Electronic Supplementary Information

Experimental section

Materials: anhydrous ferric chloride (FeCl₃), ammonium chloride (NH₄Cl), anhydrous lithium perchlorate (LiClO₄), potassium perchlorate (KClO₄), sodium perchiorate (NaClO₄), ammonium chloride (NH₄Cl), hydrazine hydrate (N₂H₄·H₂O), sodium hypochlorite (NaClO), sodium hydroxide (NaOH), sodium salicylate (C₇H₅O₃Na), sodium sulfate (Na₂SO₄), hydrochloric acid (HCl), ethanol (CH₃CH₂OH), and carbon paper were bought from Beijing Chemical Corporation. Para-(dimethylamino) benzaldehyde (C₉H₁₁NO), sodium nitroferricyanide (III) dihydrate (Na₂Fe(CN)₅NO·2H₂O), and Nafion were purchased from Aladdin Ltd. (Shanghai, China). The water used throughout all experiments was purified through a Millipore system.

Preparation of β*-FeOOH:* 5.406 g FeCl₃ 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. The autoclave was heated to 120 °C, and kept at that temperature for 12 h. After cooling to room temperature, the resulting precipitates were washed several times with eionized water and ethanol. The sample was then dried at 80 °C for 6 h and grounded to obtain homogeneous β-FeOOH.

Preparation of \beta-FeOOH/CP: Carbon paper (CP) was cleaned via brief sonication with ethanol and water for several times. To prepare the β -FeOOH/CP, 10 mg β -FeOOH and 40 μ L 5 wt% Nafion solution were dispersed in 960 μ L water/ethanol (V : V = 1 : 3) followed by 1-h sonication to form a homogeneous ink. 20 μ L ink was loaded onto a CP (1 × 1 cm²) and dried under ambient condition.

Characterizations: XRD patterns were obtained from a Shimazu XRD-6100 diffractometer with Cu Kα radiation (40 kV, 30 mA) of wavelength 0.154 nm (Japan). SEM images were collected from the tungsten lamp-equipped SU3500 scanning electron microscope at an accelerating voltage of 20 kV (HITACHI, Japan). TEM images were obtained from a Zeiss Libra 200FE transmission electron microscope 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 were measured on SHIMADZU UV-1800 ultraviolet-visible (UV-Vis) spectrophotometer. A gas chromatograph (SHIMADZU, GC-2014C) equipped with MolSieve 5A column and Ar carrier gas was used for H₂ quantifications. Gas-phase product was sampled every 1000 s using a gas-tight syringe (Hamilton). ¹H nuclear magnetic resonance (NMR) spectra were collected on a superconducting-magnet NMR spectrometer (Bruker AVANCE III HD 500 MHz) and dimethyl sulphoxide was used as an internal to calibrate the chemical shifts in the spectra.

Electrochemical measurements: Electrochemical measurements were performed with a CHI 660E electrochemical analyzer (CH Instruments, Inc., Shanghai) using a standard three-electrode system using β -FeOOH/CP as the working electrode, graphite rod as the counter electrode, and saturated Ag/AgCl electrode as the reference electrode. In all measurements, saturated Ag/AgCl electrode was calibrated with respect to reversible hydrogen electrode as following: in 0.5 M LiClO₄ aqueous solution, E(RHE) = E(Ag/AgCl) + 0.059 × pH + 0.197 V, E(RHE) = E(Hg/Hg₂SO₄) + 0.059 × pH + 0.616 V. All experiments were carried out at room temperature. For N₂ reduction experiments, the 0.5 M LiClO₄ electrolyte was purged with N₂ for 30 min before the measurement. Potentiostatic test was conducted in N₂-saturated 0.5 M LiClO₄ solution in a two-compartment cell, which was separated by Nafion 211 membrane.

Determination of NH_3 : The produced NH_3 was detected with indophenol blue by ultraviolet spectroscopy.¹ In detail, 4 mL electrolyte was obtained from the cathodic chamber and mixed with 50 µL oxidizing solution containing NaClO (ρ Cl = 4 ~ 4.9) and NaOH (0.75 M), 500 µL coloring solution containing 0.4 M C₇H₆O₃ and 0.32 M NaOH, and 50 µL catalyst solution (1 wt% Na₂[Fe(CN)₅NO]) for 2 h. Absorbance measurements were performed at λ = 650 nm. The concentration-absorbance curve was calibrated using standard NH₄⁺ solution with a serious of concentrations. The fitting curve (y = 0.388x + 0.017, R² = 0.999) shows good linear relation of absorbance value with NH₄⁺ concentration. *Determination of* N_2H_4 : The N₂H₄ present in the electrolyte was determined by the method of Watt and Chrisp.² The mixture of C₉H₁₁NO (5.99 g), HCl (30 mL), and C₂H₅OH (300 mL) was used as a color reagent. In detail, 5 mL electrolyte was removed from the electrochemical reaction vessel, and added into 5 mL above prepared color reagent and stirring 10 min at room temperature. Moreover, the absorbance of the resulting solution was measured at a wavelength of 455 nm. The concentration absorbance curves were calibrated using standard N₂H₄ solution with a series of concentrations. The fitting curve (y = 0.649x + 0.041, R² = 0.999) shows good linear relation of absorbance value with N₂H₄ concentration.

*Calculations of NH*₃ *formation rate and FE:* NH₃ formation rate was calculated using the following equation:

NH₃ formation rate = $[NH_4^+] \times V/(m_{cat.} \times t)$

FE was calculated according to following equation:

 $FE = 3 \times F \times [NH_4^+] \times V/(18 \times Q)$

Where $[NH_4^+]$ is the measured NH_4^+ concentration; V is the volume of the cathodic reaction electrolyte; t is the potential applied time; $m_{cat.}$ is the loaded quality of catalyst; F is the Faraday constant; and Q is the quantity of charge in Coulombs.

FE for H₂ was calculated according to following equation:

 $FE = 2 \times F \times n/Q$

Where F is the Faraday constant; n is the actually produced H_2 (mol), and Q is the quantity of charge in Coulombs.

Calculation Details: First-principles calculations were carried out with the generalized gradient approximation (GGA)³ in the form of the Perdew, Burke, and Ernzerhof (PBE)⁴ exchange-correlation functional, as implemented in the Dmol package.⁵ Geometry optimization was performed using a five atom layers FeOOH (110) surface with 20 Å vacuum space to avoid the interaction form nearby layers. All atoms were fully relaxed with the convergence criterion set to be 10⁻⁵ Ha, and 0.02 eV/A° was adopted for the total energy calculations. The Brillouin zone integration was set to $5 \times 1 \times 1$ Γ -centred Monkhorst-Pack k-point meshes in geometry optimization. Frequencies of each complex were calculated after geometry

optimization, and the free energy were defined as follows:

$$\triangle G = \triangle E + \triangle ZPE - T \triangle S + \triangle G_u$$

where $\triangle E$, $\triangle ZPE$, and T $\triangle S$ are the adsorption energy, zero point energy difference, the entropy difference between the adsorbed state and the gas phase, respectively; T is the temperature (298.15 K), $\triangle G_U = -neU$, where U is the electrode potential with respect to the normal hydrogen electrode, and *n* is the number of transferred charge. K). The N₂ adsorption energy is defined as: $E_{ads} = E_{N^2/substrate} - E_{substrate} - E_{N^2}$.



Fig. S1. XPS spectrum of β -FeOOH.



Fig. S2. (a) UV-Vis absorption spectra of indophenol assays with NH_4^+ concentrations after incubated for 2 h at room temperature. (b) Calibration curve used for calculation of NH_4^+ concentrations.



Fig. S3. (a) UV-Vis absorption spectra of various N_2H_4 concentrations after incubated for 10 min at room temperature. (b) Calibration curve used for calculation of N_2H_4 concentrations.



Fig. S4. (a) Amounts of H_2 from gas chromatography (GC) data of the gas from the headspace of the cell for NRR on the β -FeOOH/CP catalyst in N₂-saturated 0.5 M LiClO₄ at various potentials. (b) The calculated FEs of HER.



Fig. S5. UV-Vis absorption spectra of electrolytes stained with para-(dimethylamino) benzaldehyde indicator before and after 2 h electrolysis.



Fig. S6. UV-Vis absorption spectra of the electrolyte stained with indophenol indicator after charging at -0.70 V for 2 h at different electrochemical conditions.



Fig. S7. The NH_3 yields and FEs at -0.70 V with alternating 2-h cycles between N_2 -saturated and Ar-saturated electrolytes.



Fig. S8. ¹H nuclear magnetic resonance spectrum for the product using ${}^{15}N_2$ as feeding gas. The spectrum for ${}^{15}NH_4^+$ standard sample is also shown.



Fig. S9. Calibration curve used for calculation of NH_4^+ concentrations in 0.5 M NaClO₄.



Fig. S10. Calibration curve used for calculation of NH_4^+ concentrations in 0.5 M KClO₄.



Fig. S11. FEs and NH_3 yields at -0.70 V with different reference electrodes.



Fig. S12. SEM images of β -FeOOH after NRR test.



Fig. S13. XRD pattern of β -FeOOH after NRR test.



Table S1. Comparison of the electrocatalytic NRR performance of β -FeOOH with other aqueous-based NRR electrocatalysts at room temperature.

Catalyst	Electrolyte	NH ₃ yield	FE	Ref.
β-FeOOH	0.5 M LiClO ₄	23.32 μ g h ⁻¹ mg ⁻¹ _{cat.}	6.7%	This work
Fe ₂ O ₃ -CNT	KHCO ₃	$0.22 \ \mu g \ h^{-1} \ cm^{-2}$	0.15%	6
γ-Fe ₂ O ₃	0.1 M KOH	$0.212 \ \mu g \ h^{-1} \ mg^{-1}_{cat.}$	1.9%	7
Fe ₃ O ₄ /Ti	0.1 M Na ₂ SO ₄	$3.63 \ \mu g \ h^{-1} \ cm^{-2}$	2.6%	8
PEBCD/C	0.5 M Li ₂ SO ₄	$1.58 \ \mu g \ h^{-1} \ cm^{-2}$	2.91%	9
CNS	0.25 M LiClO ₄	97.18 μg h ⁻¹ cm ⁻²	11.56%	10
Mo nanofilm	0.01 M H ₂ SO ₄	$1.89 \ \mu g \ h^{-1} \ cm^{-2}$	0.72%	11
N-doped nanocarbon	0.05 M H ₂ SO ₄	27.2 μg h ⁻¹ mg ⁻¹ _{cat.}	1.42%	12
MoS ₂ /CC	0.1 M Na ₂ SO ₄	4.94 μ g h ⁻¹ cm ⁻²	1.17%	13
Au nanorods	0.1 M KOH	6.042 μg h ⁻¹ mg ⁻¹ _{cat.}	4%	14
Bi ₄ V ₂ O ₁₁ /CeO ₂	0.1 M HCl	23.21 μ g h ⁻¹ mg ⁻¹ _{cat.}	10.16%	15

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