Theoretical Insights into Designing Single-Atom Catalysts on Defective MXenes for Efficient Reduction of Nitrate into Ammonia

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Abstract: Electrocatalytic nitrate reduction reaction (NO₃RR) is a promising approach for converting nitrate into environmentally benign or even value-added products such as ammonia (NH₃) using renewable electricity. However, the poor understanding of the catalytic mechanism on metal-based surface catalysts hinders the development of high-performance NO₃RR catalysts. In this study, we have systematically explored the NO₃RR mechanism of single-atom catalysts (SACs) by constructing single transition metal atoms supported on MXene with oxygen vacancies (O_v-MXene) using density functional theory (DFT) calculations. Our results indicate that Ag/O_v-MXene (for precious metal) and Cu/O_v-MXene (for non-precious metal) are highly efficient SACs for NO₃RR toward NH₃, with low limiting potentials of -0.24 and -0.34 V, respectively. Furthermore, these catalysts show excellent selectivity towards ammonia due to the high energy barriers associated to the formation of byproducts such as NO₂, NO, N₂O, and N₂ on Ag/O_v-MXene and Cu/O_v-MXene, effectively suppressing the competitive hydrogen evolution reaction (HER). Our findings not only offer new strategies for promoting NH₃ production by MXene-based SACs electrocatalysts under ambient conditions but also provide insights for the development of next-generation NO₃RR electrocatalysts.

Introduction:

Nitrate (NO_3^-) pollution has become a serious human-caused issue affecting aquatic ecosystems and drinking water resources due to the release of NO or NO₂ from nitrogen-

containing fuels, the emission of NOx-containing fertilizers into soil and groundwater, and the discharge of nitrate-containing industrial wastewater.^[1,2] The accumulation of nitrate poses a significant threat to the environment and human health, including cancer and blue baby syndrome.^[3] Therefore, it is imperative to remove excess nitrate ions from contaminated water to complete the artificial nitrogen cycle. To address this challenge, various technologies, such as reverse osmosis,^[4] ion exchange,^[5] and bacterial denitrification,^[6] have been developed. However, these technologies have considerable drawbacks such as prohibitively high posttreatment costs, strict reaction conditions, and complex multi-stage processes. Recent reports showed that electrocatalytic NO₃RR is an alternative method for converting nitrate into harmless products and valued-added products using renewable electricity.^[7] Compared to the traditional approaches, NO₃RR does not require additional reducing agents to convert NO₃⁻ into products like NH₃, N₂, NO, NO₂, N₂O, and NH₂OH, as electrons are used for nitrate reduction.^[8] NH_3 is a desired product that can be generated from NO_3^- via the transfer of nine protons and eight electrons (NO₃⁻ + 9H⁺ + 8e⁻ \rightarrow NH₃ + 3H₂O E⁰ = 0.82V). Though this lowtemperature ammonia synthesis method is promising, developing catalysts with high activity and selectivity toward ammonia under ambient conditions remains a challenge due to the sluggish reaction kinetics and competitive HER.

Significant research efforts have been dedicated to developing electrocatalysts with high activity, selectivity, and durability for the reduction of NO₃⁻ into NH₃ to mitigate nitrate pollution.^[9] Previous studies have investigated the mechanism, activity, and selectivity on transition metal (TM) electrocatalysts for NO₃RR, where the rate-determining step (RDS) is deduced to be the reduction of nitrate into nitrite (NO₂⁻) on the catalyst surface in acidic condition based on the Tafel slope observed.^[10–12] Platinum group metals (PGMs) and coinage metals have shown NO₃RR activities under acidic conditions and potentials ranging from 0 to 0.4 V vs RHE, with the activities of Rh > Ru > Ir > Pd \approx Pt and Cu > Ag > Au, respectively.^[10] Although pure Rh and Cu metal catalysts display relatively high NO₃RR activities, they do not readily display high stability, activity, and selectivity towards NH₃ under other reaction conditions. To overcome these limitations, multicomponent electrocatalysts have been developed, where adjusting the ratio of transition metals in alloy catalysts can significantly enhance NO₃RR performance compared to their pure metal counterparts. For example, a stable CuNi alloy electrocatalyst displayed a higher NO₃RR performance than pure Ni and Cu metals.^[13] Besides transition metal-based electrocatalysts, other metal oxides, such as TiO₂ enriched with oxygen vacancies as well as CuO nanowire arrays, have also exhibited high NO₃RR performance with remarkable Faraday efficiency and selectivity towards ammonia.^[14–16]

The development of nitrate electrocatalysts for NO₃RR has posed a significant challenge due to the lack of a clear understanding of the catalytic mechanism on metal active sites, despite numerous transition metal-based electrocatalysts having been developed. Recently, SACs have drawn extensive attention in the heterogeneous catalysis community.^[17-21] Owing to the maximal utilization of active sites, SACs hold the promise to possess high activity and selectivity in catalytic reactions such as CO oxidation,^[22] HER,^[23] oxygen reduction reaction (ORR),^[24] oxygen evolution reaction (OER),^[25] CO₂ reduction reaction (CO₂RR),^[26] nitrogen reduction reaction (N₂RR)^[27,28] and nitrate reduction reaction (NO₃RR).^[29,30]

MXenes are a unique family of two-dimensional (2D) layered materials that exhibit excellent conductivity and chemical stability.^[31–33] MXenes themselves have been applied as electrocatalysts for HER,^[34,35] N₂RR,^[36–38] and CO₂RR.^[39,40] However, the basal plane of the MXene is readily functionalized by O²⁻, OH⁻, or F⁻ groups, resulting in no exposed metal sites on the surface of MXene. Therefore, MXenes cannot efficiently catalyze more complex reactions that involve multiple proton-coupled electron transfer (PCET) steps.^[41] Recently, engineering of vacancies has emerged as a promising strategy to stabilize SACs on MXene materials and enhance their electrocatalytic performance.^[28] Zhang et al. synthesized Mo₂TiC₂T_x MXene nanosheets with Mo vacancies serving as the anchoring sites for single Pt atoms (Mo₂TiC₂T_x-Pt_{SA}). The synthesized catalysts showed high durability and outstanding hydrogen evolution reaction activity.^[42] Chen and co-workers developed Ti-deficit 2D MXenes nanosheet and anchored Pt single atoms onto the sites previously occupied by Ti. The assynthesized Pt-based SAC, Pt₁/Ti_{3-x}C₂T_y, exhibited efficient conversion of aniline into amide.^[43]

Utilizing first-principles calculations, the feasibility of utilizing single transition metal atoms embedded on defective MXenes nanosheets, namely $Ti_{3-x}C_2O_y$ with a Ti vacancy and $Mo_{2-x}TiC_2O_2$ with a Mo vacancy, for N₂RR has been systematically explored. The results indicate that W/Ti_{3-x}C₂O_y and Mo_{2-x}TiC₂O₂-Zr_{SA} showed the lowest potential-determining step (PDS) barrier (0.11 eV and 0.15 eV) while suppressing competitive HER.^[28,44] However, to the best of our knowledge, the use of SACs supported on defective MXenes nanosheets for NO₃RR towards NH₃ has not been reported.

In this study, we chose the most extensively studied Ti₃C₂O₂ MXene as a representative substrate to construct SACs. Ti₃C₂ was the first reported type of MXene in 2011 and was the most studied for its availability, tunable modification, and unique electronic properties with applications in the fields of photocatalysis, energy conversion and storage, and electronic devices.^[45] Here, linear scaling plot and contour plot are established to explain activity trends on TM/O_v-MXene as well as to identify the metal/O_v-MXene hybrid materials with the most efficient NO₃RR activity as well as the highest selectivity toward NH₃ by suppressing competitive HER.

Results and discussion:

Screening NO₃⁻ adsorption on SACs. First, 3d-, 4d- and 5d- transition metal (TM)

atoms are embedded into the MXene support (Ti_{3-x}C₂T_y). The NO₃RR performance of SACs is then comprehensively investigated using first-principles calculations for 22 transition metals. Density functional theory calculations are performed to calculate the density of state (DOS) of the pure Ti₃C₂O₂ MXene structure (Figure S1). The calculated DOS of the MXene exhibits a conductor-like electronic structure, with a nonzero value around the Fermi level (E_F) and is mainly derived from the Ti 3d, O 2p, and C 2p orbitals, consistent with previous studies.^[32] The structure of TM/Ti₃C₂O₂ is constructed by removing one O atom from the MXene surface, leading to an O vacancy (O_v), followed by replacing the exposed Ti with different transition metal atoms to form an O vacancy TM-doped MXene (Figure 1a). The first step of the NO₃RR process is NO₃⁻ adsorption, which is critical for the entire catalytic reaction. We investigated the adsorption energies of NO_3^- on bare MXene and O_v -MXene, as shown in Figure S2. The adsorption energies are 2.02 eV and -0.94 eV for bare MXene and Ov-MXene, respectively. The introduction of an O vacancy greatly improves the NO₃⁻ adsorption energetics. Since competitive HER can disrupt the NO₃RR process, we also investigated the adsorption energies of NO₃⁻ (ΔG_{*NO3}) and proton (ΔG_{*H}) on TM/O_v-MXene for comparison (Figure 1b), and the corresponding configurations of *H and *NO₃ are shown in Figure S3. Notably, the ΔG_{*NO3} of Cr, Mn, Fe, Ni, Cu, Zr, Nb, Mo, Pd, Ag, Hf, Ta, Re, Au doped O_v-MXene are more negative than ΔG_{*H} , indicating NO₃RR is a more favorable process on these TM/O_v-MXene relative to HER.



Figure 1. a) Top and side views of the atomic structure of TM/O_v -MXene. Atom labels: C (white), Ti (blue), O (red), and TM (purple). The screened TM atoms (from Ti to Au) are listed. b) Comparison of adsorption energies of NO_3^- and H⁺ on TM/O_v-MXene. c) The scaling relation between charge transfer of TM atoms and NO_3^- adsorption energies.

The adsorption trends of NO₃⁻ on TM/O_v-MXene are investigated by probing the relationship between charge transfer of TM atoms and adsorption energy of NO₃⁻ (ΔG_{*NO_3}) (**Figure 1c**). Detailed bond lengths, binding energies, and charge transfers for NO₃⁻ adsorption on different TM/O_v-MXenes are summarized in **Table S1** in the supporting information. A good correlation coefficient (R² = 0.75) suggests a linear relationship between charge transfer and ΔG_{*NO_3} , further indicating that larger charge transfer of TM atoms results in higher NO₃⁻ adsorption energy. For instance, Hf/O_v-MXene exhibits the highest adsorption energy of NO₃⁻ of -1.41 eV with the largest charge transfer of -2.15 e⁻.

NO₃RR mechanism on TM/O_v-MXene. Electrochemical conversion of NO₃⁻ into NH₃ via 8 electron transfer steps involves various intermediates and products (e.g., NH₃, NO₂, NO, N₂O, and N₂). It has been reported that NH₃/NH₄⁺ is the most thermodynamically stable

product under negative potential bias.^[46] To understand the NO₃RR mechanism on TM/O_v-MXene, we investigate the proposed reaction pathways with one coupled proton+electron (H⁺ $+e^{-}$) pair involved in each elementary step in line with previous studies.^[13,14] The intermediates involved in the reaction pathway on TM/Ov-MXene are optimized by DFT calculation. The NO₃RR performance of TM/O_v-MXene is evaluated by comparing the computed limiting potentials ($U_L = -\Delta G_{max}/e$, where ΔG_{max} is the maximum of the free energy change among all elementary steps). Figure 2a shows the proposed reaction pathways and the generated products, while the limiting potentials (U_L) for each TM atom are summarized in Figure 2b. We find that the U_L values become less negative from going from left to right on the periodic table for 3d-, 4d- and 5d- TM atoms. Pt/O_v-MXene displayed the lowest NO₃RR energy barrier to generate NH₃. However, HER is found to outcompete NO₃RR on Pt/O_v-MXene, as shown in Figure 1b, indicating Pt/O_v-MXene is not an ideal catalyst for NO₃RR toward NH₃. The next-best NO₃RR catalyst after Pt/Ov-MXene is Ag/Ov-MXene, which exhibits efficient NO3RR activity with a limiting potential of -0.24 V. For non-precious TM, Cu/O_v-MXene displays the lowest limiting potential of -0.34 V. These two TM/O_v-MXenes also possess high preference toward NH₃ by suppressing competitive HER, demonstrating that they are promising electrocatalysts for selective NO₃RR.

Taking ΔG_{*NO_3} as a descriptor, the scaling relationship between the limiting potential on TM/O_v-MXene and ΔG_{*NO_3} is constructed in **Figure 2c**. Notably, we observe decent R² values (0.854 and 0.968), indicating that ΔG_{*NO_3} is an excellent descriptor for NO₃RR toward NH₃. In addition, we identified six TM/Ov-MXenes with the lowest limiting potentials (**Figure 2c**, red circle). Our results further demonstrate that the protonation step of *NO₃ (*NO₃ + H⁺ + e⁻ \rightarrow *HNO₃) serves as the potential-determining step (PDS) for Pt and Pd, whereas for other TMs, the protonation step of *NO₂ (*NO₂ + H⁺ + e⁻ \rightarrow *HNO₂) is the PDS. Based on these findings, we constructed a contour plot of limiting potentials as a function of two PDSs (*NO₃ $+ H^+ + e^- \rightarrow *HNO_3$ and $*NO_2 + H^+ + e^- \rightarrow *HNO_2$), as shown in **Figure 2d**. The red and blue colors on the contour plot correspond to low and high limiting potentials, respectively. Our results reveal that Pt, Ag, Pd, Au, Cu, and Ni transition metals on O_v-MXene are located close to the red region on the contour plot, indicating their high activity toward NO₃RR.



Figure 2. a) Reaction pathways of NO₃RR to NH₃ as well as byproducts including NO₂, NO, N₂O, and

N₂. b) Summary of limiting potentials on TM/O_v-MXene for NO₃RR. c) Scaling relationship between the calculated limiting potential of NO₃RR and ΔG_{*NO_3} . d) Contour plot of limiting potential as a function of two potential-determining steps (*NO₃ + H⁺ + e⁻ \rightarrow *HNO₃ and *NO₂ + H⁺ + e⁻ \rightarrow *HNO₂).

NO3RR performance of Ag/Ov-MXene and Cu/Ov-MXene. Based on our computational analysis, Ag/Ov-MXene is determined to be the most efficient electrocatalyst for NO₃RR among the TM/O_v-MXenes while concurrently inhibiting the competitive HER. Additionally, Cu/Ov-MXene has been established as the most competent earth-abundant electrocatalyst for NO₃RR featuring non-precious metals (NPMs). During the NO₃RR process, it is noted that two configurations of *NO₂ (1-O binding mode and 2-O binding mode) are considered for TM/O_v-MXene. The detailed adsorption energies and bond lengths are summarized in Table S2. Free energy diagrams for NO₃RR on Ag/O_v-MXene and Cu/O_v-MXene via the 1-O pathway are presented in Figure 3a and b, respectively, while those for the 2-O pathway are illustrated in Figure S4-5. Additionally, the corresponding structures of NO₃RR intermediates for the 1-O pathway and 2-O pathway are displayed in Figure 3c and Figure S6, respectively. We observe that the adsorption energy of NO₂ via 1-O pathway is lower than that of 2-O pathway on Ag/O_v-MXene and Cu/O_v-MXene. Consequently, the 1-O binding mode pathway is expected to be dominant despite the lower limiting potential of 2-O. We further construct free energy diagrams of NO₃RR for other TM/O_v-MXene in Figure S7-**S9** (Supporting Information) for comparison. During the NO₃RR process, NO₃⁻ initially adsorbs onto the catalyst surfaces, generating *NO₃ and *NO₃H intermediates, which subsequently form *NO₂. The reduction of NO₃⁻ into *NO₂ requires overcoming energy barriers of 0.10, 0.23, and -1.50 eV for Ag/Ov-MXene and -0.07, 0.26, and -2.05 eV for Cu/Ov-MXene, which is in agreement with experimental data.^[10] Subsequently, *NO₂ is hydrogenated by $(H^+ + e^-)$ pair to form *NO₂H intermediate, which is an endothermal process with an energy

difference of 0.24 eV for Ag/O_v-MXene and 0.34 eV for Cu/O_v-MXene. In the following step, *NO₂H is attacked by a proton to release H₂O, leaving behind *NO adsorbed on the surface. The changes in the free energy profile are -1.06 and -1.05 eV for Ag/O_v-MXene and Cu/O_v-MXene, respectively. Next, a slightly downhill step from *NO to *NOH is observed with the free energy decreased by 0.04 and 0.03 eV for Ag/O_v-MXene and Cu/O_v-MXene, respectively. In the subsequent steps (*NOH-*N-*NH-*NH₂-*NH₃), proton consecutively attacks the intermediates, and the corresponding energies drop by 0.85, 1.20, 0.91, and 0.74 eV for Ag/O_v-MXene and 0.93, 1.22, 1.00, and 0.64 eV for Cu/O_v-MXene. Eventually, *NH₃ species are desorbed from the catalyst surface.

To examine the selectivity of NO₃RR toward NH₃, the pathways leading to the formation of byproducts NO₂, NO, N₂O, and N₂ are plotted for comparison in **Figure 3a,b**. The corresponding structures of these intermediates are shown in **Figure S10-11**. The energy barriers for the release of NO₂, NO, N₂O, and N₂ on Ag/O_v-MXene reach up to 1.43, 0.91, 0.76 and 0.95 eV, respectively, while on Cu/O_v-MXene they are 1.65, 1.03, 0.97 and 0.75 eV, indicating the difficulty associated to forming these byproducts. In contrast, the desorption of NH₃ requires 0.88 and 1.09 eV for Ag/O_v-MXene and Cu/O_v-MXene, respectively. Notably, NH₃ can be further protonated to NH₄⁺ under acidic conditions with a negligible energy barrier as reported in recent studies.^[47,48]



Figure 3. a,b) Free energy diagrams of NO₃RR on Ag/O_v-MXene and Cu/O_v-MXene, respectively. The pathways to the release of NO₂, NO, N₂, and N₂O are also plotted for comparison. c) Corresponding structures of NO₃RR intermediates adsorbed on Ag/O_v-MXene (above) and Cu/O_v-MXene (below), respectively.

In order to gain insights into the underlying mechanisms behind the high NO₃RR performance of Ag/O_v -MXene and Cu/O_v-MXene, an investigation on the densities of states (DOS) of NO₃⁻ adsorption on both materials is conducted. Our results indicate that prior to NO₃⁻ adsorption, the d orbital of Ag and the 2p orbital of NO₃⁻ lie below the Fermi level, as

shown in **Figure 4a,c**. Furthermore, we observed that the energy levels of the d-orbitals of Ag and Cu, as well as the p-orbitals of NO_3^- , are well-matched. Upon NO_3^- adsorption, the d orbital of Ag and Cu mixes with the 2p orbital of NO_3^- , resulting in strong interactions between the transition metal and the adsorbed NO_3^- . To further elucidate the role of charge transfer in dictating the reduction reaction, the charge transfer from the TM atom to NO_3^- is analyzed. Our analysis reveals that there is a charge transfer of 0.74 e⁻ and 0.75 e⁻ from the TM SAC to NO_3^- for Ag/O_v-MXene and Cu/O_v-MXene, respectively, which serves as further evidence of the interaction between the TM SAC site and the adsorbed NO_3^- .



Figure 4. a,b). Partial density of states (PDOS) of NO_3^- adsorbed on Ag/O_v-MXene and Cu/O_v-MXene, respectively. E_F denotes the Fermi level, referring to 0 eV. c,d) Charge density differences of $NO_3^$ adsorbed on Ag/O_v-MXene and Cu/O_v-MXene, respectively. Iso-surfaces are 0.004 eV Å⁻³. e,f) Energy and temperature evolution versus the AIMD time for Ag/O_v-MXene and Cu/O_v-MXene, respectively. The AIMD simulation lasts for 10 ps at 500 K.

Stability of Ag/O_v-Mxene and Cu/O_v-Mxene. To evaluate the stability of TM/O_v-MXene, we conducted calculations of the formation energy (described in computational methods section). The results are summarized in **Figure S12**, which clearly shows that the

formation of TM/O_v-MXene cannot occur spontaneously. Additionally, the formation barrier of late-transition metal in the 3d, 4d, and 5d are lower than those of early-transition metals. To further investigate the stability of the catalysts, we performed ab initio molecular dynamics (AIMD) simulations at 500 K for Ag/O_v-MXene and Cu/O_v-MXene. As shown in **Figure 4e,f**, the total energy oscillates near the initial condition, and the geometric structures of Ag/O_v-MXene and Cu/O_v-MXene remain well-preserved during the 10 ps simulation. These results lead to the conclusion that Ag/O_v-MXene and Cu/O_v-MXene can serve as highly efficient and stable catalysts for selective ammonia synthesis through electrochemical NO₃RR.

Conclusions. In this work, we utilized density functional theory (DFT) calculations to investigate the potential application of SACs supported on defective Ti₃C₂O₂ nanosheets with oxygen vacancies for electrocatalytic NO₃RR to produce NH₃. By employing the scaling relationship and contour plot, our computations demonstrated that Ag/O_v-MXene (for precious metal) and Cu/O_v-MXene (for non-precious metal) exhibit outstanding low limiting potentials for NO₃RR of -0.24 and -0.34 V, respectively. Additionally, the adsorption energy of NO₃⁻⁻ on Ag/O_v-MXene and Cu/O_v-MXene is stronger than that of proton, which favors NO₃RR and suppresses the HER. With respect to selectivity, high energy barriers for the release of NO₂, NO, N₂O, and N₂ on Ag/O_v-MXene and Cu/O_v-MXene facilitate the production of ammonia. Density of state and charge density difference analysis provide insights into the superior NO₃RR performance on Ag/O_v-MXene and Cu/O_v-MXene. The stability of Ag/O_v-MXene and Cu/O_v-MXene is verified through formation energy and ab initio molecular dynamics (AIMD) simulations at 500 K. Our theoretical study suggests that Ag/O_v-MXene and Cu/O_v-MXene are highly active, selective, and robust electrocatalysts for NO₃RR to produce ammonia under ambient conditions.

Computational methods:

Spin-polarized DFT calculations were conducted to optimize the atomic positions of

the structures by VASP^[49] using the projector augmented wave (PAW) potentials with a planewave cutoff energy of 450 eV.^[50,51] The generalized gradient approximation (GGA) functional of Perdew, Burke, and Ernzerhof (PBE) was applied as the exchange-correlation functional.^[52] All structures were fully optimized until achieving the convergence criteria of 10⁻⁵ eV for electronic energies and 0.03 eV/Å for atomic forces. The grimme's semi-empirical DFT-D3 dispersion correction was utilized to describe the van der Waals (vdW) interactions.^[53] The 3 \times 3 \times 1 supercell of Ti₃C₂O₂ was used to model defective MXenes as SAC supporting substrates. In order to eliminate the effects between two adjacent layers, a vacuum region of 15 Å was added in the z-direction. For structural optimizations, the Brillouin zones integrations were performed with a gamma-centered $3 \times 3 \times 1$ Monkhorst-Pack k-point mesh grid, whereas kpoint mesh was increased to $5 \times 5 \times 1$ for the density of states (DOS) calculations. The solvation effect was not included since it has little effect on energy variation.^[47,54] Bader charge population analysis was applied to describe the charge variation of the intermediates in NO₃RR process.^[55] To evaluate the thermal stability of the catalysts, AIMD simulations were performed in the NVT canonical ensemble at 500 K for 10 ps, using a time step of 1 fs.^[56] VASPKIT, as a postprocessing program for the VASP code, was adopted to analyze the DOS diagrams and charge density difference.^[57]

The Gibbs free energy calculations for NO₃RR were based on the computational hydrogen electrode (CHE) model.^[58] The free energy of the proton-coupled electron pair of $(H^+ + e^-)$ is related to that of 1/2 H_{2(g)}. The change of Gibbs free (ΔG) of each individual step during the NO₃RR process was calculated by:

$$\Delta G = \Delta E + \Delta Z P E - T \Delta S + U e + \Delta G_{pH}$$

where ΔE is the DFT calculated reaction energy difference between the reactants and the products, ΔZPE is the zero-point energy, ΔS is the entropy change (summarized in Table S3 supporting information), T represents the finite temperature, e is the charge transferred, U is

the applied potential, and ΔG_{pH} is considered as the correction free energy of H⁺.

The Gibbs free energy change of charged $NO_{3^{-}(aq)}$ adsorbed on the electrode surface was calculating by a thermodynamic cycle (see supplementary information for details), the expression is described as:

$$\Delta G_{*NO_3} = G_{*NO_3} - G_{sur} - G_{HNO_3(g)} + \frac{1}{2}G_{H_2(g)} + \Delta G_{correct}$$

where G_{*NO3} , G_{sur} , $G_{HNO3(g)}$ and $G_{H2(g)}$ are the Gibbs free energy of NO_3^- adsorbed on TM/O_v-MXenes, O_v-MXenes, HNO₃, and H₂ gas molecule. $\Delta G_{correct}$ denotes the correction of adsorption energy and is set to 0.392 eV.

The formation energy of TM/O_v-MXene is described as:

$$\Delta E_{\text{form}} = E_{\text{TM/MXene}} - E_{\text{TM/Ov-MXene}} - \frac{1}{2} E_{O_2(g)}$$

where $E_{TM/Mxene}$, $E_{TM/Ov-MXene}$, and $E_{O_2(g)}$ are the DFT calculated energy of bare TM doped MXene, TM/O_v-MXenes, and O₂ gas molecule.

Supporting Information

Supporting Information is available online or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

Nitrate Reduction Reaction, Oxygen Vacancy MXene, Single-Atom Catalysts, DFT Calculations, Sustainable Electrochemical Upcycling

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