

Electron Sponge Effect by Dynamic-regulated Electron Self-flow towards Coupled Electrochemical Ammonia Synthesis

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Electrocatalyst, Nitrogen reduction reaction, Oxygen evolution reaction, Ammonia synthesis, Electron sponge effect

1 Experimental section

1.1 Manufacture of the working electrode and Nafion 115 membrane

Before preparation, the $1 \times 1 \text{ cm}^2$ carbon paper (Toray Paper 090) underwent a sequential immersion in ethanol, 0.05 M sulfuric acid (H_2SO_4), and deionized water,

followed by drying under vacuum conditions at 50 °C for 12 hours. In the fabrication of the working electrode, 5 mg of samples of the electrocatalyst was combined with 960 μL of isopropanol and 40 μL of Nafion solution (5 wt. %), which was then subjected to a two-hour sonication process to achieve a homogenous electrocatalyst ink. Subsequently, 40 μL of the freshly prepared ink was applied onto the pretreated carbon paper, with a mass loading of 0.2 mg cm^{-2} . In this work, the Nafion 115 membrane was initially subjected to a one-hour heating process at 80 °C within a 5 wt. % hydrogen peroxide (H_2O_2) solution, followed by a subsequent one-hour immersion in deionized water at the same temperature. After this, the membrane was treated for 1h in a 0.5 M sulfuric acid solution also at 80 °C, and then it was soaked for another hour in deionized water at an identical temperature.

1.2 Determination of ammonia

Typically, the quantitation of ammonia was achieved through the indophenol blue approach. Specifically, 2 mL of electrolyte after two-hour electrolysis was mixed with 2 mL of a 1 M NaOH solution containing 5 wt.% salicylic acid and 5 wt.% potassium sodium tartrate tetrahydrate ($\text{C}_4\text{H}_4\text{O}_6\text{KNa}\cdot 4\text{H}_2\text{O}$). Subsequently, 1 mL of 0.05 M NaClO solution was added to the above solution, followed by the incorporation of 0.2 mL of 1 wt.% sodium nitroprusside dihydrate ($\text{C}_5\text{FeN}_6\text{Na}_2\text{O}$) solution. The UV-vis absorption spectra of the aforementioned solution were examined after two-hour standing in the darkness. The absorbance at 652 nm of standard solutions containing varying concentrations of NH_4Cl was determined to construct the calibration curves for ammonia. The absorbance-concentration curves ($Y = 0.4105X - 0.0035$ for 0.1 M KOH as electrolyte, and $Y = 0.3969X + 0.0022$ for 0.05 M H_2SO_4 as electrolyte) display a good linear relationship.

1.3 Determination of Hydrazine

The possible byproduct hydrazine was determined through the previously described Watt and Chirsp approach. A combination consisting of 5.99 g of p-dimethylaminobenzaldehyde, 30 mL of concentrated hydrochloric acid, and 300 mL of

ethanol served as the color-developing reagent. 2 mL of the as-prepared color reagent was added to 2 mL of electrolyte after two-hour electrolysis, followed by mixing for 20 minutes in the dark at ambient conditions. The hydrazine absorbance of the resultant electrolyte was calculated to be 460 nm. Solutions of hydrazine hydrate with defined concentrations served as benchmarks for establishing an absolute calibration, exhibiting a pronounced linear correlation between absorbance and N₂H₄ concentration ($Y = 0.6151X + 0.0012$).

1.4 Calculation of ammonia yield rate, Faradic efficiency, and selectivity

The equation below was applied for the computation of NH₃ yield rate (R):

$$R = \frac{CV}{tS} \quad (\text{Equation 1})$$

Where C denotes the concentration of NH₃, V represents the volume of the electrolyte solution, t signifies the duration of the reaction, and S corresponds to the mass of the electrocatalyst loaded. The cumulative ammonia production within the cathodic compartment, anodic section, and the acid trap assembly was employed to determine the comprehensive ammonia yield rate throughout the NRR process.

The Faradic efficiency (η) was calculated through the following equation:

$$\eta = \frac{nFCV}{MQ} \quad (\text{Equation 2})$$

Here, n equals 3, F represents the Faraday constant ($F = 96485 \text{ C/mol}$), C denotes the NH₃ concentration derived from calculations, V signifies the volume of the electrolyte, M is the molar mass of NH₃ ($M = 17 \text{ g/mol}$), and Q indicates the total electrical charge passed through the working electrode during the electrocatalytic process.

The NRR selectivity was calculated by the following formula:

$$\gamma_{\text{NH}_3} = \frac{n_{\text{NH}_3}}{n_{\text{NH}_3} + n_{\text{H}_2}} \quad (\text{Equation 3})$$

γ_{NH_3} is the selectivity of NH₃, n_{NH_3} corresponds to the amount of substance of NH₃ in product, and n_{H_2} is the amount of substance of H₂ in product, which is obtained through gas chromatography(GC).

1.5 In-situ ATR-FTIR measurement

In-situ attenuated total reflectance Fourier-transform infrared (ATR-FTIR) analyses were performed under ambient conditions with a Nicolet iS50 FT-IR spectrometer equipped with a liquid nitrogen-cooled mercury-cadmium-telluride (MCT-B) detector. Electrochemical evaluations were executed using a CHI660E workstation within a conventional three-electrode configuration in an H-type cell, employing a platinum sheet and a saturated KCl-filled Ag/AgCl electrode as the counter and reference electrodes, respectively. 10 μ l of catalyst ink was dropped on a thin gold layer-deposited silicon prism as the working electrode, and then the N₂ flow rate was adjusted to 10 mL min⁻¹ before the test. Subsequently, the background spectrum was obtained, and all the following spectra were conducted by employing this background.

1.6 Isotopic labeling experiments

To ascertain the active origin, an isotopic labeling experiment was conducted using ¹⁵N₂ (99% purity, Shanghai Engineering Research Center of Stable Isotope) as the feeding gas. After electrolysis at -0.2 V, the as-collected electrolyte was concentrated through a rotatory evaporator from 10 mL to 1 mL. Subsequently, 0.1 mL of the as-concentrated electrolyte was mixed with 0.9 mL of d₆-DMSO (99.9% purity, procured from Sigma Aldrich). After that, the above solution was determined through ¹H nuclear magnetic on a Bruker Avance 600 MHz (¹H NMR).

1.7 Computational method

In this work, all calculations were completed based on first principle calculations with CASTEP^[1, 2]. The generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) functionals was used to process the exchange-correlation functionals^[3, 4]. A 450 eV cutoff was reached for plane-wave basis expansion. The total energy and force on each atom had convergence thresholds of 10⁻⁵ eV and 0.02 eV/Å, respectively. A 15 Å vacuum layer was added in the z direction to the slab model to prevent layer interaction. The van der Waals interaction has been investigated using the Grimme dispersion technique^[5]. The entire Gibbs free energy for the whole NRR has been

estimated using $\Delta G = -0.54$ eV to assess the computational setting, which is close to the experimental data (-0.34 eV) under standard conditions.

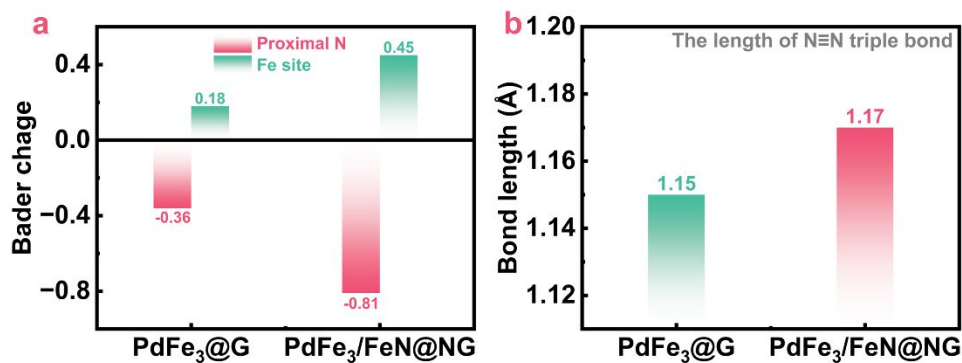


Figure S1. (a) The Bader charge of Fe sites before N₂ adsorption and proximal N from adsorbed N₂, (b) The bond length of N≡N triple bond after adsorption.

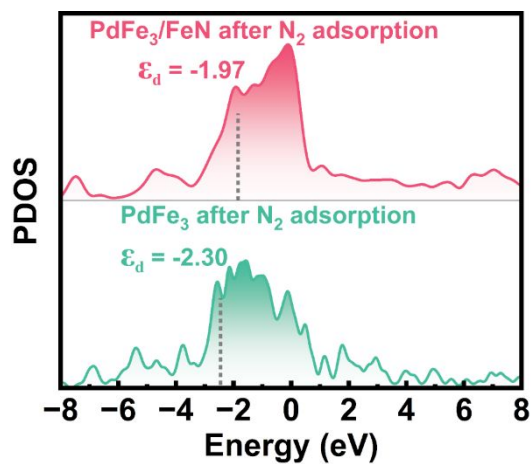


Figure S2. The PDOS of Fe site from PdFe₃@G and PdFe₃/FeN@NG after N₂ adsorption.

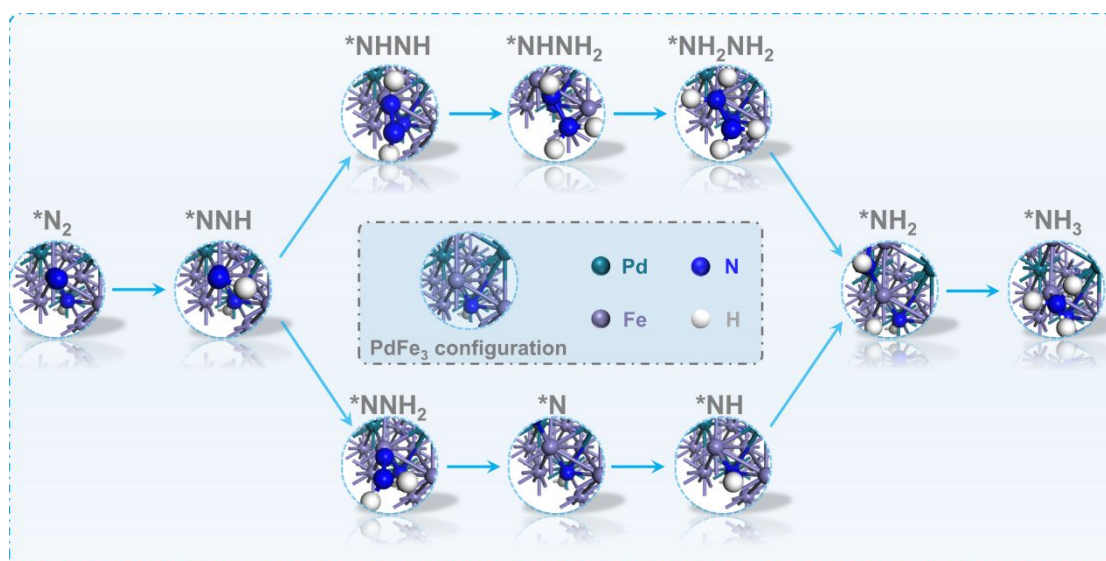


Figure S3. The structure modeling along the associative alternative and distal path over PdFe₃/FeN@NG from the top view.

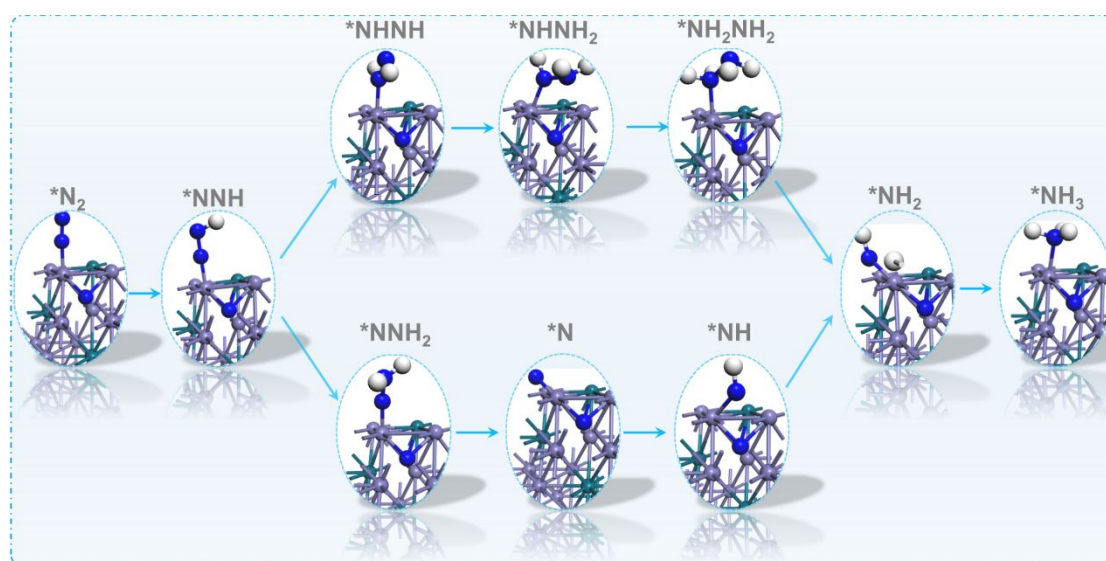


Figure S4. The structure modeling along the associative alternative and distal path over PdFe₃/FeN@NG from the top view.

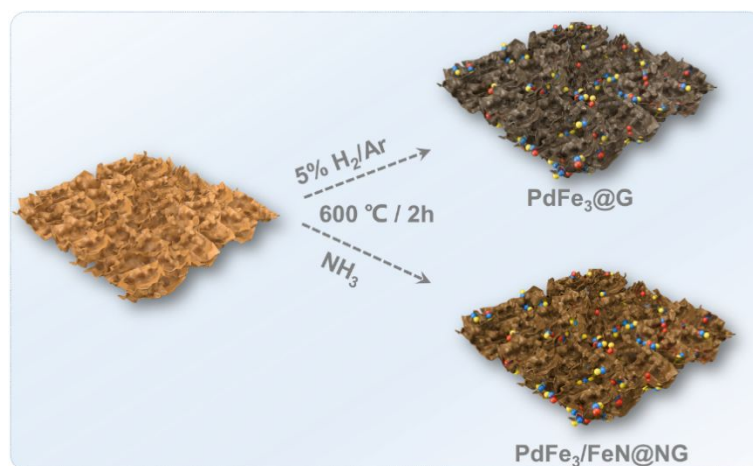


Figure S5. Schematic diagram of the synthesis process.



Figure S6. Digital image of graphene aerogels after hydrothermal treatment.

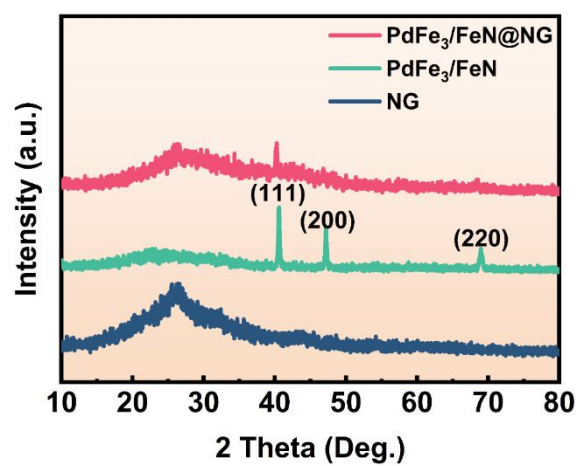


Figure S7. XRD patterns of as-synthesized PdFe₃/FeN@NG, PdFe₃/FeN, and NG.

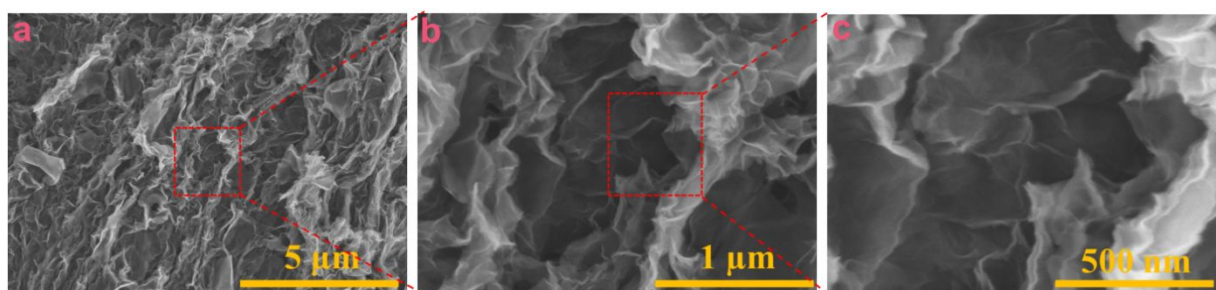


Figure S8. SEM images of PdFe₃/FeN@NG.

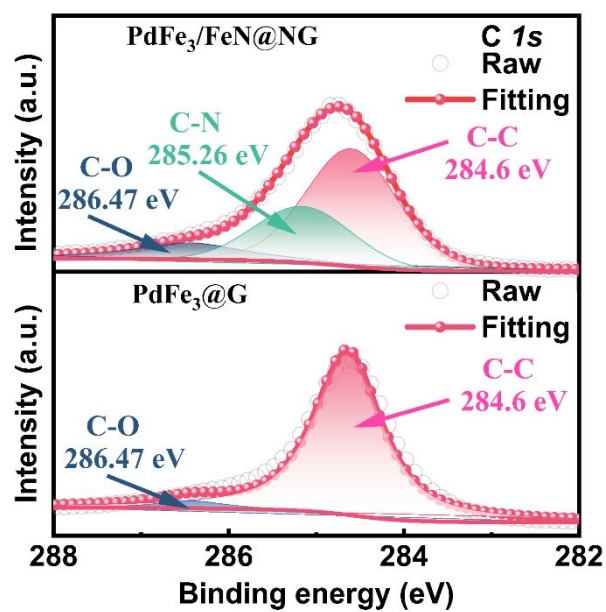


Figure S9. High-resolution C *1s* XPS spectra for PdFe₃@G and PdFe₃/FeN@NG.

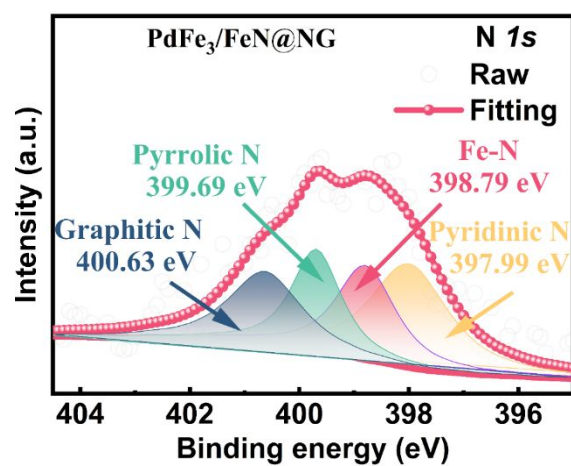


Figure S10. High-resolution N *1s* XPS spectrum for PdFe₃/FeN@NG.

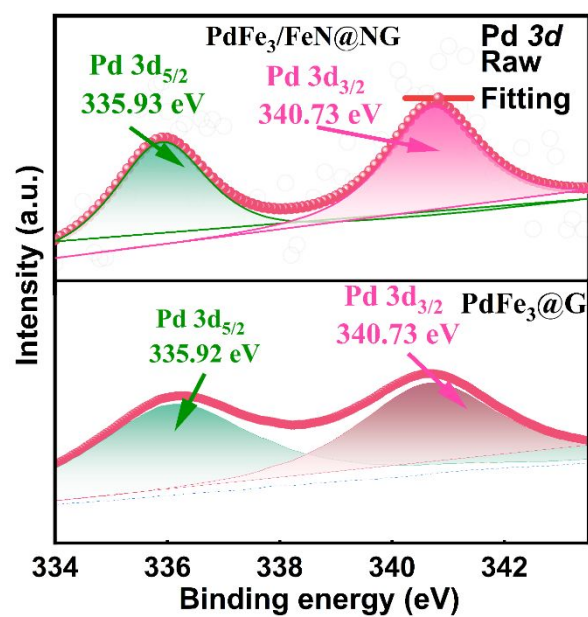


Figure S11. High-resolution Pd 3d XPS spectra for PdFe₃@G and PdFe₃/FeN@NG.

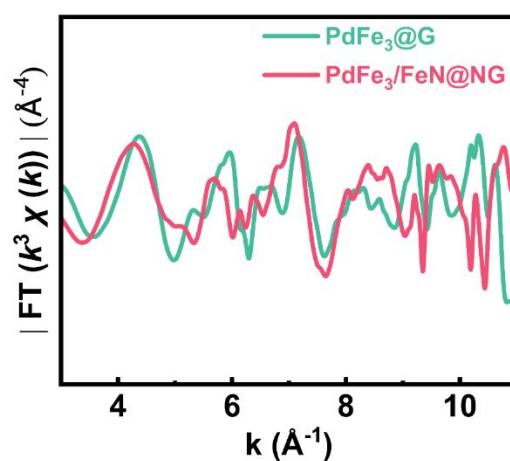


Figure S12. Fourier-transform EXAFS (FT-EXAFS) spectra of the Fe K-edge in K space.

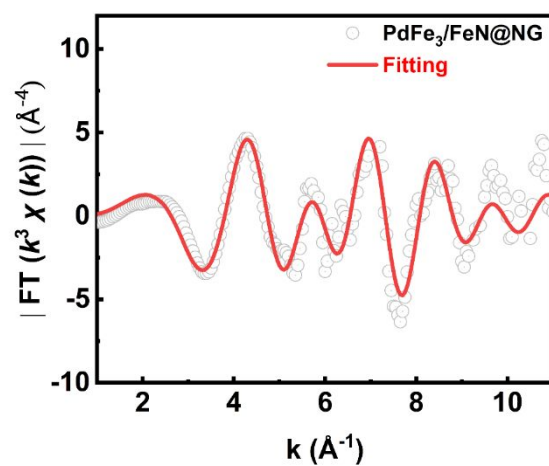


Figure S13. The corresponding fitting curves of FT-EXAFS spectra of Fe K-edge for PdFe₃/FeN@NG.

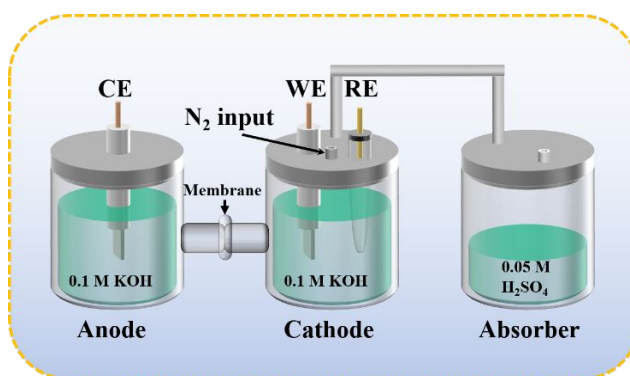


Figure S14. The schematic diagram for electrocatalytic NRR

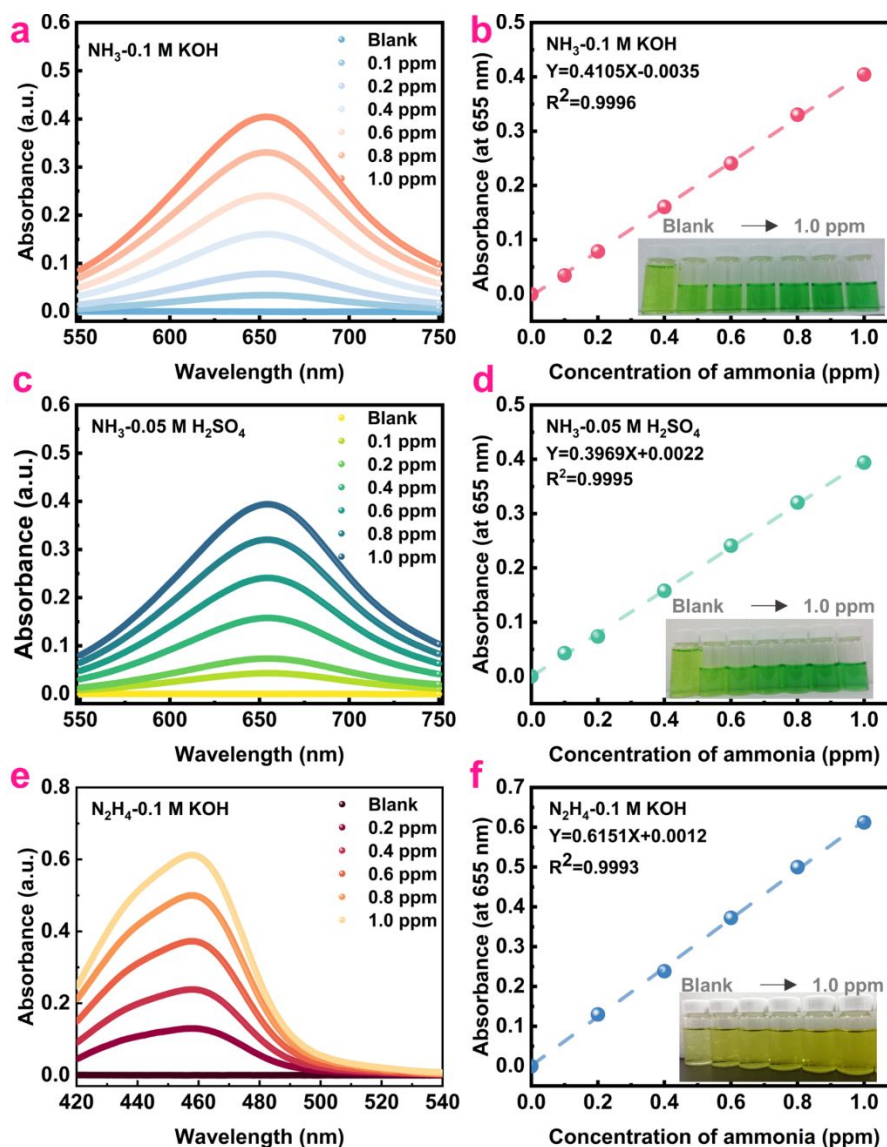


Figure S15. The approaches for detecting the amount of as-synthesized NH_3 and possible hydrazine (N_2H_4) byproduct. UV-Vis absorption spectra for known-concentration (a) NH_4Cl solution in 0.1 M KOH, (c) NH_4Cl solution in 0.05 M H_2SO_4 , and (e) N_2H_4 in 0.1 M KOH; corresponding calibration plot in (b) 0.1 M KOH for NH_3 , (d) 0.05 M H_2SO_4 for NH_3 , and (f) 0.1 M KOH for N_2H_4 .

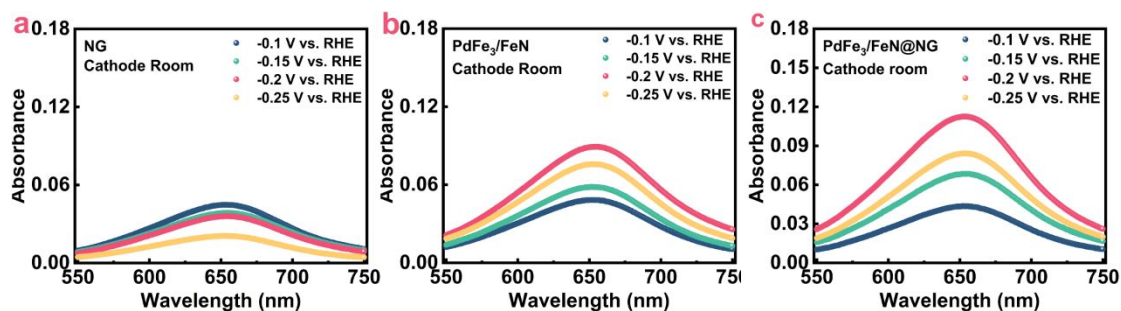


Figure S16. Potential-resolved UV-Vis spectra of the as-collected catholyte stained with the corresponding color indicator in 0.1 M KOH for (a) NG, (b) PdFe₃/FeN, and (c) PdFe₃/FeN@NG.

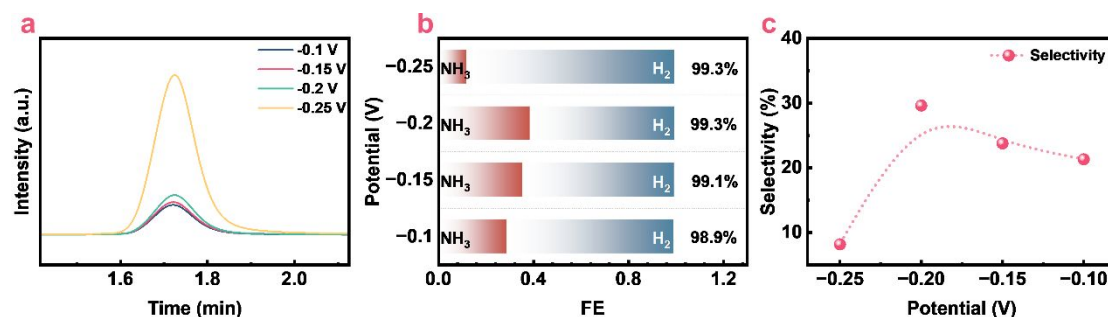


Figure S17 (a) Potential-dependent GC of H₂ production during NRR process, (b) The Faradaic efficiency of NH₃ and H₂ at different potentials, (c) The selectivity for NH₃ at different potentials.

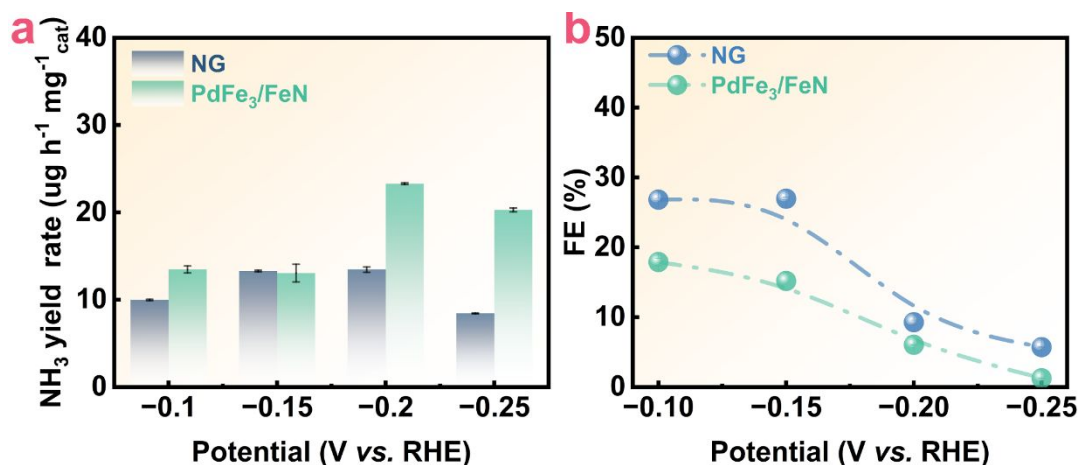


Figure S18. (a) The ammonia yield rate and (b) FE of NG and PdFe₃/FeN.

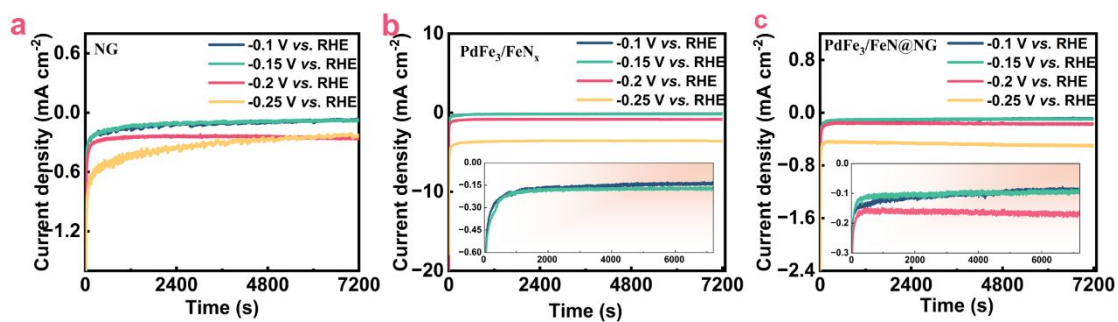


Figure S19. Chronoamperometry results at the corresponding potentials for (a) NG, (b) PdFe₃/FeN, and (c) PdFe₃/FeN@NG.

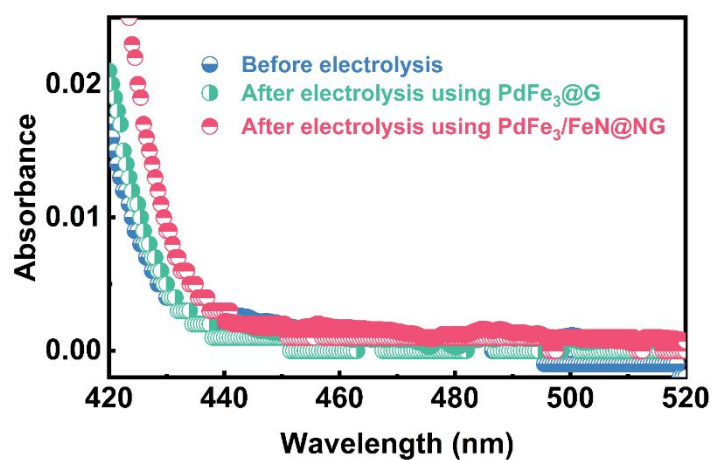


Figure S20. The UV-vis spectra of as-collected electrolytes stained with the indicator for N₂H₄·H₂O.

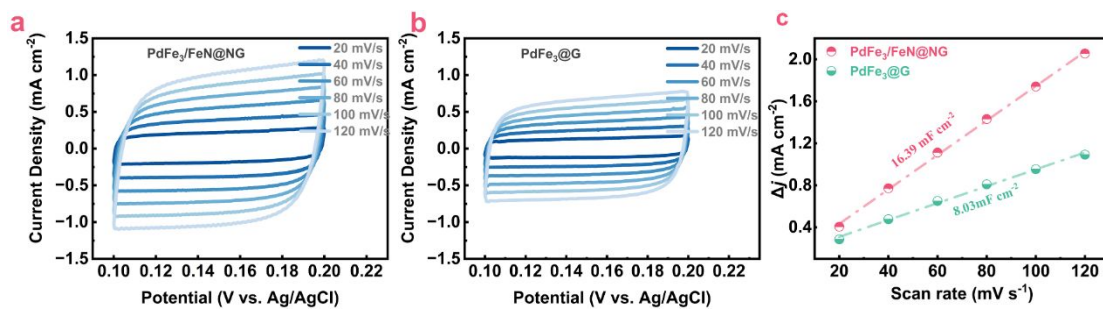


Figure S21. The cyclic voltammogram (CV) curves from 0.1 to 0.2 V vs. Ag/AgCl at various scan rates for (a) PdFe₃/FeN@NG, and (b) PdFe₃@G; (c) Corresponding plots of the specific current density vs. the scan rate.

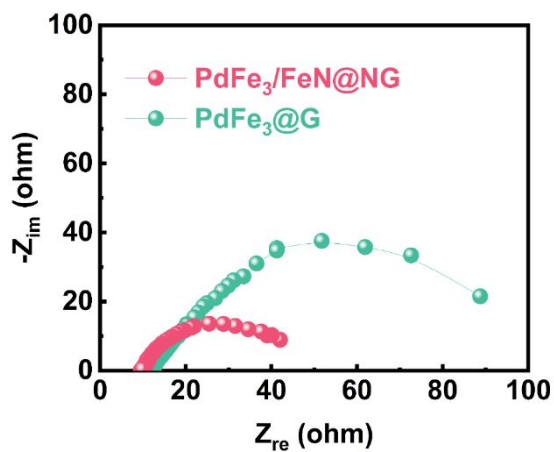


Figure S22. The electrochemical impedance spectra (EIS) of PdFe₃@G and PdFe₃/FeN@NG.

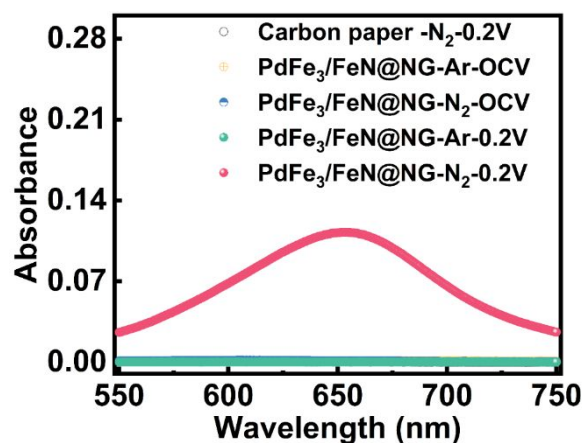


Figure S23. The UV-vis spectra of different electrolytes stained with ammonia indicator to exclude the influence of nitrogen-containing impurities.

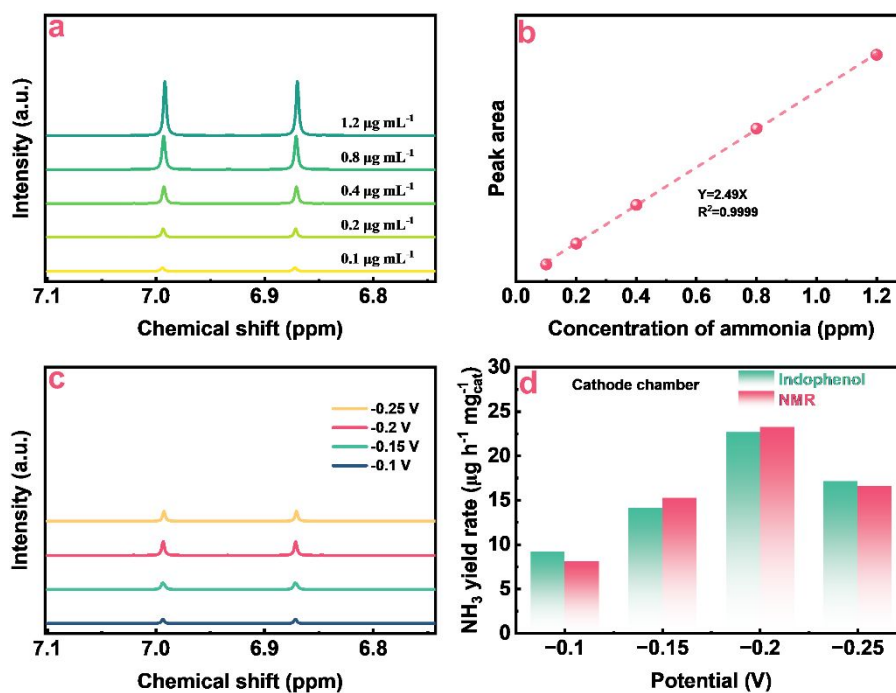


Figure S24. (a) ^1H spectra of $^{15}\text{NH}_4^+$ standard samples with specific concentrations, and (b) corresponding calibration plot versus peak area. (c) ^1H spectra of $^{15}\text{NH}_4^+$ from the NRR process fed by $^{15}\text{N}_2$ over $\text{PdFe}_3/\text{FeN@NG}$ for 2 h. (d) Comparison of $^{15}\text{NH}_3$ yield rate over $\text{PdFe}_3/\text{FeN@NG}$ from indophenol and NMR methods.

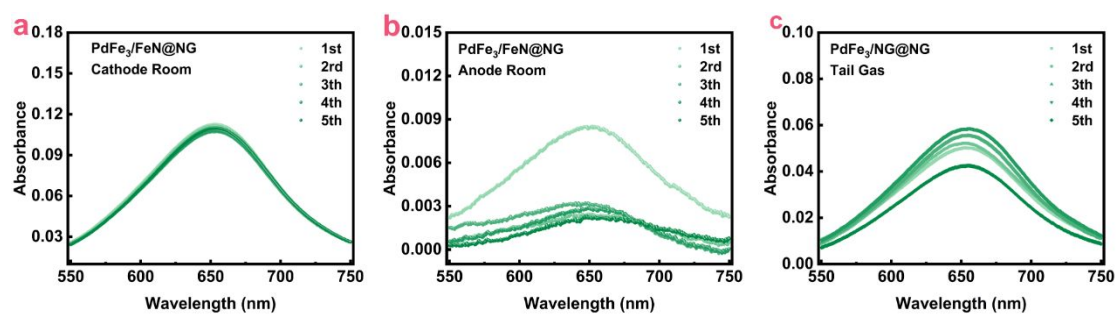


Figure S25. UV-Vis absorption spectra of the as-collected electrolyte added with color indicator after electrocatalytic reaction in N_2 -saturated 0.1 M KOH at different potentials in five consecutive cyclic measurements. (a) Cathodic chamber, (b) anodic chamber, and (c) acid trap solutions.

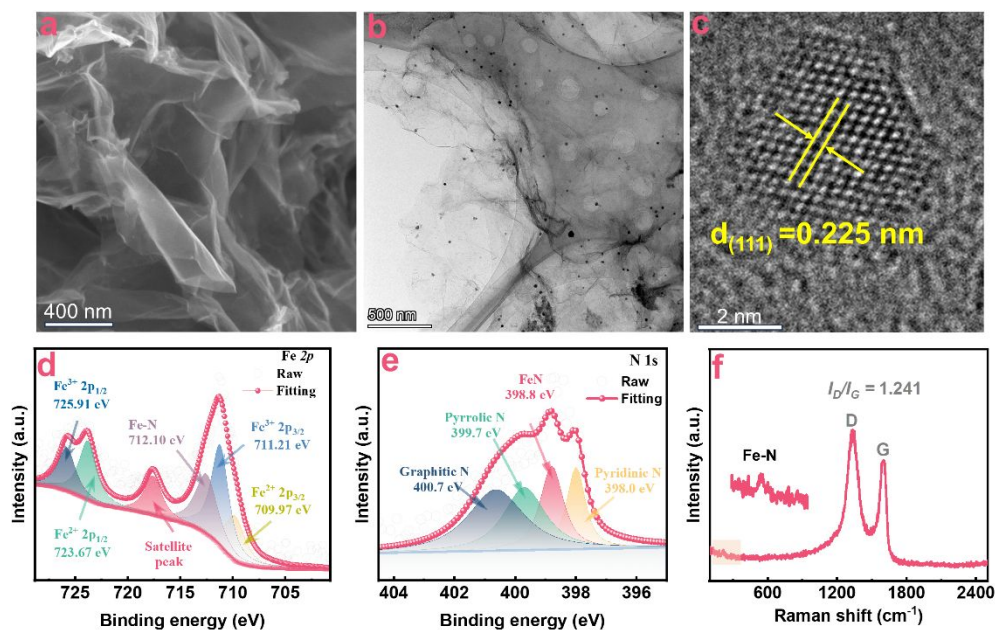


Figure S26. (a) SEM image, (b) TEM image, (c) HRTEM images, (d) Fe 2p spectrum, (e) N 1s spectrum, and (f) Raman spectrum of spent PdFe₃/FeN@NG electrode.

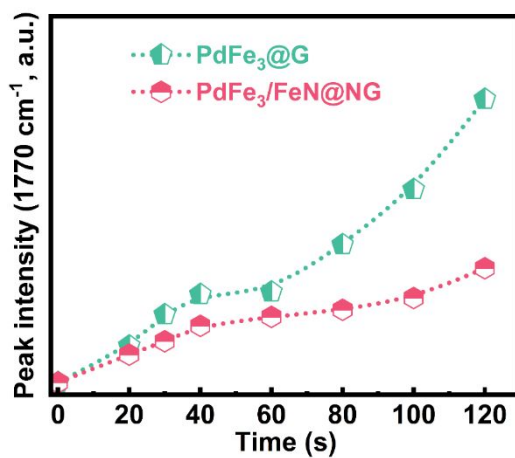


Figure S27. The spectral peak intensity of adsorbed *NH₃ at 1170 cm⁻¹ with the reaction time.

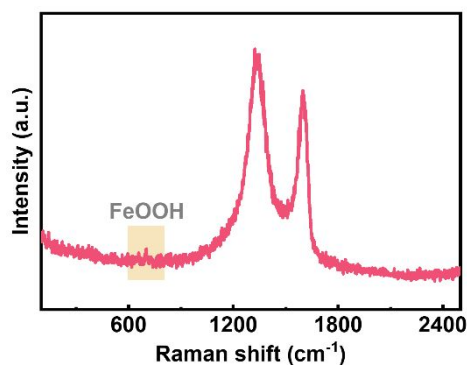


Figure S28. Raman spectrum of spent PdFe₃/FeN@NG electrode.

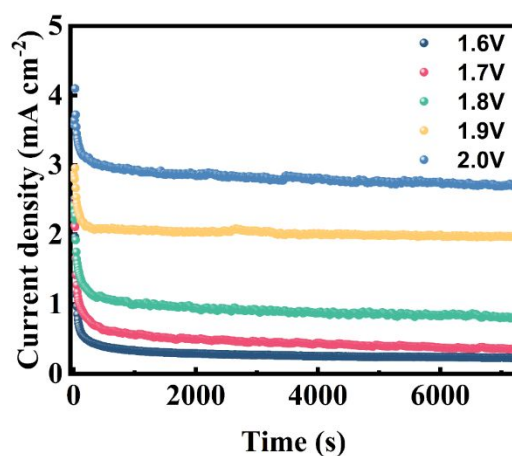


Figure S29. Full N₂ electrolysis: Chronoamperometric curves at various voltages for PdFe₃/FeN@NG as both cathodic and anodic electrodes.

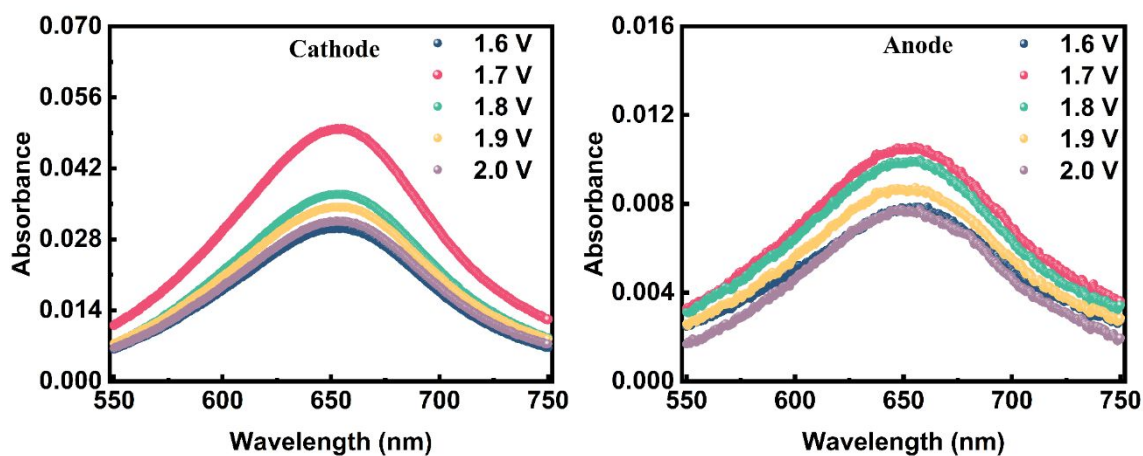


Figure S30. Full N₂ electrolysis: UV-Vis absorption spectra of the as-collected electrolyte added with color indicator after electrocatalytic reaction in N₂-saturated 0.1 M KOH at different potentials.

Table S1. The molar ratio of Fe to Pd measured by EDS and ICP-OES.

Catalysts	EDS	ICP-OES
	Atom ratio of Fe to Pd	Atom ratio of Fe to Pd
PdFe ₃ @G	3.15	2.79
PdFe ₃ /FeN@NG	3.03	2.83

Table S2. Detailed bonding information and corresponding contents of PdFe₃/FeN@NG on XPS results.

Elements	Assignment	Position (eV)	Content (at.%)
C	C–C/C=C	284.6	58.84
	C–N	285.26	27.43
	C–O	286.47	13.73
N	Pyridinic N	397.99	34.18
	Fe–N	398.79	23.54
	Pyrrolic N	399.69	20.96
	Graphitic N	400.63	21.32
Fe	Fe ²⁺ 2p _{3/2}	709.99	21.49
	Fe ²⁺ 2p _{1/2}	723.67	12.63
	Fe ³⁺ 2p _{3/2}	711.20	26.13
	Fe ³⁺ 2p _{1/2}	725.91	10.65
	Fe–N	712.10	14.61
	Satellite peak	717.60	14.49
Pd	Pd 3d _{5/2}	340.73	52.45
	Pd 3d _{3/2}	335.93	47.55

Table S3. Detailed bonding information and corresponding contents of PdFe₃@G on XPS results.

Elements	Assignment	Position (eV)	Content (at.%)
C	C–C/C=C	284.6	92.37
	C–O	286.47	7.63
Fe	Fe ²⁺ 2p _{3/2}	709.6	21.35
	Fe ²⁺ 2p _{1/2}	723.4	11.18
	Fe ³⁺ 2p _{3/2}	710.8	32.03
	Fe ³⁺ 2p _{1/2}	725.8	20.70
	Satellite peak	716.69	14.74
Pd	Pd 3d _{5/2}	340.73	57.61
	Pd 3d _{3/2}	335.92	43.39

Table S4. EXAFS fitting parameters at the Fe K-edge various samples.

Samples	Shell	CN	R(Å)	σ ² (Å ²)	ΔE ₀ (eV)	R factor
PdFe ₃ /FeN@NG	Fe-N	1.4	1.53	0.0084	6.1	0.0183
	Fe-Pd	5.3	2.55	0.0115	-7.8	

CN: coordination numbers; R: bond distance; σ²: Debye-Waller factors; ΔE₀: the inner potential correction. R factor: goodness of fit. S₀² was set to 0.74 for Fe.

Table S5. Summary of the ammonia yield rate and FE in N₂-saturated 0.1 M KOH electrolyte.

Potentials/V		Samples			
		NG	PdFe ₃ /FeN	PdFe ₃ /FeN@NG	PdFe ₃ @G
-0.10	Ammonia	9.97	13.46	13.84	
-0.15	yield	13.28	13.05	17.41	
-0.20	rate/ $\mu\text{g h}^{-1}$	13.45	23.29	29.94	27.23
-0.25	$\text{mg}_{\text{cat.}}^{-1}$	8.44	20.28	25.57	
-0.10	FE	26.82	17.90	28.63	
-0.15		26.96	15.18	35.34	
-0.20		9.28	6.05	38.43	21.37%
-0.25		5.71	1.26	11.7	

Table S6. ECSA of electrocatalysts for NRR.

Sample	C _{dl} (mF cm ⁻²)
PdFe ₃ @G	8.03
PdFe ₃ /FeN@NG	16.39

Table S7 The comparison of NH₃ synthesis performance of NRR electrolytes

Catalysts	FE (%)	Yield rate	Potential (V)
		($\mu\text{g h}^{-1} \text{mg}_{\text{cat.}}^{-1}$)	
Ru	5.1	12.1	-0.1
Fe ₃ C/Fe ₃ O ₄ @C	22.5	25.7	-0.2
PdCu/B	9	26.61	-0.4
PdFe ₃ @G	22.8	29.07	-0.2
Sn ADP	26.8	28.3	-0.3
Fe ₁ S _x @TiO ₂	17.3	18.3	-0.2
FePc@CNTS	22.2	21.7	-0.5
BCN	18.9	20.9	-0.4
Zn ¹ N-C	11.8	16.1	-0.3
W ₂ N ₃	11.67	11.66	-0.2
This work	38.43	29.94	-0.2

Table S8. Summary of OER performance in O₂-saturated 1.0 M KOH electrolyte.

Sample	Overpotential		Tafel slope / mV dec ⁻¹
	10 mA cm ⁻²	100 mA cm ⁻²	
PdFe ₃ @G	335	530	92
PdFe ₃ /FeN@NG	286	308	83

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