

## Supporting Information

### Boosting Nitrogen Reduction on Single Mo Atom by Tuning its Coordination

#### Environment

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## Theoretical faradaic efficiency

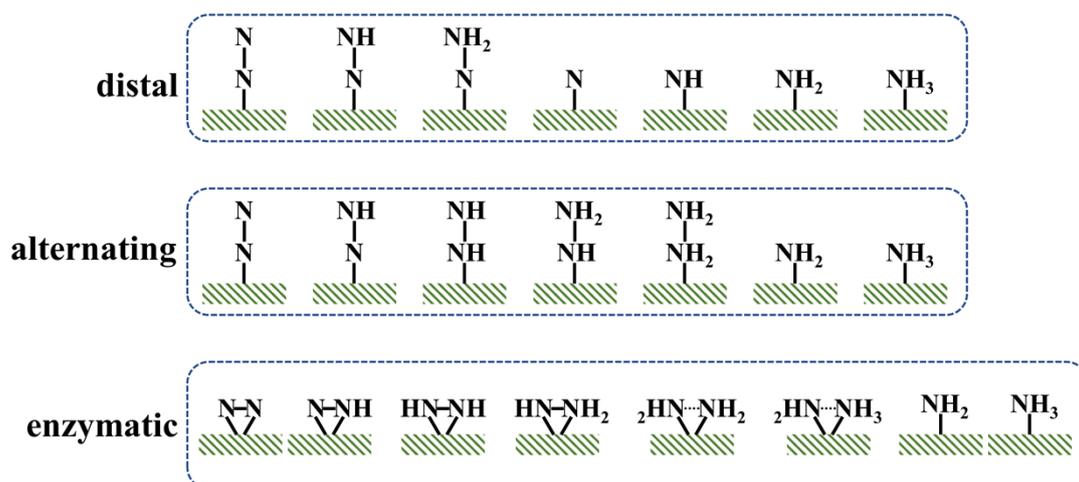
Hydrogen evolution reaction (HER) is regarded as the major competing reaction to NRR. If we assume: (1) the mass and electron transfer are not the rate determining factors for both HER and NRR, (2) only HER and NRR are competing reactions, the Faradaic efficiency of NRR ( $f_{NRR}$ ) can be estimated according to Boltzmann

distribution: 
$$f_{NRR} = \frac{1}{1 + e^{-\frac{\Delta G}{RT}}} \times 100\%$$
, where  $\Delta G$  is Gibbs free energy difference between HER and NRR limiting-potential step,  $k_B$  is the Boltzmann constant, and T is the room temperature.

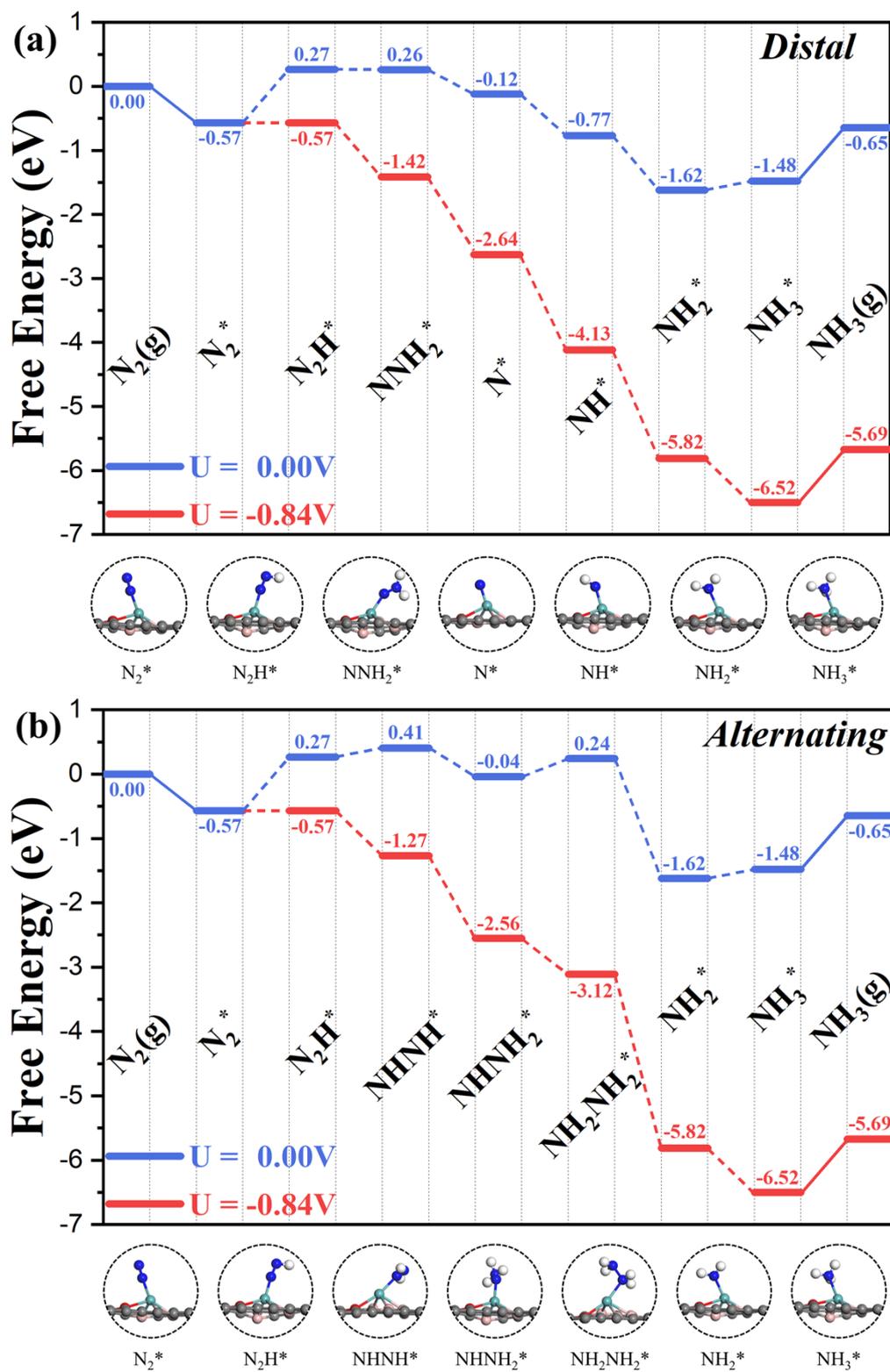
**Table S1.** The computed formation energies<sup>1</sup> ( $E_{\text{form}}$ , eV) of various substrates without single Mo atom.

substrates	$E_{\text{form}}$
CO <sub>3</sub>	-5.98
BN <sub>3</sub>	-2.86
B <sub>3</sub> N	-1.02
B <sub>3</sub> O	-1.93
O <sub>4</sub>	-9.35
O <sub>3</sub> S	-7.16

<sup>1</sup> The formation energy of these doped graphene-based substrates can be determined by:  $E_{\text{form}} = E_{\text{substrate}} - E_{\text{di-gra}} - n\mu_{\text{dopant}} + m\mu_{\text{C}}$ , where  $E_{\text{substrate}}$  and  $E_{\text{di-gra}}$  represent the total electronic energies of various substrates without Mo anchoring and defective graphene with divacancy, respectively.  $\mu_{\text{dopant}}$  and  $\mu_{\text{C}}$  are the chemical potential of dopants and C atoms, respectively, which can be derived from their most stable materials.  $n$  and  $m$  are the numbers of the introduced dopants and the removed C atoms, respectively.



**Fig. S1.** Schematic illustrations of the NRR mechanisms including distal, alternating and enzymatic pathways.



**Fig. S2.** Calculated free energy diagrams for  $N_2$  reduction on  $MoB_3O$  catalyst along the (a) distal, and (b) alternating pathways, with the corresponding atomic structures of reaction intermediates.

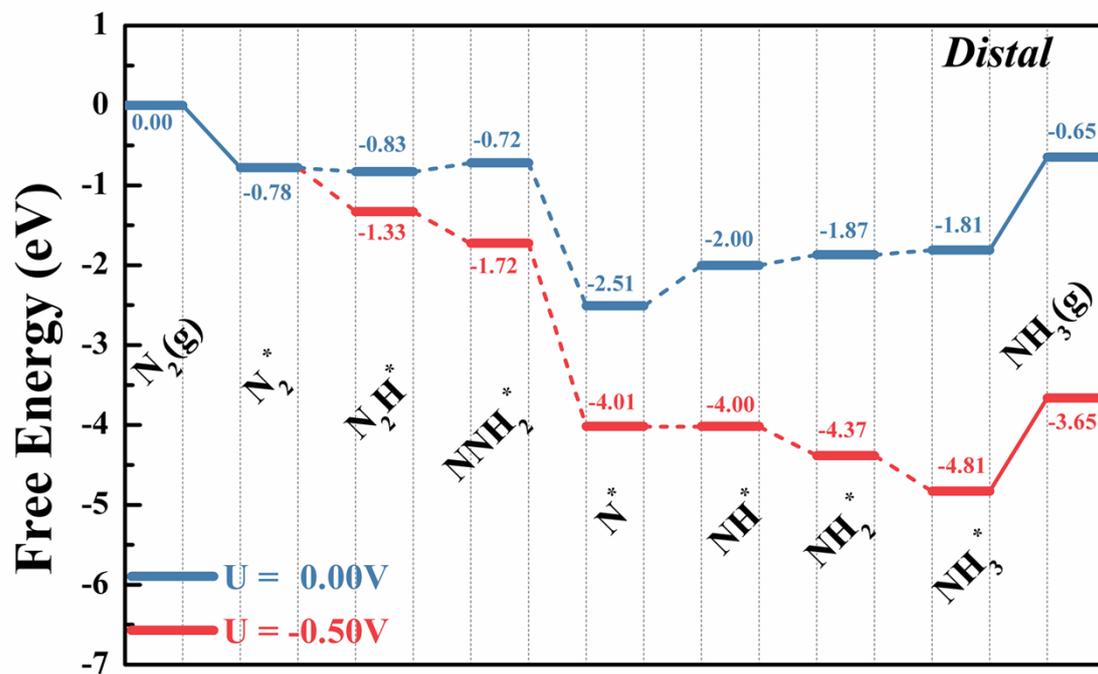
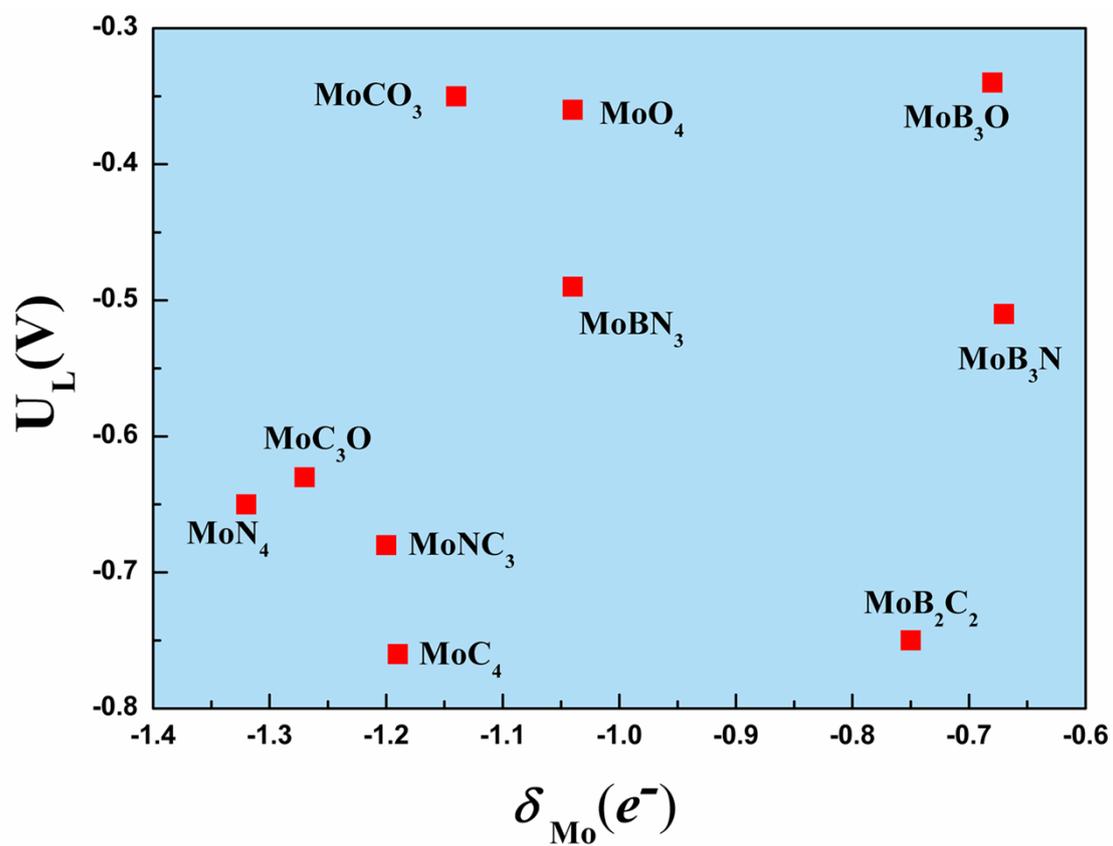
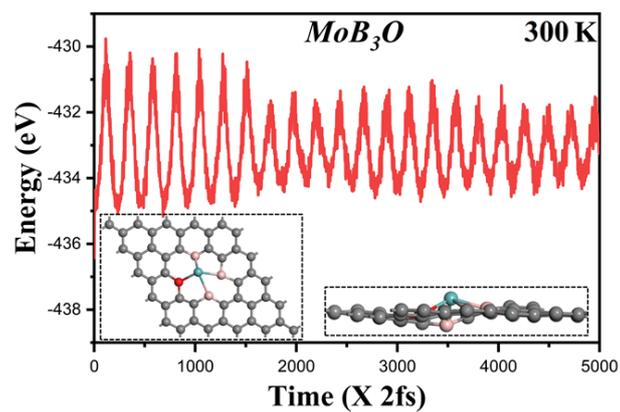


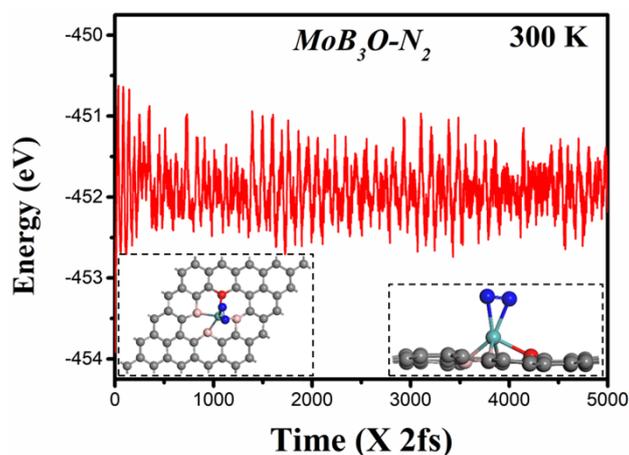
Fig. S3. The most energetically favorable free energy profile for NRR on the experimentally available MoO<sub>3</sub>S material.



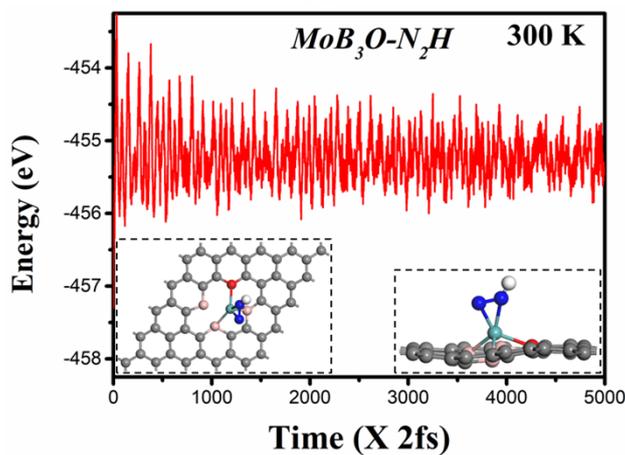
**Fig. S4.** The variation of  $U_L$  for NRR on Mo-based SACs with the charge states of Mo active site ( $\delta_{\text{Mo}}$ ).



(a)



(b)



(c)

**Fig. S5.** Variations of energy against the time for AIMD simulations for (a) MoB<sub>3</sub>O, (b) \*N<sub>2</sub>, and (c) \*N<sub>2</sub>H intermediates on MoB<sub>3</sub>O catalyst, which is run under 300 K for 10 ps with a time step of 2 fs. Schematic diagrams of corresponding atomic configurations after dynamics simulations (top and side views) are also given.