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Metal-free Electrocatalyst for Reducing Nitrogen to Ammonia Using Lewis Acid Pair

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1. Three kinds of doubly B-doped sites

In this work, we considered possible doped models (singly and doubly B-doped), which are further divided into three kinds of doped sites, para-position, meta-position and ortho-position, respectively (See Fig.S1). We further optimized three kinds of doped structures and their energies are close (~0.12eV) as shown in TableS1. Therefore, their appearing probabilities are expected to be similar in experiment.

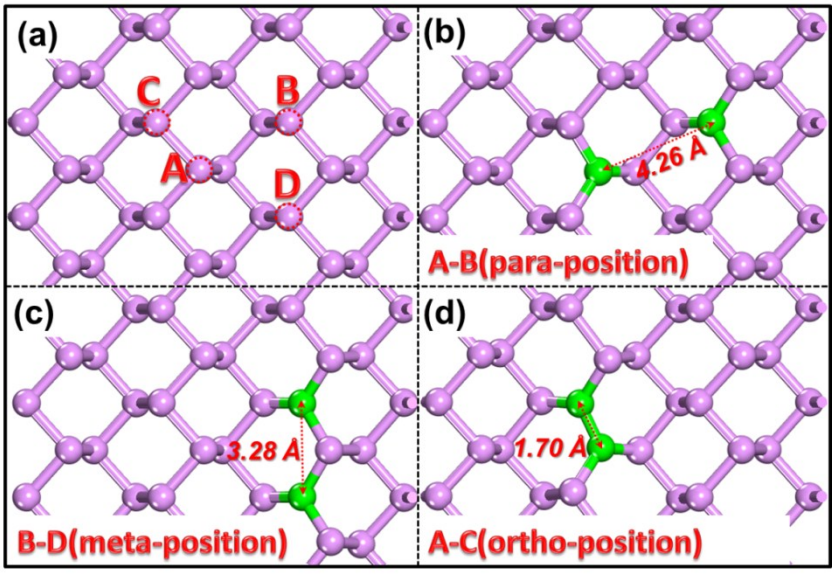


Fig. S1. (a) Possible B-doped sites. Three kinds of ways of doubly B-doped BP (b) para-position, (c) meta-position and (d) ortho-position

Table S1 Energy of three kinds of doping, para-doped, meta-doped and ortho-doped, respectively.

	Para-doped	Meta-doped	Ortho-doped
Energy (eV)	-198.673	-198.803	-198.688

2. Molecular dynamics simulations of B-doped BP

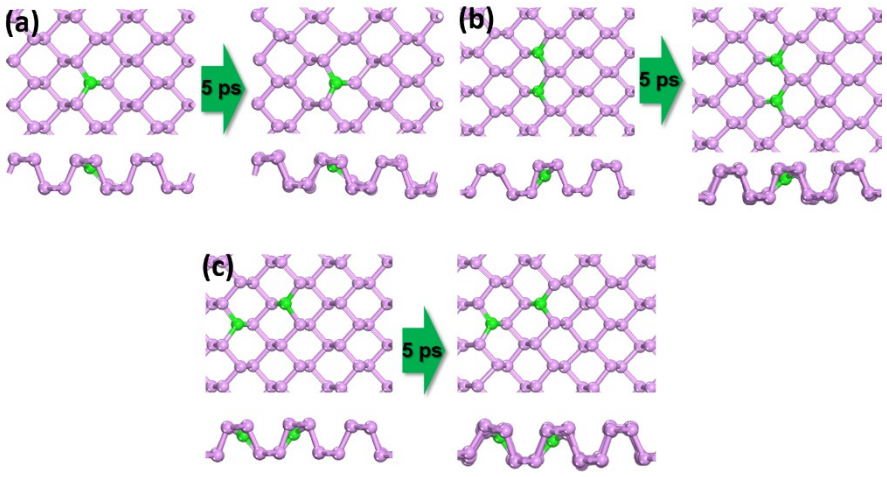


Fig. S2 Geometry snapshot: top view and front view of initial structure and final structure after 5 ps AIMD simulations. (a) B-doped BP, (b) meta-doped BP and (c) para-doped BP.

3. Nitrogen and water adsorption on para-doped and meta-doped BP.

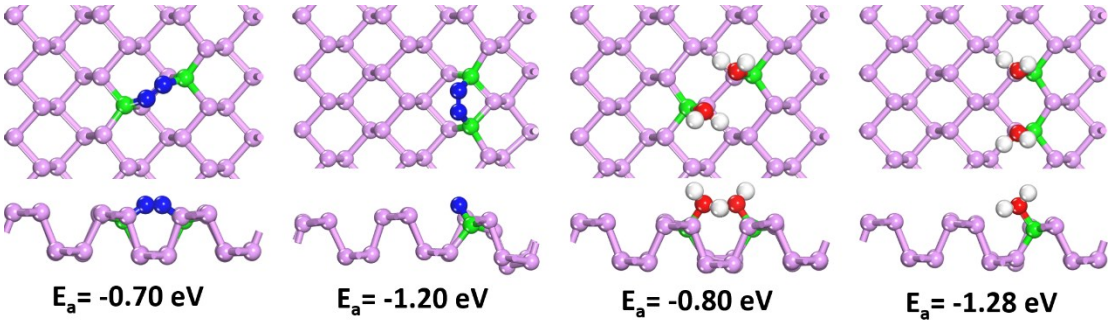
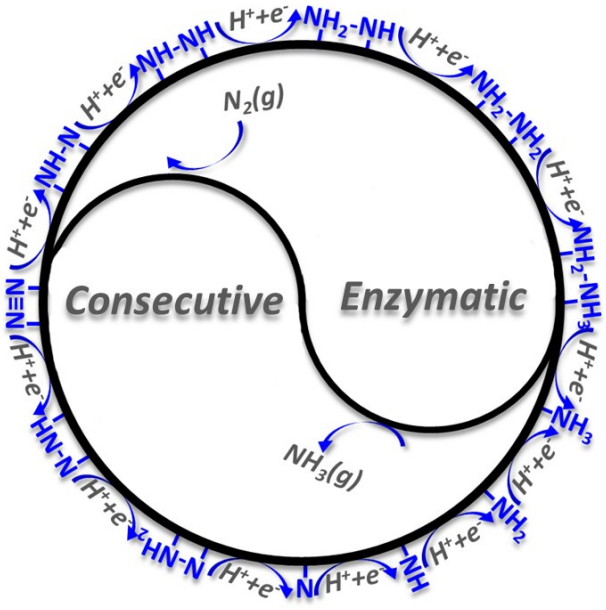


Fig. S3 Optimized geometric configurations of nitrogen and water adsorption on para-doped and meta-doped BP.

4. Schematic depictions of reaction pathways of 2B-doped BP



Scheme S1. Schematic depictions of the four reaction pathways for nitrogen reduction to ammonia on the doubly B-doped monolayer BP.

5. Optimized geometrical structures of alternating and distal pathways

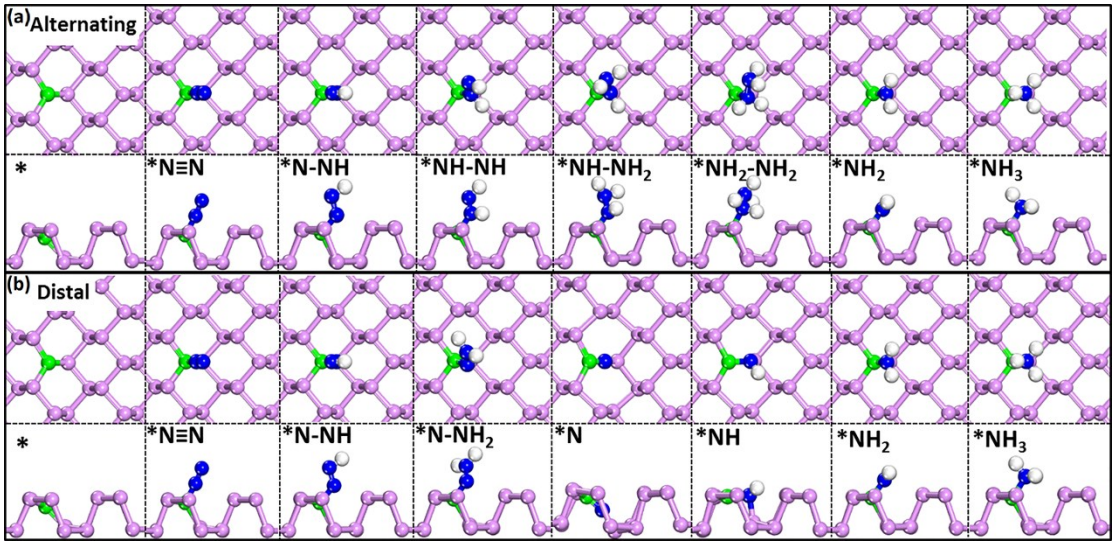


Fig. S4. Optimized geometrical structures of all the reduction processes through (a) alternating and (b) distal pathways.

6. Relationship between hydrogenation and N-N bond length on alternating and distal pathways

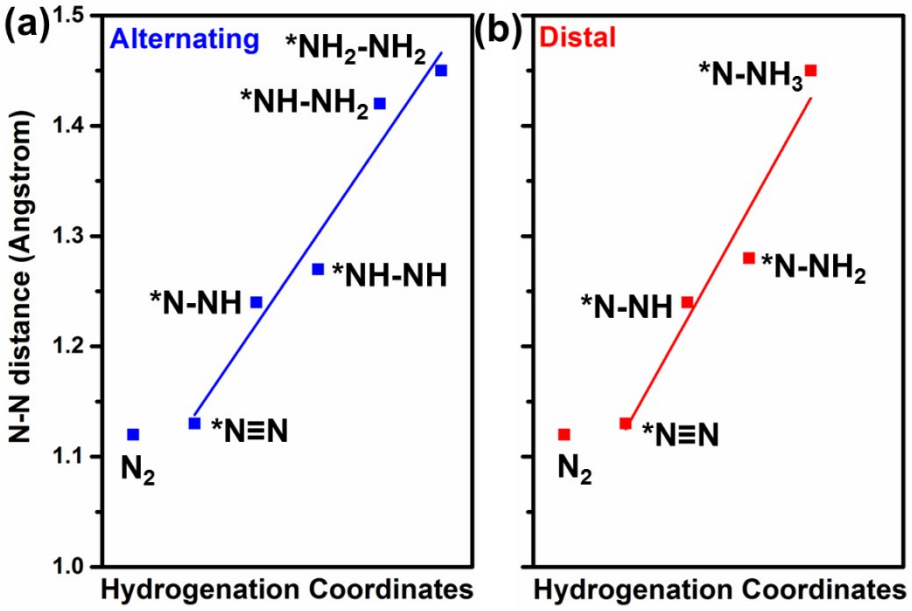


Fig. S5. Relationship between hydrogenation and N-N bond length. (a) alternating and (b) distal mechanisms on singly B-doped BP.

7. Relationship between hydrogenation and N-N bond length on consecutive and enzymatic pathways

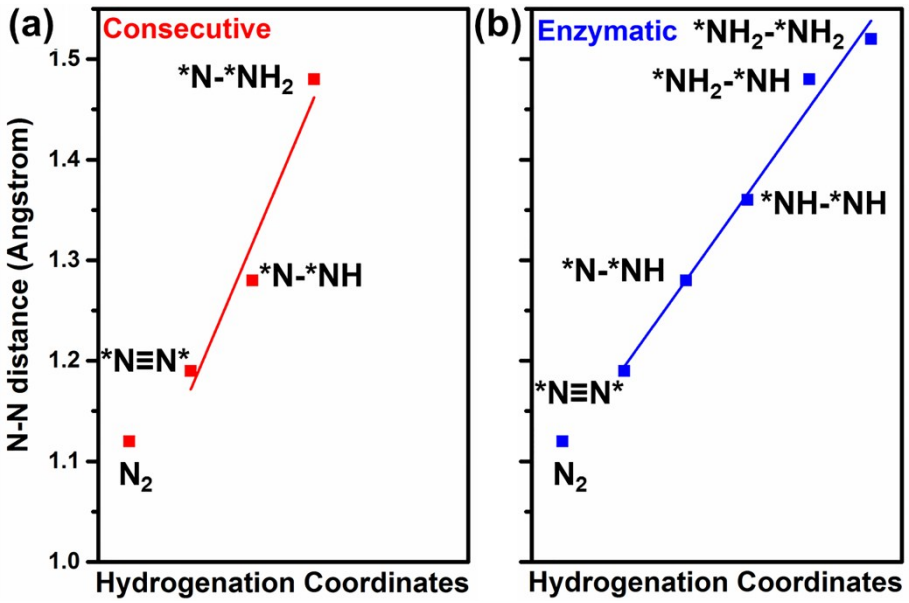


Fig. S6. Relationship between hydrogenation and N-N bond length. (a) consecutive and (b) enzymatic mechanisms on meta-position doped BP.

8. Free energy diagram for the nitrogen reduction to ammonia on meta-position doped BP

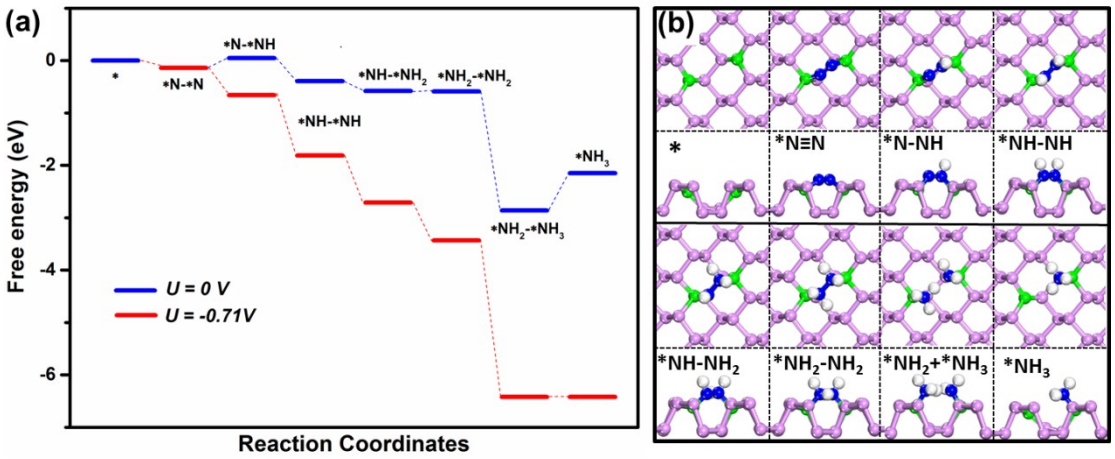


Fig. S7 (a) Free energy diagram for the nitrogen reduction to ammonia on meta-position doped BP at zero (blue line) and limited potential (red line) through enzymatic pathway. (b) Optimized geometric structures of various reaction intermediates along the reaction path of nitrogen reduction through enzymatic mechanisms.

9. Relationship between hydrogenation and N-N bond length on meta-position doped BP

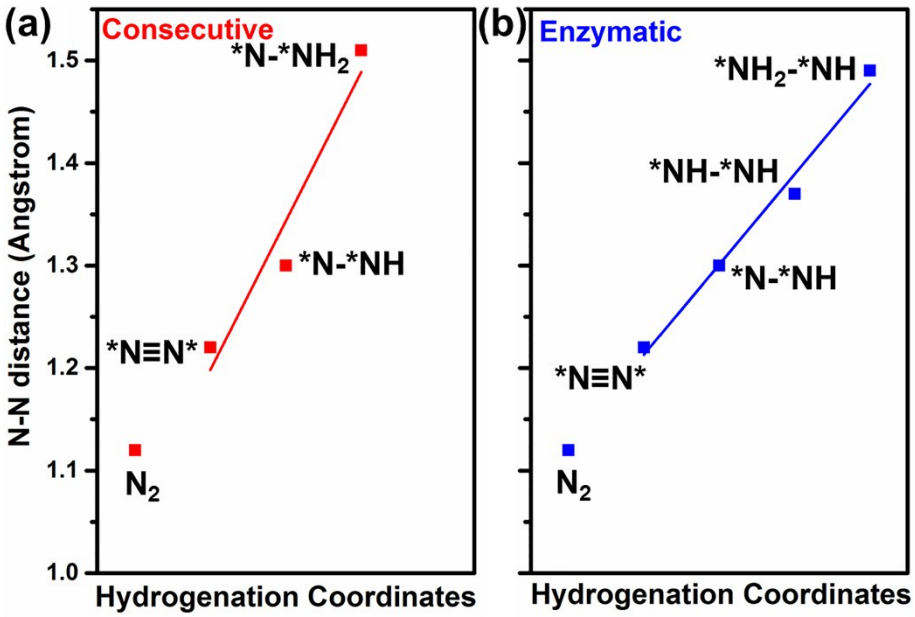


Fig. S8. Relationship between hydrogenation and N-N bond length. (a) consecutive and (b) enzymatic mechanisms on para-position doped BP.

10. Energy diagram for nitrogen direct dissociation

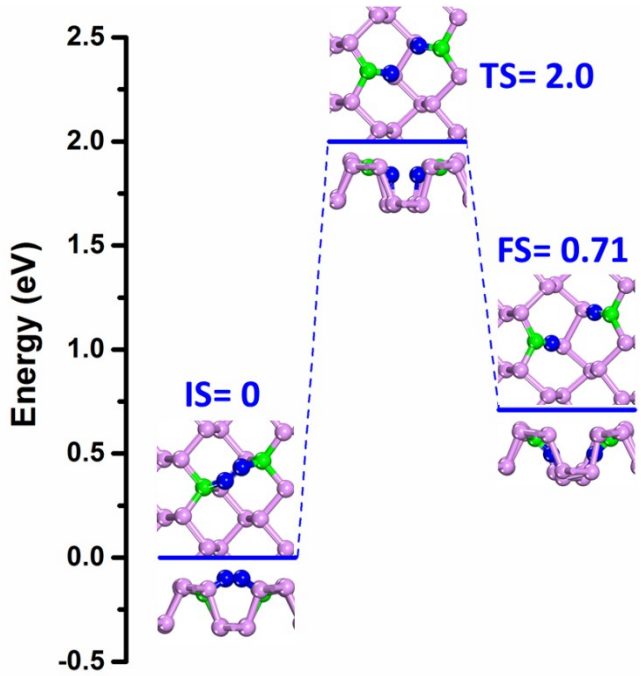


Fig. S9. Energy diagram for nitrogen direct dissociation on para-position doped BP

11. Hybridization diagrams of B and C elements

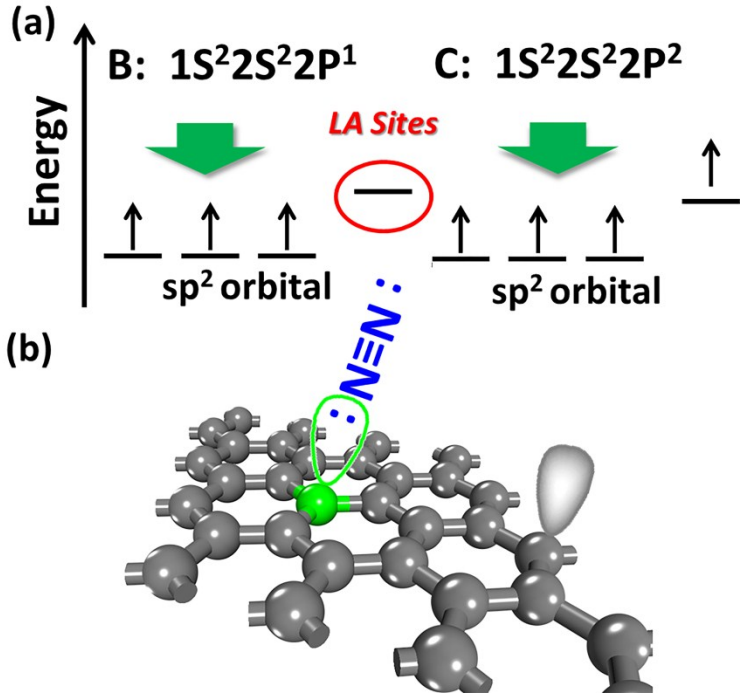


Fig. S10 (a) sp2 hybridization diagrams of B and C elements. B can form a Lewis acid site after sp2 hybridization. (b) The diagrams of B-doped graphene capture nitrogen.

12. Free energy diagram for the nitrogen reduction to ammonia on 2B-doped graphene

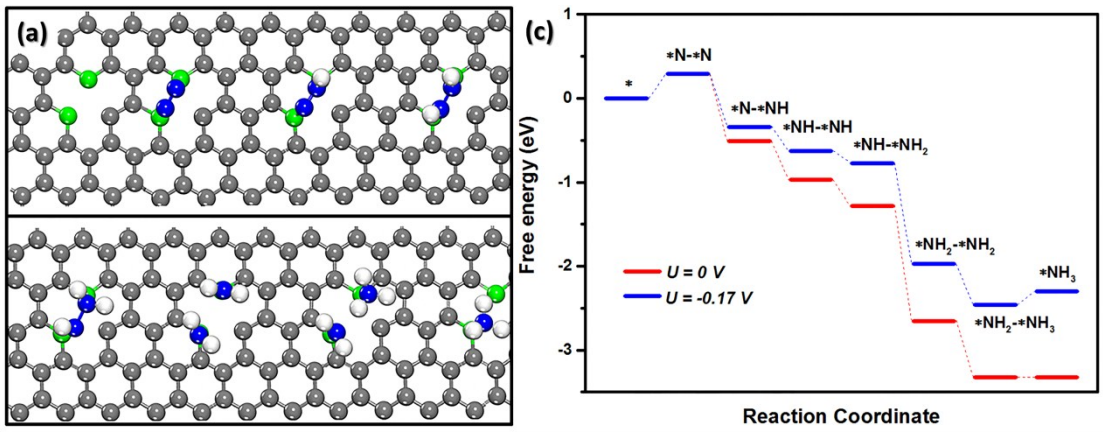


Fig. S11 (a) Optimized geometric configurations of various reaction intermediates along the reaction path of nitrogen reduction through enzymatic pathways. Free energy diagram for the nitrogen reduction to ammonia on 2B-doped graphene at zero potential (blue line) and onset-potential (red line) through enzymatic pathways. The rate-limiting step is formation of second *NH3 group and needs to overcome a high energy, the value of ΔG only is 0.17 eV.