

Reconstructed low-valent Fe single-atom sites on deficient TiO₂ enable electrocatalytic nitrate reduction to ammonia

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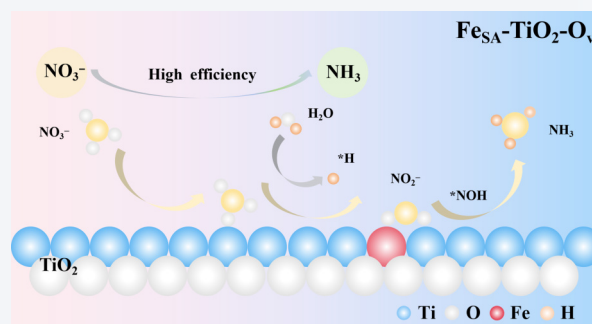
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ABSTRACT: Electrochemical nitrate (NO₃⁻) reduction reaction (NO₃RR) offers a promising route for NO₃⁻ remediation and sustainable ammonia (NH₃) synthesis, yet its efficiency is often constrained by the hydrogenation of nitrogen-containing intermediates. Herein, we report Fe single atoms anchored on oxygen-vacancy-rich TiO₂ nanosheet assemblies (Fe_{SA}-TiO₂-O_v) for efficient NO₃⁻ to NH₃ conversion. The Fe_{SA}-TiO₂-O_v catalyst achieves a high NH₃ yield rate of 16.6 mg·h⁻¹·cm⁻² at -0.5 V versus reversible hydrogen electrode (vs. RHE), accompanied by a maximum Faradaic efficiency of 92% and excellent durability over 40 h. *Operando* X-ray absorption fine structure (XAFS) spectroscopy reveals a gradual decrease in Fe valence and contraction of the Fe–O coordination shell, confirming the formation of reconstructed low-valent Fe single-atom active sites during NO₃RR. Theoretical calculations and spectroscopic analysis further indicate that Fe sites are effective for *NO hydrogenation to the *NOH intermediate, thereby promoting the efficient formation of NH₃. These findings identify the reconstructed low-valent Fe single atoms as the active sites for selective electrosynthesis of NH₃, providing a mechanistic framework for designing single-atom catalysts applicable to multistep electrocatalytic reduction reactions.



KEYWORDS: nitrate reduction reaction, metal single-atom, ammonia synthesis, electrocatalysis

1 Introduction

Nitrate contamination in aquatic systems has become a widespread environmental and public health concern owing to its high mobility, persistence, and harmful effects on ecological systems and human health [1–3]. Electrochemical nitrate reduction reaction (NO₃RR) has emerged as an attractive strategy for simultaneously removing nitrate pollutants and producing value-added ammonia (NH₃) under ambient conditions [4–7]. Compared with the

energy-intensive Haber–Bosch process, nitrate-to-ammonia electrosynthesis offers a more sustainable route by combining pollutant upgrading with renewable electricity [8–10]. Nevertheless, achieving efficient and selective NO₃RR toward NH₃ remains highly challenging. Nitrate is a thermodynamically stable oxyanion, and its complete conversion to NH₃ involves a complex electron/proton transfer process and a series of adsorbed nitrogen-containing intermediates [11–15]. The initial reduction of NO₃⁻ generally requires strong nitrate adsorption and effective activation. Moreover, the subsequent hydrogenation of intermediates toward NH₃ demands sustained electron and proton delivery, which is usually considered as the rate-determining step [16–20]. Meanwhile, the hydrogen evolution reaction (HER) competes strongly under cathodic conditions, further compromising NH₃ selectivity.

To address these challenges, catalyst design strategies, such as defect engineering, single-atom catalysis, and modulation of

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metal-support interactions, have been extensively explored in recent years. Among these approaches, single-atom catalysts have attracted particular interest, because atomically dispersed metal sites provide well-defined coordination environments and highly tunable electronic structures [21–23]. More recently, low-valent single-atom sites have garnered increasing attention in diverse catalytic reactions due to their electron-rich nature, which promotes charge transfer and enhances orbital interactions with key intermediates, thereby facilitating bond activation [24, 25]. For NO₃RR, the electronic properties of low-valent atomic sites offer distinct advantages by enhancing interfacial electron transfer and boosting the activation of nitrate and nitrogen-containing intermediates [26]. In addition, the flexible electronic configuration of low-valent atomic sites could optimize the adsorption strength of reactive intermediates while promoting the effective utilization of active atomic hydrogen (*H), thereby favoring the reduction toward NH₃ over the competing HER [27, 28]. For example, low-valent Cu single-atoms anchored on In₂S₃ nanosheets have been shown to promote exciton dissociation and charge separation, markedly enhancing photocatalytic CO₂ reduction [29]. In the context of nitrate reduction, low-valent In single-atoms on Cu-based nanosheets were recently reported to regulate ionic interference and adsorbed hydrogen, enabling near-unity NH₃ electrosynthesis in a neutral electrolyte [26]. However, most current studies still describe atomic sites primarily on the basis of *ex situ* structural characterization, whereas how low-valent single-atom sites evolve under applied potentials and operate as the catalytically relevant states during NO₃RR remains insufficiently understood.

Herein, we construct Fe single-atoms anchored on oxygen-vacancy-rich TiO₂ nanosheet assemblies (Fe_{SA}-TiO₂-O_v) for selective electrocatalytic nitrate-to-ammonia conversion. *Ex situ* X-ray absorption fine structure (XAFS) spectroscopy reveals that Fe is anchored on the defective TiO₂ support with the Fe–O₄ moiety in Fe_{SA}-TiO₂-O_v. *Operando* XAFS measurements further show that under NO₃RR conditions, the Fe sites undergo a gradual decrease in valence accompanied by a contraction of the Fe coordination shell, indicating the formation of reconstructed low-valent Fe single-atom active sites. Meanwhile, density functional theory (DFT) calculations and *in situ* attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy reveal that Fe sites more effectively promote *NO hydrogenation to the *NOH intermediate. This work identifies the reconstructed low-valent Fe atoms as the active sites for NO₃RR, offering new insight into the design of single-atom catalysts for complex multistep electrocatalytic reduction reactions.

2 Experimental section

2.1 Chemicals and material

All chemicals were of analytical grade and purchased from Aladdin Chemistry Co., Ltd., China. All chemicals were used without further purification.

2.2 Preparation of TiO₂, TiO₂-O_v, and Fe_{SA}-TiO₂-O_v catalysts

The ultrathin titanium dioxide (TiO₂) nanosheet assemblies were synthesized according to our previous study [30]. Typically, 1.7 g of titanyl sulfate was directly added to 60 mL of ammonium hydroxide, followed by the addition of 120 mL of deionized water

under vigorous stirring. The resulting mixture was stirred for 6 h, then transferred into a Teflon-lined autoclave and subjected to hydrothermal treatment at 160 °C for 6 h to obtain the titanic hydroxide precursor. The obtained precursor was then divided into two portions and treated with different thermal treatments. One portion was calcined in an air atmosphere at 500 °C for 2 h, yielding a reference sample denoted TiO₂. The other portion was thermally treated under a hydrogen atmosphere at 500 °C for 2 h, which concurrently converted the precursor into TiO₂ ultrathin nanosheet assemblies and introduced oxygen vacancies into the TiO₂ lattice. The resulting product, enriched with oxygen vacancies, was denoted as TiO₂-O_v. Subsequently, Fe single-atoms were immobilized on the TiO₂-O_v via a wet impregnation method. Specifically, 3 mL of 0.1 mol·L⁻¹ iron nitrate aqueous solution was used as the metal precursor. The impregnated sample was dried at 60 °C for 12 h and then subjected to secondary calcination in an Ar atmosphere at 300 °C for 2 h to achieve atomically dispersed Fe species, denoted as Fe_{SA}-TiO₂-O_v (also referred to as 3% Fe_{SA}-TiO₂-O_v). Control samples were synthesized via the same processes, unless the addition of iron nitrate was changed to 1, 2, 4, and 5 mL. The obtained samples were denoted as 1%, 2%, 4%, and 5% Fe_{SA}-TiO₂-O_v, respectively.

3 Results and discussion

3.1 Synthesis and structural characterization

The ultrathin TiO₂ nanosheet assemblies were synthesized according to our previously reported hydrothermal method combined with a gas-assisted liquid exfoliation strategy under alkaline conditions [30], in which the generated ammonia gas weakened the interlayer interactions within the layered precursor and promoted the formation of ultrathin nanosheet assemblies (Fig. 1(a)). The TiO₂ and TiO₂-O_v supports were prepared by calcining the precursor under air and hydrogen atmospheres, respectively. Following this approach, a series of Fe atoms with varying Fe loadings were synthesized by immobilizing Fe species onto TiO₂-O_v via an impregnation-assisted anchoring process followed by secondary calcination. In this design, oxygen vacancies serve not only as anchoring sites for isolated Fe atoms but also as electronic mediators that strengthen the metal-support interaction in Fe_{SA}-TiO₂-O_v. In addition, the actual Fe contents in the as-synthesized catalysts, as determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES), are summarized in Table S1 in the Electronic Supplementary Material (ESM). The high-resolution transmission electron microscopy (HRTEM) image displays lattice fringes with an interplanar spacing of ~ 0.362 nm, close to that of the anatase TiO₂ (101) plane (Fig. S1 in the ESM), suggesting a certain degree of local lattice expansion, which may be attributed to the local structural perturbation induced by Fe anchoring at the oxygen-deficient TiO₂ surface.

The phase structures of the as-prepared samples were further examined by X-ray diffraction (XRD, Fig. 1(b)). All samples exhibit diffraction peaks characteristic of anatase TiO₂ (JCPDS No. 21-1272). Meanwhile, no additional diffraction peaks assignable to Fe nanoparticles or iron oxide species are detected in Fe_{SA}-TiO₂-O_v, further supporting the highly dispersed nature of the Fe atoms. As shown in the enlarged inset of Fig. 1(b), the characteristic peaks of TiO₂-O_v and Fe_{SA}-TiO₂-O_v exhibit broadening and a slight shift toward lower 2θ angles compared to pristine TiO₂, indicating an

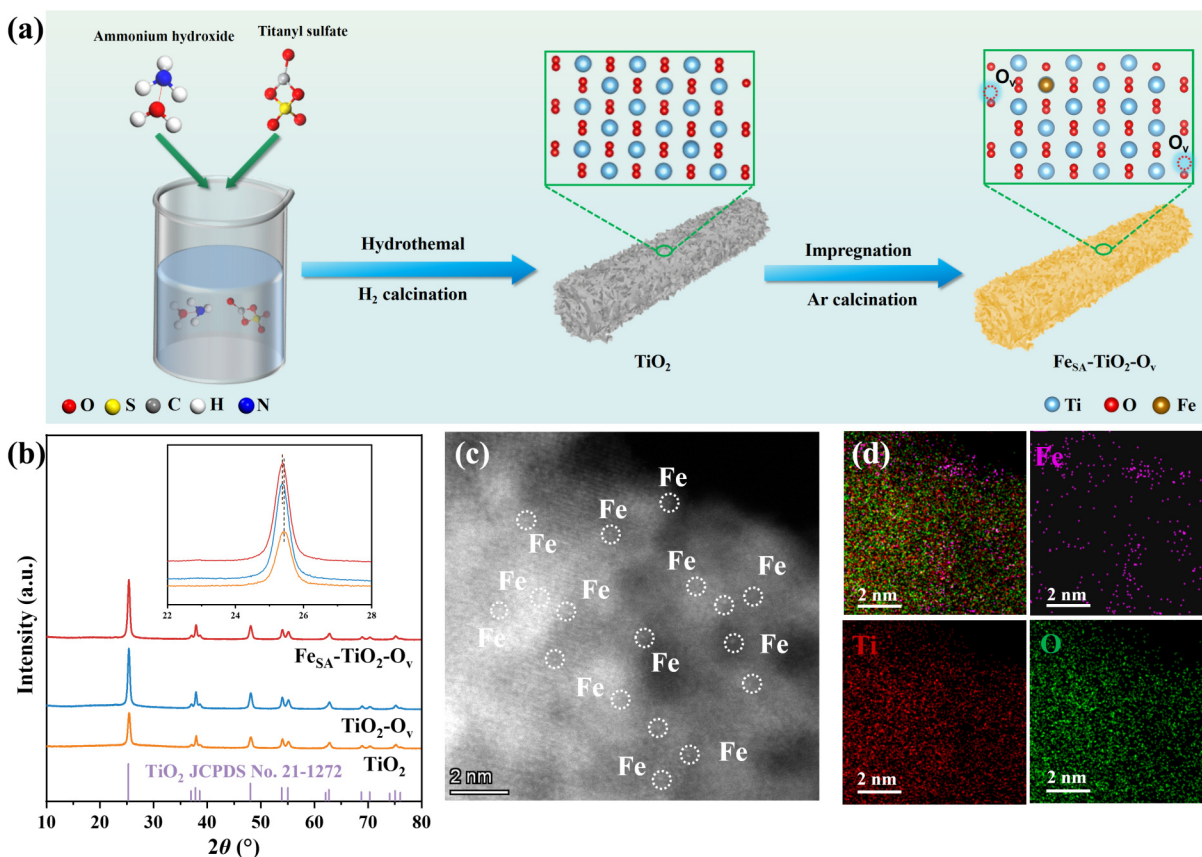


Figure 1 (a) Schematic illustration of the synthesis procedure for Fe_{SA}-TiO₂-O_v. (b) XRD patterns of TiO₂, TiO₂-O_v, and Fe_{SA}-TiO₂-O_v. (c) AC-HAADF-STEM image of Fe_{SA}-TiO₂-O_v, where individual Fe single-atoms (circled in white) are atomically dispersed on the TiO₂-O_v support. (d) Corresponding EDS elemental mapping images of Fe_{SA}-TiO₂-O_v.

increase in interlayer spacing [31]. This lattice expansion can be attributed to the combined introduction of oxygen vacancies and Fe single-atoms, which is consistent with the HRTEM results (Fig. S1 in the ESM). Consistently, the XRD patterns of various Fe_{SA}-TiO₂-O_v catalysts in Fig. S2 in the ESM also display pure anatase TiO₂ phase without any detectable crystalline Fe-related species, suggesting the possible high dispersion of Fe across different loading levels. More direct evidence for the atomic dispersion of Fe is provided by aberration-corrected high-angle annular dark-field scanning TEM (AC-HAADF-STEM). As shown in Fig. 1(c), isolated bright dots corresponding to individual Fe atoms are uniformly distributed over the TiO₂-O_v support, with no Fe clusters or nanoparticles observed. The corresponding energy-dispersive X-ray spectroscopy (EDS) elemental mapping images (Fig. 1(d)) further confirm the homogeneous distribution of Fe, Ti, and O throughout the nanosheet assemblies. These microscopic observations collectively verify the successful construction of a defect-stabilized Fe single-atom architecture. Combined with the microscopic observations above, these results confirm that the Fe species are atomically dispersed on the TiO₂-O_v support.

3.2 Electronic structure and coordination environment of Fe single-atoms in Fe_{SA}-TiO₂-O_v

To clarify the surface electronic structure and defect characteristics, high-resolution X-ray photoelectron spectroscopy (XPS) and electron paramagnetic resonance (EPR) analyses are performed. As shown in the Ti 2p spectra (Fig. 2(a)), the fraction of Ti³⁺ species

increases after hydrogen calcination and further increases upon Fe anchoring, indicating that the reductive treatment generates oxygen vacancies accompanied by the formation of reduced Ti³⁺ species [32]. Meanwhile, Fe incorporation induces additional interfacial electronic perturbation. This interpretation is supported by the high-resolution Fe 2p XPS spectra (Fig. S3 in the ESM), which reveal the coexistence of Fe²⁺ and Fe³⁺ states, confirming the successful anchoring of Fe species and their electronic interaction with the TiO₂-O_v support. In agreement with these observations, the O 1s spectra (Fig. 2(b)) can be deconvoluted into lattice oxygen, oxygen vacancies, and surface-adsorbed oxygen species, with the relative oxygen vacancy contents following the order Fe_{SA}-TiO₂-O_v > TiO₂-O_v > TiO₂. EPR spectra (Fig. 2(c)) provide further support, exhibiting a characteristic signal at *g* = 2.003 attributable to electrons trapped at oxygen vacancies [33]. Notably, the signal intensity is significantly enhanced in Fe_{SA}-TiO₂-O_v, indicating the presence of abundant oxygen vacancies. Collectively, the above results demonstrate that hydrogenation introduces abundant Ti³⁺ and oxygen-deficient states, and such a defect-rich microenvironment is expected to be crucial in stabilizing isolated Fe sites and modulating the local electronic structure of the Fe_{SA}-TiO₂-O_v.

The electronic state of Fe species in Fe_{SA}-TiO₂-O_v is further probed by XAFS spectroscopy. As shown in the *ex situ* Fe K-edge X-ray absorption near-edge structure (XANES) spectra (Fig. 2(d)), the absorption edge of Fe_{SA}-TiO₂-O_v is located between those of Fe foil and Fe₂O₃, indicating that the average oxidation state of the Fe species is between 0 and +3. The following quantitative edge-

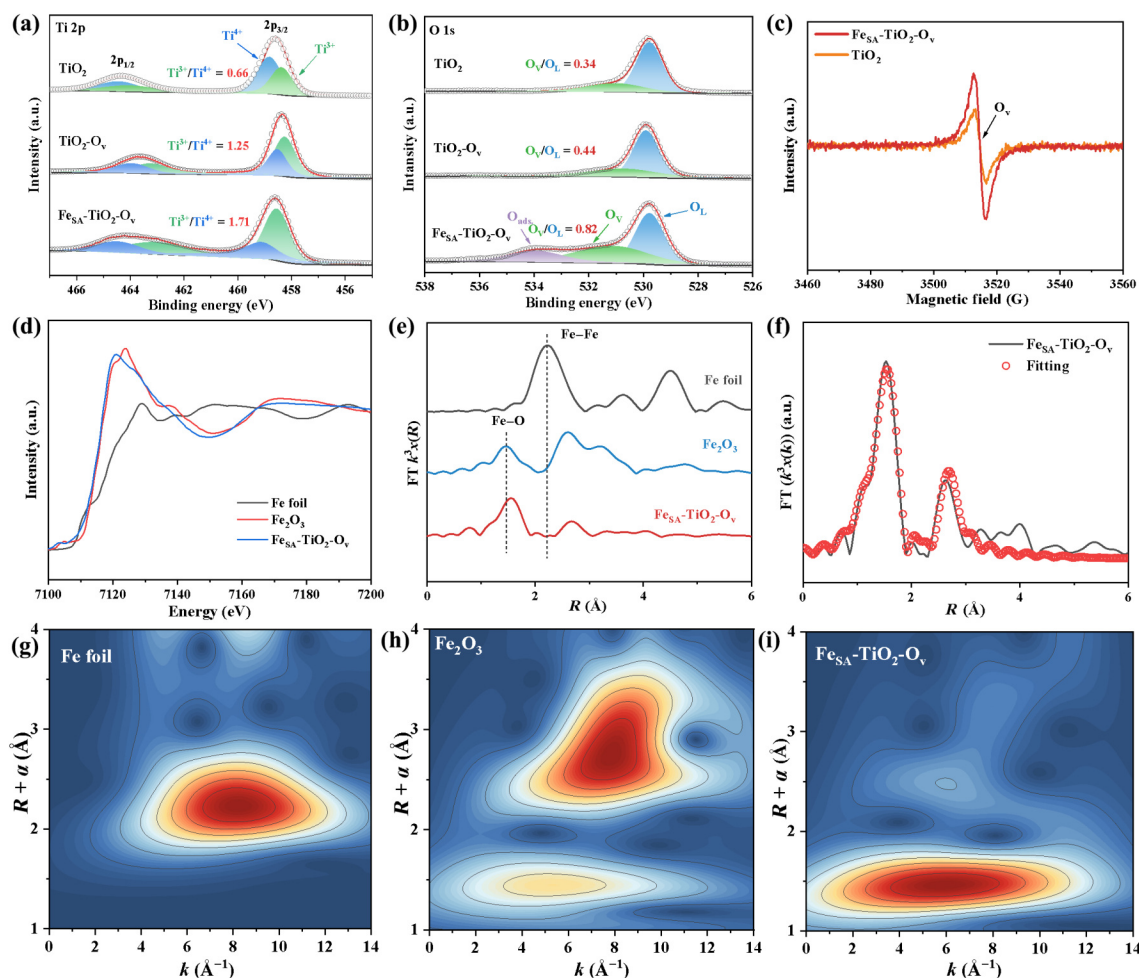


Figure 2 High-resolution XPS spectra of (a) Ti 2p and (b) O 1s of TiO₂, TiO₂-O_v, and Fe_{SA}-TiO₂-O_v. (c) EPR spectra of TiO₂ and Fe_{SA}-TiO₂-O_v. (d) Normalized XANES spectra at Fe K-edge of Fe_{SA}-TiO₂-O_v, using Fe foil and Fe₂O₃ as reference samples. (e) k³-weighted FT-EXAFS spectra and (f) R-space fitting spectra of Fe_{SA}-TiO₂-O_v. Wavelet-transformed k²-weighted EXAFS spectra of (g) Fe foil, (h) Fe₂O₃, and (i) Fe_{SA}-TiO₂-O_v.

position and linear-fitting analyses further estimate an average Fe oxidation state of +1.6 in the Fe_{SA}-TiO₂-O_v catalyst. More direct structural information is provided by the extended XAFS (EXAFS) spectra analysis. The k³-weighted FT-EXAFS spectra of Fe_{SA}-TiO₂-O_v (Fig. 2(e)) show a dominant first-shell peak at 1.54 Å, which can be assigned to Fe–O coordination, while no obvious Fe–Fe scattering contribution is observed near 2.2 Å, excluding the presence of Fe clusters or nanoparticles. Furthermore, the optimal EXAFS fitting results of Fe_{SA}-TiO₂-O_v (Fig. 2(f) and Fig. S4 and Table S2 in the ESM) reveal that the Fe site is coordinated by four light O atoms in the first coordination sphere, with an average bond distance of 1.97 Å. To further distinguish the coordination environment, wavelet-transform (WT)-EXAFS analysis was performed. Compared with Fe foil and Fe₂O₃, Fe_{SA}-TiO₂-O_v exhibits a single dominant WT intensity maximum in the low k region at 5.9 Å⁻¹ (Figs. 2(g)–2(i)), which is characteristic of Fe scattering from light atoms rather than neighboring Fe atoms. These results collectively confirm that Fe is stabilized as isolated Fe–O₄ moieties on the TiO₂-O_v support. The above results reflect strong metal–support interaction enabled by the oxygen-vacancy-rich TiO₂-O_v support.

3.3 Catalytic performance toward NO₃RR

The electrocatalytic nitrate reduction performance of Fe_{SA}-TiO₂-O_v,

TiO₂-O_v, and pristine TiO₂ is evaluated in 1 M KOH electrolyte, both with and without the addition of 0.1 M KNO₃. As shown by the linear sweep voltammetry (LSV) curves in Fig. 3(a), the cathodic current densities are markedly enhanced in the presence of nitrate compared to those in the blank electrolyte, confirming the electrocatalytic activity toward NO₃RR. Notably, Fe_{SA}-TiO₂-O_v exhibits substantially higher current densities than TiO₂ and TiO₂-O_v across the various potentials. The performance enhancement and the pivotal role of Fe doping are further validated by Fig. S5 in the ESM, which examines Fe_{SA}-TiO₂-O_v catalysts with varying Fe contents. The results establish clear composition–activity relationship, in which the current density progressively increases and the onset potential shifts positively as the Fe loading increases to an optimal value of 2.96 wt%. Chronoamperometric measurements are then conducted at various applied potentials, and the corresponding NH₃ yields and Faradaic efficiencies are summarized in Figs. 3(b) and 3(c), respectively. The NH₃ yield reaches 16.6 mg·h⁻¹·cm⁻² at –0.5 V versus reversible hydrogen electrode (vs. RHE), where Fe_{SA}-TiO₂-O_v also achieves a maximum Faradaic efficiency of 92%.

The standard curves for NH₃ and NO₂⁻ are provided in Figs. S6 and S7 in the ESM, respectively. The systematic investigation in Fig. S8 in the ESM further reveals that the superior performance with both NH₃ yield and Faradaic efficiency of Fe_{SA}-TiO₂-O_v, validating

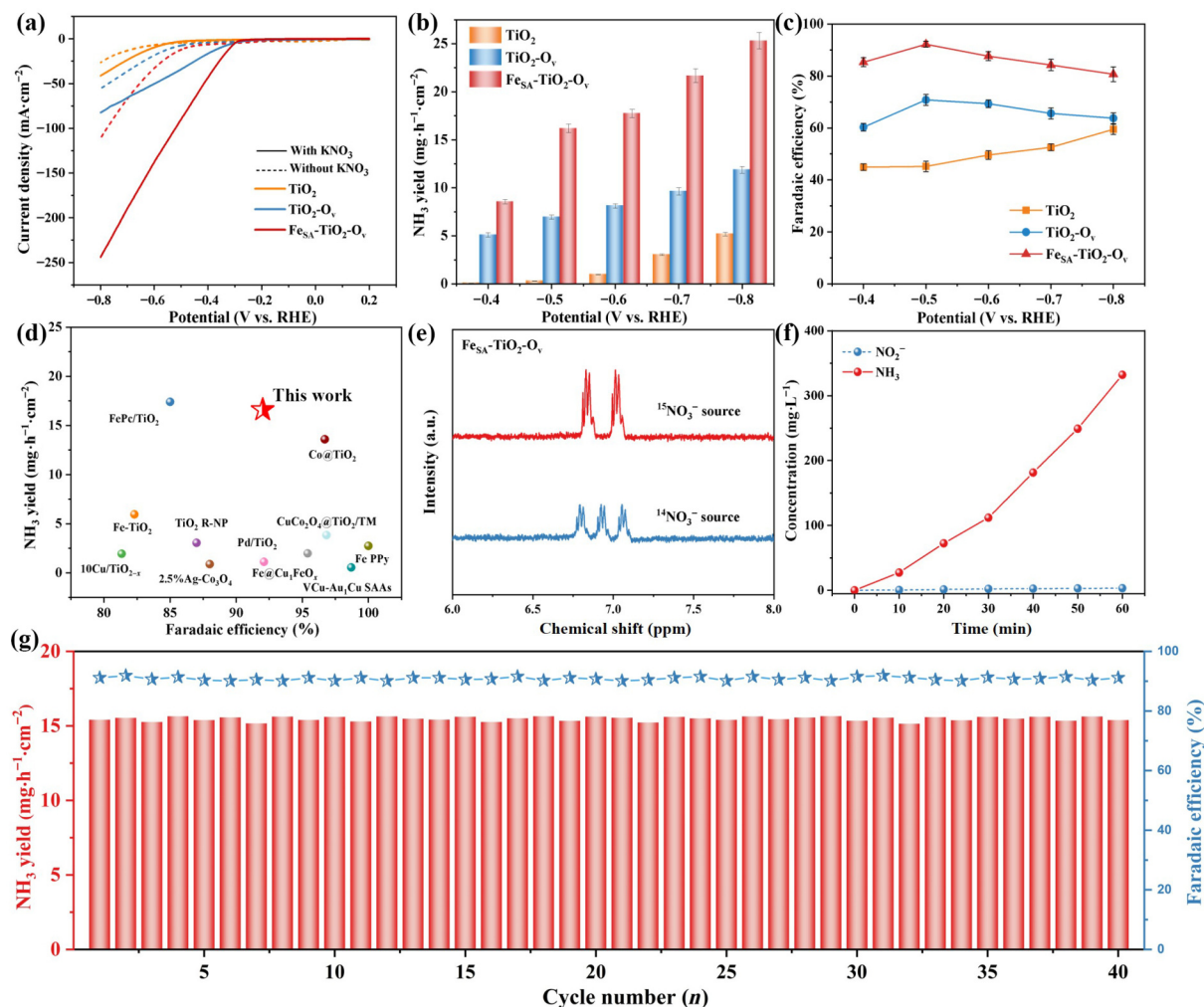


Figure 3 (a) LSV curves of TiO_2 , $\text{TiO}_2\text{-O}_v$ and $\text{Fe}_{\text{SA}}\text{-TiO}_2\text{-O}_v$ in 1 M KOH with (solid lines) and without (dashed lines) 0.1 M KNO_3 . (b) NH_3 yield rates and (c) NH_3 Faradaic efficiency of TiO_2 , $\text{TiO}_2\text{-O}_v$ and $\text{Fe}_{\text{SA}}\text{-TiO}_2\text{-O}_v$ after 1 h of NO_3RR at different potentials. (d) Comparison of the present work with previously reported nitrate reduction electrocatalysts. (e) ^1H nuclear magnetic resonance (NMR) spectra of the electrolytes produced from the NO_3RR for $\text{Fe}_{\text{SA}}\text{-TiO}_2\text{-O}_v$ using $^{15}\text{NO}_3^-$ and $^{14}\text{NO}_3^-$ standard samples. (f) Time-dependent concentration variation of NO_2^- -N and NH_3 -N during the NO_3RR on $\text{Fe}_{\text{SA}}\text{-TiO}_2\text{-O}_v$ at -0.5 V vs. RHE. (g) Recycling stability of $\text{Fe}_{\text{SA}}\text{-TiO}_2\text{-O}_v$ at -0.5 V vs. RHE.

the optimal composition identified in the activity measurements. In contrast, $\text{TiO}_2\text{-O}_v$ exhibits much lower NH_3 yields and Faradaic efficiency under identical conditions. The catalytic performance of $\text{Fe}_{\text{SA}}\text{-TiO}_2\text{-O}_v$ is further compared with previously reported nitrate reduction electrocatalysts, as shown in Fig. 3(d) and Table S3 in the ESM. The enhanced electrocatalytic activity of $\text{Fe}_{\text{SA}}\text{-TiO}_2\text{-O}_v$ is further elucidated by electrochemical impedance spectroscopy (EIS) and electrochemically active surface area (ECSA) analysis. Nyquist curves (Fig. S9 in the ESM) reveal that $\text{Fe}_{\text{SA}}\text{-TiO}_2\text{-O}_v$ exhibits the smallest charge-transfer resistance, indicating the most efficient electron-transfer kinetics [34]. Concurrently, $\text{Fe}_{\text{SA}}\text{-TiO}_2\text{-O}_v$ shows the largest ECSA among the samples, as estimated from double-layer capacitance (C_{dl}) measurements (Fig. S10 in the ESM), indicating a highly electrochemically accessible surface area. The combination of enhanced charge transfer and increased accessible surface area contributes to the accelerated kinetics of NO_3RR . Moreover, the ECSA-normalized LSV curves still exhibit higher current density for $\text{Fe}_{\text{SA}}\text{-TiO}_2\text{-O}_v$, compared to TiO_2 and $\text{TiO}_2\text{-O}_v$ (Fig. S11 in the ESM), indicating superior intrinsic catalytic activity. As a result, $\text{Fe}_{\text{SA}}\text{-TiO}_2\text{-O}_v$ exhibits a favorable combination of high NH_3 yield rate and high Faradaic efficiency.

To unequivocally identify the source of the produced ammonia, isotopic labeling experiments are carried out using $^{14}\text{NO}_3^-$ and $^{15}\text{NO}_3^-$ as nitrogen sources (Fig. 3(e)). When $^{15}\text{NO}_3^-$ is used as the reactant, characteristic doublet peaks corresponding to $^{15}\text{NH}_4^+$ are observed, while triplet peaks assigned to $^{14}\text{NH}_4^+$ are detected when $^{14}\text{NO}_3^-$ is used. These results clearly confirm that the generated NH_3 originates exclusively from nitrate electroreduction, rather than from external contamination [35]. To further investigate the reaction kinetics during nitrate electroreduction, time-dependent concentration changes of NO_2^- and NH_3 are monitored at a fixed potential (Fig. 3(f)). The NH_3 concentration increased nearly linearly with electrolysis time, indicating a stable and sustained ammonia production rate. Meanwhile, NO_2^- remained at a negligible level throughout the reaction, suggesting the absence of significant accumulation of intermediate species. These results imply that nitrogen-containing intermediates are rapidly converted during the reaction process, enabling efficient transformation of nitrate to ammonia over the $\text{Fe}_{\text{SA}}\text{-TiO}_2\text{-O}_v$ catalyst. The catalytic durability of $\text{Fe}_{\text{SA}}\text{-TiO}_2\text{-O}_v$ was evaluated through repeated electrolysis cycles. As shown in Fig. 3(g), both the NH_3 yield and Faradaic efficiency remained nearly constant over

40 h of consecutive cycles. The NH_3 yield was maintained at $16.6 \text{ mg} \cdot \text{h}^{-1} \cdot \text{cm}^{-2}$ at -0.5 V vs. RHE, while the Faradaic efficiency remained at 92%, demonstrating the excellent stability and structural robustness of the $\text{Fe}_{\text{SA}}\text{-TiO}_2\text{-O}_v$ catalyst during long-term nitrate electroreduction. In summary, the $\text{Fe}_{\text{SA}}\text{-TiO}_2\text{-O}_v$ catalyst demonstrates markedly enhanced electrocatalytic NO_3RR performance with high activity, excellent NH_3 selectivity, and outstanding durability, highlighting the crucial role of Fe single-atom active sites in promoting efficient nitrate-to-ammonia conversion.

3.4 Operando XAFS measurements and evolution of the Fe active sites

To monitor and elucidate the real-time structural evolution of Fe single-atom sites under NO_3RR conditions, *operando* Fe K-edge XAFS measurements were conducted on $\text{Fe}_{\text{SA}}\text{-TiO}_2\text{-O}_v$ at different applied potentials, including open-circuit potential (OCP), -0.2 , -0.3 , and -0.5 V vs. RHE. As shown in Fig. 4(a), the Fe K-edge position in the normalized XANES spectra for the $\text{Fe}_{\text{SA}}\text{-TiO}_2\text{-O}_v$ catalyst lies between those of Fe foil and Fe_2O_3 , indicating the initial presence of Fe single-atom states stabilized by the oxygen-vacancy-rich $\text{TiO}_2\text{-O}_v$ support. Upon electrolyte contact at OCP, only a slight spectral change is observed, suggesting that this process mainly induces interfacial coordination re-equilibration prior to catalysis. Once a cathodic bias is applied, the absorption edge progressively shifts to lower energy with increasingly negative potential, revealing a gradual decrease in the Fe valence during NO_3RR . Quantitative

linear combination fitting further shows that the average Fe valence decreases from ~ 1.62 in the $\text{Fe}_{\text{SA}}\text{-TiO}_2\text{-O}_v$ to ~ 0.97 at -0.5 V vs. RHE (Fig. 4(c)). These results suggest that, under reaction conditions, the active Fe sites are observed to reconstruct into electron-rich and low-valent Fe sites, which arise from cathodic polarization-driven electron injection into Fe 3d orbitals at the $\text{Fe}_{\text{SA}}\text{-TiO}_2\text{-O}_v$ [36], thereby enhancing electron availability and facilitating the NO_3RR process. The corresponding FT-EXAFS spectra show that the first-shell Fe-O peak gradually shifts to lower radial distances (R) values under cathodic bias, indicating the progressive contraction of the Fe-O coordination shell (Fig. 4(b)). Quantitative fitting reveals that the Fe-O bond distance decreases nearly linearly once the reaction is electrochemically initiated (Fig. 4(d)), whereas the OCP states deviate slightly from this trend because they mainly reflect surface wetting and interfacial equilibration. The nearly linear Fe-O bond contraction under working potentials, which might be associated with the adsorption of reaction intermediates on Fe and a sustained hydrogenation reaction process [37, 38].

Combined with the XANES results, these observations reveal a coupled electronic-geometric evolution of the Fe sites, in which electron accumulation at Fe is accompanied by coordination-shell compression, generating a more compact and electron-enriched reconstructed Fe-O configuration. The reconstructed Fe sites exhibit elevated electron density in their 3d orbitals, which enhances electron donation to the antibonding orbitals of N-O-containing intermediates, thereby weakening the N-O bonds and facilitating subsequent hydrogenation of $^*\text{NO}$ to form $^*\text{NOH}$ and $^*\text{NH}_x$ ($x = 1-3$) intermediates. Furthermore, the increased

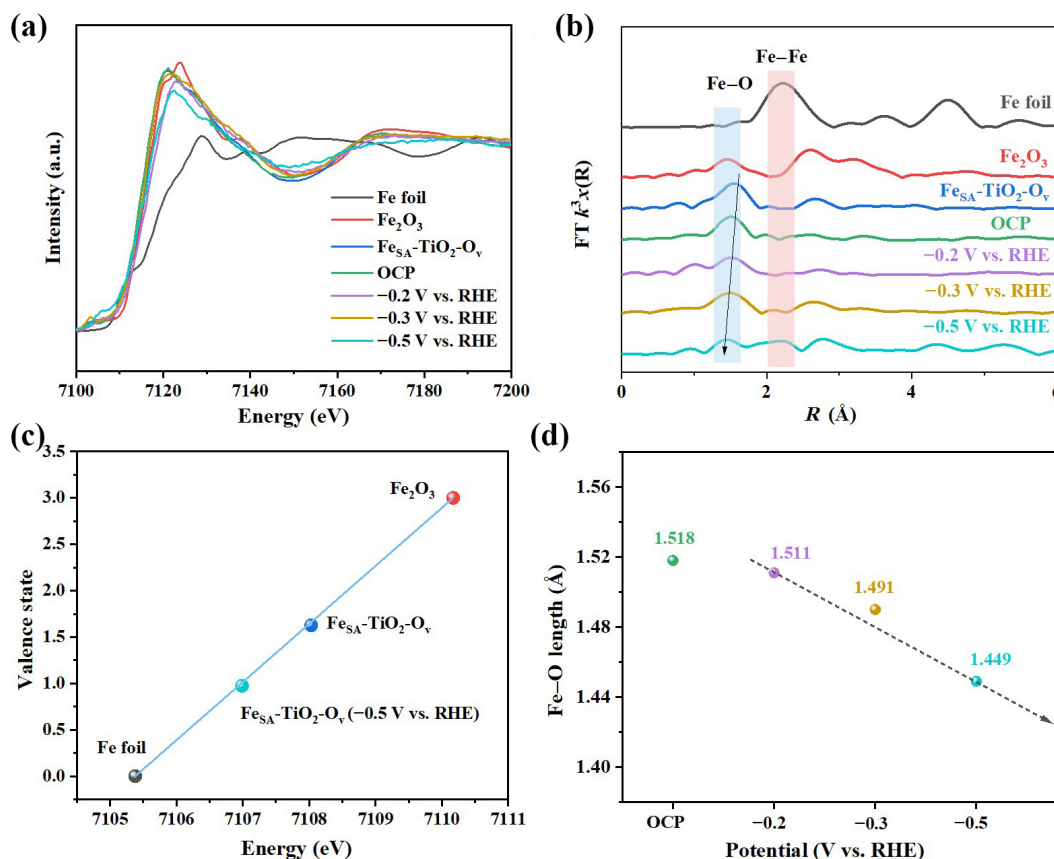


Figure 4 (a) Normalized Fe K-edge *operando* XANES spectra and (b) k^2 -weighted *operando* FT-EXAFS spectra recorded over $\text{Fe}_{\text{SA}}\text{-TiO}_2\text{-O}_v$ at OCP, -0.2 , -0.3 , and -0.5 V vs. RHE in 1 M KOH containing 0.1 M KNO_3 . Quantitative absorption energy and linear fitting analyses of (c) the Fe oxidation state and (d) Fe-O bond length in $\text{Fe}_{\text{SA}}\text{-TiO}_2\text{-O}_v$ derived from *operando* XANES and EXAFS spectra fitting results.

occupation of Fe 3d orbitals upon electron injection enhances electron–electron repulsion and modifies the shielding effect, further influencing the metal–support bond characteristics, thereby contributing to the observed structural rearrangement. Consistently, k^3 -weighted FT-EXAFS spectra analysis of the post-reaction $\text{Fe}_{\text{SA}}\text{-TiO}_2\text{-O}_v$ further shows that the contracted Fe–O coordination structure is well preserved after long-term NO_3RR (Fig. S12 in the ESM), confirming the structural stability of the reconstructed Fe sites under working conditions.

3.5 Reaction mechanistic study of $\text{Fe}_{\text{SA}}\text{-TiO}_2\text{-O}_v$ on NO_3RR

The catalytic mechanism of NO_3RR on $\text{Fe}_{\text{SA}}\text{-TiO}_2\text{-O}_v$ were investigated through a combination of online differential electrochemical mass spectrometry (DEMS) and *in situ* ATR-FTIR spectroscopy. The DEMS results provide a detailed analysis of the reaction intermediates during NO_3RR (Fig. 5(a) and Figs. S13 and S14 in the ESM), systematically comparing $\text{Fe}_{\text{SA}}\text{-TiO}_2\text{-O}_v$, $\text{TiO}_2\text{-O}_v$, and pristine TiO_2 . Upon applying step potentials, nitrogen-containing species signals were detected for all catalysts, suggesting a stepwise reduction pathway of NO_3^- . Specifically, the mass-to-charge (m/z) signals of 46, 30, 31, 17, 16, 15, and 14 were observed, corresponding to $^*\text{NO}_2$, $^*\text{NO}$, $^*\text{NOH}$, $^*\text{NH}_3$, $^*\text{NH}_2$, $^*\text{NH}$, and $^*\text{N}$, respectively [39, 40]. Based on above, the NO_3RR pathway can be proposed: The NO_3^- is initially adsorbed on the surface ($^*\text{NO}_3$), subsequently reduced to $^*\text{NO}_2$ and $^*\text{NO}$; then, the $^*\text{NO}$ is protonated into $^*\text{NOH}$, $^*\text{NH}_3$, and NH_3 as the final product. Among the three samples, $\text{Fe}_{\text{SA}}\text{-TiO}_2\text{-O}_v$ exhibits the highest signal intensities and more rapid signal evolution across all characteristic m/z ratios. In particular, the signals corresponding to NH_3 ($m/z = 17$) and NH_x -related fragments ($m/z = 15$ and 16) are consistently more pronounced on $\text{Fe}_{\text{SA}}\text{-TiO}_2\text{-O}_v$ than on the other samples, indicating enhanced formation of NH_x intermediates and more efficient conversion toward NH_3 . In contrast, poor signals of NH_x were detected on $\text{TiO}_2\text{-O}_v$, highlighting the insufficient generation of hydrogenated intermediates in the absence of Fe sites. This emphasizes that subsequent hydrogenation steps require the participation of Fe sites. *In situ* ATR-FTIR spectroscopy (Fig. 5(b)) further supports this interpretation, with distinct characteristic peaks under increasingly negative potentials. These peaks are assigned to H–O–H bending (1645 cm^{-1}), NH_4^+ deformation (1454 cm^{-1}), $^*\text{NH}_x$ intermediates (1285 cm^{-1}), and $^*\text{NOH}$ intermediates (1117 cm^{-1}), respectively [41]. Notably, compared with $\text{TiO}_2\text{-O}_v$, the characteristic $^*\text{NOH}$ -related vibrational signal and $^*\text{NH}_x$ intermediates signal on $\text{Fe}_{\text{SA}}\text{-TiO}_2\text{-O}_v$ are more pronounced (Fig. S15 in the ESM). This indicates that the gradual hydrogenation of $^*\text{NO}$ to $^*\text{NOH}$ and $^*\text{NH}_x$ is effectively promoted

by the Fe sites. The above results are consistent with the *operando* XAFS analysis, which highlights that the Fe sites play a crucial role in driving $^*\text{NO}$ hydrogenation and stabilizing $^*\text{NOH}$ and $^*\text{NH}_x$ intermediates, thereby promoting the efficient formation of NH_3 .

To gain mechanistic insight, DFT calculations were performed on $\text{Fe}_{\text{SA}}\text{-TiO}_2\text{-O}_v$ models to evaluate NO_3RR pathways. According to the above XAFS analysis, the structural models of $\text{Fe}_{\text{SA}}\text{-TiO}_2\text{-O}_v$ were proposed and further optimized through DFT calculations, as illustrated in Fig. S16 in the ESM. The incorporation of atomically dispersed Fe sites into TiO_2 with oxygen vacancies establishes an effective platform for nitrate reduction. Based on the DEMS and *in situ* ATR-FTIR spectra results, we calculated the free energy of individual intermediates on Ti sites and Fe sites over $\text{Fe}_{\text{SA}}\text{-TiO}_2\text{-O}_v$ (Fig. 6(a)). Obviously, the rate-determining step of NO_3RR is $^*\text{NO} \rightarrow ^*\text{NOH}$ step. The corresponding Gibbs free energy change on Fe site is 0.27 eV, which is much lower than that on Ti site (0.81 eV), demonstrating that Fe sites are more favorable for NO_3RR [42–44]. Bader charge calculations and charge density difference (CDD) analysis further reveal pronounced charge redistribution upon NO_3^- adsorption, indicating enhanced electronic coupling between active sites and NO_3^- species. More pronounced electron redistribution at Fe sites upon NO_3^- adsorption was observed (Fig. 6(b) and Fig. S17 in the ESM), suggesting that Fe sites facilitate charge transfer [45]. In addition, the HER-related free energy analysis (Fig. 6(c)) confirms that active $^*\text{H}$ formation is more favorable at Ti site adjacent to oxygen vacancies, highlighting Ti site as the primary site for hydrogen generation in $\text{Fe}_{\text{SA}}\text{-TiO}_2\text{-O}_v$ [46]. The Fe active sites in $\text{Fe}_{\text{SA}}\text{-TiO}_2\text{-O}_v$, on the other hand, are conducive to the hydrogenation reactions during the NO_3RR process. The results of EPR spectra show an enhanced $^*\text{H}$ signal for $\text{Fe}_{\text{SA}}\text{-TiO}_2\text{-O}_v$ relative to $\text{TiO}_2\text{-O}_v$ (Fig. 6(d)), reflecting a higher steady-state concentration of reactive $^*\text{H}$ species. This enhancement is attributed to Fe-induced electronic coupling, which promotes $^*\text{H}$ formation and stabilization at Ti and oxygen vacancy sites.

4 Conclusions

In summary, we develop $\text{Fe}_{\text{SA}}\text{-TiO}_2\text{-O}_v$ catalyst for efficient electrocatalytic NO_3^- -to- NH_3 conversion, achieving an NH_3 yield rate of $16.6\text{ mg}\cdot\text{h}^{-1}\cdot\text{cm}^{-2}$ and a maximum Faradaic efficiency of 92% at -0.5 V vs. RHE, with excellent long-term durability over 40 h. *Operando* XAFS spectroscopy shows that Fe sites undergo gradual valence descent accompanied by Fe–O bond contraction under NO_3RR conditions, confirming the formation of reconstructed low-valent Fe single-atom active sites. DFT calculations and *in situ* ATR-

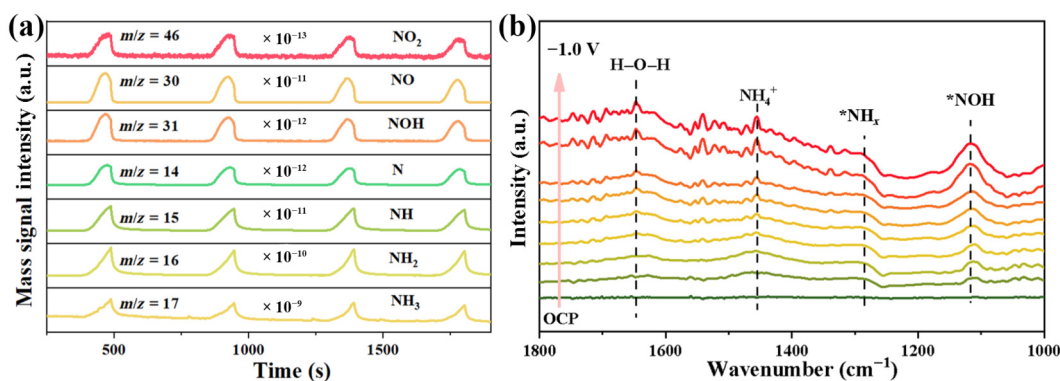


Figure 5 (a) Online DEMS of $\text{Fe}_{\text{SA}}\text{-TiO}_2\text{-O}_v$ in NO_3RR . (b) *In situ* ATR-FTIR spectra of $\text{Fe}_{\text{SA}}\text{-TiO}_2\text{-O}_v$ collected at different reaction potentials during the NO_3RR .

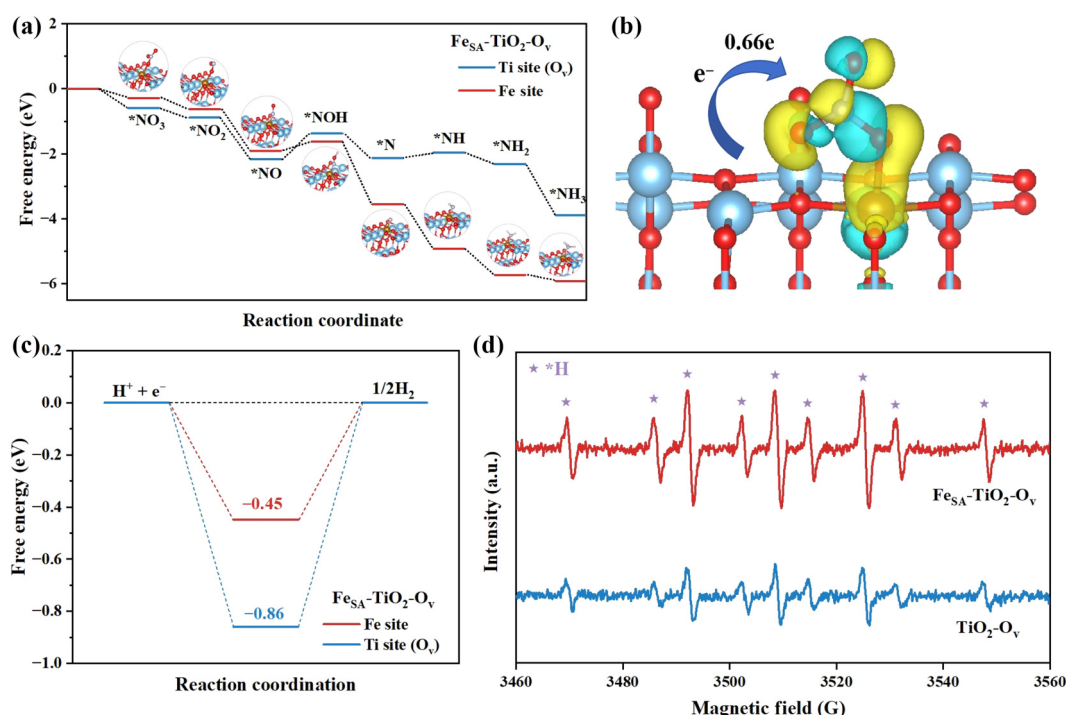


Figure 6 (a) Gibbs free energy diagrams of NO₃RR on Fe_{SA}-TiO₂-O_v at the Ti site and Fe site. (b) The adsorption configuration and CDD of NO₃⁻ adsorbed on the Fe site of Fe_{SA}-TiO₂-O_v. The light blue electronic cloud indicates charge depletion, and the yellow electronic cloud indicates charge accumulation. The isosurfaces are 0.003 eV·Å⁻³. (c) Gibbs free energy diagrams of HER on Fe_{SA}-TiO₂-O_v at the Ti site and Fe site. (d) EPR spectra of TiO₂-O_v and Fe_{SA}-TiO₂-O_v at -0.5 V vs. RHE after 10 min in 1 M KOH containing 0.1 M KNO₃ electrolytes with 5,5-dimethyl-1-pyrroline N-oxide (DMPO) under an Ar atmosphere.

FTIR spectroscopy reveal that the evolved low-valent Fe sites promote the hydrogenation of *NO to the *NOH intermediate and the subsequent reduction toward NH₃. This work identifies the active state of Fe sites, offering insights for designing single-atom catalysts for multistep electrocatalytic reduction reactions.

Electronic Supplementary Material: Supplementary material (additional experimental and computational details, including EPR spectroscopy, DEMS characterization, XAFS and *operando* XAFS measurements, electrochemical measurements, and DFT calculation models) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908792>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

S. H.: Experimental design, data curation, project administration, validation, writing manuscript. Y. X. S., and Q. N. B.: Data curation, formal analysis, investigation and writing. X. Y. L. and R. Z.: Data curation, investigation, methodology. P. Z. Q.: Data curation, formal analysis, methodology, resources. G. S. L.: Supervision, investigation. D. Q. Z.: Conceptualization, funding acquisition, supervision, manuscript preparation. All the authors have approved the final manuscript.

Use of AI statement

None.

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