Supporting Information:

Single Molybdenum Atom Anchored on N-Doped Carbon as a Promising Electrocatalyst for Nitrogen Reduction into Ammonia at Ambient Conditions

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Figures

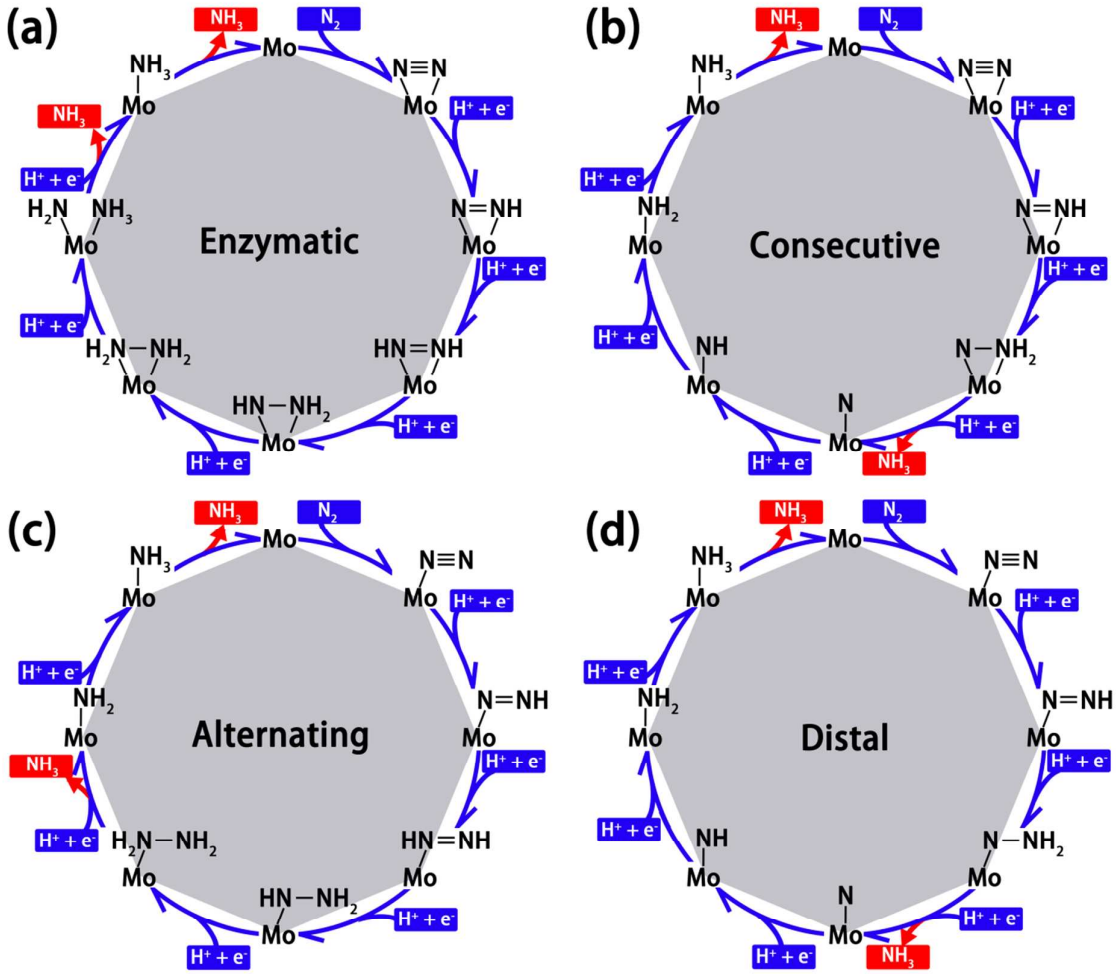

Figure S1. Schematic depiction of (a) enzymatic, (b) consecutive, (c) alternating and (d) distal mechanisms for N_2 reduction to NH_3 on Mo_1-N_1C_2.

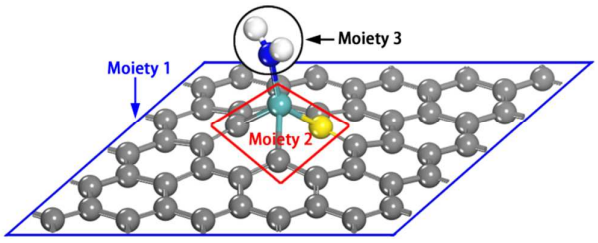

Figure S2. Definition of three moieties of N_xH_y adsorbed Mo_1-N_1C_2 by using NH_2 as prototype.

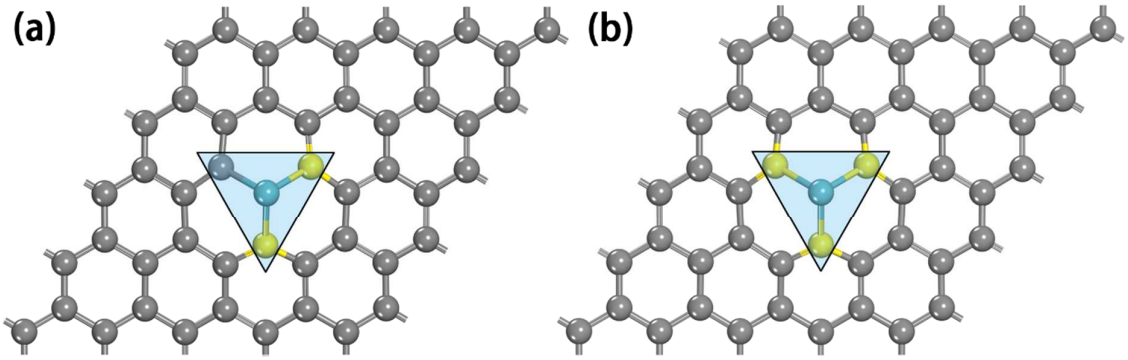

Figure S3. Structures of (a) Mo-N_2C_1 and (b) Mo-N_3 active centers. Gray, cyan and yellow balls represent the C, Mo and N atoms, respectively.

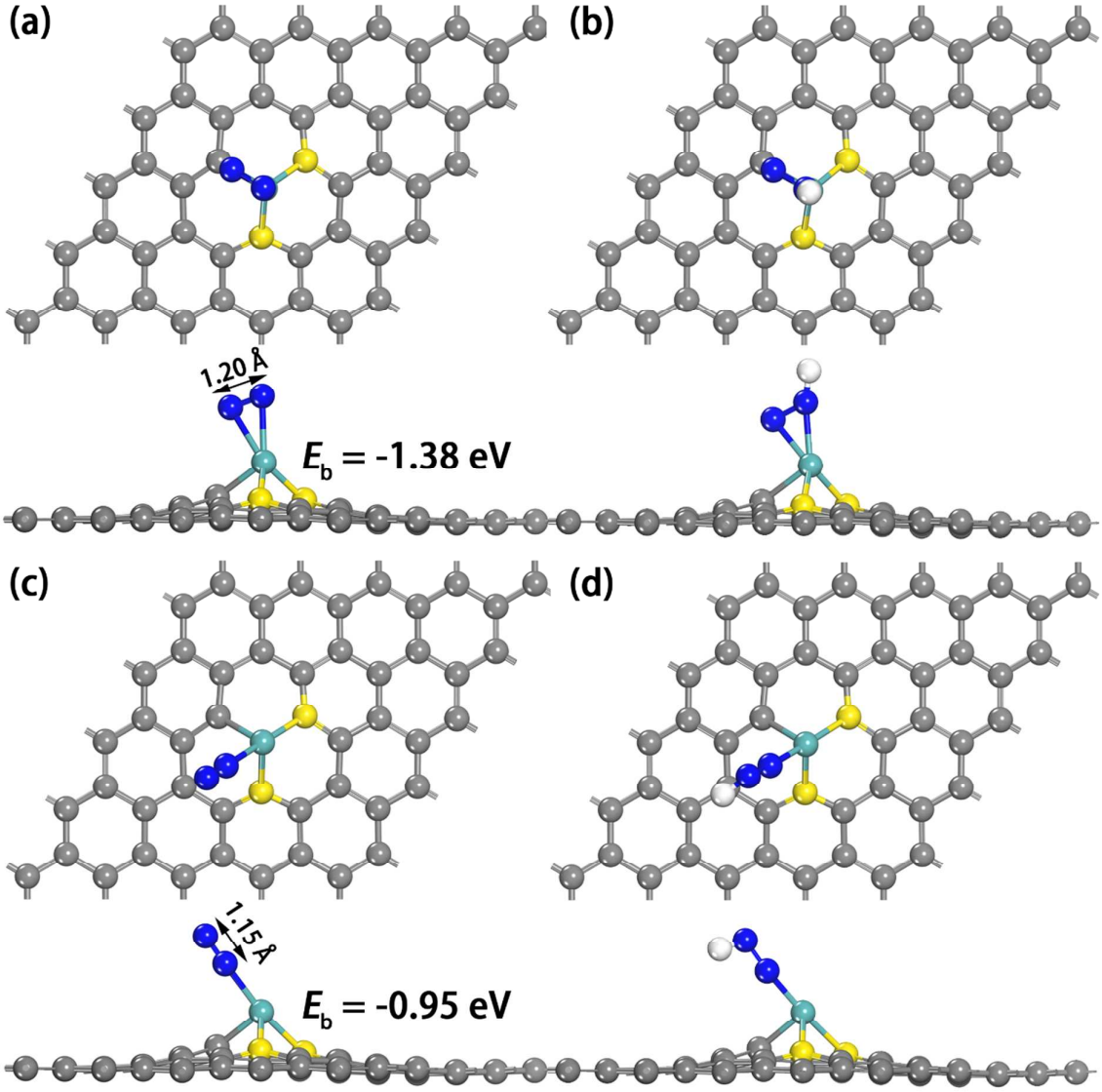

Figure S4. Top and side views of the adsorption N_2 and N_2H via the (a, b) side-on and (c, d)

end-on patterns on the Mo-N_2C_1 site. Gray, cyan, yellow and blue balls represent the C, Mo, doped N and adsorbed N atoms, respectively.

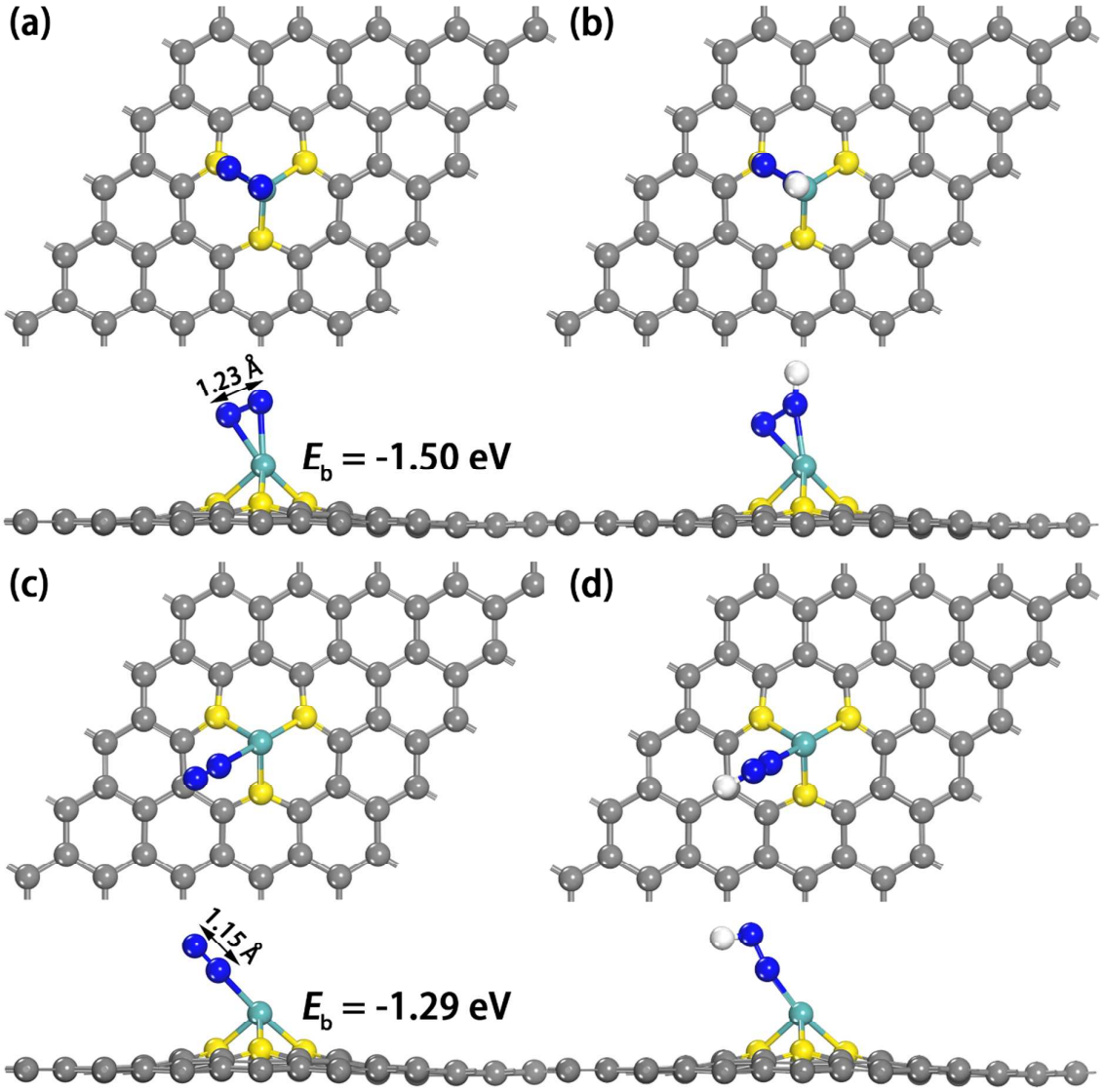

Figure S5. Top and side views of the adsorption N_2 and N_2H via the (a, b) side-on and (c, d) end-on patterns on the Mo-N_3. Gray, cyan, yellow and blue balls represent the C, Mo, doped N and adsorbed N atoms, respectively.

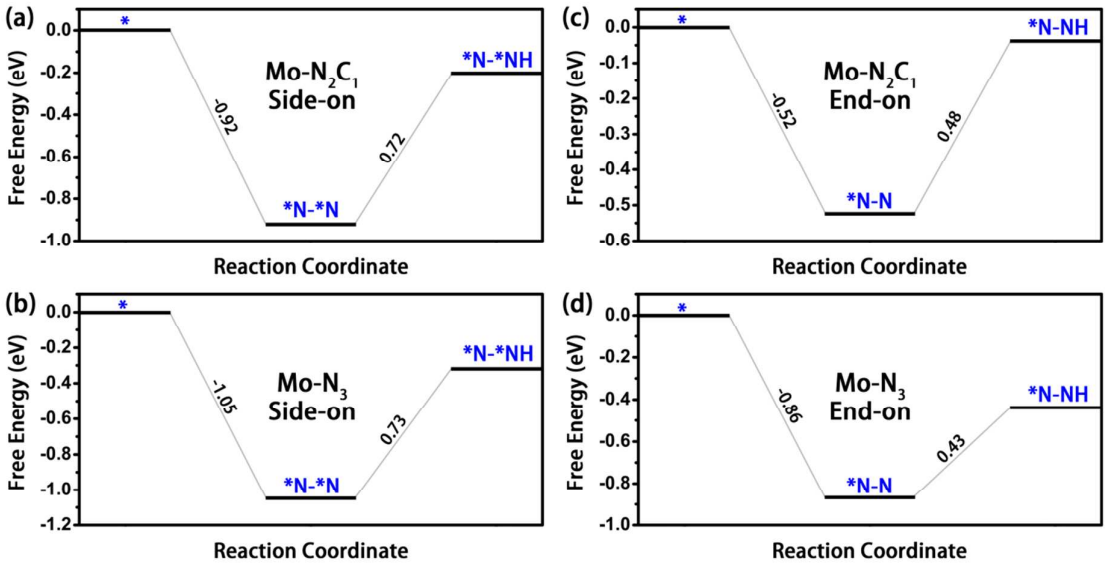

Figure S6. Calculated free energy diagrams for N_2 adsorption and protonation of side-on adsorbed N_2 on (a) Mo-N_2C_1 and (b) Mo-N_3 sites as well as of end-on adsorbed N_2 on (c) Mo-N_2C_1 and (d) Mo-N_3 sites Mo_1/N-C.

Tables

Table S1. Calculated zero point energies and entropy of different adsorption species, where the * denotes the adsorption site. Therefore, *N≡*N and *N≡N represent the side-on and end-on adsorption configurations, respectively.

Adsorption Species	E_{ZPE} (eV)	*TS* (eV)
N_2	0.15	0.58
***N≡*N**	0.19	0.15
***N=*NH**	0.49	0.13
***NH =*NH**	0.79	0.16
***NH−*NH_2**	1.14	0.17
***NH_2−*NH_2**	1.34	0.22
***NH_2−*NH_3**	1.66	0.30
***N−*NH_2**	0.83	0.15
***N**	0.08	0.06
***NH**	0.35	0.09
***NH_2**	0.65	0.14
***NH_3**	1.02	0.16
***N≡N**	0.20	0.18
***N=NH**	0.49	0.16
***NH=NH**	0.80	0.24
***NH−NH_2**	1.13	0.19
***NH_2−NH_2**	1.49	0.25
***N−NH_2**	0.82	0.18
NH_3	0.58	0.56

Table S2. Calculated adsorption energies of N_2 on various SACs that have been synthesized. For Cu_1/N-C, Pd_1/N-C and Pt_1/N-C, only the end-on configurations can be gained.

SACs	Adsorption Energies of N_2 (eV)	
	Side-on	End-on
Mo_1/N-C	-1.19	-1.18
Cu_1/N-C		-0.58
Pd_1/N-C		-0.58
Pt_1/N-C		-0.40