Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2024 This ESI replaces the original version

published on 24 Feb 2022.

Correction

We inadvertently placed the XRD pattern in Fig. S20a in Fig. S20b. We updated the XRD pattern that should have been placed in S20b. The data analysis and conclusions are not affected by these unintentional errors. Besides, for the caption of Fig. S27., "the ones with the lowest surface energies as shown in Fig. S22" should be changed to "the one with the lowest surface energy is shown in Fig. S26".

Supplementary Information

Experiment Section

Materials: FeCl₃·6H₂O, Na₂SO₄ and CP were bought from Beijing Chemical Corporation. Ethanol (C₂H₅OH), HCl, sodium hydroxide (NaOH, 99.0%), ammonium chloride (NH₄Cl), sodium salicylate (C₇H₅O₃Na), sodium nitroferricyanide dihydrate (C₅FeN₆Na₂O·2H₂O), C₉H₁₁NO, sodium hypochlorite solution (NaClO), sodium nitrate (NaNO₃), sulfamic acid was purchased from Aladdin Ltd. (Shanghai, China). The water use throughout all experiments was purified through a Millipore system. All chemicals were used of analytical grade and used as received without further purification.

Synthesis of Fe₂O₃/CP: Fe₂O₃/CP was prepared by a surfactant-free hydrothermal method with the assistance of high-temperature calcination in inert gas. 0.4 g FeCl₃·6H₂O and 0.24 g Na₂SO₄ was diluted into 35 mL aqueous solution, which was transferred to a Teflon-lined stainless autoclave having a piece of carbon paper (1.8 cm × 2 cm, pre-treated with concentrated HCl and deionized water (18.2 M Ω cm) and kept at 120 °C for 12 h. During the hydrothermal process, one-dimensional nanorod hydroxide precursor are uniformly grown on the CP substrate using Na₂SO₄ as a structure-directing agent for the one-dimensional growth (*J. Phys. Chem. C*, 2010, **114**, 21158–21164; *Nano Energy*, 2014, **9**, 345–354). Fe₂O₃/CP was obtained by annealing of the precursor in Ar gas at 450 °C for 3 h.

Characterization: Crystal phases of the samples were evaluated through the XRD (Philips PW1730). SEM (Zeiss Gemni SEM 300) and TEM (FEI TF200) were carried out to characterize the morphologies and structures of as-synthesized samples. XPS (Thermo ESCALAB 250XI) adopting Mg as the excitation source and EDX elemental mapping images were adopted to investigate further the chemical composition and element distribution of the samples.

Electrochemical measurements: Electrochemical measurements were performed in a two-compartment cell separated by a treated Nafion 117 membrane using a CHI

660E electrochemical analyzer (CHI Instruments, Inc.). Electrochemical experiments were carried out with a three-electrode configuration using the Fe₂O₃/CP as working electrodes, a platinum foil as the counter electrode, and a standard Ag/AgCl reference electrode. In all measurements, saturated Ag/AgCl electrode was calibrated to RHE if there are no special notes as following: E (RHE) = E (Ag/AgCl) + $0.059 \times pH + 0.197$ V. LSV was conducted at a scan rate of 5 mV s⁻¹ with iR correction. Before each measurement, NO or Ar was purged into the solution for at least 30 min to remove residual air in the reservoir. Controlled potential electrolysis was then performed at each potential for 2 h. ECSA was measured by CV at the potential window from 0.17 to 0.27 V versus Ag/AgCl, with different scan rates of 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mV s⁻¹. The double-layer capacitance (Cd) was estimated by plotting the $\Delta j = (j_a - j_c)$ at 0.22 V versus Ag/AgCl against the scan rates, in which the j_a and j_c were the anodic and cathodic current density, respectively. The slope is twice that of the Cdl values. Cdl was used to represent the ECSA. All the above measurements were at room temperature under atmospheric pressure and carried out without ohmic-drop correction unless noted otherwise.

Determination of NH3: The amount of NH₃ in the solution was determined by colorimetry using the indophenol blue method.

Determination of N₂H₄: The N_2H_4 presented in the electrolyte was estimated by Watt and Chrisp method.

Determination of NO₃⁻: Firstly, a certain amount of electrolyte was taken out from the electrolytic cell and diluted to 5 mL to the detection range. Then, 0.1 mL 1 M HCl and 0.01 mL 0.8 wt% sulfamic acid solution were added into the aforementioned solution. The absorption spectrum was measured using a UV-Vis spectrophotometer and the absorption intensities at a wavelength of 220 nm and 275 nm were recorded. The final absorbance value was calculated by this equation: $A = A_{220nm} - 2A_{275nm}$. The concentration-absorbance curve was calibrated using a series of standard NaNO₃ solutions and the NaNO₃ crystal was dried at 105–110 °C for 2 h in advance.

Determination of H2: The gas product (H2) was monitored by GC.

Determination of FE and NH₃ yield: The FE for NH₃ electrosynthesis was defined as the amount of electric charge used for producing NH₃ divided by the total charge passed through the electrodes during the electrolysis. The FE was calculated according to the following equation:

$$FE = n \times F \times c \times V / (M \times Q) (1)$$

The NH₃ yield was calculated using the following equation:

NH₃ yield =
$$c_{NH3} \times V / (17 \times t \times S)$$
 (2)

Where n is the number of electrons was needed to produce one product molecule, F is Faraday constant (96485 C mol⁻¹); c is the measured mass concentration of product; V is the volume of the cathodic reaction electrolyte; M is relative molecular mass of specific product; Q is the quantity of applied charge/electricity; t is the time for which the potential was applied (2 h); S is the geometric area of the working electrode.

Zn–NO battery: Fe₂O₃/CP and a polished Zn plate were directly employed as the cathode and anode in a flow cell device. NO/Ar gas (10 *vol.*% NO, Yinde City Xizhou Gas Co., Ltd (China)) was fed into cathodic chamber at a constant flow rate of 30 sccm, which passes through the gas-diffusion layer and diffuse to the catalyst surface for NO reduction catalysis. Both the anolyte (1 M KOH) and catholyte (0.1 M Na₂SO₄) used for the battery system during the discharging process were circulated by a peristaltic pump at a flow rate of 15 mL min⁻¹. The electrolyte in the cathodic compartment was sampled at intervals of 1 h during the stability tests to calculate FE and NH₃ yield. The flow rates of the electrolyte and inlet gas were optimized for NH₃ synthesis in the assembled battery. The discharging polarization curves with a scan rate of 5 mV s⁻¹ and galvanostatic tests were conducted using CHI 660E workstation. The power density (P) of Zn–NO battery was determined by P = I × V, where I and V are the discharge current density and voltage, respectively (Fig. 3a). During discharging, the electrochemical reactions on each electrode can be described as follows:

Cathode: NO +
$$4H_2O + 5e^- \rightarrow NH_3 + 5OH^-(3)$$

Anode:
$$Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^-$$
 (4)
Overall: $5Zn + 2NO + 3H_2O \rightarrow 5ZnO + 2NH_3$ (5)

Computational details: We performed first-principles calculations by using Vienna ab initio simulation package (VASP).¹ The interaction between the valence electrons and ionic cores was described with projected augment wave (PAW) pseudopotential² and the exchange-correlation effect with Perdew, Burke, and Ernzerhof (PBE) functional.³ The DFT+U method was used to account for the Fe 3*d* electrons with the effective U value of 4.5 eV.⁴ The DFT-D3 scheme was adopted to account for the long-range dispersion interaction.⁵ The total energy and force convergence criteria are 10^{-4} eV and 0.03 eVÅ⁻¹, respectively. The spin-polarization effect was considered. The (2×2) supercells were employed with the vacuum layers of ~ 18 Å to simulate the reaction on the Fe₂O₃ (104), (110), and (012) surfaces, and for all the cases the Monkhorst-Pack (MP) grid of 2×2×1 was adopted for the first Brillouin zone integration,⁶ and the cutoff energy for the plane-wave basis is taken as 450 eV.

energy change for the elemental steps,⁷

$$\Delta G = \Delta E + \Delta E_{\text{ZPE}} - T\Delta S (6)$$

DFT total energy, zero-point energy, entropy, and the absolute temperature (298.15 K), are denoted as E, E_{ZPE} , S, and T, respectively. The corrections of zero-point energy and entropy for the free molecules were taken from the NIST databases, and those of the intermediates were calculated based on the DFT results.⁸

In the framework of computational hydrogen electrode model proposed by Nørskov et al.,¹⁰ the E_{ZPE} has been calculated by equation (7):

$$E_{ZPE} = \frac{1}{2} \sum_{i} h v_i \quad (7)$$

The contributions to the free energy resulting from entropy (– TS) were calculated by equation (8):

$$-TS = K_B T \sum_i \ln\left(1 - e^{-\frac{hv_i}{K_B T}}\right) - \sum_i hv_i \left(\frac{1}{e^{\frac{hv_i}{K_B T}}-1}\right)$$
(8)

In the equation, h, v_i , and K_B are the Planck constant, vibrational frequency, and

Boltzmann constant, respectively, and the temperature is taken as 298.15 K. The zero-point energy and TS values for the gas phase molecules were taken from NIST database, while those for the adsorbates were calculated following equations (7) and (8), respectively. The vibrational frequencies of the adsorbates were calculated by the default algorithm provided by VASP. Moreover, the zero-point energy and entropy values are presented in Table S4.

Different terminations exist for Fe₂O₃ (104), (110), and (012) surfaces, and to determine the most stable one, we investigated the surface energy (γ) of the various terminations:

$$\gamma = \frac{1}{2A} \left[E_{slab}^{unrelax} - nE_{bulk} \right] + \frac{1}{A} \left[E_{slab}^{relax} - E_{slab}^{unrelax} \right]$$
(9)

where, A is the surface aera of one side of the slab; n is the number of Fe₂O₃ units of the slab; E_{bulk} is the total energy of the bulk Fe₂O₃ formula unit; E_{slab}^{relax} and $E_{slab}^{unrelax}$ are the total energies of the relaxed and unrelaxed slabs, respectively.



Fig. S1. SEM images of bare CP.



Fig. S2. SEM and EDX elemental mapping images of Fe₂O₃/CP.



Fig. S3. (a) Polarization curves obtained at scan rates of 5, 10, 20, 50 and 80 mV s⁻¹ in 0.1 M Na₂SO₄ electrolyte with 0.5 mM Fe(II)EDTA. (b) Plot showing linear dependence of I_p with $v^{1/2}$.



Fig. S4. (a) Cyclic voltammograms for Fe₂O₃/CP in the double layer region at different scan rates of 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 mV s⁻¹ in 0.1 M Na₂SO₄ electrolyte with 0.5 mM Fe(II)EDTA. (b) Capacitive current densities as a function of scan rates for Fe₂O₃/CP. (c) ECSA-normalized LSV curves for Fe₂O₃/CP in Ar- and NO-saturated 0.1 M Na₂SO₄ electrolyte with 0.5 mM Fe(II)EDTA. (d) Nyquist plots of Fe₂O₃/CP in Ar- and NO-saturated 0.1 M Na₂SO₄ electrolytes with 0.5 mM Fe(II)EDTA.



Fig. S5. NORR chronoamperometry curves for Fe_2O_3/CP in NO-saturated 0.1 M Na_2SO_4 electrolyte with 0.5 mM Fe(II)EDTA at various potentials.



Fig. S6. UV-Vis absorption spectra of the electrolytes stained with indophenol indicator after 2 h electrolysis for Fe_2O_3/CP at various applied potentials.



Fig. S7. (a) UV-Vis absorption spectra of indophenol assays with NH_4^+ after incubated for 1 h at room temperature and corresponding (b) calibration curve used for estimating NH_3 . The calibration curve (y = 0.6337 x - 0.0047, $R^2 = 0.999$) shows good linear relation of absorbance value with NH_3 concentration.



Fig. S8. (a) UV-Vis absorption spectra of various N₂H₄ concentrations after incubated for 15 min at room temperature and corresponding (b) calibration curve used for estimating N₂H₄. The calibration curve (y = 0.677 x + 0.066, R² = 0.999) demonstrates good linear relation of the peak absorbance value with NH₃ concentration.



Fig. S9. UV-Vis absorption spectra of electrolytes estimated by the method of Watt and Chrisp after 2 h electrolysis on Fe_2O_3/CP at each given potential.



Fig. S10. Photographs of pH test strips with different electrolytes drops (blank electrolyte, electrolyte after 4 h of bulk electrolysis, electrolyte after 8 h of bulk electrolysis, electrolyte after 12 h of bulk electrolysis). The gradually changed color indicates that pH values increased with the electrolysis times, which can be ascribed to the increased NH₄⁺ concentrations (accumulated via the NORR process) in the cathodic compartment of H-cell.



Fig. S11. Photographs of the different electrolytes with or without adding NH_2OH . (a) Adding 50% NH_2OH solution (0.5 mL) to the KOH solution produces bubbles. (b) Adding 50% NH_2OH (0.5 mL) solution to the Na_2SO_4 solution produces bubbles.



Fig. S12. NORR performance of Fe₂O₃/CP in NO-saturated 0.1 M Na₂SO₄ electrolyte at -0.4 V. (a) Chronoamperometry curve. (b) UV-Vis absorption spectra of indophenol assays with NH₄⁺ after incubated for 2 h at room temperature. (c) NH₃ yield and (d) FE for such electrolysis tests at -0.4 V.



Fig. S13. Polarization curves of Fe_2O_3/CP in the gas-tight (under the NO atmosphere) and open electrolytic cells (under the NO + air atmosphere). The notable current density gap in the whole potential window suggests the simultaneous reduction of NO and NO_3^- on Fe_2O_3/CP .



Fig. S14. (a) UV-Vis absorption spectra of various NO_3^- concentration after incubated for 20 min at room temperature and corresponding (b) calibration curve used for estimating NO_3^- . (c) UV-Vis absorption spectra of NO_3^- for Fe₂O₃/CP in a gas-tight (in NO-saturated electrolyte) and open electrolytic cells (under NO + air atmosphere) at -0.4 V after 2 h electrolysis.



Fig. S15. UV-Vis absorption spectra of the electrolytes stained with indophenol indicator after 2 h electrolysis for Fe_2O_3/CP in a gas-tight and open cathodic chamber at -0.4 V.



Fig. S16. UV-Vis absorption spectra of the electrolytes stained with indophenol indicator at different operating conditions: the bulk electrolysis in NO-saturated electrolyte with Fe_2O_3/CP , the bulk electrolysis in NO-saturated electrolyte with CP, NO-saturated electrolyte with the Fe_2O_3/CP under open-circuit conditions, and Ar-saturated electrolyte with the Fe_2O_3/CP at -0.4 V for 2 h. All solutions were incubated with indophenol for 2 h.



Fig. S17. NORR chronoamperometry curve of CP in NO-saturated 0.1 M Na_2SO_4 electrolyte with 0.5 mM Fe(II)EDTA at -0.4 V.



Fig. S18. (a) Chronoamperometry curves of recycling tests at -0.4 V in NO-saturated 0.1 M Na₂SO₄ electrolyte with 0.5 mM Fe(II)EDTA for Fe₂O₃/CP. (b) UV-Vis absorption spectra of the electrolytes stained with indophenol indicator after recycling tests for NORR at -0.4 V in 0.1 M Na₂SO₄ with 0.5 mM Fe(II)EDTA. The Fe₂O₃/CP electrode was subjected to a 2 h testing period at -0.4 V in NO-saturated electrolyte. The NH₃ and FE were measured at the end of the testing period. The same procedure was repeated for the next three cycles under the same conditions. This means that when the recycling testing period was completed, the tested Fe₂O₃/CP electrode was subjected to a total of 8 testing hours.



Fig. S19. UV-Vis absorption spectra of the electrolytes stained with indophenol indicator after 12 h electrolysis on Fe_2O_3/CP at -0.4 V.



Fig. S20. (a) XRD pattern for Fe_2O_3/CP (brown) after bulk NORR electrolysis, and XRD patterns for pure CP (black) and fresh powder Fe_2O_3 scraped from Fe_2O_3/CP (blue) before bulk NORR electrolysis. (b) XRD pattern for powder Fe_2O_3 scraped from Fe_2O_3/CP after bulk NORR electrolysis.



Fig. S21. SEM images for our Fe_2O_3/CP (a) before and (b) after the long-term electrolysis.



Fig. S22. Schematic illustration of the Fe₂O₃/CP-based aqueous Zn–NO battery with the capability of achieving NO abatement, NH₃ synthesis, and energy output simultaneously. The catholyte and anolyte were 0.1M Na₂SO₄ and 1 M KOH, respectively, and the bipolar membrane was used to maintain the different pH of two compartments. The battery reaction mechanism is proposed as $5Zn + 2NO + 3H_2O \rightarrow$ $5ZnO + 2NH_3$. During the discharge process, Zn anode converts to ZnO and electrons are released, meanwhile, NO-to-NH₃ conversion occurs on Fe₂O₃/CP cathode with provided electrons. Note that bipolar membrane and different electrolytes were used to further improve the battery performance in our work (*Acc. Chem. Res.*, 2019, **52**, 1721–1729; *Energy Environ. Sci.*, 2021, **14**, 3938–3944).



Fig. S23. Galvanostatic discharge curve of Fe_2O_3/CP catalyzed Zn–NO battery. The energy density (mWh g_{zn}^{-1}) is calculated according to the equation: energy density = current × service hours × average discharge voltage / weight of consumed zinc.



Fig. S24. UV-Vis absorption spectra of the electrolytes stained with indophenol indicator at different discharging current densities of Fe_2O_3/CP -based Zn–NO battery.



Fig. S25. (a) Unit cell together with the lattice parameters of the Fe₂O₃ bulk. (b) The calculated total densities of states (DOS) of the Fe₂O₃ bulk and the local DOS of the O 2p and Fe 3*d* orbitals. The dashed line in (b) denotes the position of the Fermi level (*E_f*). Brown and red spheres represent Fe and O atoms, respectively.



Fig. S26. Side views of the stab models of the (a) Fe₂O₃ (104), (b) (110), and (c) (012) (1×1) surfaces with different terminations. The bottom two repeated atomic layers in the unit cell are fixed to mimic the bulk. The surface energies (γ) are given.



Fig. S27. Top views of the most stable (a) Fe_2O_3 (104), (b) (110), and (c) (012) (2×2) supercell (the one with the lowest surface energy is shown in Fig. S26). The adsorption sites for NO are marked.



Fig. S28. Atomic structures together with the binding energies are given for NO adsorption on the Fe_2O_3 (104) surface (from (a) to (e)). In (f), the adsorption configuration for the H atom at the site most favorable for NO is displayed. Brown, red, blue, cyan, and pink spheres denote Fe, O, N, the O atom in NO, and H atoms, respectively.



Fig. S29. Atomic structures together with the binding energies are given for NO adsorption on the Fe_2O_3 (110) surface (from (a) to (e)). In (f), the adsorption configuration for the H atom at the site most favorable for NO is displayed.



Fig. S30. Atomic structures together with the binding energies are given for NO adsorption on the Fe_2O_3 (012) surface (left). On the right, the adsorption configuration for the H atom at the same site is displayed.



Fig. S31. Atomic structures of the reaction intermediates for the pathways shown in Fig. 4b, where brown, red, blue, cyan, and pink spheres denote Fe, O, N, the O atom in NO, and H atoms, respectively.



Fig. S32. Atomic structures of the reaction intermediates for the pathways shown in

Fig. 4c.



Fig. S33. Free energy changes for the NO reduction on the Fe_2O_3 (104) to produce N_2 and N_2O (a) and (b) relevant intermediates. In (b), the brown, red, blue, cyan, and pink spheres denote Fe, O, N, the O atom in NO, and H atoms, respectively.



Fig. S34. Two different NO dimer adsorption configurations on the Fe_2O_3 (110) surface.



Fig. S35. Two different NO dimer adsorption configurations on the Fe_2O_3 (012) surface.



Fig. S36. Free energy changes, calculated with considering the solvation correction, for the NO reduction on the Fe_2O_3 (a) (104), (b) (110), and (c) (012) surfaces.



Fig. S37. Local DOS of the adsorbed NO molecule and its bonded atoms of the Fe_2O_3 (104), (110), and (012) surfaces.

Table S1. Comparison of onset potential (E_{onset}), current density (*j*, at the optimal electrode potential where the maximum FE is obtained), NH₃ yield, and FE of Fe₂O₃/CP with recent NORR electrocatalysts.

Catalyst	Eonset	j	NH3 yield	FE (%)	Electrolyte	Ref.
Fe ₂ O ₃ /CP	0.2 V	~7 mA cm ⁻ ² @–0.4 V	78.02 μ mol h ⁻¹ cm ⁻² (0.0216 μ mol s ⁻¹ cm ⁻²) (221.07 μ g h ⁻¹ mg ⁻¹ _{cat.})	86.73	0.1 M Na ₂ SO ₄ + 0.5 mM Fe(II)EDTA	This work
Ru0.05Cu0.95	-0.5 V vs. Ag/Ag Cl	~5 mA cm ⁻ ² @-1.1 V vs. Ag/AgCl	17.68 μmol h ⁻¹ cm ⁻²	64.9	0.5 M Na2SO4	Sci. China. Chem., 2021, 64 , 1493–1497
CoSe2@CNTs	/	>1 mA	/	48.14	Na ₂ SO ₄ + Fe(II)EDTA	Environ. Sci. Pollut. Res., 2017, 24 , 14249–14258
Single atom Nb	-0.2 V	~50 mA cm ⁻ ² @-0.6 V	295.2 μmol h ⁻¹ cm ⁻²	77	0.1 M HCl	Nano Energy, 2020, 78 , 105321
FeNC	~0.6 V	$> 5.5 \text{ mA cm}^{-2}$	$\sim 20.2 \ \mu mol \ cm^{-2} \ h^{-1}$	5.1	0.1 M HClO4	Nat. Commun., 2021, 12 , 1856
Cu foam (NORR)	~0.6 V	~85 mA cm ⁻ ² @-0.9 V	517.1 μmol h ⁻¹ cm ⁻²	93.5		Angew. Chem. Int. Ed., 2020, 59 , 9711–9718
Cu foil (NORR)	~0.45 V	~37 mA cm ⁻ ² @-0.9 V	95.0 μmol h ⁻¹ cm ⁻²	61.9	0.25 M LiSO4	
Pt foil (NORR)	~0.45 V	~47 mA cm ⁻ ² @-0.9 V	99.4 μ mol h ⁻¹ cm ⁻²	24.1	-	
Ag nanostructure	0.1 V	~23 mA cm ⁻ ² @-0.34 V	$229 \ \mu mol \ h^{-1} \ cm^{-2}$	99%	0.1 M PSB + 200 mM Fe(II)EDTA	ACS Energy Lett., 2020, 5 , 3647–3656
MoS ₂ /GF	0.19 V	~7 mA cm ⁻ $^{2}@0.1 V$	91 μ mol h ⁻¹ cm ⁻²	75.9	0.1 M HCl + Fe(II)SB	Angew. Chem. Int. Ed., 2021, 60 , 25263–25268
Ni ₂ P/CP	0 V	~7 mA cm ⁻ ² @-0.2 V	$33 \ \mu mol \ h^{-1} \ cm^{-2}$	76.9	0.1 M HCl	J. Mater. Chem. A, 2021, 9 , 24268–24275
MnO _{2-x}	~-0.1 V	\sim 5 mA cm ⁻ $^{2}@-1.0V$	$\begin{array}{c} 99.04 \times 10^{-13} \mu mol \ h^{-1} \\ cm^{-2} \end{array}$	82.8	0.2 M Na2SO4	<i>Mater. Today Phys.</i> , 2022, 22 , 100586

incur 100, incur 1003 , and incur 102 battery systems.					
Battery systems	Catalyst	NH3 yield	Power density	Stability	Ref.
metal-NO	Fe ₂ O ₃ /CP	145.28 μg h ⁻¹ mg _{cat.} ⁻¹	1.18 mW cm ⁻²	7 h	This work
metal-NO	Ni ₂ P/CP	62.05 μ g h ⁻¹ mg _{cat.} ⁻¹	1.53 mW cm^{-2}	3 h	J. Mater. Chem. A, 2021, 9 , 24268– 24275
metal-NO	MoS ₂ /GF	411.8 μ g h ⁻¹ mg _{cat.} ⁻¹	1.04 mW cm^{-2}	/	Angew. Chem. Int. Ed., 2021, 60 , 25263–25268.
metal–NO ₃ ⁻	Pd-doped TiO ₂ nanoarray	540 $\mu g h^{-1} cm^{-2}$	0.87 mW cm^{-2}	12 h	Energy Environ. Sci., 2021, 14 , 3938–3944
metal-N ₂	Fe 1.0 HTNs	$0.172 \ \mu g \ h^{-1} \ cm^{-2}$	$0.02765 \text{ mW cm}^{-2}$	/	J. Mater. Chem. A, 2021, 9 , 4026– 4035
metal-N ₂	CoPi/HSNPC	11.62 μ g h ⁻¹ mg ⁻¹ _{cat.}	0.31 mW cm^{-2}	/	J. Mater. Chem. A, 2021, 9, 11370–11380
metal-N ₂	VN@NSC-900	$0.172 \ \mu g \ h^{-1} \ cm^{-2}$	$0.01642 \text{ mW cm}^{-2}$	/	Appl. Catal. B: Environ., 2021, 280 , 119434
metal-N ₂	CoPi/NPCS	14.7 $\mu g h^{-1}$ mg ⁻¹ _{cat.}	0.49 mW cm^{-2}	/	ACS Appl. Mater. Interfaces, 2021, 13, 12106–12117
metal-N ₂	graphene/Pd	27.1 mg g ⁻¹ cat. h ⁻¹	/	8 h	<i>Energy Environ. Sci.</i> , 2020, 13 , 2888–2895
metal-N ₂	BNFC-800	/	127 mW cm^{-2}	/	J. Mater. Chem. A, 2020, 8 , 8430–8439
metal-N ₂	NbS2	/	0.31 mW cm^{-2}	/	Appl. Catal. B: Environ., 2020, 270 , 118892
metal-N ₂	Cu-2	$0.125 \ \mu g \ h^{-1} \ cm^{-2}$	$0.0101 \text{ mW cm}^{-2}$	/	<i>Chem. Commun.</i> , 2019, 55 , 12801–12804

Table S2. Comparison of NH_3 yield and power density of our battery with recent metal-NO, metal- NO_3^- , and metal- N_2 battery systems.

BNFC-800: boron, nitrogen and fluorine ternary-doped carbon

Battery type	Chemical reaction	Theoretical voltage (V)
Zn–NO	$5Zn + 2NO + 3H_2O \rightarrow 5ZnO + 2NH_3$	2.14
Li–S	$2Li + S \rightarrow Li_2S$	2.2
Li–O ₂	$2Li + O_2 \rightarrow Li_2O_2$	3.0
Li–CO ₂	$4Li + 3CO_2 \rightarrow C + 2Li_2CO_3$	2.7
Li–N ₂	$6Li + N_2 \rightarrow 2Li_3N$	0.54
Zn–CO ₂	$Zn + CO_2 + H_2O \rightarrow ZnO + HCOOH$	0.955
Al–N ₂	$2Al + N_2 \rightarrow 2AlN$	0.99
Zn–Air	$2Zn + O_2 \rightarrow 2ZnO$	1.65
Zn-Nitrate	$4Zn+NO_{3}^{-}+3H_{2}O\rightarrow 4ZnO+NH_{4}OH+OH^{-}$	1.85

 Table S3. Theoretical voltages for different types of metal-based batteries.

Table S4. The calculated zero-point energy (E_{ZPE}) and the product (*TS*) of temperature (T = 298.15 K) and entropy (*S*) of the different species along the NORR reaction pathway, where * represents the adsorption site.

Species	ZPE (eV)	TS (eV)
NO*	0.15	0.13
NHO*	0.46	0.16
NHOH*	0.80	0.12
NH*	0.35	0.08
NH ₂ *	0.72	0.06
NH ₃ *	1.03	0.11
NH ₂ OH*	1.15	0.14
NH2O*	0.82	0.13
NH ₃ O*	1.05	0.15
NH ₃ OH*	1.39	0.17
N_2O_2*	0.36	0.17
N ₂ O ₂ H*	0.73	0.21
N_2O^*	0.31	0.29
N_2 *+OH*	0.51	0.28
N_2 *	0.18	0.17
O*	0.08	0.05
OH*	0.38	0.06
NO(g)	0.12	0.65
$H_2(g)$	0.27	0.40
$H_2O(g)$	0.56	0.67
NH ₃ (g)	0.89	0.60
N ₂ O(g)	0.29	0.68
NH ₂ OH(g)	1.05	0.73

References

- 1 G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169–11186.
- 2 P. E. Blöchl, *Phys. Rev. B*, 1994, **50**, 17953–17979.
- 3 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, 77, 3865–3868.
- H. Jani, J. Linghu, S. Hooda, R. V. Chopdekar, C. Li, G. J.Omar, S. Prakash, Y. Du, P. Yang, A. Banas, K. Banas, S. Ghosh, S. Ojha, G. R. Umapathy, D. Kanjilal, A. Ariando, S. J. Pennycook, E. Arenholz, P. G. Radaelli, J. M. D. Coey, Y. P. Feng and T. Venkatesan, *Nat. Commun.*, 2021, 12, 1668.
- 5 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, J. Chem. Phys., 2010, 132, 154104.
- 6 H. J. Monkhorst and J. D. Pack, *Phys. Rev. B*, 1976, **13**, 5188–5192.
- J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Bligaard and H. Jónsson, J. Phys. Chem. B, 2004, 108, 17886–17892.
- 8 http://webbook.nist.gov/chemistry/