Electronic Supplementary Information

Experimental section

Materials: N₂H₄·H₂O, HNO₃, HCl, and C₂H₅OH were purchased from Chengdu Kelong Chemical Reagent Factory. Sodium salicylate (C₇H₆O₃Na), ammonium chloride (NH₄Cl), *p*-dimethylaminobenzaldehyde (C₉H₁₁NO), sodium nitroferricyanide dihydrate (C₅FeN₆Na₂O·2H₂O), sodium hypochlorite solution (NaClO), red phosphorus and ferric trichloride hexahydrate (FeCl₃·6H₂O) were purchased from Beijing Chemical Corp (China). All the reagents were used as received without further purification. and carbon paper were bought from Beijing Chemical Corporation. The ultrapure water was purified through a Millipore system used throughout all experiments.

*Preparation of FeP*₂-*rGO:* First, a given amount of FeCl₃·6H₂O (2.7 g) was added in 40 mL aqueous solution. After continuously stirring for 30 min, the solution was transferred to a 50 mL Teflon-lined stainless-steel autoclave, sealed and heated at 120 °C and kept at that temperature for 12 h. The product was washed with deionized water and ethanol for several times, dried in vacuum at 60 °C for 3 h to obtain the FeOOH. Second, 40 mg rGO and 20 mg FeOOH dissolved in 40.0 mL water by ultrasonication, and then collected by centrifugation, washed with ultrapure water and dried under vacuum at 40 °C overnight to obtain the FeOOH-rGO. Third, the FeOOH-rGO was annealed in Ar gas at 450 °C for 3 h with a heating rate of 3 °C min⁻¹ to obtain the Fe₂O₃-rGO. Finally, a total weight of 200 mg mixture which the molar ratio of Fe₂O₃-rGO: red P was 1:4. After vacuum sealing, the silica tube were annealing at 600 °C in a muffle furnace for 2 h. The FeP₂-rGO was prepared well. FeP-rGO as one control catalyst can be obtained by decreasing the amount of red P (Fe₂O₃-rGO: red P = 1:2), under otherwise identical conditions for FeP₂-rGO preparation.

Characterizations: XRD patterns were recorded using a LabX XRD-6100 X-ray diffractometer, with a Cu Kα radiation (40 kV, 30 mA) of wavelength 0.154 nm (SHIMADZU, Japan). SEM measurements were carried out on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. TEM images were collected on a Zeiss Libra 200FE transmission electron microscope operated at 200 kV. XPS measurements were performed on an ESCALABMK II X-ray photoelectron

spectrometer with the exciting source of Mg. The ion chromatography data were collected on Metrohm 940 Professional IC Vario.

Electrochemical measurements: The N₂ reduction experiments were carried out in a two-compartment cell under ambient condition, which was separated by Nafion 117 membrane. The membrane was treated in H_2O_2 (5%) aqueous solution at 80 °C for 1 h and dipped in 0.1 M H₂SO₄ at 80 °C for another 1 h. And finally, the membrane was treated in ultrapure water at 80 °C for 6 h. The electrochemical measurements were conducted on a CHI660E electrochemical analyzer (CH Instruments, China) in a typical three-electrode setup with an electrolyte solution of 0.5 M LiClO₄ (40 mL), graphite rod as the counter electrode and Ag/AgCl (filled with saturated KCl solution) as the reference electrode. The potentials reported in this work were converted to RHE scale via calibration with the following equation: E (vs RHE) = E (vs Ag/AgCl) + 0.197 + 0.059 \times pH. For N₂ reduction experiments, the electrolyte solution was bubbled with N₂ for 30 min before the measurement. To ensure gas purity, a saturator filled with 0.05 M $H_2SO_4^{1}$ is used to remove possible NH₃ or NO_x impurities in the inlet gas. 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 3600 s using a gas-tight syringe (Hamilton).

Determination of NH₃: Concentration of produced NH₃ was determined by spectrophotometry measurement with salicylic acid². In detail, 4 mL of post-tested solution was got from the electrochemical reaction vessel. Then 50 µL of NaClO (4.5%) and NaOH (0.75 M), 500 µL of C₇H₅O₃Na (0.4 M) and NaOH (0.32 M) and 50 µL of 1 wt% Na₂Fe(CN)₅NO·2H₂O were added into the above solution. Absorbance measurements were performed after 1 h in dark. Absorbance measurements were performed at $\lambda = 655$ nm. The concentration-absorbance curve was calibrated using standard NH₄⁺ solution with a serious of concentrations. The fitting curve (y = 0.397x + 0.02, R² = 0.999) shows good linear relation of absorbance value with NH₄⁺ concentration by three times independent calibrations.

Determination of N_2H_4 : N_2H_4 in the electrolyte was estimated by the method of Watt and Chrisp.³ A mixed solution of C₉H₁₁NO (5.99 g), HCl (concentrated, 30 mL) and ethanol (300 mL) was used as a color reagent. Typically, 5 mL electrolyte was removed from the cathodic chamber, after that, added into 5 mL above prepared color reagent and stirring 10 min at room temperature. The absorbance of the resulting

solution was measured at 455 nm. The concentration absorbance curves were calibrated using standard N_2H_4 solution with a series of concentrations. The fitting curve shows good linear relation of the absorbance with N_2H_4 concentration (y = 0.386x + 0.055, R² = 0.999) by three times independent calibrations.

Determination of NH_3 *yield and* FE: The FE for N₂ reduction was defined as the amount of electric charge used for synthesizing NH₃ divided the total charge passed through the electrodes during the electrolysis. The total amount of NH₃ produced was measured using colorimetric methods. NH₃ yield was calculated using the following equation:

$$NH_3$$
 yield = $c_{NH3} \times V / m_{cat.} \times t$

Assuming three electrons were needed to produce one NH₃ molecule, the FE could be calculated as follows:

$$FE = 3F \times c_{NH3} \times V / 17 \times Q$$

Where F is the Faraday constant, c_{NH3} is the measured NH_3 concentration, V is the volume of the electrolyte in the cathodic chamber, Q is the total quantity of applied electricity, t is the reduction time and $m_{cat.}$ is the loaded mass of catalyst on carbon paper.

DFT calculation details: Spin-polarized DFT calculations were performed by using the plane wave-based Vienna ab initio simulation package (VASP).^{4,5} The generalized gradient approximation method with Perdew-Burke-Ernzerhof (PBE) functional was used to describe the exchange-correlation interaction among electrons.⁶ The van der Waals (vdW) correction with the Grimme approach (DFT-D3) was included in the interaction between single molecule/atoms and substrates.⁷ The energy cutoff for the plane wave-basis expansion was set to 500 eV and the atomic relaxation was continued until the forces acting on atoms were smaller than 0.01 eV Å⁻¹. The FeP (211) and FeP₂ (101) surfaces were modeled using 2×2 and 3×3 slabs, and are separated by 15 Å of vacuum. The Brillouin zone was sampled with $3 \times 3 \times 1$ Gamma-center k-point mesh, and the electronic states were smeared using the Fermi scheme with a broadening width of 0.1 eV.

The free energies of the reaction intermediates were obtained by $\Delta G = \Delta Eads + \Delta ZPE - T\Delta S + \Delta G(U) + \Delta G(pH)$, where $\Delta Eads$ is the adsorption energy, ZPE is the zero point energy and S is the entropy at 298 K. The effect of a bias was included in calculating the free energy change of elementary reactions involving transfer of

electrons by adding $\Delta G(U) = -neU$, where n is number of electrons transferred and U is the electrode potential.⁸ In our calculations, we used U = -0.40 V (vs. RHE). $\Delta G(pH) = -kBTln10 \times pH$, where kB is the Boltzmann constant, and pH = 7 for electrolyte. In this study, the entropies of molecules in the gas phase are obtained from the literature.⁹



Fig. S1. (a) XRD pattern and (b) TEM image for rGO.



Fig. S2. EDX spectrum of Fe₂-rGO.



Fig. S3. XRD pattern for FeP-rGO.



Fig. S4. (a) TEM and (b) HRTEM images of FeP-rGO. (c) STEM and corresponding EDX elemental mapping images of Fe, P, and C elements for FeP-rGO.



Fig. S5. EDX spectrum of FeP-rGO.



Fig. S6. XPS spectra in the (a) Fe 2p and (b) P 2p regions for FeP-rGO.



Fig. S7. (a) UV-Vis absorption spectra of indophenol assays with NH₃ concentrations after incubated for 1 h at room temperature. (b) Calibration curve used for calculation of NH₃ concentrations.



Fig. S8. (a) UV-Vis absorption spectra of N_2H_4 concentrations after incubated for 10 min at room temperature. (b) Calibration curve used for calculation of N_2H_4 concentrations.



Fig. S9. UV-Vis absorption spectra of the electrolytes colored with indophenol indicator using FeP_2 -rGO/CP.



Fig. S10. (a) Ion chromatograms of the standard solution with NH_4^+ concentrations in 0.5 M LiClO₄. (b) Calibration curve used for estimation of NH_4^+ . (c) Ion chromatograms of the electrolytes at a series of potentials for 2 h using FeP₂-rGO/CP. (d) NH_3 yields and FEs for FeP₂-rGO/CP at a series of potentials for 2 h determined by ion chromatography analysis.



Fig. S11. UV-Vis absorption spectra of electrolytes stained with para-(dimethylamino) benzaldehyde indicator before and after 2 h electrolysis using FeP_2 rGO/CP.



Fig. S12. UV-Vis absorption spectra of the electrolytes colored with indophenol indicator using FeP_2 -rGO/CP, rGO/CP, and bare CP at -0.40 V for 2 h.



Fig. S13. (a) Time-dependent current density curves of FeP-rGO/CP at various potentials for 2 h. (b) UV-Vis absorption spectra of the electrolytes colored with indophenol indicator using FeP-rGO/CP. (c) NH₃ yields and FEs of FeP-rGO/CP for NRR at different potentials.



Fig. S14. NH₃ yields and FEs at -0.40 V for 2 h over FeP₂-rGO/CP and FeP₂/CP.



Fig. S15. Time-dependent current density curves of FeP₂-rGO/CP at -0.40 V for 8 times.



Fig. S16. (a) Time-dependent current density curve over post-NRR FeP₂-rGO/CP at - 0.40 V in fresh N₂-saturated electrolyte. (b) UV-Vis absorption spectrum of the electrolytes colored with indophenol indicator using post-NRR FeP₂-rGO/CP.



Fig. S17. XRD pattern of FeP₂-rGO after stability test.



Fig. S18. TEM image of FeP₂-rGO after stability test.



Fig. S19. Adsorption structures and energies of N_2 molecule on FeP (211) surface. N, blue.



Fig. S20. (a) Free energy diagram of HER on FeP (211) and FeP₂ (101) surfaces at U = -0.40 V. (b) Atom configures of HER on FeP (211) and FeP₂ (101) surfaces. Free energy diagrams of NRR on FeP (211)-1 site (c) and FeP₂ (101) surface (d) at U = -0.40 V. Fe, brown; P, purple.



Fig. S21. Atom configurations of NRR on FeP (211)-1 site.







Fig. S23. P vacancy on FeP₂(101) surface.



Fig. S24. Number of active site on FeP (211) and FeP₂ (101) surfaces. Cross represents active site.



Fig. S25. Density of states of active site on FeP (211)-1 and FeP₂ (101) surfaces.

Catalyst	Electrolyte	NH ₃ yield	FE (%)	Ref.
FeP ₂ -rGO	0.5 M LiClO 4	35.26 µg h ⁻¹ mg ⁻¹ _{cat.}	21.99	This work
FeP-rGO		17.13 μ g h ⁻¹ mg ⁻¹ _{cat.}	8.57	
Fe ₂ O ₃ -CNT	KHCO ₃	$0.22 \ \mu g \ h^{-1} \ cm^{-2}$	0.15	10
30% Fe ₂ O ₃ -CNT	0.5 M KOH	$0.52~\mu g{\cdot}h^{-1}{\cdot}cm^{-2}$	0.164	11
Fe ₂ O ₃ nanorod	0.1 M Na ₂ SO ₄	$15.9 \ \mu g \ h^{-1} \ mg^{-1}_{cat.}$	0.94	12
γ-Fe ₂ O ₃	0.1 M KOH	$0.212 \ \mu g \ h^{-1} \ m g^{-1}{}_{cat.}$	1.9	13
Fe ₃ O ₄ /Ti	0.1 M Na ₂ SO ₄	$3.42 \ \mu g \ h^{-1} \ cm^{-2}$	2.6	14
o-Fe ₂ O ₃ -air	0.1 M KOH	$0.46 \ \mu g \cdot h^{-1} \cdot cm^{-2}$	6.04	15
rGO/Fe@Fe ₃ O ₄	0.2 M NaHCO ₃	$7.96 \ \mu g \ h^{-1} \ cm^{-2}$	6.25	16
OV-rich a-Fe ₂ O ₃	0.1 M KOH	$32.13 \ \mu g \ h^{-1} \ m g^{-1}_{cat.}$	6.63	17
β-FeOOH	0.5 M LiClO ₄	23.32 $\mu g h^{-1} m g^{-1}_{cat.}$	6.7	18
p-Fe ₂ O ₃ /CC	0.1 M Na ₂ SO ₄	$13.56 \ \mu g \ h^{-1} \ m g^{-1}_{cat.}$	7.69	19
Fe/Fe ₃ O ₄	0.1 M PBS	$0.19 \ \mu g \ h^{-1} \ cm^{-2}$	8.29	20
FeO(OH,F)	0.5 M LiClO ₄	42.38 $\mu g h^{-1} m g^{-1}{}_{cat.}$	9.02	21
Fe_3S_4	0.1 M HCl	$75.4 \text{ mg } h^{-1} \text{ mg}^{-1}_{\text{cat.}}$	6.45	22
Fe _{SA} –N–C	0.1 M KOH	$7.48 \ \mu g \ h^{-1} \ mg^{-1}_{cat.}$	56.55	23

Table S1. Comparison of the catalytic performances of FeP₂-rGO with other Fe-based NRR catalysts at ambient conditions.

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