

Electrochemical N₂ fixation to NH₃ under ambient conditions: porous LiFe₅O₈ nanoparticle-reduced graphene oxide as a highly efficient and selective catalyst

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Experimental section

Materials: GO, Lithium carbonate (Li_2CO_3), iron oxide (Fe_2O_3), sodium sulfate (Na_2SO_4), lithium sulfate (Li_2SO_4), methyl mercaptoacetate, ammonium chloride (NH_4Cl), hydrazine hydrate ($\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$), salicylic acid ($\text{C}_7\text{H}_6\text{O}_3$), sodium citrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$), sodium hypochlorite (NaClO), sodium hydroxide (NaOH), hydrochloric acid (HCl), ethanol ($\text{CH}_3\text{CH}_2\text{OH}$), sodium monophosphate (NaH_2PO_2) and carbon paper (CP) were bought from Beijing Chemical Corporation. Para-(dimethylamino) benzaldehyde ($\text{C}_9\text{H}_{11}\text{NO}$), sodium nitroferricyanide (III) dihydrate ($\text{Na}_2\text{Fe}(\text{CN})_5\text{NO}\cdot 2\text{H}_2\text{O}$), and Nafion were purchased from Aladdin Ltd. (Shanghai, China). The water used throughout all experiments was purified through a Millipore system. The water used throughout all experiments was purified through a Millipore system. All chemicals were used as received without further purification.

Preparation of LiFe_5O_8 -rGO: The preparation process of the porous LiFe_5O_8 -rGO composite is as follows: 0.1 g of LiFe_5O_8 particles and a certain amount of freeze-dried GO were dissolved in DMF using ultrasonication for 60 min and subsequently heated at 80 °C using a water bath. Then, 12.5 mL of hydrazine and 5 mL of methyl mercaptoacetate were added dropwise, while N_2 protection continued. The chemical reactions were stopped by cold ethanol after etching for 45 min. The obtained black powder was separated through centrifugation and washed with deionized water and ethanol.

Preparation of LiFe_5O_8 -rGO electrode: 10 mg LiFe_5O_8 -rGO powders and 40 μL of Nafion solution (5 wt%) were dispersed in 960 μL mixed solution containing 720 μL ethanol and 240 μL H_2O by 2 h sonication to form a homogeneous ink. Then, 10 μL LiFe_5O_8 -rGO was loaded on a CP with area of 1 x 1 cm^2 and dried under ambient condition.

Characterizations: XRD patterns were obtained from a Shimadzu XRD-6100 diffractometer with $\text{Cu K}\alpha$ 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 UV-Vis absorbance spectra were measured on a SHIMADZU UV-1800 UV-Vis spectrophotometer. energy dispersive X-ray analysis (EDX), and the Brunner–Emmet–Teller method (BET, ASAP 2020, Micromeritics).

Electrochemical measurements: Before NRR measures, the Nafion proton exchange film was pretreated by heating in 3% H₂O₂ solution, 0.5 M H₂SO₄ and ultrapure water at 80 °C for 1.5 h, respectively. Electrochemical measurements were carried out on a CHI 660E electrochemical analyzer (CHI Instruments, Inc., Shanghai) in a three-electrode system using Ti₃C₂T_x/CP or CP as working electrode, Ag/AgCl as reference electrode, and graphite rod as counter electrode. All experiments were performed at ambient conditions. For N₂ reduction reaction experiments, the HCl electrolyte (0.1 M) was bubbled with high-purity N₂ (99.999%) for 30 min before measurement. All potentials reported in this work were calibrated to RHE, using the following equation:

$$E \text{ (RHE)} = E \text{ (Ag/AgCl)} + (0.197 + 0.059 \text{ pH}) \text{ V}$$

Determination of NH₃: NH₃ concentration was determined by the indophenol blue method.¹ The method contains the following details: 2 mL HCl post-NRR electrolyte was collected from the cathodic chamber. Then, 2 mL of 1 M NaOH solution containing 5% salicylic acid and 5% sodium citrate was added into this solution. After mixing and standing at room temperature for 2 h, the UV-Vis absorption spectrum was measured at a wavelength of 655 nm. The concentration-absorbance curves were calibrated using standard NH₄Cl solution (0.1 HCl solution as mother solution) with a series of concentrations. The fitting curve ($y = 0.475x + 0.066$, $R^2 = 0.999$) shows good linear relation of absorbance value with NH₃ concentration by three times independent calibrations.

Determination of N₂H₄: Concentration of N₂H₄ in the electrolyte was estimated by the method of Watt and Chrisp.² Typically, a mixture solution containing p-C₉H₁₁NO (5.99 g), concentrated HCl (30 mL) and ethanol (300 mL) was used as a color reagent. In detail, 2 mL

electrolyte removed from the cathodic chamber was added into 2 mL above prepared color reagent. After standing the mixture solution at room temperature for 20 min, UV-Vis absorption spectra were measured at a wavelength of 455 nm. The concentration-absorbance curves were calibrated using standard N_2H_4 solutions with a series of concentrations for three independent calibrations.

Calculations of NH_3 yield and FE: NH_3 yield was calculated using the following equations:

$$R_{\text{NH}_3} (\mu\text{g h}^{-1} \text{mg}_{\text{cat.}}^{-1}) = (c_{\text{NH}_3} \times V) / (17 \times t \times m)$$

Where c_{NH_3} ($\mu\text{g mL}^{-1}$) is the measured NH_3 concentration; V (mL) is the volume of electrolyte (in our work 35 mL); t (s or h) is the reaction time; A (cm^2) is the geometric area of the cathode; m (mg) is the mass loading of catalyst on CP.

FE was calculated according to following equation:

$$\text{FE} = 3 \times F \times c_{\text{NH}_3} \times V / (17 \times Q) \times 100\%$$

Where F is Faraday constant (96500 C mol^{-1}); Q (C) is the quantity of applied electricity.

Computational details: To gain more in-depth insights into the mechanism for nitrogen reduction reaction (NRR) on $\text{Ti}_3\text{C}_2\text{T}_x$ ($X = \text{F}, \text{OH}$) nanosheet, density functional theory (DFT) calculations are carried out using the Vienna ab initio simulation package (VASP). Exchange-correlation energy is described by Perdew-Burke-Ernzerhof (PBE) version of the generalized gradient approximation (GGA). The projector-augmented wave (PAW) method is used to represent the core-valence electron interaction. The calculations also adopt long-range dispersion interactions (DFT-D3 (BJ)) A Hubbard U term is introduced to the PBE functional, with $U_{\text{eff}} = 4.2 \text{ eV}$ for Ti on its d orbital. An energy cutoff of 480 eV for basis-set expansion is used. A 2×2 supercell and the corresponding $5 \times 5 \times 1$ k-point mesh are modeled in the calculations. A vacuum region of about 20 Å is set to decouple the periodic replicas. Two F and OH groups attached to the hollow sites between the three neighboring carbon atoms are added on each side of $\text{Ti}_3\text{C}_2\text{T}_x$ monolayer according to previous literatures. A OH group is removed to expose active sites for N_2 adsorption. The force tolerance and total energy for the relaxations are converged to 0.02 eV \AA^{-1} and 10^{-5} eV , respectively. The Gibbs free energy is calculated via the computational hydrogen electrode model proposed by Nørskov et al.³

$$\Delta G = \Delta E + \Delta \text{ZPE} - T\Delta S$$

T and pH value are set to be 298.15K and 0 in this work, respectively. For adsorbates, ZPE and S are determined by vibrational frequencies calculations. For molecules, those are taken from the NIST database.

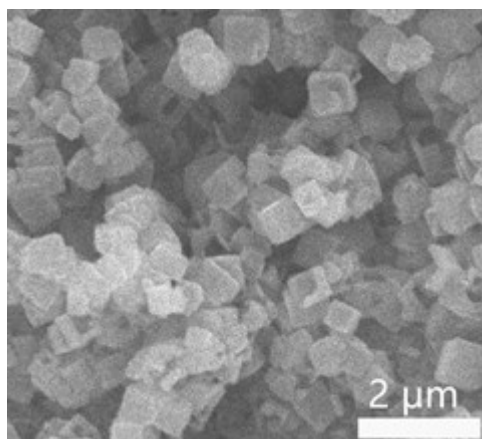


Fig. S1. SEM image of LiFe_5O_8 .

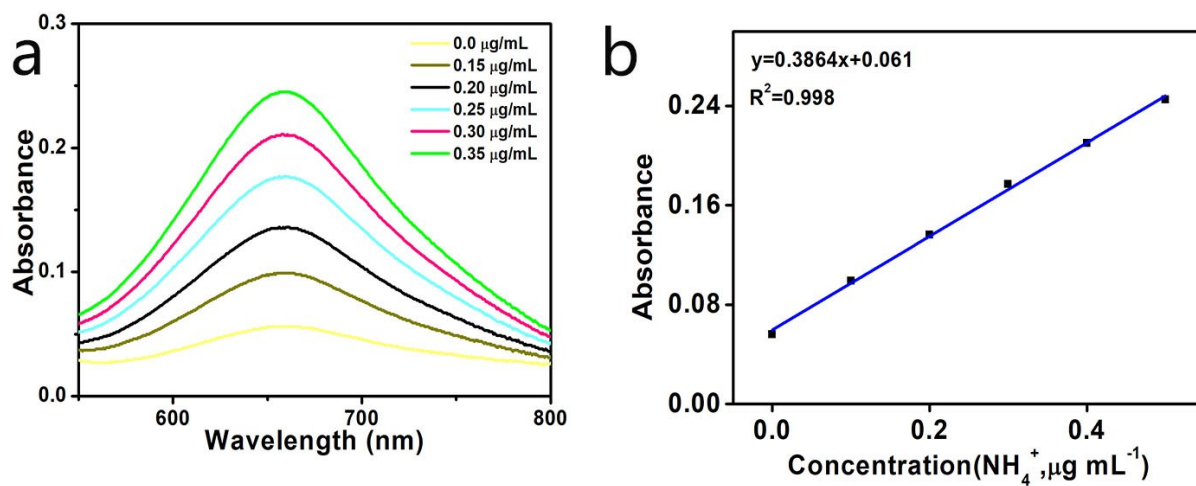


Fig. S2. (a) UV-Vis absorption spectra of indophenol assays with NH_4^+ concentrations after incubated for 2 h at room temperature. (b) Calibration curve used for calculation of NH_4^+ concentrations.

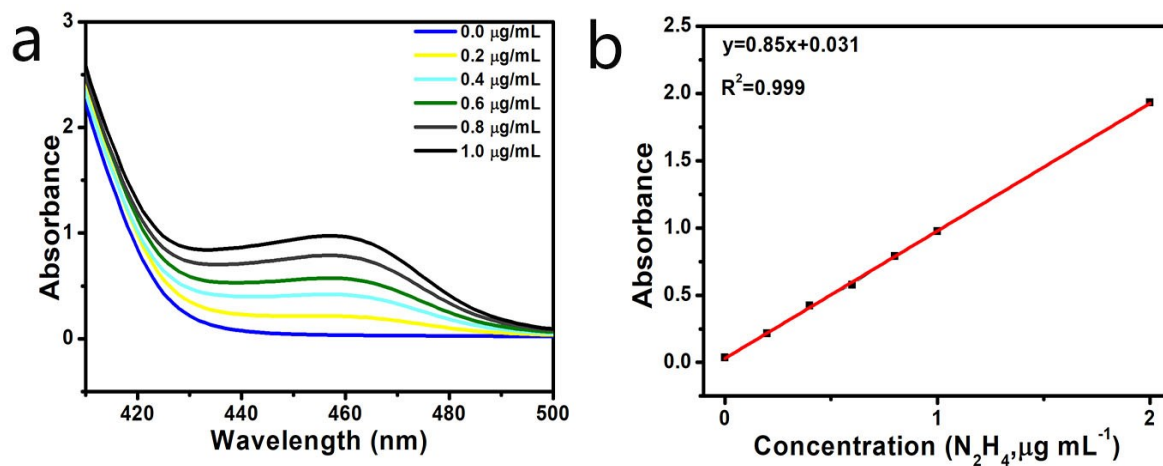


Fig. S3. (a) UV-Vis absorption spectra of various N_2H_4 concentrations after incubated for 10 min at room temperature. (b) Calibration curve used for calculation of N_2H_4 concentrations.

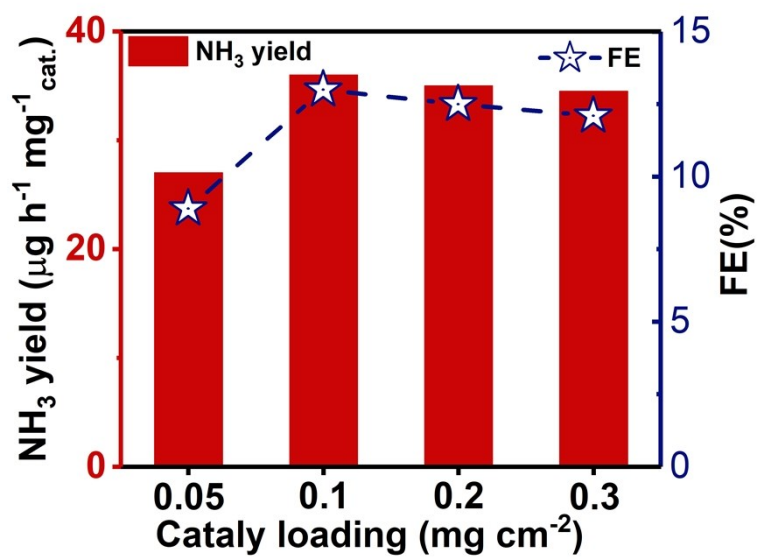


Fig. S4. The NH₃ yields and FEs for LiFe₅O₈/rGO with different catalyst loadings.

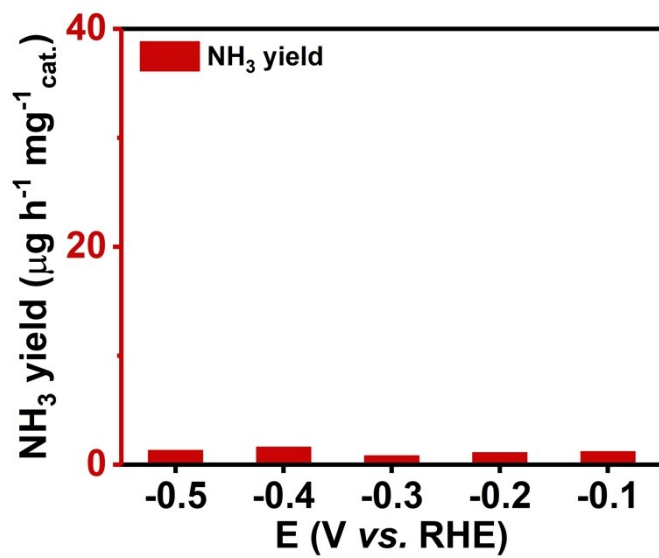


Fig. S5. The amount of NH₃ detected in the Ar-saturated electrolyte at each potential.

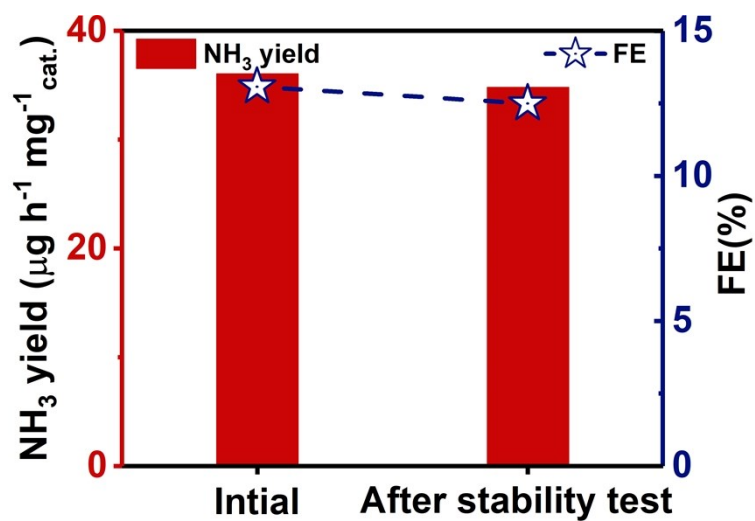


Fig. S6. NH₃ yields and FEs for LiFe₅O₈-rGO/CP after stability test.

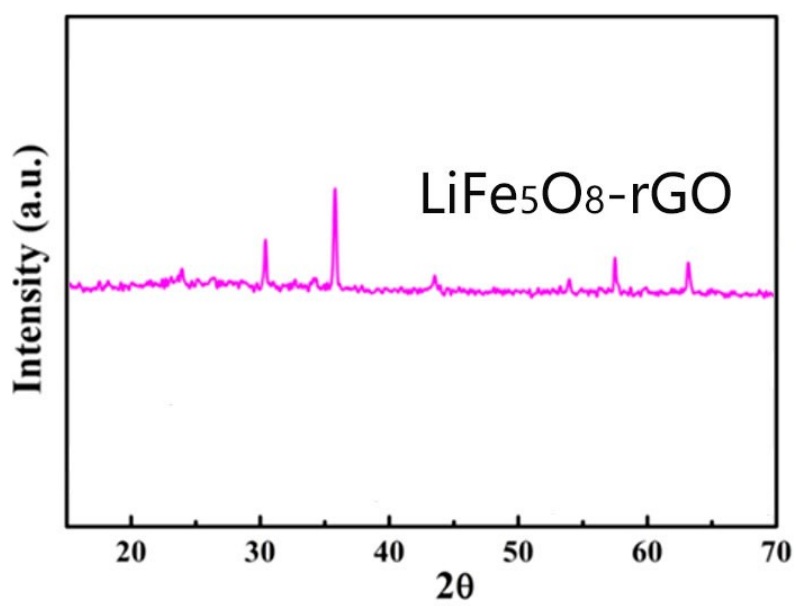


Fig. S7. XRD pattern of LiFe₅O₈-rGO after stability test.

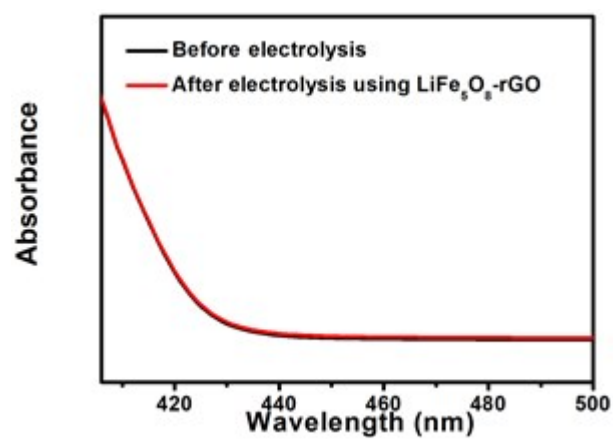


Fig. S8. UV-Vis absorption spectra of the electrolytes estimated by the method of Watt and Chrisp before and after 2 h electrolysis in N₂ atmosphere at -0.2 V.

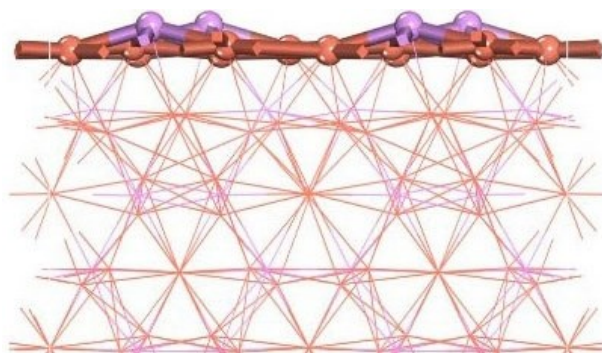


Fig. S9. Side views of the LiFe₅O₈ (111) surface.

Table S1. Comparison of electrocatalytic N₂ reduction performance for LiFe₅O₈-rGO with other aqueous-based electrocatalysts under ambient conditions.

Catalyst	Electrolyte	NH ₃ yield rate ($\mu\text{g h}^{-1} \text{mg}_{\text{cat.}}^{-1}$)	FE (%)	Ref.
LiFe₅O₈-rGO	0.1 M HCl	36.025	13.08	This work
α -Au/CeO _x -RGO	-	8.3	10.1	4
TA-reduced Au/TiO ₂	-	21.4	8.11	5
MoN NA/CC	-	18.42	1.15	6
MoO ₃	-	29.43	1.9	7
VN/TM	-	5.14	2.25	8
Bi ₄ V ₂ O ₁₁ /CeO ₂	-	23.21	1.16	9
Mo ₂ N	-	78.4	4.5	10
NPC	0.05 M H ₂ SO ₄	23.8	1.42	11
CuO/RGO	0.1 M Na ₂ SO ₄	11.02	3.9	12
TiO ₂ -rGO	0.1 M Na ₂ SO ₄	15.13	3.3	13
γ -Fe ₂ O ₃	0.1 M KOH	0.212	1.9	14
Fe ₂ O ₃ nanorods	0.1 M Na ₂ SO ₄	15.9	0.94	15

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