Supporting information for

Theoretical and experimental studies of high efficient all-solid Z-scheme TiO_2-TiC/g-C_3N_4 for photocatalytic CO_2 reduction via dry reforming of methane

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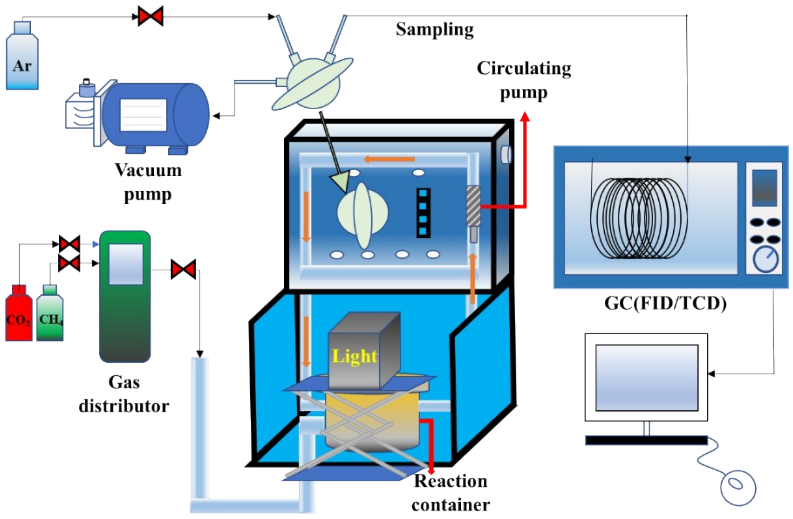

Figure S1. The diagram of the experimental device for photocatalytic CO_2 in the presence of CH_4.

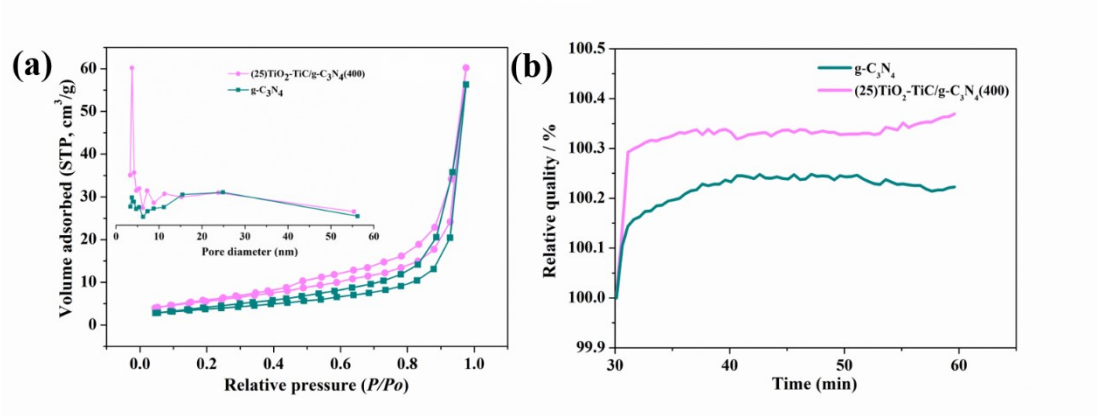

Figure S2. (a) N_2 physisorption isotherms and corresponding pore size distribution curves (inset) and (b) The CO_2 adsorption capacity of g-C_3N_4 and (25)TiO_2-TiC/g-C_3N_4(400).

Table S1. BET specific surface area and total pore volume of g-C_3N_4 and (25)TiO_2-TiC/g-C_3N_4(400).

Parameter	g-C_3N_4	(25)TiO_2-TiC/g-C_3N_4(400)
Specific surface area (m^2 /g)	16.920	21.503
Total pore volume (cm^3 /g)	0.087	0.078

Table S2. Factors and levels of the orthogonal test.

	Level 1	Level 2	Level 3	Level 4
F_A: Absolute pressure (kPa)	10	20	30	40
F_B: CH_4 to CO_2 ratio	2:1	1:1	1:2	1:3
F_C: TiC loading (mg)	15	20	25	30
F_D: Calcination temperature (℃)	350	400	450	500

Table S3. The detailed experimental conditions of four factors and four levels ($L_{16}(4^4)$) orthogonal test.

Experiment Numbers	F_A: pressure (kPa)	F_B: mole ratio of CH_4: CO_2	F_C: Loading of TiC (mg)	F_D: calcination temperature (℃)
1	10	2:1	15	350
2	10	1:1	20	400
3	10	1:2	25	450
4	10	1:3	30	500
5	20	2:1	20	450
6	20	1:1	15	500
7	20	1:2	30	350
8	20	1:3	25	400
9	30	2:1	25	500
10	30	1:1	30	450
11	30	1:2	15	400
12	30	1:3	20	350
13	40	2:1	30	400
14	40	1:1	25	350
15	40	1:2	20	500
16	40	1:3	15	450

Table S4. The experimental results of orthogonal test ($L_{16}(4^4)$).

Experiment Numbers	H_2 (μmol)	CO (μmol)	TOF_{H2} (μmol g^{-1} h^{-1})	TOF_{CO} (μmol g^{-1} h^{-1})	Conversion rates of CH_4 (%)
1	0.21	0.56	1.07	2.8	1.8
2	0.38	1.39	1.91	6.95	1.584
3	0.21	1.18	1.05	5.91	0.6
4	0.20	0.70	1.00	3.49	3.29
5	0.34	1.04	1.71	5.22	1.53
6	0.36	0.57	1.79	2.83	1.58
7	0.39	0.81	1.96	4.06	1.12
8	0.19	1.65	0.93	8.27	1.46
9	0.40	1.50	1.99	7.52	2.89
10	0.23	0.86	1.14	4.28	1.22
11	0.21	2.16	1.04	10.78	1.373
12	0.40	1.33	1.98	6.24	1.23
13	0.36	2.03	1.79	10.17	3.43
14	0.29	1.22	1.45	6.11	0.66
15	0.17	1.15	0.87	5.74	1.08
16	0.27	1.38	1.34	6.89	1.01

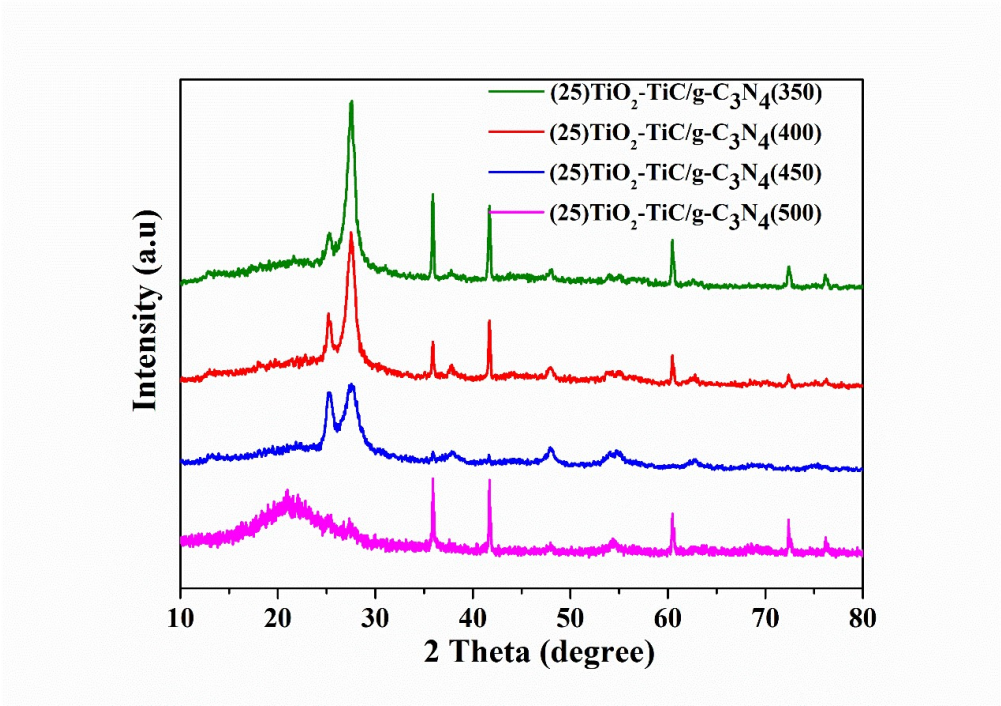

Figure S3. X-ray diffraction patterns of (25)TiO_2-TiC/g-C_3N_4(350), (25)TiO_2-TiC/g-C_3N_4(400), (25)TiO_2-TiC/g-C_3N_4(450), (25)TiO_2-TiC/g-C_3N_4(500).

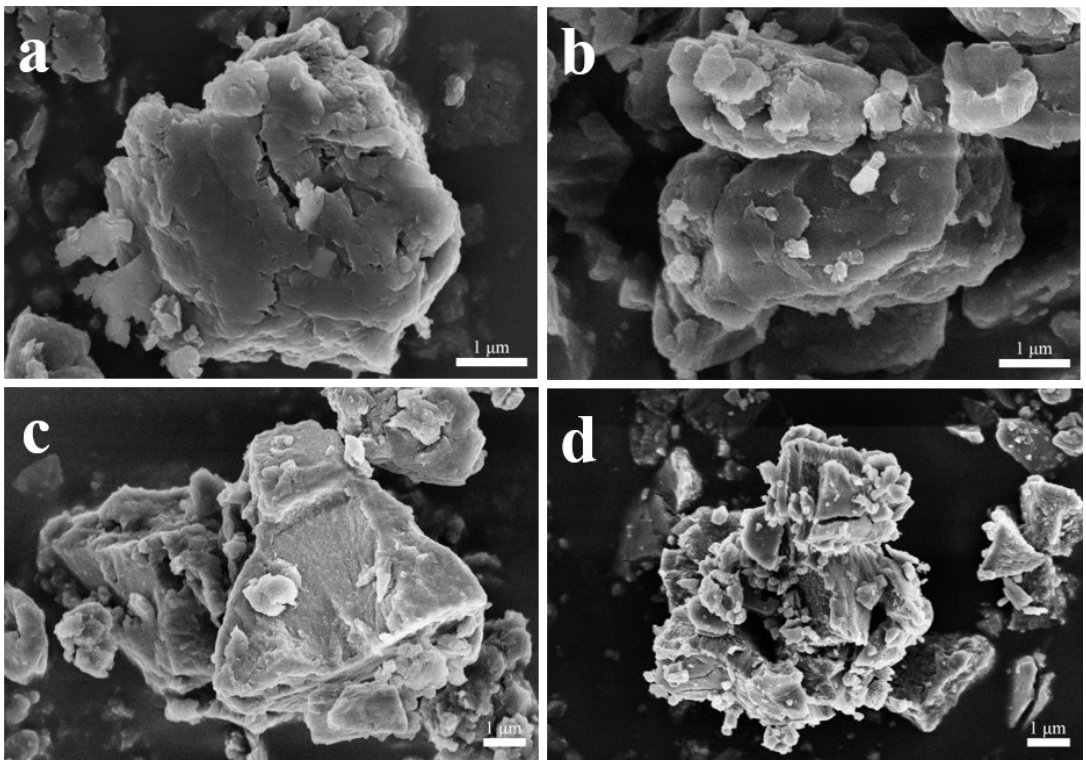

Figure S4. SEM patterns of (25)TiO_2-TiC/g-C_3N_4(350), (25)TiO_2-TiC/g-C_3N_4(400), (25)TiO_2-TiC/g-C_3N_4(450), (25)TiO_2-TiC/g-C_3N_4(500).

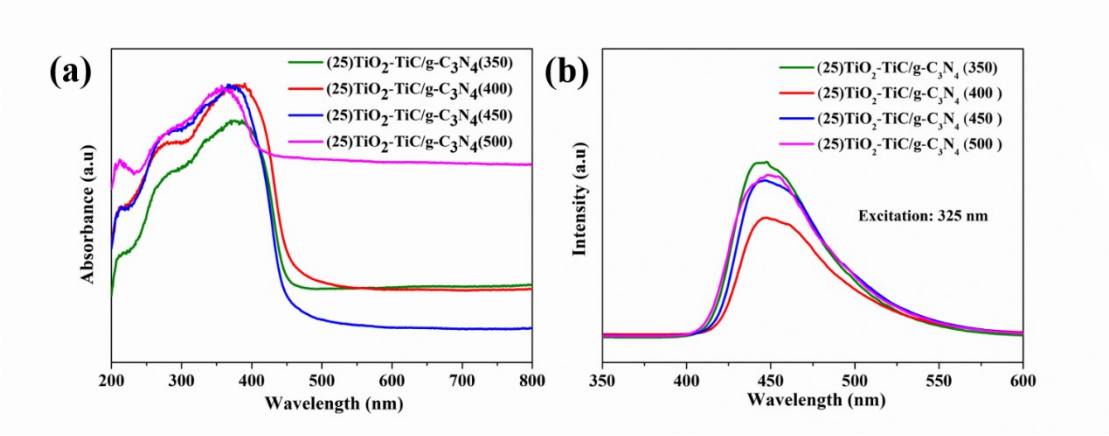

Figure S5. (a)UV−vis absorption spectra and (b) PL emission spectra of TiO_2-TiC/g-C_3N_4 calcinating under different temperature.

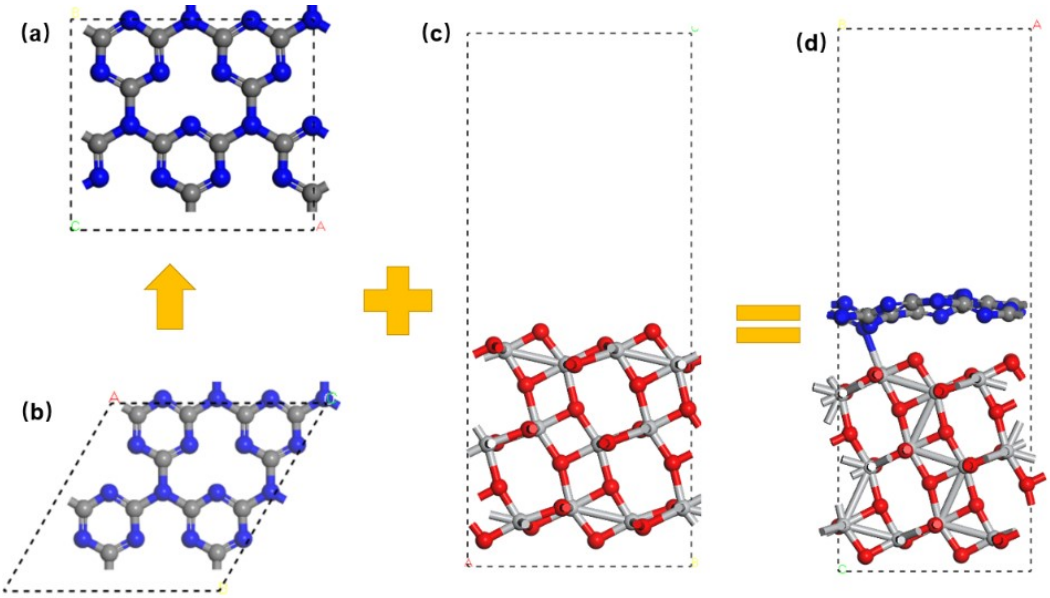

Figure S6. Illustrations of (a) 2×√3 relaxed rectangular g-C_3N_4 monolayer; (b) original g-C_3N_4 monolayer; (c) TiO_2 (101) surface; (d) TiO_2/g-C_3N_4 heterostructure. Deep gray, blue, red, and light gray balls represent C, N, O and Ti atoms, respectively; this notation is used throughout the paper.

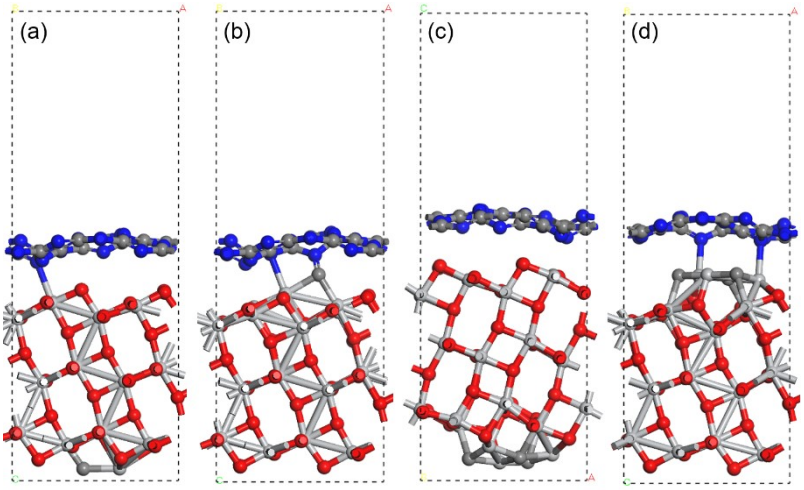

Figure S7. Illustrations of (a) TiO_2-TiC/g-C_3N_4 heterostructure with TiC on the TiO_2 side; (b) TiO_2-TiC/g-C_3N_4 heterostructure with TiC between TiO_2 and g-C_3N_4; (c) TiO_2-TiC/g-C_3N_4 heterostructure with $(TiC)_3$ on the TiO_2 side; (d) TiO_2-TiC/g-C_3N_4 heterostructure with $(TiC)_3$ between TiO_2 and g-C_3N_4.

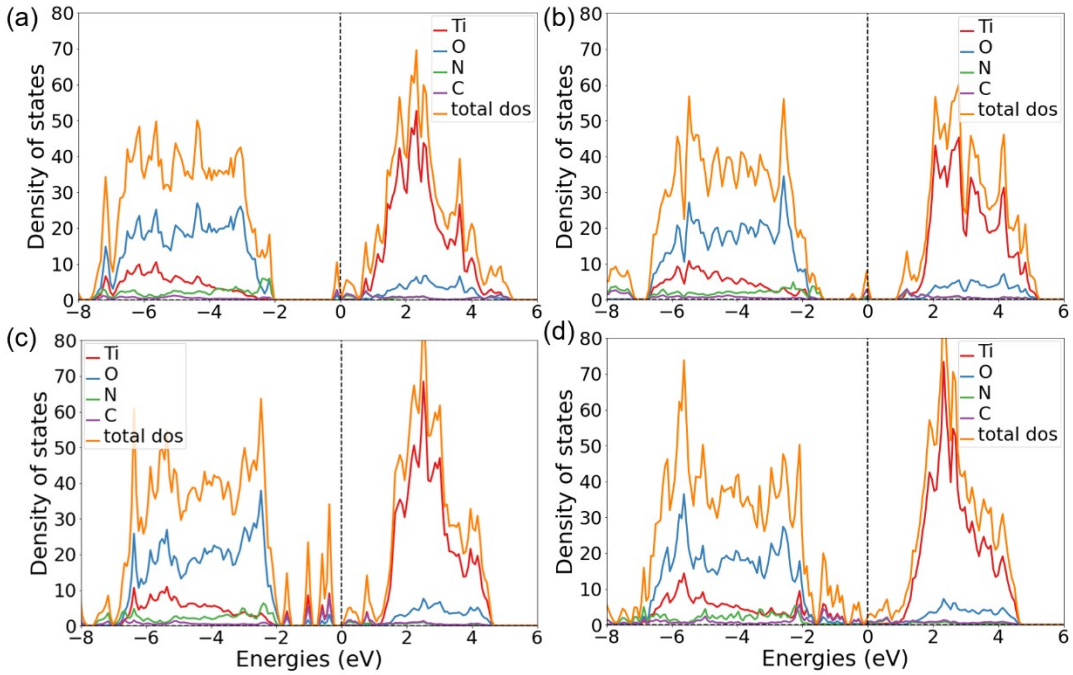

Figure S8. Density of state (DOS) of four structures in Figure S7. (a) – (d) correspond to structures (a) – (d) in Figure S7.

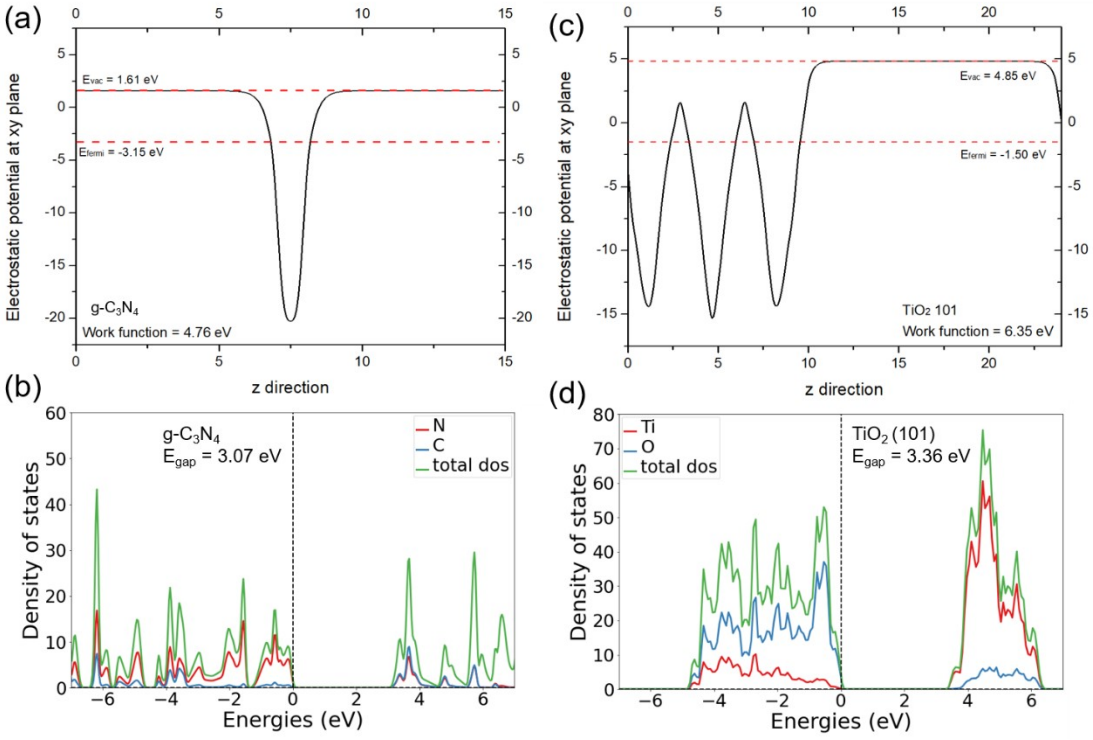

Figure S9. Electrostatic potentials and density of states of (ab) the monolayer g-C_3N_4; (cd) TiO_2(101) surface. The DOS Figures in this study are plotted using DosPlotter module in Pymatgen python package (https://pymatgen.org/).

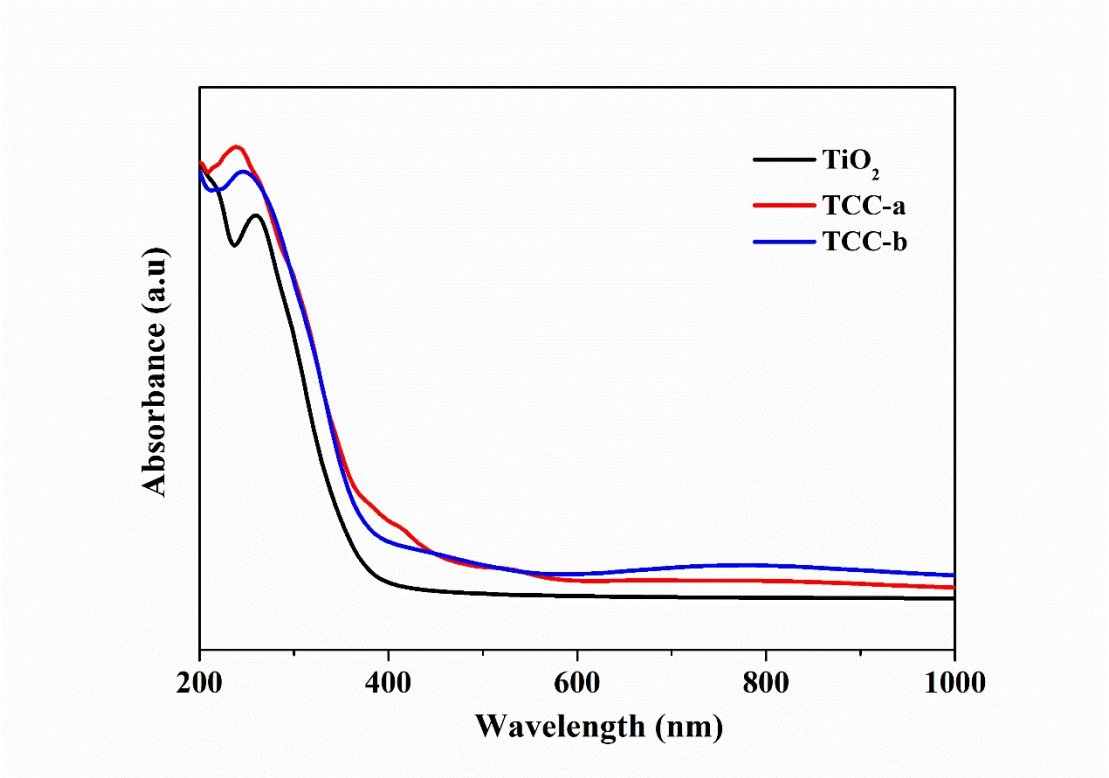

Figure S10. Calculated optical adsorption spectra of TiO_2(101), TCC-a, and TCC-b.