Supporting Information

Theoretical screening of single atoms anchored on defective graphene for electrocatalytic N_2 reduction reactions: a DFT study

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Table S1. Computed adsorption energies of single Mo atom, N_2 and NNH on MoN_3 555-777 graphene sheet using different supercell sizes.

Supercell	**5×5**	**6×6**
$\boldsymbol{E_{ads}}$**(Mo)**	**-7.23**	**-7.14**
$\boldsymbol{E_{ads}}$**(N_2)**	**-1.14**	**-1.22**
$\boldsymbol{E_{ads}}$**(NNH)**	**-1.09**	**-1.14**

Table S2. Computed N_2, N_2H and NH_2 adsorption energies on the surface of MoN_3 555-777 graphene sheets by PBE and RPBE functionals.

Functional	PBE	RPBE
E_{ads} (N_2)	-1.01	-0.86
E_{ads} (N_2H)	-2.83	-2.63
E_{ads} (NH_2)	-4.07	-3.82

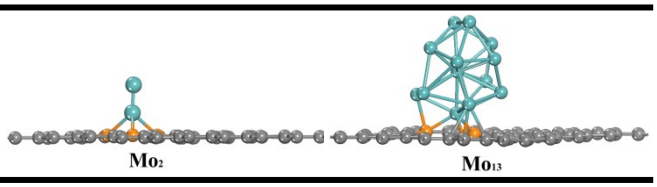
Table S3. Calculated zero point energies and entropy of different adsorption species. The entropies and vibrational frequencies of molecules in the gas phase were taken from the NIST database.

Species	E_{ZPE} (eV)	TS (eV)
N_2	0.15	0.58
H_2	0.27	0.42
NH_3	0.58	0.56
*N-*N	0.20	0.12
*N-*NH	0.48	0.13
*NH -*NH	0.80	0.16
NH-NH_2	1.14	0.18
NH_2-NH_2	1.38	0.19
NH_2-NH_3	1.69	0.21
*N-N	0.21	0.14
*N-NH	0.49	0.13
*NH-NH	0.80	0.12
*NH-NH_2	1.10	0.20
*NH_2-NH_2	1.47	0.17
*NH_2-NH_3	1.63	0.23
*N-NH_2	0.72	0.11
*N-NH_3	1.03	0.21
*NH	0.34	1.10
*NH_2	0.66	0.14
*NH_3	1.02	0.17

Table S4. The adsorption energy (E_{ads}) and free-energy variation (ΔG) of H and N_2 on MoN_3@555-777 graphene sheets.

Adsorbate	E_{ads} (eV)	ΔG (eV)
H	**-0.80**	**-0.55**
N_2-side-on	**-1.14**	**-0.63**
N_2-end-on	**-1.01**	**-0.51**

Table S5. Computed adsorption energies of N_2 and N_2H on Mo_2 and Mo_{13} cluster.

Cluster		
$E_{ads}(N_2)$/eV	-0.90	-1.03
$E_{ads}(N_2H)$/eV	-1.59	-2.22

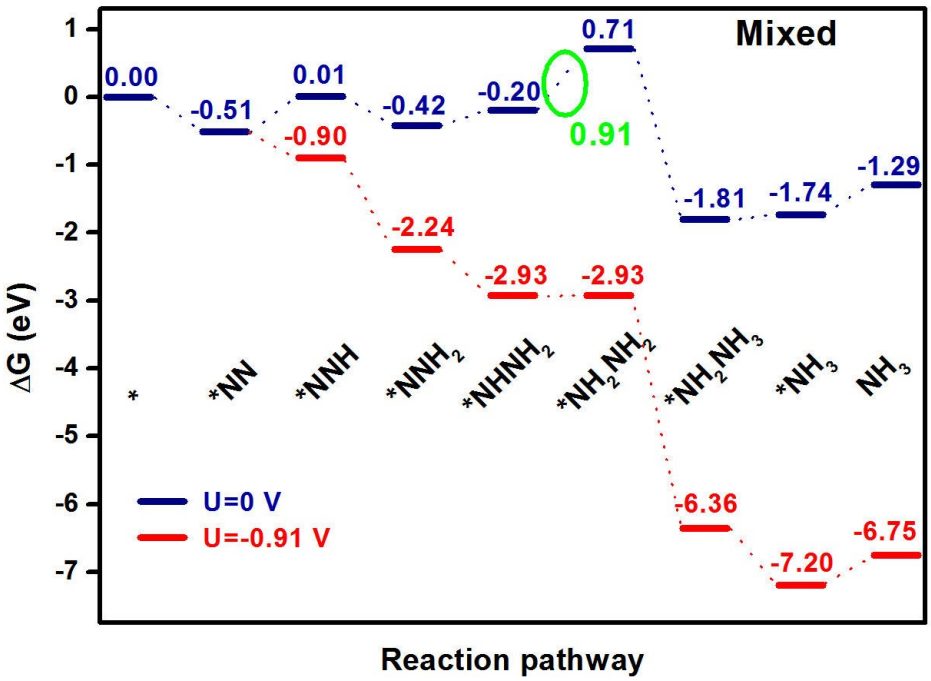


Fig. S1 Free-energy profiles at zero potential (blue line) and onset-potential (red line) along the mixed mechanism of N_2 reduction proceeded on MoN_3@555-777 graphene sheets.

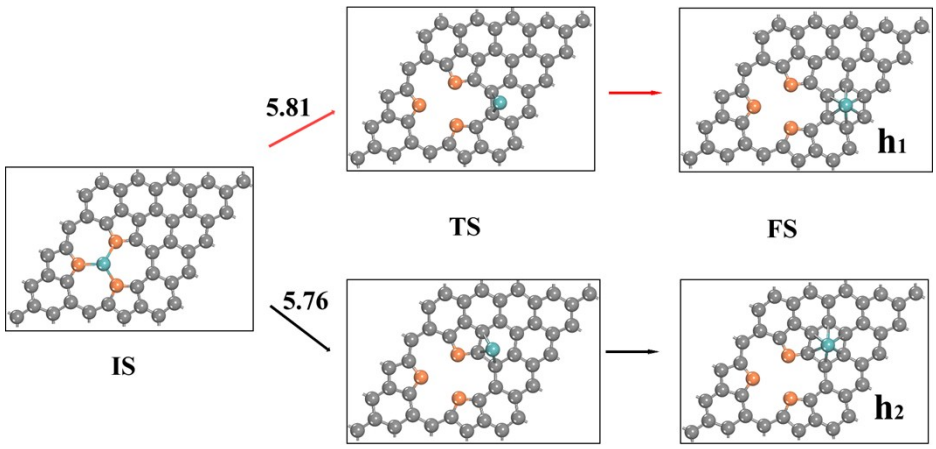


Fig. S2 The minimum energy path (MEP) for the diffusion of the adsorbed Mo atom from the defect binding site to a neighboring hollow site.

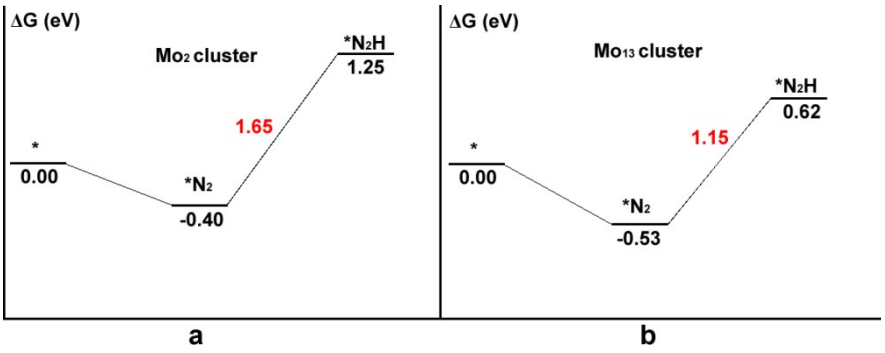


Fig. S3 Calculated free energy diagrams for N_2 adsorption and protonation of N_2 on (a) Mo_2 and (b) Mo_{13}.

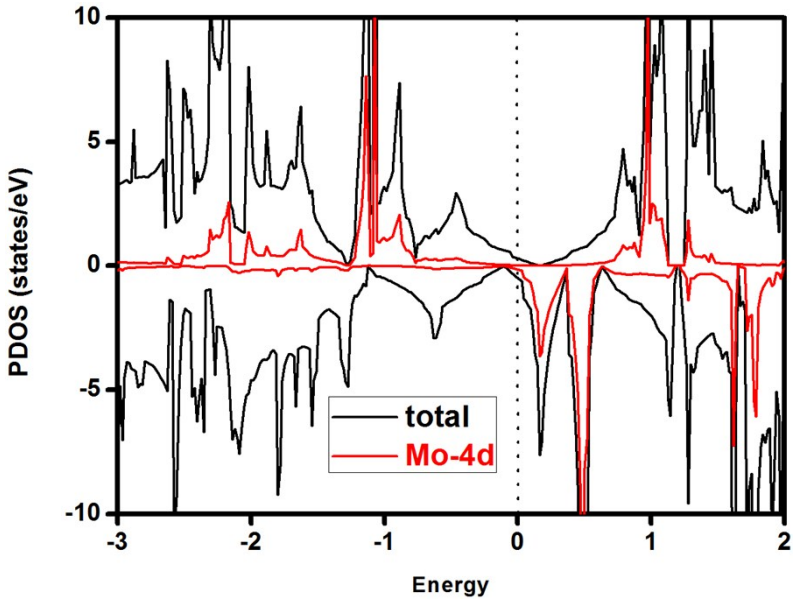


Fig. S4 DOS of MoN_3@555-777 graphene sheets and PDOS of Mo 4d orbitals

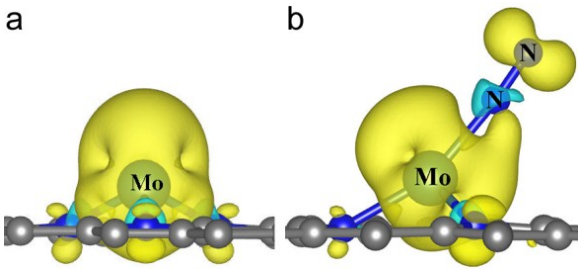


Fig. S5 Spin-polarized density for (a) MoN_3 555-777 graphene sheet and (b) N_2 adsorption on MoN_3@555-777 graphene sheets. The isovalue is set to be 0.004 e/Å^3.

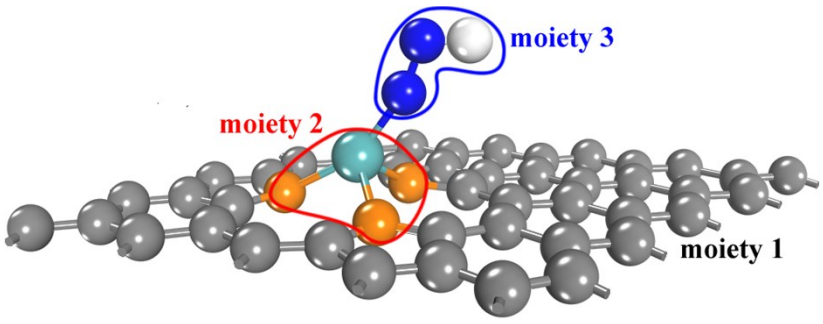


Fig. S6 Definition of three moieties of N_xH_y adsorbed MoN_3 by using N_2H as mode.

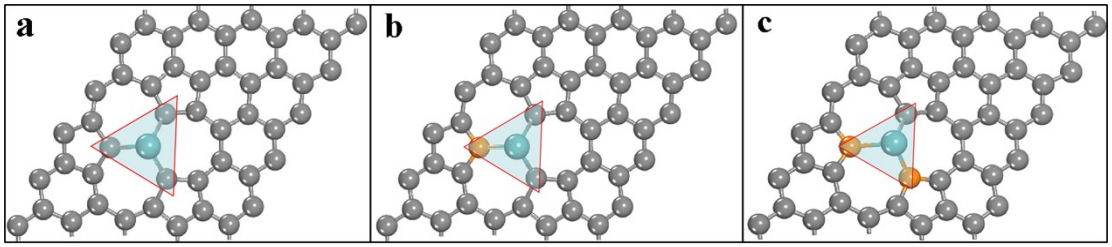


Fig. S7 Structures of (a) MoC_3, (b) MoC_2N_1 and (c) MoC_1N_2 active centers. Gray, cyan and orange balls represent the C, Mo and N atoms, respectively.

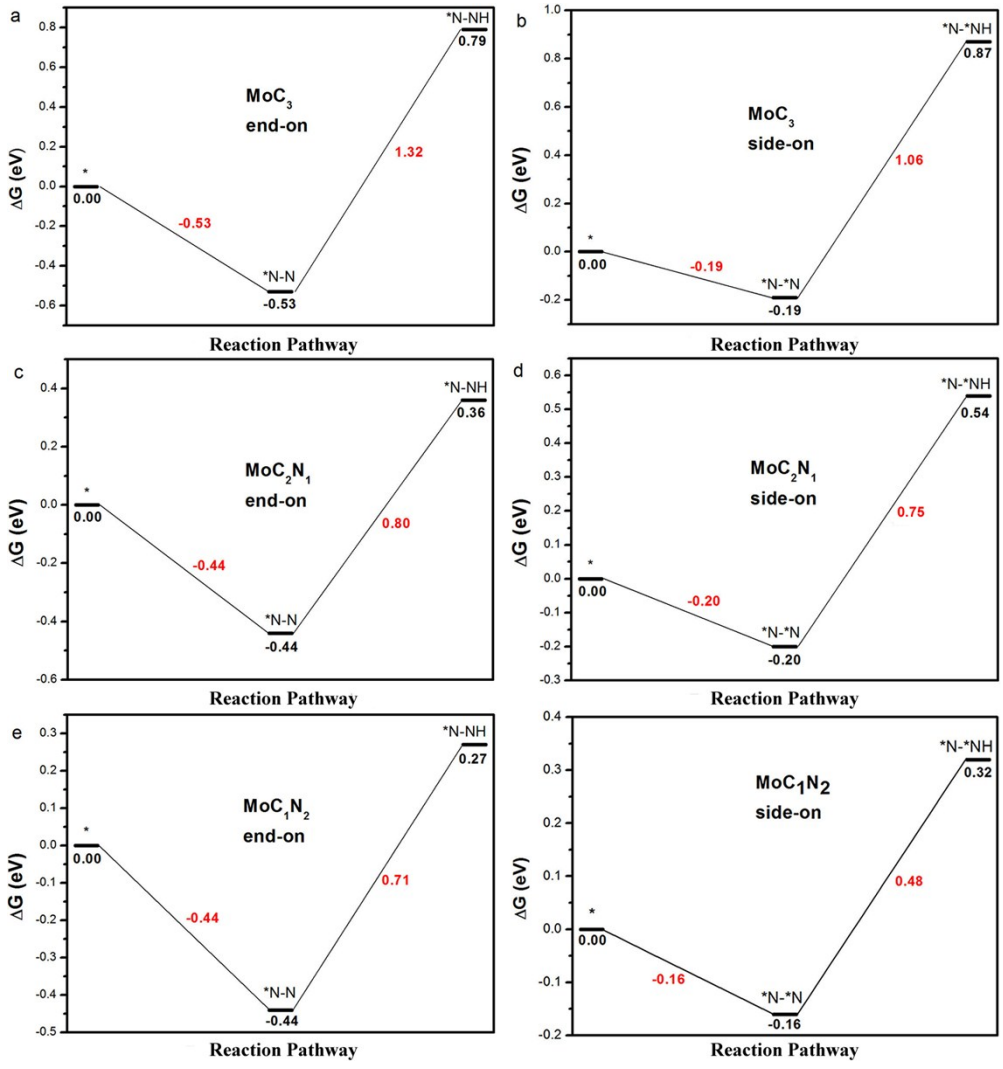


Fig. S8 Calculated free energy diagrams for N_2 and N_2H adsorption on MoC_3 (a) end-on and (b) side-on, MoC_2N_1 (c) end-on and (b) side-on as well as MoC_1N_2 (e) end-on and (f) side-on.

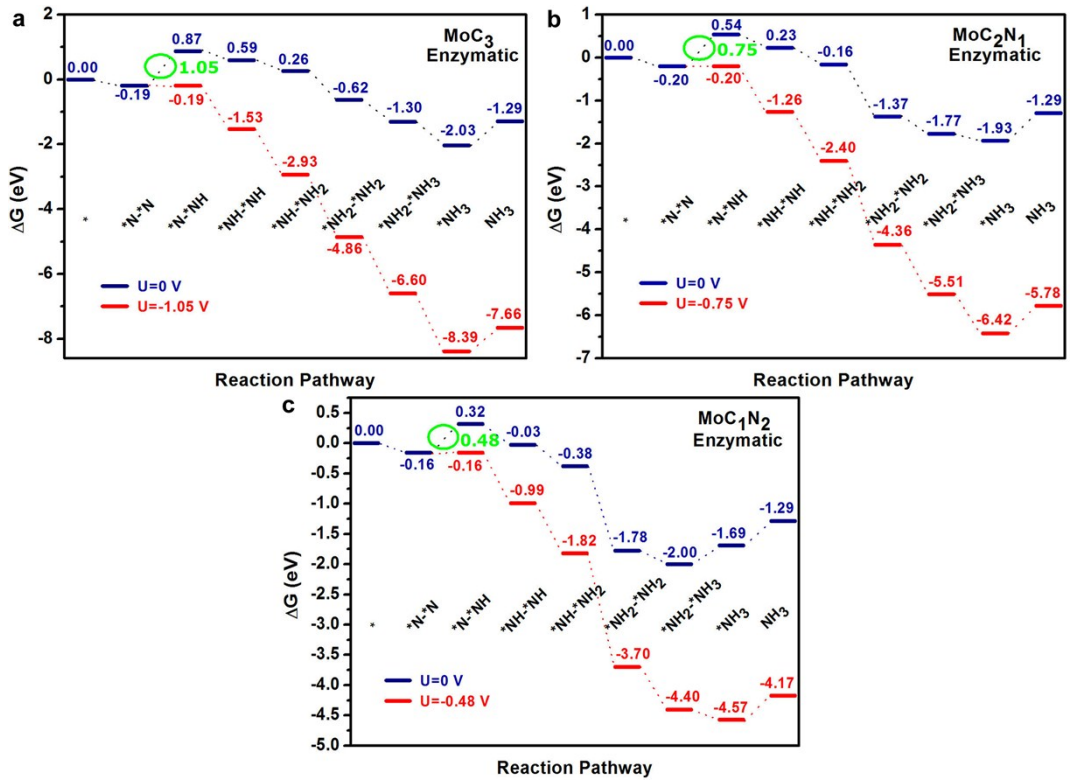


Fig. S9 Free energy profiles for N_2 reduction on (a) MoC_3, (b) MoC_2N_1 and (c) MoC_1N_2 site through enzymatic pathway