Supporting Information

Frustrated Lewis Pairs Photocatalyst for Visible Light-Driven Reduction of CO into Multi-carbon Chemicals

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Complement to Computational Detail

The adsorption energy (E_{ads}) of the single B atom on C_2N and CO species on B/C_2N substrate was calculated based on the equation: $E_{ads} = E_{total} - E_{substrate} - E_{adsorbate}$, where E_{total}, $E_{substrate}$ and $E_{adsorbate}$ represent the total energies of the systems containing the substrate and adsorbate, the substrate, and the adsorbate, respectively. According to this definition, a more negative adsorption energy indicates a stronger adsorption.

The Gibbs reaction free energy change (ΔG) of each elementary step during the CO reduction process was calculated by using the computational hydrogen electrode (CHE) model proposed by Nørskov *et al*.[1] The chemical potential of the proton-electron pair in aqueous solution is related to that of one-half of the chemical potential of an isolated hydrogen molecule. Based on this model, the ΔG value can be obtained by the formula: $\Delta G = \Delta E + \Delta ZPE - T\Delta S + \Delta G_{pH} + eU$, where ΔE is the reaction energy of reactant and product species adsorbed on the catalyst directly obtained from DFT computations; ΔZPE and ΔS are the changes between the adsorbed species and the gas phase molecules in zero point energies and entropy at 298.15 K, which can be calculated from the vibrational frequencies. ΔG_{pH} is the free energy correction of pH, and can be calculated by: $\Delta G_{pH} = K_B T \times pH \times ln10$. Notably, the pH value was set to be zero in this work for simplicity; U was the applied potential.

The reaction potentials of CO with respect to the normal hydrogen electrode (NHE, pH=0) can be calculated by :

$$\varphi = \frac{-1}{nF} \times [\, \Delta_f G^{o}_{(product)} - \Delta_f G^{o}_{(reactant)} \,]$$

where n is the number of electrons, F is the Faraday constant, and ${}^{\Delta_f G^{o}_{(x)}}$ stands for the Gibbs free energy of *x* at the standard state under the pressure of one bar and the temperature of 298.15 K, which can be obtained in the CRC handbook.[2]

Table S1. The adsorption energies of an isolated B atom at different decoration sites on monolayer C_2N. The definition of each site can be referred from Figure 1 in the main text.

Site	E_{ads} (eV)
1	-2.31
2	-5.46
3	Relax to site 2
4	-1.33
5	-1.01

Table S2. The calculated charge transfer (unit in electrons) of the decorated B atom, the host N atoms (N_{CO}) directly binding with the adsorbed CO, and the adsorbed CO molecules on B/C_2N (the charges on all the atoms of the B/C_2N substrate except for that of N_{CO} are summed into the B atom). The positive and negative data represent the charge loss and gain, respectively.

Numbers of CO	1	2	3	4	5
B atom	-0.18	-0.14	-0.15	-0.20	-0.20
N atom	+0.00	+0.11	+0.11	+0.12	+0.12
$CO_{(n)}$	+0.18	+0.03	+0.04	+0.08	+0.08

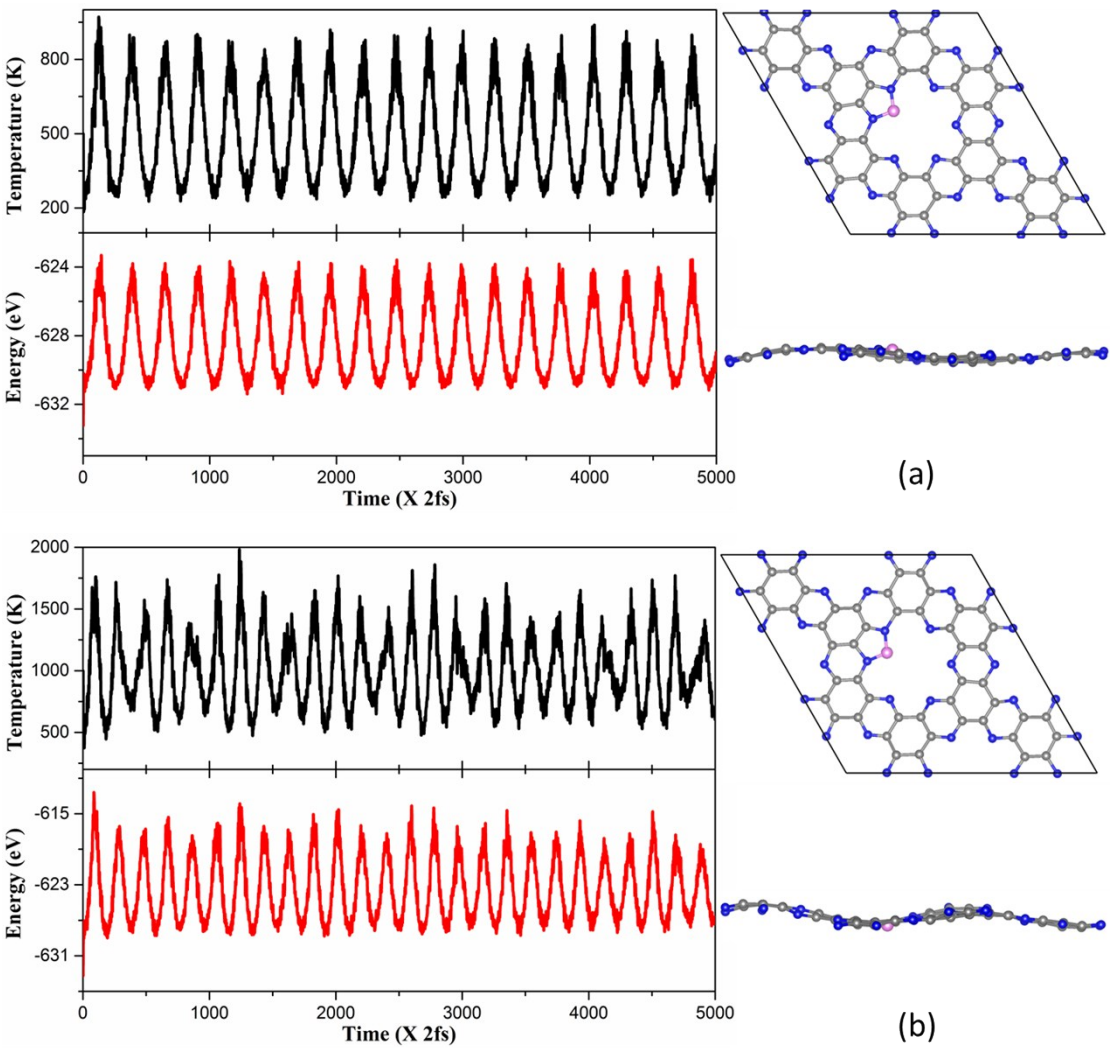

Figure S1. Variations of temperature and energy versus the time for AIMD simulations of B/C_2N, which is run under (a) 500 K and (b) 1000 K for 10 ps with a time step of 2 fs. Schematic diagrams of the B/C_2N atomic configuration after dynamics simulation (top and side views) are also given, the C, N, and B atoms are denoted by the grey, blue, and purple balls, respectively.

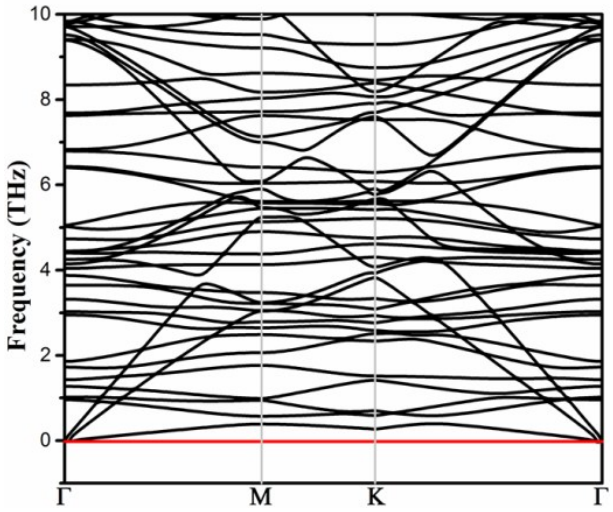

Figure S2. The calculated phonon dispersion of B/C_2N monolayer along the high-symmetry lines in the first Brillouin zone.

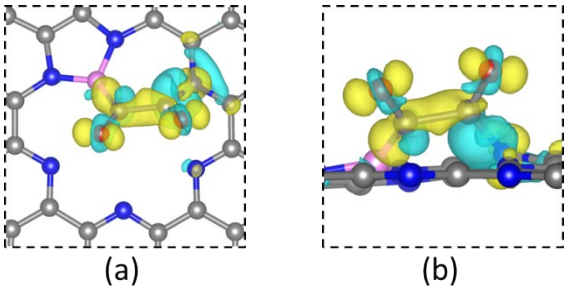

Figure S3. (a) Top view and (b) side view of the difference charge density plot for B/C_2N with two adsorbed CO molecules. The isosurface value is 0.008 $e/\text{Å}^3$, the charge accumulated and depleted regions are shown in yellow and cyan, respectively.

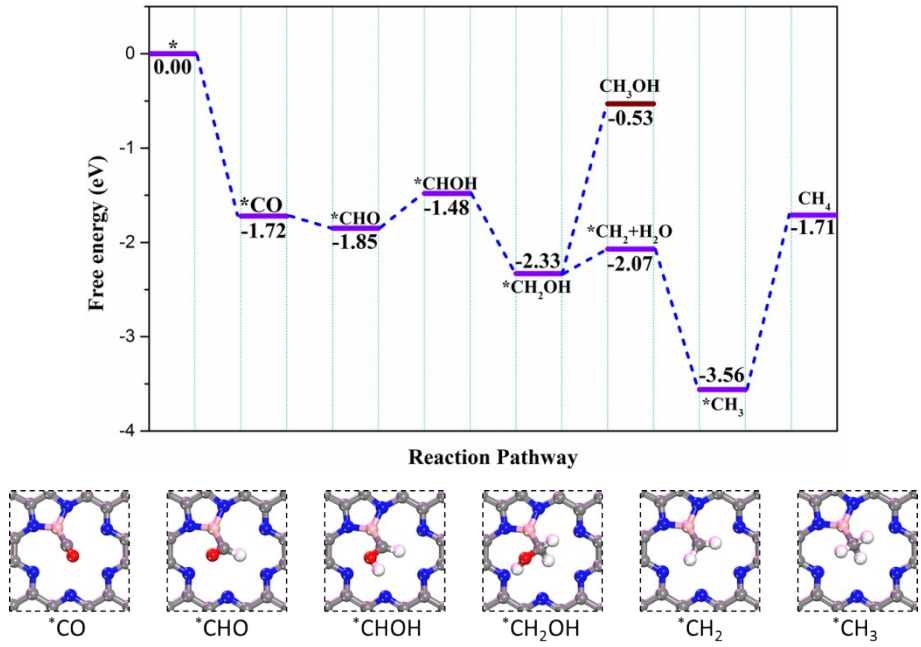

Figure S4. Gibbs free energy diagrams of CO reduction into CH_3OH and CH_4 at 0 V potentials. The structures of corresponding reaction intermediates are given in the lower panel.

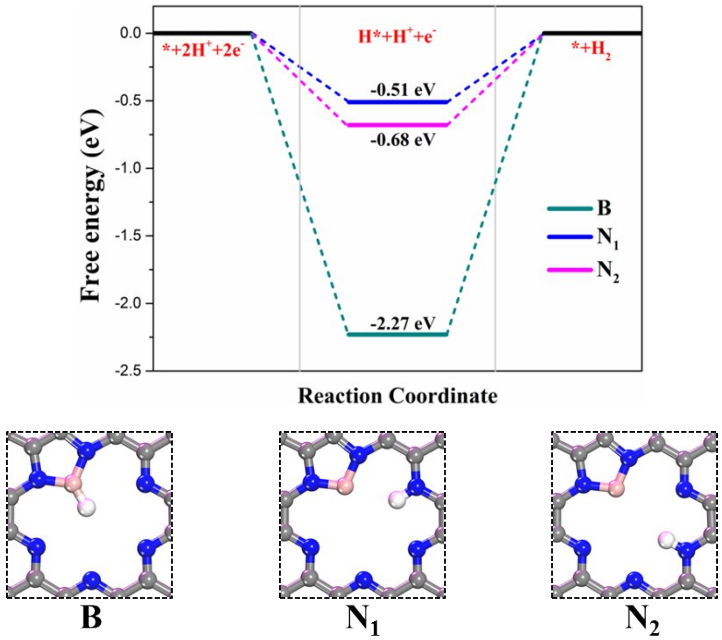

Figure S5. Gibbs free energy diagrams of HER on B/C_2N with different active sites (labeled B, N_1 and N_2). The corresponding reaction intermediates are given in the lower panel.

References

(1) J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Bligaard and H. Jonsson, *J. Phys. Chem. B,* 2004, **108**, 17886-17892.

(2) W. M. Haynes, CRC handbook of chemistry and physics; *CRC press*, 2014.