Supporting Information

Experimental Section.

Materials.

Ferric chloride (FeCl₃· $6H_2O$) was purchased from ShangHai D&B Biological Science and Technology Co.Ltd. Tetrabutylammonium fluoride (TBAF) and Sodium sulfate were purchased from Energy Chemical. Pyridine (C₅H₅N), dichloromethane (CH₂Cl₂), N,N-dimethylformamide (DMF), acetone and sodium nitrate was purchased from China National Pharmaceutical Group Chemical Reagent Co. Ltd. The CC was pretreated by sonication sequentially in concentrated nitric acid, deionized water, acetone, ethanol, and deionized water before use. All reagents used were of analytical grade. All reagents used are analytical grade and were used as received without further purification unless otherwise specified.

Synthesis of Hexaethynylbenzene

The synthesis was conducted in a 500 mL three-necked flask under inert atmosphere. Anhydrous tetrahydrofuran (100 mL) and [(trimethylsilyl)acetylene] (27.0 mL) were initially charged into the flask at -15 °C. A solution of n-butyllithium (73.36 mL) was slowly added via dropwise addition while maintaining the temperature below -10 °C, and the reaction was stirred for 15 minutes at this temperature. Anhydrous zinc chloride (25 g) was then introduced in portions, after which the system was gradually warmed to 50 °C and stirred for 0.5 h. Hexabromobenzene (8.42 g) and 100 mL paraxylene were subsequently added, along with 883 mg tetrakis(triphenylphosphine)palladium. The temperature was raised to 80 °C u and maintained for 48 hours with continuous stirring, followed by further heating to 90 °C for 24 hours. After the reaction was cooled, 100 mL of 2 M hydrochloric acid was added, and retained the organic phase after separated. Then dried the organic phase over anhydrous sodium sulfate, and purified through repeated recrystallization using a methanol/dichloromethane solvent system.

Synthesis of CC/GDY.

Graphdiyne (GDY) nanosheet arrays were grown in situ on carbon cloth (CC) fibers via a simple method. The pretreated CC $(3 \times 3 \text{ cm}^2)$ was sandwiched between two copper

foils $(4 \times 4 \text{ cm}^2)$ and immersed in a solution (pyridine: dichloromethane = 1: 19) containing hexaethynylbenzene (0.5 mg/mL). The system was sealed and stored in the dark for 72 hours to induce the in situ growth of GDY. After the completion of the reaction, the obtained samples were washed with 0.1 M HCl, ultrapure water, DMF and acetone , and dried in a vacuum oven at 60°C for at least 6 h.

Synthesis of Fe⁰/GDY.

The zero-valent Fe⁰/GDYNA were fabricated by the electrochemical method with a standard three electrode system, in which the CC/GDY, saturated calomel electrode and carbon rod were used as the working electrode, reference electrode and counter electrode, respectively. Electrodeposition was subsequently performed at a current density of 10 mA cm⁻² for 200 s after immersing the CC/GDY in a 0.5 M H₂SO₄ solution containing 5 mM FeCl₃ for 1 hour. The resulted Fe⁰/GDYNA was carefully washed with 0.5 M H₂SO₄, ultrapure H₂O, then used for catalytic reaction immediately.

Characterizations.

The electron microscopy images were taken with SEM (FEI Apreo SEM), TEM (Talos F200X TEM) and HRTEM. Energy-dispersive X-ray spectroscopy (EDX) were collected with an energy-dispersive X-ray detector in FEI Apreo SEM and Talos F200X TEM. Raman spectra was measured through the LabRAM HR800 spectrometer (473 nm excitation laser source). The surface elemental composition and chemical bonding states of the products were studied with an X-ray photoelectron spectra spectrometer (Nexsa) with Al Ka radiation (λ = 8.34 A) as the excitation source. The contact angle was measured by SL200KS. The ultraviolet-visible (UV-Vis) absorbance spectra were measured on Shimadzu UV-2600.

Electrochemical tests.

Electrochemical tests were performed in an H-type two-compartment cell separated by a membrane using CHI 660E (Shanghai Chenhua, China). In this setup, a threeelectrode system was used with a carbon rod functioned as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode, and the prepared samples directly as the working electrode. The electrolyte for NtRR measurements under neutral conditions consisted of 0.5 M Na₂SO₄ and 0.1 M NaNO₃. Linear sweep voltammetry (LSV) measurements were carried out at a scan rate of 5.0 mV/s, with the electrolyte (35 mL) being stirred at 200 rpm. Chronoamperometry tests were conducted in an Arsaturated 35 mL solution of 0.5 M Na₂SO₄ and 0.1 M NaNO₃. Potentiostatic tests were performed to evaluate the catalyst electrode's performance at potentials of -1.7, -1.8, -1.9, -2.0, and -2.1 V vs. SCE. To investigate performance changes over different reaction times, the electrolyte was sampled and tested at intervals of 1 h, and the yield rate and Faradaic efficiency were calculated over these periods. Cyclic Voltammetry (CV) scans were conducted to determine the double-layer capacity (C_{dl}) within a potential range of 0.055 V to -0.045 V vs. SCE, with increasing scan rates of 5, 10, 15, 20 and 25 mV/s.

Determination of ion concentration.

The ultraviolet-visible (UV-Vis) spectrophotometer was used to detect the ion concentration of post-test electrolytes after diluting to appropriate concentration to match the range of calibration curves. The specific detection methods are as follow:

Quantification of ammonia.

Product ammonia was used indophenol blue method to quantify. Briefly, 2.0 mL diluted electrolyte, 2.0 mL Reagent A, 1.0 mL Reagent B and 200 μ L Reagent C were fully mixed and left-standing for 1 h under dark environment. Finally, the absorbance at 655 nm was measured on the UV-vis spectrophotometer. The calibration curve was obtained by the standard ammonia chloride solution with different know concentration (Figure S4).

Reagent A: 1.0 M NaOH soultion with 5 wt.% sodium salicylate and 5 wt.% potassium sodium tartrate.

Reagent B: 5.0 mL sodium hypochlorite (available chlorine 15%) was diluted with deionized water to 100.0 mL.

Reagent C: sodium nitroferricyanide solution (1 wt.% in deionized water).

Isotope Labeling Experiments

98% Na¹⁴NO₃ was used as the feedstock to perform the nitrate reduction experiments to clarifying the source of ammonia. 0.5 M Na₂SO₄ containing 0.1 M Na¹⁵NO₃ was used as electrolyte. After electrolysis, the ion concentration in electrolyte was determined by ¹H-NMR. In details, 4 mL of electrolyte was mixed with 1 mL of 4 M H_2SO_4 , 2 mg of maleic acid was added as the internal standard. Then 0.5 mL of the above solution was mixed with 50 µL deuterated-DMSO for ¹H-NMR measurements.

Calculation of the yield and Faradaic efficiency.

For nitrate electroreduction, the yield was calculated by the following equation:

 $\text{Yield}_{\text{NH3}} = (c_{\text{NH3}} \times \text{V}) / (t \times \text{S})$

The Faradaic efficiency was defined from the electric charge consumed for synthesizing ammonia and total charge passed through the electrode according to the following equation:

Faradaic efficiency (NH₃) = $(8F \times c_{NH3} \times V) / Q$

where c_{NH3} (µM) is the molar concentration of NH₃ (aq), V (mL) is the volume of electrolyte in the cathode compartment, t (h) is the electrolysis time, S (cm²) is the geometric area of working electrode, F is the Faradaic constant (96485 C mol⁻¹), Q (C) is the total charge passing the electrode.



Fig. S1. SME images of Fe⁰/GDY.



Fig. S2. (a-d) TEM images of (a-b) CC/GDY and (c-d) Fe⁰/GDY.



Fig. S3. Calibration curves for NH_4^+ determination. (a) Absorption spectra of the solutions containing NH_4Cl at different NH_4Cl concentrations. (b) Linear relationship between the absorbance at 655 nm and the NH_4Cl concentration.



Fig. S4. The NH_3 yield rate over electrolyte with and without NO_3^- of Fe⁰/GDY catalysts.



Fig. S5. Chronoamperometry plots of Fe⁰/GDY catalysts at different potentials.

Fig. S6. Cyclic voltammograms (CV) for (a) CC/GDY, (b) Fe^{0}/GDY catalysts at different scan rates from 5 to 25 mV s⁻¹.

Fig. S7. HAADF-STEM images of Fe⁰/GDY after high current density operation.

Catalyst	Electrolyte	NH ₃ yield rate	Reference
Fe ⁰ /GDY	0.1 M NaNO ₃ + 0.5 M Na ₂ SO ₄	202.34 µmol h ⁻¹ cm ⁻²	This work
Fe-MoS ₂	0.1 M NaNO ₃ + 0.1 M Na ₂ SO ₄	$30 \ \mu mol \ h^{-1} \ cm^{-2}$	Adv. Funct. Mater. 2022, 32, 2108316
Fe@CuFeO _x	1000 ppm NO ₃ - + 0.1 M K ₂ SO ₄	116 µmol h ⁻¹ cm ⁻²	Angew. Chem. Int. Ed. 2024, 63, e202406046
Fe-PPy SAC	0.1 M KOH + 0.1 M KNO ₃	$162 \ \mu mol \ h^{-1} \ cm^{-2}$	Energy Environ. Sci. 2021, 14, 3522-3531
Cu/Cu ₂ O	1 M KOH + 0.05 M KNO ₃	$137 \ \mu mol \ h^{-1} \ cm^{-2}$	Angew. Chem. Int. Ed. 2024, 63, e202408382
Ru SA-NC	1.0 M KOH+0.5 M NO ₃ -	$110 \ \mu mol \ h^{-1} \ cm^{-2}$	ACS Nano. 2023, 7, 3483– 3491

Table S1. Comparison of NtRR activity and NH_3 production performance between and Fe⁰/GDY recently-reported electrocatalysts.