

Regulating the coordination environment of single-atom catalysts anchored on nitrogen-doped graphene for efficient nitrogen reduction reaction

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Density functional theory calculation

1.1 Formation energy and binding energy of Mo-N₄-SACs

The stabilities of different Mo-N₄-SAC structures were quantified by calculating the formation energies (E_f) as follows:

$$E_f = (E_{\text{Mo-N}_4\text{-SAC}} - n_C\mu_C - n_N\mu_N - n_H\mu_H - n_{\text{Mo}}\mu_{\text{Mo}})/M,$$

where is $E_{\text{Mo-N}_4\text{-SAC}}$ the total energy of the Mo-N₄-SAC, and n_C , n_N , n_H and n_{Mo} are the atom numbers of C, N, H and Mo. μ_C , μ_N , μ_H and μ_{Mo} are defined as the energies of a carbon atom in graphene, the energy of half N₂ molecule and H₂ molecule, and the energy of the isolated Mo atoms in a bulk, respectively. M is the total number of atoms in Mo-N₄-SAC.

The binding energy (E_b) of Mo atom with porous graphene is calculated according to the following equation:

$$E_b = (E_{\text{Mo-N}_4\text{-SAC}} - E_S - E_{\text{Mo}}),$$

where $E_{\text{A-B@S}}$, E_S , and E_{Mo} are the energies of Mo-N₄-SAC, substrate, and the isolated Mo atom, respectively.

The electrochemical stability of Mo-N₄-SAC structures were evaluated by dissolution potential (U_{diss}) which is calculated by equation:

$$U_{\text{diss}} = U_{\text{diss}}^\circ(\text{metal, bulk}) - E_f/ne,$$

where $U_{\text{diss}}^\circ(\text{metal, bulk})$, E_f and n are the standard dissolution potential of bulk metal, formation energy and the number of electrons involved in the dissolution, respectively.

The U_{diss} of Mo-ACG, Mo-AC-edge, Mo-ZZG and Mo-ZZ-edge are 0.08, 0.06, 0.09, and 0.05, respectively.

The formation energies (E_f) of the doping systems by substituting N with the O atom or S atom were calculated. E_f is defined as follows:

$$E_f = (E_{\text{O/S(1/2)-ZZ-edge}} - n_C\mu_C - n_N\mu_N - n_H\mu_H - n_{\text{Mo}}\mu_{\text{Mo}} - n_{\text{s/o}}\mu_{\text{s/o}})/M,$$

where $E_{\text{O/S(1/2)-ZZ-edge}}$ is the total energy of O/S-doped Mo-ZZ-edge system, $n_{\text{s/o}}$ are the atom numbers of S or O, $\mu_{\text{S/O}}$ is the chemical potentials of single S or O atom. In addition, μ_S is the energy per S atom in its reference phase, and μ_O is defined as $\mu_{\text{O}_2}/2$.

1.2 Calculation method of NRR activity

The change in free energy is calculated by the following formula:

$$\Delta G = \Delta E + \Delta E_{\text{ZPE}} - T\Delta S + \Delta G_{\text{U}} + \Delta G_{\text{pH}}$$

Where ΔE refers to the energy obtained by DFT calculation, where U is $\Delta G_{\text{U}} = -n \times e \times U$, the electrode potential, e is the number of transferred electrons; $\Delta G_{\text{pH}} = -k_{\text{B}} \times T \times \ln[\text{H}^+] = -k_{\text{B}} \times T \times \text{pH} \times \ln 10$, in this work, $\text{pH} = 0$ was employed. ΔE_{ZPE} is the difference between the zero point energy (ZPE) of adsorbed intermediates and gas phase intermediates, T is the temperature (298.15 K), and ΔS is the change of entropy between the adsorption state and the gas phase.

The potential-determining step (PDS), which can be used to evaluate the catalytic activity of catalysts, is identified as the elementary reaction step with the largest increase in free energy ΔG . The applied potential of at least $U = -\Delta G_{\text{max}}/e$ to make every step in the hypothetical mechanism exothermal can be an estimate of the onset potential of the overall reaction.

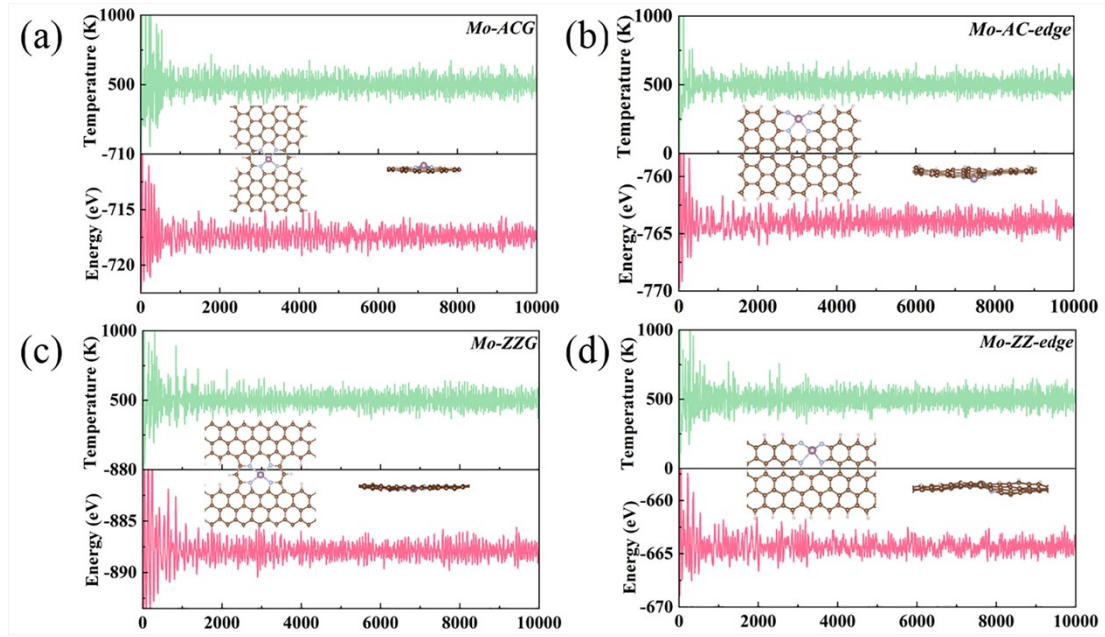


Fig. S1. Temperature and energy fluctuations of (a) Mo-ACG, (b) Mo-AC-edge, (c) Mo-ZZG, and (d) Mo-ZZ-edge. The insets illustrate the top and side view of Mo-N₄-SACs after 10 ps AIMD simulation at T = 500 K.

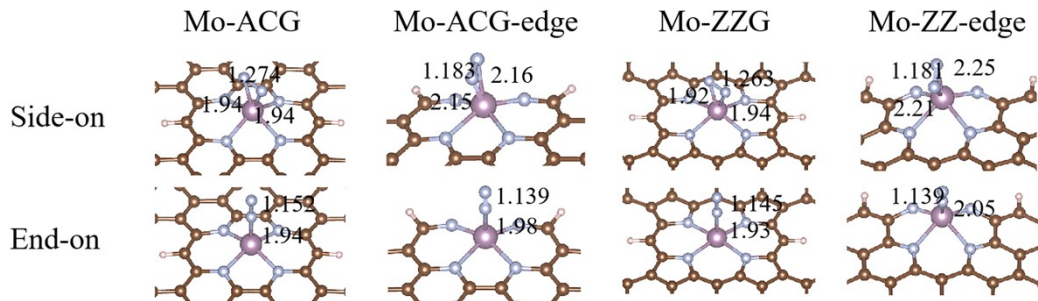


Fig. S2. Computed bond lengths of N-TM ($d_{\text{N-TM}}$, Å) and N-N ($d_{\text{N-N}}$, Å) of adsorbed N₂ with end-on and side-on adsorption configurations.

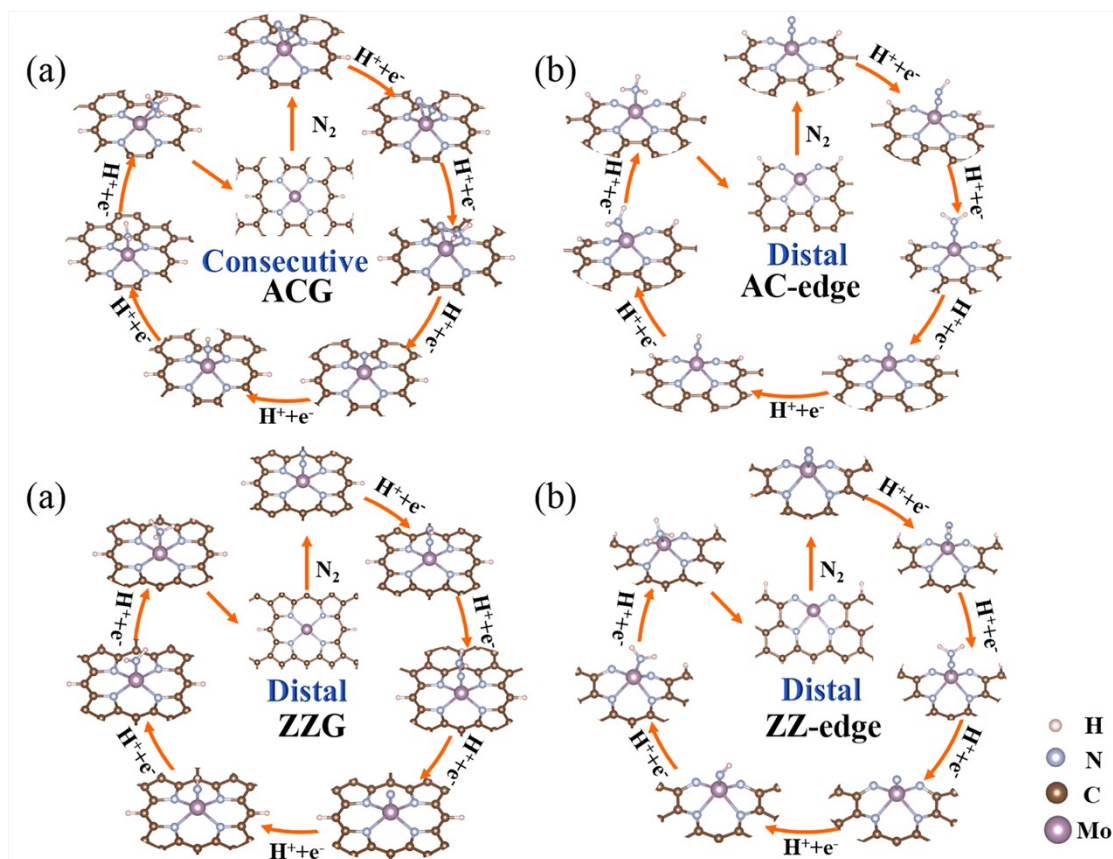


Fig. S3. Optimized structures of the involved NRR species on the (a) Mo-ACG, (b) Mo-AC-edge, (c) Mo-ZZG, and (d) Mo-ZZ-edge via the optimal pathway.

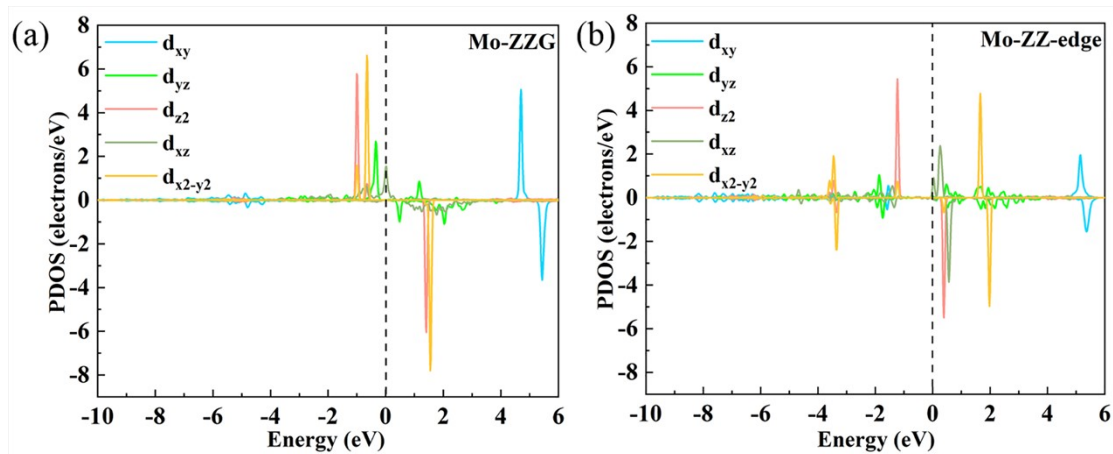


Fig. S4. Projected density of states (PDOS) of Mo 4d for Mo-ZZG and Mo-ZZ-edge. Positive and negative PDOS values represent spin-up and spin-down components, respectively.

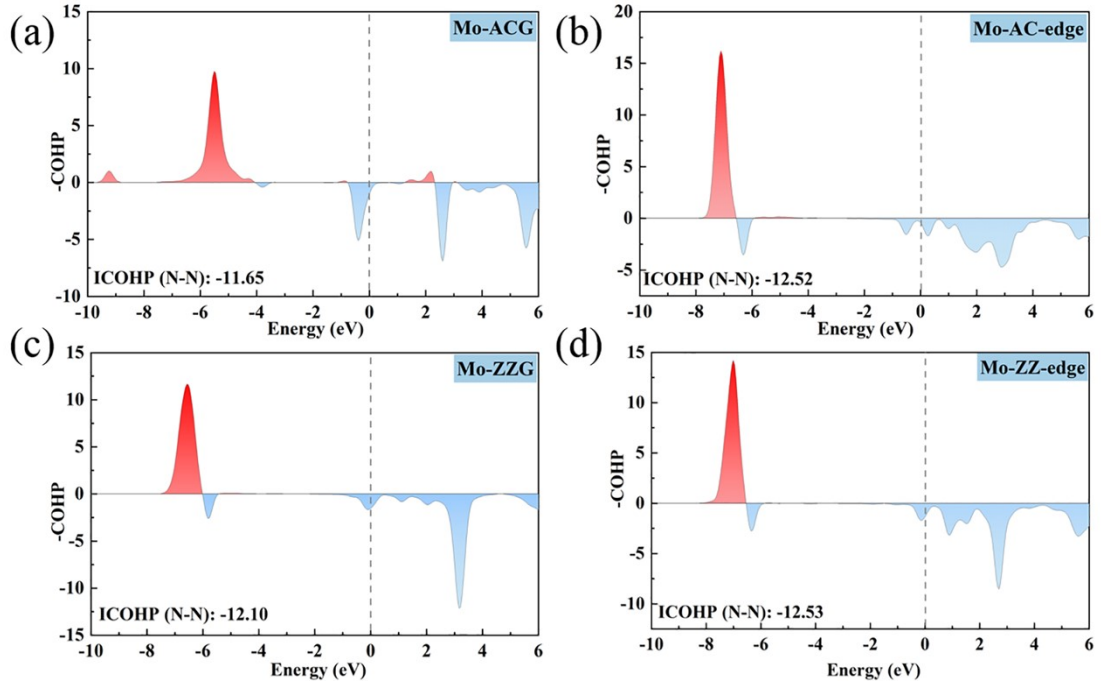


Fig. S5. Crystal orbital Hamilton population (COHP) between nitrogen atoms of N_2 on (a) Mo-ACG, (b) Mo-AC-edge, (c) Mo-ZZG, and (d) Mo-ZZ-edge.

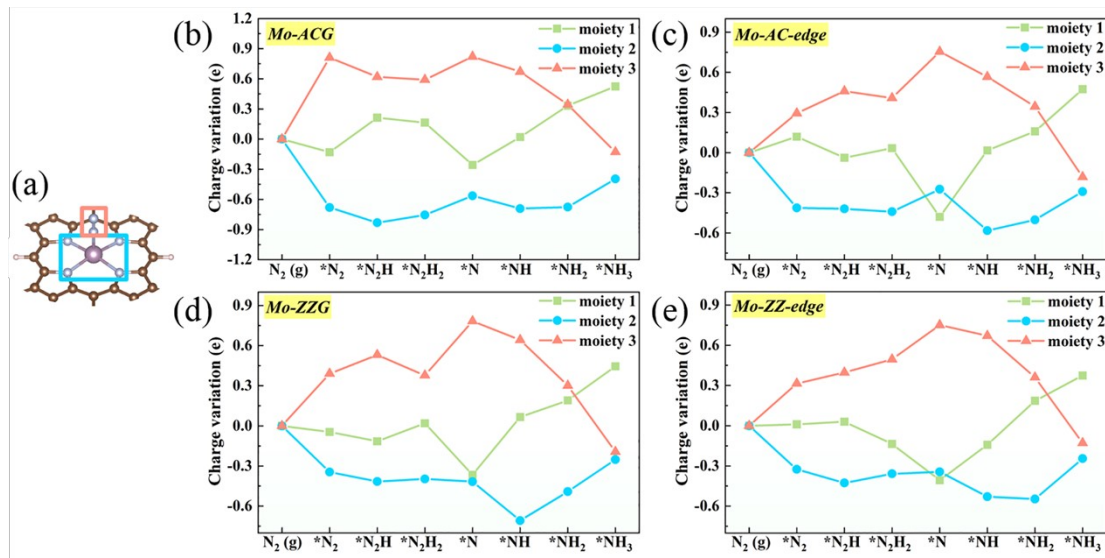


Fig. S6. (a) Schematic structure of three moieties for $*N_xH_y$ adsorbed on Mo- N_4 -SACs. The charge variations of the three moieties on (a) Mo-ACG, (b) Mo-AC-edge, (c) Mo-ZZG, (d) Mo-ZZ-edge along the optimal pathway.

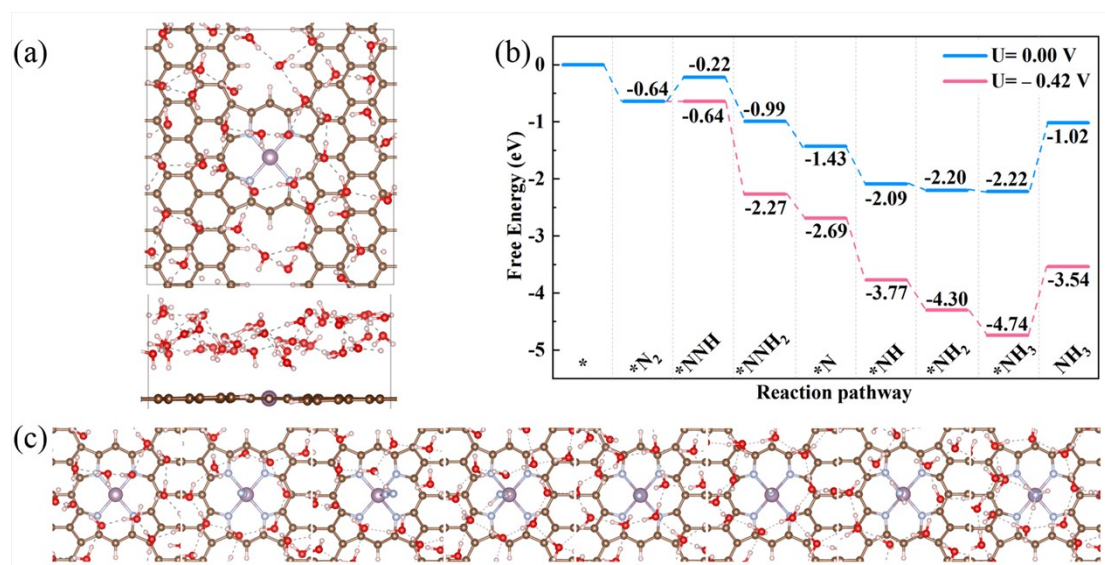


Fig. S7. Under implicit + explicit solvation condition, (a) top view and side view of Mo-ZZG; (b) Free energy diagram of NRR via the most favorable pathway on Mo-ZZG and (c) corresponding intermediate structures.

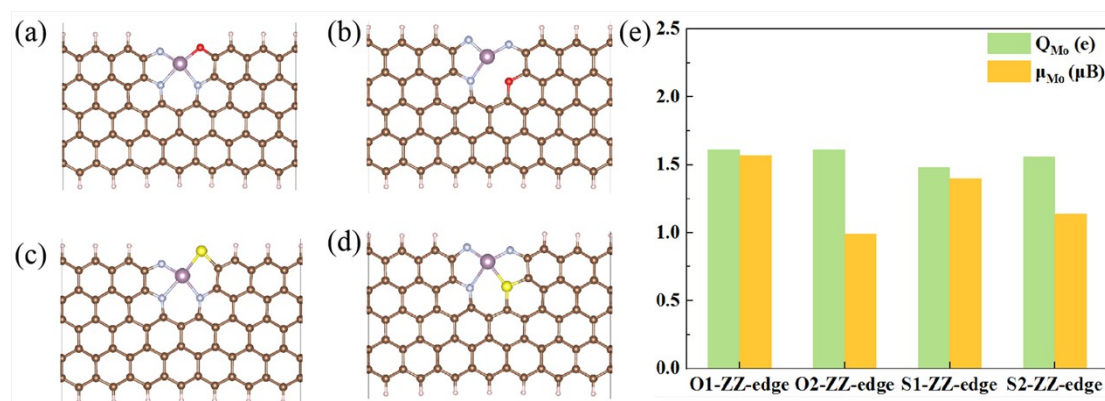


Fig. S8. (a) The optimized structural models of the O1-ZZ-edge, O2-ZZ-edge, S1-ZZ-edge, and S2-ZZ-edge. Color code: the brown, grey, purple, red, yellow, and pink balls refer to C, N, Co, O, S, and H atoms, respectively. (b) Bader charge transfer and magnetic moment of Mo atom in doped-ZZ-edge catalysts.

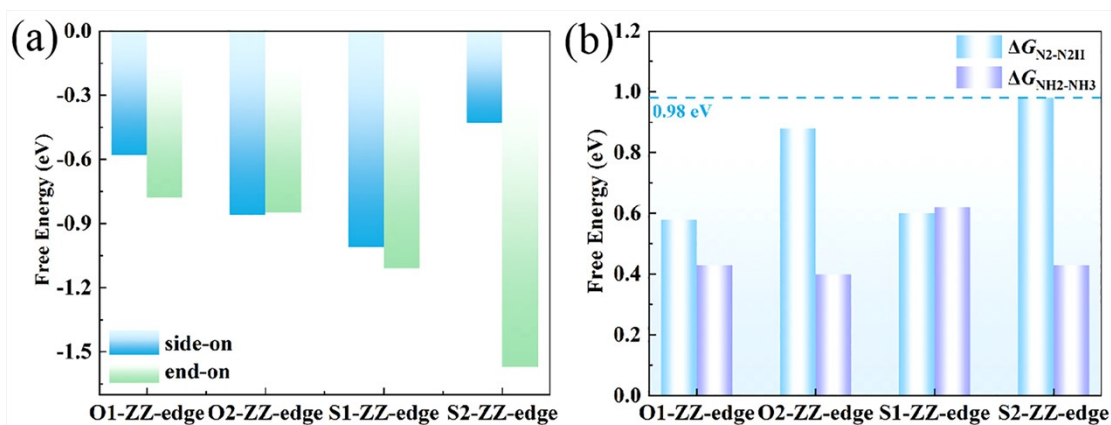


Fig. S9 (a) Gibbs free energy change $\Delta G^*_{N_2}$. (b) Free energy change of the first protonation step (ΔG_{N_2-NH}) considering end-on configurations, which is compared to the free energy change of the other crucial NRR step ($\Delta G_{NH_2-NH_3}$).

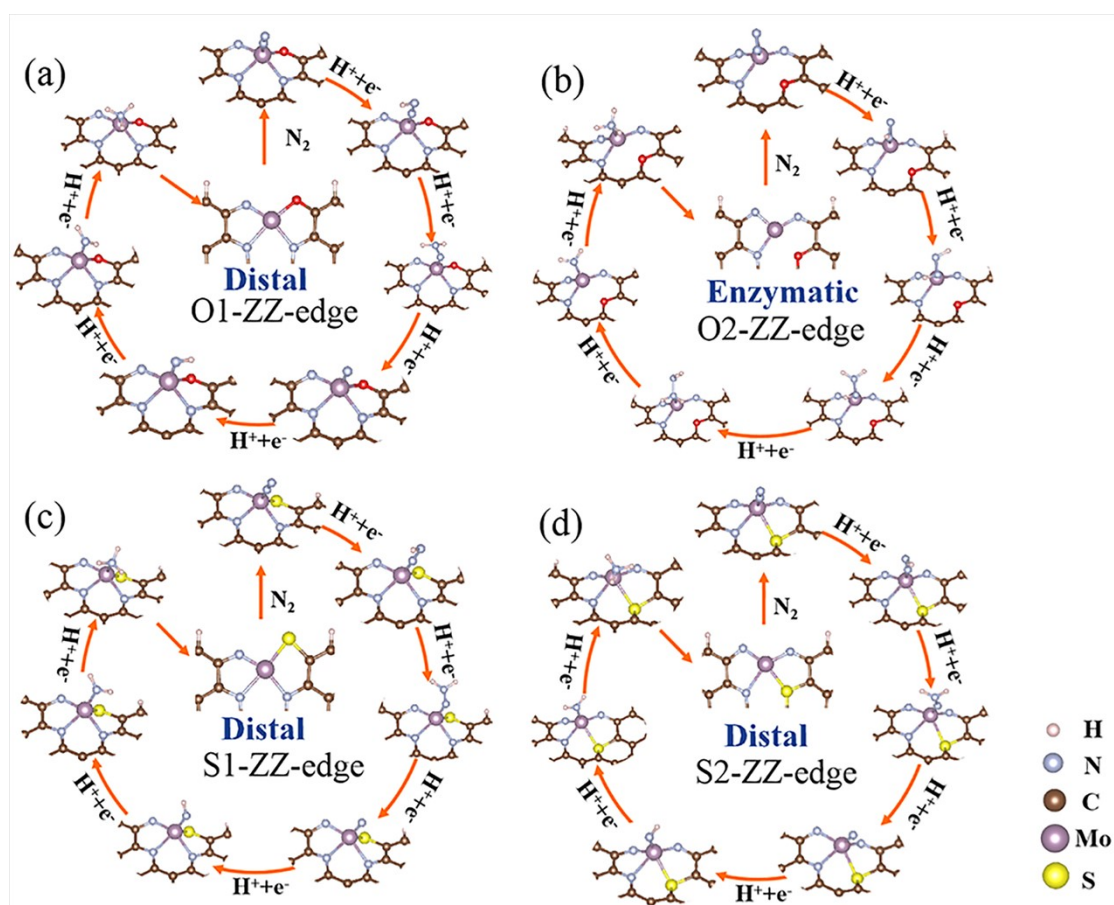


Fig. S10. Optimized structures of the involved NRR species on the (a) O1-ZZ-edge, (b) O2-ZZ-edge, (c) S1-ZZ-edge, and (d) S2-ZZ-edge.

Table S1. The calculated energy (E , eV), zero-point energy (E_{ZPE} , eV), the product (TS, eV) of temperature ($T = 298.15$ K) and entropy (S), and Gibbs free energy (G , eV).

	E	E_{ZPE}	TS	G
N ₂	-16.64	0.15	0.59	-17.08
H ₂	-6.77	0.28	0.42	-6.91
NH ₃	-19.73	0.91	0.60	-19.42