Electronic Supplementary Information

Experimental Section

Materials: Cobalt chloride hexahydrate (CoCl₂·6H₂O, 99.0%), ammonium fluoride (NH₄F), urea (CH₄N₂O), sodium hypophosphite (NaH₂PO₂, 99%), octadecanethiol (C₁₈H₃₈S), sodium sulfate (Na₂SO₄, 99.0%), sodium hydroxide (NaOH, 99.0%), ammonium chloride (NH₄Cl), ethanol (C₂H₆O, 99.0%), sodium salicylate (C₇H₅O₃Na), *p*-dimethylaminobenzaldehyde (C₉H₁₁NO), sodium nitroferricyanide dihydrate (C₅FeN₆Na₂O·2H₂O) and sodium hypochlorite solution (NaClO) were purchased from Aladdin Ltd. (Shanghai, China). Nafion (5 wt%) solution was purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. Nitric acid (HNO₃), sulfuric acid (H₂SO₄), hydrogen peroxide (H₂O₂), hydrazine monohydrate (N₂H₄·H₂O) and ethyl alcohol (C₂H₅OH) were purchased from Beijing Chemical Corp. (China). chemical Ltd. in Chengdu. Titanium mesh (TM) was provided by Suzhou Taili New Energy Co., Ltd. And it was pretreated in 0.1 M HCl and then cleaned by sonication in deionized water and C₂H₅OH for several times to remove surface impurities. The ultrapure water used throughout all experiments was purified through a Millipore system. All reagents were analytical reagent grade without further purification.

Preparation of Co(OH)F/TM: Co(OH)F/TM was prepared as follows. In a typical synthesis, $CoCl_2 \cdot 6H_2O(0.475 \text{ g})$, $NH_4F(0.186 \text{ g})$ and urea (0.60 g) were dissolved in deionized water (40 mL) in a 50 mL beaker. After continuously stirring for 30 min, the solution was then transferred to a 50 mL Teflon-lined autoclave with a piece of TM (2 cm × 3 cm). The autoclave was heated to 120 °C, and kept at that temperature for 6 h. After cooling to room temperature, the resulting precipitates were washed several times with deionized water, and then dried at 60 °C for 6 h. Then the Co(OH)F/TM was obtained.

Synthesis of CoP/TM: NaH₂PO₂ (1.0 g) was put at the center of front zone in a two-zone furnace, while Co(OH)F/TM was put at the center of back zone. The temperature of two zone were raised from 25 to 300 °C with a heating rate of 2 °C min⁻¹ and held at this temperature for 2 hours. After the conversion process, the furnace cooled down to room temperature under Ar.

Modification of CoP/TM with aliphatic thiols: In a typical experiment, required amount of developed CoP/TM were steeped in corresponding 0.05 M ethanolic solution of octadecanethiol for 24 h. Later, the resultant product was washed with ethanol twice.

Characterizations: Power XRD data were acquired by a LabX XRD-6100 X-ray diffractometer with a Cu K α radiation (40 kV, 30 mA) of wavelength 0.154 nm (SHIMADZU, Japan). SEM images were collected on a GeminiSEM 300 scanning electron microscope

(ZEISS, Germany) at an accelerating voltage of 5 kV. TEM images were acquired on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) operated at 200 kV. XPS measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. The absorbance data of spectrophotometer was measured on UV-vis spectrophotometer. The ion chromatography data were collected on Metrohm 940 Professional IC Vario.

Electrochemical measurements: In this paper, we use a H-type electrolytic cell separated by a Nafion 117 Membrane which was protonated by boiling in ultrapure water, H_2O_2 (5%) aqueous solution and 0.5 M H_2SO_4 at 80 °C for another 2 h, respectively. A three-electrode configuration is used for electrochemical experiments using C18@CoP/TM as the working electrode, Ag/AgCl (filled with saturated KCl solution) as the reference electrode, and graphite rod as the counter electrode. The electrochemical experiments were carried out with an electrochemical workstation (CHI 660E) in N₂-saturated 0.1 M Na₂SO₄ solution. The potentials reported in this work were converted to reversible hydrogen electrode (RHE) scale via calibration with the following equation: E (RHE) = E (vs. Ag/AgCl) + 0.61 V and the presented current density was normalized to the geometric surface area.

Determination of NH₃: Concentration of produced NH₃ was determined by spectrophotometry measurement with indophenol blue method.¹ In detail, 4 mL electrolyte was obtained from the cathodic chamber and mixed with 50 μ L oxidizing solution containing NaClO (4.5%) and NaOH (0.75 M), 500 μ L coloring solution containing C₇H₅O₃Na (0.4 M) and NaOH (0.32 M), and 50 μ L catalyst solution Na₂Fe(CN)₅NO·2H₂O (1 wt%) for 1 h. The concentration-absorbance curve was calibrated using the standard NH₄Cl solution with NH₃ concentrations of 0.0, 0.05, 0.10, 0.15, 0.20, 0.25 and 0.30 μ g mL⁻¹ in 0.1 M Na₂SO₄. These solutions were identified via UV-vis spectroscopy at the wavelength of 655 nm. The concentration-absorbance curves were calibrated using standard NH₃ solution with a serious of concentrations. The fitting curve (y = 0.494x + 0.028, R² = 0.999) shows good linear relation of absorbance value with NH₃ concentration.

Determination of N₂H₄: The N₂H₄ production was estimated by the method of Watt and Chrisp.² The color reagent was a mixed solution of 5.99 g C₉H₁₁NO, 30 mL HCl and 300 mL C₂H₅OH. In detail, 5 mL electrolyte was removed from the electrochemical reaction vessel, and added into 5 mL prepared color reagent and stirred 15 min at 25 °C. The absorbance of such solution at the absorbance of 455 nm was measured to quantify the hydrazine yields with a standard curve of hydrazine (y = 0.395x + 0.044, R² = 0.999).

Determination of FE and V_{NH3}: FE is calculated by equation:

$$FE = 3 \times F \times [NH_3] \times V / 17 \times Q \times 100\%$$

NH₃ yield was calculated using the following equation:

 NH_3 yield = $[NH_3] \times V / (17 \times t \times A)$

The amount of NH₃ is calculated as follows:

$$m_{\rm NH3} = [\rm NH_3] \times V$$

Where F is the Faraday constant (96500 C mol⁻¹), $[NH_3]$ is the measured NH₃ concentration, V is the volume of the Na₂SO₄ electrolyte for NH₃ collection (35 mL), Q is the total quantity of applied electricity; t is the reduction time (2 h) and A₁ is the loaded area of catalyst.

Computational method: Spin-polarized first-principles calculations based on the Density Functional Theory (DFT) were performed using the Vienna Ab initio Simulation Package (VASP).³⁻⁵ The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional⁶ within the generalized gradient approximation (GGA) was employed to describe the exchange-correlation energy. The projector-augmented-wave (PAW)⁷ method was used for simulation of the pseudopotentials. The energy cutoff was set to 450 eV. The force on each atom was set as 0.02 eV/Å for convergence. A 1 × 2 CoP (211) supercell with the lattice constants of a=8.12, b=12.60 Å, and the vacuum layer of 15 Å added in the z direction was built as the catalyst model. The gamma centered 3 × 2 × 1 k-mesh was sampled in the Brillouin zone using the Monkhorst-Pack scheme.⁸ The DFT-D3 method was employed to correct the van der Waals interactions⁹ between the adsorbates and the catalyst. The free energies of the NRR steps were calculated using the equation: $\Delta G = \Delta E_{DFT} + \Delta E_{ZPE} - T\Delta S$, where ΔE_{DFT} is the DFT calculated binding energy, the ΔE_{ZPE} and T ΔS are the zero-point energy correction and the variation of entropy, respectively, which gotten from vibration calculations.



Fig. S1. XRD patterns for CoP/TM and C18@CoP/TM.



Fig. S2. SEM images for CoP/TM.



Fig. S3. (a) UV-vis absorption curves of indophenol assays kept with different concentrations of NH_4^+ ions for 1 h at room temperature. (b) Calibration curve used for calculation of NH_4^+ concentration.



Fig. S4. LSV curves for C18@CoP/TM in N₂- and Ar-saturated 0.1 M Na₂SO₄ (scan rate 10 mV s⁻¹).



Fig. S5. UV-vis absorption spectra of the electrolytes colored with indophenol indicator for 1 h.



Fig. S6. (a) Ion chromatogram of NH_4Cl with different concentrations in 0.1 M Na_2SO_4 and (b) corresponding standard curve. (c) Ion chromatogram for the electrolytes at a series of potentials after electrolysis for 2 h. (d) NH_3 yields for C18@CoP/TM at corresponding potentials.



Fig. S7. (a) UV-vis curves of various N_2H_4 concentrations after incubated for 15 min at room temperature. (b) Calibration curve used for calculation of N_2H_4 concentration.



Fig. S8. UV-vis absorption spectra of the electrolytes estimated by the method of Watt and Chrisp before and after 2 h electrolysis in N_2 atmosphere at -0.2 V.



Fig. S9. Double layer capacitance measurements at various scan rate ranging from 10-30 mV s^{-1} (a) CoP/TM and (b) C18@CoP/TM. Capacitive current densities at 0.16 V vs. RHE as a function of scan rate (c) CoP/TM and (d) C18@CoP/TM.



Fig. S10. (a) Time-dependent current density curves of bare TM substrate, CoP/TM, and C18@CoP/TM at -0.2 V in 0.1 M Na₂SO₄. (b) UV-vis absorption spectra of the electrolytes stained with indophenol indicayor after NRR electrolysis.



Fig. S11. (a) Time-dependent current density curve of C18@CoP/TM in Ar-saturated solution at -0.2 V for 24 h. (b) UV-vis absorption spectra of the electrolytes colored with indophenol indicator after 24 h electrolysis under different conditions. (c) Comparison of NH₃ yield under different conditions.



Fig. S12. UV-vis absorption spectra of the electrolytes colored with indophenol indicator after 2 h electrolysis under different conditions.



Fig. S13. XRD pattern for C18@CoP/TM after stability test.



Fig. S14. SEM image of C18@CoP/TM after stability test.



Fig. S15. XPS spectra of C18@CoP/TM in the (a) Co 2p, (b) P 2p, and (c) S 2p regions after stability test.



Fig. S16. The initial and optimized structures in our consideration, as well as the adsorption free energies of N_2 adsorbed on the C18-thiol decorated CoP (211) surface.



Fig. S17. Free energy diagram for NRR occuring on the clean CoP (211) along distal and alternating pathways. Asterisk (*) denotes the status of adsorption.



Fig. S18. The images of the intermediates of NRR occurring on the C18-thiol decorated CoP (211) surface along the alternating pathway.

Table S1. Comparison of electrocatalytic NRR performance for C18@CoP/TM with other

 electrocatalysts under ambient conditions.

Catalyst	Electrolyte	NH ₃ yield	FE (%)	Ref.
C18@CoP/TM	0.1M Na ₂ SO ₄	$1.44 \times 10^{-10} \text{ mol s}^{-1} \text{ cm}^{-2}$	14.03	This work
CoP ₃	0.1 M Na2SO4	$3.61 \times 10^{-11} \text{ mol s}^{-1} \text{ cm}^{-2}$	11.94	10
CoFe ₂ O ₄	0.1 M Na ₂ SO ₄	$4.2 \times 10^{-11} \text{ mol s}^{-1} \text{ cm}^{-2}$	6.2	11
Co@NC	0.1 M Na ₂ SO ₄	$1.57 \times 10^{-10} \text{ mol s}^{-1} \text{ cm}^{-2}$	21.79	12
Al-Co ₃ O ₄ /NF	0.1 M KOH	$6.48 \times 10^{-11} \text{ mol s}^{-1} \text{ cm}^{-2}$	6.25	13
Ni ₁₂ P ₅ /FeP ₄	0.1 M Na ₂ SO ₄	$3.08 \times 10^{-10} \text{ mol s}^{-1} \text{ cm}^{-2}$	39.9	14
NH ₂ -MIL-88B-Fe	0.1 M Na2SO4	$1.205 \times 10^{-10} \text{ mol s}^{-1} \text{ cm}^{-2}$	12.45	15
MnO _x	0.1 M Na ₂ SO ₄	$1.63 \times 10^{-10} \text{ mol s}^{-1} \text{ cm}^{-2}$	11.4	16
Sn dendrites on Sn foil	0.1 M PBS	$5.66 \times 10^{-11} \text{ mol s}^{-1} \text{ cm}^{-2}$	3.67	17
MoS2	0.1 M Na2SO4	$8.08 \times 10^{-11} \text{ mol s}^{-1} \text{ cm}^{-2}$	1.17	18
CuO/RGO	0.1 M Na ₂ SO ₄	$1.8 \times 10^{-10} \text{ mol s}^{-1} \text{ cm}^{-2}$	3.9	19
LaFeO ₃	2 М КОН	$3.52 \times 10^{-10} \text{ mol s}^{-1} \text{ cm}^{-2}$	1.99	20
P-WO ₃ @TiO ₂	0.1 M Na ₂ SO ₄	$6.54 \times 10^{-10} \text{ mol s}^{-1} \text{ cm}^{-2}$	17.5	21
Bi	0.1 M HCl	$6.89 \times 10^{-11} \text{ mol s}^{-1} \text{ cm}^{-2}$	10.26	22
d-TiO ₂ /TM	0.1 M HCl	$1.24 \times 10^{-10} \text{ mol s}^{-1} \text{ cm}^{-2}$	9.17	23
Ti ³⁺ -TiO _{2-x}	0.1 M Na ₂ SO ₄	$3.51 \times 10^{-11} \text{ mol s}^{-1} \text{ cm}^{-2}$	14.62	24
TiN-PE	0.1 M Na ₂ SO ₄	$3.32 \times 10^{-10} \text{ mol s}^{-1} \text{ cm}^{-2}$	9.1	25

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