Supplementary Information (SI) for New Journal of Chemistry.

Electronic Supplementary Information

Co_3O_4@Co_9S_8 nanowires as tandem catalyst for efficient electrochemical reduction of nitrate to ammonia

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Materials

Nickel foam (NF), urea purchased from Tianjin Damao Chemical reagent factory. Cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), ammonium fluoride (NH_4F), urea ($CO(NH_2)_2$), sodium sulfide (Na_2S), anhydrous sodium sulfate (Na_2SO_4), sodium nitrate ($NaNO_3$), ammonium chloride (NH_4Cl), hydrochloric acid (HCl), sulfuric acid (H_2SO_4), hydrogen peroxide (H_2O_2), sodium hypochlorite (NaClO), sodium hydroxide (NaOH), sodium salicylate ($C_7H_5O_3Na$), sodium nitroferricyanide ($Na_2[Fe(CN)_5NO] \cdot H_2O$), sulfanilamide ($C_6H_4SO_2N_2H_4$), N-(1-Naphthyl) ethylenediamine dihydrochloride ($C_{12}H_{16}Cl_2N_2$), sodium hydroxide (NaOH), and phosphoric acid (H_3PO_4) were purchased from Thermo Fisher Technology Co. Ltd. (China). The ultra-pure water used in the experiment was purified by the Ulupure system.

Preparation of Co_9S_8@Co_3O_4/NF nanowire arrays

The Co_9S_8@Co_3O_4/NF were prepared by a facile combined hydrothermal-annealing-sulfurization method.[1] Firstly, 3 mmol $Co(NO_3)_2 \cdot 6H_2O$, 6 mmol NH_4F and 15 mmol $CO(NH_2)_2$ were dissolved in 80 mL deionized water to form homogeneous solution. Cleaned NF was used as the substrate. Secondly, the above solution was transferred into a Teflon-linked steel autoclave and kept at 120 °C for 8 h. After naturally cooling to room temperature, the precursor was rinsed by deionized water and annealed at 350 °C in argon for 2 h to form Co_3O_4/NF. Lastly, the Co_3O_4/NF was immersed into solution of 0.1 M Na_2S and kept at 90 °C for 9 h to form the Co_9S_8@Co_3O_4/NF.

Apparatus

The powder XRD data was tested from a SmartLab SE X-ray power diffractometer instrument (Rigaku, Japan). The morphology images were obtained from Gemini 300 field emission SEM (Zeiss, Germany) and JEM-2100 TEM (Zeiss, Germany). Elements species and distribution were obtained by an X-Max^N 50 EDS (Oxford, China). XPS spectra were obtained from an Axis Supra X-ray photoelectron spectrometer (Shimadzu, Japan). The concentration of a series of related substances in the electrolytes were detected on UV-2700 ultraviolet-visible (UV-vis) spectrophotometer

(Shimadzu, Japan). CHI660E electrochemical workstation obtained from Shanghai Chenhua Instrument Co., Ltd, China was employed for all electrochemical measurements.

Electrochemical Measurements

Before eNO_3^-RR tests, the Nafion membrane was pre-treated by heating in 5% H_2O_2 solution and ultrapure water at 80 °C for 1 h, respectively. Electrochemical measurements were performed with a CHI660E electrochemical analyzer (CHI Instruments, Inc., Shanghai) in a standard three-electrode system using Co_3O_4@Co_9S_8/NF (0.5 cm × 0.5 cm) as working electrode, Ag/AgCl as reference electrode, and graphite rod as counter electrode. All experiments were carried out at room temperature (25 °C).

The following formula was utilized to convert the potential reported in this work to RHE scale through calibration: $E \text{ (vs. RHE)} = E \text{ (vs Ag/AgCl)} + 0.197 + 0.059 \times \text{pH}$, and the polarization curve was the steady-state curve after a few cycles. During NO_3^- reduction test, 0.1 M Na_2SO_4 and 0.1 M Na_2SO_4 + 0.01 M $NaNO_3$ electrolyte in two chambers of the H–type electrolytic cell was separated by a Nafion membrane, so that the anode chamber can continuously provide the H^+ required for the reaction to the cathode chamber.

Determination of NH_3

The produced ammonia was estimated by indophenol blue method by ultraviolet spectroscopy.[2] Firstly, taken 0.5 mL of electrolyte from the cathodic cell with a pipette gun and diluted it to 4 mL. Then, 50 µL of oxidizing agent (NaClO) and 0.75 M NaOH), 500 µL of coloring agent (0.4 M $C_7H_5O_3Na$ and 0.32 M NaOH), and 50 µL of catalyst (1.0 wt% $Na_2[Fe(CN)_5NO]\cdot H_2O$) were added into the diluted electrolyte accordingly and mixed uniformly. After standing at 25 °C for 2 h, the UV–Vis absorption spectrum was measured. The concentration of indophenol blue was determined using the absorbance at a wavelength of 660 nm. In this study, a concentration-absorbance curve was obtained using a standard ammonium chloride solution firstly. The fitted curve ($y = 0.1539x + 0.0001071$, $R^2 = 0.9960$) indicates a good linear relationship between the absorbance value and the NH_3 concentration. Next, electrolyte was obtained from the electrochemical reaction cathode vessel for UV–Vis spectrometry.

Determination of NO_2^-

The chromogenic agent of NO_2^- contains 4 g $C_6H_4SO_2N_2H_4$, 0.2 g $C_{12}H_{16}Cl_2N_2$, 10 mL H_3PO_4 (ρ = 1.70 g mL^{-1}), and 50 mL H_2O.[3] Firstly, taken 20 µL of electrolyte from the cathodic cell with a pipette gun and diluted it to 5 mL. Then, 100 µL of chromogenic agent was added into the diluted electrolyte and mixed uniformly. The absorbance intensity of the aforementioned solution after keeping 25 min was recorded at the wavelengths of 540 nm. The related concentration-absorbance curve was recorded from a series of known standard concentration of $NaNO_2$ solutions and the fitted curve is $y = 0.1960x - 0.001190$, $R^2 = 0.9996$.

The Y_{NH_3}, FE_{NH_3}, and $FE_{NO_2^-}$ were calculated using the following formulas:

$$Y_{NH_3} = (1000 \times c_{NH_3} \times V) / (17 \times t \times A) \quad (1)$$

$$FE_{NH_3} = [(8 \times F \times c_{NH_3} \times V) / (17 \times 10^6 \times Q)] \times 100\% \quad (2)$$

$$FE_{NO_2^-} = [(2 \times F \times c_{NO_2^-} \times V) / (46 \times 10^6 \times Q)] \times 100\% \quad (3)$$

Where c_{NH_3} (mg L^{-1}) is the measured NH_3 concentration; V (L) is the volume of the electrolyte; t (h) is the reduction reaction time; and A (cm^2) is the geometric area of the cathode; F is the Faraday constant (96485 C mol^{-1}); Q (C) is the quantity of applied electricity; $c_{NO_2^-}$ (mg L^{-1}) is the measured NO_2^- concentration.

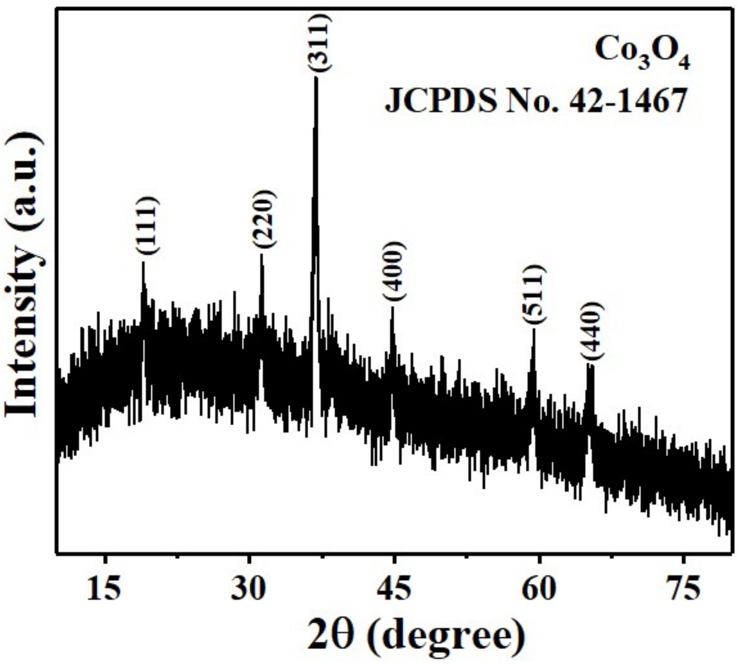

Fig. S1 XRD pattern of Co_3O_4.

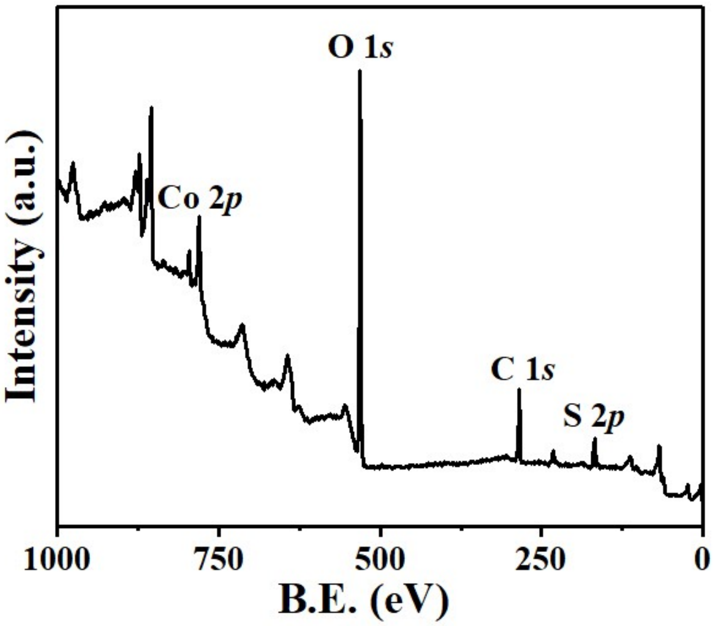

Fig. S2 (a) XPS total spectrum of Co_3O_4@Co_9S_8.

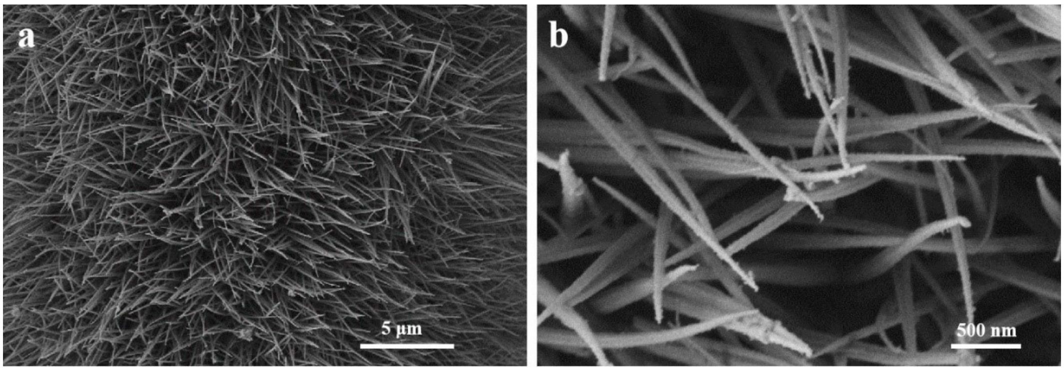

Fig. S3 (a) and (b) SEM images of Co_3O_4.

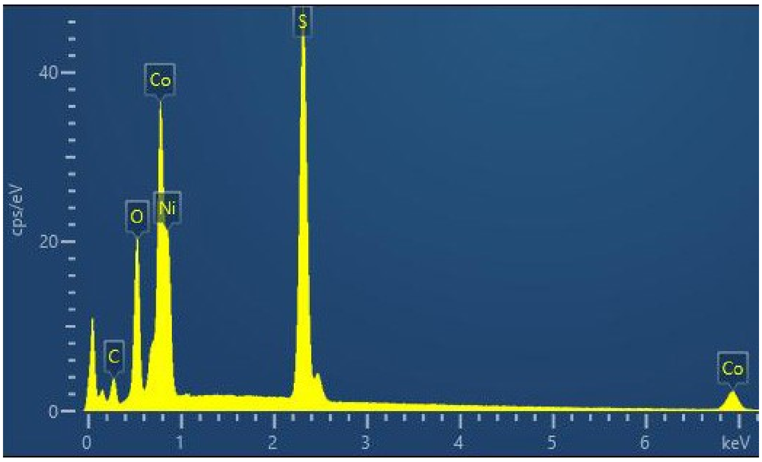

Fig. S4 EDX images of $Co_3O_4@Co_9S_8/NF$.

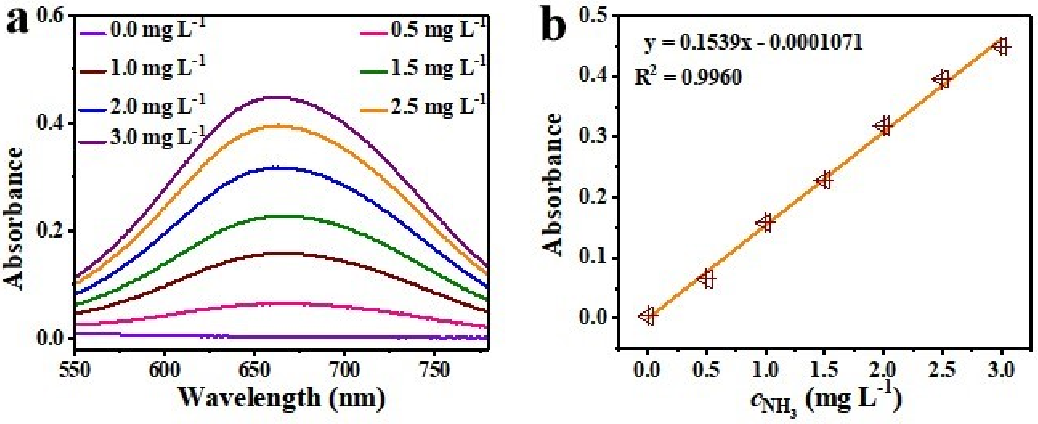

Fig. S5 (a) UV-Vis absorption spectra with different NH_3 concentrations. (b) Calibration curve used for calculation of NH_3 concentrations.

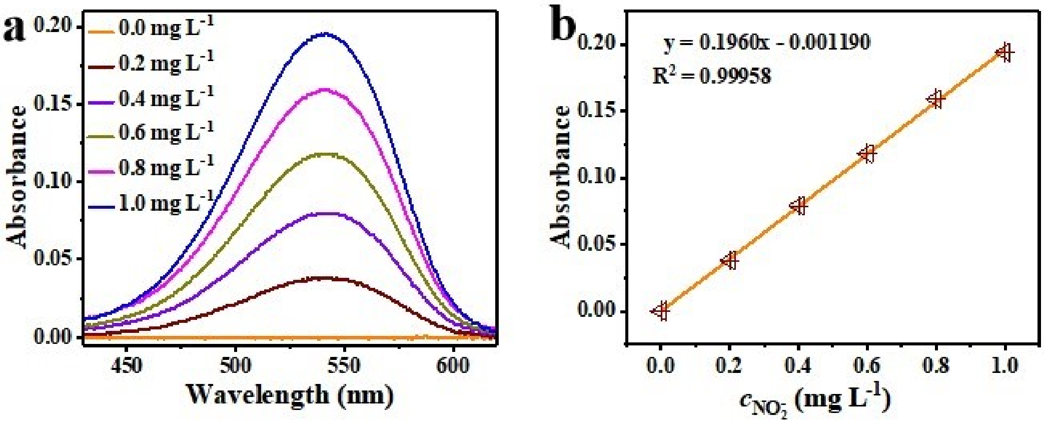

Fig. S6 (a) UV-Vis absorption spectra with different NO_2^- concentrations. (b) Calibration curve used for calculation of NO_2^- concentrations.

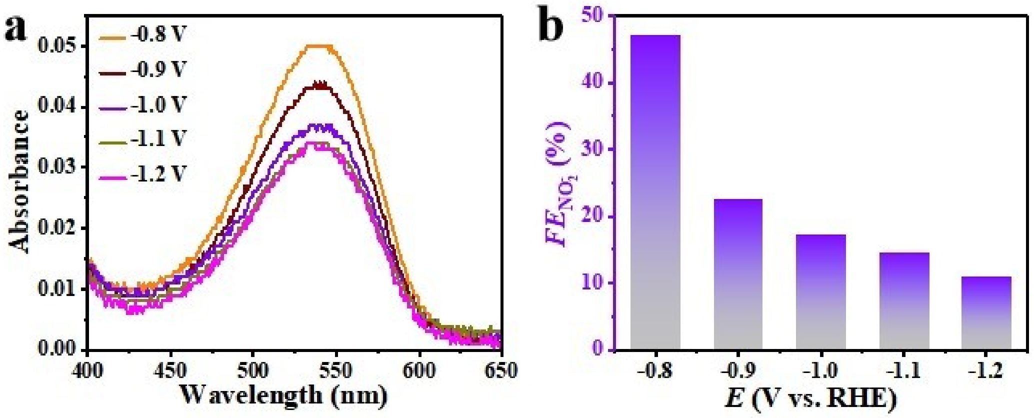

Fig. S7 (a) UV-Vis absorption spectra of NO_2^- for the electrolytes and (b) $FE_{NO_2^-}$ at a series of potentials.

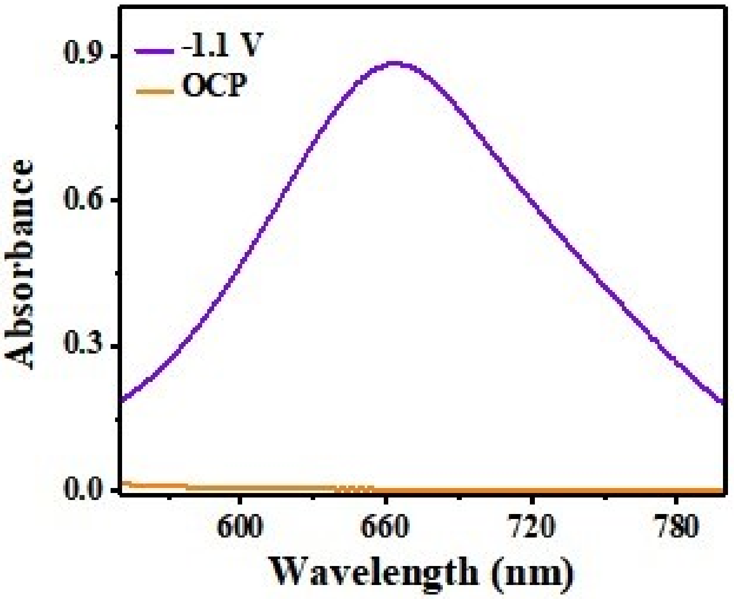

Fig. S8 UV-Vis absorption spectra of NH_3 at OCP and −1.1 V vs. RHE.

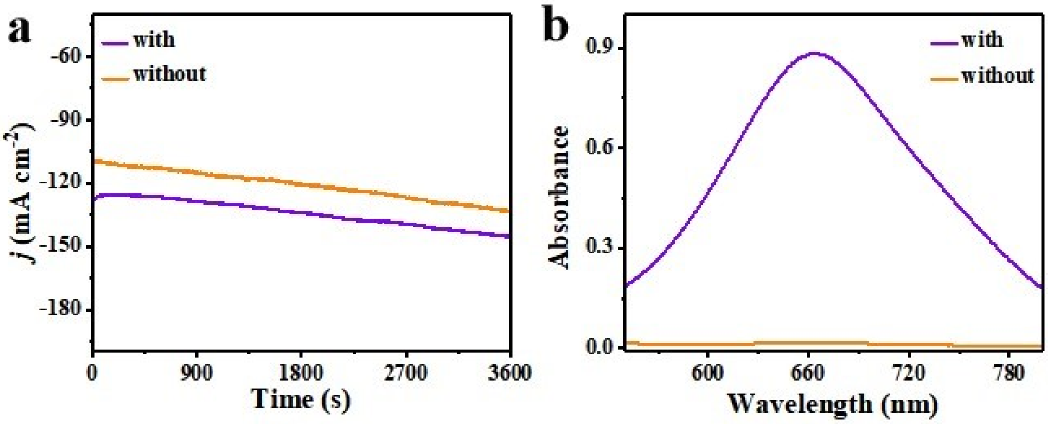

Fig. S9 Chronoamperometry current density curves of $Co_3O_4@Co_9S_8$/NF in 0.1 M Na_2SO_4 with or without 0.01 M $NaNO_3$ electrolytes at −1.1 V vs. RHE.

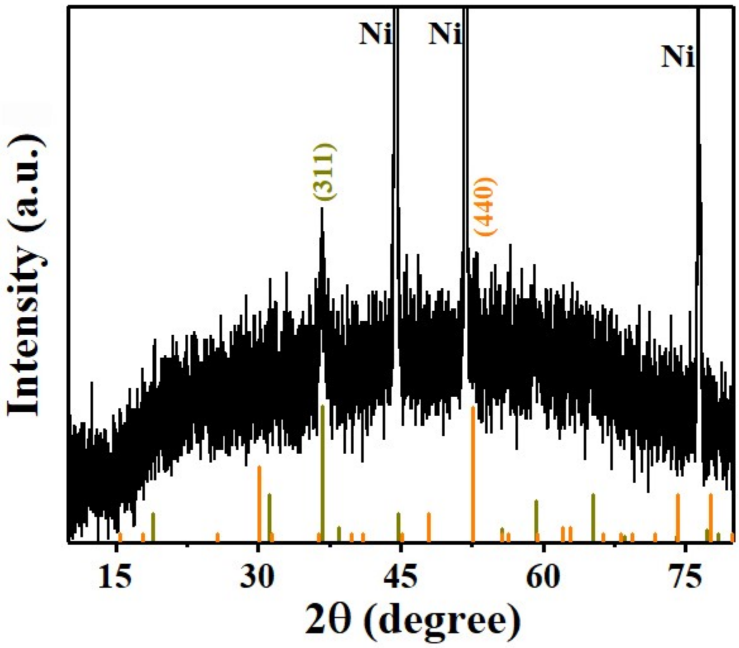

Fig. S10 XRD pattern of Co_3O_4@Co_9S_8 after long-term electrochemical NO_3^-RR test.

Table S1 Comparison of different electrocatalysts for NO_3^- to NH_3.

Catalyst	**Electrolyte**	Y_{NH_3} **(%)**	FE_{NH_3} **(%)**	**Ref.**
Pd	0.1 M Na_2SO_4 + 0.1 M NO_3^-	548.50 mmol h^{-1} cm^{-2}	79.91	4
TiO_2-OVs	0.5 M Na_2SO_4 + 50 ppm NO_3^-	45.00 μmol h^{-1} mg^{-1}	85.00	5
Cu/Cu_2O	0.5 M Na_2SO_4 + 200 ppm NO_3^-	244.90 μmol h^{-1} cm^{-2}	95.80	6
O-Cu-PTCDA	0.1M PBS + 500 ppm NO_3^-	436.00 ± 85.00 μg h^{-1} cm^{-2}	85.90	7
Pd/TiO_2	0.25 M NO_3^-	66.00 μmol h^{-1} cm^{-2}	92.10	8
Co_2AlO_4 nanoarray	0.1 M PBS + 0.1 M NO_3^-	467.70 μmol h^{-1} cm^{-2}	92.60	9
Co_3O_4@Co_9S_8/NF	0.1 M Na_2SO_4 + 0.05 mM $NaNO_3$	538.09 μmol h^{-1} cm^{-2}	85.88	This work

References

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