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# Strain effect on the catalytic activities of B- and B/N-doped black phosphorene for electrochemical conversion of CO to valuable chemicals

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## Complement to Computational Detail

The adsorption energy ($E_{ads}$) of the intermediate species of CO reduction on the designed B@BP and B-N@BP catalysts 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 ($\Delta G$) 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 $\Delta G$ value can be obtained by the formula: $\Delta G = \Delta E + \Delta ZPE - T\Delta S + \Delta G_{pH} + eU$, where $\Delta E$ is the reaction energy of reactant and product species adsorbed on the catalyst directly obtained from DFT computations; $\Delta ZPE$ and $\Delta S$ 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. $\Delta G_{pH}$ 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.

**Table S1.** The calculated cohesive energies ($E_{coh}$, eV per atom) and formation energies ($E_f$, eV) of B@BP with different compressive strain along the armchair direction.

| Strain | 0% | 3% | 5% | 7% |
|---|---|---|---|---|
| $E_{coh}$ | 3.613 | 3.611 | 3.607 | 3.604 |
| $E_f$ | 0.806 | 0.887 | 1.068 | 1.257 |

**Table S2.** The calculated adsorption energies ($E_{ads}$, eV) of CO molecule and $CH_2$ species on B@BP with different compressive strain along the armchair direction.

| Strain | 0% | 3% | 5% | 7% |
|---|---|---|---|---|
| $E_{ads}$(CO) | -1.27 | -1.32 | -1.34 | -1.36 |
| $E_{ads}$($CH_2$) | -4.38 | -3.78 | -3.78 | -3.77 |

**Table S3.** The calculated cohesive energies ($E_{coh}$, eV per atom), formation energies ($E_f$, eV) and distances between B and N dopants ($L_d$, Å) of para-B-N@BP with different compressive strain along the armchair direction.

| Strain | 0% | 3% | 5% | 7% |
|---|---|---|---|---|
| $E_{coh}$ | 3.631 | 3.630 | 3.628 | 3.623 |
| $E_f$ | 1.566 | 1.590 | 1.726 | 1.937 |
| $L_d$ | 4.19 | 4.06 | 3.96 | 3.88 |

**Table S4.** The calculated adsorption free energy (eV) of proton ($^*$H) at B sites on B@BP and B-N@BP with different compressive strain.

| Strain | 0% | 3% | 5% | 7% |
|---|---|---|---|---|
| B@BP | -0.39 | -0.47 | -0.51 | -0.54 |
| B-N@BP | -0.38 | -0.47 | -0.51 | -0.55 |

**Table S5.** The calculated adsorption energies (eV) of water ($H_2O$) at active sites of designed catalysts with different compressive strain.

| Strain | 0% | 3% | 5% | 7% |
|---|---|---|---|---|
| B site in B@BP | -0.80 | -0.81 | -0.81 | -0.91 |
| B site in B-N@BP | -0.90 | -0.91 | -0.91 | -0.86 |
| N site in B-N@BP | -0.16 | -0.19 | -0.18 | -0.16 |

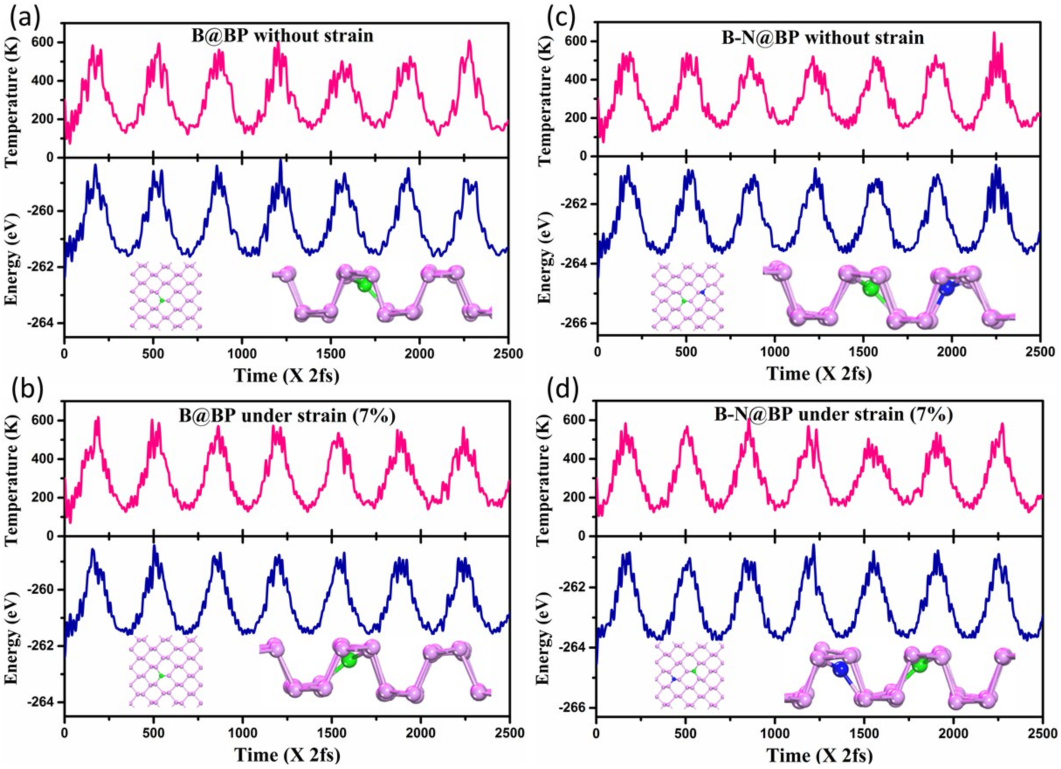

**Fig. S1** The variations of temperature and energy versus the time for AIMD simulations of (a) B@BP without strain, (b) B@BP with 7% compressive strain, (c) para-B-N@BP without strain and (d) para-B-N@BP with 7% compressive strain, which is run under 300 K for 5 ps with a time step of 2 fs. Schematic diagrams of these two atomic configurations after dynamics simulation (top and side views) are also given.

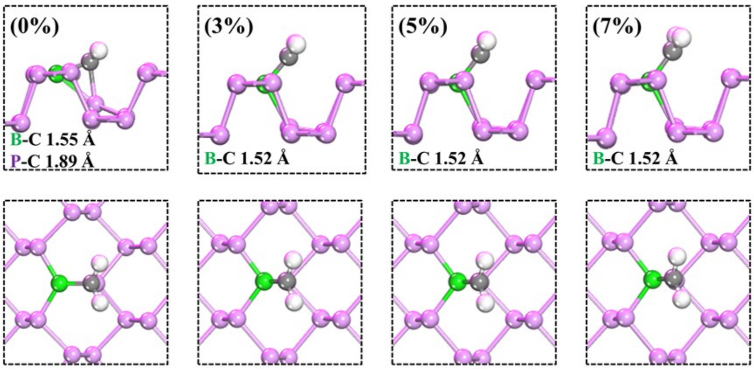

**Fig. S2** The atomic structures of $^*CH_2$ species adsorbed on B@BP with different compressive strain.

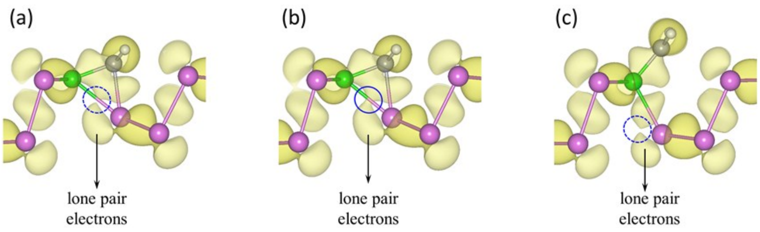

**Fig. S3** The deformation charge density of $^{*}CH_2$ species adsorbed on B@BP (a) without strain, (b) with 3% compressive strain before relaxation and (c) with 3% compressive strain after full relaxation. The isosurface value of the charge density plots is set to be 0.004 e Å$^{-3}$. For clarity, only the charge accumulation region (in yellow) was shown in this figure.

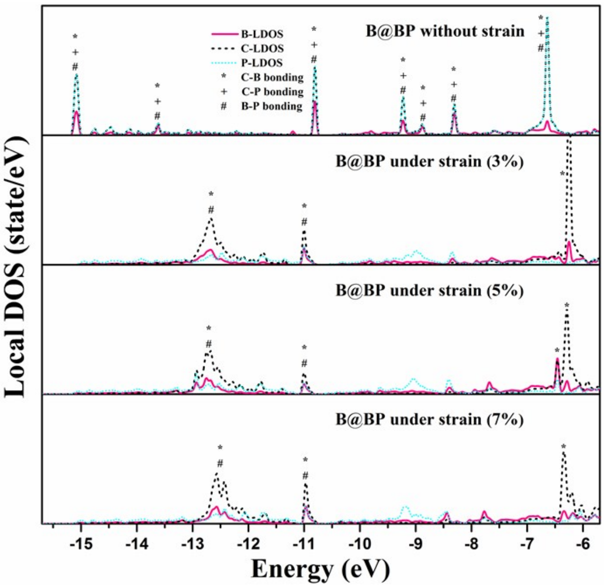

**Fig. S4** Local density of states (LDOS) of B@BP with the $^{*}CH_2$ species under different compressive strain (from 0% to 7%, respectively).

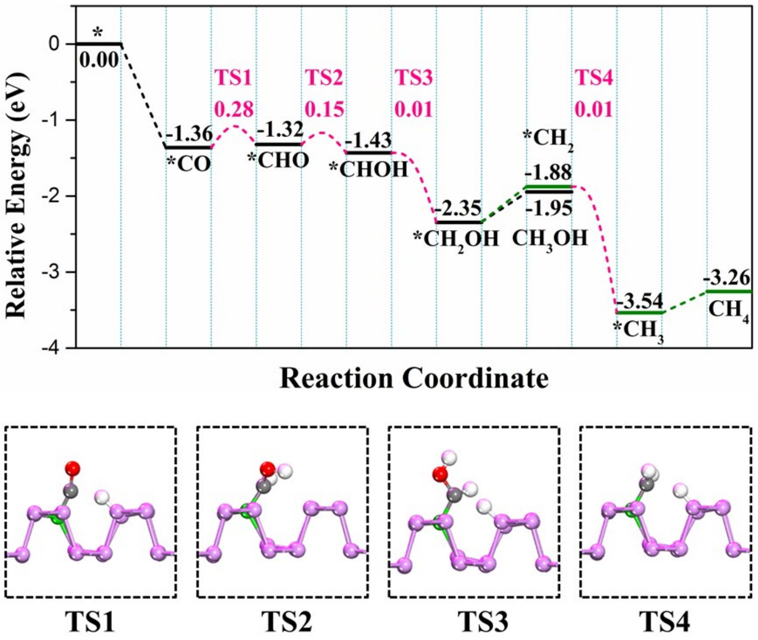

**Fig. S5** The detailed kinetic energy diagram of CO reduction towards $C_1$ products on B@BP with 7% compressive strain, and the structures of transition state are also given.

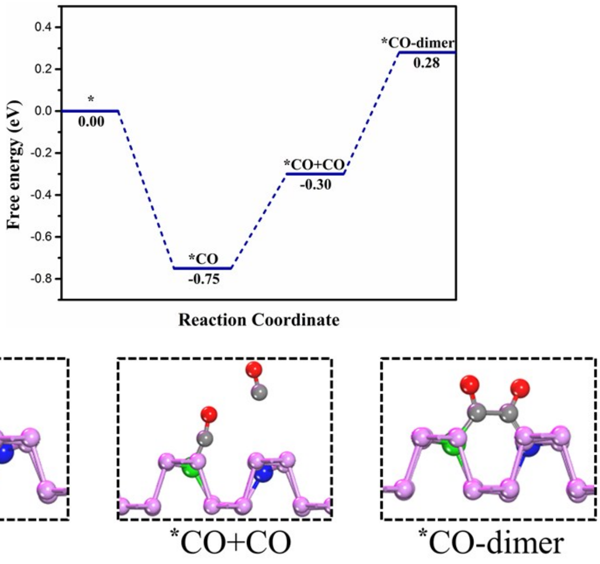

**Fig. S6** The detailed free energy pathway of C-C coupling on para-B-N@BP with 7% compressive strain. The relevant atomic structures are also given.

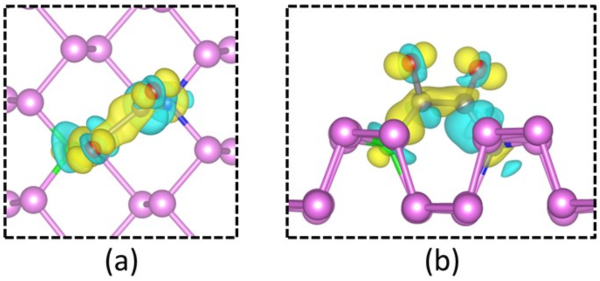

**Fig. S7** (a) Top view and (b) side view of the difference charge density plots for CO-dimer on para-B-N@BP with 7% compressive strain. The isosurface value is set to be 0.008 e Å$^{-3}$, the charge accumulated and depleted regions are shown in yellow and cyan, respectively.

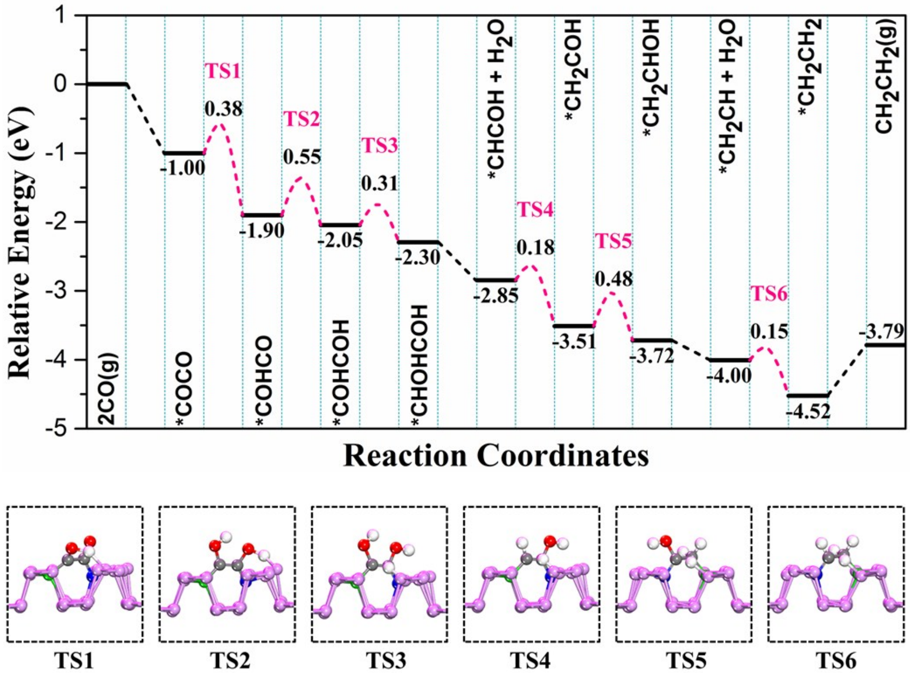

**Fig. S8** The detailed kinetic energy diagram of CO reduction towards $C_2$ product on B-N@BP with 7% compressive strain, and the structures of transition state are also given.

## 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.