

Validation of nitrate adsorption energy as an activity descriptor for nitrate electroreduction on single-atom catalysts supported by chiral carbon nanotubes: DFT calculations and machine learning

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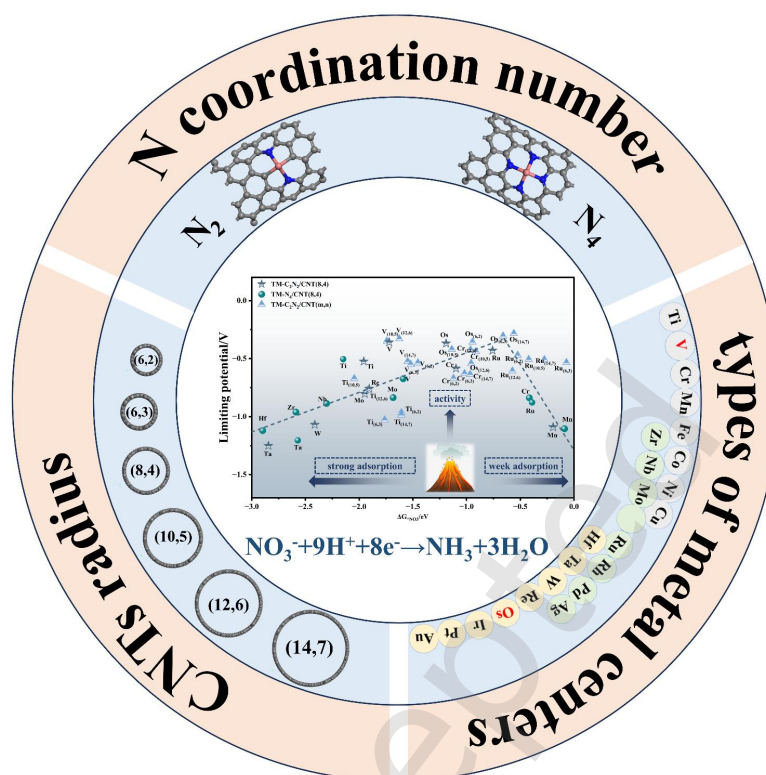
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A robust volcano relationship is established between the limiting potential of the nitrate reduction reaction and the adsorption energy of NO_3^- across 71 diverse single-atom catalysts. This highlights the adsorption energy of NO_3^- as a universal activity descriptor that remains consistent regardless of the metal center, nitrogen coordination, or carbon nanotube curvature

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ABSTRACT: Single-atom catalysts have attracted extensive attention for the electrochemical nitrate reduction reaction (NO₃RR). However, effective catalyst design principles, particularly transferable activity descriptors across different structures, remain limited. Based on single-atom systems supported on chiral carbon nanotubes (CNTs), a total of 71 SAC models were constructed, comprising different metal centers, coordination environments, and CNT diameters. After stability, nitrate-adsorption, and selectivity screening, 45 systems were selected for complete free-energy pathway calculations. Our results show that V-C₂N₂/CNT and Os-C₂N₂/CNT exhibit favorable catalytic performance with limiting potentials of -0.36 and -0.37 V. A consistent volcano-type relationship was identified between catalytic activity and the adsorption energy of NO₃⁻. This relationship remains consistent across different doping configurations and CNT sizes. The adsorption energy of NO₃⁻ exhibits a linear relationship with key intermediate species, providing a thermodynamic rationale for using nitrate adsorption energy as an activity descriptor. Machine-learning analysis identifies the valence-electron count and local TM–N coordination as influential features for predicting ΔG*_{NO₃} within the present dataset. These findings provide useful insights into the design of chiral-CNT-supported NO₃RR catalysts.

KEYWORDS: NO₃⁻ electroreduction, single-atom catalysts, activity descriptor, Density functional theory, N-doped nanotube

1 Introduction

Ammonia (NH₃) is not only an essential chemical feedstock for modern agriculture but also a key molecule in pharmaceuticals, fine chemicals, explosives, and emerging energy systems^[1, 2]. Currently, more than 90% of global ammonia production relies on the Haber-Bosch process, which operates under harsh conditions of 400–500°C and 150–300 atm^[3–5]. This process consumes approximately 1–2% of the global energy supply and emits substantial CO₂, making it a typical high-energy and high-emission industrial route^[6, 7]. Therefore, developing alternative ammonia synthesis pathways under mild conditions with low or even zero carbon emissions has become an important scientific challenge. The electrochemical nitrate reduction reaction offers a promising strategy for ammonia synthesis under ambient conditions^[8]. In this process, NO₃⁻ can be stepwise reduced to NH₃ using water as the proton source and renewable electricity as the driving force^[9, 10]. Compared with other electrochemical ammonia synthesis routes, such as the nitrogen reduction reaction (NRR) and nitric oxide reduction reaction (NORR), nitrate exhibits higher solubility. In addition, this approach can

simultaneously remove nitrate pollutants from water systems^[11].

However, the NO₃RR still faces challenges such as limited catalytic activity and competing side reactions^[12, 13]. Addressing these issues requires the development of electrocatalysts with high activity, selectivity, and stability^[14, 15].

Early studies on NO₃RR mainly focused on noble metal catalysts and their alloys^[16–18]. Although these materials exhibit certain activity for nitrate reduction, they generally suffer from high cost, limited selectivity, and susceptibility to poisoning. In recent years, the emergence of single-atom catalysts (SACs) has brought new opportunities to the field of catalysis^[19–21]. SACs feature maximized atomic utilization and well-defined active sites that can be precisely tuned, enabling outstanding catalytic activity and selectivity in various electrocatalytic reactions^[22–24]. For example, Liu and co-workers^[25] recently developed a nitrogen-rich carbon nitride catalyst embedded with single-atom copper (C₃N₄/Cu). This catalyst exhibited excellent piezophotocatalytic nitrate reduction performance over a wide pH range and nitrate concentration window, achieving a high ammonia production rate of 25.2 mg h⁻¹ g_{cat}⁻¹ without the use of sacrificial agents. Cheng and co-workers^[26] reported an iron

single-atom catalyst supported on a three-dimensional carbon-nitrogen framework (Fe SCAs/NC), which achieved a Faradaic efficiency of 98.2% and an ammonia yield rate of $22515 \mu\text{g}\cdot\text{h}^{-1}\cdot\text{mg}_{\text{cat}}^{-1}$. Spectroscopic analysis revealed that its activity originates from the reversible structural evolution of the Fe active center from pyrrole- N_4 -Fe to pyrrole- N_3 -Fe, which significantly lowers the energy change of the key $\text{NO} \rightarrow \text{NHO}$ step. Meanwhile, Niu and co-workers^[27] conducted density functional theory (DFT) studies and found that Ti and Zr single atoms anchored on g-CN can achieve highly selective nitrate reduction to ammonia at low limiting potentials of -0.39 V and -0.41 V, respectively. Their results further indicated that the N-end pathway is the most favorable reaction route. Despite these advances, the rational design of SACs for NO_3RR still relies largely on empirical approaches. Existing studies typically focus on specific metal-support combinations, and the identified structure-activity relationships are often system-dependent. In contrast, studies on general activity descriptors that can guide catalyst design across different local coordination environments and support structures remain limited^[28, 29].

Following the Sabatier principle, adsorption free energies of key reaction intermediates have been widely used as descriptors for evaluating electrocatalytic activity, because they connect the binding strength of surface species with the thermodynamic difficulty of elementary proton-electron transfer steps. For NO_3RR and related electrochemical reactions, recent theoretical and machine-learning studies have further shown that adsorption-energy descriptors can be used to rationalize activity trends and accelerate catalyst screening^[30-34]. For the nitrate reduction reaction, the adsorption strength of nitrate (NO_3^-) plays a critical role in determining the activation of the NO_3^- molecule and the subsequent hydrogenation steps^[35]. Previous studies have reported volcano-type relationships between catalytic activity and adsorption energy in various electrochemical reactions^[36, 37]. However, whether such a general relationship exists for NO_3RR on single-atom catalysts (SACs), particularly under different support geometries and coordination environments, remains an open question. Carbon nanotubes (CNTs) have been widely used as catalyst supports^[38], especially chiral carbon nanotubes, which provide a unique platform for exploring this issue. Unlike planar graphene or symmetric achiral CNTs^[39], chiral CNTs possess intrinsically asymmetric local electronic environments and curvature-induced strain^[40-42], which can significantly influence the electronic structure of anchored single atoms. In addition, the coordination environment of single atoms on CNTs can be flexibly tuned by adjusting the number of nitrogen dopants and the tube diameter. This tunability makes CNTs an ideal model system for systematically investigating the transferability of potential activity descriptors.

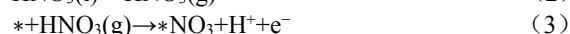
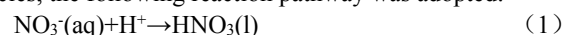
In this work, we performed a comprehensive density functional theory study of NO_3RR on transition-metal single-atom catalysts supported on nitrogen-doped chiral CNTs. Chiral CNTs were selected not to claim a direct chirality-induced spin-selectivity mechanism, but to provide a helical, asymmetric, and curvature-tunable carbon support for examining how local coordination geometry and CNT diameter regulate the electronic structure of anchored single atoms. The 71 single-atom catalyst models comprise 23 TM- $\text{C}_2\text{N}_2/\text{CNT}$ (8,4) catalysts, 23 TM- N_4/CNT (8,4) catalysts, and 25 TM- $\text{C}_2\text{N}_2/\text{CNT}$ catalysts constructed by

combining five representative metals (Ti, V, Cr, Ru, and Os) with five additional CNT diameters. After stability, nitrate-adsorption, and selectivity screening, 45 systems were selected for complete free-energy pathway calculations. V- $\text{C}_2\text{N}_2/\text{CNT}$ and Os- $\text{C}_2\text{N}_2/\text{CNT}$ were identified as promising catalysts, with limiting potentials of -0.36 and -0.37 V, respectively. A consistent volcano-type relationship between NO_3RR activity and $\Delta G^*\text{NO}_3$ was observed across the examined coordination motifs and CNT diameters, supporting $\Delta G^*\text{NO}_3$ as an effective activity descriptor within the present chiral-CNT-supported SAC space. Machine-learning models were subsequently used to correlate elemental and local structural features with $\Delta G^*\text{NO}_3$ rather than directly predicting catalytic activity. These results provide useful structure-activity insights for the design of chiral-CNT-supported NO_3RR catalysts.

2 Computational Details

All spin-polarized density functional theory (DFT) calculations were performed using the Vienna ab initio Simulation Package (VASP)^[43, 44]. The Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation was employed to describe the exchange-correlation interactions^[45]. The projector-augmented wave (PAW) method was applied with a kinetic energy cutoff of 450 eV for the expansion of the electronic wavefunctions^[46, 47]. Long-range van der Waals interactions were incorporated using Grimme's DFT-D3 correction scheme^[48]. All atomic configurations were fully relaxed until the convergence criteria for energy and forces reached 10^{-4} eV and 0.02 eV/Å, respectively. A Γ -centered $1\times 1\times 3$ Monkhorst-Pack k-point mesh was used for structural relaxation within the first Brillouin zone, while a finer $1\times 1\times 6$ k-point grid was adopted for density of states (DOS) calculations. Spin polarization was included in all computations.

The Gibbs free energy change for nitrate adsorption ($\Delta G^*\text{NO}_3$) was calculated using the computational hydrogen electrode (CHE) model^[49, 50]. To avoid direct computation of charged species, the following reaction pathway was adopted:



The adsorption energy of NO_3^- was then obtained as:

$$\Delta G^*\text{NO}_3 = G^*\text{NO}_3 - G_* - G_{\text{HNO}_3(\text{g})} + 0.5 G_{\text{H}_2(\text{g})} + \Delta G_{\text{correct}} \quad (4)$$

where $G^*\text{NO}_3$ and G_* are the Gibbs free energies of the system with and without adsorbed NO_3^- , respectively; $G_{\text{HNO}_3(\text{g})}$ and $G_{\text{H}_2(\text{g})}$ are the Gibbs free energies of gaseous HNO_3 and H_2 ; and $\Delta G_{\text{correct}} = 0.392\text{eV}$ is an empirical correction term based on previous studies^[51]. To simulate the aqueous environment, an implicit continuum solvation model implemented in VASPsol was employed, with the dielectric constant of water set to 78.4^[52, 53]. All Gibbs free energies include corrections for zero-point energy and entropy at 298.15 K (Table S12 and Table S13).

It should be noted that the present calculations were performed using standard constant-charge DFT together with the CHE model. Although this approach is widely used for comparing relative electrocatalytic trends, it does not explicitly describe the potential-dependent charging of the catalyst surface, the structure of the electric double layer, or specific ion effects at the electrode-electrolyte interface. Accordingly, the calculated limiting potentials should be interpreted mainly as relative activity indicators obtained under a consistent computational protocol. Future constant-potential grand-canonical DFT studies

would be valuable for more quantitative assessment of the electrode-electrolyte interface^[54].

3. Results and discussion

3.1 NO₃⁻ Adsorption on TM-C₂N₂/CNT

The chiral carbon nanotube CNT (8,4) used in this study exhibits a typical helical structure. As shown in Figure 1(a), the carbon rings are helically arranged along the tube axis. The C-C bond lengths is approximately 1.42 Å, and the tube diameter is 8.29 Å. A series of transition metal atoms (TM = Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Hf, Ta, W, Re, Os, Ir, Pt, Au) were anchored on a chiral CNT with two radially doped nitrogen atoms, denoted as TM-C₂N₂/CNT. The bond lengths of the TM-N bonds vary from 1.91 to 2.20 Å. Bader charge analysis indicates significant electron transfer between the metal atom and the support, with transferred charges ranging from 0.50 to 1.68 e⁻ (Figure 1(c)). To evaluate the stability of these catalysts, the binding energy (E_b), formation energy (E_f), and dissolution potential (U_{diss}) of the metal atoms on CNT were calculated, as illustrated in Figure 1(b). The calculated E_b and E_f values for all metals are negative, with ranges of -4.22 to -10.69 eV and -0.97 to -4.29 eV, respectively. These values indicate strong interactions between the metal atoms and the CNT support. The stability of these catalysts under electrochemical conditions was further evaluated using the dissolution potential. The calculated U_{diss} values range from -0.54 to 2.94 V, and most metals exhibit positive values, suggesting good thermodynamic and electrochemical stability under reduction conditions. However, Zr, Nb, and Hf show negative U_{diss} values (-0.38, -0.14, and -0.54 V), indicating that these metal atoms may undergo migration or aggregation under reaction conditions. Therefore, these three metals were excluded from further analysis. The detailed data are summarized in Table S1.

The adsorption of nitrate (NO₃⁻) on the catalyst surface is the

key initial step that triggers the NO₃RR. Its adsorption strength directly affects the NH₃ selectivity and catalytic efficiency. The adsorption structure of NO₃⁻ on the remaining stable TM-C₂N₂/CNT catalysts was examined, considering two possible configurations: single-oxygen adsorption (1O mode) and double-oxygen adsorption (2O mode). Structural optimization results (Table S2) show that the 2O mode forms a stable O-N-O-TM four-membered ring structure and exhibits lower adsorption energies than the 1O configuration. Therefore, the 2O adsorption mode is more stable and is adopted in the following analysis. Figure 1(d) shows that Fe, Co, Ni, Cu, Rh, Pd, Ag, Pt, and Au exhibit positive $\Delta G^*_{NO_3}$ values of 0.12, 0.32, 1.19, 1.06, 0.07, 1.53, 1.24, 1.64, and 1.59 eV. These results indicate that the adsorption of NO₃⁻ on these metal sites is thermodynamically unfavorable, making it difficult to effectively activate the reactant molecules during subsequent reactions. Therefore, these metals were excluded from further investigation. In contrast, the remaining metals (Ti, V, Cr, Mn, Mo, Ru, Ta, W, Re, Os, and Ir) exhibit negative $\Delta G^*_{NO_3}$ values ranging from -0.07 to -2.84 eV, indicating that these sites can effectively activate NO₃⁻ and facilitate subsequent reduction steps toward ammonia formation. Under practical electrochemical reduction conditions, the hydrogen evolution reaction (HER) is the major competing reaction for NO₃RR. Therefore, we compared the adsorption strengths of NO₃⁻ and H⁺ on the catalyst surface. As displayed in Figure 1(d), among the remaining candidates, only Ir shows stronger adsorption for H⁺ than for NO₃⁻, which is unfavorable for the NO₃RR process. In contrast, the other metals (Ti, V, Cr, Mn, Mo, Ru, Ta, W, Re, and Os) exhibit more negative adsorption energies for NO₃⁻ than for H⁺, indicating a stronger affinity for nitrate species. This characteristic is beneficial for suppressing the HER side reaction and promoting nitrate reduction.

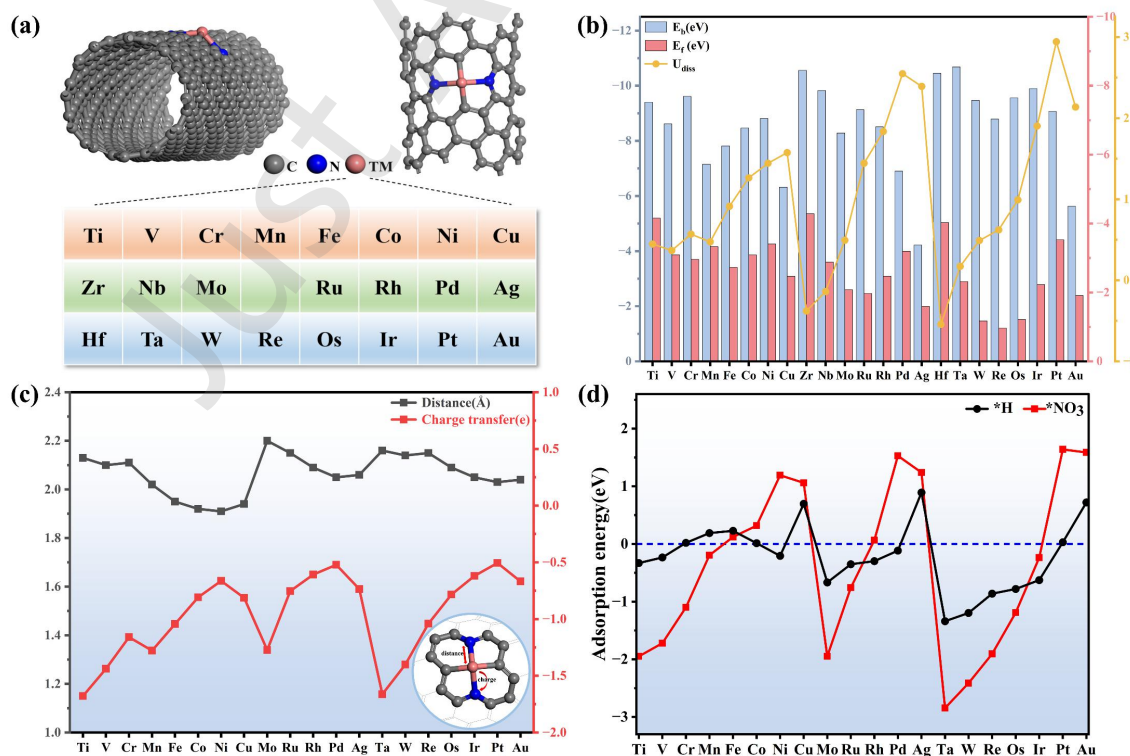


Figure 1. (a) Front and top views of the atomic structure of C₂N₂/CNT. Atom labels: C (gray), N (blue), and TM (pink). The loaded single atoms range from Ti to Au. (b) Binding energy, formation energy, and dissolution potential of TM-C₂N₂/CNT catalysts. (c) Bond lengths between single-atom TMs and N atoms (the corresponding structure is shown in the lower-right inset) and the line plot of Bader charge analysis. (d) Comparison of the adsorption energies of H⁺ and NO₃⁻.

on TM-C₂N₂/CNT catalysts.

3.2 NO₃RR Mechanism on TM-C₂N₂/CNT

To systematically clarify the reaction mechanism and selectivity of NO₃RR, mechanistic studies were performed for the above catalyst systems. Previous results show that NO preferentially adsorbs on the catalyst surface through the N end, which is energetically more favorable than O-end adsorption or dual-end configurations. Based on this observation, three representative reaction pathways were analyzed, as presented in Figure 2(a): (1) N-end hydrogenation forming the *NHO intermediate for NH₃ production; (2) O-end hydrogenation forming the *NOH intermediate for NH₃ formation; and (3) NO-NO coupling leading to direct N₂ formation. In pathway (1), further hydrogenation of *NHO may occur at either the N or O site, leading to the formation of *NH₂O and *NHOH, respectively. The adsorption energies of key intermediates involved in the NO₃RR on TM-C₂N₂/CNT catalysts are summarized in Table S3, and the detailed reaction pathways are depicted in Figure S1.

The reaction mechanisms on V-C₂N₂/CNT and Os-C₂N₂/CNT were analyzed as representative examples to evaluate their catalytic performance for electrochemical nitrate reduction to ammonia. The optimized structures of key intermediates along the most favorable pathways are given in Figures 2(b) and 2(c). NO₃⁻ can stably adsorb on both V and Os sites through two TM-O bonds, forming *NO₃ with adsorption energies of -1.72 and -1.19 eV, respectively. Due to the stronger adsorption on V-C₂N₂/CNT, the subsequent proton-electron coupling step converting *NO₃ to *NO₃H is slightly uphill and requires an energy change of 0.22 eV. In contrast, this step is spontaneous on Os-C₂N₂/CNT. Subsequently, *NO₃H undergoes successive protonation steps, forming the *NO₂ intermediate and releasing two H₂O molecules, ultimately generating the key intermediate *NO. For the V-C₂N₂/CNT, although the formation of *NHO is energetically favorable ($\Delta G = -0.55$ eV), the further hydrogenation of *NHO to *NHOH requires a relatively high energy change of 0.55 eV. The alternative hydrogenation route through *NH₂O followed by reduction to *NH₂OH has an even higher change of 1.33 eV. Therefore, the *NOH pathway is more favorable on V-C₂N₂/CNT. In the subsequent reaction steps, the transformations *NOH → *N → *NH → *NH₂ → *NH₃ are largely exergonic. Only the final step (*NH₂ → *NH₃) requires a small energy input of 0.32 eV, while the other hydrogenation steps show negative free energy changes of -1.14, -0.90, and -0.75 eV, respectively. Overall, four hydrogenation steps *NO₃ → *NO₃H, *NO₂ → *NOOH, *NO → *NOH, and

*NH₂ → *NH₃ require additional energies of 0.22, 0.24, 0.36, and 0.32 eV, respectively. Among these non-spontaneous steps, the *NO → *NOH conversion exhibits the largest free energy change and is therefore identified as the potential-determining step (PDS) for NO₃RR on V-C₂N₂/CNT. For the Os-C₂N₂/CNT catalyst, the energy change for *NO hydrogenation to *NOH (0.52 eV) is higher than that for forming *NHO (0.37 eV), indicating that the *NHO pathway is more favorable on this catalyst. During the overall reduction process, the *NO → *NHO step is identified as the PDS on the Os-C₂N₂/CNT surface. Further hydrogenation produces *NHOH and *NH₂O with free energy changes of 0.28 and -0.08 eV, respectively. However, *NH₂OH is prone to dissociation, and the subsequent hydrogenation steps of *NHOH leading to *NH₃ formation proceed spontaneously, with free energy changes of -2.22, -0.06, and -0.03 eV. To examine the solvent effect on NO₃RR, the reaction mechanisms were further calculated using an implicit solvation model implemented in VASPsol. The results reveal that solvation does not alter the overall reaction trend or the identity of the potential-determining step. Moreover, the catalytic activity toward NO₃RR changes only slightly under solvent conditions. Detailed results are provided in Figure S2.

To further evaluate the NH₃ selectivity of the two highly active catalysts (V-C₂N₂/CNT and Os-C₂N₂/CNT), we analyzed the adsorption energies and limiting potentials associated with possible byproducts, including NO, NO₂, and N₂. The corresponding reaction pathways are displayed in Figures 2(b) and 2(c). On V-C₂N₂/CNT, the calculated desorption free energies of NO and NO₂ are 2.94 and 3.14 eV, whereas the corresponding values on Os-C₂N₂/CNT are 3.47 and 3.02 eV. These values are significantly higher than the desorption energies of NH₃ (1.45 and 1.30 eV), indicating that the desorption of these byproducts is unfavorable. This result further confirms the high NH₃ selectivity of V-C₂N₂/CNT and Os-C₂N₂/CNT in NO₃RR. In addition, the NO-NO coupling pathway leading to N₂ formation on V-C₂N₂/CNT and Os-C₂N₂/CNT was investigated (see Figure S3 for adsorption structures). The hydrogenation step *N₂O₂ → *N₂O₂H is thermodynamically uphill by 0.80 and 0.79 eV, respectively, and can be regarded as the PDS for N₂ formation. These changes are significantly higher than the maximum changes for NH₃ formation from NO₃⁻ (0.36 eV and 0.37 eV), indicating that NH₃ formation is thermodynamically more favorable. This observation further supports the high selectivity of these catalysts toward ammonia production.

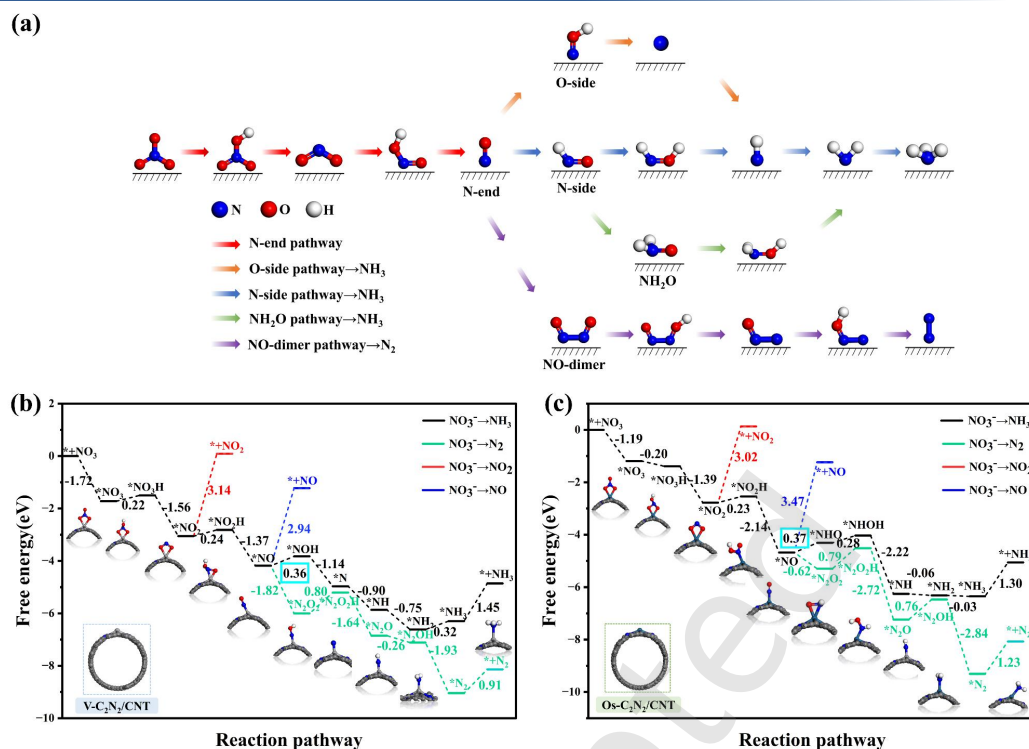


Figure 2. (a) Proposed reaction pathways for different products of the NO_3RR . (b) Gibbs free energy profile for the reduction of NO_3^- to NH_3 on $\text{V-C}_2\text{N}_2/\text{CNT}$. (c) Gibbs free energy profile for the reduction of NO_3^- to NH_3 on $\text{Os-C}_2\text{N}_2/\text{CNT}$.

3.3 NO_3RR Activity Origin on $\text{V-C}_2\text{N}_2/\text{CNT}$ and $\text{Os-C}_2\text{N}_2/\text{CNT}$

To quantitatively evaluate the NO_3RR performance of the catalysts, the limiting potential (U_L) was used as the activity metric. It is defined as ($U_L = -\Delta G_{\text{max}}/e$), where ΔG_{max} is the largest Gibbs free energy change among all elementary steps and (e) is the elementary charge. A more positive (less negative) limiting potential indicates a lower thermodynamic potential requirement and therefore higher predicted catalytic activity. As depicted in Figure 3(a), the calculated limiting potentials for the remaining screened metal catalysts were obtained. Among them, $\text{V-C}_2\text{N}_2/\text{CNT}$ and $\text{Os-C}_2\text{N}_2/\text{CNT}$ exhibit the most positive limiting potentials of -0.36 V and -0.37 V, respectively, corresponding to the ΔG_{max} values in the full reaction pathway. The potential-determining steps and limiting potentials of the other catalysts are summarized in Table S4. These results indicate that nitrate electroreduction to ammonia occurs most readily on $\text{V-C}_2\text{N}_2/\text{CNT}$ and $\text{Os-C}_2\text{N}_2/\text{CNT}$ catalysts.

We then focused on the first step of the reaction, namely the adsorption of NO_3^- . The adsorption configuration of NO_3^- on the TM active center involves two oxygen atoms (O_1 and O_2) bonding with the metal atom, forming two O-TM bonds (d_1 and d_2). Since the coordination environments of d_1 and d_2 are identical, their bond lengths are the same, and similarly ($d_3 = d_4$). A volcano-type relationship is observed between ΔG_{NO_3} and the bond length d_1 (or d_2) in Figure 3(c). This trend suggests that moderate adsorption strength is favorable for balancing the activation process. It can also be seen that early transition metals lie on the left branch of the volcano plot, while late transition metals (Cu, Ni, Pd, Pt, Au, and Ag) are located on the right branch. This observation further confirms that these late metals

bind NO_3^- too weakly to effectively activate the reactant. In addition, Figure 3(d) shows a clear linear negative correlation between ΔG_{NO_3} and the N-O bond length (d_3 or d_4) in the adsorbed NO_3^- species. This relationship directly reflects the influence of adsorption strength on reactant activation. The N-O bond becomes elongated as ΔG_{NO_3} becomes more negative. For example, catalysts with Ta and W active centers exhibit the strongest NO_3^- adsorption and the longest N-O bond length (d_3). This also indicates that excessively strong adsorption may hinder subsequent hydrogenation steps. More importantly, the linear relationships between ΔG_{NO_3} and the free-energy change of the subsequent hydrogenation steps ($\text{NO} \rightarrow \text{NOH}$ and $\text{NH}_2 \rightarrow \text{NH}_3$), shown in Figures 3(e) and 3(f), further demonstrate that the initial adsorption strength of NO_3^- can systematically influence the thermodynamic requirements of subsequent protonation steps throughout the reaction pathway. Therefore, ΔG_{NO_3} effectively links the activation of reactants with the difficulty of subsequent elementary steps, and its optimal value corresponds to the coordinated optimization of these free-energy changes. To further understand the role of NO_3^- adsorption, a volcano plot correlating ΔG_{NO_3} with the limiting potential (U_L) was constructed. Figure 3(b) presents the two catalysts with outstanding NO_3RR performance, $\text{V-C}_2\text{N}_2/\text{CNT}$ and $\text{Os-C}_2\text{N}_2/\text{CNT}$, which exhibit moderate adsorption energies for NO_3^- (-1.72 and -1.19 eV). These values place them near the top of the volcano plot. This result indicates that moderate NO_3^- adsorption strength not only facilitates the activation and conversion of reactant molecules but also promotes the desorption of reaction intermediates, thereby significantly enhancing the catalytic efficiency. These findings further support the effectiveness of ΔG_{NO_3} as an activity descriptor for NO_3RR catalysis.

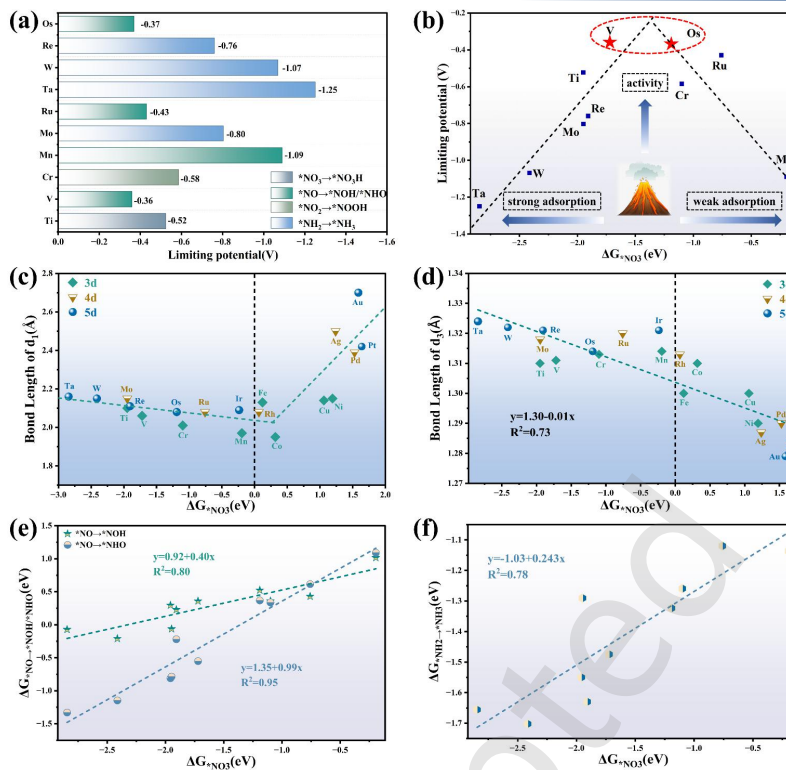


Figure 3. (a) Theoretical limiting potentials (U_L) of the ten selected TM-C₂N₂/CNT. (b) Volcano plot of NO₃RR activity on TM-C₂N₂/CNT using $\Delta G^*_{NO_3}$ as the descriptor. (c) Correlation between the bond length d_1 (distance between the lower-left O atom in $*NO_3$ and the TM active center) and $\Delta G^*_{NO_3}$. (d) Correlation between the bond length d_3 (distance between the lower-left O atom in $*NO_3$ and the central N atom) and $\Delta G^*_{NO_3}$. (e) Scaling relationship between $\Delta G^*_{NO \rightarrow *NOH/*NHO}$ and $\Delta G^*_{NO_3}$. (f) Scaling relationship between $\Delta G^*_{NH_2 \rightarrow *NH_3}$ and $\Delta G^*_{NO_3}$.

To further understand the electronic origin of the high NO₃RR activity on V-C₂N₂/CNT and Os-C₂N₂/CNT, the electronic properties were analyzed. As can be seen in Figure 4(a), the amount of charge transfer during NO₃⁻ adsorption exhibits a significant linear relationship with the adsorption energy of NO₃⁻. This indicates that the electronic interaction between the surface and nitrate is the key factor determining the adsorption strength. Figure 4(b) presents the projected crystal orbital Hamiltonian population (pCOHP) analysis for the NO₃⁻ adsorption configurations on the two catalysts. The hybridization between the metal 3d orbitals and the O 2p orbitals of NO₃⁻ splits into bonding and antibonding states. The antibonding states play a key role in determining the adsorption strength of the adsorbate. When antibonding states are located below the Fermi level, the adsorption strength of NO₃⁻ becomes relatively weak, and the activation effect is limited. For V-C₂N₂/CNT and Os-C₂N₂/CNT, only a small fraction of the antibonding states appears below the Fermi level. This result indicates that the V and Os active

centers exhibit relatively strong adsorption toward NO₃⁻, leading to effective activation of the reactant and reduced free-energy changes, which facilitates the NO₃RR process. From the pCOHP results shown in Figures 4(b), Os-C₂N₂/CNT displays a larger number of antibonding states below the Fermi level compared with V-C₂N₂/CNT. This observation suggests that the adsorption of NO₃⁻ on Os-C₂N₂/CNT is slightly weaker than that on V-C₂N₂/CNT, which is consistent with the trends observed in the $\Delta G^*_{NO_3}$ values. Figure 4(c) shows the projected density of states (PDOS) for V-C₂N₂/CNT. It can be observed that the 3d orbital of V overlap with the 2p orbitals of O, indicating strong interactions between the single metal atoms and the adsorbed NO₃⁻ species. Finally, the thermal stability of the catalysts was evaluated using ab initio molecular dynamics (AIMD) simulations. As shown in Figure 4(d), the total energy of V-C₂N₂/CNT fluctuates within a narrow range during a 10 ps simulation at 500 K. This result confirms the good thermodynamic stability of the catalyst and suggests that V-C₂N₂/CNT is a promising candidate for NO₃RR catalysis.

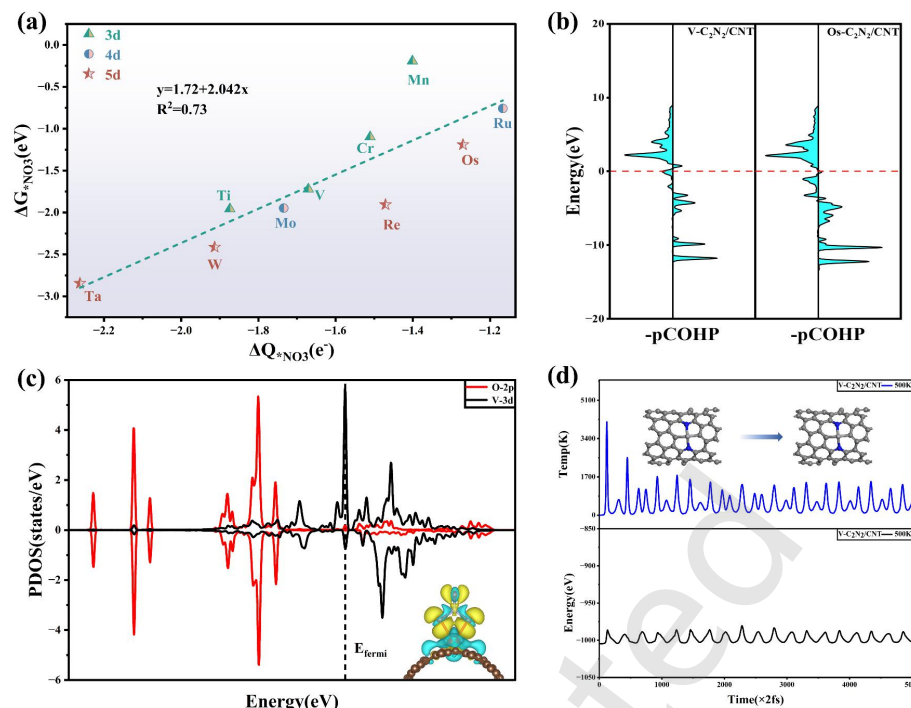


Figure 4. (a) Linear relationship between charge transfer for NO_3^- adsorption and the adsorption energy of NO_3^- . (b) Projected crystal orbital Hamiltonian population (pCOHP) analyses for NO_3^- adsorption on $\text{Os-C}_2\text{N}_2/\text{CNT}$ and $\text{V-C}_2\text{N}_2/\text{CNT}$. (c) Projected density of states (PDOS) of V-3d/O-2p orbitals, with the Fermi level (E_f) set to 0 eV. (The lower right panel shows the charge density difference plot.) (d) Evolution of energy and temperature during ab initio molecular dynamics (AIMD) simulations at 500 K for 10 ps.

3.4 Effect of carbon nanotube curvature on activity

This study further investigated the influence of CNT support curvature on NO_3RR catalytic activity. Using the most active catalyst, $\text{V-C}_2\text{N}_2/\text{CNT}$, as a representative system, we systematically examined catalysts supported on CNTs with different diameters, including CNT (6,2), (6,3), (10,5), (12,6), and (14,7), whose diameters are 5.65, 6.21, 10.36, 12.43, and 14.50 Å. The calculations indicate that the d-band center of the same active metal (V) shifts with changes in CNT curvature, indicating that the support curvature can modulate the electronic structure of the active center. This electronic tuning directly affects the adsorption behavior of the key intermediate NO_3^- . As shown in Figure 5(a), the d-band center exhibits an inverted volcano-type relationship with $\Delta G_{\text{NO}_3^-}$. Under moderate curvature conditions, such as CNT (8,4) and CNT (10,5), the d-band center falls within an optimal range, which promotes effective activation of NO_3^- and facilitates the subsequent reaction steps. The adsorption behavior of another key species, NH_3 , also displays a similar inverted volcano-type trend (Figure S4). This observation further confirms that electronic structure modulation strongly influences adsorption strength. In addition to electronic effects, CNT curvature also affects the geometric structure of the catalyst. As illustrated in Figure 5(b), with increasing CNT diameter, the distance between the active metal center (V) and the coordinated nitrogen atoms ($d_{\text{TM-N}}$) first increases and then decreases. At moderate curvature, the $d_{\text{TM-N}}$ distance reaches its maximum value, corresponding to the strongest NO_3^- adsorption. This geometry is therefore favorable for efficient NO_3^- activation and promotes the subsequent reaction pathway.

To further explore the influence of the coordination environment on NO_3RR activity, we also calculated nitrate reduction on N_4/CNT (8,4) catalysts. The corresponding structures can be seen in Figure S5. The results indicate that $\text{Ti-N}_4/\text{CNT}$ exhibits the highest activity, with a limiting potential of -0.48 V. This result further confirms the important role of the coordination environment in determining catalytic performance. The detailed computational results for all $\text{TM-N}_4/\text{CNT}$ catalysts are summarized in Tables S5-S8. In the previous sections, we systematically revealed a volcano-type relationship between NO_3RR activity and $\Delta G_{\text{NO}_3^-}$ on single-atom CNT catalysts. Using $\text{C}_2\text{N}_2/\text{CNT}$ (8,4) as the reference system, we further extended the analysis to N_4/CNT (8,4) catalysts with different coordination environments and to CNT supports with various diameters, including CNT (6,2), (6,3), (10,5), (12,6), and (14,7), each loaded with Ti, V, Cr, Os, and Ru single atoms. The detailed computational results for all $\text{TM-C}_2\text{N}_2/\text{CNT}$ with different diameters catalysts are summarized in Table S9. The screening workflow of all catalysts is illustrated in Figure 5(c). Figure 5(d) displays that all catalyst systems follow the same volcano-type trend, and the corresponding reaction pathways are presented in Figure S6 and Figure S7. Catalysts located near the apex of the volcano exhibit intermediate nitrate adsorption strengths and relatively favorable limiting potentials. This result further supports the conclusion that the adsorption energy of NO_3^- can serve as an effective activity descriptor for NO_3RR catalysis. It also indicates that tuning the adsorption strength of NO_3^- by adjusting the support curvature and coordination environment is a key strategy for designing highly efficient NO_3RR catalysts.

To distinguish the effects of support geometry from a possible chirality-induced spin selectivity mechanism, we further compared the chiral CNT (8,4) system with a diameter-matched

achiral armchair CNT (6,6) and a planar graphene support using the same V-C₂N₂ active-site motif (Figure S8). The calculated limiting potentials are -0.36, -0.49, and -0.50 V, respectively. The enhanced activity of the CNT (8,4) system mainly arises from a more balanced distribution of the uphill protonation steps. These results demonstrate that support geometry and local

curvature can influence NO₃RR thermodynamics, but they do not establish a CISS-driven mechanism. CISS-related effects were not evaluated in the present collinear spin-polarized DFT/CHE framework; rigorous assessment of CISS would require non-collinear spin-orbit and transport-level calculations.

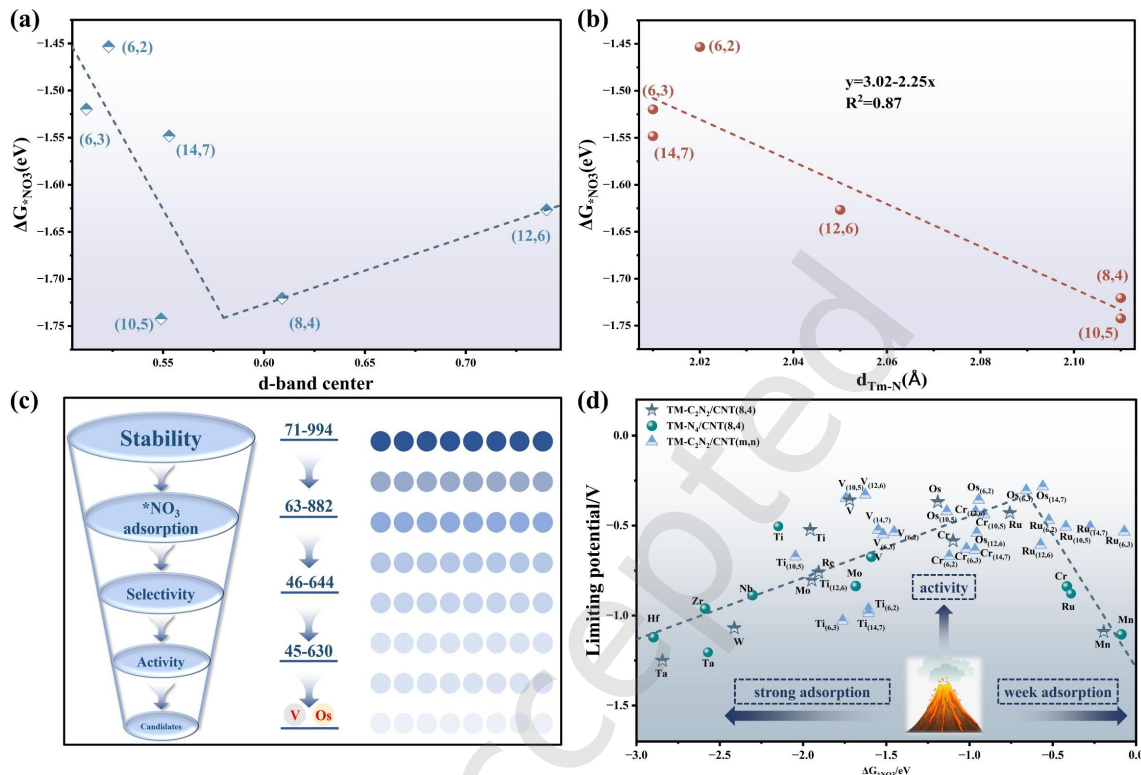


Figure 5. (a) Correlation between the d-band center of the active V site and $\Delta G^*_{\text{NO}_3}$ on V-C₂N₂/CNT with different diameters. (b) Scaling relationship between the V-N bond length and $\Delta G^*_{\text{NO}_3}$ on V-C₂N₂/CNT with different diameters. (c) Screening process of the NO₃ RR catalyst set. (d) Volcano plot of NO₃RR activity for TM-C₂N₂/CNT (8,4), TM-C₂N₂/CNT with different diameters (TM = Ti, V, Cr, Os, Ru), and TM-N_x/CNT (8,4) catalysts with different coordination environments.

3.5 Machine Learning

Although the above volcano analysis demonstrates that $\Delta G^*_{\text{NO}_3}$ can serve as an effective activity descriptor for NO₃RR, the adsorption strength of NO₃⁻ is ultimately determined by the intrinsic electronic properties of the metal center and its local coordination environment. Therefore, machine learning (ML) models were further constructed to identify the key factors controlling $\Delta G^*_{\text{NO}_3}$ from a data-driven perspective. The DFT-calculated $\Delta G^*_{\text{NO}_3}$ values were used as the target variable, while a series of physically meaningful descriptors were selected as candidate inputs, including the atomic number of the metal atom (M_{atom}), atomic radius (R_{TM}), number of valence electrons (M_{val}), first ionization energy (IE_1), electronegativity (χ_p), N coordination number (N_x), CNT diameter (D_{tube}), TM-N bond length ($d_{\text{TM-N}}$), charge transfer (Q), and d-band center (ϵ_d) (Table S10). Subsequently, five regression algorithms, including support vector regression (SVR), gradient boosting regression (GBR), fast random forest regression (FRF), random forest regression (RFR), and k-nearest-neighbor regression (KNN), were employed to predict the NO₃⁻ adsorption free energy ($\Delta G^*_{\text{NO}_3}$). The models were evaluated using the fixed hyperparameter settings summarized in Table S11. Considering the relatively limited size of the DFT dataset, ten repetitions of

five-fold cross-validation were first employed for model comparison, with a random seed of 42, while leave-one-out cross-validation (LOOCV) was subsequently used to provide an additional sample-wise assessment of the best-performing regression algorithm. In each cross-validation split, correlation-based descriptor filtering, standardization, and model fitting were incorporated into a unified pipeline and fitted exclusively using the corresponding training subset. The model hyperparameters were held fixed throughout the validation procedure and were not reoptimized within individual cross-validation folds. The pairwise Pearson correlation matrix of all ten candidate descriptors and the DFT-calculated $\Delta G^*_{\text{NO}_3}$ was constructed to provide an overall view of descriptor interdependence (Figure 6a). The full-data correlation matrix was used only for descriptive visualization, whereas descriptor filtering during model evaluation was conducted independently within each training fold. For each descriptor pair with $|r| > 0.80$, the descriptor showing the weaker correlation with $\Delta G^*_{\text{NO}_3}$ was removed. Because correlation-based filtering was refitted independently within each training subset, the retained descriptor combination was allowed to vary among cross-validation splits. When the same filtering procedure was subsequently applied to the complete dataset solely for final interpretation, six representative descriptors, namely M_{val} , R_{TM} ,

$d_{\text{TM-N}}$, IE_1 , N_x , and D_{tube} , were retained. Among these descriptors, M_{val} and R_{TM} exhibited the strongest pairwise correlations with $\Delta G^*_{\text{NO}_3}$, with Pearson correlation coefficients of 0.75 and -0.72, respectively. These associations suggest that the valence-electron count and atomic size of the metal center are closely related to nitrate adsorption. In contrast, $d_{\text{TM-N}}$, N_x , and D_{tube} encode complementary information regarding the local coordination geometry and CNT curvature. Collectively, these descriptors provide a compact and physically interpretable representation of the intrinsic and environmental factors governing NO_3^- adsorption. As shown in Figure 6b, among the five evaluated regression algorithms, SVR exhibited the best overall predictive performance, with a repeated-CV R^2 of 0.89 and RMSE of 0.22 eV. GBR gave slightly lower accuracy, with $R^2 = 0.86$ and RMSE = 0.26 eV, whereas FRF, RFR, and KNR showed larger prediction errors. The superior performance of SVR suggests that the relationship between the selected descriptors and $\Delta G^*_{\text{NO}_3}$ is nonlinear but can be effectively captured using a regularized kernel-based model, which is particularly suitable for datasets with limited sample size. Cross-validated permutation importance was further used to quantify the model-specific sensitivity to the retained descriptors (Figure 6c). This analysis employed five repetitions of five-fold cross-validation. For each cross-validation split, the SVR pipeline was fitted using the corresponding training subset, whereas descriptor permutation and performance evaluation were conducted exclusively on the held-out validation subset. Each descriptor was independently permuted five times, and its importance was quantified as the resulting increase in validation RMSE relative to the unpermuted baseline. M_{val} produced the largest RMSE increase of 0.46 eV, indicating that the valence-electron count was the most influential predictive feature for the present SVR model and dataset. This finding is physically reasonable because M_{val} affects the electron-donation ability and orbital interaction between the metal center and the adsorbed NO_3^- species. The second most influential descriptor was $d_{\text{TM-N}}$, with an RMSE increase of 0.16 eV, followed by R_{TM} , IE_1 , N_x , and D_{tube} . These results suggest that the adsorption tendency is mainly governed by the intrinsic electronic properties of the metal atom, while the local coordination structure and CNT curvature regulate the magnitude of adsorption strength. The feature importance in Figure 6(c) should be interpreted as model-specific sensitivity within the present chemical space, not as an independent universal descriptor formulation. The

subsequent LOOCV prediction results are shown in Figure 6d. The SVR model achieved an LOOCV R^2 of 0.937, an RMSE of 0.190 eV, and an MAE of 0.152 eV, showing good agreement between the DFT-calculated and ML-predicted $\Delta G^*_{\text{NO}_3}$ values for the investigated catalyst systems. These results indicate that the selected physicochemical descriptors capture the principal predictive trends within the chemical and structural space represented by the present dataset. Because SVR was selected on the basis of the preceding repeated cross-validation comparison, the reported LOOCV metrics should be interpreted as an internal sample-wise assessment rather than a fully nested estimate of model-selection performance. To further examine the role of local atomic environments, wACSF-inspired radial descriptors were additionally introduced as supplementary descriptors by considering the neighboring C/N atoms around the metal center^[55]. The corresponding results are provided in Figure S9. After including these local radial descriptors, SVR remained the best-performing model, with a repeated-CV R^2 of 0.89 and RMSE of 0.23 eV, and an LOOCV R^2 of 0.922, RMSE of 0.211 eV, and MAE of 0.160 eV. Although the inclusion of the radial descriptor did not further improve the prediction accuracy, the retained radial descriptor $G_2^x(R_c = 4 \text{ \AA}, \eta = 0.2)$ ranked second in the permutation importance analysis, with an RMSE increase of 0.17 eV. This result indicates that the local atomic environment indeed contributes to the modulation of NO_3^- adsorption. However, for the present CNT-supported SAC dataset, part of the local-environment information may already be captured by compact structural descriptors, such as $d_{\text{TM-N}}$, N_x , and D_{tube} . Therefore, the baseline model without radial descriptors was kept in the main text owing to its compact descriptor set and marginally higher LOOCV accuracy, while the radial-descriptor model is presented in the Supporting Information as complementary validation of the physical relevance of local atomic environment effects.

In this work, $\Delta G^*_{\text{NO}_3}$ is used as the activity descriptor for NO_3RR , whereas the variables employed in the ML model are predictive input features rather than a newly derived universal or dimensionless descriptor formula. The present model is intended primarily for interpolation within the chemical and structural space represented by the training data, including the selected transition metals, coordination motifs, and CNT diameters. Predictions for unseen support families, substantially different active-site geometries, or electrochemical environments require additional DFT or experimental validation.

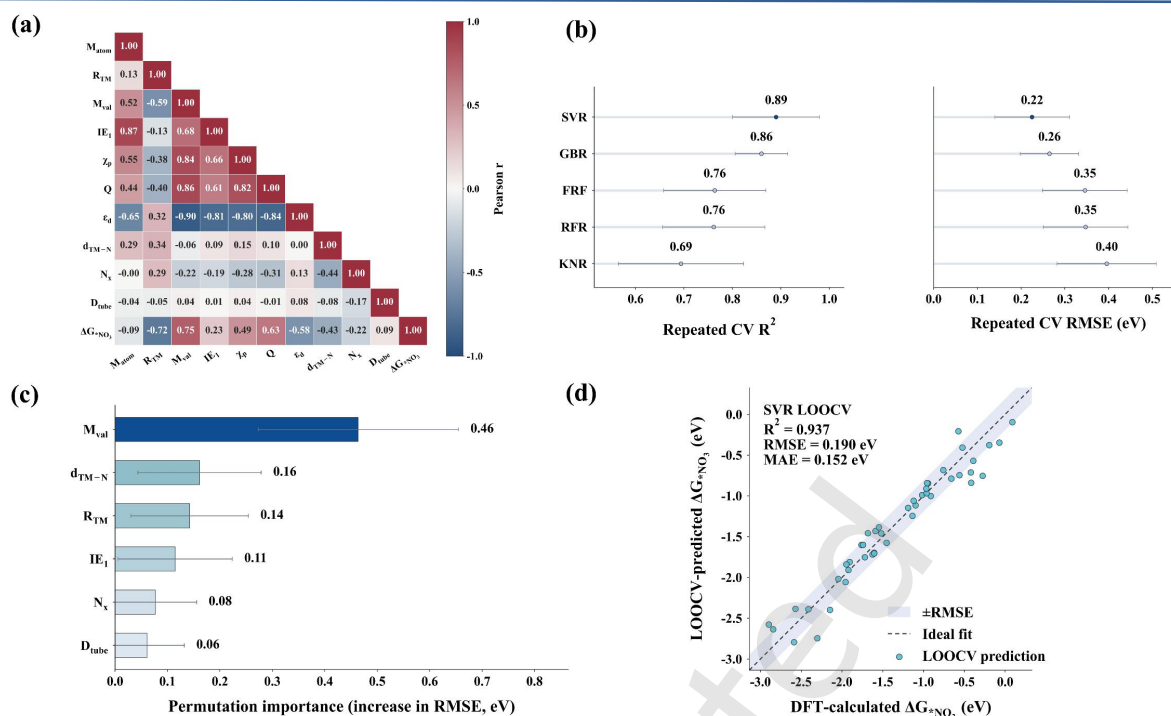


Figure 6. (a) Pairwise Pearson correlation matrix of all ten candidate descriptors and the DFT-calculated ΔG_{NO_3} . Numerical entries denote the Pearson correlation coefficients (r), with red and blue indicating positive and negative correlations, respectively. The full-data correlation matrix was used only for descriptive visualization and interpretation. (b) Comparison of the predictive performance of different regression models based on ten repetitions of five-fold cross-validation, using R^2 and RMSE as evaluation metrics. Error bars denote the standard deviations over the repeated cross-validation splits. (c) Cross-validated permutation importance of the retained descriptors for the SVR model, expressed as the increase in RMSE after descriptor permutation exclusively within the held-out validation subsets. (d) Comparison between DFT-calculated and LOOCV-predicted ΔG_{NO_3} values using the SVR model. The dashed line represents ideal agreement, and the shaded region denotes $\pm \text{RMSE}$.

4 Conclusion

In summary, we systematically investigated NO_3RR on transition-metal single-atom catalysts supported on N-doped chiral CNTs with different metal centers, coordination environments, and CNT diameters. $\text{V-C}_2\text{N}_2/\text{CNT}$ and $\text{Os-C}_2\text{N}_2/\text{CNT}$ exhibit favorable limiting potentials of -0.36 and -0.37 V, respectively. The potential-determining steps are the hydrogenation of NO to NOH on $\text{V-C}_2\text{N}_2/\text{CNT}$ and of NO to NHO on $\text{Os-C}_2\text{N}_2/\text{CNT}$. The release of NO and NO_2 and the pathway toward N_2 formation are thermodynamically less favorable than NH_3 formation. Across the examined chiral-CNT-supported catalyst space, a consistent volcano-type relationship was observed between NO_3RR activity and ΔG_{NO_3} , validating nitrate adsorption free energy as a useful activity descriptor within the investigated coordination environments and CNT diameters. Machine-learning models were further developed to predict ΔG_{NO_3} from elemental and local structural features. Within the present dataset and SVR model, the metal valence-electron count and TM–N coordination were identified as influential predictive features. These results provide useful structure–activity insights into the design of chiral-CNT-supported single-atom catalysts for NO_3RR .

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and/or the Supplementary Material. The complete dataset used for machine-learning model development and validation is provided in Table S10 and the machine-readable dataset is additionally provided as Dataset S1 in CSV format from <https://doi.org/10.5281/zenodo.21429459>.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author contribution statement

Xiaofei Song: Writing - original draft, Data curation, Visualization, Investigation. Xinyu Sui: Software, Data curation. Baowen He: Data curation. Xiaoxue Sang: Data curation. Chi Ding: Data curation. Yangyang Song: Software, Supervision. Zean Xie: Formal analysis, Validation. Yu Ren: Supervision, Writing, reviewing, and editing. Zhen Zhao: Methodology, Conceptualization, Writing - review & editing.

Informed consent

Not applicable

Ethics statement

Not applicable

Use of AI statement

Used generative AI for language polishing.

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Electronic Supplementary Material

Validation of nitrate adsorption energy as an activity descriptor for nitrate electroreduction on single-atom catalysts supported by chiral carbon nanotubes: DFT calculations and machine learning

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Computational methods

A chiral (8,4) single-walled carbon nanotube (CNT) with a diameter of 8.29 Å was chosen as the base structure. A periodic supercell measuring 25×25×11.3 Å containing 112 carbon atoms was built to minimize inter-tube interactions. Carbon vacancy defects were introduced by removing two carbon atoms. Ab initio molecular dynamics (AIMD) simulations were conducted in VASP to assess the thermodynamic stability of candidate structures. These simulations employed the canonical ensemble (NVT) with a Nosé–Hoover thermostat at 500 K, running for 10 ps with a time step of 2 fs.

The binding energy (E_{bind}) between the transition metal (TM) atom and the carbon nanotube (CNT) support was calculated as:

$$E_{\text{bind}} = E_{\text{TM-C}_2\text{N}_2/\text{CNT}} - E_{\text{C}_2\text{N}_2/\text{CNT}} - E_{\text{TM}} \quad (1)$$

Where $E_{\text{TM-C}_2\text{N}_2/\text{CNT}}$ is the total energy of the TM atom adsorbed on the CNT, $E_{\text{C}_2\text{N}_2/\text{CNT}}$ is the energy of the pristine CNT, and E_{TM} is the energy of an isolated TM atom in its ground state. A negative value of E_{bind} indicates stable adsorption.

The formation energy (E_f) of the TM/CNT system was evaluated as:

$$E_f = \frac{E_{\text{TM-C}_2\text{N}_2/\text{CNT}} - E_{\text{C}_2\text{N}_2/\text{CNT}} - nE_{\text{TM,bulk}}}{n} \quad (2)$$

Where $E_{\text{TM,bulk}}$ is the energy per atom in the bulk TM metal, and n is the number of TM atoms. A negative E_f implies thermodynamic stability.

The dissolution potential (U_{diss}) was computed to assess electrochemical stability:

$$U_{\text{diss}} = U_{\text{diss}}^0(\text{metal, bulk}) - \frac{E_f}{ne} \quad (3)$$

where $U_{\text{diss}}^0(\text{metal, bulk})$ is the standard dissolution potential of the bulk metal, e is the elementary charge, and n is the number of electrons involved in the dissolution reaction. A positive U_{diss} value indicates resistance against electrochemical dissolution.

Table S1. Binding energy (E_b), formation energy (E_f), dissolution potential (U_{diss}), bond length $d_{\text{N-M}}$, bond length $d_{\text{C-M}}$ and Bader charge of TM adsorbed on $\text{C}_2\text{N}_2/\text{CNT}(8,4)$.

Metal	$E_b(\text{eV})$	$E_f(\text{eV})$	U_{diss}	$d_{\text{N-M}}(\text{\AA})$	$d_{\text{C-M}}(\text{\AA})$	Bader(e^-)
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Ti	-9.40	-4.16	0.45	2.13	2.00	-1.68
V	-8.62	-3.10	0.37	2.10	1.98	-1.44
Cr	-9.62	-2.96	0.57	2.11	1.96	-1.16
Mn	-7.16	-3.33	0.47	2.02	1.94	-1.28
Fe	-7.82	-2.73	0.91	1.95	1.90	-1.04
Co	-8.46	-3.09	1.26	1.92	1.88	-0.81
Ni	-8.81	-3.41	1.44	1.91	1.87	-0.66
Cu	-6.33	-2.47	1.58	1.94	1.90	-0.81
Zr	-10.56	-4.28	-0.38	2.26	2.09	-1.87
Nb	-9.82	-2.89	-0.14	2.27	2.04	-1.57
Mo	-8.29	-2.08	0.49	2.20	2.02	-1.27
Ru	-9.13	-1.97	1.45	2.15	1.97	-0.75
Rh	-8.51	-2.47	1.84	2.09	1.95	-0.61
Pd	-6.90	-3.20	2.55	2.05	1.95	-0.52
Ag	-4.22	-1.59	2.39	2.06	1.98	-0.74
Hf	-10.46	-4.03	-0.54	2.22	2.08	-1.90
Ta	-10.69	-2.32	0.17	2.16	2.04	-1.66
W	-9.47	-1.17	0.49	2.14	2.02	-1.40
Re	-8.79	-0.97	0.62	2.15	1.99	-1.04
Os	-9.56	-1.22	0.99	2.09	1.97	-0.78
Ir	-9.89	-2.23	1.90	2.05	1.96	-0.62
Pt	-9.07	-3.53	2.94	2.03	1.96	-0.50
Au	-5.63	-1.91	2.14	2.04	1.98	-0.67

Table S2. The adsorption free energies of NO_3^- on TM- $\text{C}_2\text{N}_2/\text{CNT}(8,4)$ via 1-O patterns model or 2-O patterns model and the adsorption free energies of H on TM- $\text{C}_2\text{N}_2/\text{CNT}(8,4)$, with the unit of eV.

Metal	$\Delta G^*_{\text{NO}_3-1\text{O}}$	$\Delta G^*_{\text{NO}_3-2\text{O}}$	ΔG^*_{H}
Ti	-1.25	-1.96	-0.33
V	-1.11	-1.72	-0.23

Cr	-1.07	-1.10	0.02
Mn	-0.12	-0.19	0.19
Fe	0.17	0.12	0.23
Co	0.73	0.32	0.01
Ni	1.49	1.19	-0.21
Cu	1.37	1.06	0.70
Mo	-1.63	-1.95	-0.67
Ru	-0.45	-0.76	-0.35
Rh	0.11	0.07	-0.30
Pd	1.64	1.53	-0.11
Ag	1.37	1.24	0.89
Ta	-1.96	-2.84	-1.34
W	-2.35	-2.41	-1.20
Re	-1.85	-1.91	-0.86
Os	-1.01	-1.19	-0.78
Ir	0.37	-0.24	-0.63
Pt	1.73	1.64	0.03
Au	1.68	1.59	0.72

Table S3. Adsorption energy of *NO₂, *NO, *N, and *NH₃ on TM-C₂N₂/CNT(8,4) SACs calculated using their corresponding gas-phase energy as the reference, with the unit of eV.

Catalyst	*NO ₂	*NO	*N	*NH ₃
V-C ₂ N ₂ /CNT(8,4)	-3.15	-2.96	-5.44	-1.47
Ru-C ₂ N ₂ /CNT(8,4)	-2.37	-3.00	-5.71	-1.12
Ta-C ₂ N ₂ /CNT(8,4)	-4.32	-3.32	-5.54	-1.66
Re-C ₂ N ₂ /CNT(8,4)	-3.49	-3.67	-6.65	-1.63
Os-C ₂ N ₂ /CNT(8,4)	-2.91	-3.44	-6.41	-1.32

Cr-C ₂ N ₂ /CNT(8,4)	-2.53	-2.82	-5.54	-1.26
Mn-C ₂ N ₂ /CNT(8,4)	-1.77	-2.69	-4.88	-1.14
Ti-C ₂ N ₂ /CNT(8,4)	-3.38	-2.30	-3.59	-1.55
Mo-C ₂ N ₂ /CNT(8,4)	-3.39	-2.87	-5.92	-1.29
W-C ₂ N ₂ /CNT(8,4)	-3.89	-3.34	-6.47	-1.70

Table S4. The potential-determining step (PDS) and limiting potential (U_L) for the nitrate reduction reaction (NO₃RR) on TM-C₂N₂/CNT(8,4) catalysts, with the unit of V.

Catalyst	PDS	U _L
V-C ₂ N ₂ /CNT(8,4)	*NO→*NOH	-0.36
Ru-C ₂ N ₂ /CNT(8,4)	*NO→*NOH	-0.43
Ta-C ₂ N ₂ /CNT(8,4)	*NH ₂ →*NH ₃	-1.25
Re-C ₂ N ₂ /CNT(8,4)	*NH ₂ →*NH ₃	-0.76
Os-C ₂ N ₂ /CNT(8,4)	*NO→*NHO	-0.37
Cr-C ₂ N ₂ /CNT(8,4)	*NO ₂ →*NO ₂ H	-0.59
Mn-C ₂ N ₂ /CNT(8,4)	*NO→*NHO	-1.09

Ti-C ₂ N ₂ /CNT(8,4)	*NO ₃ →*NO ₃ H	-0.52
Mo-C ₂ N ₂ /CNT(8,4)	*NH ₂ →*NH ₃	-0.80
W-C ₂ N ₂ /CNT(8,4)	*NH ₂ →*NH ₃	-1.07

Table S5. Binding energy (E_b), formation energy (E_f), dissolution potential (U_{diss}), bond length($d_{TM-N-1/2}$), Bader charge of TM and d-band center (ϵ_d) adsorbed on N₄/CNT(8,4).

Metal	E_b (eV)	E_f (eV)	U_{diss}	d_{TM-N-1} (Å)	d_{TM-N-2} (Å)	Bader(e^-)	ϵ_d
Ti	-8.12	-2.87	-0.195	1.994	2.071	-1.63	0.790
V	-7.82	-2.30	-0.032	1.971	2.027	-1.44	0.714
Cr	-9.10	-2.44	0.312	1.953	2.002	-1.30	0.453
Mn	-6.16	-2.34	-0.022	1.914	1.935	-1.35	-1.139
Fe	-6.99	-1.90	0.498	1.896	1.901	-1.13	-1.222
Co	-7.44	-2.07	0.753	1.875	1.869	-0.92	-1.147
Ni	-7.54	-2.14	0.808	1.881	1.876	-0.75	-3.081
Cu	-4.94	-1.09	0.885	1.924	1.979	-0.91	-3.190
Zr	-8.82	-2.54	-0.814	2.062	2.172	-2.03	0.603
Nb	-8.16	-1.22	-0.693	2.050	2.141	-1.58	0.666

Mo	-6.52	-0.32	-0.094	1.998	2.044	-1.54	-0.531
Ru	-7.70	-0.54	0.731	1.963	1.999	-1.09	-0.954
Rh	-7.38	-1.35	1.273	1.947	1.989	-0.75	-1.100
Pd	-5.58	-1.88	1.888	1.955	1.999	-0.76	-3.195
Ag	-2.41	0.22	0.584	2.174	2.397	-0.62	/
Hf	-8.92	-2.49	-0.928	2.062	2.158	-1.82	0.775
Ta	-9.06	-0.69	-0.370	1.998	2.101	-1.83	0.088
W	-7.88	0.42	-0.039	1.993	2.033	-1.64	/
Re	-7.07	0.75	0.049	1.985	2.027	-1.35	/
Os	-8.05	0.29	0.804	1.965	1.993	-1.01	/
Ir	-8.63	-0.96	1.481	1.950	1.981	-0.82	-1.422
Pt	-7.62	-2.07	2.217	1.957	1.992	-0.74	-3.075
Au	-2.91	0.81	1.230	1.972	2.034	-0.88	/

Table S6. The adsorption free energies of NO₃⁻ on TM-N₄/CNT(8,4) via 2-O patterns model, the adsorption free energies of H on TM-N₄/CNT(8,4) and the difference between them, with the unit of eV.

Metal	ΔG^{*NO_3}	ΔG^{*H}	$\Delta G^{*NO_3}-\Delta G^{*H}$
Ti	-2.15	-0.68	-1.47
V	-1.59	-0.33	-1.26
Cr	-0.42	0.08	-0.49
Mn	-0.09	0.18	-0.27
Fe	0.35	0.15	0.20
Co	0.75	-0.03	0.78
Ni	1.43	1.23	0.21
Cu	1.10	1.21	-0.10
Zr	-2.59	-0.99	-1.60
Nb	-2.30	-0.92	-1.39
Mo	-1.68	-0.74	-0.94
Ru	-0.39	-0.38	-0.01
Rh	0.85	-0.40	1.24

Pd	1.77	1.63	0.13
Ag	/	/	/
Hf	-2.90	-1.30	-1.60
Ta	-2.57	-1.32	-1.25
W	/	/	/
Re	/	/	/
Os	/	/	/
Ir	0.70	-0.66	1.35
Pt	1.86	1.30	0.57
Au	/	/	/

Table S7. Adsorption energy of *NO₂, *NO, *N, and *NH₃ on TM-N₄/CNT(8,4) SACs calculated using their corresponding gas-phase energy as the reference, with the unit of eV.

Catalyst	*NO ₂	*NO	*N	*NH ₃
Cr-N ₄ /CNT(8,4)	-1.95	-2.82	-5.29	-0.78
Ru-N ₄ /CNT(8,4)	-2.04	-2.70	-4.96	-0.88
Ti-N ₄ /CNT(8,4)	-3.71	-3.16	-4.78	-1.61
V-N ₄ /CNT(8,4)	-3.17	-2.98	-5.51	-1.25
Zr-N ₄ /CNT(8,4)	-4.13	-3.05	-4.56	-1.50
Nb-N ₄ /CNT(8,4)	-3.92	-3.51	-6.23	-1.47
Mo-N ₄ /CNT(8,4)	-3.43	-3.87	-6.90	-1.18
Ta-N ₄ /CNT(8,4)	-4.32	-3.82	-6.34	-1.53
Mn-N ₄ /CNT(8,4)	-1.55	-2.57	-4.90	-0.80
Hf-N ₄ /CNT(8,4)	-4.49	-3.29	-4.53	-1.68

Table S8. The potential-determining step (PDS) and limiting potential (U_L) for the nitrate reduction reaction (NO_3RR) on TM-N₄/CNT(8,4) catalysts, with the unit of V.

Catalyst	PDS	U_L
Cr-N ₄ /CNT(8,4)	*NO→*NHO	-0.84
Ru-N ₄ /CNT(8,4)	*NO ₃ →*NO ₃ H	-0.88
Ti-N ₄ /CNT(8,4)	*NH ₂ →*NH ₃	-0.48
V-N ₄ /CNT(8,4)	*NO ₂ →*NO ₂ H	-0.67
Zr-N ₄ /CNT(8,4)	*NH ₂ →*NH ₃	-0.96
Nb-N ₄ /CNT(8,4)	*NH ₂ →*NH ₃	-0.89
Mo-N ₄ /CNT(8,4)	*NH ₂ →*NH ₃	-0.84
Ta-N ₄ /CNT(8,4)	*NH ₂ →*NH ₃	-1.20
Mn-N ₄ /CNT(8,4)	*NO→*NHO	-1.10
Hf-N ₄ /CNT(8,4)	*NH ₂ →*NH ₃	-1.12

Table S9. Binding energy (E_b), formation energy (E_f), dissolution potential (U_{diss}), bond length d_{N-M} , bond length d_{C-M} , Bader charge of TM, adsorption free energies of NO_3^- and H of TM adsorbed on C_2N_2/CNT with different diameters (TM = Ti, V, Cr, Os, Ru).

Catalyst	E_b (eV)	E_f (eV)	U_{diss}	d_{N-M} (Å)	d_{C-M} (Å)	Bader(e^-)	ΔG^{*NO_3}	ΔG^{*H}
Ti- $C_2N_2/CNT(6,2)$	-9.55	-4.30	0.52	2.08	1.98	-1.65	-1.61	-0.09
V- $C_2N_2/CNT(6,2)$	-8.87	-3.35	0.50	2.03	1.95	-1.42	-1.45	-0.25
Cr- $C_2N_2/CNT(6,2)$	-9.60	-2.95	0.56	2.05	1.91	-1.69	-1.12	0.03
Ru- $C_2N_2/CNT(6,2)$	-9.20	-2.04	1.48	2.10	1.91	-0.28	-0.52	-0.04
Os- $C_2N_2/CNT(6,2)$	-9.54	-1.21	0.99	2.07	1.92	-0.81	-0.95	-0.53
Ti- $C_2N_2/CNT(6,3)$	-9.66	-4.41	0.58	2.06	1.98	-1.65	-1.76	-0.25
V- $C_2N_2/CNT(6,3)$	-9.01	-3.49	0.57	2.01	1.95	-1.41	-1.52	-0.28
Cr- $C_2N_2/CNT(6,3)$	-9.77	-3.12	0.65	2.03	1.91	-1.73	-1.02	0.01
Ru- $C_2N_2/CNT(6,3)$	-9.46	-2.30	1.61	2.07	1.90	-0.75	-0.07	0.09
Os- $C_2N_2/CNT(6,3)$	-9.82	-1.48	1.03	2.05	1.92	-0.83	-0.66	-0.41
Ti- $C_2N_2/CNT(10,5)$	-9.54	-4.29	0.51	2.14	2.04	-1.69	-2.05	-0.43
V- $C_2N_2/CNT(10,5)$	-8.80	-3.28	0.46	2.11	2.02	-1.44	-1.74	-0.24
Cr- $C_2N_2/CNT(10,5)$	-9.88	-3.22	0.70	2.08	2.00	-1.73	-0.91	0.10
Ru- $C_2N_2/CNT(10,5)$	-9.36	-2.20	1.56	2.13	1.98	-0.68	-0.42	-0.27
Os- $C_2N_2/CNT(10,5)$	-9.88	-1.54	1.03	2.09	1.99	-0.79	-1.14	-0.70
Ti- $C_2N_2/CNT(12,6)$	-9.88	-4.63	0.69	2.08	2.05	-1.72	-1.92	-0.35
V- $C_2N_2/CNT(12,6)$	-9.13	-3.61	0.62	2.05	2.03	-1.44	-1.63	-0.22
Cr- $C_2N_2/CNT(12,6)$	-10.15	-3.49	0.84	2.04	1.98	-1.75	-0.96	0.05
Ru- $C_2N_2/CNT(12,6)$	-9.99	-2.83	1.87	2.07	1.96	-0.41	-0.57	0.01
Os- $C_2N_2/CNT(12,6)$	-10.52	-2.18	1.11	2.05	1.97	-0.81	-0.96	-0.54
Ti- $C_2N_2/CNT(14,7)$	-9.85	-4.60	0.67	2.06	1.98	-1.66	-1.61	-0.08
V- $C_2N_2/CNT(14,7)$	-9.08	-3.56	0.60	2.01	1.95	-1.43	-1.55	-0.32
Cr- $C_2N_2/CNT(14,7)$	-9.96	-3.30	0.74	2.02	1.92	-1.70	-0.97	0.03
Ru- $C_2N_2/CNT(14,7)$	-9.65	-2.49	1.71	2.05	1.92	-1.02	-0.28	0.002
Os- $C_2N_2/CNT(14,7)$	-10.04	-1.70	1.05	2.03	1.93	-0.84	-0.56	-0.54

Table S10. Complete dataset for machine learning.

Catalyst	M_{atom}	R_{TM}	M_{val}	IE_1	χ_p	Q	ϵ_d	d_{TM-N}	N_x	D_{tube}	ΔG^{*NO_3}
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Catalyst	M _{atom}	R _{TM}	M _{val}	IE ₁	χ _p	Q	ε _d	d _{TM-N}	N _x	D _{tube}	ΔG*NO ₃
V-C ₂ N ₂ /CNT(8,4)	23	134	5	650.9	1.63	-1.44	0.609	2.10	2	8.29	-1.72
Ru-C ₂ N ₂ /CNT(8,4)	44	134	8	710.2	2.20	-0.75	-0.916	2.15	2	8.29	-0.76
Ta-C ₂ N ₂ /CNT(8,4)	73	143	5	761.0	1.50	-1.66	0.043	2.16	2	8.29	-2.84
Re-C ₂ N ₂ /CNT(8,4)	75	137	7	760.0	1.90	-1.04	-0.790	2.15	2	8.29	-1.91
Os-C ₂ N ₂ /CNT(8,4)	76	135	8	840.0	2.20	-0.78	-1.260	2.09	2	8.29	-1.19
Cr-C ₂ N ₂ /CNT(8,4)	24	128	6	652.9	1.66	-1.16	0.198	2.11	2	8.29	-1.10
Mn-C ₂ N ₂ /CNT(8,4)	25	127	7	717.3	1.55	-1.28	-0.974	2.02	2	8.29	-0.19
Ti-C ₂ N ₂ /CNT(8,4)	22	147	4	658.8	1.54	-1.68	0.670	2.13	2	8.29	-1.96
Mo-C ₂ N ₂ /CNT(8,4)	42	136	6	684.3	2.16	-1.27	-0.110	2.20	2	8.29	-1.95
W-C ₂ N ₂ /CNT(8,4)	74	137	6	770.0	2.36	-1.40	-0.175	2.14	2	8.29	-2.41
Os-C ₂ N ₂ /CNT(6,2)	76	135	8	840.0	2.20	-0.81	-1.667	2.07	2	5.65	-0.95
Os-C ₂ N ₂ /CNT(6,3)	76	135	8	840.0	2.20	-0.83	-1.652	2.05	2	6.21	-0.66
Ru-C ₂ N ₂ /CNT(6,3)	44	134	8	710.2	2.20	-0.75	-1.227	2.07	2	6.21	-0.07
Ti-C ₂ N ₂ /CNT(6,3)	22	147	4	658.8	1.54	-1.65	0.722	2.06	2	6.21	-1.76
V-C ₂ N ₂ /CNT(6,3)	23	134	5	650.9	1.63	-1.41	0.512	2.01	2	6.21	-1.52
Os-C ₂ N ₂ /CNT(10,5)	76	135	8	840.0	2.20	-0.79	-1.079	2.09	2	10.36	-1.14
Ru-C ₂ N ₂ /CNT(10,5)	44	134	8	710.2	2.20	-0.68	-0.839	2.13	2	10.36	-0.42
Ti-C ₂ N ₂ /CNT(10,5)	22	147	4	658.8	1.54	-1.69	0.668	2.14	2	10.36	-2.05
V-C ₂ N ₂ /CNT(10,5)	23	134	5	650.9	1.63	-1.44	0.549	2.11	2	10.36	-1.74
Os-C ₂ N ₂ /CNT(12,6)	76	135	8	840.0	2.20	-0.81	-1.085	2.05	2	12.43	-0.96
Ru-C ₂ N ₂ /CNT(12,6)	44	134	8	710.2	2.20	-0.41	-0.893	2.07	2	12.43	-0.57
Ti-C ₂ N ₂ /CNT(12,6)	22	147	4	658.8	1.54	-1.72	0.706	2.08	2	12.43	-1.92
V-C ₂ N ₂ /CNT(12,6)	23	134	5	650.9	1.63	-1.44	0.740	2.05	2	12.43	-1.63
Cr-N ₄ /CNT(8,4)	24	128	6	652.9	1.66	-1.30	0.453	1.97	4	8.29	-0.42
Ru-N ₄ /CNT(8,4)	44	134	8	710.2	2.20	-1.09	-0.954	1.98	4	8.29	-0.39

Catalyst	M _{atom}	R _{TM}	M _{val}	IE ₁	χ _p	Q	ε _d	d _{TM-N}	N _x	D _{tube}	ΔG*NO ₃
Ti-N ₄ /CNT(8,4)	22	147	4	658.8	1.54	-1.63	0.790	2.00	4	8.29	-2.15
V-N ₄ /CNT(8,4)	23	134	5	650.9	1.63	-1.44	0.714	1.99	4	8.29	-1.59
Zr-N ₄ /CNT(8,4)	40	160	4	640.1	1.33	-2.03	0.603	2.10	4	8.29	-2.59
Nb-N ₄ /CNT(8,4)	41	143	5	652.1	1.60	-1.58	0.666	2.10	4	8.29	-2.30
Mo-N ₄ /CNT(8,4)	42	136	6	684.3	2.16	-1.54	-0.531	2.01	4	8.29	-1.68
Ta-N ₄ /CNT(8,4)	73	143	5	761.0	1.50	-1.83	0.088	2.03	4	8.29	-2.57
Mn-N ₄ /CNT(8,4)	25	127	7	717.3	1.55	-1.35	-1.139	1.92	4	8.29	-0.09
Hf-N ₄ /CNT(8,4)	72	159	4	658.5	1.30	-1.82	0.775	2.11	4	8.29	-2.90
Ti-C ₂ N ₂ /CNT(6,2)	22	147	4	658.8	1.54	-1.65	0.838	2.08	2	5.65	-1.61
Ru-C ₂ N ₂ /CNT(6,2)	44	134	8	710.2	2.20	-0.28	-1.253	2.10	2	5.65	-0.52
V-C ₂ N ₂ /CNT(6,2)	23	134	5	650.9	1.63	-1.42	0.523	2.03	2	5.65	-1.45
Ti-C ₂ N ₂ /CNT(14,7)	22	147	4	658.8	1.54	-1.66	0.939	2.06	2	14.50	-1.61
Ru-C ₂ N ₂ /CNT(14,7)	44	134	8	710.2	2.20	-1.02	-0.975	2.05	2	14.50	-0.28
Os-C ₂ N ₂ /CNT(14,7)	76	135	8	840.0	2.20	-0.84	-1.277	2.03	2	14.50	-0.56
V-C ₂ N ₂ /CNT(14,7)	23	134	5	650.9	1.63	-1.43	0.553	2.01	2	14.50	-1.55
Cr-C ₂ N ₂ /CNT(6,2)	24	128	6	652.9	1.66	-1.69	0.671	2.05	2	5.65	-1.12
Cr-C ₂ N ₂ /CNT(6,3)	24	128	6	652.9	1.66	-1.73	0.573	2.03	2	6.21	-1.02
Cr-C ₂ N ₂ /CNT(10,5)	24	128	6	652.9	1.66	-1.73	0.771	2.08	2	10.36	-0.91
Cr-C ₂ N ₂ /CNT(12,6)	24	128	6	652.9	1.66	-1.75	0.754	2.04	2	12.43	-0.96
Cr-C ₂ N ₂ /CNT(14,7)	24	128	6	652.9	1.66	-1.70	0.862	2.02	2	14.50	-0.97

Table S11. Detailed parameters of the ML models.

ML	Parameters
GBR	number of estimators: 150 learning rate: 0.03 max depth: 2 min samples leaf: 3 subsample: 0.80 random state: 42
FRF	number of estimators: 120 max depth: 6 min samples split: 5 min samples leaf: 2 max features: sqrt bootstrap: True random state: 42
RFR	number of estimators: 150 max depth: 6 min samples split: 5 min samples leaf: 2 max features: sqrt random state: 42
KNR	number of neighbors: 5 weights: uniform p: 1
SVR	C: 10 kernel: rbf gamma: scale epsilon: 0.03

Table S12. Zero-point energy (ZPE) values of nitrate reduction reaction (NO₃ RR) intermediates over catalysts with various coordination environments, including TM-C₂ N₂ /CNT (8,4), TM-C₂ N₂ /CNT with different diameters (TM = Ti, V, Cr, Os, Ru), and TM-N₄ /CNT (8,4).

Catalyst	*NO ₃	*NO ₃ H	*NO ₂	*NOOH	*NO	*NHO	*NOH	*NH ₂ O	*NHOH	*NH ₂ OH	*N	*NH	*NH ₂	*NH ₃
Ti-C ₂ N ₂ /CNT(6,2)	0.42	0.66	0.26	0.55	0.16	0.44	0.46	0.82	0.78	1.00	0.05	0.33	0.65	1.00
V-C ₂ N ₂ /CNT(6,2)	0.42	0.65	0.27	0.54	0.20	0.47	0.46	0.83	0.78	1.11	0.08	0.33	0.66	1.01
Cr-C ₂ N ₂ /CNT(6,2)	0.42	0.65	0.27	0.55	0.19	0.43	0.45	0.83	0.77	1.02	0.09	0.34	0.65	1.01
Ru-C ₂ N ₂ /CNT(6,2)	0.42	0.66	0.27	0.54	0.19	0.48	0.46	0.83	0.78	1.11	0.09	0.34	0.66	1.01
Os-C ₂ N ₂ /CNT(6,2)	0.41	0.66	0.27	0.57	0.19	0.44	0.47	0.83	0.71	0.97	0.09	0.34	0.67	1.02
Ti-C ₂ N ₂ /CNT(6,3)	0.42	0.66	0.26	0.54	0.15	0.44	0.44	0.82	0.78	1.01	0.06	0.33	0.65	1.01
V-C ₂ N ₂ /CNT(6,3)	0.42	0.65	0.26	0.54	0.19	0.47	0.47	0.83	0.78	1.12	0.08	0.34	0.66	1.01
Cr-C ₂ N ₂ /CNT(6,3)	0.42	0.66	0.27	0.56	0.19	0.47	0.46	0.83	0.78	1.11	0.09	0.34	0.65	1.00
Ru-C ₂ N ₂ /CNT(6,3)	0.40	0.65	0.27	0.55	0.19	0.47	0.46	0.82	0.78	1.12	0.09	0.34	0.65	1.01
Os-C ₂ N ₂ /CNT(6,3)	0.41	0.65	0.27	0.57	0.19	0.47	0.47	0.83	0.78	1.11	0.09	0.34	0.67	1.02
Ti-C ₂ N ₂ /CNT(10,5)	0.42	0.63	0.26	0.55	0.16	0.45	0.45	0.83	0.77	1.10	0.05	0.33	0.64	1.00
V-C ₂ N ₂ /CNT(10,5)	0.41	0.65	0.26	0.54	0.19	0.46	0.46	0.83	0.78	1.11	0.08	0.34	0.65	1.01
Cr-C ₂ N ₂ /CNT(10,5)	0.42	0.65	0.26	0.55	0.18	0.47	0.46	0.83	0.78	1.11	0.09	0.34	0.65	1.01
Ru-C ₂ N ₂ /CNT(10,5)	0.40	0.67	0.26	0.58	0.19	0.48	0.47	0.83	0.77	1.10	0.09	0.35	0.67	1.03
Os-C ₂ N ₂ /CNT(10,5)	0.40	0.67	0.27	0.58	0.19	0.48	0.46	0.84	0.78	0.96	0.09	0.35	0.68	1.03
Ti-C ₂ N ₂ /CNT(12,6)	0.42	0.63	0.26	0.54	0.15	0.45	0.45	0.83	0.77	1.08	0.05	0.32	0.64	1.00
V-C ₂ N ₂ /CNT(12,6)	0.41	0.67	0.25	0.54	0.19	0.46	0.46	0.83	0.75	1.11	0.08	0.34	0.65	1.00
Cr-C ₂ N ₂ /CNT(12,6)	0.41	0.66	0.27	0.55	0.20	0.45	0.46	0.82	0.77	1.12	0.09	0.34	0.66	1.00
Ru-C ₂ N ₂ /CNT(12,6)	0.41	0.67	0.27	0.58	0.20	0.42	0.47	0.82	0.77	1.12	0.09	0.31	0.67	1.00
Os-C ₂ N ₂ /CNT(12,6)	0.41	0.67	0.28	0.58	0.19	0.48	0.47	0.82	0.78	1.12	0.09	0.33	0.67	1.03
Ti-C ₂ N ₂ /CNT(14,7)	0.42	0.67	0.26	0.55	0.16	0.45	0.46	0.83	0.78	1.10	0.06	0.34	0.65	1.01
V-C ₂ N ₂ /CNT(14,7)	0.42	0.66	0.27	0.54	0.18	0.47	0.46	0.83	0.78	1.11	0.09	0.34	0.66	1.01
Cr-C ₂ N ₂ /CNT(14,7)	0.42	0.65	0.27	0.56	0.20	0.46	0.45	0.83	0.77	1.11	0.09	0.34	0.66	1.00
Ru-C ₂ N ₂ /CNT(14,7)	0.41	0.66	0.27	0.57	0.19	0.47	0.47	0.82	0.78	1.11	0.09	0.33	0.65	1.01
Os-C ₂ N ₂ /CNT(14,7)	0.40	0.67	0.27	0.57	0.20	0.48	0.47	0.83	0.77	1.11	0.09	0.34	0.67	1.01
Cr-N ₄ /CNT(8,4)	0.42	0.65	0.28	0.57	0.20	0.46	0.47	0.82	0.77	1.11	0.09	0.33	0.64	1.01
Ru-N ₄ /CNT(8,4)	0.42	0.66	0.28	0.55	0.67	0.49	0.47	0.83	0.78	1.03	0.09	0.36	0.67	1.03
Ti-N ₄ /CNT(8,4)	0.41	0.64	0.24	0.54	0.17	0.44	0.45	0.82	0.77	1.02	0.07	0.34	0.64	1.01
V-N ₄ /CNT(8,4)	0.42	0.66	0.27	0.56	0.19	0.45	0.46	0.83	0.77	1.03	0.09	0.35	0.66	1.02
Zr-N ₄ /CNT(8,4)	0.39	0.62	0.22	0.48	0.16	0.44	0.45	0.82	0.76	0.99	0.06	0.34	0.64	1.00
Nb-N ₄ /CNT(8,4)	0.40	0.63	0.24	0.55	0.19	0.45	0.45	0.82	0.77	1.03	0.08	0.34	0.65	1.01
Mo-N ₄ /CNT(8,4)	0.41	0.65	0.27	0.57	0.19	0.46	0.45	0.83	0.77	1.03	0.09	0.35	0.67	1.01
Ta-N ₄ /CNT(8,4)	0.40	0.64	0.25	0.55	0.19	0.45	0.46	0.83	0.78	1.04	0.08	0.36	0.66	1.02
Mn-N ₄ /CNT(8,4)	0.40	0.69	0.26	0.54	0.20	0.46	0.46	0.83	0.76	1.11	0.09	0.34	0.64	0.99
Hf-N ₄ /CNT(8,4)	0.40	0.64	0.23	0.50	0.16	0.44	0.45	0.82	0.77	1.00	0.06	0.35	0.65	1.02
Ru-C ₂ N ₂ /CNT(8,4)	0.42	0.66	0.27	0.58	0.19	0.48	0.46	0.83	0.76	1.09	0.09	0.34	0.67	1.02
Ta-C ₂ N ₂ /CNT(8,4)	0.42	0.64	0.24	0.55	0.17	0.46	0.46	0.83	0.78	1.02	0.08	0.35	0.67	1.02
Re-C ₂ N ₂ /CNT(8,4)	0.41	0.66	0.27	0.55	0.19	0.47	0.47	0.90	0.78	1.04	0.09	0.34	0.67	1.04
Os-C ₂ N ₂ /CNT(8,4)	0.40	0.67	0.27	0.58	0.19	0.47	0.45	0.84	0.78	1.07	0.09	0.34	0.68	1.04
Cr-C ₂ N ₂ /CNT(8,4)	0.42	0.65	0.26	0.55	0.19	0.44	0.46	0.83	0.77	1.12	0.09	0.33	0.65	1.01
Mn-C ₂ N ₂ /CNT(8,4)	0.42	0.69	0.27	0.56	0.19	0.46	0.44	0.83	0.75	1.13	0.09	0.33	0.64	1.01
Ti-C ₂ N ₂ /CNT(8,4)	0.42	0.63	0.26	0.53	0.16	0.45	0.45	0.82	0.77	0.99	0.06	0.32	0.65	1.01
Mo-C ₂ N ₂ /CNT(8,4)	0.41	0.65	0.26	0.57	0.16	0.45	0.46	0.83	0.78	1.04	0.08	0.34	0.66	1.00
W-C ₂ N ₂ /CNT(8,4)	0.41	0.64	0.26	0.56	0.16	0.46	0.48	0.83	0.77	1.05	0.09	0.33	0.67	1.01
V-C ₂ N ₂ /CNT(8,4)	0.42	0.65	0.26	0.55	0.19	0.47	0.47	0.83	0.78	1.10	0.08	0.34	0.65	1.00

Table S13. TS values of nitrate reduction reaction (NO₃ RR) intermediates for catalysts with diverse coordination environments, including TM-C₂N₂/CNT (8,4), TM-C₂N₂/CNT with different diameters (TM = Ti, V, Cr, Os, Ru), and TM-N₄/CNT (8,4).

Catalyst	*NO ₃	*NO ₃ H	*NO ₂	*NOOH	*NO	*NHO	*NOH	*NH ₂ O	*NHOH	*NH ₂ OH	*N	*NH	*NH ₂	*NH ₃
Ti-C ₂ N ₂ /CNT(6,2)	0.20	0.31	0.23	0.19	0.20	0.19	0.13	0.17	0.18	0.22	0.10	0.11	0.13	0.03
V-C ₂ N ₂ /CNT(6,2)	0.18	0.27	0.21	0.25	0.13	0.13	0.14	0.16	0.18	0.26	0.06	0.10	0.11	0.21
Cr-C ₂ N ₂ /CNT(6,2)	0.25	0.27	0.21	0.23	0.14	0.15	0.21	0.16	0.21	0.20	0.06	0.08	0.13	0.14
Ru-C ₂ N ₂ /CNT(6,2)	0.24	0.27	0.20	0.19	0.15	0.17	0.18	0.17	0.21	0.19	0.05	0.09	0.12	0.20
Os-C ₂ N ₂ /CNT(6,2)	0.24	0.26	0.18	0.19	0.15	0.19	0.18	0.16	0.16	0.26	0.05	0.10	0.12	0.17
Ti-C ₂ N ₂ /CNT(6,3)	0.27	0.30	0.24	0.21	0.15	0.18	0.22	0.17	0.18	0.21	0.09	0.11	0.13	0.15
V-C ₂ N ₂ /CNT(6,3)	0.25	0.28	0.23	0.23	0.13	0.13	0.18	0.16	0.17	0.25	0.06	0.10	0.12	0.14
Cr-C ₂ N ₂ /CNT(6,3)	0.26	0.28	0.20	0.27	0.15	0.13	0.19	0.16	0.18	0.20	0.05	0.09	0.13	0.10
Ru-C ₂ N ₂ /CNT(6,3)	0.22	0.28	0.22	0.24	0.09	0.17	0.18	0.16	0.20	0.19	0.05	0.09	0.09	0.19
Os-C ₂ N ₂ /CNT(6,3)	0.24	0.22	0.19	0.24	0.15	0.19	0.18	0.16	0.19	0.13	0.05	0.09	0.13	0.13
Ti-C ₂ N ₂ /CNT(10,5)	0.20	0.25	0.24	0.20	0.19	0.16	0.20	0.17	0.20	0.21	0.10	0.13	0.14	0.15
V-C ₂ N ₂ /CNT(10,5)	0.20	0.21	0.24	0.25	0.14	0.14	0.21	0.16	0.17	0.25	0.07	0.11	0.13	0.14
Cr-C ₂ N ₂ /CNT(10,5)	0.25	0.28	0.20	0.27	0.10	0.14	0.14	0.16	0.18	0.14	0.06	0.11	0.14	0.16
Ru-C ₂ N ₂ /CNT(10,5)	0.22	0.26	0.20	0.20	0.15	0.18	0.17	0.17	0.16	0.24	0.05	0.09	0.11	0.17
Os-C ₂ N ₂ /CNT(10,5)	0.17	0.24	0.18	0.23	0.16	0.18	0.12	0.15	0.20	0.28	0.05	0.10	0.10	0.10
Ti-C ₂ N ₂ /CNT(12,6)	0.26	0.19	0.23	0.22	0.20	0.16	0.19	0.17	0.19	0.20	0.10	0.13	0.14	0.10
V-C ₂ N ₂ /CNT(12,6)	0.21	0.26	0.19	0.18	0.14	0.14	0.20	0.17	0.19	0.20	0.07	0.11	0.13	0.03
Cr-C ₂ N ₂ /CNT(12,6)	0.21	0.26	0.22	0.29	0.14	0.18	0.19	0.13	0.17	0.19	0.06	0.10	0.13	0.16
Ru-C ₂ N ₂ /CNT(12,6)	0.20	0.25	0.22	0.19	0.15	0.17	0.11	0.17	0.15	0.25	0.05	0.08	0.13	0.09
Os-C ₂ N ₂ /CNT(12,6)	0.18	0.24	0.20	0.23	0.16	0.17	0.12	0.17	0.20	0.17	0.05	0.11	0.07	0.11
Ti-C ₂ N ₂ /CNT(14,7)	0.26	0.29	0.23	0.19	0.13	0.17	0.18	0.16	0.17	0.22	0.09	0.10	0.14	0.15
V-C ₂ N ₂ /CNT(14,7)	0.25	0.27	0.22	0.25	0.14	0.13	0.13	0.15	0.12	0.19	0.06	0.10	0.12	0.15
Cr-C ₂ N ₂ /CNT(14,7)	0.25	0.28	0.20	0.21	0.14	0.14	0.14	0.16	0.15	0.14	0.05	0.08	0.12	0.10
Ru-C ₂ N ₂ /CNT(14,7)	0.21	0.26	0.22	0.19	0.15	0.18	0.16	0.17	0.19	0.24	0.05	0.11	0.09	0.19
Os-C ₂ N ₂ /CNT(14,7)	0.27	0.27	0.20	0.19	0.13	0.14	0.12	0.17	0.14	0.23	0.05	0.09	0.12	0.03
Cr-N ₄ /CNT(8,4)	0.23	0.27	0.19	0.26	0.15	0.19	0.18	0.16	0.21	0.19	0.05	0.09	0.15	0.08
Ru-N ₄ /CNT(8,4)	0.23	0.26	0.18	0.22	0.12	0.15	0.15	0.16	0.21	0.20	0.05	0.07	0.12	0.12
Ti-N ₄ /CNT(8,4)	0.27	0.30	0.23	0.22	0.17	0.12	0.14	0.19	0.19	0.21	0.07	0.10	0.14	0.16
V-N ₄ /CNT(8,4)	0.25	0.28	0.20	0.25	0.08	0.16	0.19	0.17	0.21	0.20	0.06	0.09	0.12	0.13
Zr-N ₄ /CNT(8,4)	0.22	0.26	0.26	0.22	0.11	0.18	0.21	0.12	0.21	0.26	0.09	0.12	0.15	0.09
Nb-N ₄ /CNT(8,4)	0.25	0.34	0.22	0.20	0.15	0.16	0.15	0.19	0.21	0.22	0.07	0.10	0.13	0.14
Mo-N ₄ /CNT(8,4)	0.25	0.34	0.22	0.20	0.15	0.16	0.15	0.19	0.21	0.22	0.07	0.10	0.13	0.14
Ta-N ₄ /CNT(8,4)	0.26	0.24	0.22	0.24	0.15	0.16	0.20	0.18	0.19	0.20	0.07	0.10	0.12	0.20
Mn-N ₄ /CNT(8,4)	0.23	0.28	0.25	0.16	0.09	0.14	0.12	0.15	0.23	0.19	0.05	0.08	0.10	0.15
Hf-N ₄ /CNT(8,4)	0.20	0.30	0.25	0.27	0.18	0.18	0.14	0.19	0.20	0.24	0.08	0.10	0.14	0.20
Ru-C ₂ N ₂ /CNT(8,4)	0.22	0.26	0.19	0.24	0.15	0.17	0.18	0.16	0.23	0.24	0.06	0.09	0.11	0.19
Ta-C ₂ N ₂ /CNT(8,4)	0.25	0.25	0.22	0.24	0.16	0.15	0.21	0.18	0.18	0.21	0.07	0.10	0.12	0.13
Re-C ₂ N ₂ /CNT(8,4)	0.20	0.27	0.20	0.21	0.15	0.14	0.18	0.07	0.17	0.19	0.06	0.11	0.11	0.14
Os-C ₂ N ₂ /CNT(8,4)	0.24	0.25	0.18	0.24	0.15	0.15	0.10	0.16	0.19	0.17	0.05	0.10	0.12	0.16
Cr-C ₂ N ₂ /CNT(8,4)	0.25	0.28	0.21	0.25	0.14	0.11	0.21	0.16	0.20	0.20	0.06	0.10	0.13	0.15
Mn-C ₂ N ₂ /CNT(8,4)	0.25	0.34	0.20	0.26	0.15	0.16	0.04	0.16	0.26	0.24	0.05	0.12	0.16	0.15
Ti-C ₂ N ₂ /CNT(8,4)	0.26	0.23	0.23	0.24	0.19	0.17	0.14	0.18	0.20	0.24	0.09	0.13	0.12	0.13
Mo-C ₂ N ₂ /CNT(8,4)	0.26	0.25	0.22	0.22	0.12	0.10	0.14	0.16	0.18	0.19	0.07	0.09	0.13	0.10
W-C ₂ N ₂ /CNT(8,4)	0.19	0.25	0.22	0.25	0.12	0.16	0.18	0.17	0.21	0.18	0.05	0.08	0.11	0.09
V-C ₂ N ₂ /CNT(8,4)	0.26	0.28	0.24	0.22	0.14	0.13	0.18	0.17	0.19	0.23	0.06	0.11	0.12	0.16

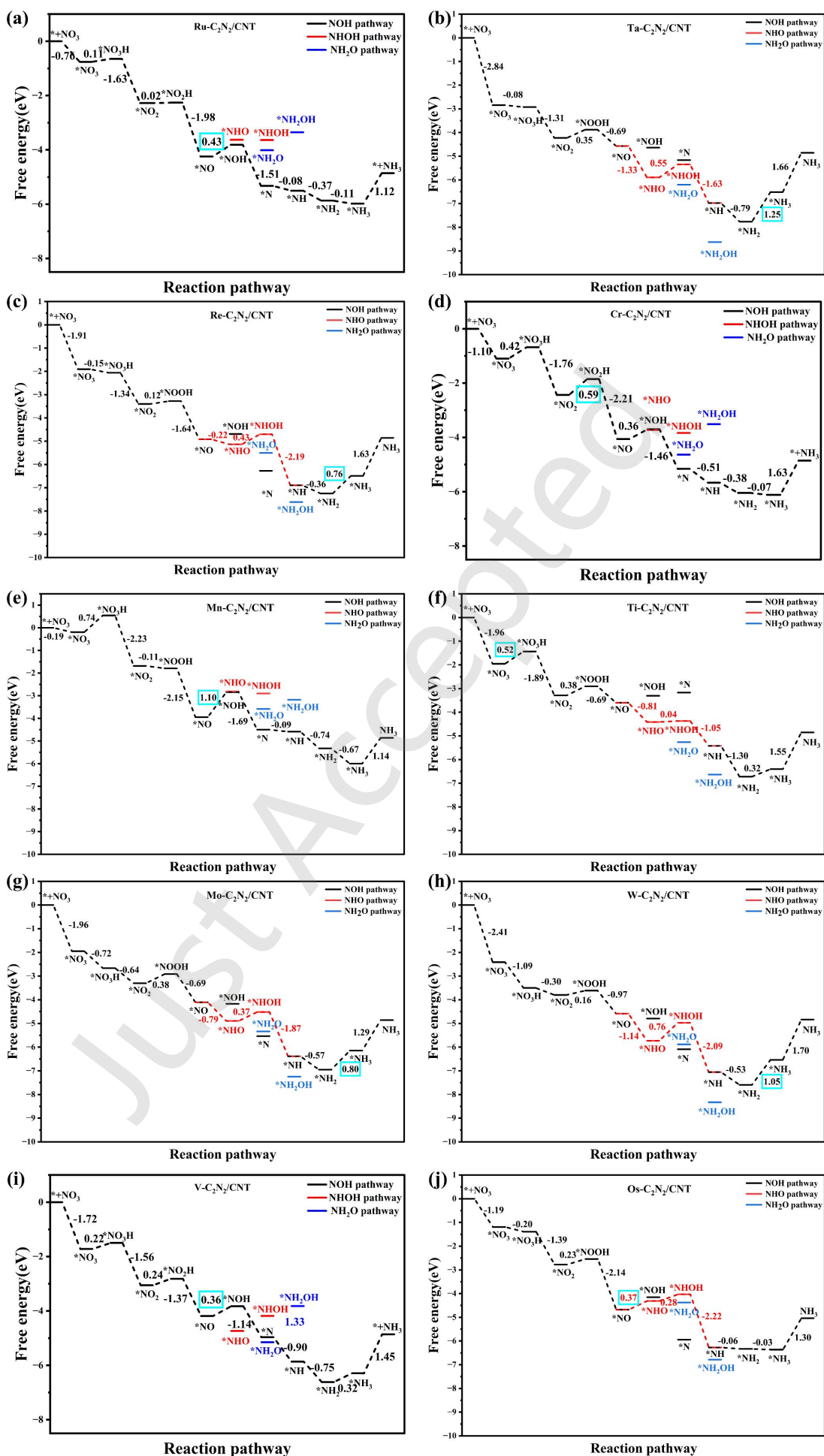


Figure S1. Free energy diagrams for the NO_3^- reduction reaction on $\text{TM-C}_2\text{N}_2/\text{CNT}$ ($\text{M} = \text{Ru}, \text{Ta}, \text{Re}, \text{Cr}, \text{Mn}, \text{Ti}, \text{Mo}, \text{W}, \text{V}, \text{Os}$).

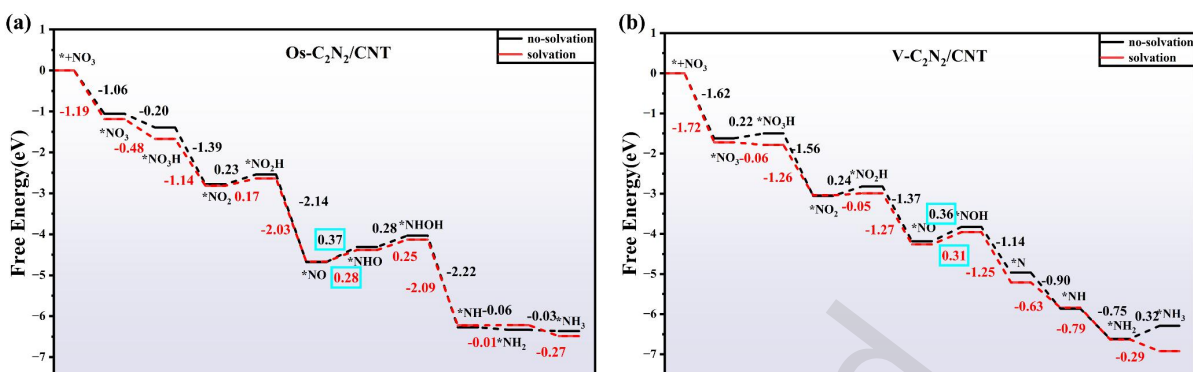


Figure S2. Free energy reaction pathway diagrams of $\text{V-C}_2\text{N}_2/\text{CNT}$ and $\text{Os-C}_2\text{N}_2/\text{CNT}$ considering the effect of solvation energy.

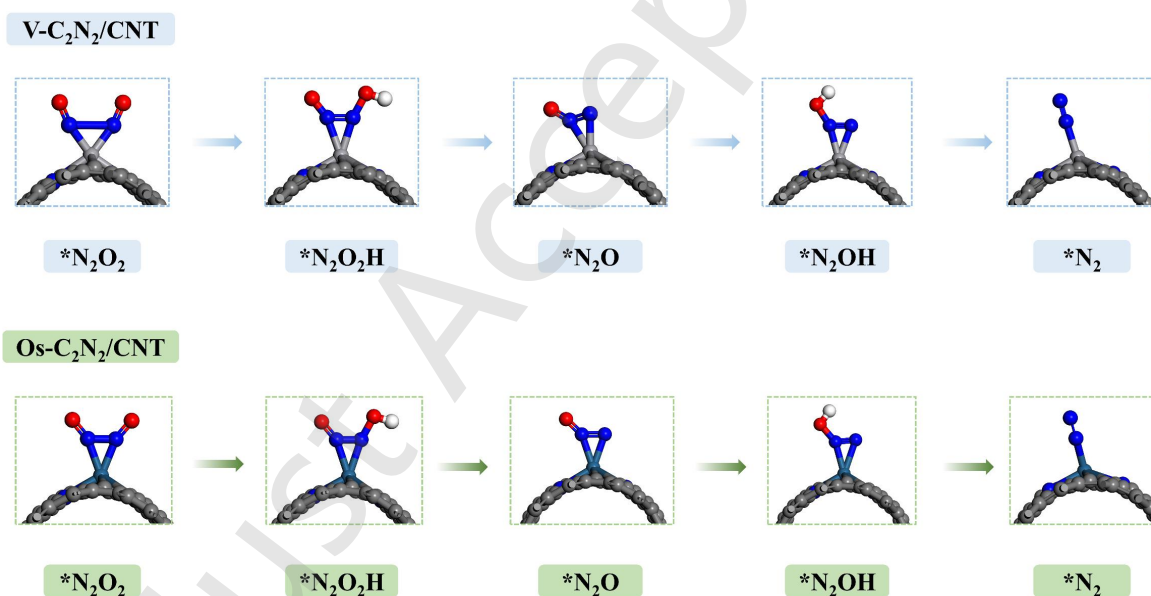


Figure S3. Corresponding structures of NO_3RR intermediates (via NO -dimer pathway) adsorbed on $\text{V-C}_2\text{N}_2/\text{CNT}$ and $\text{Os-C}_2\text{N}_2/\text{CNT}$, respectively.

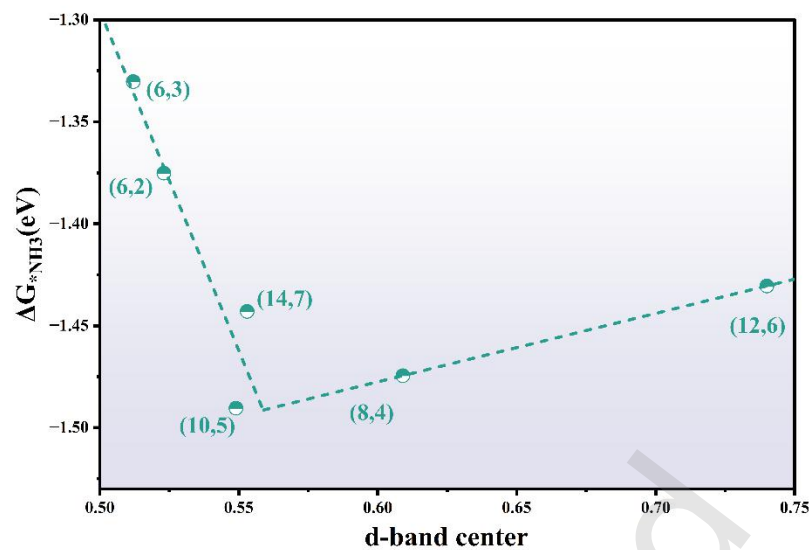


Figure S4. Correlation between the d-band center of the active V site and $\Delta G_{\text{NH}_3}^*$ on V-C₂N₂/CNT with different diameters.

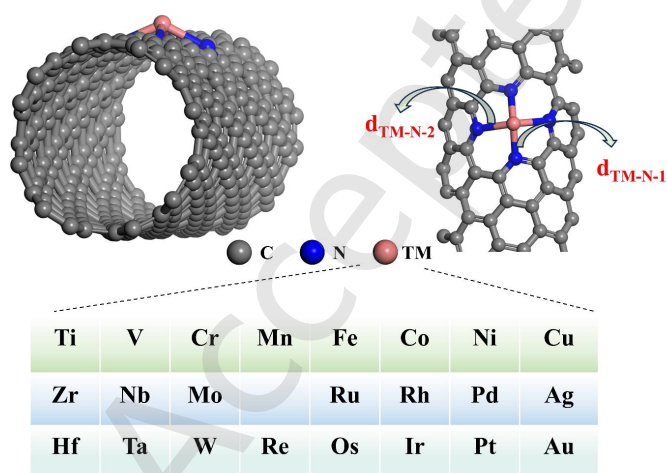


Figure S5. Front view and top view of the atomic structure of N₄/CNT. Atomic labels: C (gray), N (blue), TM (pink).

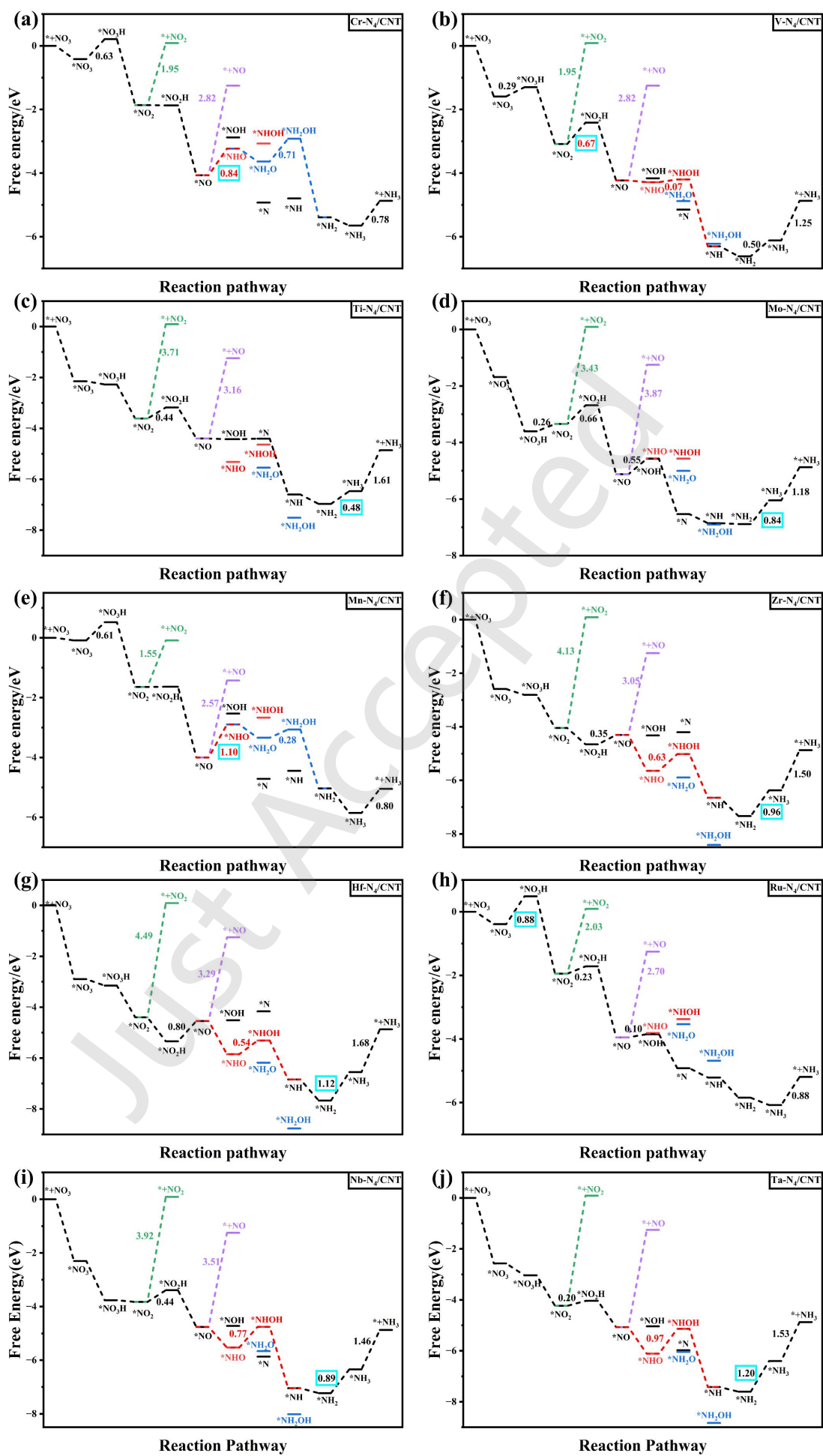
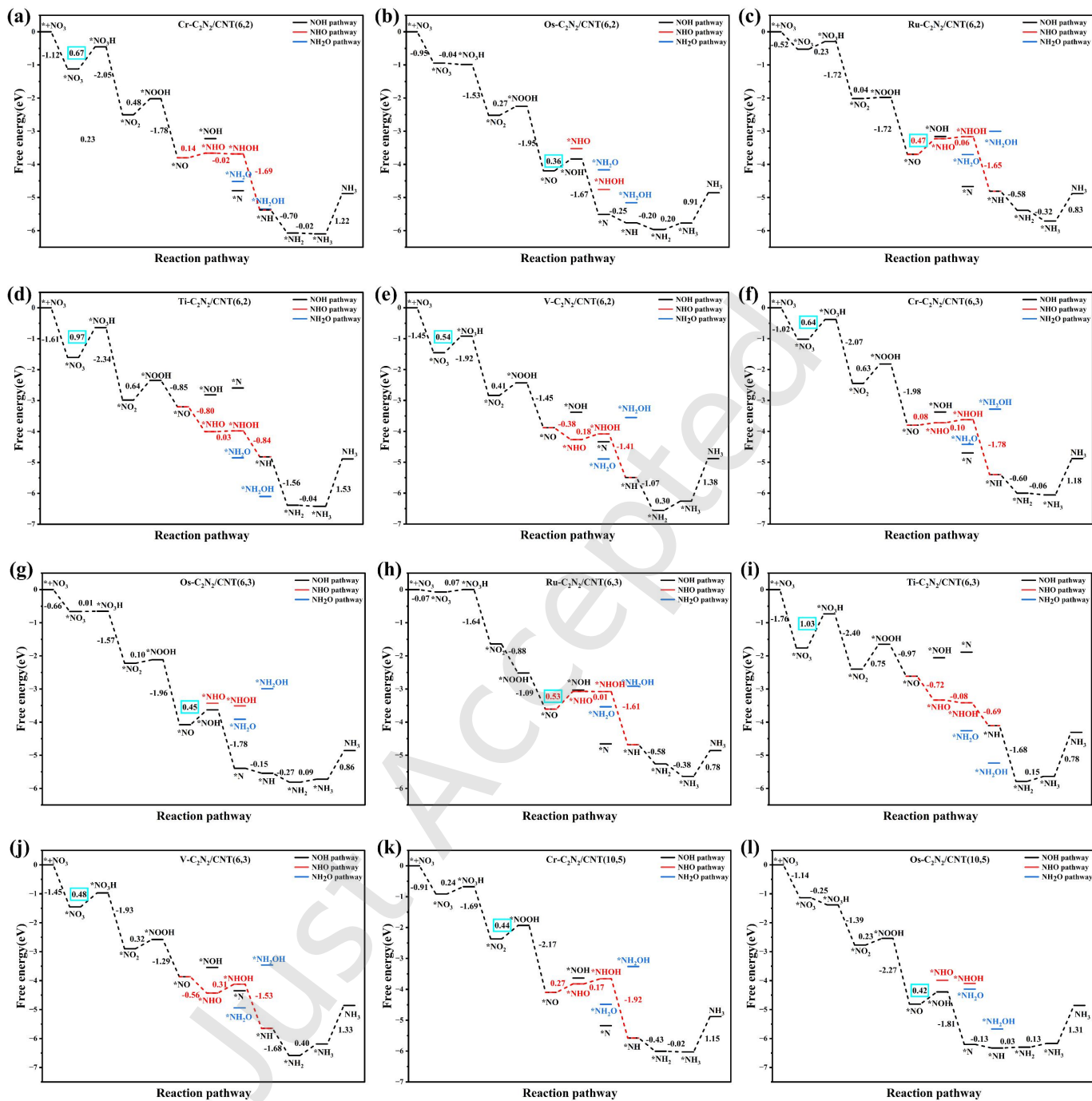


Figure S6. Free energy diagrams for the NO_3^- reduction reaction on TM- N_4/CNT ($M = \text{Cr}, \text{V}, \text{Ti}, \text{Mo}, \text{Mn}, \text{Zr}, \text{Hf}, \text{Ru}, \text{Nb}, \text{Ta}$).



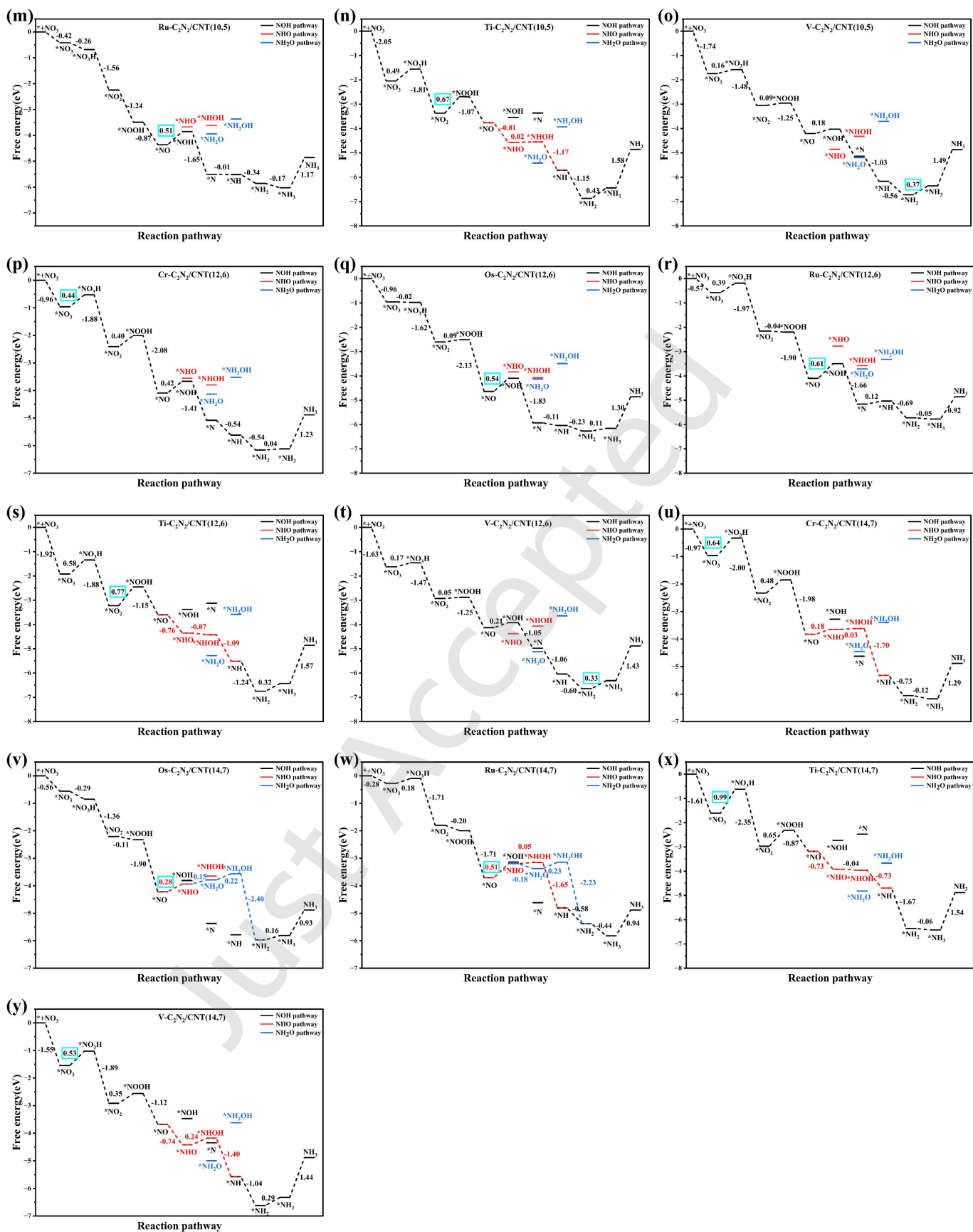


Figure S7. Free energy diagrams for the NO_3^- reduction reaction on TM- $\text{C}_2\text{N}_2/\text{CNT}$ with varying diameters (TM = Cr, Os, Ru, Ti, V)

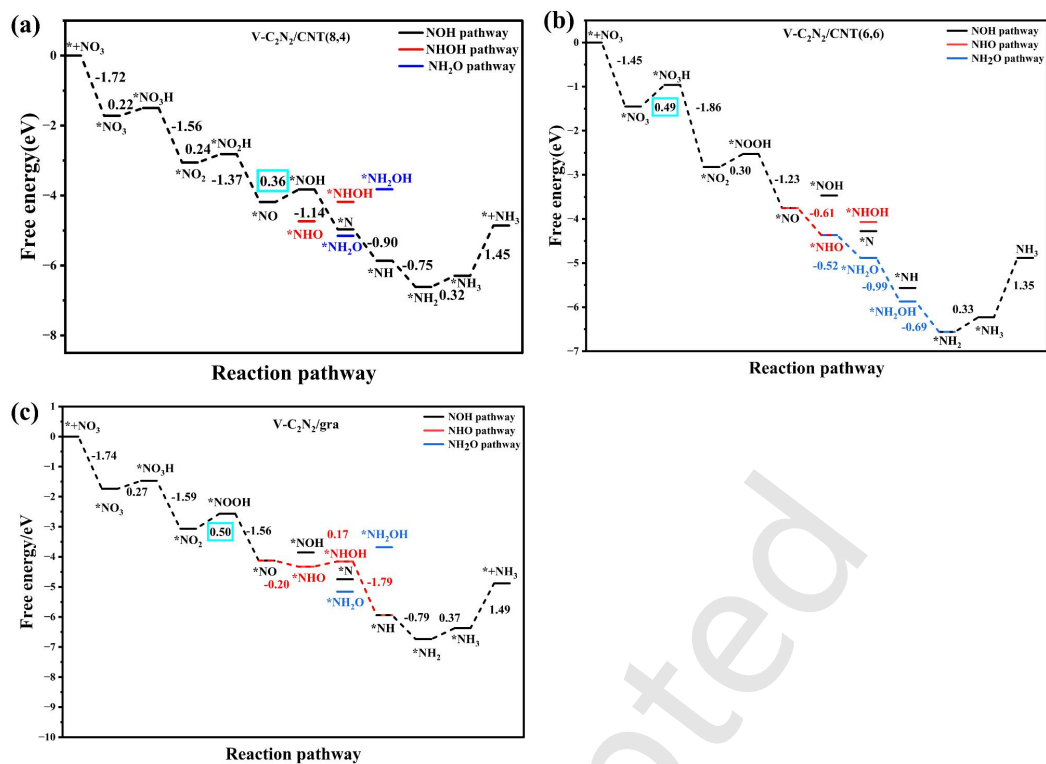


Figure S8. Gibbs free energy profile for the reduction of NO_3^- to NH_3 on $\text{V-C}_2\text{N}_2/\text{CNT}(8,4)$, $\text{V-C}_2\text{N}_2/\text{CNT}(6,6)$, $\text{V-C}_2\text{N}_2/\text{gra}$.

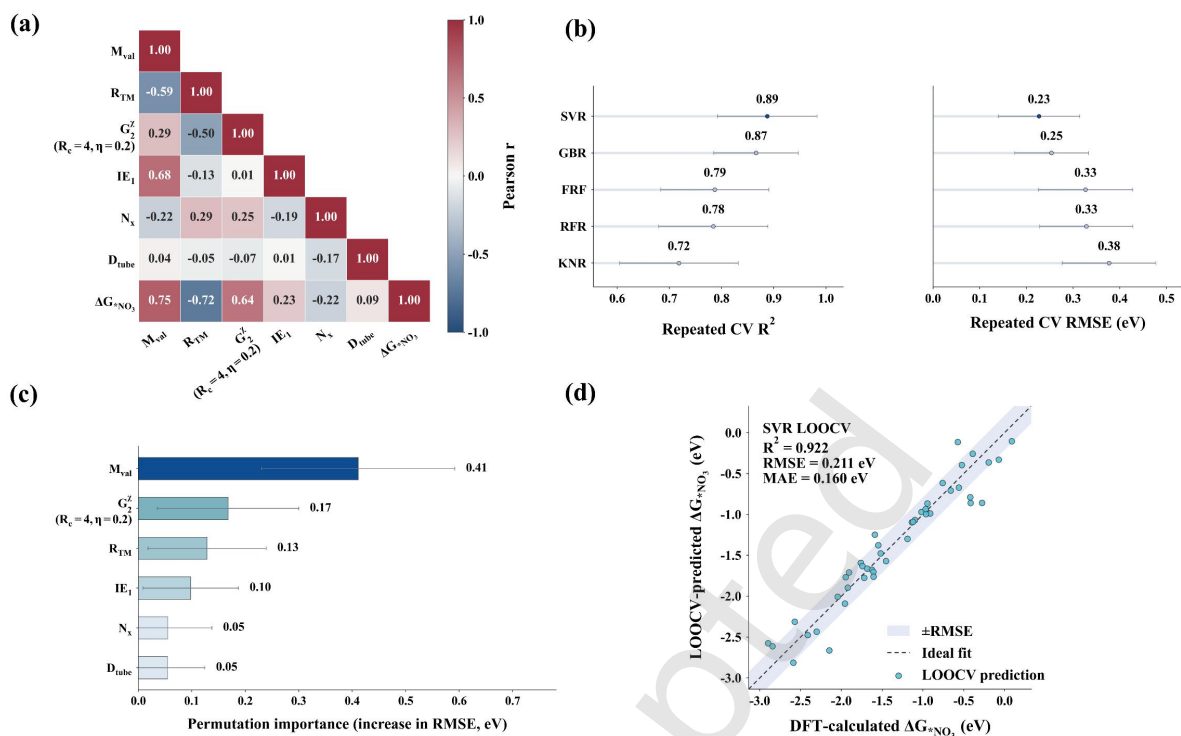


Figure S9. Machine learning analysis of $\Delta G_{\text{NO}_3}^*$ after including wACSF-inspired radial local atomic environment descriptors.

(a) Pearson correlation matrix of the retained descriptors and $\Delta G_{\text{NO}_3}^*$ after correlation filtering, including the retained radial descriptor $G_2^x(R_c = 4 \text{ \AA}, \eta = 0.2)$. Red and blue colors represent positive and negative correlations, respectively. (b) Comparison of the predictive performance of different regression models based on repeated five-fold cross-validation, using R^2 and RMSE as evaluation metrics. Error bars denote the standard deviations over repeated cross-validation splits. (c) Cross-validated permutation importance of the retained descriptors for the SVR model, expressed as the RMSE increase after feature permutation. (d) Comparison between DFT-calculated and LOOCV-predicted $\Delta G_{\text{NO}_3}^*$ values using the SVR model. The dashed line represents the ideal fit, and the shaded region denotes $\pm \text{RMSE}$.