

**Synergistic effects of B-F/B-S and nitrogen vacancy co-doping on g-C₃N₄ and
photocatalytic CO₂ reduction mechanisms: A DFT study**

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Table S1. Formation energy (eV) of B-F-N_v and B-S-N_v co-doped g-C₃N₄.

	B-F-N _v		B-S-N _v	
	E _{doped}	E _{form}	E _{doped}	E _{form}
N _v 1	-467.79	3.62	-459.07	3.25
N _v 2	-468.11	3.30	-461.25	1.07
N _v 3	-467.70	3.71	-458.97	3.35
N _v 4	-471.96	-0.55	-459.78	2.54
N _v 5	-466.05	5.35	-456.33	5.99

Table S2. The bond length parameters of intrinsic and doped g-C₃N₄.

g-C ₃ N ₄					B-F			B-F-N _v		B-S-N _v	
bond length/Å	our work	PBE ^a	PW91 ^b	Expt ^b	bond length/Å	our work	PW91 ^b	bond length/Å	our work	bond length/Å	our work
a ^c	7.13	7.15	7.13	7.30	—	—	—	—	—	—	—
N1-C2	1.47	1.47	1.47	—	B-N1	1.51	1.51	B-N1	1.62	B-N1	1.53
C2-N3	1.33	1.34	1.34	—	B-N2	1.49	1.47	B-N2	1.54	B-S	1.98
N3-C4	1.33	1.33	1.33	—	N2-C3	1.38	1.37	N2-C3	1.19	S-C2	1.76
C4-N5	1.39	1.39	1.40	—	B-N6	1.40	1.41	B-N5	1.55	C2-N3	1.39
—	—	—	—	—	F-N2	1.41	1.41	B-F	1.40	B-N5	1.38

^a The parameters are from ref. [28]. ^b The parameters are from ref. [48]. ^c a represents the unit cell parameter.

Table S3. The band gap energy (eV) for the intrinsic and doped g-C₃N₄.

	E _g /eV			Expt
	PBE	HSE06		
g-C ₃ N ₄	1.21	2.77	2.68 ^[a]	2.73 ^[b] , 2.77 ^[c]
B-F	1.83	3.06	2.94 ^[a]	2.86 ^[c]
B-F-N _v	1.19	2.67	—	
B-S-N _v	1.16	—	—	

^a The results for g-C₃N₄ and B-F are from ref. [31]. ^b The value is from ref. [50]. ^c The results for g-C₃N₄ and B-F are from ref. [28].

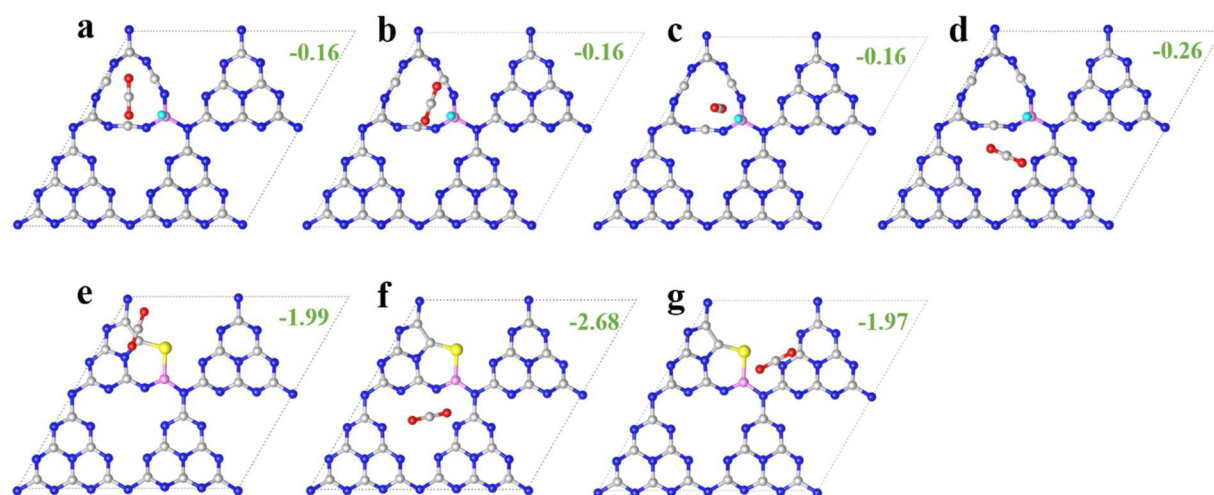


Figure S1. The possible adsorption sites for CO₂ on B-F-N_v (a-d) and B-S-N_v (e-g), and corresponding adsorption energy (eV).

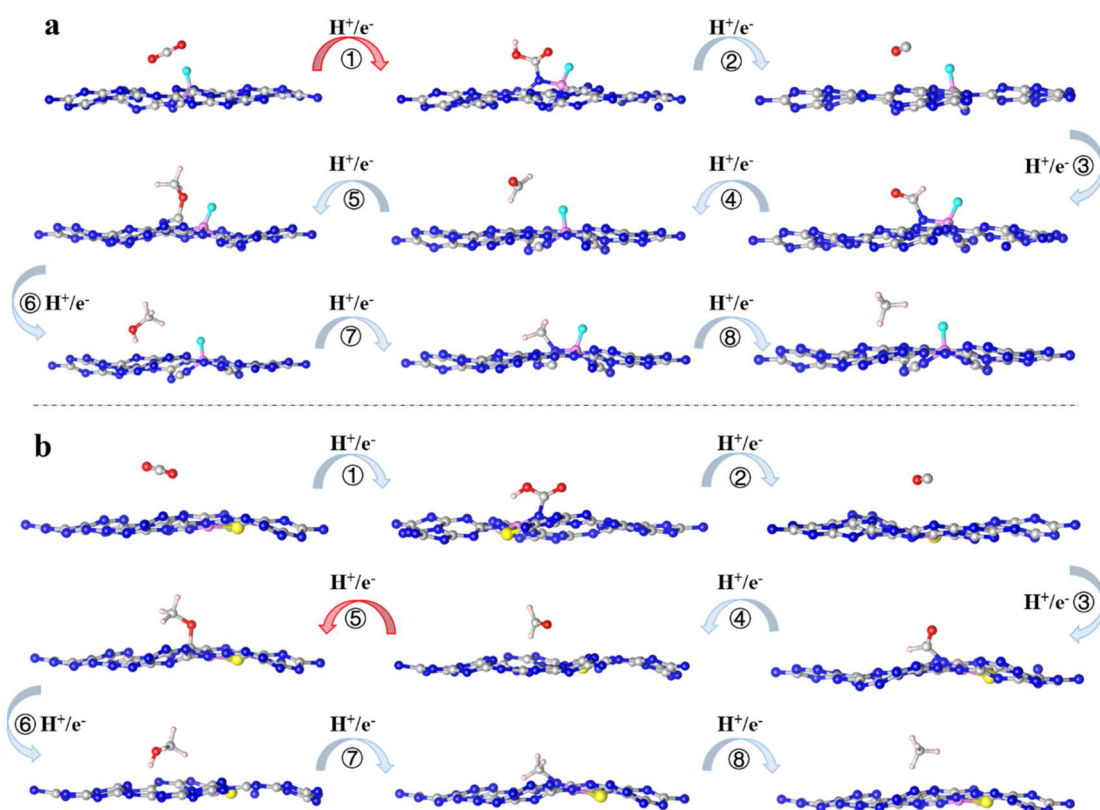


Figure S2. The reaction pathways for B-F-N_v (a) and B-S-N_v (b).

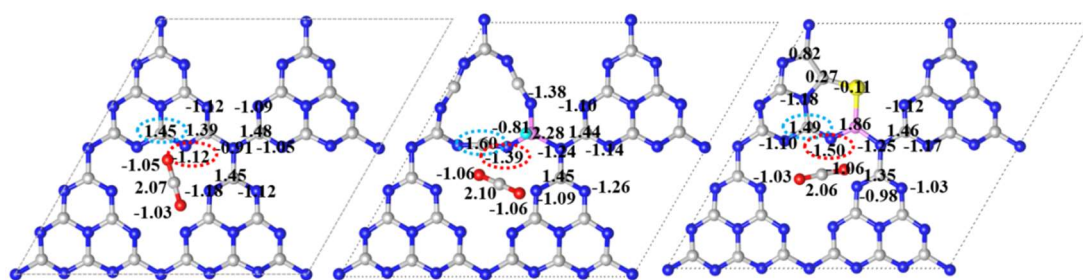


Figure S3. The bader charge (unit e) of g-C₃N₄ (left), B-F-N_v (middle), and B-S-N_v (right). Negative and positive values mean gaining and losing electrons. The elements are colored in pink for B, gray for C, blue for N, red for O, cyan for F, and yellow for S.

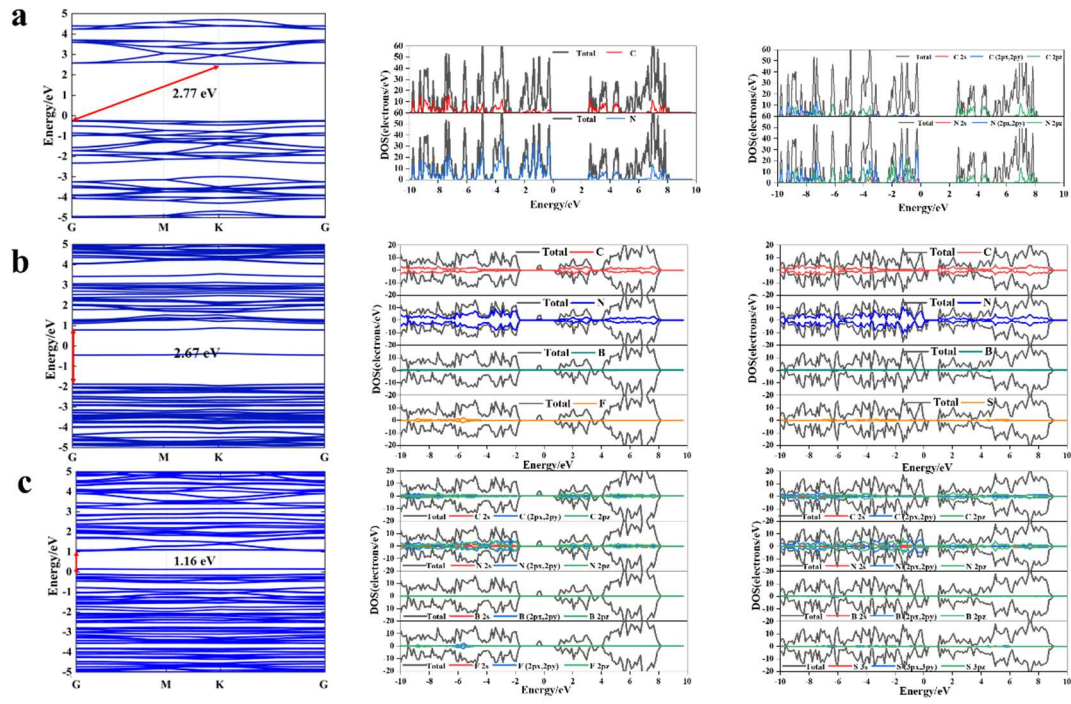


Figure S4. Calculated band structure (left), density of states (middle), and partial density of states (right) diagrams of g-C₃N₄ (a), B-F-N_v (b) and B-S-N_v (c), the energy range is from -10 eV to 10 eV.