Electrochemically converting nitrate, a widespread water pollutant, back to valuable ammonia is a green and delocalized route for ammonia synthesis, and can be an appealing and supplementary alternative to the Haber-Bosch process. However, as there are other nitrate reduction pathways present, selectively guiding the reaction pathway towards ammonia is currently challenged by the lack of efficient catalysts. Here we report a selective and active nitrate reduction to ammonia on Fe single atom catalyst, with a maximal ammonia Faradaic efficiency of ~75% and a yield rate of up to ~20,000 μg h⁻¹ mgcat.⁻¹ (0.46 mmol h⁻¹ cm⁻²). Our Fe single atom catalyst can effectively prevent the N-N coupling step required for N₂ due to the lack of neighboring metal sites, promoting ammonia product selectivity. Density functional theory calculations reveal the reaction mechanisms and the potential limiting steps for nitrate reduction on atomically dispersed Fe sites.
Ammonia (NH₃) is one of the most fundamental chemical feedstocks in the world, as it is not only an indispensable chemical for fertilizer, pharmaceutical, dyes, etc., but also considered as an important energy storage medium and carbon-free energy carrier. Currently, the industrial-scale NH₃ synthesis relies on the century-old Haber–Bosch process, which requires harsh operating conditions including high temperature (400–500 °C) and high pressure (150–300 atm) using heterogeneous iron-based catalysts. Due to its enormous annual production and energy-intensive processes, the NH₃ synthesis industry accounts for 1–2% of the world’s energy supply, and causes ca. 1% of total global energy-related CO₂ emissions. As an attractive alternative to the Haber–Bosch process, the electrochemical NH₃ synthesis route, with renewable electricity inputs such as solar or wind, has attracted tremendous interests over the past few years. Nitrogen gas (N₂) from air was identified as one major nitrogen source for this renewable route via electrochemical nitrogen reduction reaction (NRR); however, due to the extremely stable N≡N triple bond (941 kJ mol⁻¹) and its non-polarity, NRR suffers from low selectivity (referring to Faradaic efficiency in this work unless otherwise specified) and activity. While exciting progresses in NRR catalyst development have been made, in many cases it is still challenging to firmly attribute the detected NH₃ to NRR process rather than contaminations due to the extremely low NH₃ production rate (mostly <200 μg h⁻¹ mg⁻¹). Therefore, using N₂ as the N source for electrochemical synthesis of NH₃, as promising as it is, still has a long way to go to deliver considerable yields for practical applications.

Nitrate (NO₃⁻) ions as one of the world’s most widespread water pollutants become an attractive nitrogen source, alternative to the inert N₂, for electrochemical synthesis of NH₃ (refs. 22–27). Nitrate source mainly comes from industrial wastewater, liquid nuclear wastes, livestock excrements, and chemical fertilizers, with a wide range of concentrations up to ca. 2 M. Using electrochemical methods to remove nitrate contaminants from industrial wastewater has been an important topic in environmental research field, and their targeted product of nitrate reduction is N₂ instead of NH₃ (refs. 29–33). A variety of metal catalysts (including Ru, Rh, Ir, Cu, Au, and Ag) and their alloys have been developed over the years to selectively convert NO₃⁻ to N₂, with NH₃ as the byproduct. The development of high-performance electrocatalysts to selectively reduce nitrate wastes into value-added NH₃ will open up a different route of nitrate reaction pathways, which are highly complex and poorly understood.

Inspired by the Fe active sites in both Haber–Bosch catalysts (Fe-based compounds) and nitrogenase enzymes (mainly containing Fe–Mo cofactor), here we report excellent activity and selectivity of Fe single atomic sites in reducing NO₃⁻ towards NH₃. Deposited on a standard glassy carbon electrode, our Fe SAC delivered a maximal NH₃ Faradaic efficiency (FE) of ~75% at ~0.66 V vs. reversible hydrogen electrode (RHE), with NH₃ partial current density of up to ~100 mA cm⁻² at ~0.85 V. This corresponds to an impressive NH₃ yield rate of ~20,000 μg h⁻¹ mg⁻¹. Importantly, the Fe SAC displayed a significantly improved NH₃ yield rate than that of Fe nanoparticle catalysts despite much lower Fe contents. We used density functional theory (DFT) calculations to elucidate reaction mechanism for NO₃⁻ reduction to NH₃ on Fe single atomic site. In addition, we show that NO⁺ reduction to HNO⁺ and HNO⁺ reduction to N₂ are the potential limiting steps.

Results

Synthesis and characterizations of Fe SAC. The Fe SAC was synthesized by a TM-assisted carbonization method using SiO₂ powers as hard templates. The strategy involves mixing precursors including FeCl₃, o-phenylenediamine with SiO₂ powder, followed by pyrolysis of the mixture, then NaOH and H₂SO₄ etching and second pyrolysis (Fig. 1a; “Methods”). The low-magnification transmission electron microscopy (TEM) image of Fe SAC indicates an interconnected vesicle-like structure with well-defined pores originating from SiO₂ hard templates (Fig. 1b and Supplementary Fig. 1). No nanoparticles can be found on the carbon frameworks. Isolated Fe single atoms dispersed on the porous carbon matrix can be clearly identified as bright dots by the aberration-corrected medium-angle annular dark-field scanning transmission electron microscopy (AC MAADF-STEM) image in Fig. 1c (“Methods”). No Fe clusters or nanoparticles are observed in many different areas of Fe SAC (Supplementary Fig. 2). The Fe metal loading is estimated to be 1.51 wt% based on inductively coupled plasma-optical emission spectroscopy (ICP-OES) analysis. Energy-dispersive X-ray spectroscopy (EDS) mapping analysis confirms the existence of Fe, N, and C elements throughout the porous structure (Fig. 1d). A sophisticated point analysis of electron energy loss spectroscopy (EELS) on a single Fe atomic site, as shown in Fig. 1e, confirms the Fe–N–C coordination environment. Considering the angstrom resolution of the electron probe, the signals in EELS point spectrum comes from the Fe atom and its closest neighboring atoms, suggesting a high possibility of Fe–N direct coordination in Fe SAC. Other point spectra acquired from different areas confirmed similar coordination environments (Supplementary Fig. 3). The X-ray diffraction (XRD) pattern of the Fe SAC exhibits two distinct characteristic peaks at ca. 26.2° and 43.7°, corresponding to the (002) and (101) planes of graphitic carbon (Fig. 1f). There are no characteristic peaks of Fe-based crystals, demonstrating that no large Fe-based crystalline nanoparticles exist in the catalyst. The graphitic carbon structures are also shown by high-resolution TEM as well as Raman spectroscopy (Supplementary Figs. 4 and 5). We used N₂ sorption method to analyze the pore structures of the Fe SAC (Fig. 1g), where a remarkable hysteresis loop of type-IV indicates the presence of highly mesoporous structures in Fe SAC. The mesopore size distribution is centered at 18.3 nm (inset in Fig. 1g), and the Brunauer–Emmett–Teller (BET) surface area and pore volume are 285.8 m² g⁻¹ and 0.80 cm³ g⁻¹, respectively (Supplementary Table 1).

We further analyzed the chemical and atomic structure of our Fe SAC using X-ray photoelectron spectroscopy (XPS) and X-ray
absorption spectroscopy (XAS). In XPS results (Fig. 2a and Supplementary Fig. 6a), the high-resolution N 1s spectrum contains four peaks at 398.5, 399.8, 401.0, and 402.6 eV, which are assigned to pyridinic N, pyrrolic N, graphitic N, and oxidized N, respectively.46,49 No obvious Si 2p XPS signal was found, indicating that SiO2 templates have been completely removed (Supplementary Fig. 6b). The high-resolution Fe 2p spectrum with two relatively weak peaks centered at 711.1 eV (Fe 2p3/2) and 723.9 eV (Fe 2p1/2) suggests the positive oxidation states of Fe species in the Fe SAC (Supplementary Fig. 6c).50 This is consistent with our XAS analysis (Fig. 2b). The Fe K-edge X-ray absorption near-edge structure (XANES) of Fe SAC presents a near-edge absorption energy between Fe metal foil and Fe2O3 references, indicating that the oxidation state of Fe single atoms sits between Fe0 and Fe3+.49–51 No Fe–Fe interaction peak at 2.2 Å can be observed, excluding the possibility of any Fe clusters or nanoparticles in our catalyst. These results conclude that the Fe atoms are atomically dispersed in the N-doped carbon (NC) matrix, consistent with our STEM observations. Owing to the powerful resolutions in both k and R spaces, wavelet transform (WT) of Fe K-edge EXAFS oscillations was employed to further explore the atomic dispersion of Fe in Fe SAC. Only one intensity maximum is observed at ~4.6 Å−1 in the WT contour plots, which corresponds to the Fe–N coordination. No intensity maximum belonging to Fe–Fe contribution can be observed, compared with the WT plots of Fe foil and Fe2O3 (Fig. 2d). To better understand the Fe coordination environment, we also conducted the EXAFS fitting to obtain the structural parameters and extract the quantitative chemical configuration of Fe atoms (Fig. 2e, f). Each Fe atom is coordinated by about 4N atoms in average, and the mean bond length is 1.92 Å (Supplementary Table 2). According to these fitting results, the proposed coordination structure of Fe SAC is Fe–N4, which is shown as the inset in Fig. 2f. The EXAFS fitting results of Fe foil and Fe2O3 are presented in Supplementary Fig. 7 and Supplementary Table 2. Additionally, only one peak at the L3-edge and no clear multiple structures are found in the Fe L-edge XANES spectrum of Fe SAC, which suggests a unique feature of delocalized Fe 3d electrons of Fe SAC.19 The itinerant Fe 3d electrons of Fe SAC can be shared by the porphyrin-like structures (as analyzed by Fe K-edge EXAFS fitting) and enhance the electrical conductivity of the catalyst (Fig. 2g).19 Other TM SACs including Co and Ni were
also prepared using the same synthesis method, and characterized to confirm their atomic dispersion of TM atoms in NC support (Supplementary Figs. 8–21, Supplementary Tables 1 and 2 and Supplementary Note 1).

Electrocatalytic nitrate reduction performance. Electrochemical nitrate reduction was conducted in a customized H-cell under ambient conditions. The Fe SAC was deposited onto a mirror-polished glassy carbon electrode with a fixed catalyst mass loading of 0.4 mg cm$^{-2}$. We first performed the linear sweep voltammetry (LSV) in K$_2$SO$_4$ electrolyte with and without KNO$_3$ to study the nitrate reduction catalytic activity of Fe SAC (Fig. 3a). The obviously enhanced current density under the same potential suggests that NO$_3^-$ ions can be effectively reduced by the Fe SAC. Product selectivity was performed in K$_2$SO$_4$/KNO$_3$ electrolyte by holding a certain potential each time for 0.5 h, with generated NH$_3$ products quantified by ultraviolet-visible (UV–Vis) spectrophotometry (Supplementary Fig. 22; see “Methods”). As shown in Fig. 3b, c, our Fe SAC shows high selectivity and superior yield rate for electrocatalytic NO$_3^-$-to-NH$_3$ conversion.

At $-0.50$ V vs. RHE when the reaction starts to onset (an overall current density of 4.3 mA cm$^{-2}$), NH$_3$ product can be readily detected with an FE of 39%, representing a yield rate of $331$ μg h$^{-1}$ mg$_{cat}$$^{-1}$ (Fig. 3b, c). The NH$_3$ selectivity gradually increases to a maximal of $75\%$ at $-0.66$ V under an overall current density of $35.3$ mA cm$^{-2}$, delivering a yield rate of $5245$ μg h$^{-1}$ mg$_{cat}$$^{-1}$. The NH$_3$ Faradaic efficiency does not change with time and keeps around $75\%$ during $2$ h (Supplementary Fig. 23). A large NH$_3$ partial current density of $\sim 100$ mA cm$^{-2}$ is achieved at $-0.85$ V, corresponding to an impressive yield rate of $\sim 20,000$ μg h$^{-1}$ mg$_{cat}$$^{-1}$. The bare glassy carbon electrode shows a negligible nitrate reduction activity to ammonia (Supplementary Fig. 24). The FE and yield rate of NO$_3^-$-to-NH$_3$ conversion on Fe SAC are orders of magnitude higher than reported N$_2$-to-NH$_3$ conversions$^{10,21}$, due to the dramatically different kinetic energy barriers to overcome$^{39}$; more importantly, the ammonia activity per metal active site favorably compare with other nitrate reduction systems which typically used bulk or nanostructured transition metal catalysts (Supplementary Table 3)$^{22–24,52–55}$. Different from N$_2$ reduction studies where the concentrations of generated NH$_3$ are typically much lower than H nuclear magnetic resonance (NMR) detection limit, in our case the generated NH$_3$ has concentrations high enough to be accurately quantified by NMR test, which helps to independently confirm our UV–Vis test. We chose the maximal FE point to be validated by NMR (see “Methods”). As shown in Fig. 3d, e, two peaks corresponding to $^{14}$NH$_4^+$ are clearly observed in electrolytes after 0.5-h electrolysis under $-0.66$ V. Based on the averaged NMR peak areas of three independent electrolysis tests and the calibration curve of $^{14}$NH$_4^+$ (Supplementary Fig. 25), we obtained an FE of NH$_3$ at $76\%$ (Fig. 3b, e), in good agreement with our UV–Vis spectrophotometry measurements. Additionally, we used NMR to confirm that the NH$_3$ produced actually came from NO$_3^-$ ions using $^{15}$N-labeled NO$_3^-$ (Fig. 3e).

**Fig. 2 Structural analysis of Fe SAC.** a High-resolution N 1s of the Fe SAC. b XANES spectra at the Fe K-edge of the Fe SAC, referenced Fe foil and Fe$_2$O$_3$. c FT $k^2$-weighted $\chi(k)$-function of the EXAFS spectra at Fe K-edge. d WT of the Fe K-edge. Fitting results of the EXAFS spectra of Fe SAC at e $k$-space and f $R$ space. Inset: Schematic model of Fe SAC: Fe (yellow), N (blue), and C (gray). g XANES spectrum at Fe L-edge of Fe SAC.
appear in $^1$H NMR spectra with their peak intensity increasing with the electrolysis time, confirming that the NH$_3$ generated is from electrochemical nitrate reduction rather than contaminations. Also, no NH$_3$ could be detected if KNO$_3$ was absent in the electrolyte during the electrolysis (Supplementary Fig. 26).

The main byproduct of nitrate reduction on Fe SAC is NO$_2$–, the simplest nitrate reduction product, as detected and quantified by UV–Vis (Supplementary Figs. 27 and 28). The FE of NO$_2$– starts from as high as 66% at the onset potential, followed by a gradual decease to a minimal of ~9%. This trend correlates to the gradual increase of NH$_3$ selectivity, suggesting that NO$_2$– could be an intermediate product and can be further reduced to NH$_3$ under more negative potentials. This hypothesis was further validated by performing NO$_2$– reduction on Fe SAC, where more than 90% FE of NH$_3$ and higher production rates can be achieved under the studied potential window (Supplementary Fig. 29). Other possible minor products such as N$_2$ and H$_2$ were further quantified by gas chromatography, with FEs less than 1%. In fact, gas bubbles could hardly be observed on the working electrode during electrolysis until the potential is more negative than $-0.73$ V.

As various nitrate concentrations exist in different sources, we also evaluated the catalytic performance of Fe SAC at initial KNO$_3$ concentrations ranging from 0.05 to 1.0 M. The maximal FEs of NO$_3$–-to-NH$_3$ conversion were 74.3, 71.8, and 73.5% in 0.05, 0.1, and 1 M KNO$_3$, respectively, similar to the performance tested in 0.5 M KNO$_3$ solution (Supplementary Fig. 30). This suggests that the NO$_3$– concentration has no obvious impacts on Fe SAC’s NH$_3$ selectivity. In addition, we observed that the NH$_3$ yield rate was greatly enhanced by increasing the KNO$_3$ concentrations from 0.05 to 0.5 M, but remained nearly unchanged with further increase to 1.0 M. We found that this performance difference was not due to the mass diffusion limit or the concentration of K$^+$ (Supplementary Figs. 31 and 32). There could be a transition of rate-limiting step in the kinetic regime from positive to zero order in nitrate from 0.05 to 1.0 M. For some practical applications, when the nitrate concentrations are much lower or higher in some sources, some strategies could be adopted, such as using mature industrial concentrating processes to concentrate those low-concentration nitrates, and diluting highly concentrated nitrates before conversion, as well as electrochemical cell engineering technology.$^{56,57}$ Besides, we found that the presence of NaCl in the electrolyte did not affect the catalytic performance of Fe SAC for nitrate reduction (Supplementary Fig. 33). We also investigated nitrate reduction on Fe SAC at different pH (Supplementary Fig. 34). The FE of NO$_3$–-to-NH$_3$ conversion in the alkaline solution (pH = 13) is similar to that at neutral pH, with significantly improved overpotentials, while the catalytic activity and selectivity are
Nitrate reduction to ammonia is accompanied by nine proton and eight electron transfers. The first step is protonation of NO$_3^-$ which is a solution-mediated proton transfer to form HNO$_3$ and does not require electron transfer. The intermediates and their energy profile across the reaction coordinate are displayed in the free energy diagram in Supplementary Fig. 50. Figure 4a (also the green arrows in Supplementary Fig. 49 and green line in Supplementary Fig. 50) indicate the minimum energy pathway (MEP) for nitrate reduction to NH$_3$ on Fe single atom site. We find that reduction of NO$_3^-$ to NO is downhill in free energy. This finding is in agreement with previous computational report on Pd surface$^{46}$. Nitrate reduction on polycrystalline and single crystals of transition metals have been studied in the past.$^{44,51-54}$ Liu et al.$^{40}$ suggested that N* and O* binding energies can be used as descriptors for nitrate reduction performance on TMs. In addition, it has been shown that the main product of nitrate reduction reaction on all transition metals is nitrogen with low selectivity towards ammonia. The latter is due to the dominance of parasitic hydrogen evolution reaction. Moreover, NO* has been suggested as a key intermediate for nitrate reduction on metal surfaces such as Pt where its reduction to HNO* or NOH* is a critical step for production of NH$_4^+$. Our analysis on Fe SAC shows that NO* is a key intermediate for nitrate reduction reaction which is consistent with previous computational reports on Pt and Pd.$^{58,65}$ We would like to emphasize that while NO$_3^-$ is confirmed as an intermediate product in the experimental result, our DFT calculations show that the potential limiting steps are the NO* reduction to HNO* and HNO* reduction to N* in agreement with previous computational reports on transition metals such as Pt and Pd.$^{58,65}$ Compared to the MEP at $U = 0.0$ V vs. RHE (green line) in Fig. 4b, a limiting potential of $U = -0.30$ V (black line) is needed to make all steps downhill in free energy. Although not exactly the same, the calculated limiting potential ($-0.30$ V) is reasonably comparable with the observed experimental onset potential at $-0.40$ V. The 0.10 V difference can be attributed to the additional kinetic barriers that need to be overcome. We note here that due to the single atom nature of active sites in our catalyst, it is energetically unfavorable to make N–N coupling intermediates or products such as N$_2$O or N$_2$ (Supplementary Fig. 50), which is why we did not observe any N$_2$ products from nitrate reduction on Fe SAC. In addition, our DFT calculations show that the MEP on Fe(110) is different from the one on Fe SAC and the potential limiting step is reduction of NH* to NH$_2^+$ (Supplementary Fig. 51). The DFT calculated limiting potential on Fe(110) is 0.50 V indicating that Fe(110) exhibits lower catalytic activity than Fe SAC. We also calculated the free energy diagrams for Co and Ni SACs (Supplementary Fig. 52). As it can be seen the potential limiting step is the reduction of NO* to HNO* on both Co and Ni SACs. The calculated limiting potentials for nitrate reduction on Co and Ni, and Fe SACs are 0.42, 0.39, and 0.3 V, respectively, explaining why Fe SAC is more active than Co and Ni SACs. Of note, the potential limiting steps on Co and Ni SAC are highly close and within the range of DFT calculations error, indicating that they have very similar nitrate reduction activity, consistent with our experimental data (Fig. 3f). Combining experimental results and DFT calculations, the high NH$_3$ yield rate or activity of Fe SAC in this study can be attributed to the following two aspects. On the one hand, the Fe SAC has intrinsically high-efficiency active sites, i.e. Fe–N$_4$ centers, which exhibit much lower thermodynamic barriers, evidencing from smaller calculated limiting potentials than that of FeNP of FeNP/NC, Co–N$_4$ of Co SAC, and Ni–N$_4$ of Ni SAC. One the other hand, the optimized electrocatalytic conditions, including the concentration of KNO$_3$, pH of

$\text{NO}_3^- + 9\text{H}^+ + 8\text{e}^- \rightarrow \text{NH}_3 + 3\text{H}_2\text{O} \quad E^0 = 0.88 \text{ V}$  (1)
electrolyte, and applied potential, also play an important role in high NH3 yield rate of Fe SAC.

Discussion
In summary, we have demonstrated Fe SAC as an active and selective electrocatalyst to reduce nitrate to valuable ammonia. Our DFT simulations reveal the reaction pathways and potential limiting steps for nitrate reduction on Fe single atomic site. We believe this nitrate reduction to ammonia route could stimulate a different perspective towards how delocalized ammonia generation could be achieved. Future works should focus on further enhancing the catalytic selectivity, activity, and energy conversion efficiency in nitrate reduction to ammonia, testing the system in real wastewater system, and designing electrochemical reactors for more concentrated ammonia product generated from low-concentration nitrate sources.

Methods

Synthesis of Fe SAC. In a typical synthesis, 2.0 g o-phenylenediamine, 0.58 g FeCl3, and 2.0 g SiO2 powder (10–20 nm, Aldrich) were added into 240 mL iso-propyl alcohol and then vigorously stirred for ca. 12 h. After drying the mixture by using a rotary evaporator, the obtained dried powder was subsequently carbonized under flowing Ar for 2 h at 800 °C. After drying the mixture by using a rotary evaporator, the obtained dried powder was subsequently carbonized under flowing Ar for 2 h at 800 °C. Then, the product underwent alkaline (2.0 M NaOH) and acidic (2.0 M H2SO4) leaching successively to remove SiO2 templates and unstable metallic species, respectively. Finally, the Fe SAC was obtained by second heat treatment at the same temperature (i.e. 800 °C) under flowing Ar for another 2 h.

Synthesis of Co SAC and Ni SAC. The synthesis processes of Co SAC and Ni SAC are similar to that of Fe SAC, with the only difference being that 0.44 g CoCl2 and 0.44 g NiCl2·6H2O were used for synthesizing Co SAC and Ni SAC, respectively.

Synthesis of NC catalyst. For comparison, the NC catalyst was also prepared. Typically, 2 g o-phenylenediamine was firstly dissolved in 30 mL 1.0 M HCl, and then 2.0 g SiO2 powder was added into the above solution. After stirring for 0.5 h, 24 mL 1.0 M HCl solution containing 6.0 g ammonium peroxydisulfate, i.e., (NH4)2S2O8, was added dropwise with stirring. The polymerization process was carried out in an ice bath for ca. 24 h. The mixture was dried by using a rotary evaporator, and then carbonized under flowing Ar for 2 h at 800 °C. The SiO2 templates were removed by 2.0 M NaOH solution. Finally, the NC catalyst was obtained by second heat treatment at the same temperature (800 °C) under flowing Ar for another 2 h.

Synthesis of FeNP/NC catalyst. Firstly, 0.528 g FeSO4·7H2O and 0.16 g NC were added into 15 mL deionized water and sonicated for 30 min. Then, 10 mL NaBH4 (containing 0.284 g NaBH4) aqueous solution was added dropwise into the above solution with vigorous stirring. Then, the mixed solution was stirred for 3 h. The sample was finally obtained by centrifugation collection, thoroughly washing with ethanol and deionized water and drying in an oven. The content of Fe in the FeNP/NC catalyst was 22.2 wt%, which was determined by ICP-OES analysis.

Characterization. TEM observations and EDS elemental mapping were carried out on a Talos F200X transmission electron microscope at an accelerating voltage of 200 kV equipped with an energy-dispersive detector. XPS was performed on an X-ray photoelectron spectrometer (ESCALab MKII) with an excitation source of Mg Kα radiation (1253.6 eV). XRD data were collected on a Rigaku D/Max Ultima II Powder X-ray diffractometer. N2 adsorption–desorption isotherms were recorded on an ASAP 2020 accelerated surface area and porosimetry instrument.
passing the electrode, \( t \) is the reduction time, and \( m_{\text{cat}} \) is the loading mass of catalysts.

**Determination of ammonia.** The concentration of produced \( \text{NH}_3 \) was spectrophotometrically determined by the indophenol blue method with modification\(^a\).

First, a certain amount of electrolyte was taken out from the electrolytic cell and diluted in the detection range. Then, 2 mL of solution was removed from the diluted electrolyte. Subsequently, 2 mL of a 1 M \( \text{NaOH} \) solution containing 5 wt% salicylic acid and 5 wt% sodium citrate was added to the aforementioned solution, followed by the addition of 1 mL of 0.05 M \( \text{NaClO} \) and 0.2 mL of 1.0 wt% \( \text{C}_{12}\text{FeN}_{6}\text{Na}_{4}\text{O} \) (sodium nitrofurazycycane) solution. After 2 h at room temperature, the absorption spectrum was measured by using a UV–vis spectrophotometer (UV-2600). The formation of indophenol blue was determined using the absorbance at a wavelength of 655 nm. The concentration–absorbance curve was made using a series of standard ammonium chloride solutions.

**Determination of nitrite**\(^b\). Secondly, 0.2 g of \( \text{N}-(1\text{-naphthyl}) \) ethylenediamine dihydrochloride, 4 g of \( \text{p}-\text{aminobenzenesulfonyl} \), and 10 mL of phosphoric acid \((\rho = 1.685 \text{ g mL}^{-1})\) were added into 50 mL of deionized water and mixed thoroughly as the color reagent. When testing the electrolyte from electrolytic cell, it should be diluted to the detection range. Then 5 mL of the diluted electrolyte and 0.1 mL of color reagent were mixed together. After 20 min at room temperature, the absorption spectrum was measured by using a UV–vis spectrophotometer (UV-2600), and the absorption intensity was recorded at a wavelength of 540 nm. A series of standard potassium nitrite solutions were used to obtain the concentration–absorbance curve by the same process.

**NMR determination of ammonia.** The \( \text{NH}_3 \) concentration was also quantitatively determined by \( ^{1} \text{H} \) nuclear magnetic resonance (NMR, 500 MHz) with using DMSo-d\(_{6}\) as a solvent and maleic acid \((\text{C}_5\text{H}_4\text{O}_4)\) as the internal standard. The calibration curve was made as follows. First, a series of ammonium chloride solutions with known concentration were prepared in 0.01 M HCl containing 0.5 M KNO\(_3\) as standards; second, 0.5 mL of the standard solution was mixed with 0.1 mL DMSo-d\(_{6}\) (with 0.04 wt% \( \text{C}_6\text{H}_5\text{O}_2\) \( \text{Na} \)); third, the mixture was tested by a 500 MHz Bruker Advance NMR spectrometer at 60 °C; finally, the calibration curve was achieved using the peak area ratio between \( \text{NH}_4^+ \) and \( \text{CH}_3\text{COO}^- \) because the \( \text{NH}_4^+ \) concentration and the area ratio are positively correlated. For testing the produced \( \text{NH}_4^+ \) from \( \text{NO}_3^- \) reduction, the pH of obtained electrolyte must be adjusted to 2.0 before the test. Then, the processes of testing produced \( \text{NH}_4^+ \) are the same to that for making the calibration curve. The amount of produced \( \text{NH}_4^+ \) can be calculated from the peak area using the calibration curve.

**15N isotope-labeling experiment.** An isotope-labeling experiment using 0.10 M K\( \text{SO}_4\)/0.50 M K\( ^{15}\text{NO}_3 \) (98 atom% \( ^{15}\text{N} \)) mixed solution as the electrolyte was carried out to clarify the source of \( \text{NH}_4^+ \). After \( ^{15}\text{NO}_3^- \) electroreduction for 0.5 to 2 h at −0.66 V (vs. RHE), the obtained \( ^{15}\text{NH}_4^+ \) was tested by \( ^{1} \text{H} \) nuclear magnetic resonance (NMR, 500 MHz). The NMR test method of15NH\(_4^+\) is the same to that of \( ^{14}\text{NH}_4^+\).

**Computational details.** Atomic simulation environment (ASE) was used to handle the simulation\(^a\). All electronic structure relaxations were performed using QUANTUM ESPRESSO code\(^68\). The electronic wavefunctions were expanded in plane waves with a cutoff energy of 500 eV while 5000 grids were used for electronic density representation. To approximate the core electrons ultrasoft pseudopotentials were adopted\(^a\). Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional was used to calculate the adsorption energies\(^a\). A one-layer two-dimensional graphene structure was used with a 5 × 5 super cell lateral size. The periodic images were separated by adding a vacuum of 18 Å. Additional layers of graphene have been shown to have negligible effect on the adsorption energies of the intermediates\(^a\). A \( (4 \times 4 \times 1) \) Monkhorst–Pack \( k \)-point was used to sample the Brillouin zone. We apply computational hydrogen electrode method to calculate the adsorption free energies, which assumes the chemical potential of an electron–proton pair is equal to that of \( \text{H}_2 \) in the gas phase. The free energies of adsorption are then calculated as \( \Delta G = \Delta G_{\text{DFT}} + \Delta G_{\text{PE}} - T \Delta S \), where \( \Delta G_{\text{DFT}} \), \( \Delta G_{\text{PE}} \), \( T \), and \( S \) are adsorption enthalpy, zero-point energy, temperature, and entropy, respectively. The limiting potential is calculated by taking the negative of the maximum free energy difference between each two successive steps in the free energy diagram.

Adsorption free energies are calculated using HNO\(_3\) as a reference suggested by Calle-Vallejo et al.\(^a\). We applied 1.12 eV correction to compensate for the DFT error of calculated formation energy of HNO\(_3\). (ref. \(^{22}\)). We investigated the effect of solution on the adsorption energies of the critical step \( \text{NO}_3^- \) reduction to \( \text{HNO}_2\) using an optimized explicit solvent model (Supplementary Fig. 3). This analysis showed a negligible change in the calculated limiting potential due to the solvent interaction. 

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\(^{a}\) Authors for correspondence.
Data availability
The data that support the plots within this paper and other findings of this study are available from the corresponding authors upon reasonable request.

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Author contributions

Z.-Y.W. and H.W. conceptualized the project. H.W. and S.S. supervised the project. Z.-Y.W. developed and performed catalyst synthesis. Z.-Y.W., Q.H., F.Y.C., and C.X. conducted the catalytic tests of catalysts and the related data processing. Z.-Y.W. performed materials characterization with the help of D.A.C., Q.X., M.S., J.Y.K., Y.X., K.H., and Y.H. 1H NMR experiments and analysis was carried out by P.Z., Z.-Y.W., and Q.Z.H. S.S., M.K., X.Y., and I.G. performed the DFT simulation. Z.-Y.W., H.W., and S.S. wrote the manuscript. M.S.W. and Q.L. helped the revision of the manuscript. All authors discussed the results and commented on the manuscript.

Competing interests

The authors declare no competing interests.

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