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Activity and selectivity of N_2 fixation on B doped g-C_9N_{10}: A density functional theory study

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In our work, the phonon contribution of solids to free energy is negligible. To verify this point, we estimated the $\Delta E_{ZPE} - T\Delta S$ term of $N_2 + * \rightarrow N_2*$ process on B_A doped g-C_9N_{10} with and without phonon contribution using harmonic approximation[1], the equation is as shown in following:[2]

$$E_{ZPE} = \frac{1}{2}\sum_i h\upsilon_i \tag{1}$$

$$-TS = k_B T \sum_i \ln\left(1 - e^{-\frac{h\upsilon_i}{K_B T}}\right) - \sum_i h\upsilon_i \left(\frac{1}{e^{\frac{h\upsilon_i}{k_B T}} - 1}\right) \tag{2}$$

where h, υ_i and k_B are Planck constant, vibrational frequencies and Boltzmann constant, respectively. Vibrational analyses were performed using the finite difference method at the Γ point only.

As shown in Table S1, we found that $\Delta E_{ZPE} - T\Delta S$ values with and without phonon contribution differ by only 40 meV. Therefore, only the calculation of E_{ZPE} and S of reaction intermediates are needed as the contribution of substrate can be offset.

Table S1. Calculated E_{ZPE} and TS values (in eV) of N_2 adsorbed B_A doped g-C_9N_{10}, B_A doped g-C_9N_{10} and N_2 gas with and without phonon contribution. Calculated $\Delta E_{ZPE} - T\Delta S$ *of* $N_2 + * \rightarrow N_2*$ process on B_A doped g-C_9N_{10} with and without phonon contribution.

	with phonon contribution			**without phonon contribution**		
system	N_2 adsorbed B_A doped g-C_9N_{10}	B_A doped g-C_9N_{10}	N_2 gas	N_2 adsorbed B_A doped g-C_9N_{10}	B_A doped g-C_9N_{10}	N_2 gas
E_{ZPE}	3.02	2.87	0.148	0.22	0	0.148
TS	0.64	0.74	0.593	0	0	0.593
process	$N_2 + * \rightarrow N_2*$			$N_2 + * \rightarrow N_2*$		
ΔE_{ZPE}	0.002			0.072		
$T\Delta S$	-0.703			-0.593		
$\Delta E_{ZPE} - T\Delta S$	0.705			0.665		

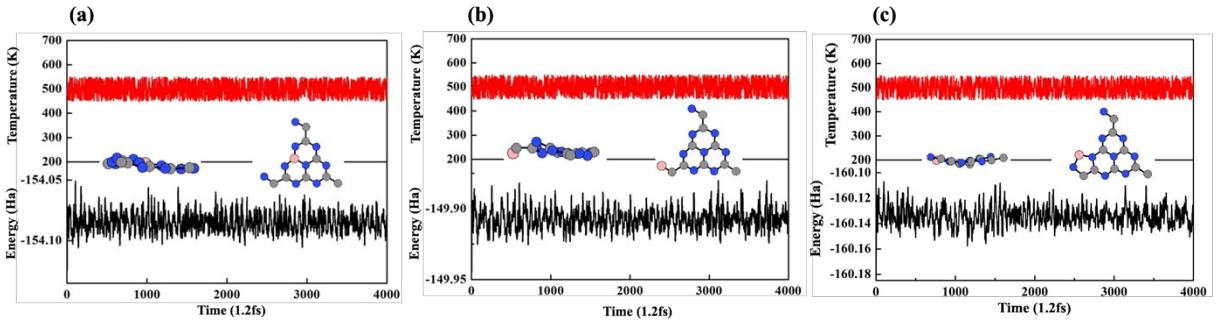

Figure S1. Variations of temperature and energy against time for *ab-initio* molecular dynamics (AIMD) simulations of the B_{C1} (a), B_{N1} (b) and B_A doped g-C_9N_{10} (c), and the insets show top and side views of the snapshot of the atomic configuration. The simulation is run at 500 K for 4.8 ps with a time step of 1.2 fs.

To study kinetics of end-on N_2 to side on N_2, rotation process was first calculated using the nudged elastic band (NEB) method[3] and the transition state was further refined by using climbing image nudged elastic band (CI-NEB) method[4,5]. The activation free energy (G_a) can be evaluated by the following equation:

$$G_a = G_{TS} - G_{IS}$$

where G_{IS} and G_{TS} stand for the free energy of initial and transition state, respectively.

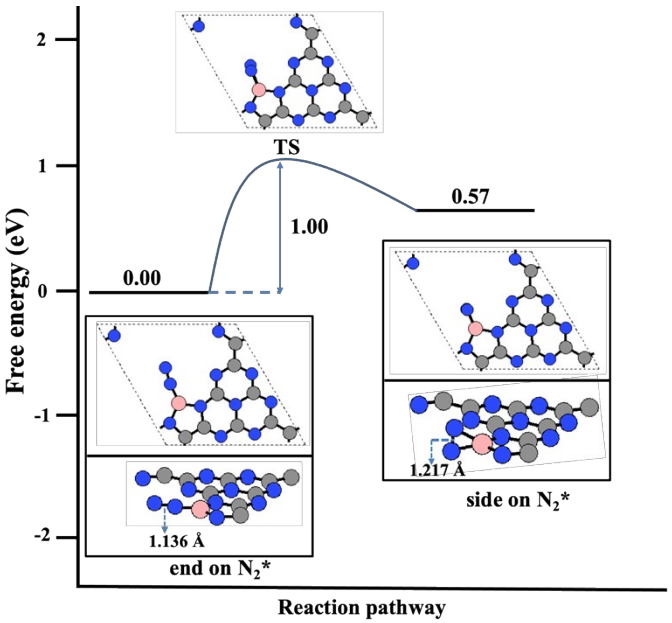

Figure S2. Free energy barrier diagram of N_2 rotation process on B_A doped g-C_9N_{10} (end on N_2* → side on N_2*).

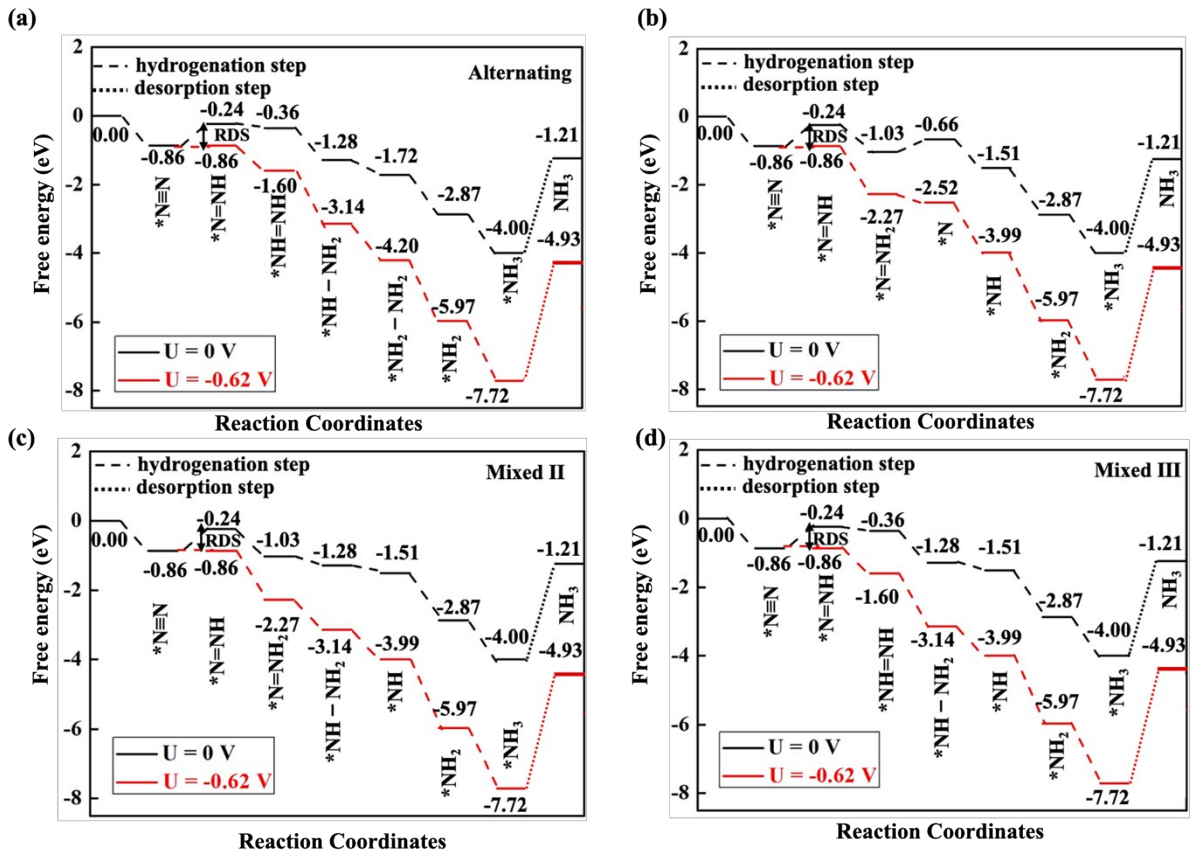

Figure S3. Free energy diagrams for N_2 reduction on B_{N1} doped g-C_9N_{10} through (a) alternating, (b) distal, (c) mixed II and (d) mixed III mechanisms at different applied potentials.

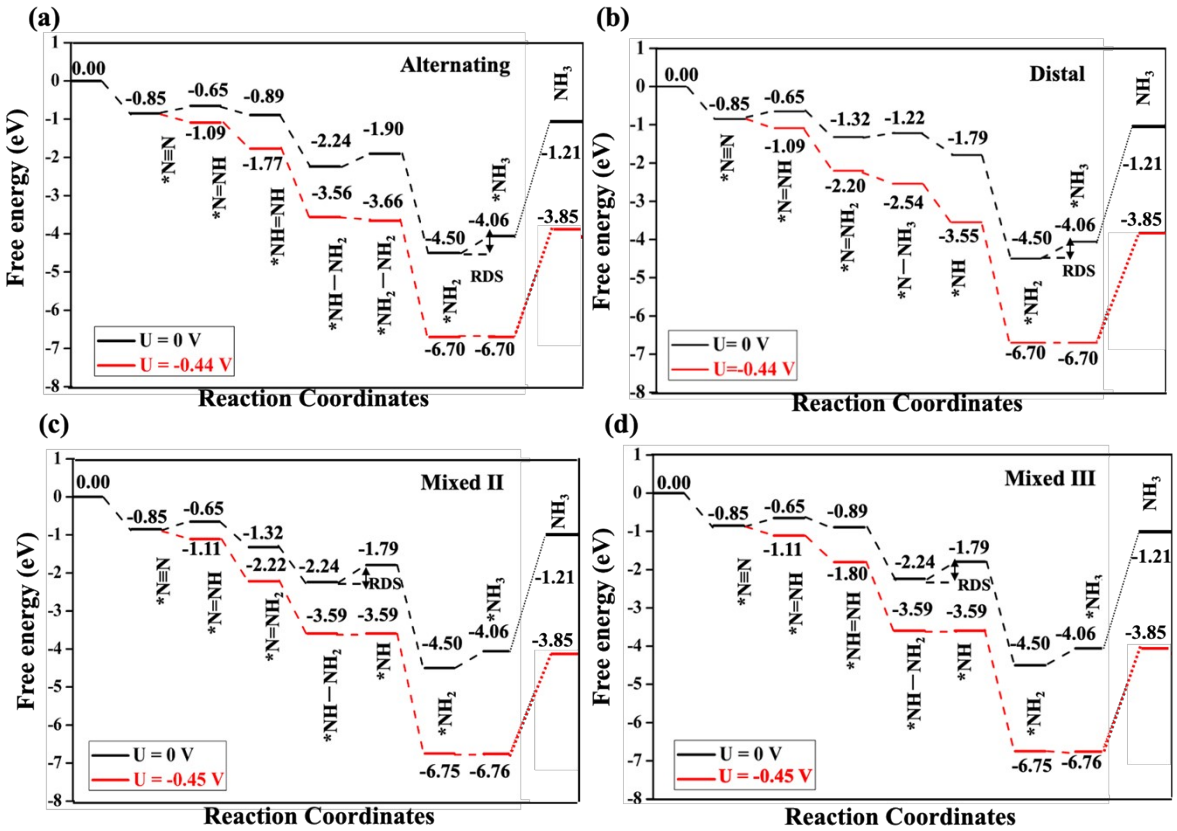

Figure S4. Free energy diagrams for N_2 reduction on B_A doped g-C_9N_{10} through (a) alternating, (b) distal, (c) mixed II and (d) mixed III mechanisms at different applied potentials.

Table S2. Calculated free energy of the reaction path followed by N_2RR on B_{N1} doped g-C_9N_{10}.

process		B_{N1} case
		ΔG (eV)
adsorption	$N_2 + * \rightarrow NN*$	-0.90
1e$^-$	$NN* + e^- + H^+ \rightarrow NNH*$	0.62
2e$^-$	$NNH* + e^- + H^+ \rightarrow NH_2N*$	-0.75
	$NNH* + e^- + H^+ \rightarrow NHNH*$	-0.08
3e$^-$	$NH_2N* + e^- + H^+ \rightarrow NH_2NH*$	-0.25
	$NH_2N* + e^- + H^+ \rightarrow N* + NH_3$	0.37
	$NHNH* + e^- + H^+ \rightarrow NH_2NH*$	-1.44
4e$^-$	$NH_2NH* + e^- + H^+ \rightarrow NH_2NH_2*$	-0.44
	$N* + e^- + H^+ \rightarrow NH*$	-0.85
	$NH_2NH* + e^- + H^+ \rightarrow NH*+NH_3$	-0.13
5e$^-$	$NH_2NH_2* + e^- + H^+ \rightarrow NH_2* + NH_3$	-1.15
	$NH* + e^- + H^+ \rightarrow NH_2*$	-1.36
6e$^-$	$NH_2* + e^- + H^+ \rightarrow NH_3*$	-1.13
desorption	$NH_3* \rightarrow NH_3 + *$	2.79

Table S3. Calculated free energy of the reaction path followed by N_2RR on B_A doped g-C_9N_{10}.

process		B_A case ΔG (eV)
adsorption	$N_2 + * \rightarrow NN*$	-0.85
1e$^-$	$NN* + e^- + H^+ \rightarrow NNH*$	0.20
2e$^-$	$NNH* + e^- + H^+ \rightarrow NH_2N*$	-0.67
	$NNH* + e^- + H^+ \rightarrow NHNH*$	-0.24
3e$^-$	$NH_2N* + e^- + H^+ \rightarrow NH_2NH*$	-0.92
	$NH_2N* + e^- + H^+ \rightarrow NNH_3*$	0.1
	$NHNH* + e^- + H^+ \rightarrow NH_2NH*$	-1.35
4e$^-$	$NH_2NH* + e^- + H^+ \rightarrow NH_2NH_2*$	0.34
	$NNH_3 + e^- + H^+ \rightarrow NH* + NH_3$	-0.57
	$NH_2NH* + e^- + H^+ \rightarrow NH* + NH_3$	0.45
5e$^-$	$NH_2NH_2* + e^- + H^+ \rightarrow NH_2* + NH_3$	-2.60
	$NH* + e^- + H^+ \rightarrow NH_2*$	-2.71
6e$^-$	$NH_2* + e^- + H^+ \rightarrow NH_3*$	0.44
desorption	$NH_3* \rightarrow NH_3 + *$	2.85

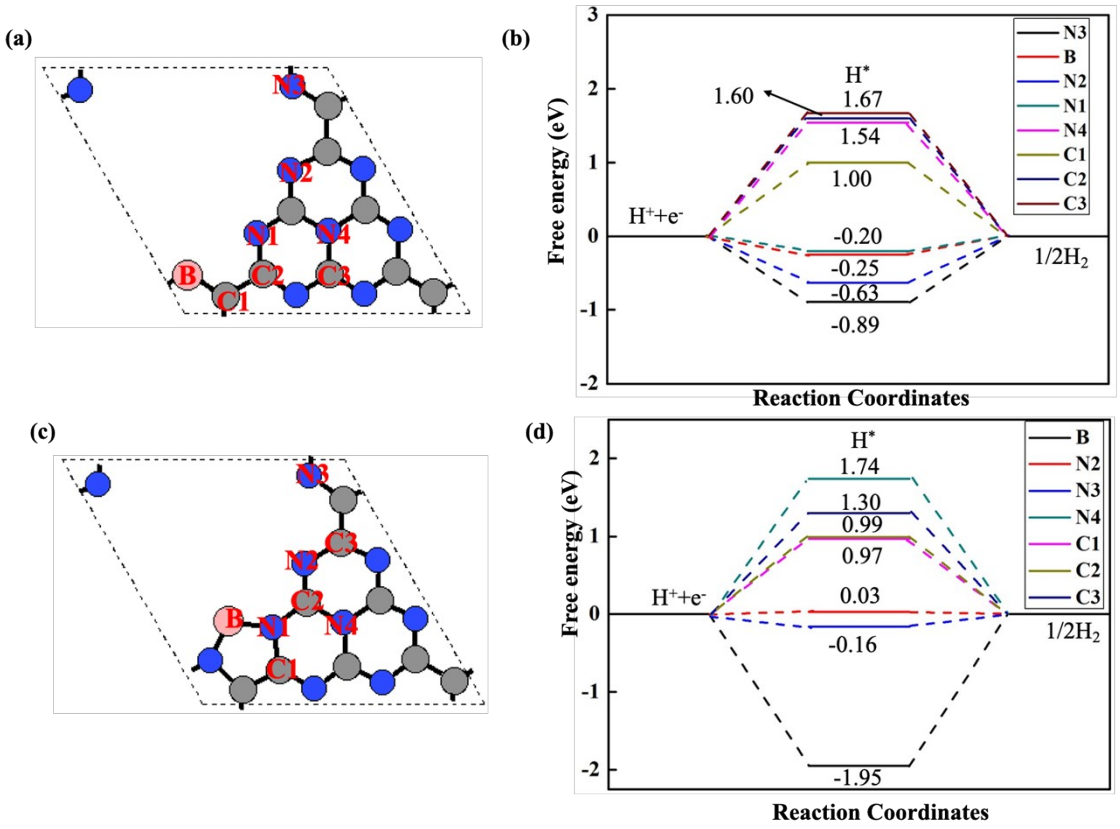

Figure S5. The eight possible H adsorption sites on B_{N1} doped *g*-C_9N_{10} (a) and B_A doped g-C_9N_{10} (c). The pink, blue, and gray balls denote boron, nitrogen, and carbon atoms, respectively. The Gibbs free energy profile of hydrogen evolution reaction (HER) of B_{N1} doped *g*-C_9N_{10} (b) and B_A doped g-C_9N_{10} (d). H adsorption on N1 site of B_A doped g-C_9N_{10} broke the structure, so it is not shown in HER diagram.

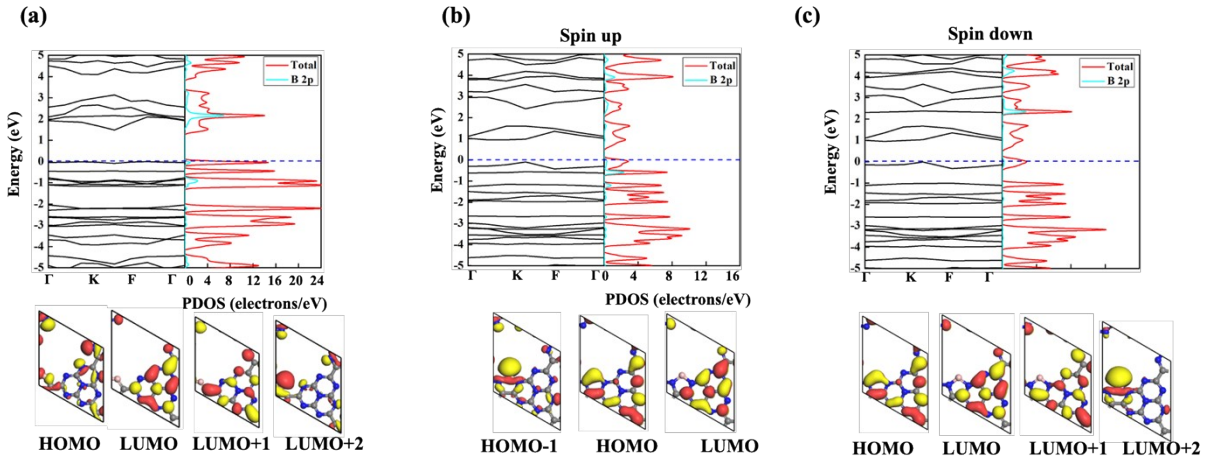

Figure S6. The band gap, PDOS HOMO and LUMO distributions of B_{N1} doped g-C_9N_{10} (a), B_A doped g-C_9N_{10} in spin up channel (b) and spin down channel (c) by using GGA/PBE functional.

Reference

1. D. R. Lide, CRC handbook of physics and chemistry, CRC Press, Boca Raton, USA 2001, 76,1995-1996.
2. C. Ling, X. Niu, Q. Li, A. Du, J. Wang, J. Am. Chem. Soc., 2018, 140, 14161-14168.
3. H. Kim, A. Tkatchenko, J. Cho, M. Scheffler, Phys. Rev. B., 2012, 85, 041403.
4. G. Henkelman, Jonsson, H. J. Chem. Phys., 2000, 113, 9978-9985.
5. G. Henkelman, B. P. Uberuaga, H. Jónsson, J. Chem. Phys., 2000, 113, 9901-9904.