Supporting Information

A Novel Phosphotungstic Acid Supported Single Metal Atom Catalyst with High Activity and Selectivity for the Synthesis of NH_3 from Electrochemical N_2 Reduction：A DFT Prediction

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

Adsorption Species	E_{ZPE} (eV)	TS (eV)
H_2	0.27	0.40
N_2	0.15	0.59
*N≡*N	0.20	0.13
*N═*NH	0.50	0.12
N-NH_2	0.84	0.09
NH-NH_2	1.12	0.15
NH_2-NH_2	1.47	0.12
NH_2-NH_3	1.68	0.18
*N	0.09	0.06
*NH	0.35	0.10
*NH_2	0.67	0.12
*NH_3	1.03	0.16
*N≡N	0.20	0.18
*N═NH	0.46	0.20
*NH-NH	0.81	020
*NH-NH_2	1.14	0.21
*NH_2-NH_2	1.49	0.21
*N-NH_2	0.81	0.20
NH_3	0.89	0.60

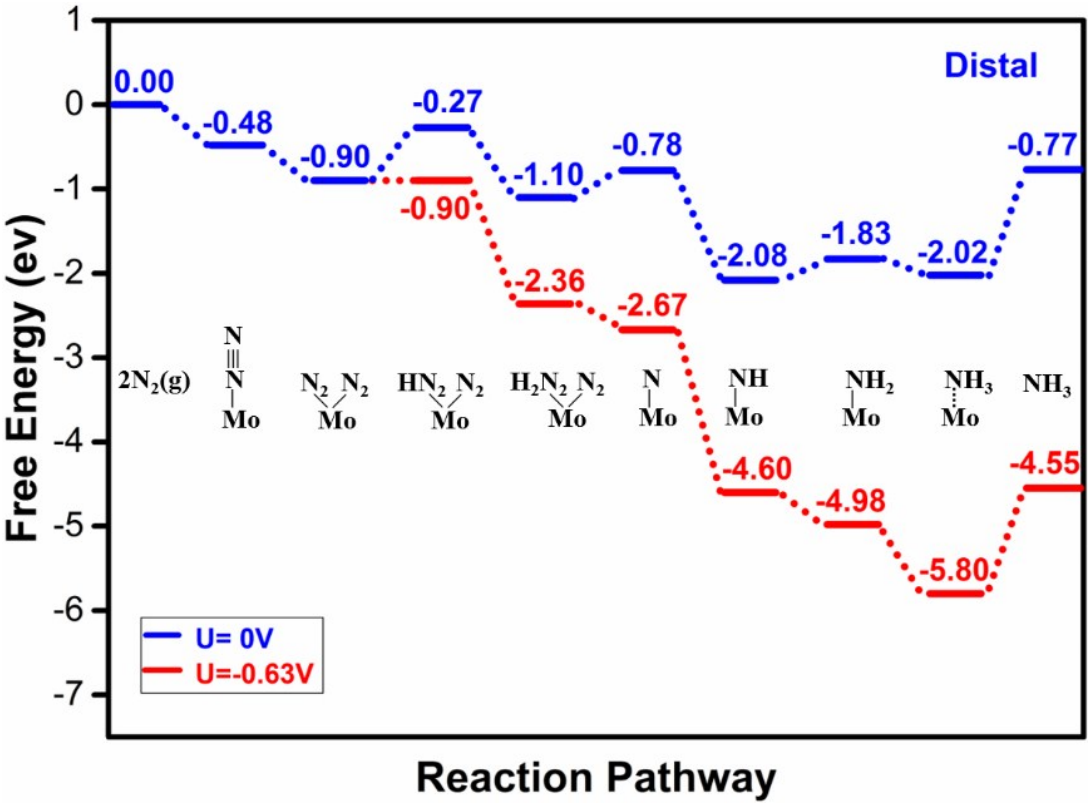

Figure S1. Calculated free energy diagrams for NRR on Mo-PTA through distal mechanism when two N_2* are coadsorbed in the reaction state at different applied potentials.

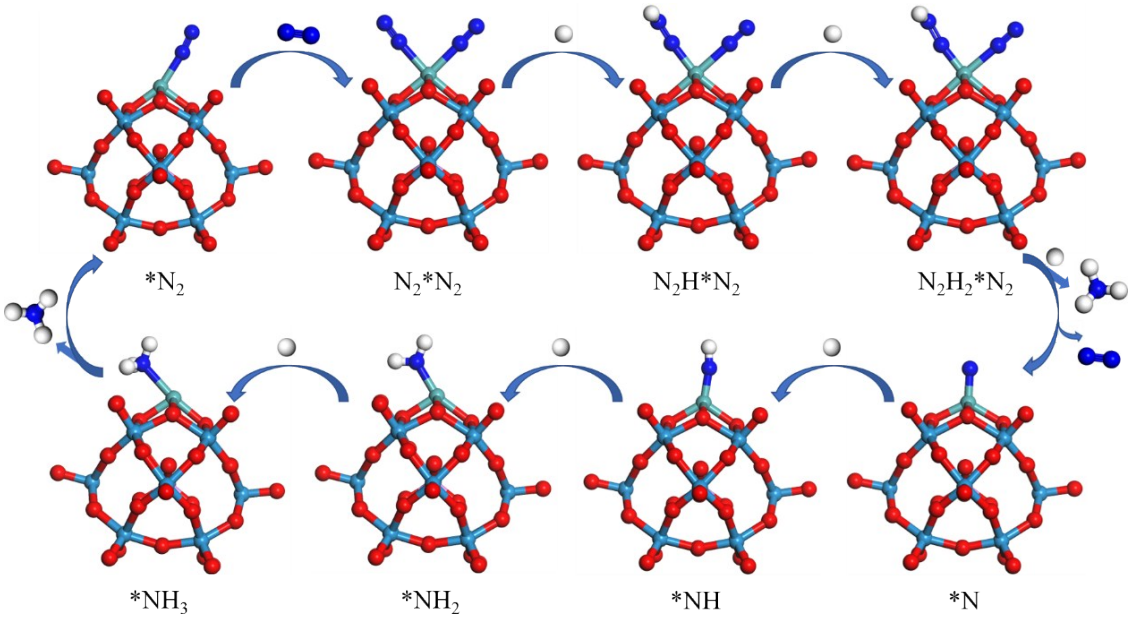

Figure S2. The optimized structures of the intermediates on Mo-PTA following the distal mechanism when two nitrogen molecules are coadsorbed in the reaction state. Color scheme: P, pink; O, red; W, blue; Mo, cyan; N, navy blue; and H, white.

For the coadsortpion of $*N_2$ and *H, when N_2 firstly adsorbed on Mo-PTA, the ΔG of second H adsorption is computed by $\Delta G = (E_{H*N2} - E_{*N2} - 1/2E_{H2}) + (E_{H*N2} - E_{*N2} - 1/2E_{H2})_{ZPE} - T(S_{H*N2} - S_{*N2} - 1/2S_{H2})$.

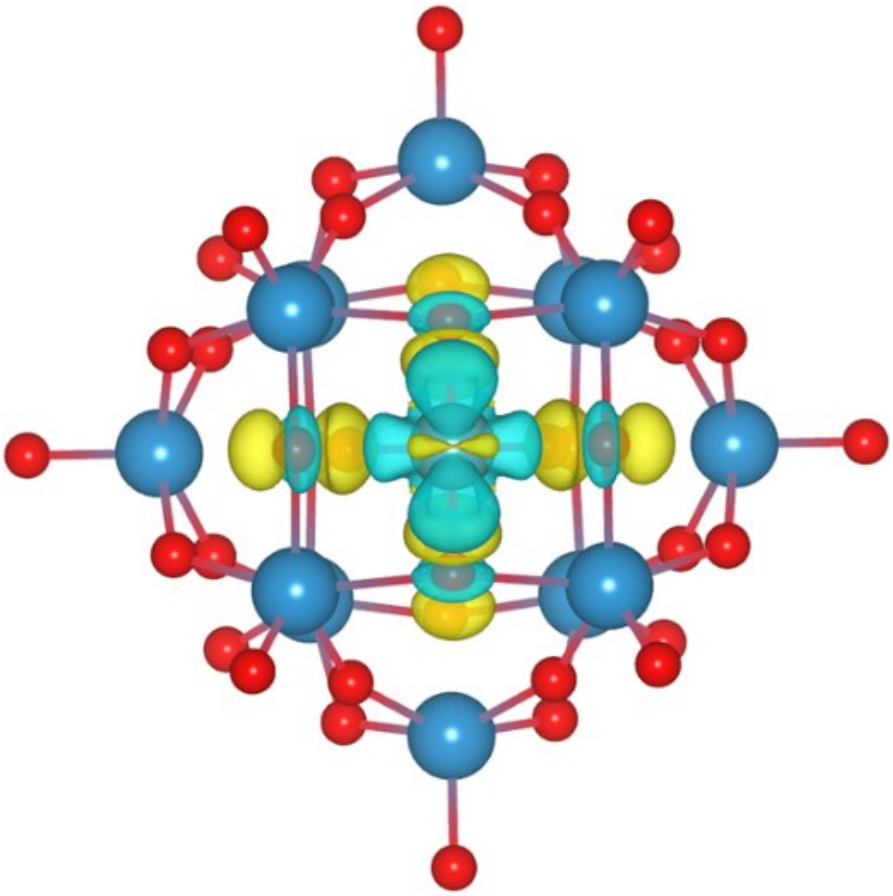

Figure S3. Charge differential density Of Mo-PTA. Isosurface levels is 0.008 e $Å^{-3}$, and charge density difference is computed as ρ(Mo-PTA) − ρ(PTA) − ρ(Mo). Cyan and yellow represent charge depletion and accumulation, respectively