Structural insight into [Fe–S$_2$–Mo] motif in electrochemical reduction of N$_2$ over Fe$_1$-supported molecular MoS$_2$†

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The catalytic synthesis of NH$_3$ from the thermodynamically challenging N$_2$ reduction reaction under mild conditions is currently a significant problem for scientists. Accordingly, herein, we report the development of a nitrogenase-inspired inorganic-based chalcogenide system for the efficient electrochemical conversion of N$_2$ to NH$_3$, which is comprised of the basic structure of [Fe–S$_2$–Mo]. This material showed high activity of 8.7 mg$_{NH_3}$/mg$_{Fe}^{-1}$ h$^{-1}$ (24 mg$_{NH_3}$/cm$^2$ h$^{-1}$) with an excellent faradaic efficiency of 27% for the conversion of N$_2$ to NH$_3$ in aqueous medium. It was demonstrated that the Fe$_1$ single atom on [Fe–S$_2$–Mo] under the optimal negative potential favors the reduction of N$_2$ to NH$_3$ over the competitive proton reduction to H$_2$. *Operando* X-ray absorption and simulations combined with theoretical DFT calculations provided the first and important insights on the particular electron-mediating and catalytic roles of the [Fe–S$_2$–Mo] motifs and Fe$_1$, respectively, on this two-dimensional (2D) molecular layer slab.

Introduction

NH$_3$ is a chemical that can be used as a fertilizer and carbon-free energy store. The industrial production of NH$_3$ from N$_2$ and hydrogen (H$_2$) via the Haber Bosch (HB) process is well developed, but simultaneously, it is very energy demanding and environmentally unfriendly. The HB process is normally conducted at high pressure and high temperature (400–500 °C and 100–200 bar, respectively), which accounts for 1–2% of the global annual energy output. This is due to the difficulty in this reaction route to dissociate the strong N≡N triple bond of N$_2$ for the production of ammonia. In addition, H$_2$ as a reactant for the HB process is predominately derived from fossil fuel, which is responsible for about 1% of the global greenhouse gas emission. Thus, several new attempts have been developed to replace the HB process using renewable energies. For example, decentralized pilot plants have been built to convert solar, wind, and tidal power to H$_2$ via renewable electricity for the synthesis of NH$_3$ (eHB) (see Fig. S1†). Furthermore, as a potential new process, it is even more attractive to produce NH$_3$ directly from the electrochemical reaction of N$_2$ and H$_2$O under ambient conditions. However, this still has to be developed using more effective catalysts.

For low-temperature N$_2$ catalytic fixation to NH$_3$, the associative mechanism most likely occurs through enzymatic, photo- or electro-chemical means. For these processes, N$_2$ fixation through enzyme nitrogenase is the most efficient route to produce NH$_3$, which has also been adopted in nature. Thus, substantial efforts have been devoted to understanding and mimicking how the nitrogenase enzyme accomplishes the reduction of N$_2$ at ambient temperature and pressure. Many homogeneous catalysts act as well-defined molecular systems to provide important mechanistic insights. On the other hand, inorganic-based nitrogenase mimics can potentially accomplish N$_2$ fixation and convert it into NH$_3$ under ambient conditions with light or electricity input. For example, heterogeneous catalysts in the form of transition metal chalcogenides, including Mo- and Fe-containing sulphide clusters, have been reported to catalyze the reduction of N$_2$ to NH$_3$. However, these structures are not well-defined and cannot provide as much mechanistic guidance as that of the homogeneous catalysts.

In addition, a number of these solid electrocatalysts suffer from slow kinetics due to the low N$_2$ reduction. Also, H$_2$ from competitive proton (water) reduction occurs over the same active sites. It has been reported that proton reduction is
thermodynamically more favorable than N2 reduction under negative potentials (see Fig. S2†). The adsorption and reduction of H+ to surface H* are potential dependent and can be rate-limiting on a specific catalyst. If this competitive route is suppressed, then it may dramatically enhance the faradaic efficiency (ηFE) for N2 reduction. Therefore, the design of inherently active and selective electrocatalysts with a suitable surface for N2 reduction relies on controlling the applied potential to attenuate or totally inhibit the H2 evolution process, while enhancing the activation of N2. The activity of transition metals for the synthesis of NH3 has been rationalized in terms of the N2 binding energy by Norskov and co-workers. Their results showed that transition metals with half-electron filled 3d orbitals, such as Ru, Os and Fe, have a relative lower adsorption energy (−55–10 kJ mol−1 N2) for N2, which results in higher turnover frequencies for the synthesis of NH3. As both a non-noble metal and the active ingredient of the nitrogenase enzyme, Fe is a potential candidate for the electrochemical synthesis of NH3.

Herein, we developed a structurally well-defined single-atom catalyst consisting of isolated Fe1 anchored on exfoliated molecular-layered MoS2 for the efficient N2 reduction reaction (NRR) to NH3 of 8.7 mgNH3 mgFe−1 h−1 in water under an applied potential, which could also offer a high ηFE of 27% over H2 evolution from water electrolysis. It is interesting to find that this single-atom Fe1 catalyst possesses similar [Fe–S2–Mo] motifs to the core-structure of the FeMo sulfur (S) clusters in the nitrogenase enzyme. This makes the single-atom Fe1 the catalytic redox active centers, which combined with the electronic-mediating [Fe–S2–Mo] units, boost the electrochemical reduction of N2 in water. The electrochemical reduction of N2 over the Fe1 single-atom catalyst was investigated via operando synchrotron-radiation X-ray absorption fine structure (opXAFS), X-ray absorption near edge structure (XANES) spectroscopy and density functional theory (DFT) calculations. The mechanistic pathways and structure–activity relationships were deduced over this inorganic nitrogenase mimic [Fe–S2–Mo], providing guiding principles for the NRR.

Results and discussion

Structure of Fe1 single-atom on single-layer MoS2

The MoS2 matrix was firstly treated with n-butyllithium solution in hexane to exfoliate bulk MoS2 to form 2D mono-layered MoS2. The X-ray diffraction (XRD, Fig. S3†) pattern and atomic force microscopy (AFM, Fig. S4†) image show that around 60% of the exfoliated MoS2 is single molecular layers. Subsequently, single-atom Fe1 was introduced on the three-sublayer S-Mo–S in trigonal prismatic 2-H structure mono-layered MoS2 via the hydrothermal method. No peaks corresponding to Fe-based aggregated species were detected in the XRD patterns and TEM images, demonstrating the high dispersion of the Fe1 atoms.

The existence of dispersed Fe atoms on the basal plane of MoS2 was clearly verified by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), as shown in Fig. 1. Single-layer MoS2 nanosheets with a 2H trigonal prismatic symmetry pattern can be clearly seen. For single-atom catalysis, the specific chemical environment of the atom is critical since its coordinated feature can significantly affect its catalytic behavior and performance. For most of the reported supported single-atom (active site) materials, although the atoms could be directly visualized using the recently developed HADDF-STEM technique, their atomic positions with respect to the support structures were not clear and well-defined; hence, obscuring the derivation of the important structure–activity relationships. In contrast, our single-atom Fe on single-molecular layered MoS2 (sMoS2) exhibited clear

![Fig. 1 Morphology and structural characterization of Fe-sMoS2. (a) HAADF-STEM image of Fe-sMoS2 sheet, scale bar is 1 nm. Chemical environments of Fe1 can be seen in the two enlarged square boxes, where Scan 1 (blue line) shows the Fe1 atom on the Mo atop site and Scan 2 (pink line) shows the Fe1 atom substituted on the S site. The red arrows indicate individual Fe1 atoms on the Mo atop site. (b) HAADF-STEM scan, (c) corresponding DFT optimized model and (f) ADF intensity profile analysis of the Fe1 atom on the Mo atop site. (d) HAADF-STEM scan, (e) corresponding DFT optimized model and (g) ADF intensity profile analysis of the Fe1 atom as the substituted S site.](image-url)
bonding environments. As shown in Fig. 1, isolated Fe1 atoms are located at two types of preferred positions on the basal plane of sMoS2, namely the Mo atop site and substituted S atom site. They were revealed by the brighter spots than the surrounding Mo or S2 sites in the 2-H arrangement, typically as presented in the blue and pink squares, respectively. Further evidence was obtained from the DFT simulations (Fig. S5†), enlarged HAADF-STEM image, corresponding model and intensity profile analysis, as shown in Fig. 1b, c and f, respectively showing that the Fe1 atom sits on the triangle S sites, which is directly on the top position of Mo as the atop site. Similarly, Fig. 1d, e and g show that the Fe atom is located on the S basal site of 2H-sMoS2, where the intensity profile suggests that S is substituted by the Fe atom. It should be noted that most of the Fe1 single atoms were found on the Mo atop sites, and occasionally on the S substitution sites.

To obtain bonding information on the anchored Fe1 atom, experimental XAFS (Fig. 2a) spectra were collected together with DFT simulations. Fig. 2a shows the Fourier transform spectrum of the Fe K-edge XAFS oscillations of the as-reduced Fe-sMoS2 in comparison with the standard Fe foil. The absence of Fe–Fe interaction in the FT-XAFS spectra indicates the single-atom configuration of Fe1. The peak at approximately 1.7 Å is mainly attributed to the Fe–S bonds at the Mo atop site. The simulation of the structure with the corresponding bonding distance is shown in the inset of Fig. 2a. Wavelet transformed analysis of XAFS (WT-XAFS, Fig. 2c) based on Morlet wavelets was conducted to differentiate the closely-related spatial interactions of the Fe1 atoms with their proximal atoms. As displayed in Fig. 2c, the Fe–Fe bonds in the Fe foil show an energy maximum in the range of 7–11 Å⁻¹, while that for Fe-sMoS2 is in the range of 4–9 Å⁻¹. This again supports the fact that the Fe species are individually dispersed as single atoms, as shown by the HAADF-STEM image (Fig. 1), mainly at the Mo atop sites.

The bonding environment of the Fe1 atom at the Mo atop site was simulated by DFT, and the result is shown in Fig. S5.† Interestingly, the structure in the model of Fe1 at the Mo atop site has almost the same inorganic motif of [Fe–S2–Mo] with that of the core structure of FeMoco, the primary cofactor of nitrogenase, giving equivalent bond lengths and geometries of the coordinated Fe1 shells (see Table S1†).24,25 In addition to the similar bonding environment of Fe, according to the XANES analysis, the absorption edge is clearly located between FeII and FeIII, indicating that the oxidation state of the Fe species in Fe-sMoS2 is also close to that of the working state of FeMoco,26 as shown in Fig. 2b. Of particular interest is the characteristic peak below the absorption edge of Fe-sMoS2. It is well known that this pre-edge feature is due to the 1s → 3d orbital forbidden transition, which would be excluded by dipole selection rules for a symmetry site.27 The observed pre-edge peak matches with the characterized isolated Fe1 on s-MoS2.

**Electrochemical N2 reduction**

The material was then tested for electrochemical N2 conversion to NH3 in water under ambient conditions. The catalyst was deposited on carbon paper as a cathode under a flowing stream of N2 feed gas. It has been noted in the literature in this field that carefully designed blanks must be employed to confirm the nitrogen reduction reaction activity of any material. For example, it has been reported that contaminants such as NOx may also participate in the synthesis of ammonia.16,31 NaClO3 is known to be one of the most efficient chemicals for NOx oxidation due to its strong oxidation power.26,32 Thus, to remove the interference of NOx, two traps filled with 0.2 M NaClO3 solution and 1 mM H2SO4 solution were used to purify the feed gas before it was flowed into the three-electrode single cell. The ability to remove NOx is evidenced in Fig. S6.† In a previously established N2 purification protocol, gas cleaning of the filters following by acid trapping were employed to remove NOx.26 The two methods were compared, and the results were within an acceptable deviation of 8.3%. Prior to each test, blank measurements in the absence of N2 and catalyst were conducted.15,38 The obtained reaction assay was measured by two independent methods, namely the indophenol blue method (Fig. S7†) and ammonia selective electrode.29 The detail mechanism of the ammonia selective electrode is presented in the ESL.† The calibration curves are shown in Fig. S8 and S9,† respectively. The results from the two methods were in a good agreement. We firstly optimized the over-potential required for the maximum production of NH3 over Fe-sMoS2 in the range of –0.05 V to –1.00 V (versus the reversible H2 electrode (RHE)). As shown in Fig. S10,† the current density increased as the applied potential increased, and was more stable at low potential. The highest rate of NH3 production was 24.5 μgNH3 cm⁻² h⁻¹ (8.7 mgNH3 mg⁻¹ h⁻¹) at –0.10 V (versus RHE, see Fig. 3a) with a maximum ηFe of ca. 27.0% (Fig. 3b). To the best of our knowledge, this electrocatalytic performance is among the best.
reported results for the electrochemical synthesis of NH₃ using non-noble Fe-based systems in the literature (Table S2†). However, both the rate and ηFF decreased dramatically when the applied potential was beyond −0.20 V (Fig. 3b). The Tafel plot in Fig. S11† was used to determine the rate-determining step for the H₂ evolution reaction and oxygen reduction reaction. Mechanistically, three principal steps can participate in the conversion of 2H⁺ to H₂, namely the Volmer, Heyrovsky and Tafel steps. If the Volmer process is the rate-determining step (rds), a slope of ∼120 mV per decade will likely be obtained. In contrast, a rate-determining Heyrovsky or Tafel step gives characteristic slopes between 30−40 mV per decade.† Our Tafel slope for Fe-Sm0S₂ in argon gas was measured to be ∼156 mV per decade at a low over-potential range (Fig. S11†), which suggests the rds is the Volmer step, involving the initial highly activated adsorption and reduction of H⁺ to produce active surface H* (H⁺ + e⁻ + * = *H). On the other hand, the corresponding Tafel slope for Fe-Sm0S₂ for N₂ reduction to ammonia was measured to be ∼121 mV per decade, which is substantially lower than that of the proton reduction. Therefore, to reduce the extent of H₂ production on this surface during N₂ reduction, it appears to be necessary to apply an optimal potential.

It is well known that exposed lattice vacancies can act as active sites for the activation of H₂ and N₂.†,‡,†† Consequently, different concentrations of S vacancies in different-layered MoS₂ samples using electron paramagnetic resonance were obtained (EPR, Fig. 3d). As can be seen in Fig. 3d, the peak intensity due to S vacancies (unpaired electrons at g = 2.00 detected infer the formation of S vacancies) increased with S decrease in the thickness of the MoS₂ layers (S vacancies were created during exfoliation†), which correlates well with their electrochemical performances at a potential of −0.1 V (versus RHE, Fig. 3d and S12†). The activity for both N₂ reduction and H₂ evolution appeared to be greatly promoted when single-layered MoS₂ was used. Notably, the activity for NH₃ yield apparently increased with a reduction in the thickness of the MoS₂ slab. However, the overall ηFF for N₂ reduction to NH₃ by the single-layered MoS₂ was significantly lower than that of few-layered MoS₂ and bulk MoS₂. This implies that S vacancies promote a greater degree of H₂ evolution than N₂ reduction due to the more favorable thermodynamics in the former case. The addition of a transition metal causes an obvious decrease in the EPR signal, presumably because the transition metal dopant can occupy the S vacancies of 2H-MoS₂, as shown by the HAADF-STEM analysis (Fig. 1c). Fe-Sm0S₂ exerts strong magnetic perturbation due to the presence of paramagnetic Fe, which accounts for the perturbed zig-zag oscillation of the background ESR signal. Fig. S13† shows a comparison of the activities and ηFF for N₂ reduction to NH₃ over different metal-doped MoS₂ such as Au and Ru with the previously reported values.†,‡ The presence of trace Li⁺ during the preparation of the molecular layer of MoS₂ may facilitate the activity and ηFF since Li⁺ has been reported to play a vital role in the NRR. However, the result from Fig. S13† indicates that the metal doping affects much more than the residual Li⁺. Polarization due to protruded transition metal atoms on the thin MoS₂ surface suggested by L. Zhang and co-workers may play a role in their activity. However, we believe that the intrinsic atomic arrangements of Fe-Sm0S₂, which has the core structure of nitrogenase, can give the best activity and ηFF. In fact, among the Haber-Bosch catalysts and biological enzymes, Fe is well-known to bind N and H competitively to give ammonia compared to other metals. This is further supported by the high electron consumption for the nitrogen reduction reaction over Fe-Sm0S₂, as shown in Fig. 3c.

The electrochemical performance for N₂ fixation to NH₃ on Fe-Sm0S₂ was also studied by linear sweep voltammetry (LSV), as shown in Fig. 3b, a clearly higher cathodic current density can be observed in the sweeping potential range of −50 mV to −300 mV versus RHE when the electrolyte was purged with N₂ instead of Ar. In addition, the ηFF for N₂ reduction by dividing the current density in Ar is very close to that in the synthesis of NH₃ (maximum of 27%), verifying that N₂ is activated and converted to NH₃ by the Fe-Sm0S₂ catalyst. Isotopic labeling using 98% ¹⁵N-enriched N₂ gas was carried out to prove the derivation of NH₃. Controlled experiments in the absence of ¹⁵N₂, catalyst, and applied potential were firstly conducted, and no clear ammonia signal was observed in the proton NMR spectra, as shown in Fig. S14.† In contrast, a doublet in the region near 7.0 ppm was found for the test over Fe-Sm0S₂ at −0.10 V with a flow of ¹⁵N₂. The quantitative results (Fig. S15†) indicated that the product rate is around 22 μg cm⁻² h⁻¹, which is consistent with the result using ¹⁴N₂. These results show that both the catalyst and the applied potential are necessary for
nitrogen fixation. Thus, based on the result from LSV, nitrogen fixation occurs at a potential in the range of 0 to \(-0.5\) V. Subsequently, liquid chromatography-mass spectrometry (LC-MS) analysis was conducted, which identified two major species containing indophenol derivatives from natural \(^{14}\text{N}\) and enriched \(^{15}\text{N}\) (see Fig. S16†). The fragments containing \(^{15}\text{N}\) have a much higher area ratio at \(199/198\ m/z\) (mass/charge ratio) compared to that of the control fragments containing \(^{14}\text{N}\). The isotopically labeled \(^{15}\text{N}_2\) authenticated that the \(\text{NH}_3\) synthesized originated from \(\text{N}_2\) reduction. These results gave sufficient proof that \(\text{N}_2\) can be fixed to \(\text{NH}_3\) over \(\text{Fe-sMoS}_2\). We conducted a 10 h chronoamperometry test, which demonstrated that the activity and \(\eta_{\text{Fe}}\) slightly changed, as shown in Fig. S17.†

**Molecular activation and reduction of \(\text{N}_2\)**

Operando Fe K-edge opXAFS and opXANES are sensitive techniques to monitor the chemical environment of Fe atoms, which were performed in this study at the B18 Beamline, Diamond Light Source, UK to study the structural dynamics involving the single Fe atoms upon the competitive adsorption and activation of \(\text{N}_2\) with a proton from water over \(\text{Fe-sMoS}_2\). Fig. 4a and c show the Fourier transform (FT) opEXAFS spectra and the corresponding Fe K-edge opXANES spectra under different experimental conditions. Particularly, the peak relative to the Fe–S bond attributed to the Mo atop site (see Fig. 3a) under open-circuit voltage is compared in \(\text{N}_2\), \(\text{Ar}/\text{H}_2\text{O}\), and \(\text{N}_2/\text{H}_2\text{O}\), and at \(-0.1\) V (versus RHE) in \(\text{N}_2/\text{H}_2\text{O}\). It is clear that the FT intensity near the Fe–S bonds at the Mo atop site clearly changes in this region to the different treatments. After switching to highly acidic electrolyte solution purged with \(\text{Ar}\), the intensity of the Fe–S peak attributed to the Fe atop site exhibited the lowest value, which indicates the lowest coordination number for this Fe species. Based on our DFT simulation, the Fe–N bonding interactions of these molecule-absorbed Fe-sMoS2 species are at around \(1.8\ \text{Å}\) (Fig. S18†), which is comparable in distance with the Fe–S interactions. Thus, it was anticipated that competitive replacement of this absorbed \(\text{N}_2\) species from Fe by \(\text{H}^+\) would cause a reduction in the intensity of this peak. Interestingly, upon switching the gas stream back to \(\text{N}_2\), we noted that the peak intensity increased to a higher value, resuming the higher contribution from the Fe–N scattering. These results clearly show that \(\text{N}_2\) and \(\text{H}^+\) can be competitively activated by the Fe1 atoms on MoS2, as reflected by the atop Fe–S peak modulations. During the typical conditions for electrochemical \(\text{N}_2\) reduction to \(\text{NH}_3\) at the previously optimized \(-0.1\) V versus RHE, the

![Fig. 4 Operando X-ray absorption spectroscopy and \(\text{N}_2\) activation process. (a) Fourier transform magnitudes of the experimental Fe K-edge srXAFS spectra of Fe-sMoS2 under open-circuit voltage bias in \(\text{N}_2\), \(\text{Ar}/\text{H}_2\text{O}\), and \(\text{N}_2/\text{H}_2\text{O}\), and at \(-0.1\) V (versus RHE) in \(\text{N}_2/\text{H}_2\text{O}\). \(\text{H}_2\text{O}\) represents electrolyte solution containing 0.1 M hydrogen chloride. (b) Structural evolution of the active site in electrochemical \(\text{NH}_3\) synthesis with \(\text{N}_2\) absorption and applied potential. (1) Before \(\text{N}_2\) adsorption, the Fe–S bond is 2.14 Å in length. (2) After the adsorption of \(\text{N}_2\) on the Fe1 atom, the Fe–S bond is extended to 2.20 Å in length. (3) Low unoccupied molecular orbital of Fe1 Mo atop site. Green net represents positively charged orbital and orange net represents negatively charged orbital. After applying a potential, the electron will transfer to the Fe1 atom. Blue, yellow, brown, green, and red balls are Mo, S, Fe, N, and H atoms, respectively. (c) Normalized operando Fe K-edge XANES spectra for Fe-sMoS2 under open-circuit voltage bias in \(\text{Ar}/\text{H}_2\text{O}\), and \(\text{N}_2/\text{H}_2\text{O}\), and at \(-0.1\) V (versus RHE) in \(\text{N}_2/\text{H}_2\text{O}\). (d) Simulated Fe K-edge XANES spectra for Fe-sMoS2, \(\text{N}_2\)-adsorbed Fe-sMoS2, and electron-rich Fe. Blue, yellow, brown, cyan, and red balls are N, S, Fe, and Mo atoms, respectively.](#)
The introduction of N$_2$ caused a shift of the absorption edge at 7118 eV, corresponding to the same phenomenon observed in Fig. 3a. This also indicates that the electron from the applied potential is biased at the Fe$^+_1$ atom and could be used for competitive N$_2$ activation to NH$_3$. In addition, the Fourier transform spectra showed that there was a slight but significant shift in the Fe–S interaction of the atop site during N$_2$ activation, as shown in Fig. 4a. The main peak of Fe–S shifted to a shorter length (~4.04 Å) upon switching to Ar flushing and returned to the original position when the N$_2$ flow was resumed. Clearly, the electron back-donation of Fe orbitals from the adsorbed N$_2$ can attenuate its bonding with the S ligands, accounting for the longer Fe–S interaction. Apparently, applying a negative over-potential for N$_2$ over H$^+$ in the dynamic synthesis of ammonia places the peak position between these two values.

The processes for N$_2$ activation were then investigated by DFT calculations (Fig. S19†). Fig. 4b(1) shows that the DFT-optimised Fe–S bond of the initial Fe$^+_1$ atom at the Mo atop site is 2.14 Å. After the absorption of N$_2$, the bond is extended by absorbed N$_2$ to 2.20 Å (Fig. 4c(2)). The increment in the bond length (~0.06 Å) is close to the observed value (~0.04 Å), as measured by opXAFS. The electron ground state of Fe-sMoS$_2$ was simulated in the form of the highest occupied molecular orbital (HOMO). As shown in Fig. 4c(3), Fe$^+_1$ is relatively positively charged under H$_2$, which allows the external electrons to occupy it under HOMO excitation. The experimental result from opXAFS also confirmed that the external electrons from the applied potential will be accommodated at the Fe$^+_1$ atom, as above. Therefore, the electron can then be used for the activation and reduction of N$_2$ to NH$_3$ on [Fe–S$_2$–Mo].

Fig. 4c shows the corresponding normalized operando Fe K-edge opXANES spectra in Ar. The shoulder signal of the main absorption edge at ~7118 eV is due to the 1s → 4p transition. The introduction of N$_2$ caused a shift to the right, showing an electron withdrawing effect from the Fe species to N$_2$, indicating the electronic effects on the Fe$_1$ atom via N$_2$ adsorption. The shift to a higher oxidative state is due to the effective delocalization of the unpaired electron in the 3d orbitals of Fe and the spontaneous charge transfer from Fe to both the N$_2$ 2p orbital and proton 1s orbital. During electrochemical N$_2$ reduction, the Fe K-edge of Fe-sMoS$_2$ shifted back to a lower shift value, indicating the recovery of the electronic state of the orbitals of Fe$_1$ due to the injection of external electrons. We further monitored this process using XANES simulations for Fe-sMoS$_2$ under different conditions (Fig. 4d). As shown, the N$_2$ adsorption on the Fe$_1$ atom significantly shifted the edge of 1s → 4p transition, which returned to a lower energy value after applying one electron to the Fe atom. The simulations confirmed the trend of the effect of N$_2$ activation and potential applied. Similar phenomena of opXAFS and opXANES were observed for the molecular activation and reduction of CO$_2$.

Thus, based on these operando studies, the Fe$_1$ single atom on Fe-sMoS$_2$ serves as the active site for the electrochemical fixation of N$_2$ to NH$_3$. During the adsorption and electrochemical reduction of N$_2$, [Fe–S$_2$–Mo] responds to the tension and contraction of the Fe–S bond by changing the bond length and Fe electronic state.

To demonstrate the electron-mediating and catalytic roles of the [Fe–S$_2$–Mo] unit in promoting the synthesis of ammonia, we compared the electronic structure of N$_2$–Fe-sMoS$_2$ and N$_2$–Fe$_3$S$_4$. As shown in Fig. 5, the Bader charge of adsorbed N$_2$ is ~0.29 electrons (~0.01–0.28) over Fe-sMoS$_2$. This value is much lower than that (0.23–0.43 = ~0.20 electrons) over Fe$_3$S$_4$, indicating that more electrons are donated from the Fe$_1$ site to the antibonding orbital of the adsorbed N$_2$ on Fe-sMoS$_2$ with [Fe–S$_2$–Mo] units than Fe$_3$S$_4$ without Mo. Consequently, the activation of N$_2$ is promoted with a longer N–N bond length from 1.10 Å to 1.15 Å (see Table S3†). Meanwhile, the bond length of Fe–N is shortened within the unit of [Fe–S$_2$–Mo]. In addition, the average Bader charge of the S atom in the [Fe–S$_2$–Mo] unit is also more negative than that without the nitrogenase-mimic structure (~0.61 vs. ~0.54 electrons), indicating that the removal of a proton from the competitive active site of the Fe atom is easier for a higher efficiency of nitrogen reduction over the nitrogenase mimic Fe-sMoS$_2$ under the same potential.

**Conclusions**

In summary, a new inorganic-based electrocatalyst with Fe$_1$ on a 2D single-layer MoS$_2$ slab was described. The structure contained dispersed Fe atoms on nitrogenase-like [Fe–S$_2$–Mo] motifs, which showed superior electrochemical activity and $\eta_{Fe}$ for electrochemical N$_2$ fixation to NH$_3$ over proton reduction in water under the application of the optimal potential at 0.1 V. Operando Fe K-edge srXAFS, XANES and DFT calculations indicated that N$_2$ can be adsorbed and reduced at the catalytic Fe$_1$ site on the essential electron-mediating [Fe–S$_2$–Mo] motifs. To activate the N$_2$ molecule, the strain of the Fe–S bonds and redox states of the Fe$_1$ atom will adapt to accelerate the absorption and reduction processes. This work not only demonstrated that single-atom heterogeneous catalysis accelerates the electrochemical reduction of N$_2$, but also offers unique insight into the synergistic active site with electronic...
and structural transitions during N₂ fixation over the nitrogenase mimic [Fe-S₂-Mo] structure.

Conflicts of interest

The authors declare no competing financial interest.

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