Electronic Supporting Information

Coordination Tunes Activity and Selectivity of Nitrogen Reduction Reaction on Single-Atom Iron Catalysts: A Computational Study

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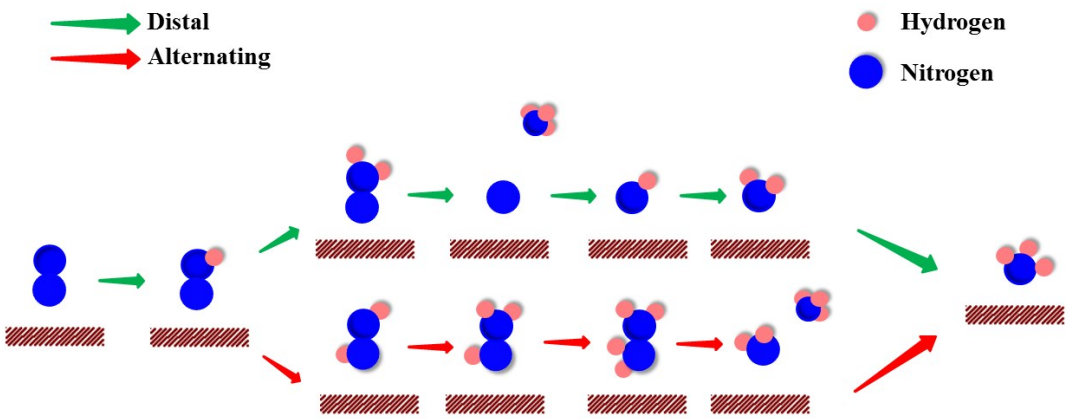
Computational Details on Free Energy Changes

The widely–accepted computational hydrogen electrode (CHE) model[1,2] was used to compute the change in the Gibbs free energy change (ΔG) for all NRR steps, in which one–half of the chemical potential of hydrogen molecule is equal to the chemical potential of proton-electron pair. In this CHE model, the ΔG value of each elementary step in NRR can be obtained by: $\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S + \Delta G_{pH} + \Delta G_{U,}$ where ΔE that represents the reaction energy difference of reactant and product, which can be directly computed from DFT computations. ΔE_{ZPE} and ΔS are the change in the zero–point energies and entropy at room temperature (T = 298.15K), which can be computed from the vibrational frequencies. Notably, the entropies of the free molecules, including N_2, NH_3, and H_2, were taken from the NIST database. ΔG_{pH} is the free energy correction of pH, which can be determined as: $\Delta G_{pH} = k_B T \times pH \times \ln 10$, and in this work the pH value was set to be zero. $\Delta G_U = -eU$, where e is the transferred charge and U represents the applied potential at the electrode. The limiting potential (U_L) was employed to assess the NRR catalytic activity, which can be computed by: $U_L = -\max(\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4 \ldots, \Delta G_i)/e$, where ΔG_i represents the free energy change of each elementary step in the whole NRR process. According to this definition, a less negative U_L on a given catalyst denotes a less energy input, thus suggesting its higher NRR catalytic activity.



Scheme S1. The involved reaction pathways for NRR on B-doped Fe-N_4/G

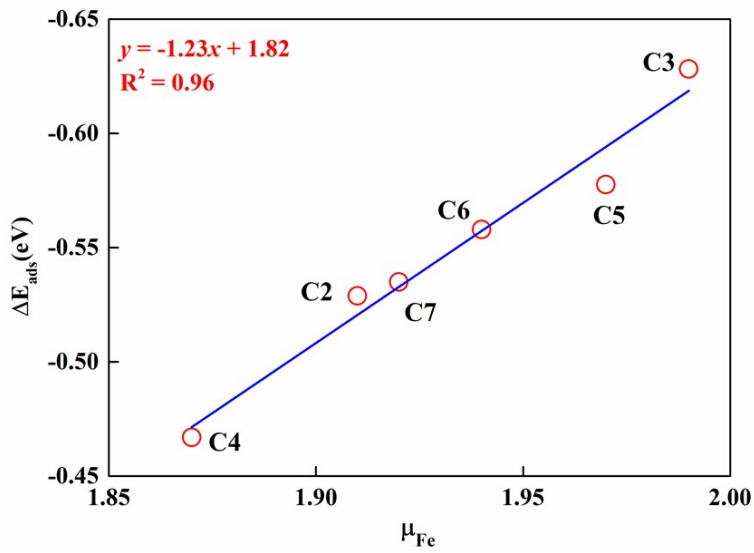


Fig. S1. The scaling relationship between adsorption energy (E_{ads}) of N_2 molecule and spin moment of the central Fe atom (μ_{Fe}).

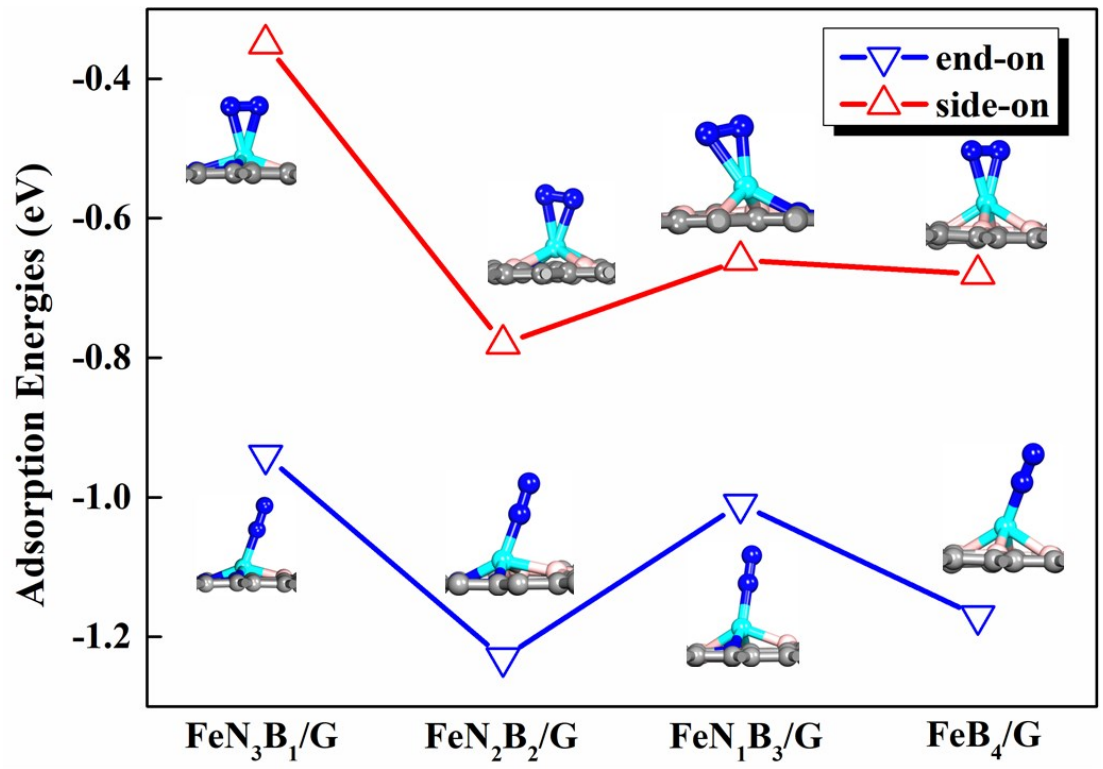


Fig. S2. The optimized adsorption configurations of N_2 molecule on Fe-B_xN_{4-x}/G in end-on and side-on patterns and the corresponding adsorption energies.

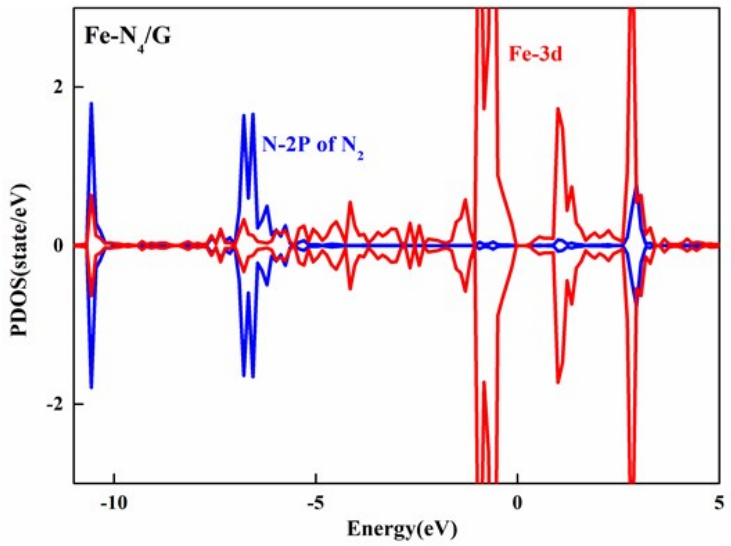


Fig. S3. The computed partial density of states of N_2 adsorption on pristine Fe-N_4/G.

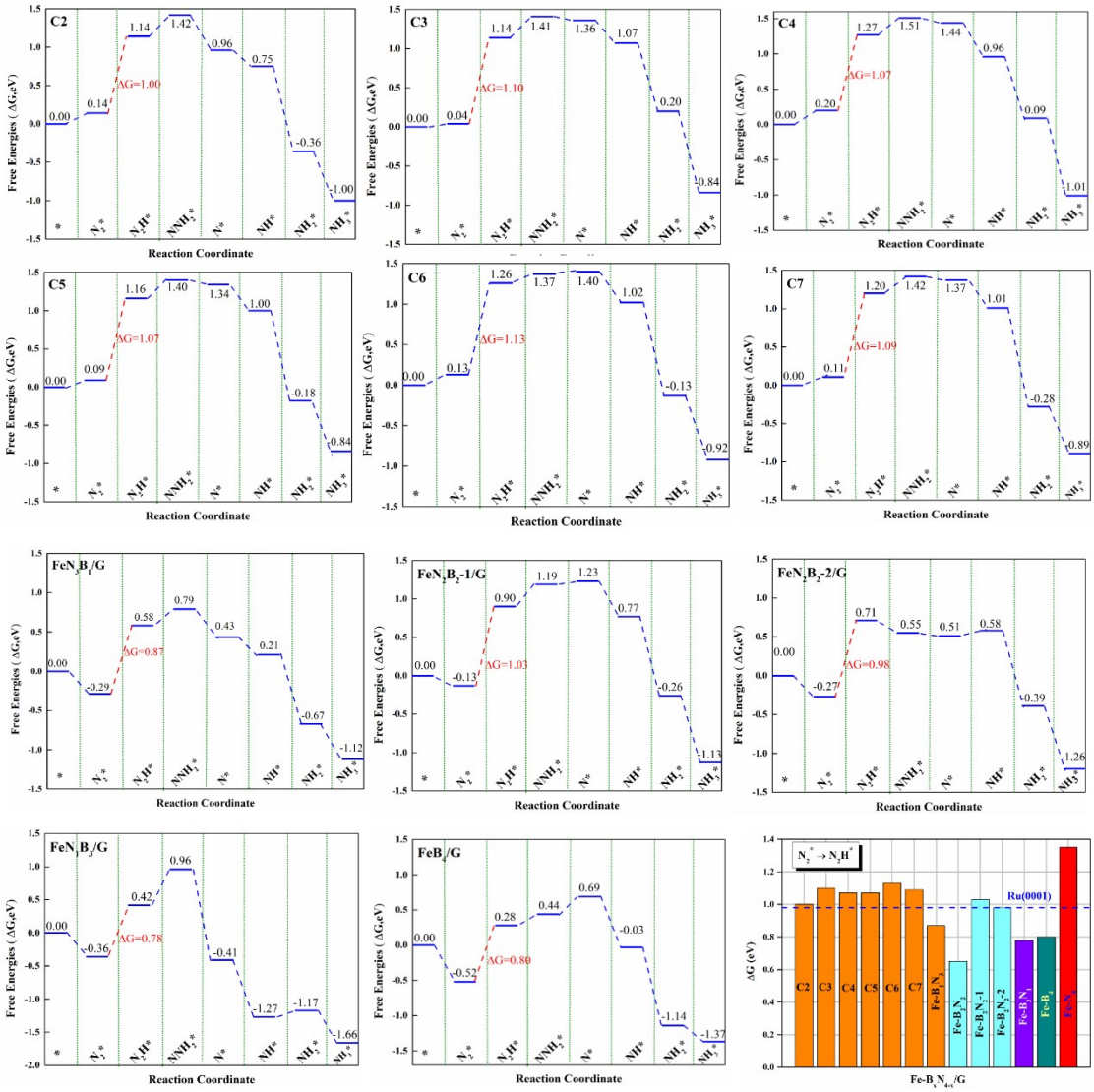


Fig. S4. The obtained free energy profiles of NRR on various Fe-B_xN_{4-x}/G systems along distal pathways, and the computed ΔG values for $N_2^* \rightarrow N_2H^*$.

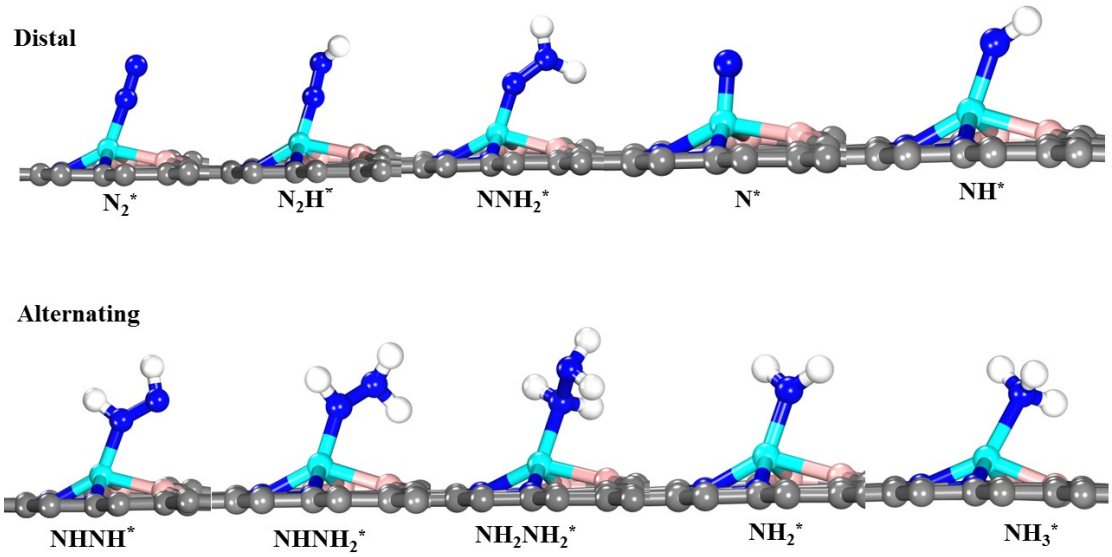


Fig. S5. The involed NRR intermediates on Fe-B_1N_3/G along distal and alternative pathways.

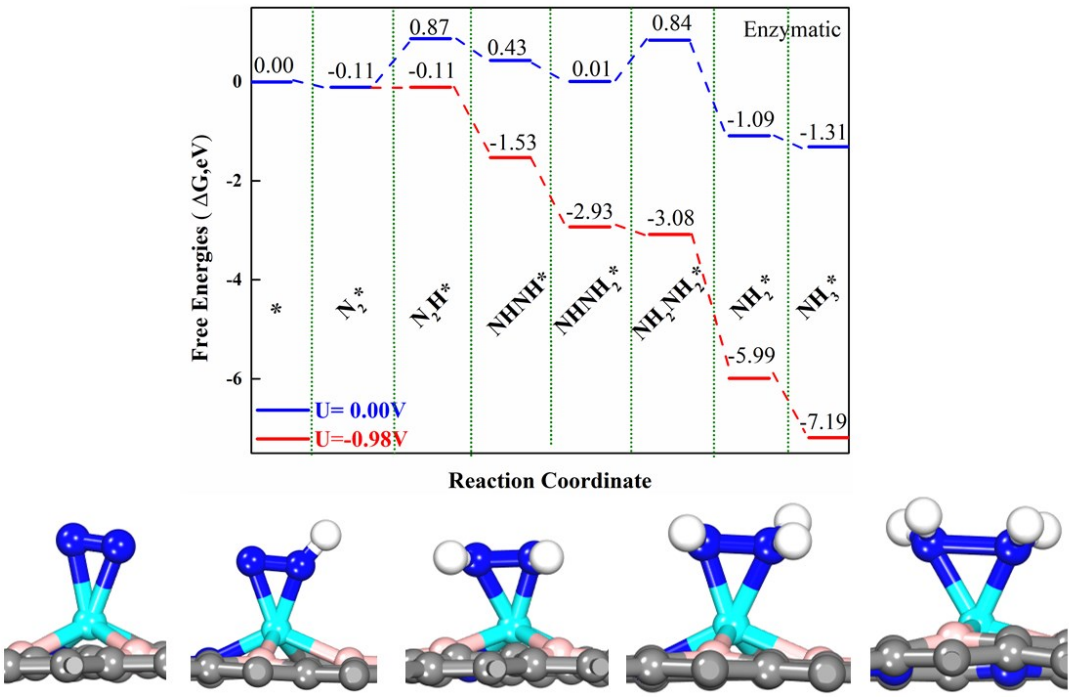
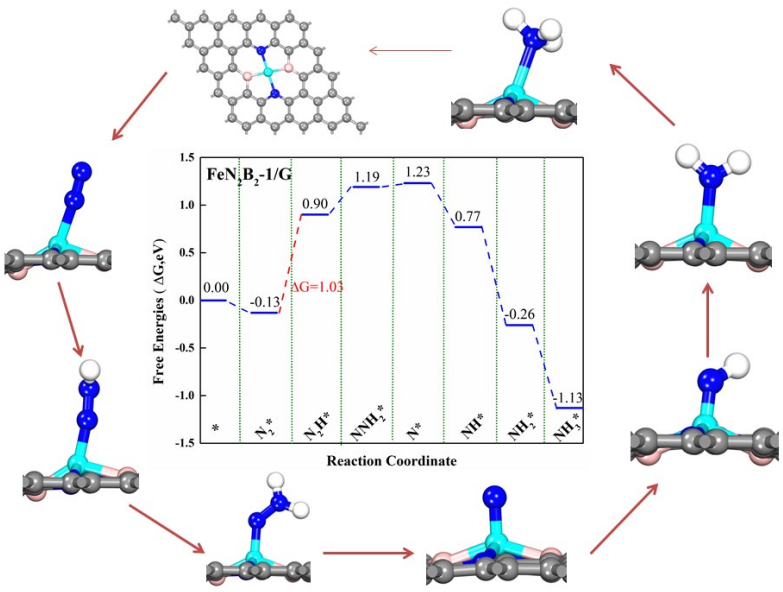
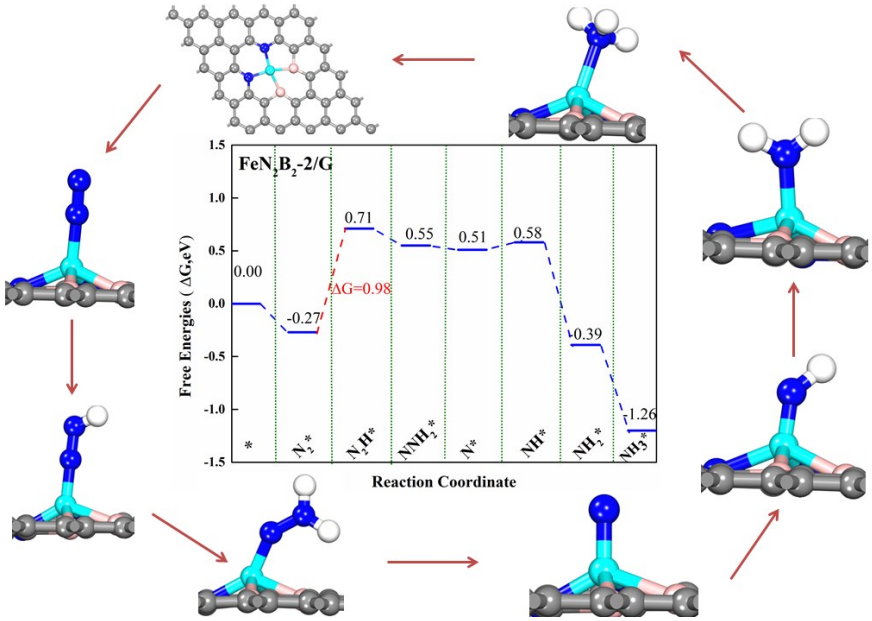


Fig. S6. The computed free energy profiles for NRR on Fe-B_2N_2/G along enzymatic pathway, and the involved reaction intermediates.



(a)



(b)

Fig. S7. The computed free energy profiles of NRR on (a) Fe-B_2N_2-1 and (b) Fe-B_2N_2-2, and the corresponding NRR intermediates.

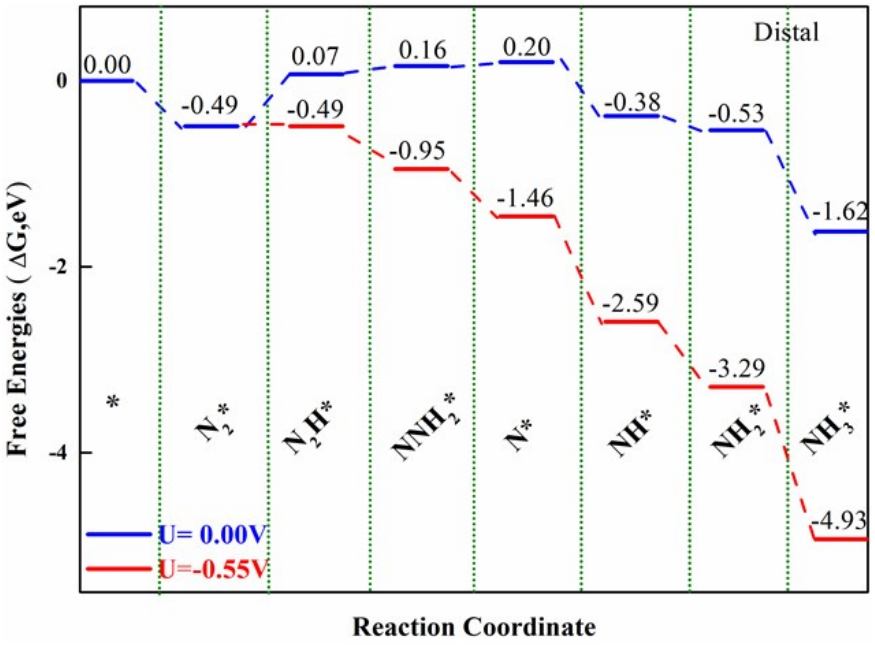


Fig. S8. Gibbs free energy (ΔG) diagram for NRR on Fe-B_2N_2/G with solvent effect.

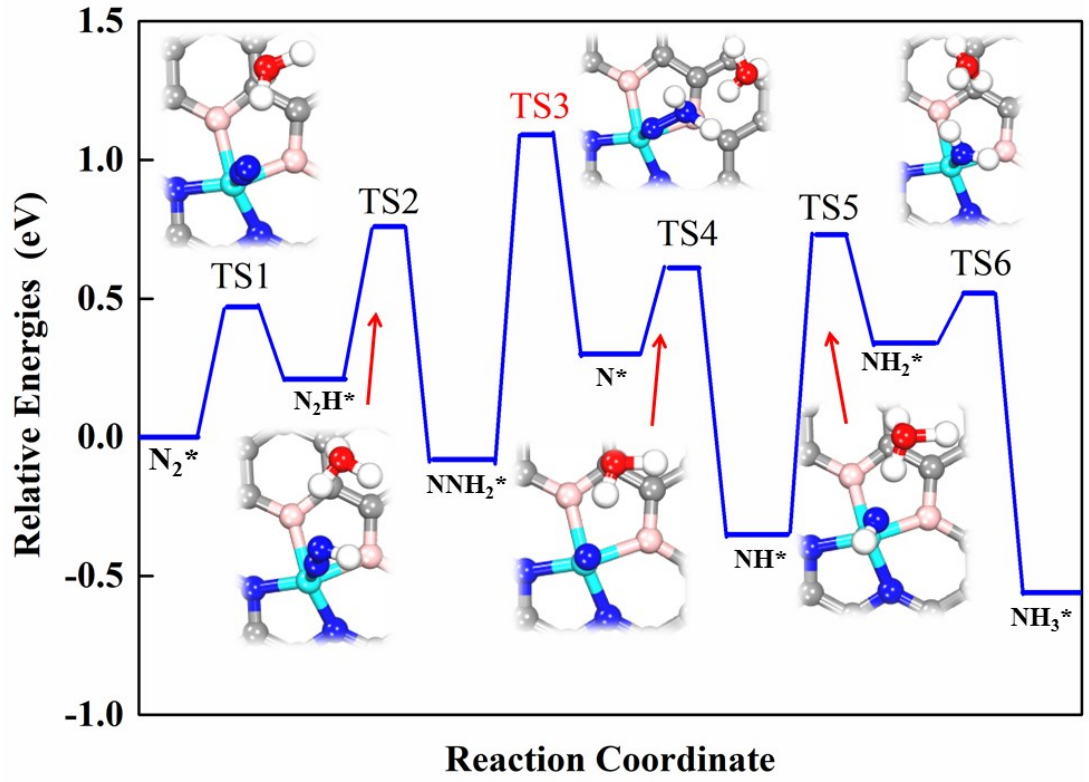


Fig. S9. The computed minimum energy path for N_2 reduction to NH_3, and the corresponding structures of transition states (TSs).

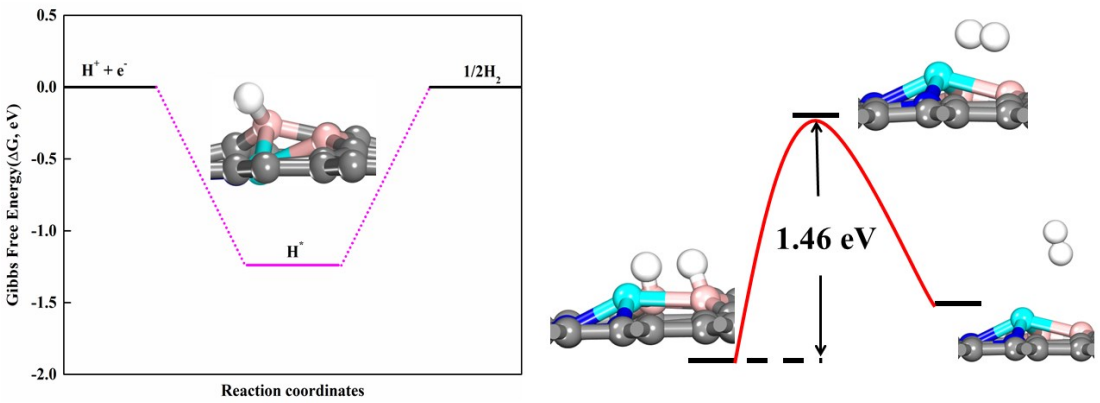


Fig. S10. The computed (a) free energy profile and (b) minimum energy path for HER on Fe-B_2N_2/G.

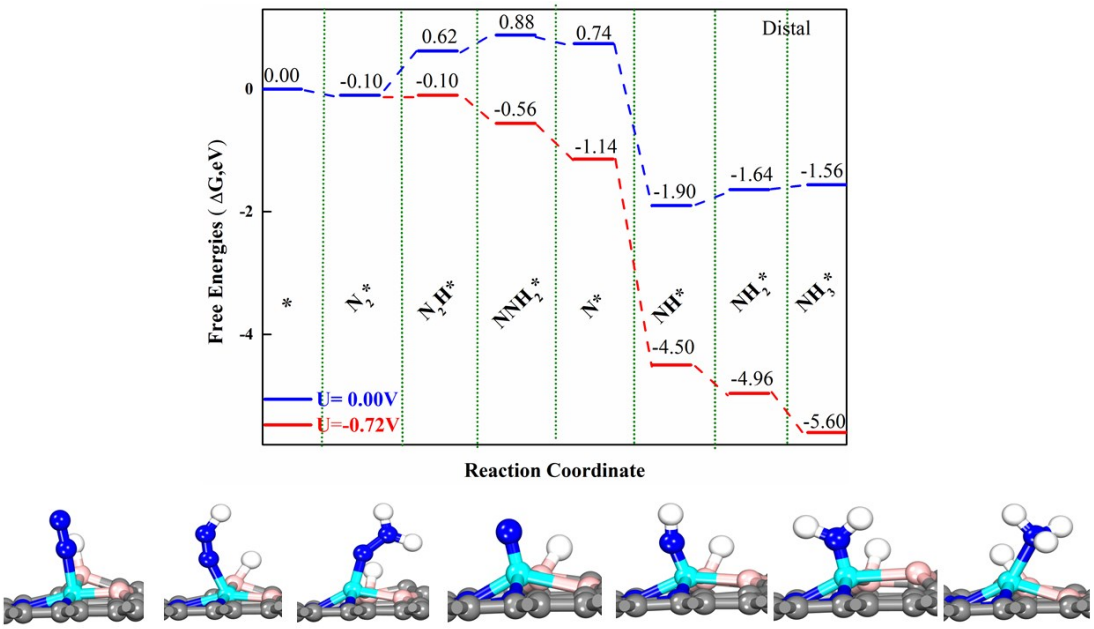


Fig. S11. Gibbs free energy (ΔG) diagram for NRR on Fe-B_2N_2/G with H-preadsorption on B site.

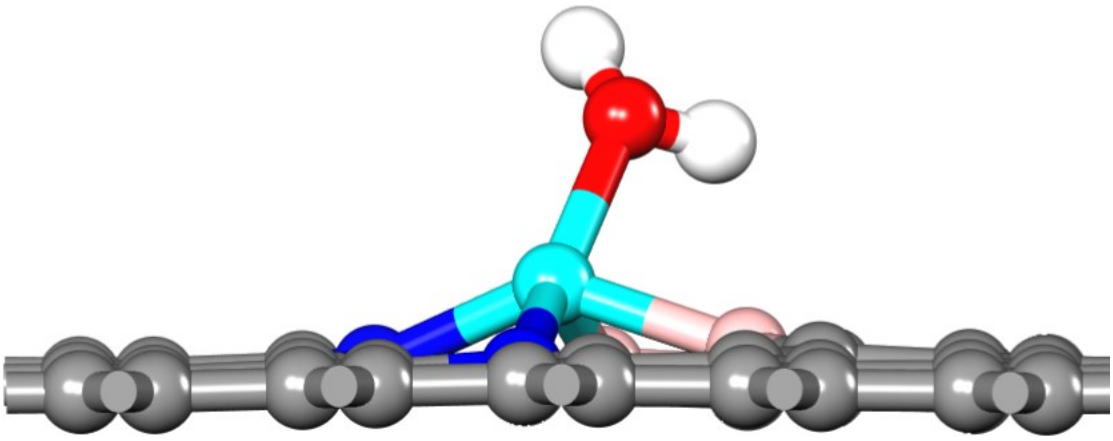


Fig. S12. The optimized adsorption configuration for H_2O on Fe-B_2N_2/G.

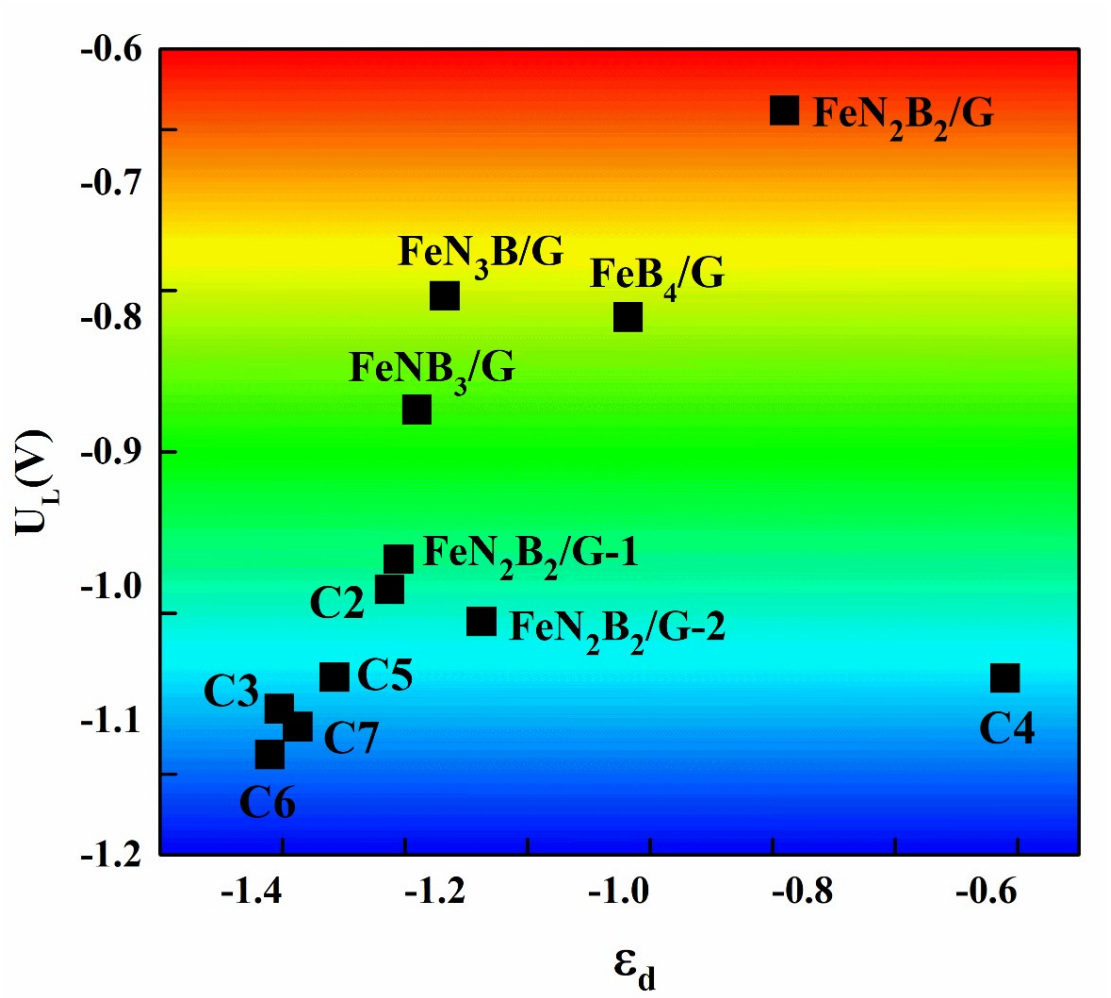


Fig. S13. The scaling relationships of limiting potential of NRR (U_L) *vs* d-band center (ε_d) of the central Fe atoms.

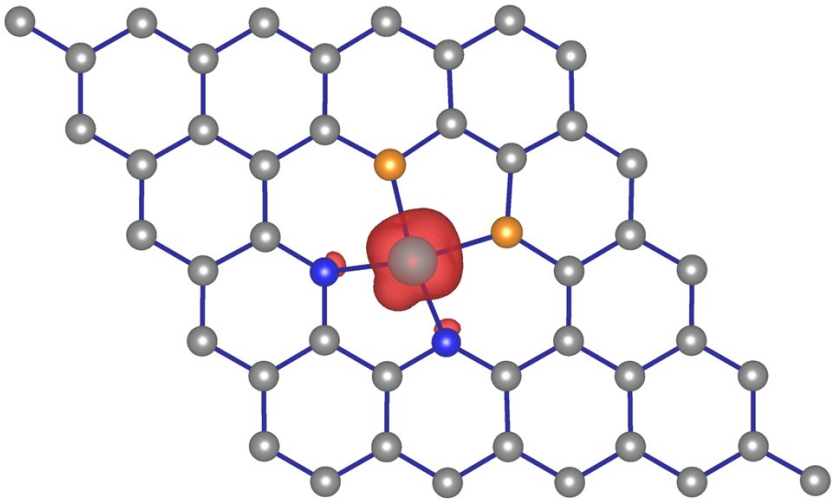


Fig. S14. The spin density of Fe-B_2N_2/G. The isosurface value was set as 0.01 e/Å^2.

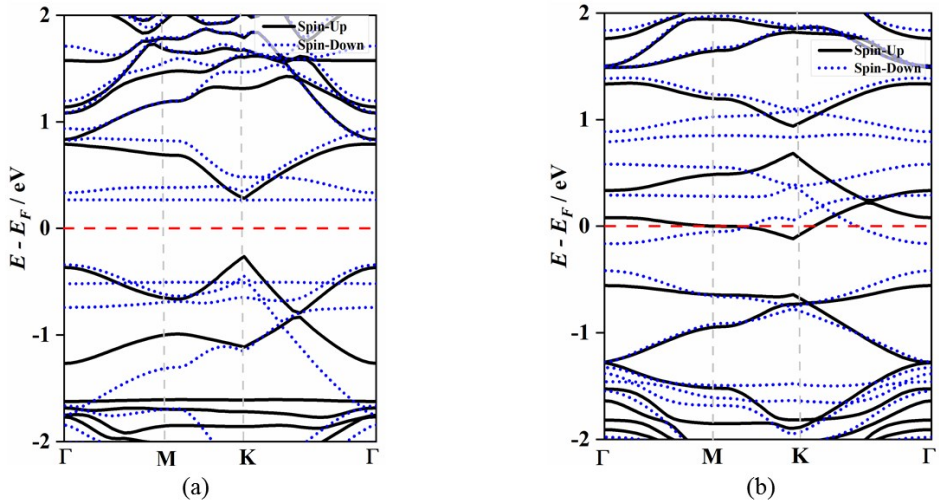


Fig. S15. The computed band structures of (a) Fe-N_4/G and (b) Fe-B_2N_2/G. The Fermi level was set to zero in red dotted line.

References

1. J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Bligaard and H. Jonsson, *J. Phys. Chem. B*, 2004, 108, 17886-17892.

2. A. A. Peterson, F. Abild-Pedersen, F. Studt, J. Rossmeisl and J. K. Nørskov, *Energy & Environ. Sci.*, 2010, 3, 1311-1315.

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