Unravelling the adsorption and electroreduction performance of CO$_2$ and N$_2$ over defective and B, P, Si-doped C$_3$Ns: a DFT study

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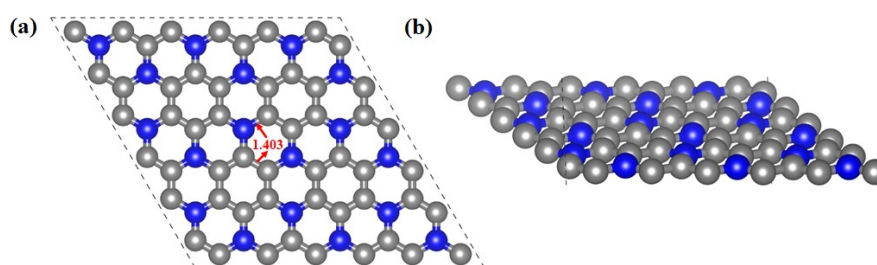
Fig. S1 Top and side views of optimized pri-C$_3$N structure. The grey and blue balls represent C and N atoms, respectively.
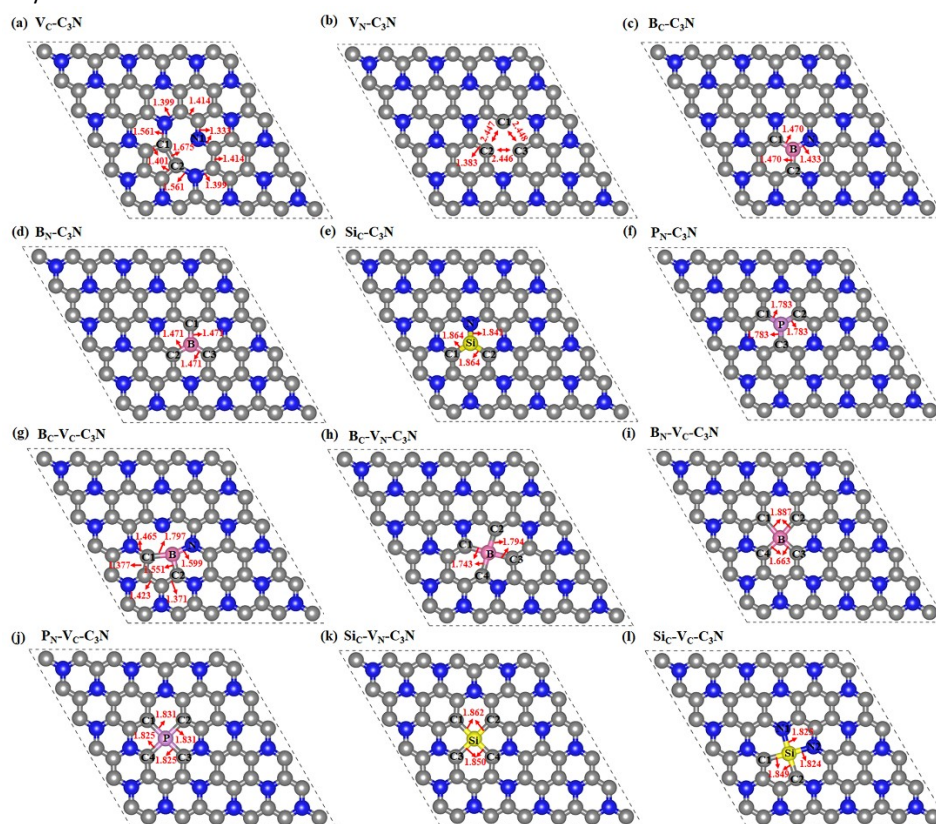

Fig. S2 Top views of optimized defective and doped C$_3$N structures with (a) V$_C$, (b) V$_N$, (c) B$_C$, (d) B$_N$, (e) Si$_C$, (f) P$_N$, (g) B$_C$-V$_C$, (h) B$_C$-V$_N$, (i) B$_N$-V$_C$, (j) P$_N$-V$_C$, (k) Si$_C$-V$_N$ and (l) Si$_C$-V$_C$. The grey, blue, pink, yellow and purple balls represent C, N, B, Si and P atoms, respectively.
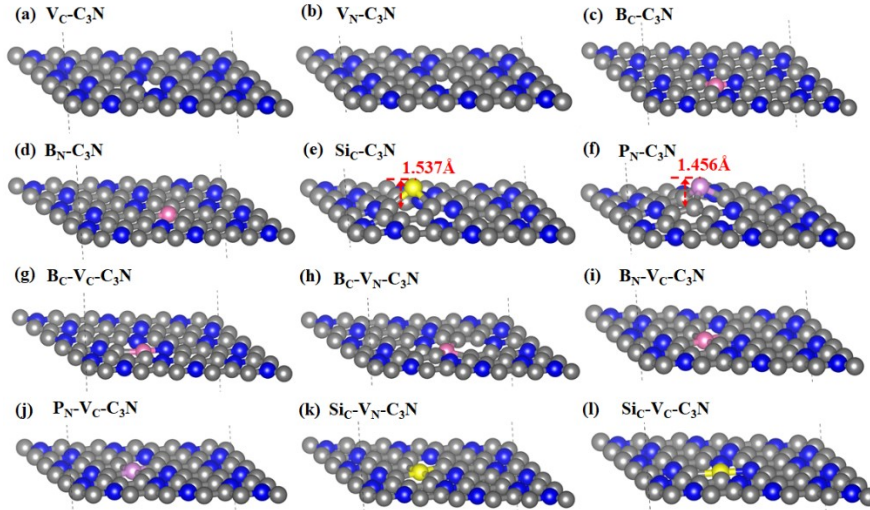
Fig. S3 Side views of optimized defective and doped C_3N structures with (a) V_C, (b) V_N, (c) B_C, (d) B_N, (e) Si_C, (f) P_N, (g) B_C-V_C, (h) B_C-V_N, (i) B_N-V_C, (j) P_N-V_C, (k) Si_C-V_N and (l) Si_C-V_C. The grey, blue, pink, yellow and purple balls represent C, N, B, Si and P atoms, respectively.
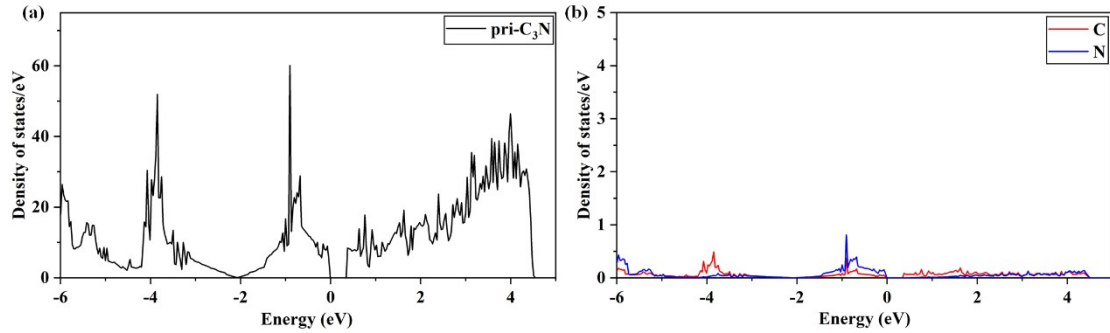

Fig. S4 (a) The total density of states (TDOS) plots for pri-C_3N, (b) The partial total density of states (PDOS) plots for one C and one N atom of pri-C_3N. The Fermi level was assigned at 0 eV.
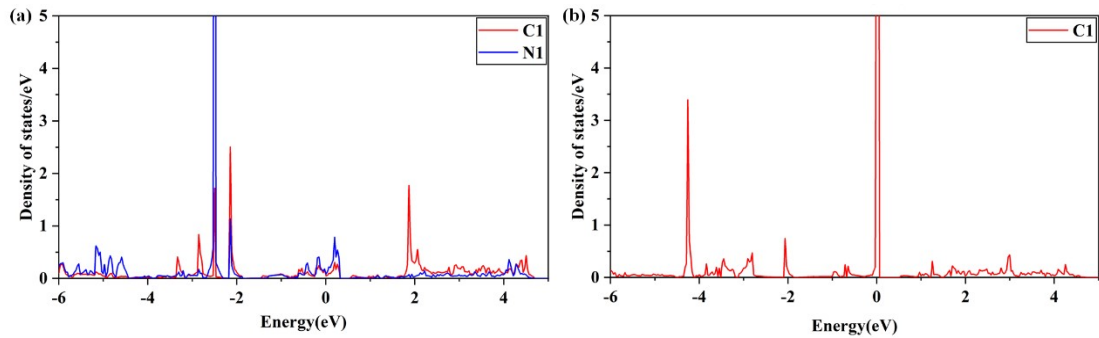

Fig. S5 PDOS plots for (a) C1 and N atoms at V_C site of V_C-C_3N, (b) C1 atom at V_N site of V_N-C_3N. The Fermi level was assigned at 0 eV. The atoms labelled by numbers in this diagram correspond to those in **Fig. 1**.
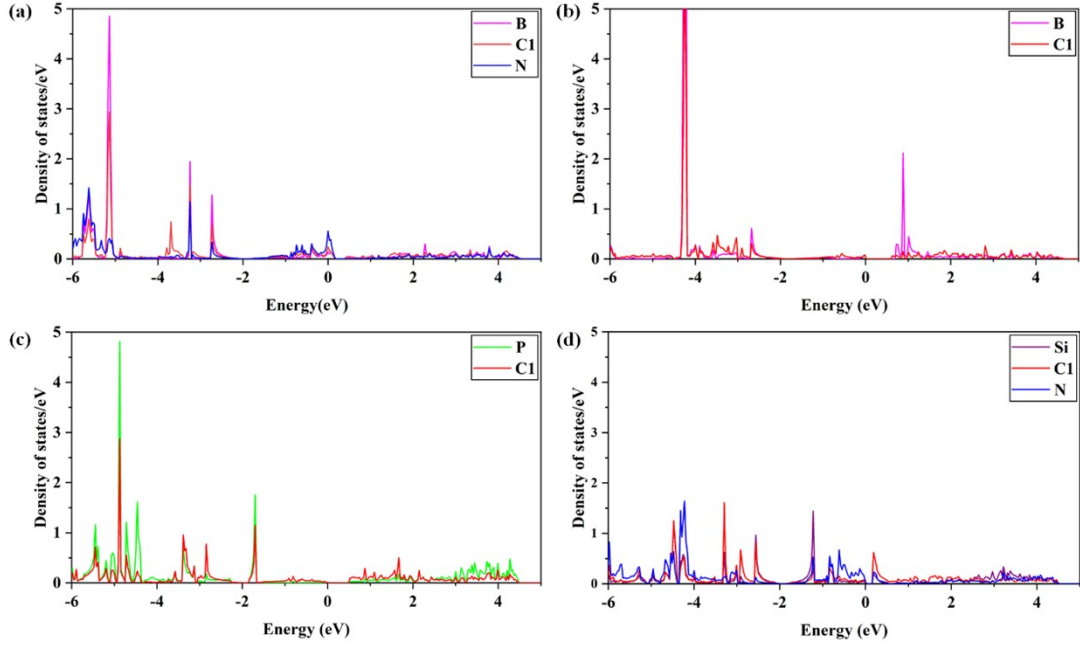
Fig. S6 PDOS plots for (a) B, C1 and N atoms at B_C site of B_C-C_3N, (b) B and C1 atom at B_N site of B_N-C_3N, (c) P and C1 atoms at P_N site of P_N-C_3N, (d) Si, C1 and N atom at Si_C site of Si_C-C_3N. The Fermi level was assigned at 0 eV. The atoms labelled by numbers in this diagram correspond to those in **Fig. 1**.
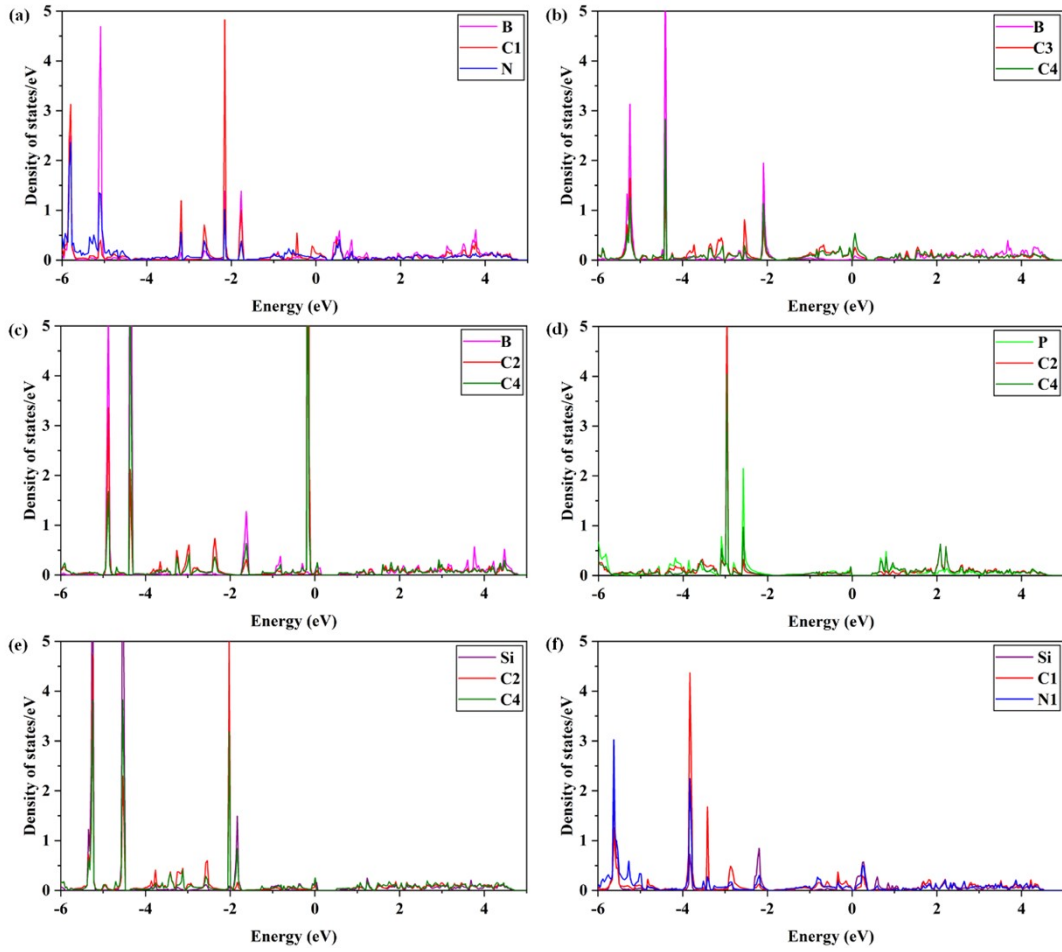

Fig. S7 PDOS plots for (a) B, C1 and N atoms at defect site of B_C-V_C-C_3N, (b) B, C3, and C4 atom at defect site of B_C-V_N-C_3N, (c) B, C2, and C4 atoms at defect site of B_N-V_C -C_3N, (d) P, C2, and C4 atoms at defect site of P_N-V_C-C_3N, (e) Si, C2 and C4 atoms at defect site of Si_C-V_N-C_3N, (f) Si, C1 and N1 atoms at defect site of Si_C-V_C-C_3N. The Fermi level was assigned at 0 eV. The atoms labelled by numbers in this diagram correspond to those in **Fig. 1**.
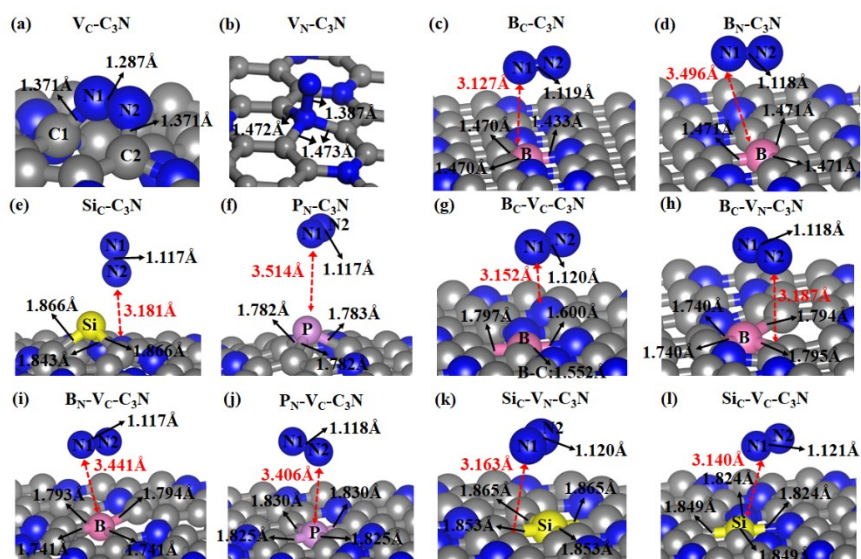
Fig. S8 The optimized structures for the most stable N_2 adsorption configurations on (a) V_C-C_3N, (b) V_N-C_3N, (c) B_C-C_3N, (d) B_N-C_3N, (e) Si_C-C_3N, (f) P_N-C_3N, (g) B_C-V_C-C_3N, (h) B_C-V_N-C_3N, (i) B_N-V_C-C_3N, (j) P_N-V_C-C_3N, (k) Si_C-V_N-C_3N and (l) Si_C-V_C-C_3N. The grey, blue, pink, yellow and purple balls represent C, N, B, Si and P atoms, respectively.
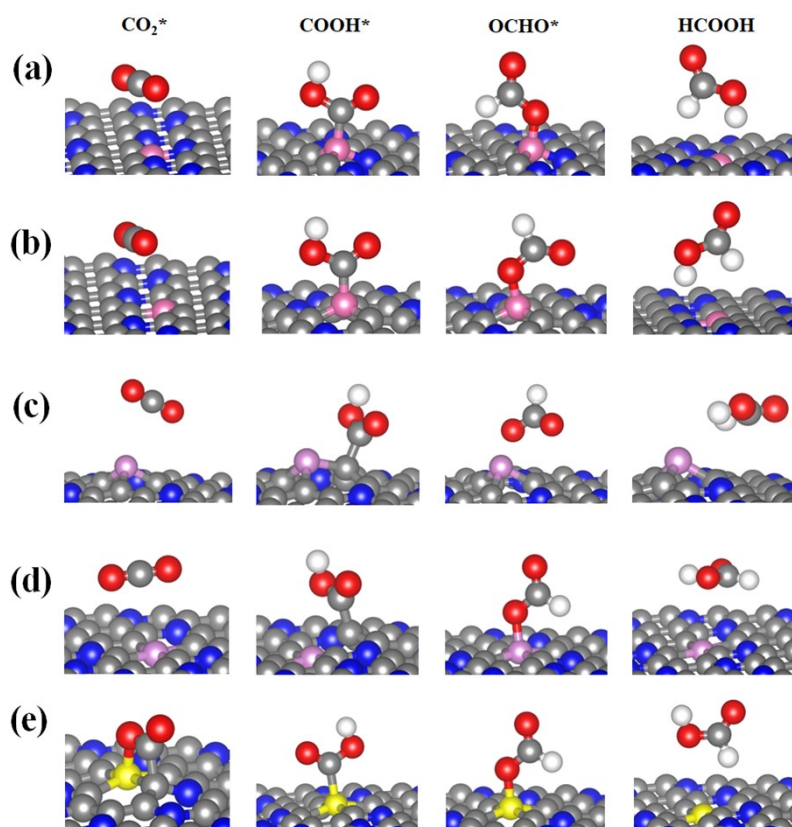
Fig. S9 The optimized structures of the intermediates in electrocatalytic CO_2RR towards HCOOH on (a) B_C-C_3N, (b) B_N-C_3N, (c) P_N-C_3N, (d) P_N-V_C-C_3N, (e) Si_C-V_N-C_3N. The grey, blue, pink, yellow and purple balls represent C, N, B, Si and P atoms, respectively.
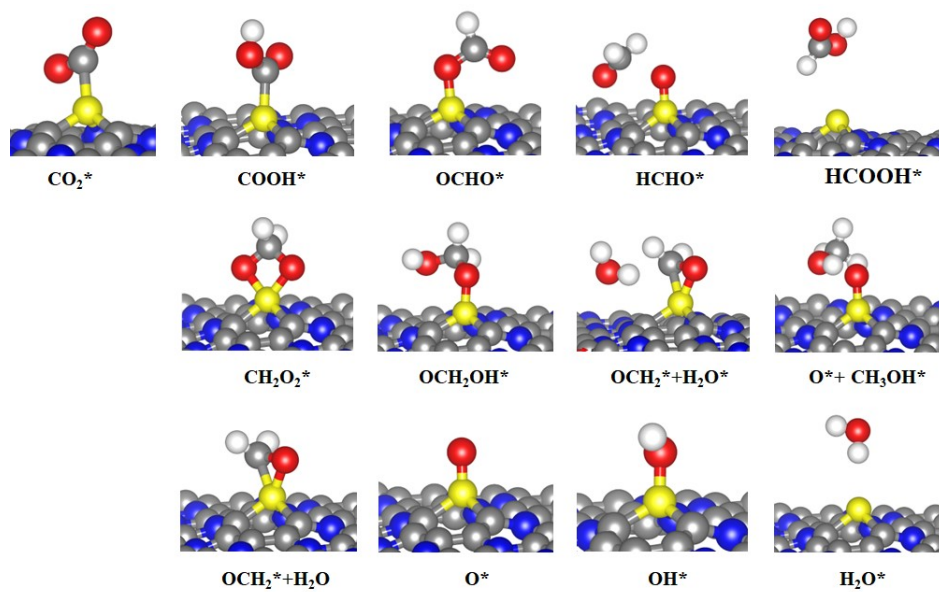
Fig. S10 The optimized structures of the intermediates in electrocatalytic CO_2RR towards CH_3OH on Si_C-C_3N. The grey, blue, pink, yellow and purple balls represent C, N, B, Si and P atoms, respectively.