[共同研究成果]

Density functional theory of N_2 fixation on B doped g-C$_9$N$_{10}$

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N_2 fixation to produce NH_3 is vital for fertilizers and energy storage. Converting N_2 to NH_3 under ambient conditions is challenging due to the stable $N\equiv N$ bond. The industrial Haber-Bosch method, though effective, requires extreme conditions and generates CO_2 [1-2]. Photocatalysis and electrocatalysis of N_2 provide eco-friendly alternatives, improving reaction rates, selectivity, and energy efficiency while avoiding CO_2 emissions. Discovering a suitable N_2RR catalyst is crucial for sustainable development [3]. Metal-free carbon materials have gained significant attention over metal-based catalysts due to their excellent stability, low cost, high surface area, and environmental friendliness [4]. B atom is electron-deficient atom, and it has Lewis-acid characteristics, which can drive the "σ donation-π backdonation" process when the B atom is attacked by Lewis base (such as N_2) [5]. Thus, in this project, we have systematically investigated N_2RR on B doped g-C$_9$N$_{10}$ with three doping configurations, i. e. B substituted N (B_{N1}), B substituted C (B_{C1}), and B anchored (B_A) on g-C$_9$N$_{10}$ using density functional theory (DFT) calculations [6].

First, we construct the seven B atom doping structures, namely B substituted C or N and anchored on g-C$_9$N$_{10}$ (Figure 1(a-h)). The stability of different doping sites is evaluated by formation energy, and B_{N1} and B_A (B_{C1}) are stable at N-poor (rich) conditions. (Figure 1(i)). We found that for B_{C1}, the N_2 molecule is physisorbed at B site due to the large boron-nitrogen distance (3.298 Å), while N_2 adsorbed on B_{N1} only has an end-on configuration with an adsorption energy of -1.53 eV and N_2 adsorbed on B_A has two different end-on and side-on configurations with E_{ads}'s of -1.48 eV and -0.91 eV, respectively. we found that N_2 is preferably

adsorbed in the end-on configuration than the side-on one by a large energy difference of 0.57

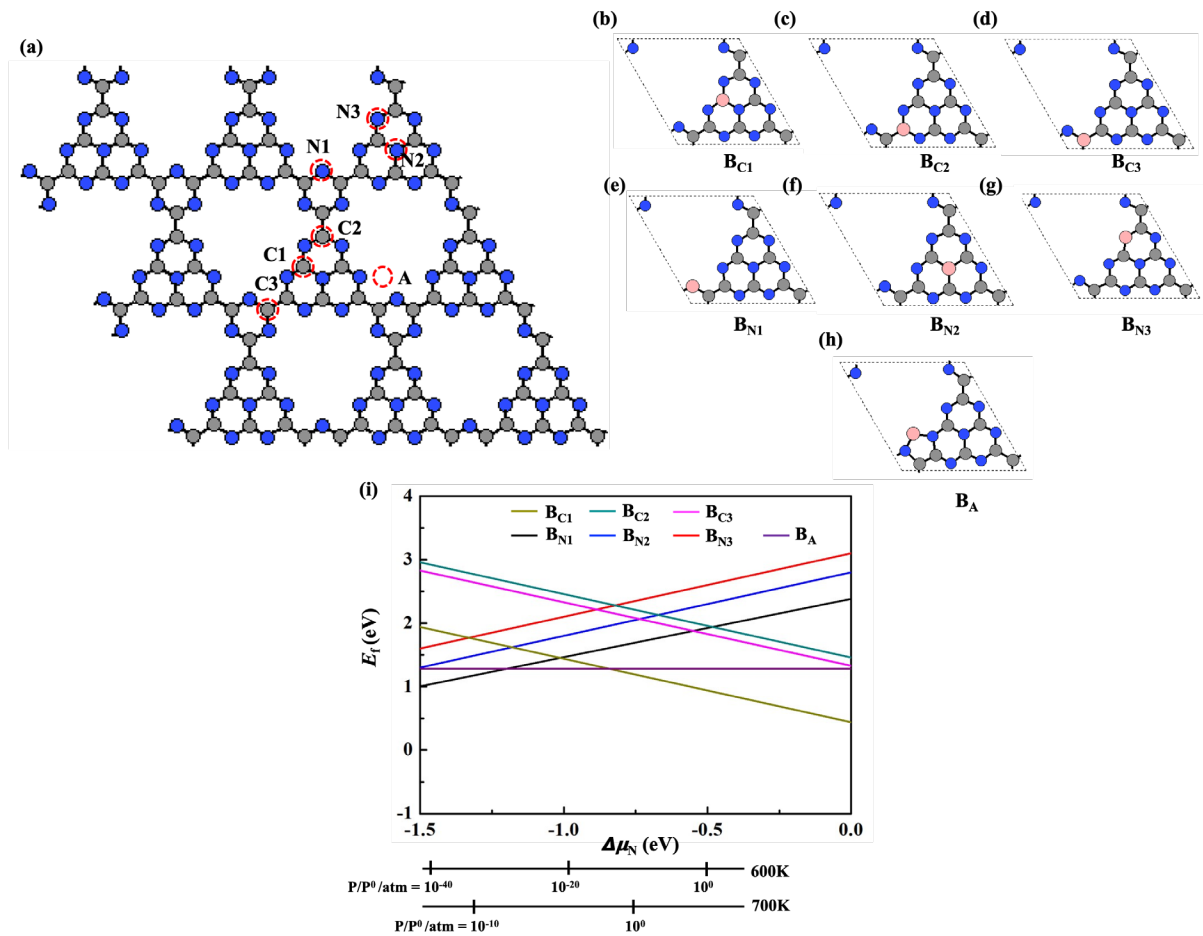eV and the transition from end-on to side-on N_2 requires a barrier of 1.00 eV by CI-NEB [7-8].

Figure 1. The possible site of B doped g-C_9N_{10} (a). The optimal structure of B_{C1} doped g-C_9N_{10} (b), B_{C2} doped g-C_9N_{10} (c), B_{C3} doped g-C_9N_{10} (d), B_{N1} doped g-C_9N_{10} (e), B_{N2} doped g-C_9N_{10} (f), B_{N3} doped g-C_9N_{10} (g) and B_A doped g-C_9N_{10} (h). (i) The formation energy of seven B doped g-C_9N_{10} structures as a function of N chemical potential. $\Delta\mu_N = 1/2(\mu_{N2} - E_{N2})$ where E_{N2} is the total energy of a gas-phase N_2 molecule at 0 K. The bottom axes show the corresponding N_2 chemical potentials at the absolute temperature T and partial pressure P (with $P° = 1$ atm), $\mu_{N2} = H°(T) - H°(0) - TS°(T) + k_BT\ln(P/P°)$, where the enthalpy $H°$ and the entropy $S°$ are obtained from ref. 9.

Then, we investigated the five possible N_2RR pathways [10-12] starting by end-on N_2

adsorption, including alternating, distal, mixed I, mixed II and mixed III pathways. The free energy

calculations show that B_{N1} and B_A doped g-C_9N_{10} proceeds via mix I mechanism (Figure 2) starting

from the stable end-on N_2 with low limiting potentials of -0.62 V and -0.44 V, respectively. Importantly,

H blocks active site in the case of B_A doped g-C_9N_{10} due to stronger E_{ads} of H* (-1.95 eV), resulting in

lower N_2RR selectivity, while B_{N1} doped g-C_9N_{10} can effectively prevent the H poisoning due to the weaker H adsorption relative to N_2 adsorption (-0.25 eV vs. -0.9 eV), thus improving the N_2RR activity and selectivity.

Finally, we also perform the band structure and adsorption spectrum to investigate the photocatalytic activity. The band structures and absorption spectra indicate that introducing B atom can decrease the band gap and enhance the light absorption ability in the visible range.

In summary, in this project, partly DFT works were performed by Simulation Tool for the Atom Technology (STATE) program using AOBA-B system of the supercomputer in tohoku university to study atomistic insights into the N_2RR on B-doped g-C_9N_{10}. The supercomputer offers very effective and time-saving to run the work. We think that our work would motivate experimental work to prove and explore the more carbon nitride materials for N_2RR. Detailed results are published in reference [6].
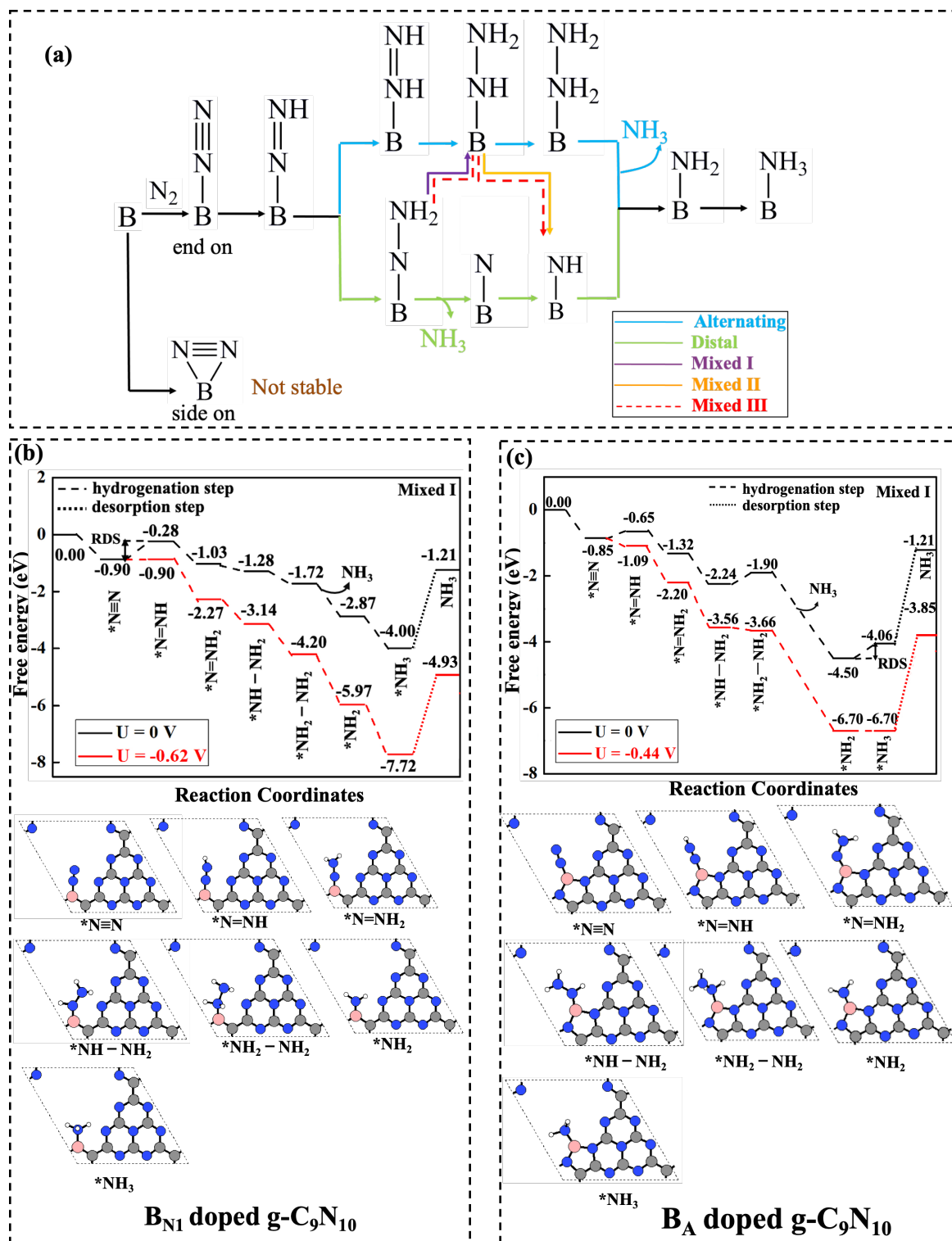
Figure 2. (a) Schematic depiction of distal, alternating, enzymatic and Mixed mechanisms for N_2RR. (b) Free energy diagrams for optimal N_2 reduction pathway on B_{N1} doped g-C_9N_{10} through mixed I mechanisms with the optimized structure of each intermediate. (c) Free energy diagrams for optimal N_2 reduction pathway on B_A doped g-C_9N_{10} through enzymatic mechanism with the optimized structure of each intermediate.

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