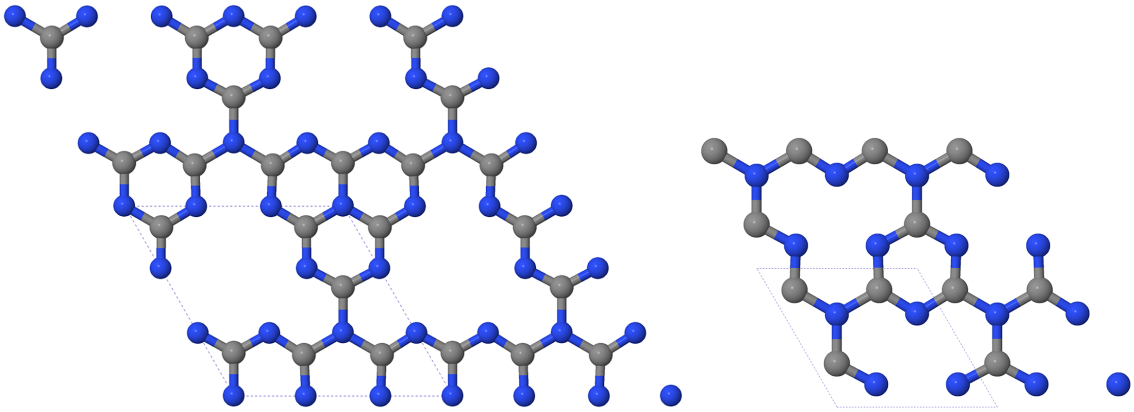
Sulfur-doped g-C_3N_4/TiO_2 anatase (101) composites for photocatalytic applications: a DFT-based computational investigation

— Supplementary Information —

Zihan Wang and Frédéric Labat*

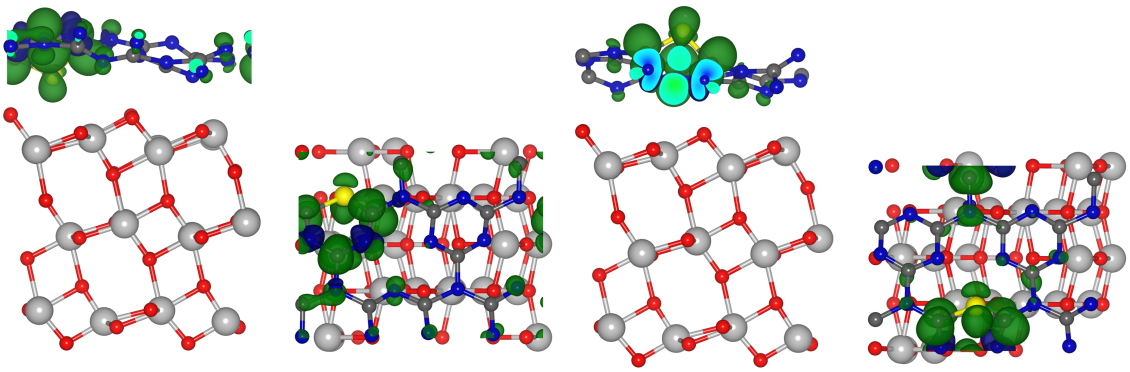
Chimie ParisTech, PSL University, CNRS, Institute of Chemistry for Life and Health Sciences, Chemical Theory and Modelling Group, F-75005 Paris, France

E-mail: frederic.labat@chimieparistech.psl.eu



(a) (b)

Figure S1: Relaxed structures of: (a) tri-s-triazine- (C_6N_8 unit cell) and (b) s-triazine-based g-C_3N_4 (C_3N_4 unit cell), calculated at the HSE06-D2 level and shown in a (2×2) supercell. C and N shown as gray and blue spheres, respectively. The unit cell is shown as blue dotted lines. Based on the computed total energy difference per unit cell, the heptazine-based system is found -0.193 eV more stable than the s-triazine-based one, in line with previous findings.[1,2]



(a) (b)

Figure S2: Spin densities of the (a) S_b-g-C_3N_4/TiO_2 and (b) S_t-g-C_3N_4/TiO_2 composite models in a doublet spin state. C, N, S, Ti and O shown as brown, blue, yellow, grey and red spheres, respectively. Isosurface values of $|0.0025|$ e.bohr^{-3}.

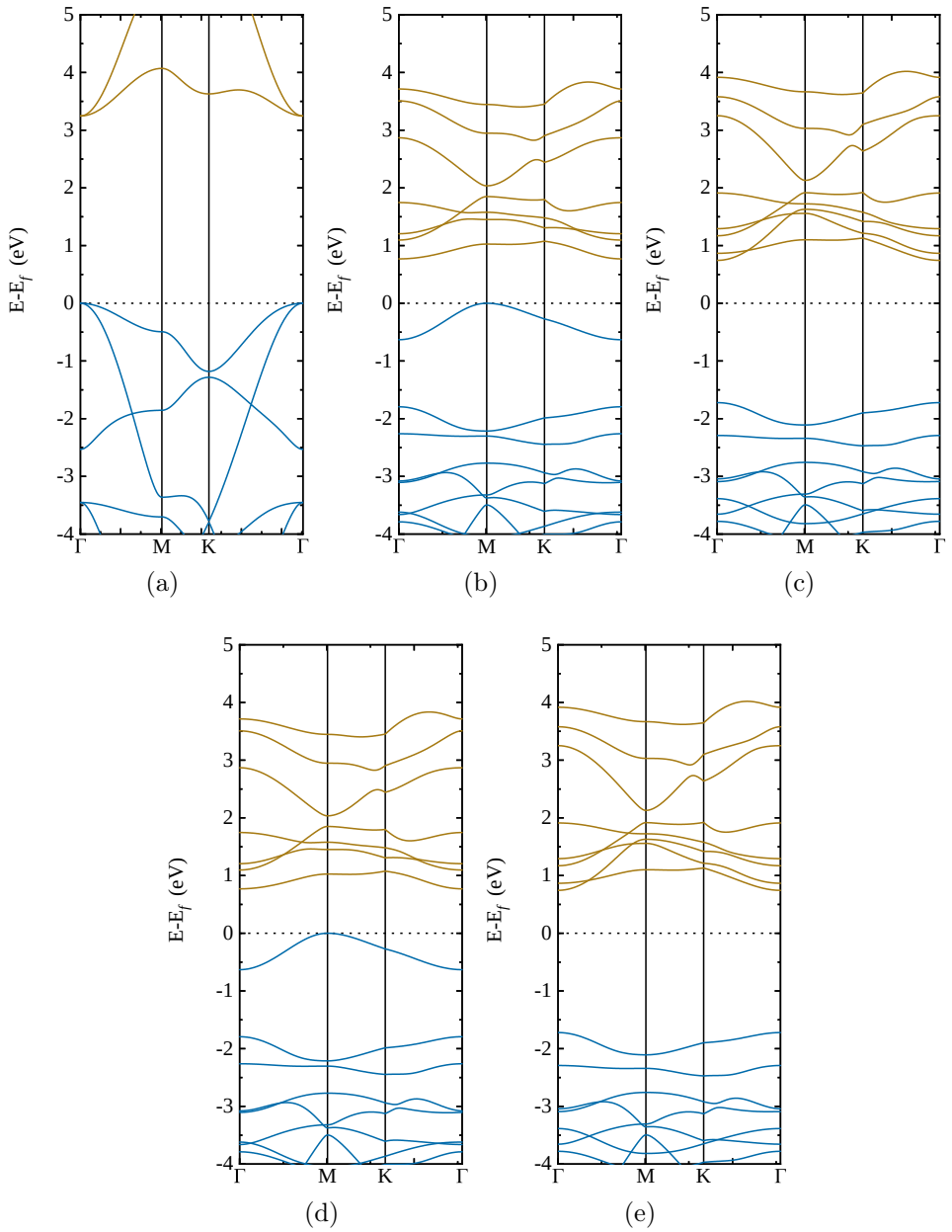
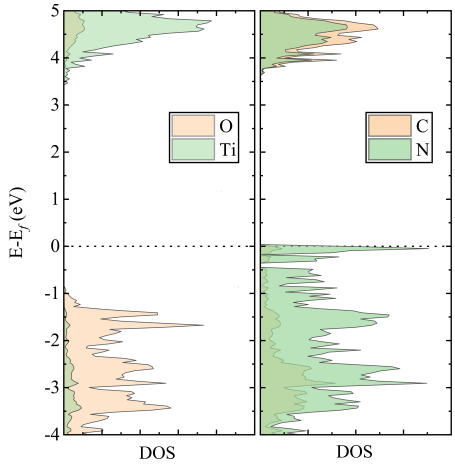
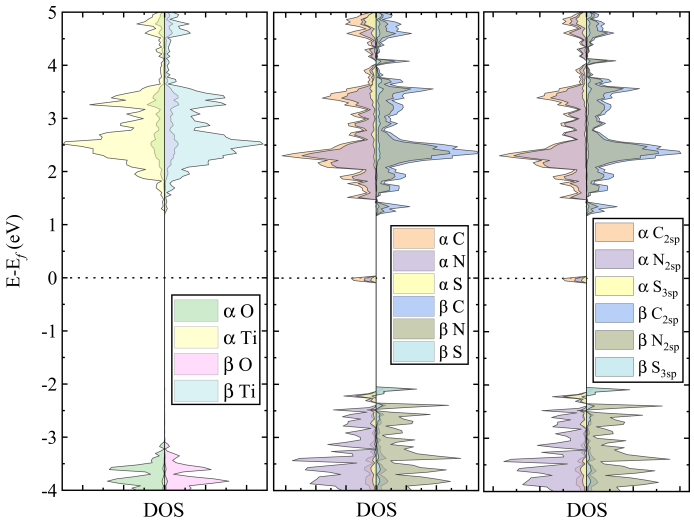


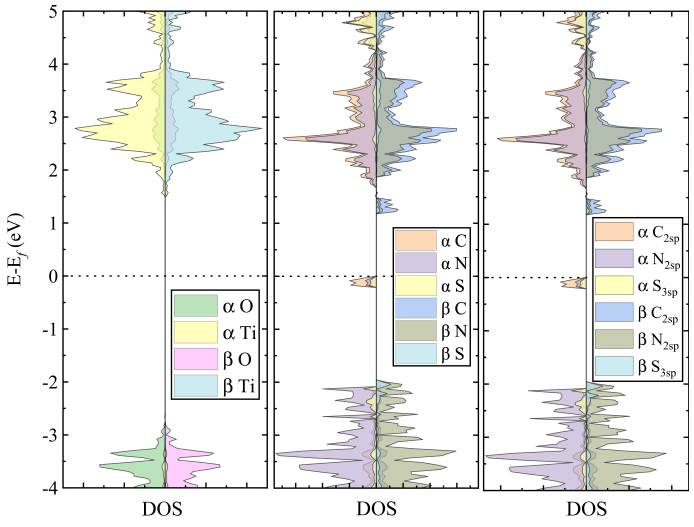
Figure S3: Band structures of freestanding (a) g-C_3N_4, (b) α S_b-g-C_3N_4, (c) β S_b-g-C_3N_4, (d) α S_t-g-C_3N_4, and (e) β S_t-g-C_3N_4. All data obtained at the HSE06-D2 level.



(a)



(b)



(c)

Figure S4: Atom and atomic orbital projected Density of states of (a) g-C_3N_4/TiO_2, (b) S_b-g-C_3N_4/TiO_2 and (c) S_t-g-C_3N_4/TiO_2 interface models. The Fermi level (shown as thin dotted line) has been set to 0 eV.

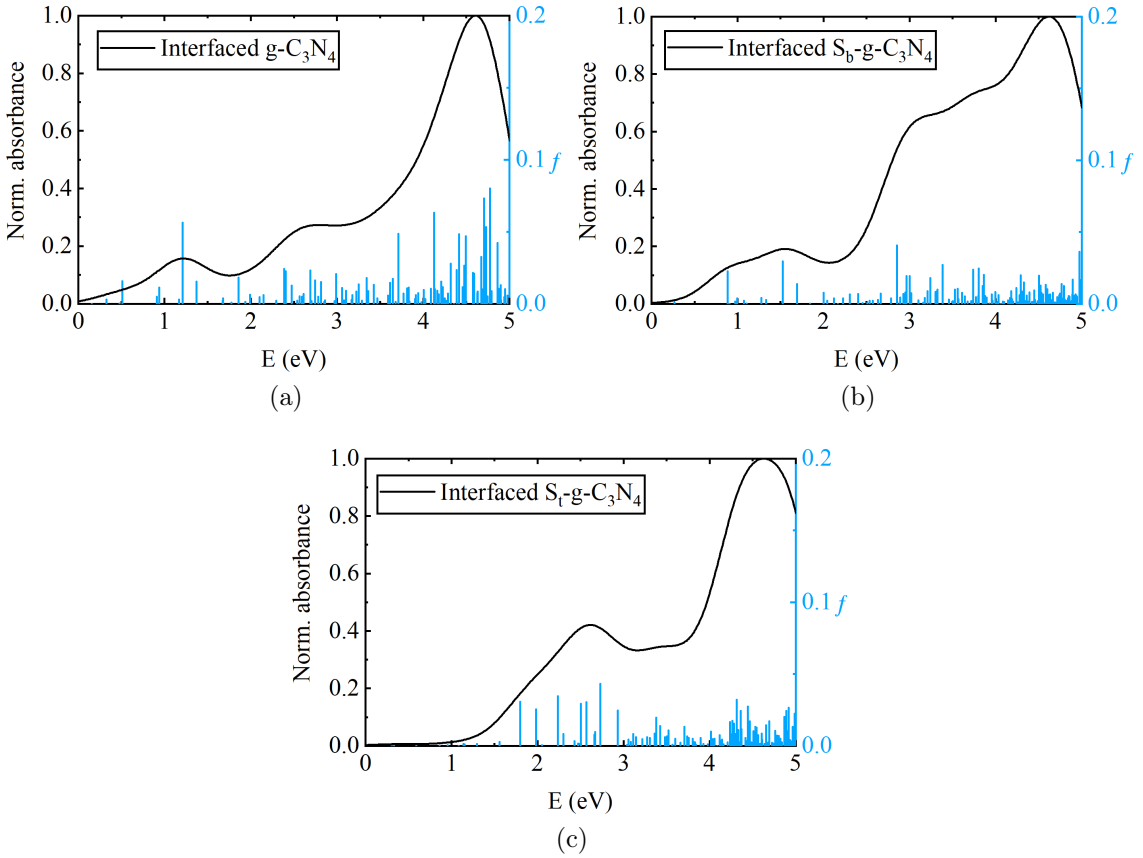


Figure S5: Simulated UV-Vis. spectra of interfaced (a) g-C_3N_4, (b) S_b-g-C_3N_4 and (c) S_t-g-C_3N_4 along with the computed stick spectrum (in blue) with heights corresponding to the computed oscillator strengths of the electronic transitions.

Table S1: Computed main vertical electronic transitions of the supercells of (a) freestanding and (b) interfaced g-C_3N_4, indicating transition energies (E, in eV), oscillator strengths (f), approximate exciton size ($\widetilde{d}_{exc}$, in Å), D_{CT} index (in Å) and exciton binding energy (E_b) (in eV). Only transitions with $f \geq 0.03$ are reported.

Excited State	E	f	$\widetilde{d}_{exc}$	D_{CT}	E_b
S_8	0.97	0.05	5.30	0.683	4.11
S_{19}	2.00	0.04	5.30	1.465	4.24
S_{38}	3.06	0.03	7.05	1.713	2.75
S_{43}	3.20	0.04	5.17	0.720	4.14
S_{59}	3.90	0.07	5.23	0.678	3.88
S_{63}	4.06	0.04	5.45	0.485	4.22
S_{68}	4.21	0.07	4.84	1.135	4.22
S_{78}	4.50	0.04	5.07	1.076	4.08
S_{79}	4.56	0.06	4.92	0.708	4.25
S_{89}	4.89	0.06	4.29	0.396	4.38
S_{91}	4.95	0.04	4.48	0.767	4.29

(a)

Excited State	E	f	$\widetilde{d}_{exc}$	D_{CT}
S_8	1.21	0.06	4.26	0.326
S_{64}	4.12	0.06	5.16	0.996
S_{86}	4.71	0.07	5.19	0.371
S_{87}	4.73	0.05	5.85	0.045
S_{89}	4.78	0.08	5.92	1.102

(b)

Table S2: Computed main vertical electronic transitions of the supercells of (a) freestanding and (b) interfaced S_b-g-C_3N_4, indicating transition energies (*E*, in eV), oscillator strengths (f), approximate exciton size ($\widetilde{d}_{exc}$, in Å), D_{CT} index (in Å) and exciton binding energy (E_b) (in eV). Only transitions with $f \geq 0.02$ are reported.

Excited State	E	f	$\widetilde{d}_{exc,\alpha}$	$\widetilde{d}_{exc,\beta}$	D_{CT}	E_b
D_{12}	1.43	0.04	3.89	2.38	1.392	4.50
D_{13}	1.64	0.03	4.88	2.41	1.309	4.07
D_{22}	2.47	0.04	4.05	2.74	1.402	4.70
D_{25}	2.59	0.08	3.59	2.47	0.654	4.99
D_{29}	2.68	0.06	4.72	2.75	1.927	3.87
D_{31}	2.74	0.04	4.44	2.96	1.868	4.34
D_{59}	3.58	0.03	3.72	4.71	1.744	4.34
D_{71}	3.84	0.07	3.83	4.10	0.637	4.39
D_{74}	3.90	0.04	3.70	3.62	0.166	4.65
D_{114}	4.56	0.07	4.92	4.16	1.159	4.34
D_{138}	4.85	0.03	4.30	5.99	1.524	3.92
D_{143}	4.90	0.03	4.78	5.41	0.289	4.04

(a)

Excited State	E	f	$\widetilde{d}_{exc,\alpha}$	$\widetilde{d}_{exc,\beta}$	D_{CT}
D_2	0.88	0.02	2.30	2.35	0.819
D_{10}	1.53	0.03	2.32	2.76	1.108
D_{27}	2.85	0.04	2.86	3.70	0.764
D_{43}	3.38	0.03	4.07	4.06	0.699
D_{54}	3.74	0.02	3.21	4.44	1.442
D_{57}	3.80	0.02	3.64	4.86	1.030
D_{59}	3.86	0.02	3.18	4.32	0.770
D_{79}	4.29	0.02	4.22	4.15	0.266
D_{93}	4.51	0.02	5.06	4.33	1.414
D_{129}	4.97	0.04	3.64	4.46	0.100

(b)

Table S3: Computed main vertical electronic transitions of the supercells of (a) freestanding and (b) interfaced S_t-C_3N_4, indicating transition energies (*E*, in eV), oscillator strengths (f), approximate exciton size ($\widetilde{d}_{exc}$, in Å), D_{CT} index (in Å) and exciton binding energy (E_b) (in eV). Only transitions with $f \geq 0.03$ are reported.

Excited State	E	f	$\widetilde{d}_{exc,\alpha}$	$\widetilde{d}_{exc,\beta}$	D_{CT}	E_b
D_9	1.05	0.10	3.84	3.92	1.069	5.22
D_{20}	2.20	0.07	3.86	3.30	1.191	4.28
D_{25}	2.51	0.11	4.16	3.96	1.836	4.48
D_{58}	3.82	0.09	4.74	3.07	0.831	4.23
D_{100}	4.67	0.05	4.31	4.87	1.461	3.90
D_{115}	4.85	0.07	4.52	3.97	0.778	4.10

(a)

Excited State	E	f	$\widetilde{d}_{exc,\alpha}$	$\widetilde{d}_{exc,\beta}$	D_{CT}
D_{11}	1.80	0.03	2.67	2.94	0.850
D_{14}	2.23	0.03	3.07	3.00	0.852
D_{18}	2.50	0.03	3.88	2.63	0.430
D_{19}	2.57	0.03	3.43	2.69	0.523
D_{22}	2.73	0.04	4.30	2.88	1.124
D_{69}	4.31	0.03	4.09	4.18	0.682
D_{76}	4.45	0.03	4.08	4.40	0.851

(b)

Table S4: Computed main vertical electronic transitions of g-C_3N_4/TiO_2 with 2 Ti layers, indicating transition energies (*E*, in eV), oscillator strengths (f), approximate exciton size ($\widetilde{d}_{exc}$, in Å), D_{CT} index (in Å) and exciton binding energy (E_b) (in eV). Only transitions with $f \geq 0.02$ are reported.

Excited State	E	f	$\widetilde{d}_{exc}$	D_{CT}	E_b
S_7	1.18	0.04	4.50	0.420	4.00
S_{32}	2.89	0.04	4.98	0.270	3.53
S_{97}	4.15	0.03	5.12	0.886	3.37
S_{100}	4.20	0.03	5.05	0.666	3.34
S_{113}	4.33	0.03	5.55	1.040	3.27
S_{166}	4.70	0.02	5.49	0.841	3.14
S_{171}	4.74	0.03	5.90	0.817	3.11

Table S5: Computed main vertical electronic transitions of S_b-g-C_3N_4/TiO_2 with 2 Ti layers, indicating transition energies (*E*, in eV), oscillator strengths (f), approximate exciton size ($\widetilde{d}_{exc}$, in Å), D_{CT} index (in Å) and exciton binding energy (E_b) (in eV). Only transitions with $f \geq 0.01$ are reported.

Excited State	E	f	$\widetilde{d}_{exc,\alpha}$	$\widetilde{d}_{exc,\beta}$	D_{CT}	E_b
D_6	0.68	0.01	4.61	3.31	0.716	4.74
D_{28}	1.98	0.01	4.61	4.33	0.498	3.84
D_{45}	2.54	0.01	4.55	5.67	0.674	3.74
D_{49}	2.65	0.02	3.92	2.75	1.025	4.44
D_{299}	4.53	0.01	5.08	4.57	0.668	3.15
D_{425}	4.91	0.01	4.40	4.47	0.464	3.17

Table S6: Computed main vertical electronic transitions of S_t-g-C_3N_4/TiO_2 with 2 Ti layers, indicating transition energies (*E*, in eV), oscillator strengths (f), approximate exciton size ($\widetilde{d}_{exc}$, in Å), D_{CT} index (in Å) and exciton binding energy (E_b) (in eV). Only transitions with $f \geq 0.01$ are reported.

Excited State	E	f	$\widetilde{d}_{exc,\alpha}$	$\widetilde{d}_{exc,\beta}$	D_{CT}	E_b
D_{10}	0.98	0.01	3.29	2.51	0.273	5.11
D_{15}	1.43	0.02	3.79	3.18	0.463	4.20
D_{19}	1.82	0.01	3.90	2.94	0.480	4.67
D_{22}	1.99	0.02	3.61	2.60	0.386	5.06
D_{35}	2.70	0.05	3.17	3.15	0.254	4.02
D_{38}	2.85	0.03	4.18	4.04	0.370	4.23
D_{47}	3.10	0.02	4.57	2.71	1.015	4.14
D_{66}	3.59	0.02	4.79	5.61	0.705	3.67
D_{133}	4.21	0.02	4.85	4.53	0.932	3.27
D_{264}	4.81	0.01	4.35	4.52	0.432	3.22

References

(1) Zhu, B.; Zhang, L.; Cheng, B.; Yu, J. First-principle calculation study of tri-s-triazine-based g-C_3N_4: a review. *Applied Catalysis B: Environmental* **2018**, *224*, 983–999.

(2) Dong, G.; Zhang, Y.; Pan, Q.; Qiu, J. A fantastic graphitic carbon nitride (g-C_3N_4) material: electronic structure, photocatalytic and photoelectronic properties. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* **2014**, *20*, 33–50.