Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Unleashing Power of Boron: Enhancing Nitrogen Reduction Reaction Through Defective ReS_2 Monolayers

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Table S1. Adsorption energies of N2 on the active B site, categorized by both end-on and side-on configurations.

Structures	**B@V_{Re}**	**B@V_S**	**B@V_{ReS}**	**B@V_{ReS2}**	**dB@V_{Re}**
E_{End-on} (eV)	0.439	-0.944	0.181	-0.261	0.357
$E_{Side-on}$ (eV)	No interaction	0.561	0.235	-0.101	No interaction

Table S2. Overview of NH_3* adsorption energy values ($^{\Delta G_{NH_3*}}$) on B-doped defective ReS_2, derived from activity assessments. The $^{\Delta G_{NH_3*}}$ represents the free energy of gaseous NH_3.

Structures	**ZPE**	**TS**	ΔG_{NH_3*}
B@V_{Re}	1.07	0.01	-0.19
B@V_S	1.06	0.01	-1.16
B@V_{ReS}	1.06	0.01	-0.46
B@V_{ReS2}	1.06	0.01	-0.43
dB@V_{Re}	1.08	0.01	-0.25

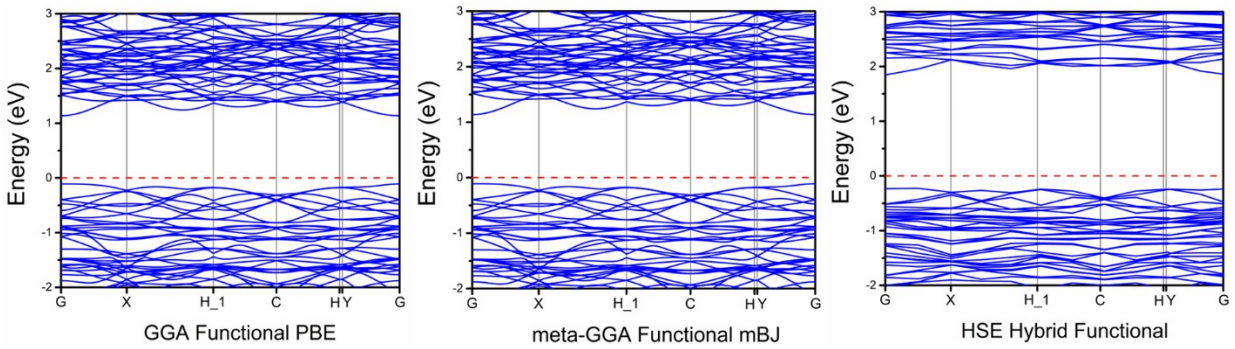

Figure S1. The band structures of ReS2 were determined using DFT with GGA-PBE, metaGGA-mBJ,[S1] and the HSE06 hybrid functional[S2,S3] methods.

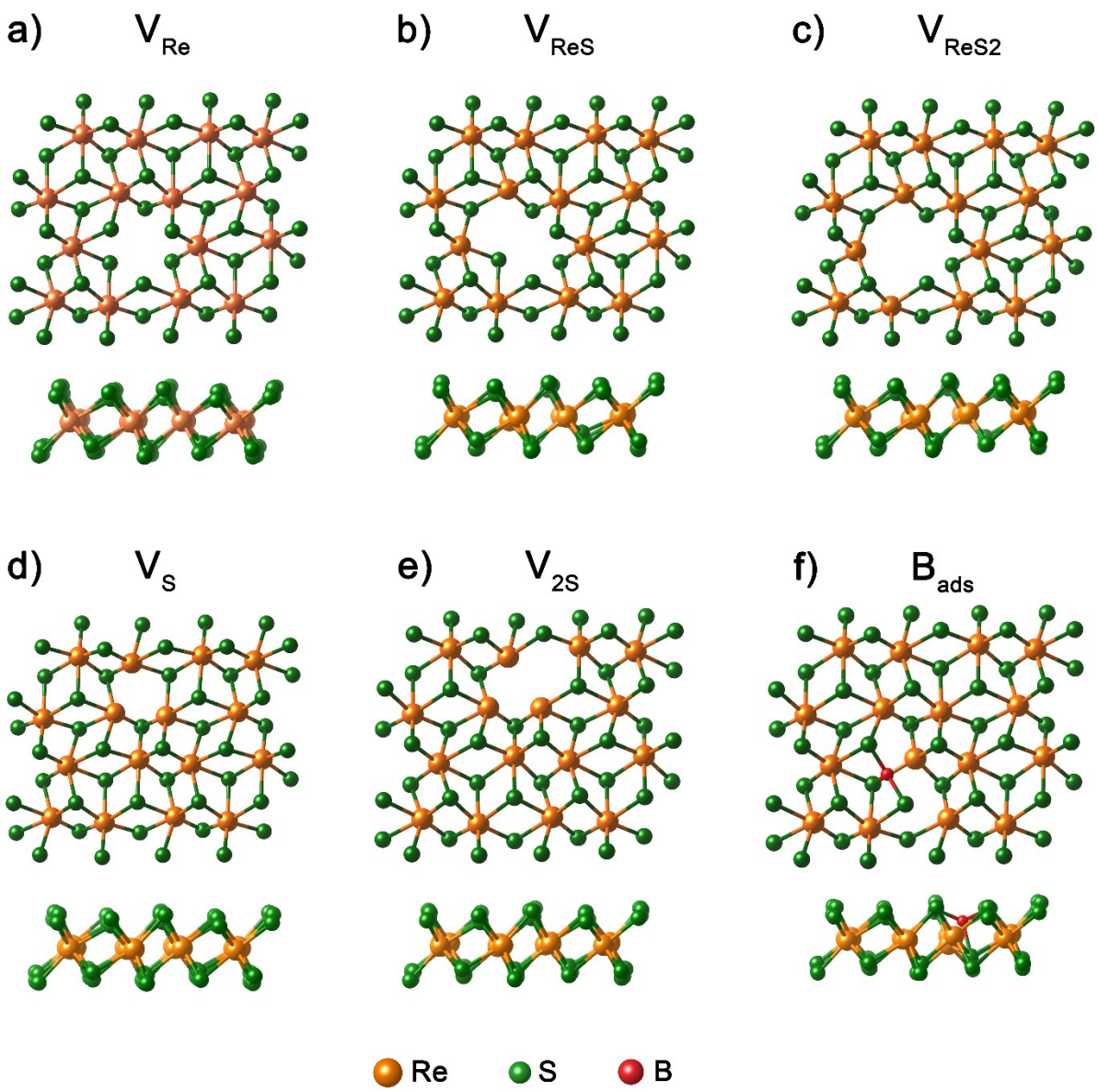

Figure S2. Optimized configurations of other five defective ReS_2 structures: (a) one-Re vacancy, (b) one-Re-and-one-S vacancy, (c) one-Re-and-two-S vacancy, (d) one-S vacancy, (e) two-S vacancy, and (f) B-adsorbed ReS_2, respectively. Orange, green, and red spheres represent Re, S, and B atoms. Symbol (V) denotes the vacancy sites of the ReS_2 substrate. Top and side views are provided for each configuration.

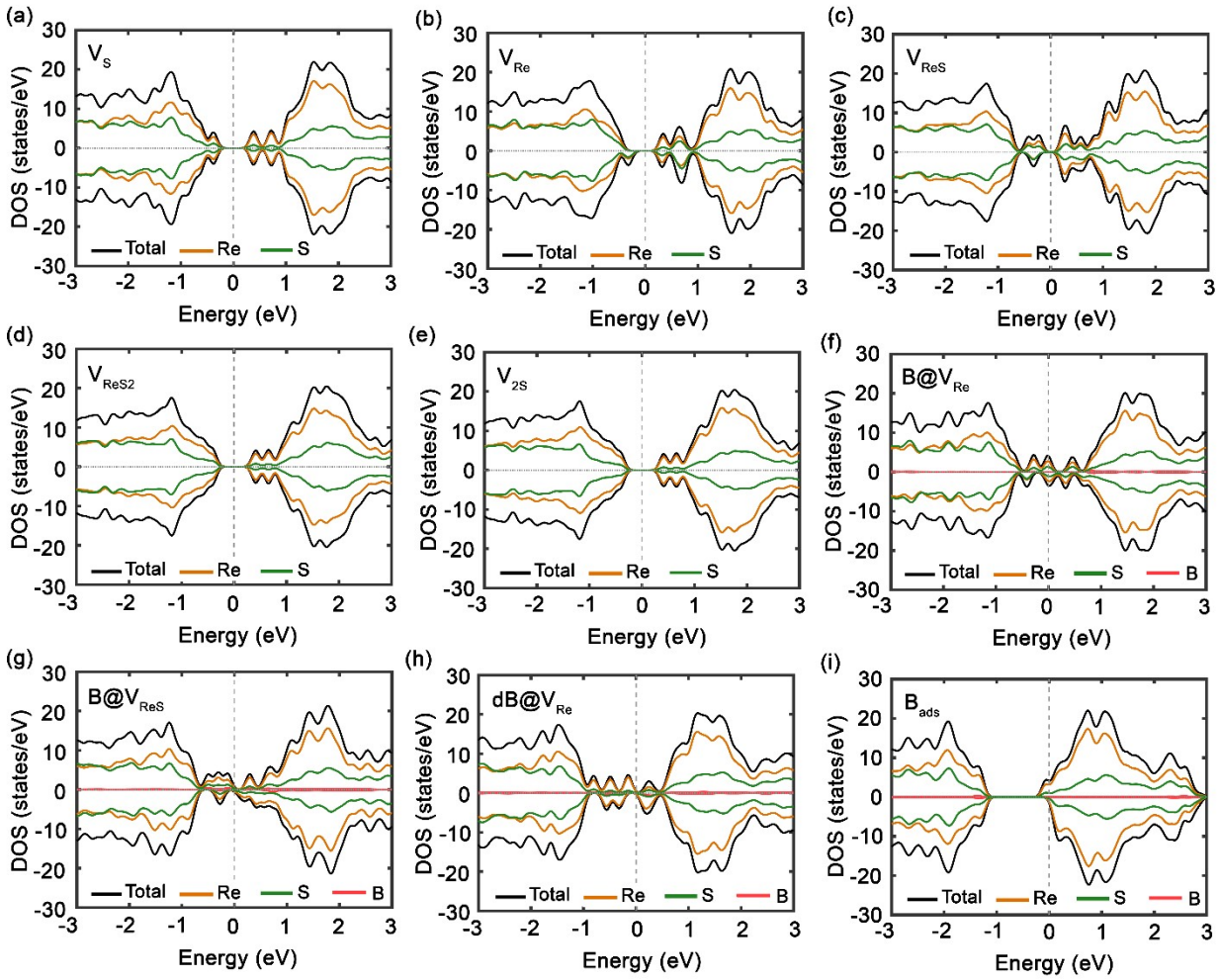

Figure S3. Partial density of states (PDOS) for (a) V_S, (b) V_{Re}, (c) V_{ReS}, (d) V_{ReS2}, (e) V_{2S}, (f) $B@V_{Re}$, (g) $B@V_{ReS}$, (h) $dB@V_{Re}$, and (i) B_{ads}. Black, orange, green, and red lines represent total DOS, PDOS of Re, S, and B atoms, respectively.

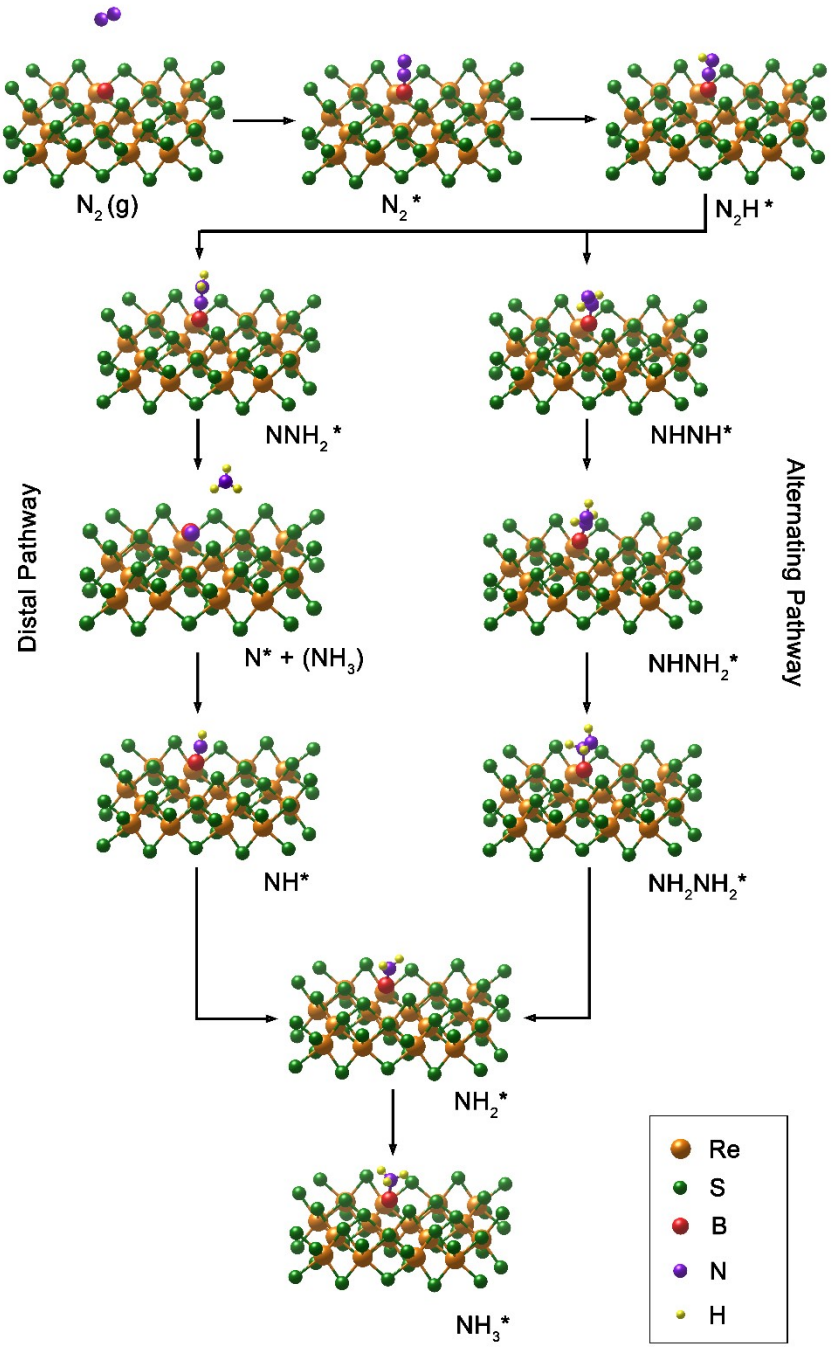

Figure S4. Schematic view of distal (left) and alternating (right) NRR reaction pathways for B-doped ReS_2 with S defect. Orange, green, red, purple, and yellow spheres represent Re, S, B, N, and H atoms, respectively.

References

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S3. F. Tran and P. Blaha, *Phys. Rev. Lett.*, 2009, **102**, 226401.