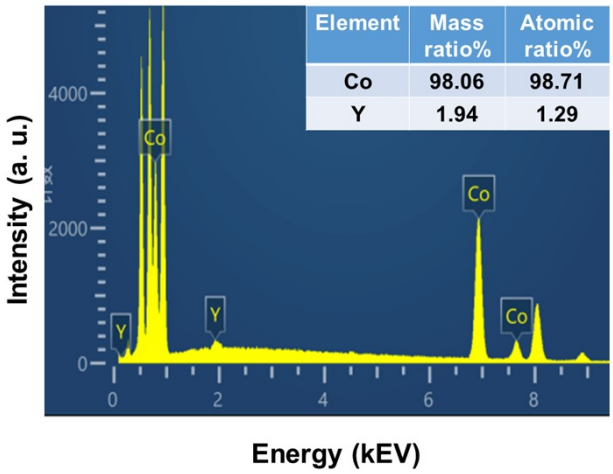

Fig. S10 EDS spectrum of Y-Co(OH)F/CF after NO_3RR testing.

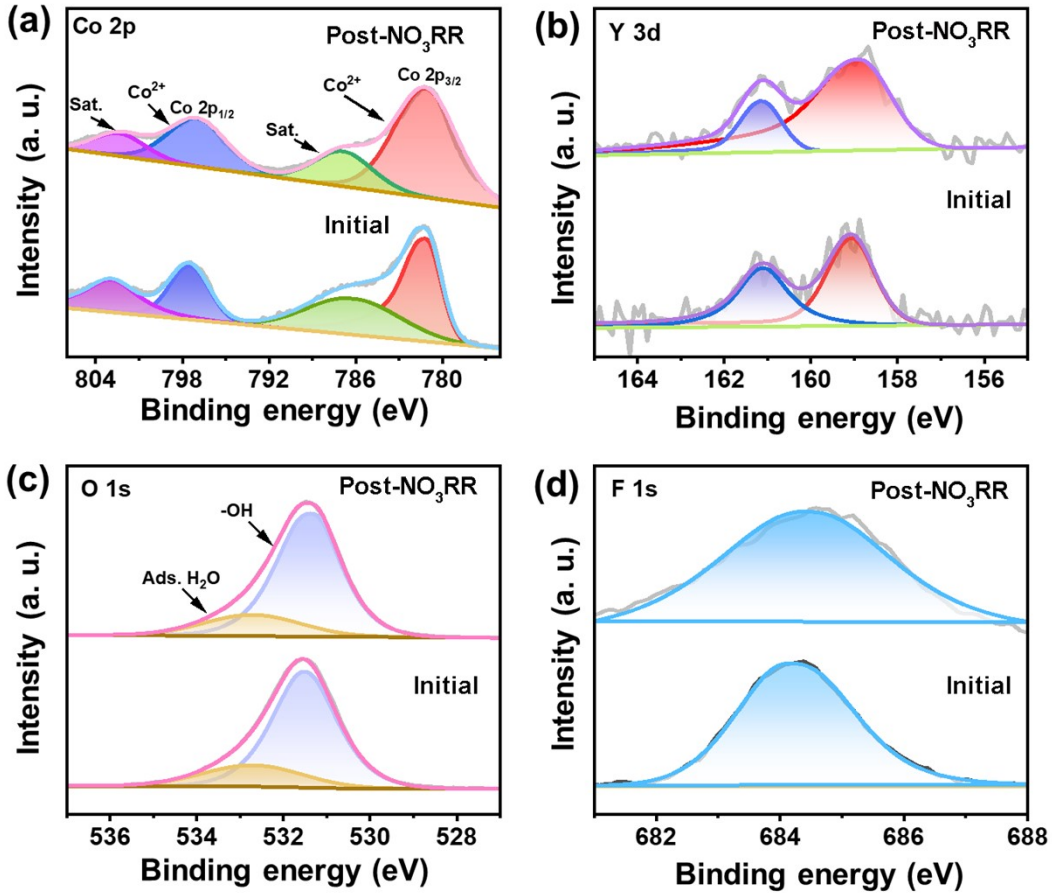

Fig. R11 (a) High-resolution Co 2p XPS spectra, (b) high-resolution Y 3d XPS spectra, (c) high-resolution O 1s XPS spectra, (d) high-resolution F 1s XPS spectra of Y-Co(OH)F/CF before and after NO_3RR testing

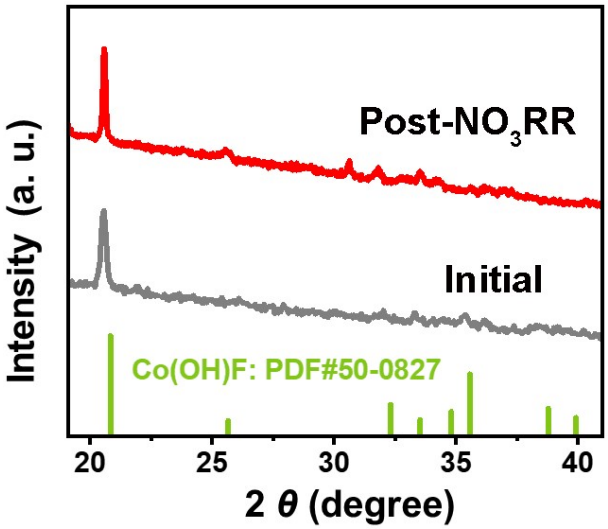

Fig. S12 XRD patterns of Y-Co(OH)F/CF before and after NO_3RR testing.

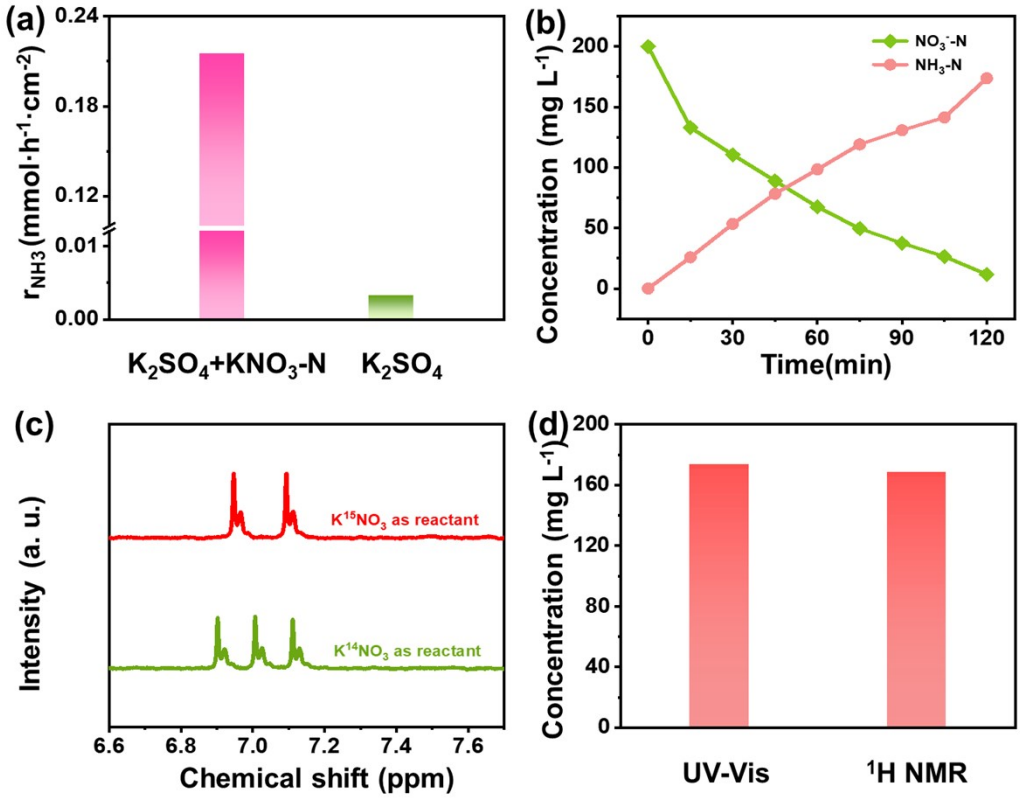

Fig. S13 (a) Yield rates of ammonia from Y-Co(OH)F/CF in a K_2SO_4 electrolyte with and without nitrate. (b) NO_3^--N and NH_3-N concentrations over the Y-Co(OH)F/CF at −1.3 V vs. SCE change with time. (c) ^1H NMR spectra of the electrolytes after electrolysis using $^{15}NO_3^-$ and $^{14}NO_3^-$ as the nitrogen source. (d) UV-Vis and ^1H NMR measurements of generated NH_3 concentrations using $^{14}NO_{3-}$ and $^{15}NO_{3-}$ as nitrogen sources.

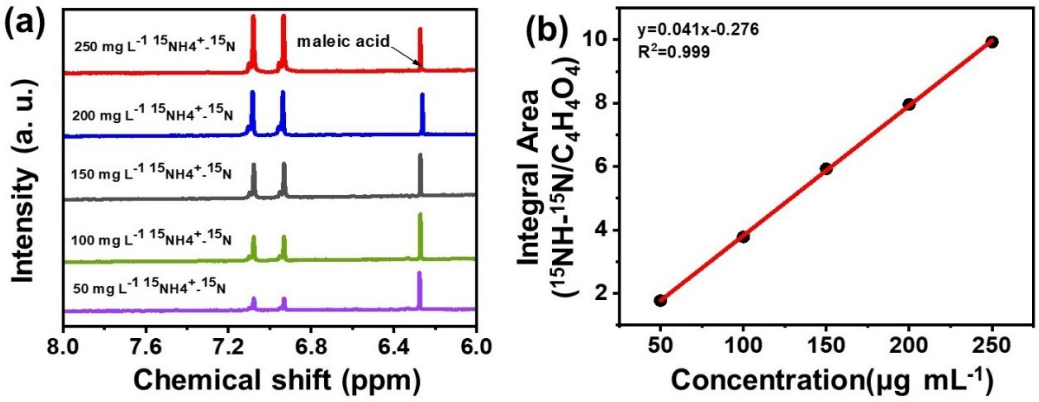

Fig. S14 (a) ^{1}H NMR spectra of $^{15}NH_4^+$-^{15}N with different concentrations. (b) The standard curve of integral area ($^{15}NH_4^+$-$^{15}N/C_4H_4O_4$) against $^{15}NH_4^+$-^{15}N concentration.

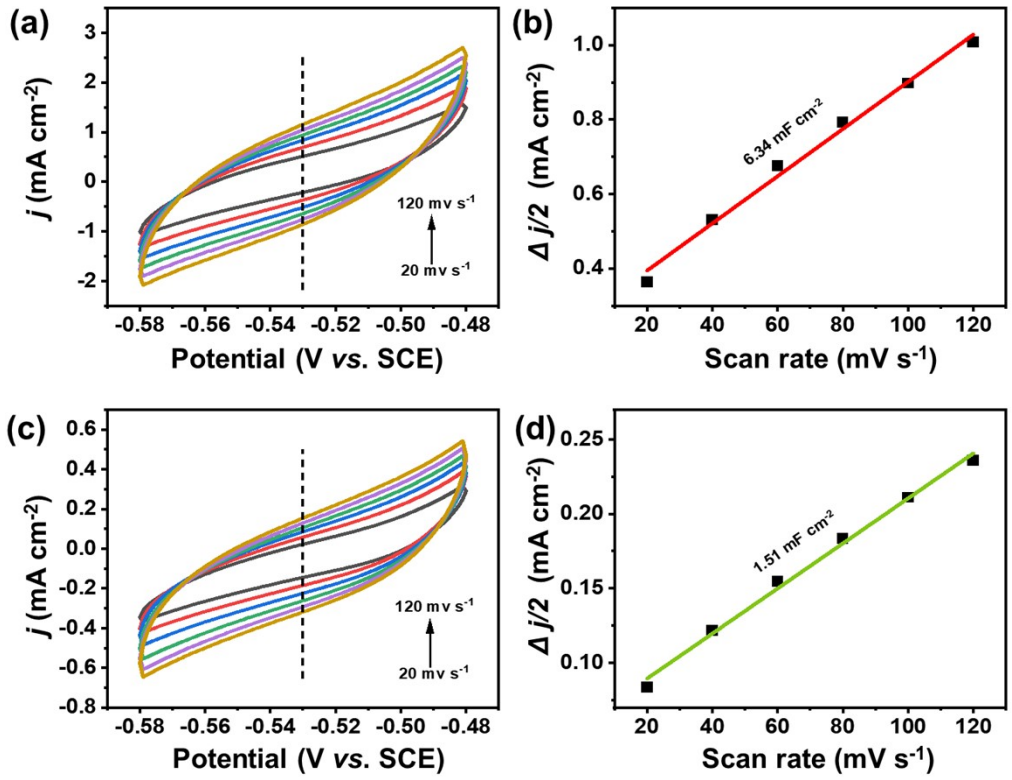

Fig. S15 CV curves of (a) Y-Co(OH)F/CF and (c) Co(OH)F/CF at different scanning rates; Capacitance current densities of (b) Y-Co(OH)F/CF and (d) Co(OH)F/CF at -0.53 V (vs. SCE).

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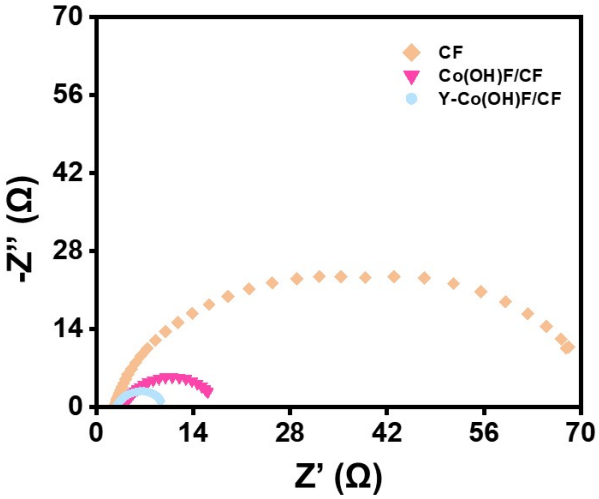

Fig. S16 EIS spectra of Y-Co(OH)F/CF, Co(OH)F/CF and CF.

Table S1 Comparison of electrochemical nitrate-to-ammonia performance between the Y-Co(OH)F/CF and some other reported Co-based electrocatalysts.

Electrocatalyst	Electrolyte	Faradaic Efficiency (Potential)	Ref.
Y-Co(OH)F/CF	0.5mol K_2SO_4 + 200 mg L^{-1} KNO_3	91.81% (-1.3V *vs.* SCE)	This work
Co_3O_4/Ti mesh	0.1 M Na_2SO_4 + 100 g L^{-1} NO_3^-	1.23% (2.19 V *vs.* RHE)	1
Co_3O_4@NiO HNTs	0.5mol K_2SO_4 + 200 mg L^{-1} KNO_3	54.97% (-0.7V *vs*. RHE)	2
Co/NC-800	0.1 M Na_2SO_4 + 100 mg L^{-1} NO_3^-	81.2 % (-1.2 V *vs.* Ag/AgCl)	3
Co_3O_4/CF	50 mM Na_2SO_4 + 50 mg L^{-1} NO_3^-	22.19% (-1.3 V *vs.* Ag/AgCl)	4
[Bim]NTf_2-Co_3O_{4-x}	0.1 M Na_2SO_4 + 500 mg L^{-1} KNO_3	84.74% (-1.41 V *vs.* Ag/AgCl)	5
PP-Co	0.1 M NaOH + 0.1 M KNO_3	90.1% (-0.6 V *vs*. RHE)	6
Co_3O_4/Co	0.1 M Na_2SO_4 + 1 mg mL^{-1} NO_3^-	88.7% (-0.8 *vs*. RHE)	7
Co−CuO_x	500 mg L^{-1} Na_2SO_4 + 144.4 mg L^{-1} KNO_3	53.5%(-1.1 V *vs.* Ag/AgCl)	8

References

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