Electronic Supporting Information

How does the B,F-monodoping and B/F-codoping Affect the Photocatalytic Water-splitting Performance of g-C_3N_4

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S1. Computational methods

In order to find the most appropriate method to describe the electronic states of the systems our investigation, standard functionals (GGA/PBE, GGA/PW91, LDA/CA-PZ[1]) and hybrid functionals (HSE06, PBE0)[2] were carried out to calculate the band gap of the pure monolayer g-C_3N_4.

In order to describe the electronic properties of g-C_3N_4 precisely, several DFT calculations were preformed to research the undoped g-C_3N_4, and the corresponding band gaps are listed in Table S1. The results show that the band gaps of 0.99 and 1.13 eV for pure g-C_3N_4 produced from LDA and GGA, respectively, have obviously underestimated the band gap compared with the experimental value of 2.67-2.73 eV[3-5] due to the well-known shortcoming in these two functionals. Besides, the band gap determined by PBE0 (3.44 eV) is larger than the experimental value. While the result calculated by HSE06 (2.68 eV) is quite comparable to the experimental reports, and the band gap of doping systems well agree with the experimental values[6, 7]. Hence, in the following sections, we will display only the electronic properties of pure and doped g-C_3N_4 systems calculated by HSE06 functional.

Table S1. Band gaps with different methods for pure and doped g-C_3N_4.

Systems	E_g/eV				
	LDA	GGA	PBE0	HSE06	Experimental
pure	0.99	1.13	3.44	2.68	2.67 [a], 2.7[b], 2.73[c]
B-doped	-	-	-	2.64	2.66[d]
F-doped	-	-	-	2.81	2.63[e]
B/F-codoped	-	-	-	2.94	-

a Ref.S3; b Ref.S4; c Ref.S5; d Ref.S6; e Ref.S7

Table S2. The dopant formation energies *(E_{from}*/eV) of g-C_3N_4.

Doping$_{-kind}$	**Doping$_{-site}$**	***E_{from}*/eV**
	B@C1	1.13
	B@C2	1.42
B-doped	B@N1	3.10
	B@N2	3.16
	B@N3	4.36
	F@C1	-2.68
	F@C2	-2.38
F-doped	F@N1	0.97
	F@N2	-2.01
	F@N3	-0.06
	F@C1- B@C1	-1.49
	F@C2- B@C1	-1.18
B/F-codoped	F@N1- B@C1	0.81
	F@N2- B@C1	-1.85
	F@N3- B@C1	0.61

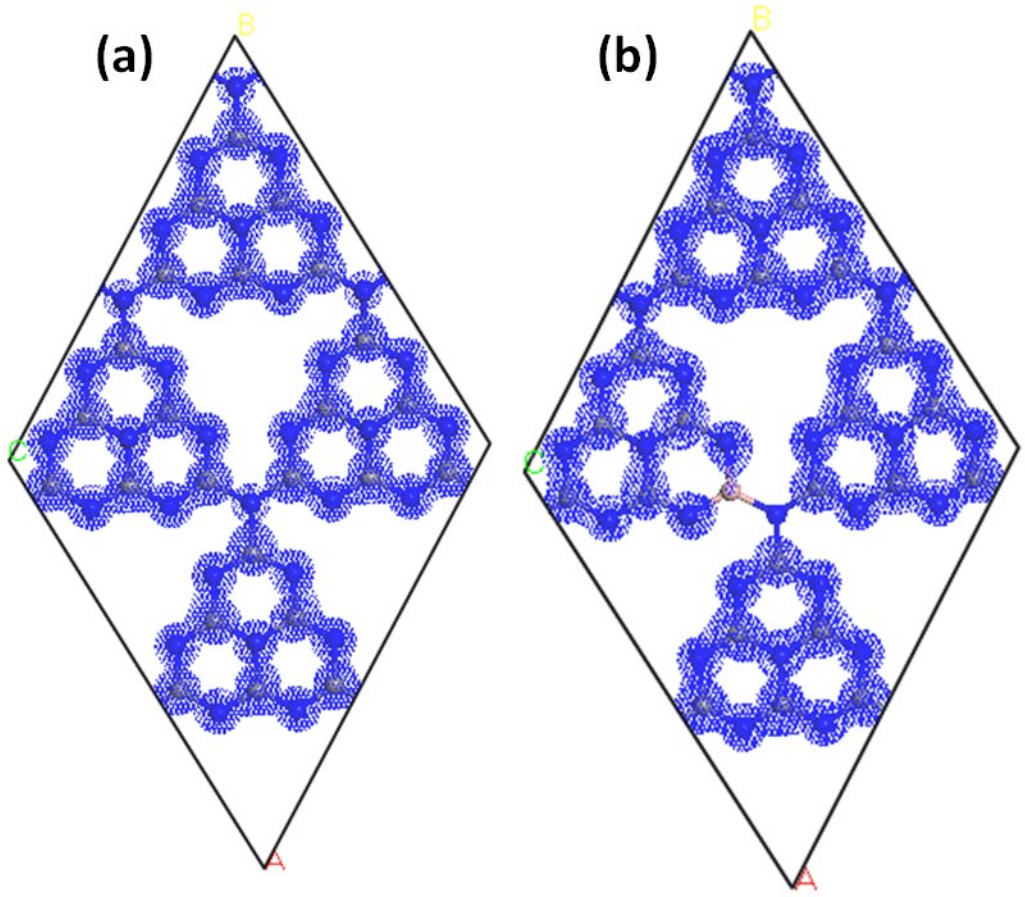

Figure S1. The corresponding π-conjugated orbital diagram of pure (a) and B-doped (b) g-C_3N_4.

Table S3. The peak position distribution of imaginary parts ε_2 and transition assignments. [a]

	Assignment of the transition	Description	Energy range of the transition (eV)	Imaginary parts ε_2
	n → π*	E1	2.684 ~ 2.920	2.8×10^{-5} (at 2.847 eV)[b]
	n → π*	E2	2.920 ~ 3.157	8.0×10^{-5} (at 3.068 eV)
pure	n → π*	E3	3.157 ~ 3.674	0.347 (at 3.541 eV)
	n → π*	E4	3.674 ~ 3.984	0.408 (at 3.881 eV)
	π→ π*	E5	3.984 ~ 4.590	2.369 (at 4.368 eV)
	n → π*	E1	1.256 ~ 1.700	0.075 (at 1.461 eV)
	n → π*	E2	1.700 ~ 2.239	0.324 (at 1.985 eV)
B-doped	n → π*	E3	2.239 ~ 3.106	0.098 (at 2.359 eV)
	n → π*	E4	3.106 ~ 3.630	0.208 (at 3.581 eV)
	π → π*	E5	3.630 ~ 4.737	1.751 (at 4.378 eV)
	n → π*	E1	1.095 ~ 1.432	0.185 (at 1.271 eV)
	n → π*	E2	1.432 ~ 2.435	0.257 (at 1.691 eV)
F-doped	n → π*	E3	2.435 ~ 2.726	0.024 (at 2.645 eV)
	π→ π*	E4	2.726 ~ 4.148	0.846 (at 4.051 eV)
	π → π*	E5	4.148 ~ 4.795	1.109 (at 4.552 eV)
	n → π*	E1	2.942 ~ 3.076	0.088 (at 3.026 eV)
	n → π*	E2	3.076 ~ 3.342	0.152 (at 3.226 eV)
B/F-codoped	n → π*	E3	3.342 ~ 3.559	0.284 (at 3.475 eV)
	π → π*	E4	3.559 ~ 3.975	0.943 (at 3.875 eV)
	π → π*	E5	3.975 ~ 4.142	0.871 (at 4.001 eV)

[a] Only shown the first five peaks of electronic transitions.

[b] The energy associated with the maximum amplitude of transition is shown in parentheses.

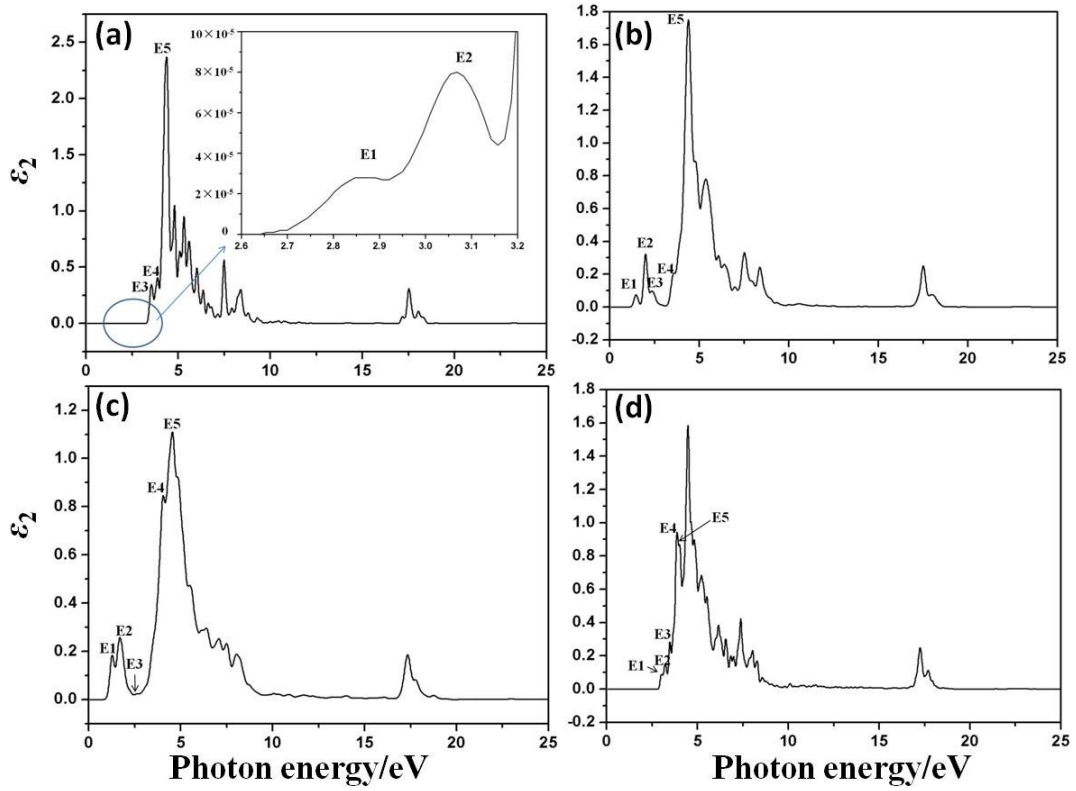

Figure S2. The calculated imaginary parts of dielectric function of pure(a), B-doped(b), F-doped(c), B/F-codoped(d) g-C_3N_4. The inset shows a detail with enlarged scale in the range from 2.6 to 3.2 eV.

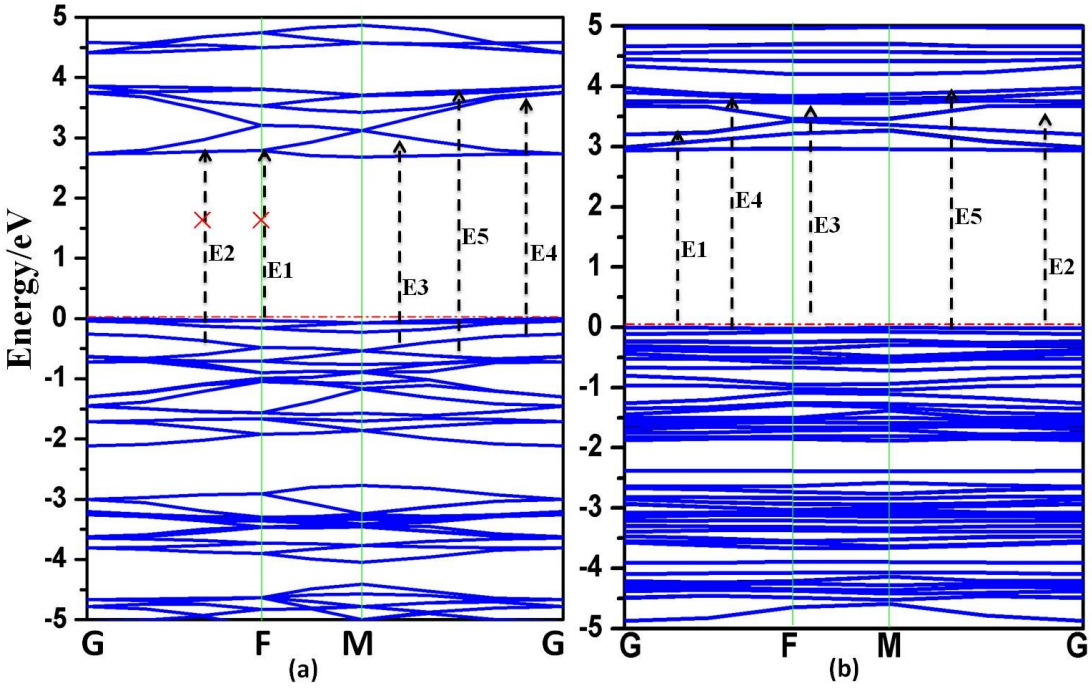

Figure S3. The first five main peaks distribution of imaginary parts ε_2 in band structure of pure (a) and B/F-codoped (b) g-C_3N_4.

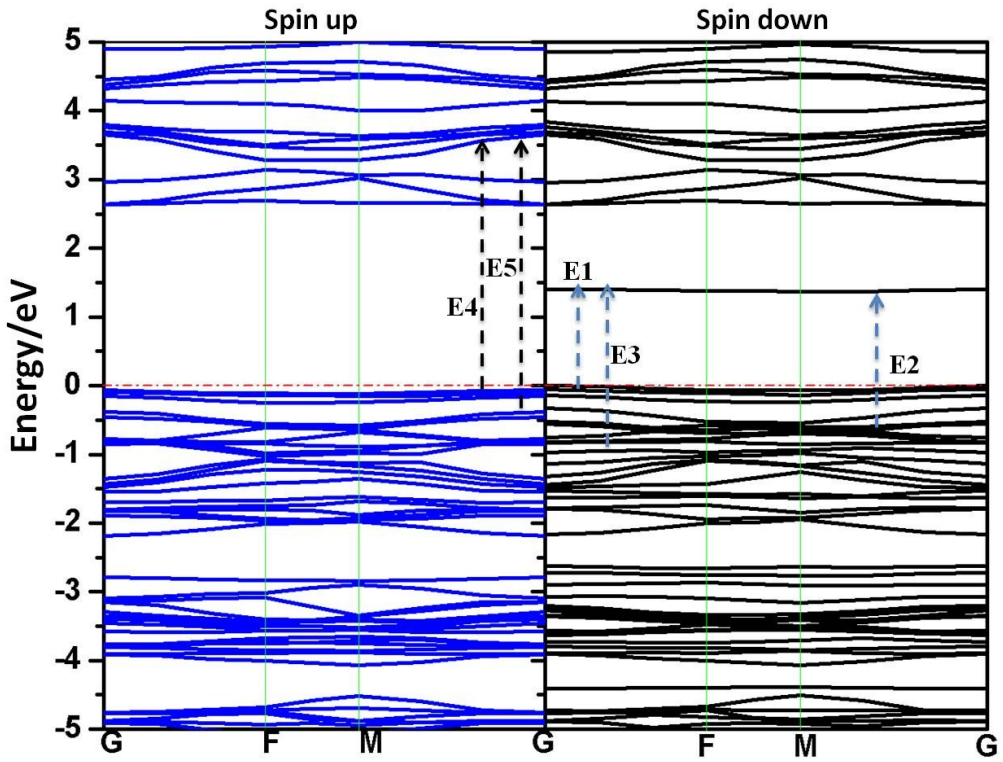

Figure S4. The first five main peaks distribution of imaginary parts ε_2 in band structure of B-doped g-C_3N_4.

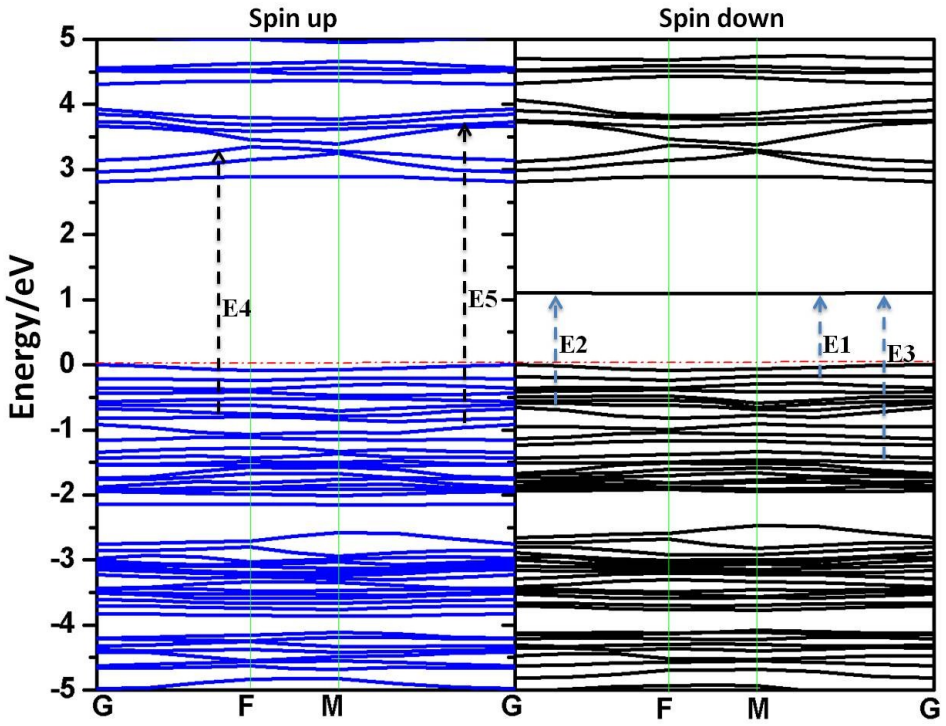

Figure S5. The first five main peaks distribution of imaginary parts ε_2 in band structure of F-doped g-C_3N_4.

References

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