Large-scale ammonia synthesis under ambient environment is a highly demanding technology which is promising to replace the energy-consuming Haber–Bosch process. Motivated by the crucial iron–sulfur interaction in nitrogenase, the performance of 2D iron monochalcogenides (FeX, X=S, or Se) toward electrochemical nitrogen reduction reaction (e-N2RR) by means of density functional theory calculations is explored. It is confirmed that pristine 2D FeX is inert for even N2 adsorption while defective 2D FeX with single-anion-point vacancy (VX) demonstrates considerable activity for NRR. The enhancement is attributed to the interaction between defect-induced states and p-orbitals of nitrogen, which greatly alters the adsorption behavior of N2 molecule. Meanwhile, the relation between the N2 adsorption free energy and theoretical limiting potential (UL) agrees well with the previous report. Moreover, the 2D nature of FeX provides flexible adsorption sites for both N2 and proton, alleviating the competition between e-N2RR and hydrogen evolution reaction. As the existence of V5 and VSe in tetragonal iron monochalcogenides has been validated by experiments, a facile strategy for designing practical and economical NRR electrocatalysts is provided and might be extended to the study of other species of defects in catalysis.

1. Introduction

Fixing earth-abundant nitrogen element into more advanced chemicals is a delicate process for both nature and mankind.[1] Compared with the amount of ammonia generated by natural events such as lightning and biological enzymes, artificial ammonia synthesis makes significant contribution in feeding the world’s population and circulating economy. Consequently, studies relating artificial ammonia synthesis were awarded three Nobel Prizes[2] in the past century. Although the productivity of artificial ammonia synthesis continued increasing ever since it was practiced, the industrial techniques and reaction mechanisms remained almost unchanged from the original Haber–Bosch (HB) process, which requires numerous energy consumption to create a reaction environment under high temperature (∼500 °C) and high pressure (>100 atm).[3] At the same time, HB process may cause severe environmental concerns due to the great deal of CO2 emission.[4] In order to explore more economical and environmental-friendly alternatives of HB process, electrochemical methods emerged as another option in recent years to conduct nitrogen fixation and have achieved much progress.[5–7] Electrochemical nitrogen reduction reaction (e-N2RR) generally takes advantage of renewable electricity to weaken the stable N≡N bond in electrolytic cells with the aid of electrocatalysts. Electrocatalysts play a key role in this process by optimizing the N2 adsorption energy and energy barrier of each electrochemical step, and perfect candidates should balance among several factors like cost, activity, and selectivity.[8] Therefore, searching for the ideal e-N2RR electrocatalysts is an urgent and challenging task which meets broad interests of researchers.

In the practical HB process, iron acts as the active component of the thermocatalysts mainly because of its cheap price while its catalytic activity is far from satisfying. Naturally, iron and iron-based compounds were first considered when switching to electrocatalysis. General strategies to modulate the properties of iron (oxide) include morphology engineering and alloying iron with other elements. For the first point, Liang and co-workers synthesized Fe nanoparticles with the diameter of few nanometers on fluorine-doped graphene and observed a faradic efficiency of 41.6% and ammonia yield rate of 53.3 μg h⁻¹ mg⁻¹.[9] Zheng and collaborators developed a metal-organic framework-aided strategy to synthesize single-Fe atom active sites hosted by carbon nanotubes (CNT) and reported a slightly lower ammonia yield rate of 34.83 μg h⁻¹ mg⁻¹.[10] In addition, iron oxide is also commonly studied for e-N2RR due to its facile synthesis and excellent stability. Chen et al. prepared Fe2O3 nanoparticles supported on CNTs for direct electrochemical ammonia synthesis.[11] The catalyst remained stable for at least 12 h and ammonia yield rate reached 41.6 μg h⁻¹ mg⁻¹. Feng’s group prepared Fe/Fe3O4 catalyst toward e-N2RR by oxidizing iron foil at...
300 °C. In their electrochemical test, a 120-fold enhancement of Faradic efficiency and ninefold N2RR activity were observed compared with the original iron foil.[12] The effect of oxygen vacancy (V_O) on the catalytic performance of iron oxide was also reported as V_O is the most common defect in metal oxide. Zhang’s group investigated the performance of FeO_x nanorods with oxygen vacancies for N2RR and reported a decent NH_3 production rate but poor durability.[13] Second, alloy engineering has also been adopted to modulate the catalytic performance of iron. Sun and coworkers synthesized porous LaFeO_3 perovskite nanofiber and achieved ammonia yield rate of 18.59 μg h^{-1} mg^{-1} with faradic efficiency of 8.77%.[14] Density functional theory (DFT) calculation indicated the La-induced states near the Fermi level is the key factor for N_2 activation. Ahmed et al. proposed CoFeO_x cluster on reduced graphene oxide as a promising catalyst to reduce N_2 to ammonia.[15] This catalyst provided different types of active sites (Co and Fe) for N_2 adsorption and its 2D nature ensured a large density of active sites, surpassing the performance of its monometallic counterparts. Synergy of other transition metals and iron was also reported to boost catalytic activity toward e-N2RR, including Cu[16] and Mo[17] and Ni[18] just to list a few. Within the approach of alloy engineering, it is worthy to draw special attention on nitrogenase-inspired catalysts. Nitrogenase is a natural nitrogen fixation enzyme which usually contains iron, molybdenum, and sulfur as key elements. Inspired by this biological model, researchers designed lots of catalysts which mimic the structure and function of nitrogenase. Sun’s group proposed a FeMoS composite consisting of carbon fiber cloth covered by FeS-dotted MoS_2 nanosheets,[19] which can maintain a high ammonia yield rate over a wide pH range. Similarly in Chu’s work, the authors reported FeMoO_xS_y nanorods as an effective e-N2RR catalyst with high yield rate (65.3 μg h^{-1} mg^{-1}) and Faradic efficiency (19.2%).[20] Kanatzidis’s group developed chalcosols containing [Mo_2Fe_xS_y (SPh)_3]^3- and [Sn_2S_6]^{4-} clusters to effectively catalyze N_2 to NH_3 under ambient environment and white light irradiation.[21] Although these works enlightened the prospect of enzyme-inspired strategy, all of them are currently restricted on lab scale and possess quite complex structures, making it ambiguous to clarify the mechanism on these delicate assemblies.

Bulk iron sulfide prevails in minerals with diverse forms such as Fe_S_3 (greigite), FeS_2 (marcasite or pyrite), and Fe_S_3 (pyrrhotite). Among all these compounds, tetragonal FeS is of great physical interests due to the observation of superconductivity at 5 K.[22] Bulk tetragonal FeS has a layer-by-layer structure which indicates the possibility of being exfoliated to monolayer. Marzari et al. theoretically proved that tetragonal FeS could be cleaved down to atomical thickness[23] and single-layer FeS was successfully synthesized later.[24] FeSe has the same structure as FeS, and high-T_c superconductivity was observed in monolayer FeSe.[25–27] Meanwhile, anion-point vacancy (V_S or V_S) was also detected in both FeS[27] and FeSe[28–29] but the impact of point defect on their catalytic performance was rarely reported.

2D materials have attracted global interests since the discovery of graphene.[30] Owing to their unique dimension-reduced structure, 2D materials were regarded as an ideal platform to achieve unconventional physics, such as topological states[31] and superconductivity.[32] Later, the potential of 2D materials as catalysts was also explored because their 2D nature provides abundant and well-defined active sites which is crucial to clarify reaction mechanisms. There are plenty of works reporting the application of 2D materials as high-efficient catalysts for various reactions such as hydrogen evolution reaction (HER)[33,34] oxygen evolution/reduction reaction (OER/ORR)[35,36] and carbon dioxide reduction (CO_2RR).[37,38] In regard to e-N2RR, 2D materials were reported not only to directly act as catalysts[39,40] but also capable of supporting the active center.[41,42] Therefore, designing 2D e-N2RR electrocatalysts is a practical topic and enriches the knowledge for nitrogen reduction mechanism.

Combining the two inspirations mentioned earlier, we studied 2D defective iron monochalcogenides (FeS and FeSe) as potential e-N2RR catalysts by DFT calculations since defects were reported to play an attractive role in various catalytic processes[43–46] and especially in e-N2RR.[47–50] We found that pristine 2D FeS is inert for e-N2RR due to the poor adsorption of N_2 while anion point vacancy could stimulate their activities toward nitrogen fixation. Especially on V_S–FeS, the theoretical overpotential is only 0.49 V which ranks among the outstanding results. The N_2 adsorption free energies and limiting potentials (U_1) of both two candidates agree well with the inverse volcano plot suggested by previous work,[51] endorsing the credibility of our results. At the same time, competition of active sites between N_2 and proton is not severe due to the atomically thin morphology of 2D FeS, which decouples the commonly competitive N2RR and HER. Therefore, our work validated defect engineering on 2D iron monochalcogenides as a promising strategy for designing practical e-N2RR catalysts and might inspire more studies on defects in catalysis.

2. Results and Discussion

The lattice constant of 2D FeS was identified as a=b=3.557 Å which is close to the previous report (3.584 Å).[23] The structure of 2D FeS 3 × 3 supercell used in this work is shown in Figure 1a, and the anion point vacancy is introduced by removing one chalcogen atom. This resulted in a vacancy density of 1/9 (11.1%) which is close to the previously reported values of FeS_{0.94} (11.1%) and FeSe_{0.88} (13.1%) separately. Meanwhile, we also evaluated the formation energy of the point vacancy and performed AIMD simulation to check its stability. These details can be found in the Supporting Information from which we can confirm that the single-anion-point vacancy in tetragonal FeS is dynamically stable. These calculational evidences together with the experimentally observed defect density endorsed the rationality of our models for further investigation.

As the initial step of nitrogen reduction, N_2 adsorption was first studied on both pristine and defective FeS. According to our calculations, N_2 could not be adsorbed stably by any configuration on perfect FeS, as shown in Figure S2 and S3. Supporting Information. However, after introducing one chalcogen vacancy, the vacant site could capture the N_2 molecule via an associative manner, as shown in Figure 1b. The bond length of adsorbed N_2 (1.27 Å) is significantly stretched compared with the free N_2 molecule (1.10 Å), facilitating stable adsorption and weakening the N≡N bond for further reduction.[52] To investigate the nature of stable N_2 adsorption at point vacancy, we performed charge density difference and density of states (DOS) calculations. For charge density difference plot in Figure 1c,d,
there is clearly bidirectional charge transfer which implies the “acceptance-donation” mechanism\[^{41}\] between adsorbed N\(_2\) molecule and defective site in both FeS and FeSe, resulting in the weakening of the triple bond in N\(_2\). This can be further warranted by DOS plot in Figure 2. DOS of pure and defective Fe\(X\) were almost identical except for the zoomed part near \(E_F\), where some vacancy-induced states are populated into a small range well below the Fermi level as marked out. These vacancy-generated states are energetically close to \(p\)-orbitals of nitrogen molecule and would interact with nitrogen for activation. It was also observed that the defect-induced states in FeSe are less substantial than that of FeS, indicating a weaker N\(_2\) adsorption on FeSe. This can be quantitatively verified by the \(d\)-band center of iron in FeS (–0.18 eV) and FeSe (–0.37 eV), respectively, as a higher \(d\)-band center always implies a stronger interaction with the adsorbent molecule. This is consistent with our calculations that the nitrogen adsorption free energies on FeS and FeSe are –0.45 and –0.33 eV, separately.

After validating the initial adsorption pattern of N\(_2\) on defective FeS, we proceeded to the energy evolution profile of the reaction as in Figure 3. The associative adsorption mode in our work resembles the enzymatic mode which facilitates an alternative hydrogenation of both nitrogen atoms.\[^{41,54}\] The first H\(^+\) hits either of the nitrogen atoms as both of them are equivalent with each other, and the following protons attack two nitrogen atoms one by one till the formation of the first ammonia molecule.

**Figure 1.** a) Structure of 3 × 3 FeS supercell in this work with anion point vacancy. b) Optimized N\(_2\) adsorption of associative manner on 2D FeS. c) Charge density difference plot of associative N\(_2\) adsorption mode on defective FeS. d) Charge density difference plot of associative N\(_2\) adsorption mode on defective FeSe. c,d) Yellow indicates charge accumulation and cyan represents charge depletion. The isosurface value is set to be 0.01e Bohr\(^{-3}\). The top panels are top views while bottom panels are side views. Color map: yellow—S; green—Se; brown—Fe; blue—N.

**Figure 2.** a) Comparison of DOS in pristine and defective 2D FeS, with the DOS of nitrogen molecule plotted for reference. b) Zoomed details near Fermi level in the dashed region of (a), marking out states induced by S-vacancy and the \(d\)-band center of surrounding Fe atoms. c) Comparison of DOS in pristine and defective 2D FeSe. d) Zoomed details near Fermi level in the dashed region of (c), marking out states induced by Se vacancy and the \(d\)-band center of surrounding Fe atoms.
Then the last $H^+$ hits the lone-standing $^*NH_2$ to generate another NH$_3$. During the six-electron transfer process, the first two hydrogenation steps would release free energies of 0.14 and 0.29 eV, separately. The third and fourth steps are energetically uphill with the third step as the potential-determining step (PDS) with a free energy change of 0.653 eV, and the last two steps go energetically downhill. The intermediate configurations during the whole process on FeS are displayed in Figure 3c while the configurations on FeSe can be checked in Figure S4, Supporting Information. Because the equilibrium potential of $(N_2 + 6H^+ + 6e^- \rightarrow 2NH_3)$ is $-0.16$ V$^{[55]}$ within the framework of the computational hydrogen electrode (CHE) model, the theoretical overpotential ($\eta = U_{eq} - U_L$) is calculated to be only 0.49 V which is among the outstanding results ever reported. To make our work more reasonable and convincing, we also investigated a single-anion vacancy in $4\times4$ supercell, which corresponds to a defect density of $1/16(6.25\%)$, for its performance toward NRR. The comparison of these two ratios (11.1% and 6.25%) is put in Figure S5, Supporting Information, where only negligible difference was observed. This proves the robustness of catalytic activity of 2D defective FeX(X=S, Se) within a practical range of impurity densities. The results of defective 2D FeSe are similar as FeS except that the PDS is the last hydrogenation step with the largest $\Delta G = 0.842$ eV. This corresponds to an overpotential of 0.68 V which is not so good as FeS but can still be accepted in practice. It is worthy to mention that the relation between $N_2$ adsorption free energy and limiting potential agrees well with an inverse volcano described by the previous work$^{[51]}$ verifying the credibility of our calculation. Considering that electrocatalytic processes are usually conducted in solvent environment which may possibly affect the results,$^{[56]}$ we performed extra calculations where an implicit solvation model$^{[57]}$ was adopted. It was found that solvation plays a minor role in the performance of defective FeS while it can even elevate the activity of defective FeSe, which is shown in Figure S6, Supporting Information. The inclusion of solvation effect confirmed the performance of the catalysts and improved the credibility of this work.

Selectivity to desired products is also an important factor of evaluating the performance of electrocatalysts. For e-N2RR, HER is commonly regarded as a competitive reaction due to their close equilibrium potentials. Therefore, we also checked the HER activity on defective 2D FeS. The proton adsorption energy ($\Delta G_H$) is an effective descriptor to reflect HER activity, and the ideal catalysts should have $\Delta G_H$ close to zero. We screened all possible adsorption sites for $H^+$ on FeS–V$_S$ as in Figure 4a and concluded later. It is found that the defective site has the lowest $H^+$ adsorption free energy which is about $0.37$ eV, while $H^+$ initially adsorbed on bridge or hollow sites would move to the vacancy, and $H^+$ initially adsorbed on top of sulfur has a positive binding energy. In Figure 4b, we also plotted the $\Delta G_H$ of commercial Pt|C as a comparison with defective FeS. A clearly large deviation between $0.37$ eV and the commercial Pt|C indicates that FeS–V$_S$ is not a good HER catalyst. Moreover, the adsorption free energy of proton ($-0.37$ eV) is smaller than that of $N_2$ ($-0.45$ eV), implying that $N_2$ is much preferred in competing the adsorption sites. Finally, as shown in Figure 4c, we proved even a proton is preadsorbed on the vacant site, and it would migrate to the other side of FeS to make room for $N_2$ adsorption owing to the 2D nature of monolayer FeS.

Figure 3. a) Free energy diagram of FeS–V$_S$ via associative pathway with $U_L = -0.653$ V. b) Free energy diagram of FeSe–V$_{Se}$ via associative pathway with $U_L = -0.842$ V. c) Configurations of all intermediates during e-N2RR on defective 2D FeS. The top panels in c) are top views while bottom panels are side views. Color map: yellow—S; brown—Fe; blue—N; red—H.
This joint adsorption yields a free energy of −0.38 eV which suggested its feasibility. All these factors steer the selectivity to e-N2RR other than HER, increasing the catalytic performance of 2D defective FeS for e-N2RR. For further evaluation and comparison of the HER performance for iron monochalcogenide monolayer, the complete data for all possible adsorption sites on pristine and defective FeS/Se are provided in Table S1 and S2, Supporting Information, proving their bad performances toward HER.

3. Conclusions

In summary, we studied pristine and point-vacant 2D FeX as the potential electrocatalyst toward e-N2RR by DFT calculations. We confirmed that pristine monolayer FeS and FeSe are inert due to their poor adsorption ability for N2. However, both of them become active after introducing single-anion-point vacancy, because the interaction between defect-induced states and nitrogen molecule could decrease the strength of N≡N bond and activate it for further electrochemical hydrogenation. Especially on 2D FeS−V S, a small overpotential of 0.49 V is predicted together with the suppression of competing HER. Considering that anion point defects were experimentally verified in iron monochalcogenides, our work demonstrates the importance of defect engineering in catalysts design and provides a practical system to be further investigated for catalyzing e-N2RR.

4. Computational Methods

DFT calculations were performed using Vienna ab initio simulation package (VASP) including spin polarization effects.

The projector-augmented wave (PAW) method was applied to depict the relation between valence electrons and ions, while generalized gradient approximation functional (GGA) was realized by the Perdew–Burke–Ernzerhof form. A 400 eV threshold was set as the cutoff energy of plane-wave basis sets, and convergence criteria for the energy and the force were set to be 10−5 eV and 0.01 eV Å−1 separately. Grids for sampling the Brillouin zone were set as 3 × 3 × 1 gamma-centered mesh. In the 3 × 3 supercell of 2D FeX, vacuum thickness was about 16 Å to avoid impacts from neighboring cells in z-direction.

CHE model was adopted to calculate the free energy change of each electrochemical step.

\[
\Delta G = \Delta E_{\text{DFT}} + \Delta E_{\text{ZPE}} - T \Delta S + eU + \Delta G_{\text{pH}}
\]

where \(\Delta E_{\text{DFT}}\) is the electronic energy difference from standard DFT calculation, \(\Delta E_{\text{ZPE}}\) is the modification of zero point energy which accounts for the vibration energy of intermediates adsorbed on the catalyst surface, and \(T \Delta S\) is the entropic contribution where \(T\) was set as 298 K. The \((\Delta E_{\text{ZPE}} - T \Delta S)\) term was calculated by VASPKIT package. \(U\) is the potential of external circuit and \(\Delta G_{\text{pH}}\) is the modification originating from pH. The last two terms were omitted because \(U\) and pH were assumed to be constant in this work.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

anion point vacancies, defect engineering, density functional theory, iron monochalcogenides, nitrogen reduction, 2D
