Boron-decorated C_9N_4 monolayers as promising metal-free catalysts for electrocatalytic nitrogen reduction reaction: A first-principle study

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Electronic Supplementary Information

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Table S1. Calculated zero-point energy and entropy of different adsorption species along the alternating pathway for NRR on B-C_9N_4, where ∗ denotes the adsorption site.

Species	E_{ZPE} **(eV)**	TS **(eV)**
N_2	0.15	0.58
***N≡N**	0.23	0.11
***N=NH**	0.51	0.15
***NH=NH**	0.87	0.10
***NH-NH_2**	1.20	0.12
***NH_2-NH_2**	1.50	0.14
***NH_2-NH_3**	1.70	0.33
***N-NH_2**	0.84	0.12
***N-NH_3**	1.19	0.11
***N**	0.08	0.06
***NH**	0.38	0.07
***NH_2**	0.74	0.06
***NH_3**	1.04	0.07
NH_3	0.89	0.06

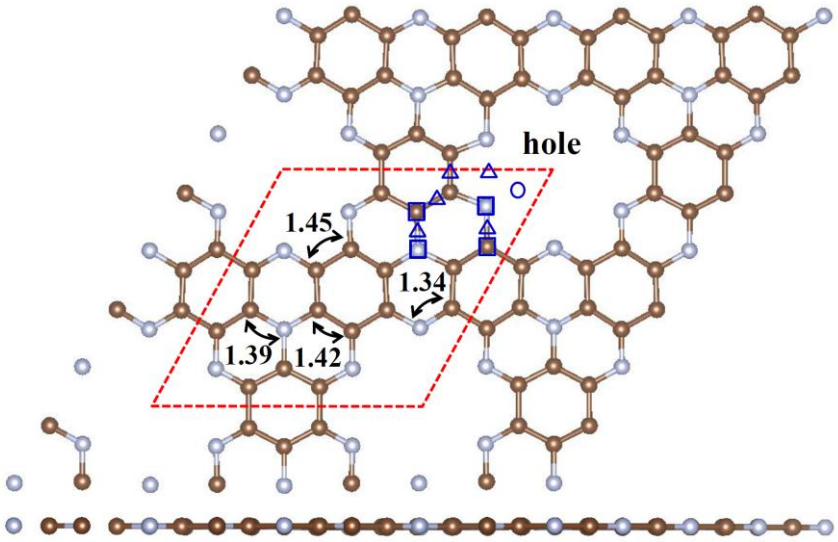

Fig. S1. Top and side views of the pristine (2×2) C_9N_4 monolayer, where the unit cell is enclosed by the red lines. The brown and silvery balls represent C and N atoms, respectively. The key bond lengths (in Å) are also given.

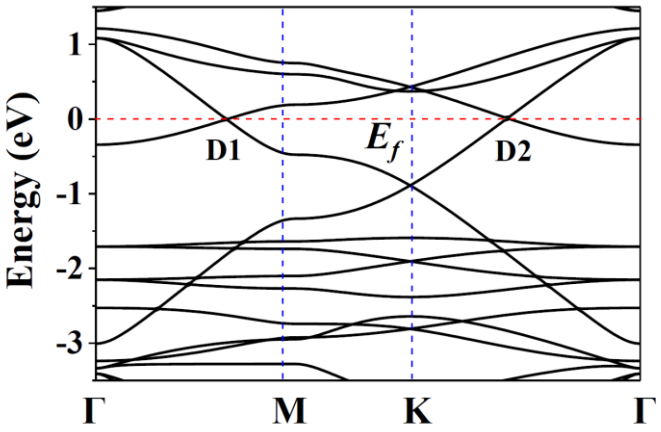

Fig. S2. Band structure of the pristine C_9N_4 monolayer unit cell. The horizontal dashed line denotes the position of Fermi level.

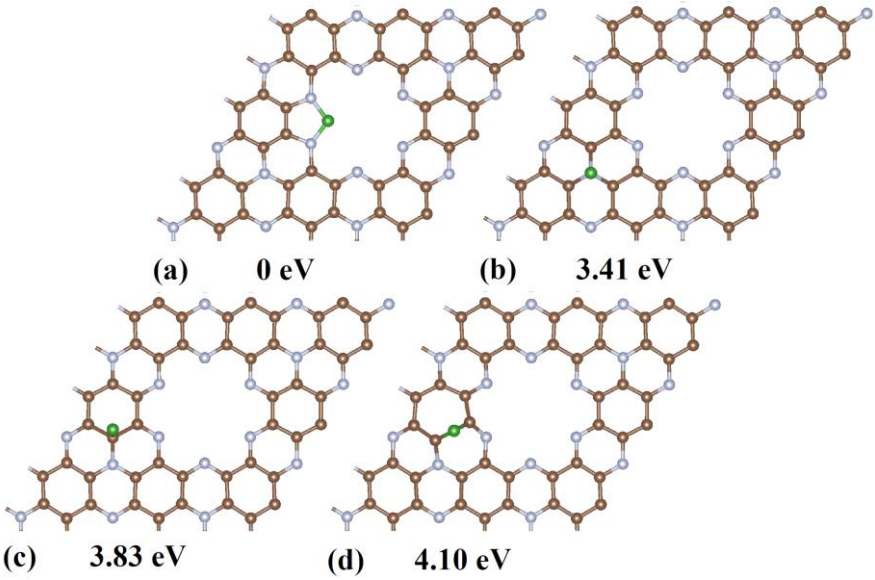

Fig. S3. Top views of the four stable B-C_9N_4 and their relative energies.

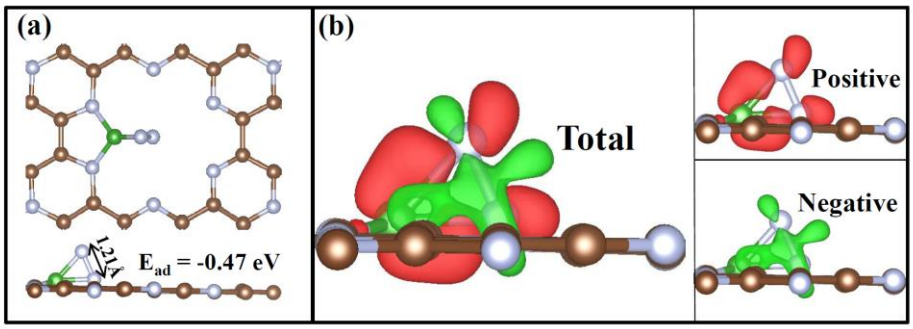

Fig. S4. (a) Top and side views of B-C_9N_4 with the adsorbed N_2 on the side-on pattern, where the adsorption energy and bond length of N_2 are shown. (b) Charge density difference of B-C_9N_4 with the adsorbed N_2 via the side-on pattern. The red and green regions represent the areas of electron accumulation and depletion, respectively. The isosurfaces are taken as 0.005 e/bohr^3.