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Single-atom catalysts templated by metal–organic frameworks for electrochemical nitrogen reduction†

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The electrocatalytic nitrogen reduction reaction (NRR) has much prospect for substituting the energy-consuming Haber–Bosch process. Nevertheless, its sluggish reaction kinetics and the competing hydrogen evolution reaction always result in limited ammonia yield and low faradaic efficiency (FE). In this work, an Fe-decorated porphyrinic metal–organic framework (MOF) is employed as a precursor to construct single-atom Fe implanted nitrogen-doped carbon catalysts (Fe₁-N-C) through a mixed ligand strategy. Benefiting from the highly dispersed single-atom Fe sites, hierarchically porous structure and good conductivity, Fe₁-N-C shows a FE of 4.51% and an ammonia yield rate of 1.56×10^{-11} mol cm⁻² s⁻¹ at -0.05 V *versus* the reversible hydrogen electrode, superior to those of Co₁-N-C and Ni₁-N-C. Theoretical calculations reveal that Fe₁-N-C shows the lowest energy barrier of the rate-determining step during the NRR process, consistent with its highest activity obtained in experiments. This work reveals the unique potential of single-atom catalysts for the electrochemical NRR and provides in-depth insights into the catalytic mechanism of the NRR.

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Introduction

Single-atom catalysts (SACs), presenting the utmost utilisation of metal atoms at the atomic scale, possess coordinatively unsaturated metal atoms acting as active sites and provide a great variety of opportunities for application in chemical reactions.^{1–5} Due to their remarkable activity, high selectivity, considerable stability and good recyclability, SACs are capable of bridging the gap between homogeneous and heterogeneous catalysts.^{6–13} Recently, SACs have been found to be promising in electrocatalysis, such as the efficient CO₂ reduction reaction (CO₂RR).^{14–16} Due to the atomic dispersion of metal atoms in SACs, only top site adsorption is permitted, resulting in sluggish kinetics of hydrogen evolution.¹⁷ Moreover, the positively charged metal atoms in SACs are effective to impede the

adsorption of protons, further preventing the competitive hydrogen evolution reaction.¹⁷ Thus, compared with other heterogeneous catalysts, some SACs might possess particular advantages to suppress the HER process.

Ammonia synthesis *via* electrocatalytic nitrogen reduction similar to the CO₂RR is also performed at a potential range overlapped with that of HER, where SACs might be also promising but are rarely reported so far.^{18–27} Reports have illustrated homogeneous Fe-dinitrogen complexes as efficient NRR catalysts.^{28,29} Besides, the Fe site has also been found to be essential for the biological fixation in nitrogenase.^{30–35} Based on the facts above, single-atom Fe catalysts, with a well-defined structure similar to Fe-dinitrogen complexes, might be promising electrocatalysts for the NRR.^{36,37} Relevant theoretical predictions have also been reported to support the promising NRR application of Fe-N-C materials.^{38,39} Thus, the accurate construction of SACs, especially single-atom Fe catalysts, is much needed in the exploration of the efficient NRR.

Metal–organic frameworks (MOFs), a kind of porous crystalline structure assembled with metal clusters/ions and organic ligands, have aroused widespread concern in the research frontier.^{40–65} Featuring a well-defined crystalline structure, a large surface area and excellent tailorability, MOFs have been extensively applied for the rational construction of efficient catalysts.^{40–65} On account of the structural regularity and synthetic tunability, MOFs have also been proven to be ideal precursors/templates to produce SACs with improved metal loading *via* pyrolysis.^{66–70} In addition, the porous characteristic of the MOF precursor can also be largely inherited to

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its derivative, which can greatly accelerate the catalytic process of MOF-derived SACs.

Taking the above into consideration, single-atom Fe embedded nitrogen-doped carbon was constructed with a porphyrinic MOF (PCN-222) for the investigation of the electrocatalytic NRR. Based on ligand modulation, PCN-222(Fe), with a suitable molar ratio of Fe-TCPP (iron(III)*meso*-tetra(4-carboxyphenyl)porphine chloride) and H₂-TCPP (tetra(4-carboxyphenyl)porphine), was synthesized. With the assistance of the high-content of H₂-TCPP in PCN-222(Fe), the distance of the neighboring Fe atoms in Fe-TCPP can be effectively expanded. Upon pyrolysis, the agglomeration of Fe atoms in PCN-222(Fe) can be effectively inhibited and single Fe atom decorated nitrogen-doped porous carbon (designated as Fe₁-N-C) can be finally obtained (Schemes 1 and S1†). In virtue of the single-atom Fe sites and hierarchically porous structure, Fe₁-N-C shows efficient ammonia synthesis with a yield rate of $1.56 \times 10^{-11} \text{ mol cm}^{-2} \text{ s}^{-1}$ and a high FE of 4.51% at $-0.05 \text{ V vs. the reversible hydrogen electrode (RHE)}$, much better than that of Co₁-N-C and Ni₁-N-C synthesized using the same procedure. Density functional theory (DFT) calculations demonstrate that the energy barrier for the rate-determining step (RDS) of Fe₁-N-C is lower than that of Co₁-N-C and Ni₁-N-C, confirming the excellent activity of Fe₁-N-C toward the NRR.

Experimental

Synthesis of *meso*-tetra(4-carboxyphenyl)porphine tetramethyl ester (TPPCOOMe)

The ligands were prepared on the basis of a reported procedure.⁷¹ Pyrrole (6.0 g), methyl 4-formylbenzoate (13.8 g) and propionic acid (200 mL) were homogeneously mixed and heated at 140 °C under reflux for 12 h. The sample was acquired *via* suction-filtration and subsequent washing with ethanol, ethyl acetate and THF. The solid was eventually dried at 60 °C under vacuum.

Synthesis of iron(III) *meso*-tetra(4-methoxycarbonylphenyl)porphine chloride (Fe-TPPCOOMeCl)

Generally, TPPCOOMe (1.8820 g) and FeCl₂·4H₂O (5.51 g) were dispersed in DMF (100 mL) and heated at 160 °C for 6 h under reflux. Then H₂O (150 mL) was replenished and the precipitate was acquired by suction-filtration and subsequent washing with

H₂O three times. The sample was dissolved in chloroform (150 mL) and extracted with 1 M HCl three times and water twice.

Synthesis of Co-TPPCOOMe and Ni-TPPCOOMe

The procedures were identical to those of Fe-TPPCOOMeCl, except for the amount of CoCl₂·6H₂O (6.59 g) and NiCl₂·6H₂O (6.59 g).

Synthesis of Fe-TCPP

A mixture of Fe-TPPCOOMeCl (0.75 g), THF (25 mL), MeOH (25 mL) and 25 mL KOH (2.63 g) solution was heated under reflux at 85 °C for 6 h. The organic solvent was evaporated and H₂O was replenished to the mixture. The resultant solution underwent acidification with 1 M HCl until the pH reached 3. Then the resultant precipitate was acquired by suction-filtration and subsequent washing with H₂O twice. The solid was eventually dried at 60 °C under vacuum.

Synthesis of Co-TCPP, Ni-TCPP and H₂-TCPP

The procedures were identical to those of Fe-TCPP, except for utilizing Co-TPPCOOMe (0.75 g), Ni-TPPCOOMe (0.75 g) and TPPCOOMe (0.75 g).

Synthesis of PCN-222(Fe)

The catalyst preparation is similar to a reported procedure.⁶⁶ Typically, ZrOCl₂·8H₂O (108.6 mg), Fe-TCPP (6.8 mg), H₂-TCPP (24 mg), DMF (10 mL) and CF₃COOH (0.45 mL) were placed in a Pyrex vial (20 mL) and were subsequently ultrasonically dissolved and heated at 120 °C for 18 h. Then the resultant sample was acquired by centrifugation and subsequent washing with DMF three times and acetone twice. The solid was eventually dried at 60 °C under vacuum.

Synthesis of PCN-222(Co) and PCN-222(Ni)

The procedures were identical to those of PCN-222(Fe), except for utilizing Co-TCPP (7 mg) and Ni-TCPP (7 mg).

Synthesis of Fe₁-N-C

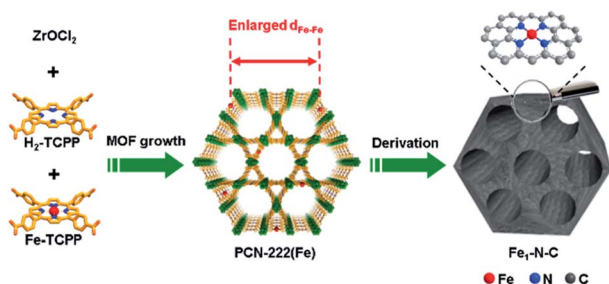
Typically, PCN-222(Fe) was transferred to a tube furnace, heated to 800 °C in 3 h and kept for 2 h under a N₂ atmosphere. The metal oxide was further etched by soaking the sample in a HF (20 wt%) solution at 80 °C. Then the resultant precipitate was acquired by centrifugation and subsequent washing with H₂O three times and EtOH twice. The solid was eventually dried at 60 °C under vacuum.

Synthesis of Fe_{NP}-N-C and N-C

The procedures were identical to those of Fe₁-N-C, except for respectively utilizing Fe-TCPP (32 mg) and H₂-TCPP (30 mg) as the ligand in the synthesis of the MOF precursor.

Synthesis of Co₁-N-C and Ni₁-N-C

The procedures were identical to those of Fe₁-N-C, except for utilizing PCN-222(Co) and PCN-222(Ni).



Scheme 1 The fabrication of Fe₁-N-C from PCN-222(Fe).

Electrochemical NRR tests

Electrochemical tests were performed with a Zahner Zennium system by utilizing a Ag/AgCl reference electrode and a Pt counter electrode. Before measurement, N₂ was bubbled for 30 min. In the electrochemical NRR, a chronoamperometry test was performed with continuous bubbling of N₂ at 40 sccm. For electrode preparation, the catalyst (5 mg) and Nafion solution (30 μ L) were added to 500 μ L absolute ethanol. After sonication, the ink (120 μ L) was coated on both sides of carbon paper (1 \times 1 cm²) and dried at 85 $^{\circ}$ C.

Determination of NH₃

Typically, 2 mL NaOH solution (1 M) including sodium citrate (5 wt%) and *o*-hydroxybenzoic acid (5 wt%) was transferred to the electrolyte (2 mL). Next, 1 mL NaClO (0.05 M) and 200 μ L C₅FeN₆Na₂O (sodium nitroprusside) solution (1 wt%) were replenished. When the system was maintained at 25 $^{\circ}$ C for 2 h, the concentration of the obtained solution was quantified on the basis of UV-vis absorption at 655 nm. The calibration curve was acquired with standard NH₄Cl solutions, as depicted in Fig. S1 and S2.† The limit of detection of the method is calculated to be 0.0095 μ g mL⁻¹. The standard NH₄Cl solution was prepared with 0.1 M HCl, which is consistent with the electrolyte utilized in the electrocatalytic experiments.

Determination of N₂H₄

As for the preparation of the coloring reagent, generally 4 g *p*-dimethylaminobenzaldehyde was added to a mixture of 20 mL concentrated HCl and 200 mL ethanol. Typically, 2 mL coloring reagent was added to 2 mL electrolyte. When the solution was maintained at 25 $^{\circ}$ C for 15 min, the concentration of the obtained solution was quantified on the basis of the UV-vis absorption wavelength at 455 nm. The calibration curve was acquired with standard N₂H₄ solutions, as depicted in Fig. S3.† The standard N₂H₄ solution was prepared with 0.1 M HCl, which is consistent with the electrolyte utilized in the electrocatalytic experiments.

Calculations of the NH₃ yield rate and FE

Typically, the NH₃ yield rate (*r*) and FE are quantified as below,

$$r = \frac{[\text{NH}_3] \times V}{s \times t}$$

$$\text{FE} = \frac{Q_{\text{NH}_3}}{Q} = \frac{3 \times F \times [\text{NH}_3] \times V}{\int I dt}$$

where [NH₃] is the NH₃ concentration measured from UV-vis absorption spectra, *V* represents the volume of the electrolyte (*V* = 25 mL), *s* is the practical surface area, *t* is the time applied for the chronoamperometry test (*t* = 2 h) and *F* is the Faraday constant.

Nuclear magnetic resonance (NMR) measurement

After electrolysis, 0.9 mL electrolyte was taken out and mixed with 0.1 mL deuterium oxide containing dimethyl sulphoxide as the internal standard. The ¹H NMR measurement was performed with water suppression (Bruker Avance III 400 MHz). To quantify the amount of ¹⁵NH₄⁺, a series of standard ¹⁵NH₄Cl solutions (0.05 μ g mL⁻¹, 0.075 μ g mL⁻¹, 0.1 μ g mL⁻¹ and 0.15 μ g mL⁻¹) were prepared with 0.1 M HCl. The calibration curve was obtained by integrating the ¹⁵N doublet of the NMR signal.

Results and discussion

PCN-222(Fe), with a uniform rod shaped morphology, was successfully synthesized (Fig. 1a and S4†). The type-IV isotherm features a high Brunauer–Emmett–Teller (BET) surface area of 2011 m² g⁻¹ and the corresponding pore size distribution shows the existence of micropores (1.2 nm) and mesopores (3.2 nm) (Fig. S5†). The transmission electron microscopy (TEM) image of PCN-222(Fe) can further illustrate the existence of mesopores with high orientation (Fig. 1b). After pyrolysis of PCN-222(Fe) followed by the removal of ZrO₂, Fe₁-N-C with the retained rod-shape was finally obtained (Fig. 1c). N₂ sorption measurement of Fe₁-N-C indicates a large BET surface area (440 m² g⁻¹); the hysteresis loop reveals the mesoporous structure (Fig. S6†). In the powder X-ray diffraction result, the broad peaks at around 25 $^{\circ}$ and 44 $^{\circ}$ correspond to the (002) and (101) facets of the graphitized carbons (Fig. S7†). Any exceptional peaks corresponding to the diffraction of Fe species cannot be observed, which is consistent with the absence of Fe particles in the TEM image (Fig. 1c). Furthermore, energy-dispersive spectroscopy (EDS) mapping reveals the homogeneous distribution of Fe and N in the carbon matrix (Fig. S8†).

In the Raman scattering spectra of Fe₁-N-C, two peaks around 1352 cm⁻¹ (D band) and 1591 cm⁻¹ (G band) correspond to disordered and graphitic carbon structures (Fig. S9†). The relatively low intensity ratio (0.93) *I*_D/*I*_G illustrates the high

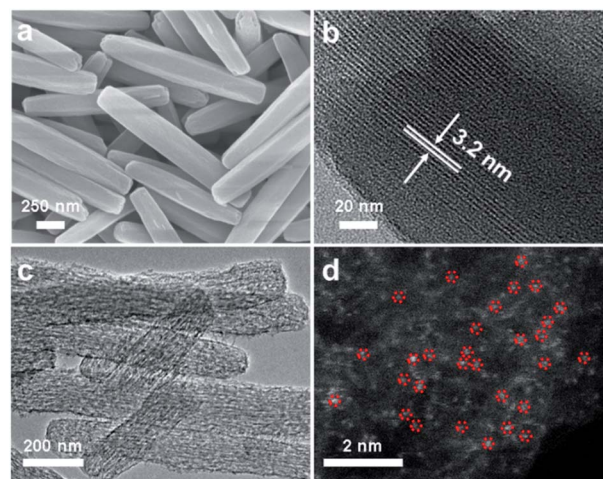


Fig. 1 (a) Scanning electron microscopy and (b) TEM images of PCN-222(Fe). (c) TEM and (d) aberration-corrected HAADF-STEM images of Fe₁-N-C.

graphitization degree of Fe₁-N-C. With respect to the high-resolution N 1s X-ray photoelectron spectroscopy (XPS) spectrum, the binding energies at 398.5 eV, 400.2 eV, 401.1 eV and 402.8 eV correspond to pyridinic N, pyrrolic N, graphitic N and oxidized N. The peak at 399.2 eV reveals the existence of Fe-N_x species in Fe₁-N-C (Fig. 2a). Besides, the Fe 2p spectrum of Fe₁-N-C sheds light on the oxidized state of Fe, reflecting the presence of Fe-N_x series (Fig. S10†). Inductively coupled plasma atomic emission spectroscopy and elemental analysis were also performed to further quantify the content of Fe and N, indicating an Fe loading of 1.71 wt% and a N content of 4.81 wt% in Fe₁-N-C (Tables S1 and S2†).

To further investigate the existing forms of the Fe atom in Fe₁-N-C, aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was utilized.

The isolated bright spots exhibit the atomic distribution of Fe atoms (Fig. 1d). Apart from this, X-ray absorption spectroscopy (XAS) was performed for understanding the coordination environment and electronic state of Fe metal atoms. In the Fe K-edge X-ray absorption near-edge structure (XANES) spectra, Fe₁-N-C exhibits an energy absorption profile located between that of Fe foil and Fe₂O₃, demonstrating a positive valence state of Fe atoms in Fe₁-N-C (Fig. 2b). The Fourier transform-extended X-ray absorption fine structure (FT-EXAFS) curve of Fe₁-N-C presents a main peak at *ca.* 1.4 Å, corresponding to Fe-N coordination. The Fe-Fe peak at 2.2 Å cannot be observed, exhibiting the exclusive existence of single-atom Fe (Fig. 2c). To recognise the coordination structure of Fe₁-N-C, EXAFS fitting was also applied. According to the best fitting result, the single Fe atom is coordinated by ~4 N atoms, suggesting the existence of Fe-N₄ sites in Fe₁-N-C (Fig. 2d and Table S3†).

With regard to the NRR performance of the prepared SACs, a linear sweep voltammetry (LSV) test was first performed. As for Fe₁-N-C, the current density in the N₂ saturated electrolyte is higher than that in the Ar saturated counterpart (Fig. 3a), demonstrating that the NRR can be successfully catalyzed by

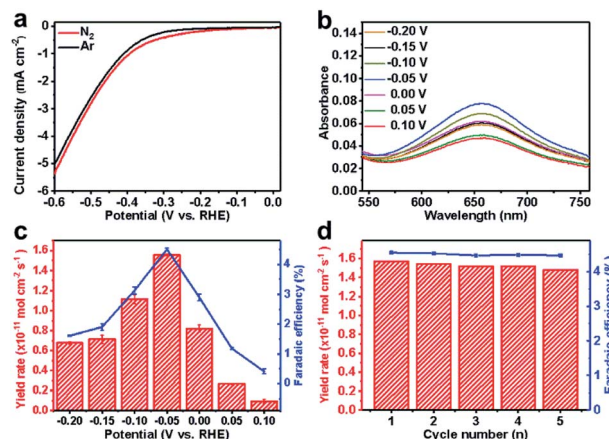


Fig. 3 (a) LSV curves of Fe₁-N-C in N₂ and Ar-saturated electrolyte. (b) UV-vis spectra of the electrolyte at various potentials on Fe₁-N-C. (c) NH₃ yield rate and FE of Fe₁-N-C at various potentials. (d) Recycling test of Fe₁-N-C at -0.05 V.

Fe₁-N-C. Proved by the fact above, potentiostatic tests were systematically performed at a sequence of potentials under atmospheric pressure so that the optimal conditions for NH₃ formation can be achieved. As exhibited in the UV-vis spectra, the generated ammonia reacts with phenol and hypochlorite in the coloring reagent. The electrolyte obtained at -0.05 V has the maximum absorption at 655 nm, corresponding to the highest concentration of ammonia (Fig. 3b). This result manifests that the best NRR performance of Fe₁-N-C can be realized at -0.05 V vs. RHE. To further quantify the accurate ammonia yield, a set of control experiments were performed.^{72–74} The Ar control experiments and the N₂ control experiments were subsequently conducted and all of the potential distractions (including ammonia and NO_x) to the NRR activity are well ruled out (Fig. S11†). Under these circumstances, the highest NH₃ yield rate is calculated to be $1.56 \times 10^{-11} \text{ mol cm}^{-2} \text{ s}^{-1}$, with a FE of 4.51% (Fig. 3c). During five successive recycling tests at -0.05 V, no obvious decay of the NH₃ yield rate or FE can be observed, demonstrating excellent stability of Fe₁-N-C (Fig. 3d). Furthermore, during 60 h of continuous electrolysis, the NH₃ yield rate increases linearly and reaches a turnover number (TON) of 11, further illustrating the excellent stability of Fe₁-N-C (Fig. S12†). Apart from ammonia, hydrazine (N₂H₄) might be another potential product obtained in the NRR. In the electrocatalytic NRR of Fe₁-N-C, no N₂H₄ can be obtained, demonstrating the specific selectivity of Fe₁-N-C toward NH₃ in nitrogen reduction (Fig. S13†).

Accurately, the quantitative isotopic labelling experiment using ¹⁵N₂ as the feed gas was also performed to strictly determine the origin of ammonia. When Fe₁-N-C underwent the chronoamperometry test at -0.05 V for 2 h under ¹⁵N₂, the sample was analyzed by ¹H nuclear magnetic resonance (NMR).

From the spectra, only the doublet coupling for ¹⁵NH₄⁺ can be identified (Fig. 4a). Furthermore, the integral of the ¹⁵N doublet was calculated to be 0.151, corresponding to an ¹⁵NH₄⁺ concentration of 0.076 μg mL⁻¹ (Fig. 4b). A similar result was also obtained from the indophenol blue method, with an

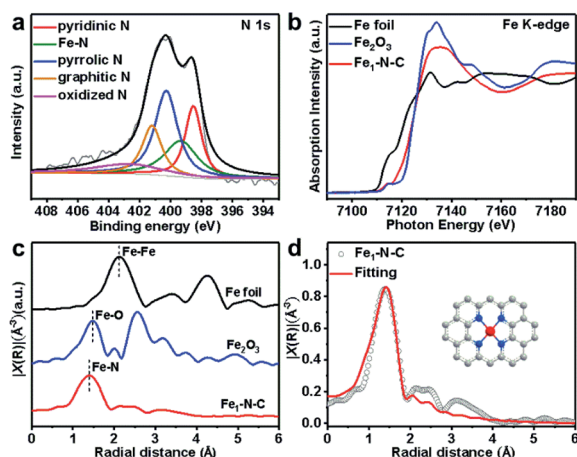


Fig. 2 (a) XPS result of N 1s of Fe₁-N-C. (b) Fe K-edge XANES and (c) FT-EXAFS curves of Fe foil, Fe₁-N-C and Fe₂O₃. (d) EXAFS fitting result of Fe₁-N-C.

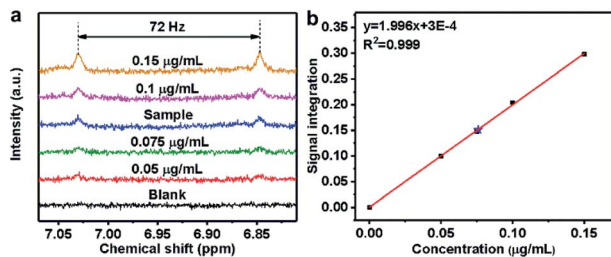


Fig. 4 (a) ^1H NMR result of standard $^{15}\text{NH}_4\text{Cl}$ solutions. (b) The ^1H NMR calibration curve of $^{15}\text{NH}_4\text{Cl}$. The blue asterisk stands for the NRR sample of $\text{Fe}_1\text{-N-C}$ at -0.05 V.

amount of $0.077\ \mu\text{g mL}^{-1}$. Therefore, the quantitative isotopic labelling experiments provide solid evidence to support that NH_3 is produced from the NRR.^{75–78} To rule out the activity of nitrogen-doped carbon, N-C, from pyrolysed PCN-222, without Fe was tested for the NRR. At -0.15 V, N-C exhibited poor NRR performance, with a FE of 0.1% (Fig. S14†). To have a better comparison, a catalyst featuring Fe nanoparticles (denoted as $\text{Fe}_{\text{NP}}\text{-N-C}$) was also synthesized (Fig. S15†), which exhibited poor NRR performance, with a faradaic efficiency of 0.21% and an ammonia yield rate of $0.79 \times 10^{-11}\ \text{mol cm}^{-2}\ \text{s}^{-1}$ at -0.05 V (Fig. S16†). Furthermore, SCN^- , which can block the single-atom Fe sites, has been added and leads to the decrease of the ammonia yield rate (Fig. S17†).⁷⁰ The results manifest that the single-atom Fe sites are the real source of the high NRR activity of $\text{Fe}_1\text{-N-C}$. In order to make a further comparison, PCN-222(Co) and PCN-222(Ni) have also been synthesized and used to construct $\text{Co}_1\text{-N-C}$ and $\text{Ni}_1\text{-N-C}$, both of which show similar characteristics (including morphology, pore characteristics, metal loading, N configurations and content, as well as graphitization degree) to $\text{Fe}_1\text{-N-C}$ (Fig. S18–S20, Tables S4 and S5†). Besides, the state of Co and Ni in $\text{Co}_1\text{-N-C}$ and $\text{Ni}_1\text{-N-C}$ has also been confirmed with aberration-corrected HAADF-STEM and XAS characterization studies (Fig. S21–S24, Tables S6 and S7†). When used as NRR catalysts, both $\text{Co}_1\text{-N-C}$ and $\text{Ni}_1\text{-N-C}$ show a much inferior ammonia yield rate and FE to those of $\text{Fe}_1\text{-N-C}$, following the trend $\text{Fe}_1\text{-N-C} > \text{Co}_1\text{-N-C} > \text{Ni}_1\text{-N-C}$, which further manifests the advantage of the single-atom Fe catalyst for efficient NRR (Fig. 5 and S25–S27†). Moreover, no N_2H_4 can be detected in the NRR of $\text{Co}_1\text{-N-C}$ or $\text{Ni}_1\text{-N-C}$, presenting their excellent selectivity toward NH_3 in nitrogen reduction (Fig. S28 and S29†).

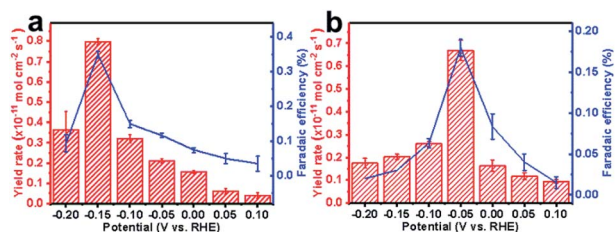


Fig. 5 NH_3 yield rate and FE of (a) $\text{Co}_1\text{-N-C}$ and (b) $\text{Ni}_1\text{-N-C}$ at various potentials.

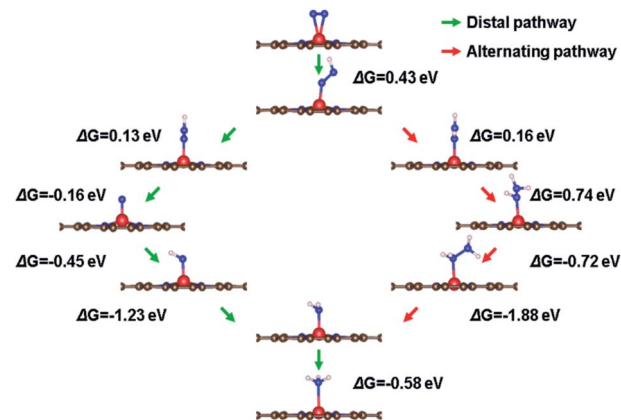


Fig. 6 The reaction diagram of the NRR on the surface of $\text{Fe}_1\text{-N-C}$.

To better understand the capability of $\text{Fe}_1\text{-N-C}$ for efficient NRR, the variation of Gibbs free energy (ΔG) along the NRR reaction pathway at the zero electrode potential ($U = 0$) was studied by DFT.⁷⁹ The result exhibits that the NRR on $\text{Fe}_1\text{-N-C}$ proceeds through the distal pathway, where N_2 adsorption is the RDS with a ΔG of 1.03 eV (Fig. 6, 7a and 7b). In comparison, the RDS for both $\text{Co}_1\text{-N-C}$ and $\text{Ni}_1\text{-N-C}$ is the conversion from N_2^* to N_2H^* , with a ΔG of 1.30 eV and 2.29 eV respectively, which is consistent with experimental catalytic performance and supports the high catalytic activity of $\text{Fe}_1\text{-N-C}$ theoretically (Fig. 7a and S30†). To further investigate the difference of FE among these catalysts, Bader charge analysis was performed. The charge values of Fe, Co and Ni were +1.08 e, +0.87 e and +0.84 e, respectively (Fig. 7c). Considering the electrostatic repulsion between protons and positively charged metal atoms, the most positive charge on the Fe atom can prevent the approach of protons, significantly suppressing the HER process.¹⁷ With the lowest energy barrier of the RDS toward the NRR and the most sluggish HER kinetics, the best NRR performance of $\text{Fe}_1\text{-N-C}$ can be well understood.

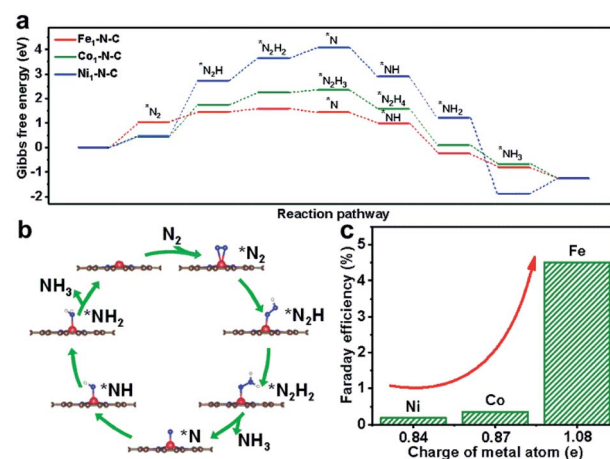


Fig. 7 (a) Free energy plot of the NRR on $\text{Fe}_1\text{-N-C}$, $\text{Co}_1\text{-N-C}$ and $\text{Ni}_1\text{-N-C}$. (b) The intermediates in the distal path of the NRR on $\text{Fe}_1\text{-N-C}$. (c) The Bader charge analysis of $\text{Fe}_1\text{-N-C}$, $\text{Co}_1\text{-N-C}$ and $\text{Ni}_1\text{-N-C}$.

Conclusions

In summary, Fe₁-N-C with atomically dispersed Fe has been successfully constructed by rational control over the distance of adjacent Fe atoms in a porphyrinic MOF. Thanks to the single-atom Fe sites (excellent performance for the NRR) and hierarchically porous structure (accessibility of active sites), Fe₁-N-C has a superior NRR performance with an NH₃ yield rate of 1.56×10^{-11} mol cm⁻² s⁻¹ and a FE of 4.51% at -0.05 V vs. RHE, which surpass those of Co₁-N-C and Ni₁-N-C. DFT calculations reveal that the RDS of Fe₁-N-C toward the NRR shows a much lower energy barrier than that of Co and Ni counterparts, explaining the much better performance of Fe₁-N-C theoretically. This work offers a guideline for the construction of outstanding SACs for the NRR and provides insightful understanding of the related catalytic mechanism.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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