Supporting information for:

Single Boron Atom doped Boron Nitride Edge as Metal-free Catalyst for N_2 Fixation

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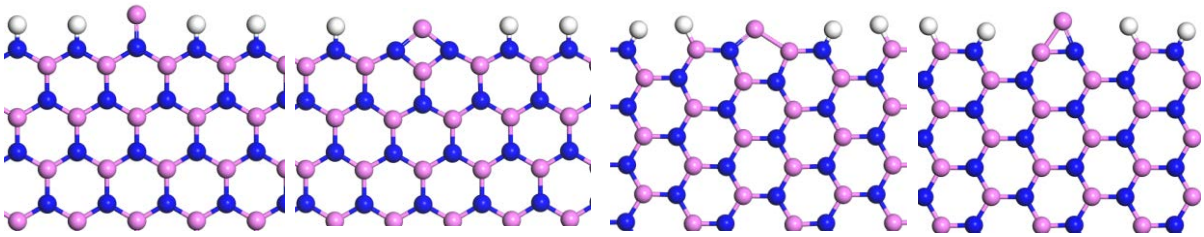
Table S1. Calculated zero point energies and entropy of different adsorption species, where the * represents the active site.

Adsorption species	**E_{ZPE} (eV)**	**-TS (eV)**
N_2	0.15	-0.58
*N_2(end-on)	0.22	-0.14
*NNH	0.51	-0.16
*NNH_2	0.82	-0.17
*NNH_3	1.19	-0.16
*NH	0.35	-0.09
*NH_2	0.76	-0.12
*NH_3	0.97	-0.16
*NHNH	0.85	-0.15
*$NHNH_2$	1.15	-0.19
*NH_2NH_2	1.35	-0.22
*NH_2NH_3	1.60	-0.28
*N_2(side-on)	0.19	-0.12
*NNH	0.49	-0.14
*NHNH	0.81	-0.13
*$NHNH_2$	1.14	-0.17
*NH_2NH_2	1.34	-0.21
*NH_2NH_3	1.60	-0.28
NH_3	0.58[1-2]	-0.56

Table S2. The formation energy for B decorated at different adsorption site of BN zigzag edge and armchair edge.



ΔE_{ad} = -1.01 eV	ΔE_{ad} = -3.04 eV	ΔE_{ad} = -1.46 eV	ΔE_{ad} =1.18 eV

The formation energy of B at BN edge is calculated by,

$E_{ad}=E_{B@BN}-E_B-E_{BN}$

Where $E_{B@BN}$, E_B, and E_{BN} is the total energy of single B decorated at BN edge, single B atom in bulk phase, and pure BN edge.

Figure S1.

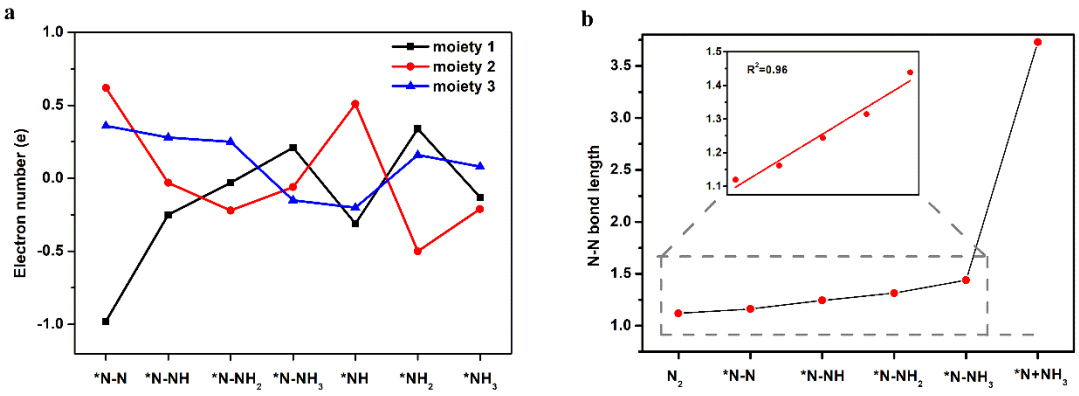


Figure S1. a) Charge variation of three moieties. b) N-N bond distance along the distal mechanism via end-on adsorption pathway, where the bond length increases linearly before broken.

1. Azofra, L. M.; Li, N.; MacFarlane, D. R.; Sun, C., Promising prospects for 2D d2–d4 M3C2 transition metal carbides (MXenes) in N2 capture and conversion into ammonia. *Energ Environ Sci* **2016,** *9* (8), 2545-2549.
2. Ling, C.; Bai, X.; Ouyang, Y.; Du, A.; Wang, J., Single Molybdenum Atom Anchored on N-Doped Carbon as a Promising Electrocatalyst for Nitrogen Reduction into Ammonia at Ambient Conditions. *The Journal of Physical Chemistry C* **2018,** *122* (29), 16842-16847.