Supplementary Information

Nitrogen-Doped Graphene Encapsulating Fe₂N for Enhanced Electrocatalytic

Conversion of Nitrate to Ammonia

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Experimental section

Materials. Dicyandiamide ($C_2H_4N_4,98\%$) was purchased from Sinopharm Chemical Reagent Co. Ltd. Glucose ($C_6H_{12}O_6$, 99%) was purchased from Macklin. FeCl₃·6H₂O (99%) was purchased from Kermel. Ferric oxide (Fe₂O₃, 98%) was purchased from Macklin. All chemicals were used as received without further purification.

Synthesis of electrocatalysts

Synthesis of Fe₂N@NG: Dicyandiamide and glucose (0.1 g) were combined in mass ratios of 10:1 and subsequently dissolved in 35 mL of deionized water containing 61 mg of FeCl₃·6H₂O, stirring for 12 h to get homogeneous solution. Subsequently, the solution was frozen dried in a freeze dryer with vacuum after freezing by liquid nitrogen. The resultant powders were pyrolyzed at 550 °C for 2 h and 800 °C for 2 h under flowing Ar atmosphere. The heating rate was 4°C/min from 25°C to 550°C and 3°C/min from 550°C to 800°C, with an Ar gas flow rate of 85 mL/min. The powder was treated with NH₃ and held at 900 °C for 30 min. The obtained products were denoted as Fe₂N@NG. The heating rate was 10°C/min from 25°C to 900°C, with a gas flow rate of 25 mL/min.

Synthesis of Fe₂N: Commercial Fe₂O₃ with a particle size identical to that of the synthesized Fe₂N@NG was purchased, followed by heat treatment of the Fe₂O₃ in NH₃ at 900 °C for 30 minutes to ultimately obtain Fe₂N.

Synthesis of NG: The NG samples were synthesized using the same method, excluding the addition of Fe salt.

Synthesis of Fe₂N/NG: The mass fraction of Fe in Fe₂N@NG was measured by Inductively coupled plasma mass spectrometry (ICP-MS) to assess the amount of Fe₂N. The mass ratio of Fe₂N to NG was approximately 2.5:7.5, and the mixture was thoroughly ground using a mortar.

Physical characterization. Transmission electron microscopy (TEM) and high-resolution TEM images were obtained by a FEI Talos F200XG2 AEMC. XRD patterns were recorded on a Rigaku Smart Lab 9 KW

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with Cu K α radiation (λ = 1.5418 Å), employing a scan rate of 6° min⁻¹ under operational parameters of 40 kV and 40 mA. XPS spectroscopy was performed using a Thermo Scientific K-Alpha with non-monochromatic Al K α x-rays as the excitation source. The binding energy was calibrated using the C 1s peak energy of 284.8 eV and valence spectrum. The Fourier transform infrared (FTIR) transmittance spectra were obtained using a Thermo Scientific Nicolet iS20. Isotope labeling experiments were conducted through ¹H NMR on a Bruker 400 MHz AVANCE NEO spectrometer.

Electrochemical Measurements. The electrochemical measurements were performed in a traditional three electrode H-type electrolysis cell with an electrochemical workstation (CHI 660E). For fabrication of the working electrode, 4.0 mg of Fe₂N@NG powder was uniformly dispersed with 50 μ L of 5 wt% Nafion solution in a mixed solvent system containing 475 μ L ethanol and 475 μ L ultrapure water (18.2 M Ω ·cm), followed by ultrasonication treatment for 30 minutes to achieve homogeneous ink formation. Subsequently, the resultant electrocatalyst ink was dropped to the carbon paper in a uniform layer to maintain a loading of 0.2 mg cm⁻². The nitrate reduction reaction (NO₃RR) was investigated in the H-cell, employing the 1 cm⁻² carbon paper (with catalyst) as the working electrode. A Hg/HgO reference electrode and the platinum wire counter electrode completed the three-electrode system. The catholyte composition comprised 0.5 M Na₂SO₄ with or without variable concentrations of NaNO₃ (0.01-0.5 M).

Calculation of the NH₃ Faradaic Efficiency (FE), and Yield Rate

The FE of electrocatalytic NO₃⁻-NH₃ conversion was calculated as follows:

$$FE = \frac{8 \times V \times C_{NH_3} \times F}{Q}$$

The rate of NH₃ yield rate was calculated using the following equation:

Yield NH₃ =
$$\frac{C_{NH_3} \times V}{17 \times m \times t}$$

where V is the volume of the cathodic electrolyte, C_{NH3} is the measured NH₃ concentration, F is the Faraday constant (96500 C mol⁻¹), Q is the total charge passing the electrode, m is the loading mass of catalysts and t is the reduction time.

The electrochemically active surface area (ECSA) was determined from CV curves at various scan rates within a non-Faraday potential window. The absolute value of capacitance corresponding to the potential in the middle of the CV curve at different sweep rates yields a straight line, with a slope equal to the electrochemical double-layer capacitance (C_{dl}).

The ECSA was calculated using the following equation:

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$$ECSA = \frac{C_{dl}}{C_{ref}}$$

Where C_{ref} is specific capacitance of a flat surface. We take 40 μ F cm⁻² to be a moderate value for the C_{ref} .



Fig. S1. XPS Survey spectra of $Fe_2N@NG$ and NG.



Fig. S2. UV-vis absorption spectra of the standard solutions containing (a) NH_3 and (c) NO_2^- . The plot of standard curves of (b) NH_3 and (d) NO_2^- .



Fig. S3. The NH_3 yield rate of $Fe_2N@NG$, Fe_2N/NG and NG different potentials.



Fig. S4. H_2 FE of Fe₂N@NG, Fe₂N/NG and NG at different potentials.



Fig. S5. NH_3 current densities at different applied potentials of $Fe_2N@NG$, Fe_2N/NG and NG.





Fig. S7. Double layer capacitance (C_{dl}) of Fe₂N@NG, Fe₂N/NG and NG.



Fig. S8. NH₃ current densities normalized by ECSA of NO₃RR at different applied potentials of Fe₂N@NG, Fe₂N/NG and NG.



Fig. S9. Comparisons of NO₃RR performance of Fe₂N@NG with other reported electrocatalysts.



Fig. S10. Tafel plots of Fe₂N@NG, Fe₂N/NG and NG.





Fig. S12. NO_2^- FE of Fe₂N@NG at different concentrations of NO_3^- .



Fig. S13. (a) Bode phase plots of Fe_2N/NG at different potentials in electrolyte of 0.5 M Na_2SO_4 without NO_3^- or (b) with NO_3^- (c) NG at different potentials in electrolyte of 0.5 M Na_2SO_4 without NO_3^- .



 $\begin{array}{c} \hline & -& -& 0 \\ \hline & -& 0.4 \\ \hline & -& 0.8 \\ \hline & -& 0.6 \\ \hline & -& 0.4 \\ \hline & -& 0.2 \\ \hline & -& 0.5 \\ \hline & -& 0.6 \\ \hline & -& 0.6 \\ \hline & -& 0.7 \\ \hline & -& 0.8 \\ \hline & -& 0.6 \\ \hline & -& 0.7 \\ \hline & -& 0.8 \\ \hline & -& 0.6 \\ \hline & -& 0.7 \\ \hline & -& 0.8 \\ \hline & -& 0.6 \\ \hline & -& 0.7 \\ \hline & -& 0.8 \\ \hline & -& 0.6 \\ \hline & -& 0.7 \\ \hline & -& 0.8 \\ \hline & -& 0.6 \\ \hline & -& 0.7 \\ \hline & -& 0.8 \\ \hline & -& 0.6 \\ \hline & -& 0.8 \\ \hline & -& 0.6 \\ \hline & -& 0.8 \\ \hline & -& 0.6 \\ \hline & -& 0.8 \\ \hline & -& 0.8$



Fig. S15. The ¹H NMR spectra of electrolytes after NO₃RR using ¹⁴NO₃⁻ or ¹⁵NO₃⁻ as the N-source, respectively.



 $NO_3^{\text{-}} \qquad NO_3^{\text{-}}$ Fig. S16. The yield rate of NH_3 with or without NO_3', and without potential.



Fig. S17. Successive recycling test at -0.5 V vs. RHE for Fe₂N@NG.

Table S1. Elemental compositions obtained by ICP-MS of Fe₂N@NG.

Sample	Element	Content (wt %)	
Fe ₂ N@NG	Fe	23.368	

Table S2. Comparison of the C_{dl} and ESCA.

Samples	C _{dl} (mF cm ⁻²)	ESCA
Fe ₂ N@NG	2.71	67.75
Fe ₂ N/NG	11.35	283.75
NG	9.56	239

Table S3. Performance comparison of Fe₂N@NG with the reported catalysts.

Catalysts	Electrolyte	FE (%)	NH₃ Yield Rate	Potential	Ref
			(mmol h ⁻¹ g _{cat} ⁻¹)	(V <i>vs</i> . RHE)	
Fe₂N@NG	0.025 M NaNO₃ + 0.5 M	96.16	618.35	-0.5	This
	Na ₂ SO ₄				work
Co@CC	0.1 M NaOH + 0.1 M	93.4	600	-0.8	1
	NO ₃ -				T
aCu@B-SnS ₂ -x	0.1 M KOH + 0.1MKNO ₃	94.6	550	-0.67	2
Cu@Ni ₂ P-NF	$1 \text{ M KOH} + 20 \text{ mM KNO}_3$	92.4	374.11	-0.4	3
Cu@ZnO NWA	0.1 M KOH + 0.05 M	89.14	354.7	-0.6	4
	KNO₃				4
Cu/JDC	0.1 M NaOH + 0.1 M	93.2	520	-0.6	5
	NO ₂ ⁻				
FeMo-N-C	0.05 M PBS + 0.16 M	93	170	-0.45	6
	NO ₃ -				
MWCNTs	0.1 M KOH + 0.1 M KNO ₃	84.72	237.05	-0.16	7
Ni@JBC-800	0.1 M NaOH + 0.1 M	83.4	242.35	-0.5	8
	NO ₂ ⁻				
CoS ₂ /MoS ₂	0.1 M KOH + 600 ppm	97.07	441.18	-0.25	0
	KNO ₃				Э

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