Electronic Supplementary Information

Chemicals and materials

Sodium palladium(II) tetrachloride (Na₂PdCl₄) and DM-970 (α -(dinonylphenyl)- ω -hydroxypoly(oxy-2-ethanediyl), (C₂H₄O)n·C₂₄H₄₂O·C₁₅H₂₄O)) were received from Sigma-Aldrich. Potassium bromide (KBr), Sodium borohydride (NaBH₄), hydrazine hydrate, sodium hypophosphite (NaH₂PO₂), sodium nitrite (NaNO₂), ammonium chloride (NH₄Cl), ammonium chloride-¹⁵N (¹⁵NH₄Cl-¹⁵N), sulfamic acid, phosphoric acid, p-aminobenzenesulfonamide, N-(1-Naphthyl) ethylenediamine dihydrochloride, potassium sodium tartrate, Nessler's reagent, potassium nitrate (KNO₃), potassium nitrate-¹⁵N (K¹⁵NO₃-¹⁵N) and potassium sulfate (K₂SO₄) were obtained from Aladdin (Shanghai, China). HCl and ethanol (C₂H₅OH) were purchased from Beijing Chemical Works.

Quantification of ion concentrations¹

Quantification of NO₃--N: Nitrate has a typical absorption of UV light at a wavelength of 220 nm and the absorption value is proportional to the nitrate concentration. First, 5.0 mL of standard solution, or (diluted) sample solution was added to a test-tube followed by addition of 0.10 mL of 1 M HCl and 10 μ L of 0.8 wt%) sulfamic acid. Following shaking and left-standing for 10 min, the absorbance of the mixture at a wavelength of 220 nm and 275 nm is determined by using UV-Vis spectrophotometry. Based on the equation of A = A_{220nm} - 2A_{275nm}, the final absorbance of NO₃--N was obtained. The concentration-absorbance curve was calibrated using different concentrations of KNO₃(Fig. S3).

Quantification of $NO_2^{-}N$: The Nitrite (NO_2^{-}) can be diazotized by sulphonamide in an acidic environment and the diazotized compound can be coupled with N-(1-Naphthyl) ethylenediamine dihydrochloride to produce a pink azo dye with typical absorption at 540 nm. Thus, the color reagent was consisted of 0.8 g p-aminobenzenesulfonamide, 0.04 g N-(1-Naphthyl) ethylenediamine dihydrochloride, 2 mL phosphoric acid (ρ =1.70 g/mL) and 10 mL deionized water. Then, 1 mL of color developer was added to the 5 mL of solution which was diluted to detection range and mixed well. After 20 minutes, the wavelength of 540 nm was determined by using UV-vis spectrophotometry to reveal the absorbance of NO₂⁻-N. The concentration-dependent absorption spectra were calibrated using standard potassium nitrite (NaNO₂) solutions with different known concentrations (Fig. S4).

Quantification of NH₃(NH₄⁺)-N: Nessler's reagent was used to detect the NH₃ concentration. Firstly, the corresponding calibration curve was obtained by UV-vis curves for known concentration of NH₃ in DI water(Fig. S5). After running chronoamperometry test for 2 h, 0.1 mL of ρ =0.5 g/mL sodium potassium tartrate solution and 0.1 mL of Nessler's reagent mixed into the electrolyte which was diluted to detection range. After shaking and standing for 20 minutes, the value of absorbance was tested by the UV-Vis spectrophotometry at a wavelength of 540 nm can be determined by the UV-Vis spectrophotometry. Finally, NH₃ concentration was calculated according to the UV-vis curve and calibration curve.

¹⁵N Isotope Labeling Experiments:

Isotope labelling experiments were carried out using $K^{15}NO_3^{-15}N$ as the nitrogen supply source to clarify the source of ammonia. The electrolyte containing ${}^{15}NH_4^{-15}N$ was removed after electroreduction and the pH was adjusted to a weak acid containing 4M H₂SO₄, which was further quantified by 1H NMR (600 MHz) and maleic acid external standard. For preparation of calibration curve, different concentration of ${}^{15}NH_4^{+}$ - ${}^{15}N$ solutions (25, 50, 75, 100, 125 mg L⁻¹) and 50 mg L⁻¹ maleic acid were added in 0.5 M K₂SO₄. Then, The D₂O was added aforementioned solution for the

NMR detection. On account of ${}^{15}NH_4^{+}-{}^{15}N$ concentration and the area ratio were positively correlated, the calibration curve can be obtained by using the peak area ratio between ${}^{15}NH_4^{+}-{}^{15}N$ and maleic acid. Similarly, the amount of ${}^{14}NH_4^{+}-{}^{14}N$ was quantified by this approach when K ${}^{14}NO_3$ was used as the feeding N-source.

Calculation of the conversion rate, yield, selectivity, and Faradaic efficiency

The concentrations of NO_3^- , NO_2^- and NH_3 were determined by the absorbance measured by the UV-Vis spectrophotometer. The calculation of the percentages of NO_3^- conversion, and NH_3 generation, the NO_2^- and NH_3 selectivity, and the Faradaic efficiency of NO_3RR were as follows:

$$\begin{split} &\text{NO}_3^- \text{ Conversion} = \Delta C_{_{NO_3^-}} / C_0 \times 100\% \\ &\text{NO}_2^- \text{ Selectivity} = C_{_{NO_2^-}} / \Delta C_{_{NO_3^-}} \times 100\% \\ &\text{NH}_3 \text{ Selectivity} = C_{_{NH_3}} / \Delta C_{_{NO_3^-}} \times 100\% \\ &\text{Faradaic efficiency} = (8F \times C_{_{NH_3}} \times V) / (M_{_{NH_3}} \times Q) \times 100\% \\ &\text{Yield}_{_{\text{NH}_3}} = (C_{_{NH_3}} \times V) / (M_{_{NH_3}} \times t \times S) \end{split}$$

where C_{NH3} is the concentration of NH_{3(aq)}, C_{NO2} is the concentration of NO_{2^{-(aq)}}, ΔC_{NO3} is the concentration difference of NO₃ before and after electrolysis, C_0 is the initial concentration of NO₃, V is the electrolyte volume, M_{NH3} is the molar mass of NH₃, t is the electrolysis time, S the geometric area of catalyst(cm²), F is the Faradaic constant (96485 C mol⁻¹), Q is the overall charge during electrolysis.



Fig. S1 SEM images of PdB NAs/NF (a) and PdP NAs/NF (b).



Fig. S2 Schematic illustration showing the electrocatalytic system for nitration reduction to ammonia.



Fig. S3 (a) UV-vis absorption spectroscopy for various concentrations of NO_3 -N. (b) Calibration curve used to estimate the concentrations of NO_3 -N.



Fig. S4 (a) UV-vis absorption spectroscopy for various concentrations of NO_2^--N . (b) Calibration curve used to estimate the concentrations of NO_2^--N .



Fig. S5 (a) UV–vis absorption spectroscopy for various concentrations of NH₃-N. (b) Calibration curve used to estimate the concentrations of NH₃-N.



Fig. S6. (a) NO₃⁻-N conversation, (b) selectivity of NH₃-N and NO₂⁻-N and (c) NH₃ yield rates and (d)

Faradaic efficiency of various PdBP NAs/NF samples at -0.66 V (vs. RHE).



Fig. S7 LSV curves of PdBP NAs/NF and Pd NAs/NF showing successful HER suppression by B and P co-doping.



Fig. S8 EIS spectra of the PdBP NAs/NF and Pd NAs/NF measured at -0.66V(vs. RHE) in a 0.5 M K_2SO_4 solution comtaining 100 mg L⁻¹ of NO₃⁻, with the frequency range of 0.1 Hz ~100 kHz and the AC amplitude of 5 mV.



Fig. S9 (a) The CV curves at various scan rates and (b) capacitive current densities of the Pd NAs/NF.(c) The CV curves at various scan rates and (d) capacitive current densities of the PdBP NAs/NF.



Fig. S10 (a) SEM image and (b)TEM image of the PdBP NAs/NF after stability testing.



Fig. S11 (a) XRD pattern, (b) Pd 3d high-resolution XPS spectrum, (c) P 2p high-resolution XPS spectrum, (d) B 1s high-resolution XPS spectrum of PdBP NAs/NF after stability testing.



Fig. S12 NO₃⁻-N conversition and NH₃-N selectivity on the PdBP NAs/NF with various NO₃⁻-N concentrations.



Fig. S13 (a) The ¹H NMR spectra of ¹⁵NH⁴⁺ with different ¹⁵NH⁴⁺-¹⁵N concentrations. (b) The standard curve of integral area (15 NH⁴⁺- 15 N / C₄H₄O₄) against ¹⁵NH⁴⁺- 15 N concentration.

Table S1 Comparison of electrochemical nitrate-to-ammonia performance between the PdBP NAs/NFand some other reported electrocatalysts.

Electrocatalysts	Electrolytes	Performance	Ref.	
PdBP NAs/NF	0.5 M K ₂ SO ₄ , 100 mg L ⁻¹ NO ₃ ⁻ -N	r _{NH3} : 0.11 mmol h ⁻¹ cm ⁻² _{cat.} S _{NH3} : 88.44 % FE _{NH3} : 64.73 % (-0.66 V vs. RHE, 2 h)	This work	
Co ₃ O ₄ -TiO ₂ - PVP	0.1 M Na ₂ SO ₄ 0.1 M NaNO ₃	S _{NH3} : 73 % (10 mA cm ⁻²)	2	
CuPd@DCLMCS/CNT s	100 mg L ⁻¹ NO ₃ ⁻ -N 0.1 M Na ₂ SO ₄	S _{NH3} : 5% FE _{NH3} : 36% (-1.35 V <i>vs.</i> RHE, 24 h)	3	
Cu/rGO/ graphite plate(GP)	0.02 M NaCl, 0.02 M NaNO ₃	S _{NH3} : 29.93% (-1.4 V <i>vs.</i> SCE, 3 h)	4	
CuO-Co ₃ O ₄ /Ti	100 mg L ⁻¹ NO ₃ ⁻ -N, 0.05 M Na ₂ SO ₄	S _{NH3} :44% FE _{NH3} : 54.5% (20 mA cm-2, 3 h)	5	
Pd _{0.27} Cu _{0.73} /SS	0.1 M Na2SO4 50 mg L ⁻¹ NO ₃ ⁻ -N	S _{NH3} : 34.0% (3 mA cm ⁻² , 4 h)	6	
Pd-Cu/SS	0.01 M NaClO ₄ 0.6 mM NaNO ₃	S _{NH3} : 6% (-0.2 V <i>vs.</i> SCE, 3 h)	7	
Cu@Cu ₂₊₁ O NWs	0.5 M K ₂ SO ₄ , 50 mg L ⁻¹ NO ₃ ⁻ -N	S _{NH3} : 76% (-1.2 V <i>vs.</i> SCE, 2 h)	8	
Co ₃ O ₄ /Ti	0.05 M Na ₂ SO ₄ , 100 mg L ⁻¹ NO ₃ -	S _{NH3} : ~ 70% (10 mA cm ⁻² , 3 h)	9	
Ni-Fe ⁰ @Fe ₃ O ₄	10 mM NaCl, 50 mg L ⁻¹ NO ₃ -	S _{NH3} : 10.4% (5 mA cm ⁻² , 4 h)	10	
Cu-Pt/CF	0.0125 M K ₂ SO ₄ , 30 mg L ⁻¹ NO ₃ ⁻ -N	S _{NH3} : 84.0% FE _{NH3} : 22 % (90 mA cm ⁻² , 4 h)	11	

Electrocatalyst s	NaBH₄ Amount (mmol)	NaH ₂ PO ₂ Amount (mmol)	NO3 ⁻ -N Conversion	NH3-N Selectivity	NH3 Yield (mmol h ⁻¹ cm ⁻²)	FE
PdBP NAs/NF (Our typical sample)	1.2	0.3	99.79%	88.44%	0.110	64.73%
PdBP NAs/NF-1	0.6	0.3	98.13%	76.91%	0.086	55.40%
PdBP NAs/NF-2	1.8	0.3	97.35%	78.95%	0.087	56.39%
PdBP NAs/NF-3	1.2	0.15	98.23%	66.28%	0.073	39.21%
PdBP NAs/NF-4	1.2	0.6	99.05%	83.96%	0.094	56.81%

Table S2 Comparison of the nitrate-to-ammonia activity of various PdBP NAs/NF samples with different contents of B and P at -0.66 V (*vs.* RHE).

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