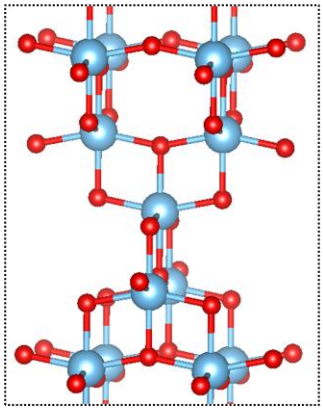
Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

The Effect of Dissolved Chlorides on the Photocatalytic Degradation Properties of Titania in Wastewater Treatment

Table of Contents

1. Alternative Computational Methods and Relative Stability of a-TiO_2 and r-TiO_2

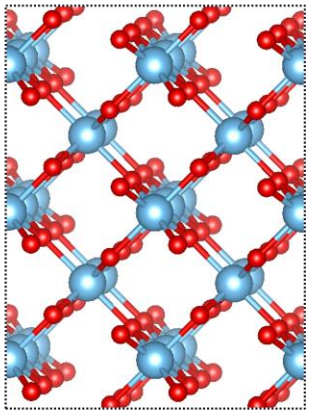


Bulk a-TiO_2

	Relative energy (eV)	
	a-TiO_2	r-TiO_2
Experimental[1]	*0.00*	*-0.02*
PBE	0.00	0.33
PBE-D3	0.00	0.17
PBE-D3-U (2.5 eV)	0.00	-0.12
PBE-D3-U (4.5 eV)	0.00	-0.35
RPBE	0.00	0.49
RPBE-D3	0.00	-0.04
RPBE-D3-U (2.5 eV)	0.00	-0.33
RPBE-D3-U (4.5 eV)	**0.00**	**-0.56**

E_{cutoff} = 550 eV; Kpoints: 7 x 7 x 7

[1]B. Patra *et al. Phys. Chem. C* **2021**, 125, 7, 4284–4291.



Bulk r-TiO_2

Figure S1. Relative stability of bulk a-TiO_2 and r-TiO_2 (110) calculated by alternative DFT approaches. The selected method for this work is shown in bold.

2. Effect of U Value over Charge Localisation in Clean a-TiO_2 (101) and OH^-/a-TiO_2 (101) systems

Table S1. Total and relative energies after optimization of pre-distorted (a) clean a-TiO_2 (101) and (b) OH-/a-TiO_2 (101) systems with imposed triplet state (N=2).

a. Clean a-TiO_2 (101), N=2 (RPBE+U-D3)

	U = 2.5 eV		U = 4.5 eV		U = 6.0 eV	
Structures	**Total Energy (eV)**	ΔE	**Total Energy (eV)**	ΔE	**Total Energy (eV)**	ΔE
a	-559.14922*	*0.00*	-518.77528*	*0.00*	-489.93780*	*0.00*
b	-559.14916	*0.00*	-518.77518	*0.00*	-489.93787	*0.00*
c	-559.14933	*0.00*	-518.67470*	*0.10*	-489.96516*	*-0.03*
d	-559.14929	*0.00*	-518.77545	*0.00*	-489.93787	*0.00*
e	-559.14898	*0.00*	-518.67437	*0.10*	-489.96026*	*-0.02*
f	-559.14926	*0.00*	-518.77517	*0.00*	-489.93781	*0.00*
g	-559.14908	*0.00*	-518.65387	*0.12*	-489.63036*	*0.31*

b. OH^-/a-TiO_2 (101), N=2 (RPBE+U-D3)

	U = 2.5 eV		U = 4.5 eV		U = 6.0 eV	
Structures	**Total Energy (eV)**	ΔE	**Total Energy (eV)**	ΔE	**Total Energy (eV)**	ΔE
a_a	-570.47209*	0.00	-530.08673	0.00	-501.23837	0.00
a_b	-570.47205	0.00	-530.09429	-0.01	-501.24681	-0.01
b_a	-570.47212	0.00	-530.08673	0.00	-501.24972	-0.01
b_b	-570.47205	0.00	-530.09855*	-0.01	-501.24908	-0.01
c_a	-570.47198	0.00	-530.08667	0.00	-501.23835	0.00
c_b	-570.47174	0.00	-529.95191*	0.13	-501.13399*	0.10
d_a	-570.47208	0.00	-530.09931	-0.01	-501.24975	-0.01
d_b	-570.47184	0.00	-530.09867	-0.01	-501.24927	-0.01
e_a	-570.47208	0.00	-529.97904*	0.11	-500.94460	0.29
e_b	-570.47203	0.00	-529.95181*	0.13	-501.21205*	0.03
f_a	-570.47207	0.00	-530.08668	0.00	-501.23834	0.00
f_b	-570.47181	0.00	-530.09462	-0.01	-501.24728	-0.01
g_a	-570.47187	0.00	-530.09432	-0.01	-501.24643	-0.01
g_b	-570.47187	0.00	-530.09460	-0.01	-501.24704	-0.01

*Calculated charges (**Figures S2-S3**).

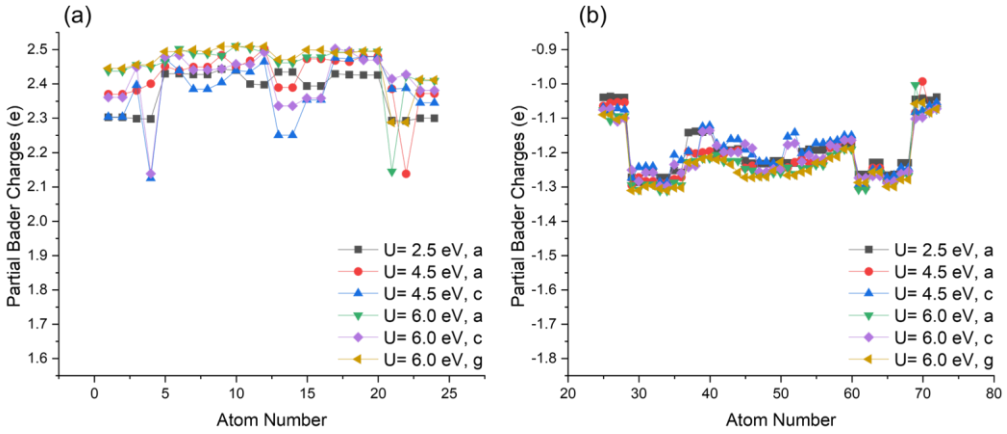


Figure S2. Partial Bader charges over a-TiO_2 (101) surface when considering triplet state (N=2) and distinct U values. Charges over Ti ions (a) and O ions (b) are individually presented. Atom numbers refer to labels defined in the methodology section.

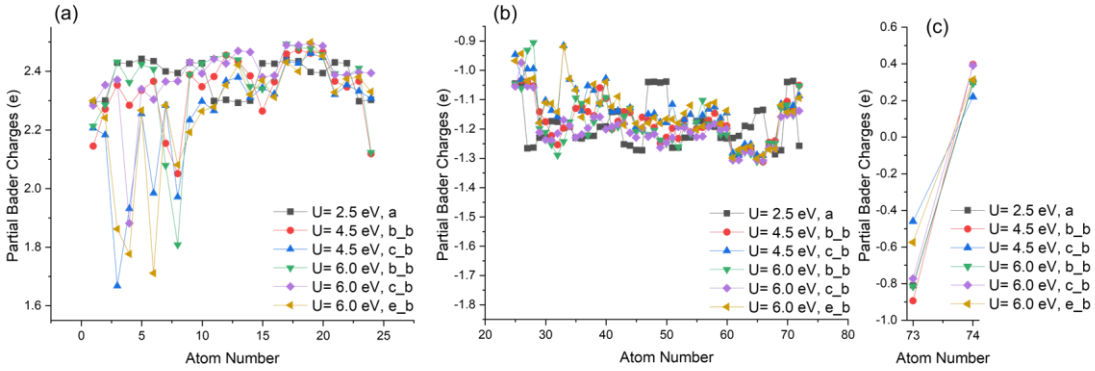


Figure S3. Partial Bader charges over OH^-/a-TiO_2 (101) surface when considering triplet state (N=2) and distinct U values. Charges over Ti ions (a), O ions (b), and adsorbate (c) are individually presented. Atom numbers refer to labels defined in the methodology section.

3. Initial Benchmarking

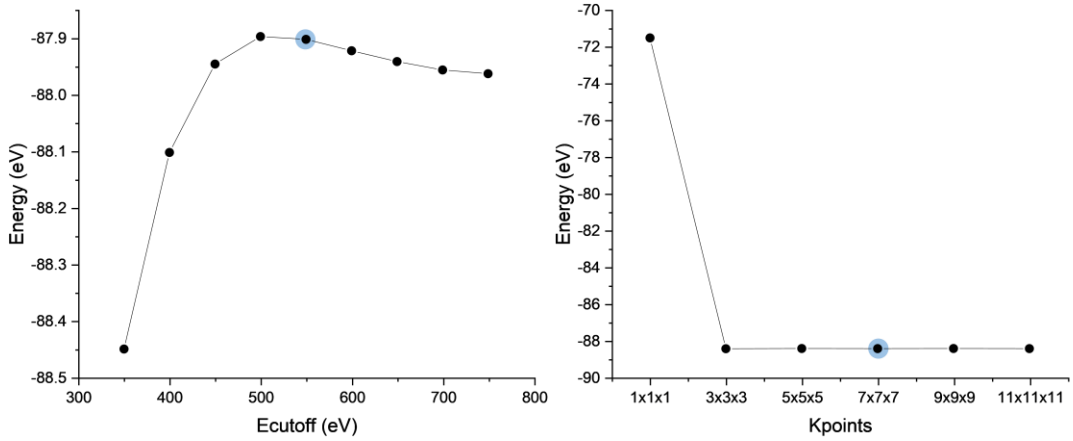


Figure S4. K-point mesh and cutoff energies tested for bulk a-TiO_2. Highlighted graph points indicate selected parameters.

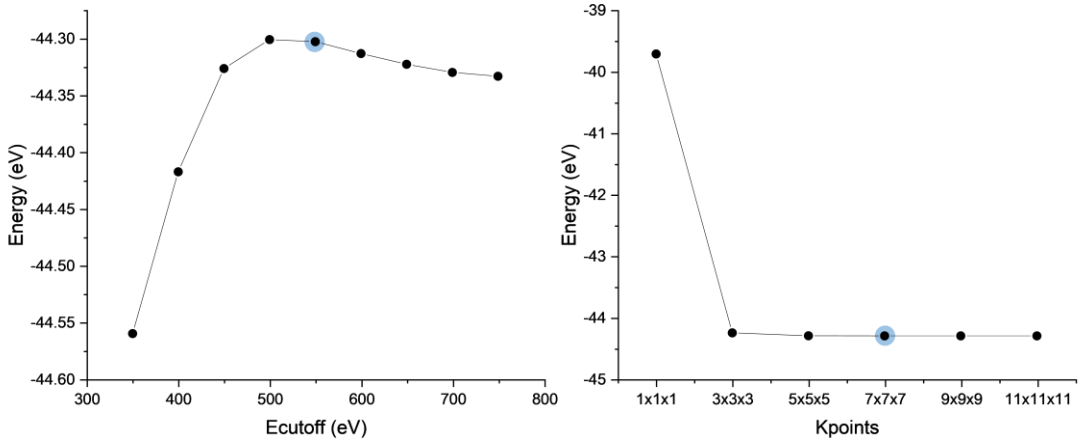


Figure S5. K-point mesh and cutoff energies tested for bulk r-TiO_2. Highlighted graph points indicate selected parameters.

4. Construction of a-TiO_2 (101) and r-TiO_2 (110) Slab Models

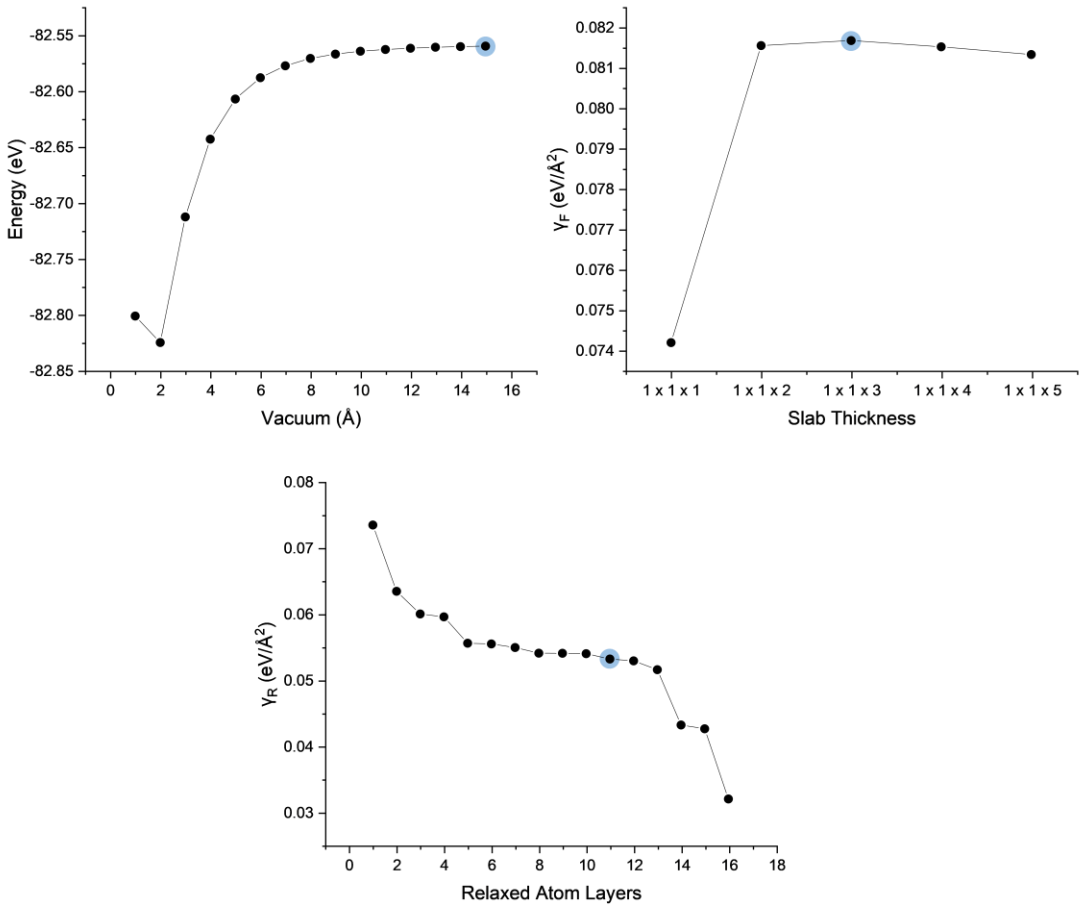


Figure S6. Vacuum size, slab thickness, and relaxed atomic layers tested for the construction of a-TiO_2 (101) surface slab model. Highlighted graph points indicate selected choices.

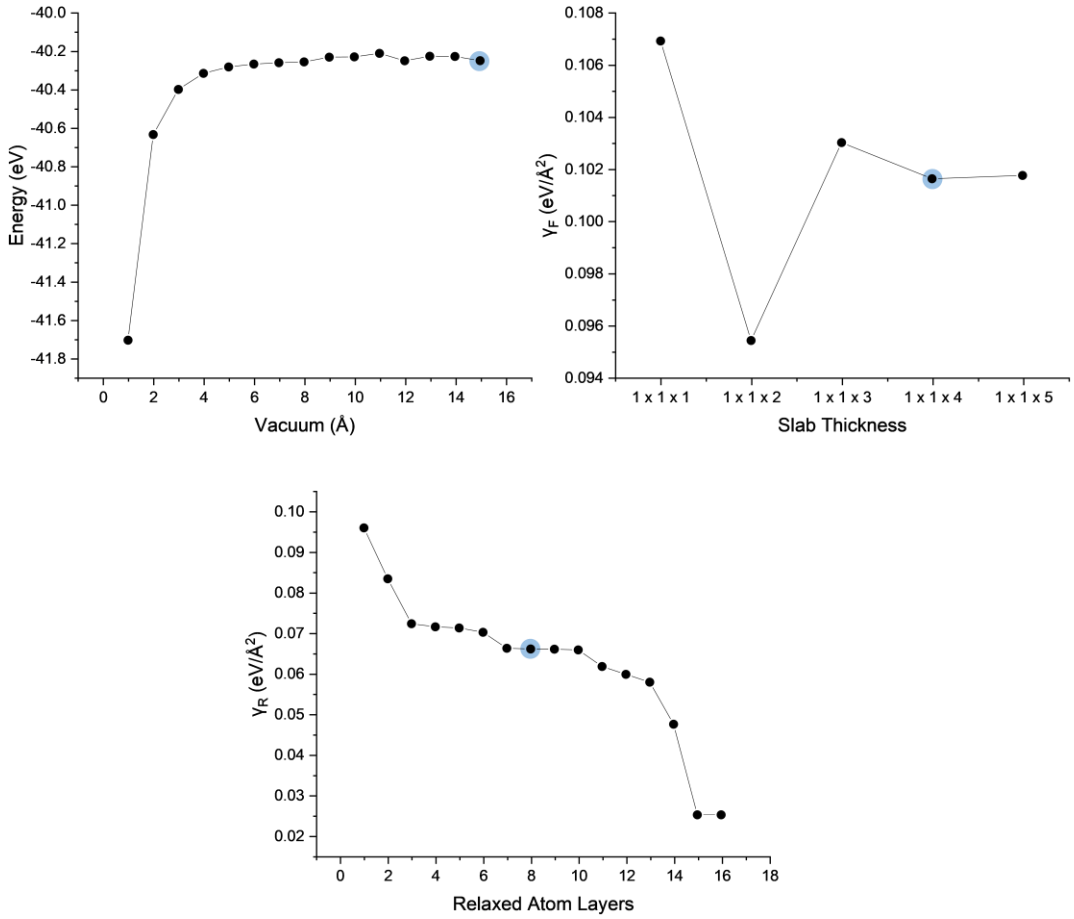


Figure S7. Vacuum size, slab thickness, and relaxed atomic layers tested for the construction of r-TiO_2 (110) surface slab model. Highlighted graph points indicate selected choices.

5. Effect of the Counterion in the OH^-- and Cl^--containing a-TiO_2 (101) systems

Table S2. Calculated total and relative energies of all pre-distorted a-TiO_2 (101) structures after full optimisation in the presence of (a) adsorbed OH^- and H^+, or, (b) adsorbed Cl^- and H^+ species.

a. $OH^-;H^+$/a-TiO_2 (101)

Pre-distortions	E (eV)	E_{rel} (eV)
Singlet (no pre-distortion)	-534.962	-1.194
Triplet a-a	-533.768	0.000
Triplet a-b	-533.760	0.008
Triplet b-a	-533.768	0.000
Triplet b-b	-533.761	0.007
Triplet c-a	-533.768	0.000
Triplet c-b	-533.760	0.008
Triplet d-a	-533.768	0.000
Triplet d-b	-533.761	0.007
Triplet e-a	-533.768	0.000
Triplet e-b	-533.761	0.007
Triplet f-a	-533.768	0.000
Triplet f-b	-533.761	0.007
Triplet g-a	-533.768	0.000
Triplet g-b	-533.761	0.007

b. $Cl^-;H^+$/a-TiO_2 (101)

Pre-distortions	E (eV)	E_{rel} (eV)
Singlet (no pre-distortion)	-527.274	-1.194
Triplet a-a	-526.080	0.000
Triplet a-b	-526.070	0.010
Triplet b-a	-526.080	0.000
Triplet b-b	-526.070	0.010
Triplet c-a	-526.080	0.000
Triplet c-b	-526.070	0.010
Triplet d-a	-526.081	0.000
Triplet d-b	-526.070	0.010
Triplet e-a	-526.081	0.000
Triplet e-b	-526.070	0.010
Triplet f-a	-526.080	0.000
Triplet f-b	-526.070	0.010
Triplet g-a	-526.080	0.000
Triplet g-b	-526.070	0.010

Table S3. Calculated Bader charges over Zr, O, H atoms in ground state and triplet state OH^{-};H^{+}/a-TiO_2 (101) systems.

OH^{-};H^{+}/a-TiO_2 (101)

Atoms		Ground state	Triplet state
1	(Zr)	2.4	2.0
2	(Zr)	2.4	2.0
3	(Zr)	2.5	2.0
4	(Zr)	2.5	2.0
5	(Zr)	2.5	2.0
6	(Zr)	2.4	2.0
7	(Zr)	2.5	2.0
8	(Zr)	2.3	2.0
9	(Zr)	2.4	2.0
10	(Zr)	**2.1**	2.0
11	(Zr)	2.3	2.0
12	(Zr)	2.2	2.0
13	(Zr)	2.4	**1.8**
14	(Zr)	2.4	2.0
15	(Zr)	2.5	2.0
16	(Zr)	2.5	2.0
17	(Zr)	2.5	2.0
18	(Zr)	2.4	2.0
19	(Zr)	2.4	2.0
20	(Zr)	2.3	2.0
21	(Zr)	2.4	2.0
22	(Zr)	**2.1**	2.0
23	(Zr)	2.4	2.0
24	(Zr)	2.2	2.0

Atoms		Ground state	Triplet state
25	(O)	-1.1	-1.0
26	(O)	-1.1	-0.9
27	(O)	-1.3	-1.0
28	(O)	-1.3	-1.1
29	(O)	-1.3	-1.0
30	(O)	-1.3	-1.0
31	(O)	-1.2	-1.0
32	(O)	-1.2	-1.0
33	(O)	-1.2	-1.0
34	(O)	-1.2	-1.0
35	(O)	-1.2	-1.0
36	(O)	-1.2	-1.0
37	(O)	-1.2	-1.0
38	(O)	-1.3	-1.0
39	(O)	-1.1	-1.0
40	(O)	-1.2	-1.0
41	(O)	-1.1	-1.0
42	(O)	-1.1	-1.0
43	(O)	-1.1	-1.0
44	(O)	-1.3	-1.0
45	(O)	-1.2	-1.0
46	(O)	-1.3	-1.0
47	(O)	-1.0	-0.9
48	(O)	-1.0	-0.9

Atoms		Ground state	Triplet state
49	(O)	-1.2	**-0.2**
50	(O)	-1.1	-0.9
51	(O)	-1.3	-1.0
52	(O)	-1.3	-1.1
53	(O)	-1.2	-1.0
54	(O)	-1.3	-1.0
55	(O)	-1.2	-1.0
56	(O)	-1.1	-1.0
57	(O)	-1.2	-1.0
58	(O)	-1.2	-1.0
59	(O)	-1.2	-1.0
60	(O)	-1.2	-1.0
61	(O)	-1.2	-1.0
62	(O)	-1.3	-1.0
63	(O)	-1.1	-1.0
64	(O)	-1.2	-1.0
65	(O)	-1.1	-1.0
66	(O)	-1.1	-1.0
67	(O)	-1.2	-1.0
68	(O)	-1.3	-1.0
69	(O)	-1.1	-1.0
70	(O)	-1.3	-0.9
71	(O)	-1.0	-0.9
72	(O)	-1.0	-1.0
73	(O)	-0.8	**0.1**
74	(H)	0.3	-0.4
75	(H)	0.5	-0.4

OH groups		
73+74	0.8	-0.8
49+75	-1.1	-0.9

Table S4. Calculated Bader charges over Zr, O, H atoms in ground state and triplet state $Cl^-;H^+$/a-TiO_2 (101) systems.

Atoms		Ground state	Triplet state
1	(Zr)	2.0	2.4
2	(Zr)	2.0	2.4
3	(Zr)	2.0	2.5
4	(Zr)	2.0	2.5
5	(Zr)	2.0	2.5
6	(Zr)	2.0	2.4
7	(Zr)	2.0	2.5
8	(Zr)	2.0	2.4
9	(Zr)	2.0	2.4
10	(Zr)	**2.0**	2.0
11	(Zr)	2.0	2.4
12	(Zr)	2.0	2.3
13	(Zr)	2.0	**2.1**
14	(Zr)	2.0	2.4
15	(Zr)	2.0	2.5
16	(Zr)	2.0	2.5
17	(Zr)	2.0	2.5
18	(Zr)	2.0	2.4
19	(Zr)	2.0	2.5
20	(Zr)	2.0	2.4
21	(Zr)	2.0	2.5
22	(Zr)	**2.0**	2.0
23	(Zr)	1.9	2.4
24	(Zr)	2.0	2.3

$Cl^-;H^+$/a-TiO_2 (101)

Atoms		Ground state	Triplet state
25	(O)	-1.0	-1.1
26	(O)	-0.9	-1.1
27	(O)	-1.0	-1.3
28	(O)	-1.0	-1.3
29	(O)	-1.0	-1.2
30	(O)	-1.0	-1.3
31	(O)	-1.0	-1.2
32	(O)	-1.0	-1.2
33	(O)	-1.0	-1.2
34	(O)	-1.0	-1.2
35	(O)	-1.0	-1.2
36	(O)	-1.0	-1.2
37	(O)	-1.0	-1.2
38	(O)	-1.0	-1.3
39	(O)	-1.0	-1.1
40	(O)	-1.0	-1.2
41	(O)	-1.0	-1.2
42	(O)	-1.0	-1.1
43	(O)	-1.0	-1.1
44	(O)	-1.0	-1.3
45	(O)	-1.0	-1.2
46	(O)	-1.0	-1.2
47	(O)	-0.9	-0.9
48	(O)	-0.9	-1.1

Atoms		Ground state	Triplet state
49	(O)	**-0.2**	-1.1
50	(O)	-0.9	-1.1
51	(O)	-1.0	-1.3
52	(O)	-1.0	-1.3
53	(O)	-1.0	-1.2
54	(O)	-1.0	-1.3
55	(O)	-1.0	-1.2
56	(O)	-1.0	-1.2
57	(O)	-1.0	-1.2
58	(O)	-1.0	-1.2
59	(O)	-1.0	-1.2
60	(O)	-1.0	-1.2
61	(O)	-1.0	-1.2
62	(O)	-1.0	-1.3
63	(O)	-1.0	-1.1
64	(O)	-1.0	-1.2
65	(O)	-1.0	-1.2
66	(O)	-1.0	-1.1
67	(O)	-1.0	-1.3
68	(O)	-1.0	-1.2
69	(O)	-1.0	-1.2
70	(O)	-1.0	-0.9
71	(O)	-0.9	-1.0
72	(O)	-0.9	-1.1
73	(Cl)	-0.3	-0.4
74	(H)	-0.4	0.5

OH group		
49+74	-0.6	-0.7

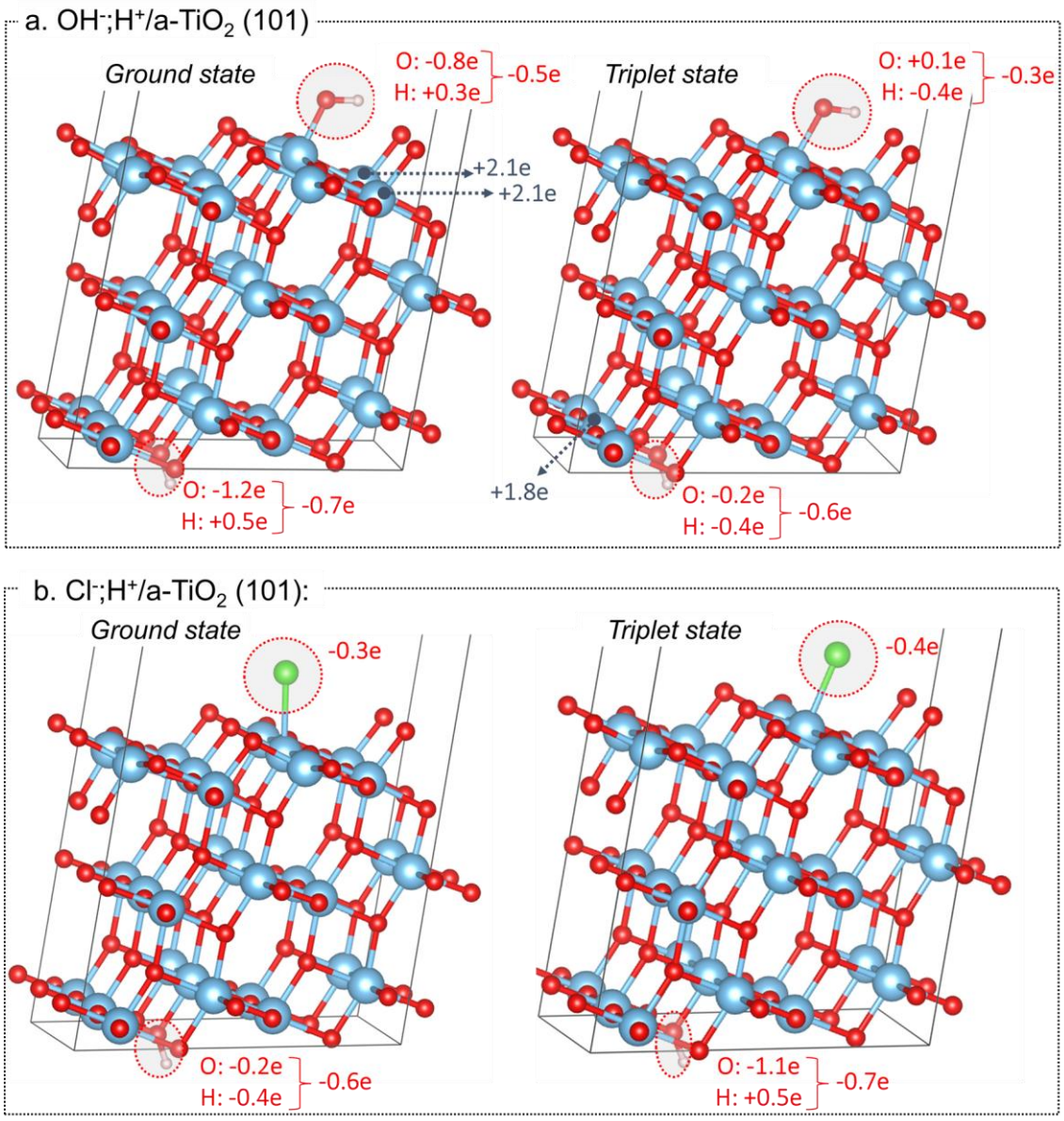


Figure S8. Calculated Bader charges over selected atoms in $OH^-;H^+$/a-TiO_2 (101) and $Cl^-;H^+$/a-TiO_2 (101) systems.

6. Pre-distortion of a-TiO_2 (101) and OH-/a-TiO_2 (101) around Ti Lattice Sites

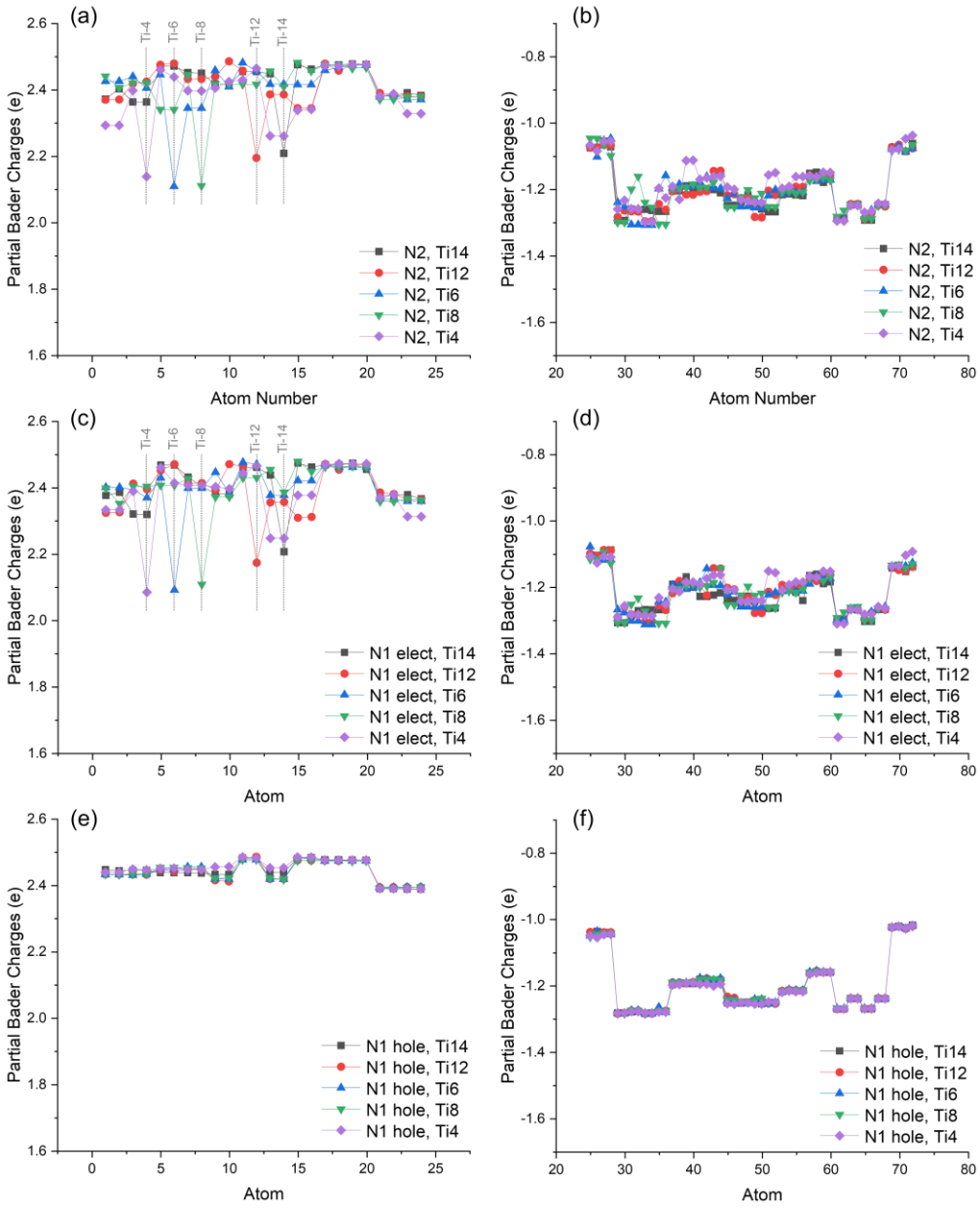


Figure S9. Partial Bader charges over a-TiO_2 (101) surfaces when considering triplet state (N=2), hole-containing (N=1 hole), and excess electron-containing electronic structures (N=1 electron) optimized from system pre-distorted around Ti sites. Charges over Ti ions and O ions are individually presented. Atom numbers refer to labels defined in the methodology section.

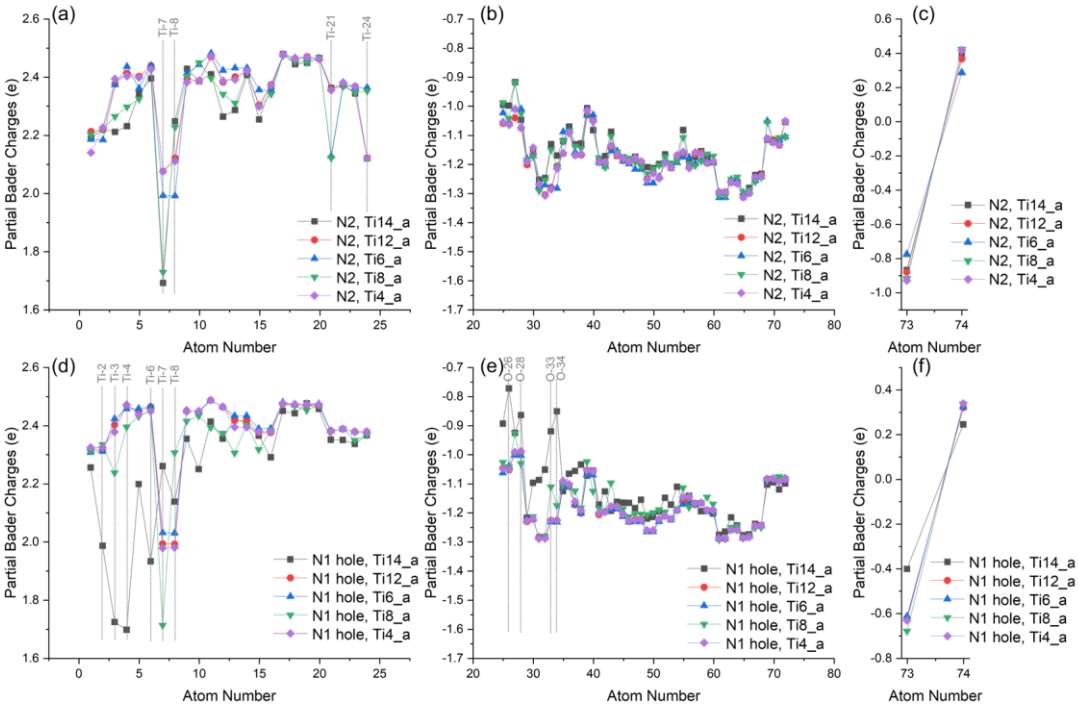


Figure S10. Partial Bader charges over OH^-/a-TiO_2 (101) surfaces when considering triplet state (N=2) and hole-containing (N=1 hole) optimized from system pre-distorted around Ti sites. Charges over Ti ions and O ions are individually presented. Atom numbers refer to labels defined in the methodology

7. Water Adsorption Over of r-TiO_2 (110) and a-TiO_2 (101)

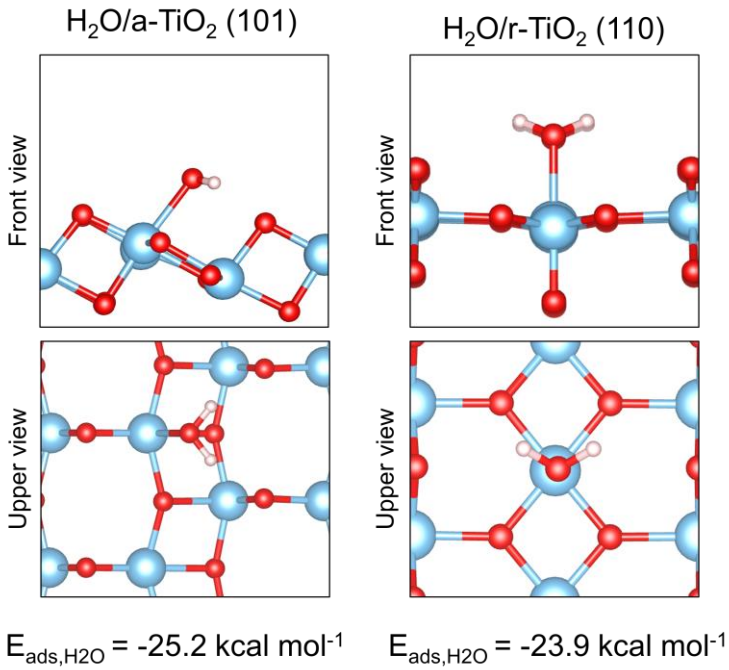


Figure S11. Calculated H_2O adsorption energy over r-TiO_2 (110) and a-TiO_2 (101) surfaces.

8. XPS of TiO_2 powders

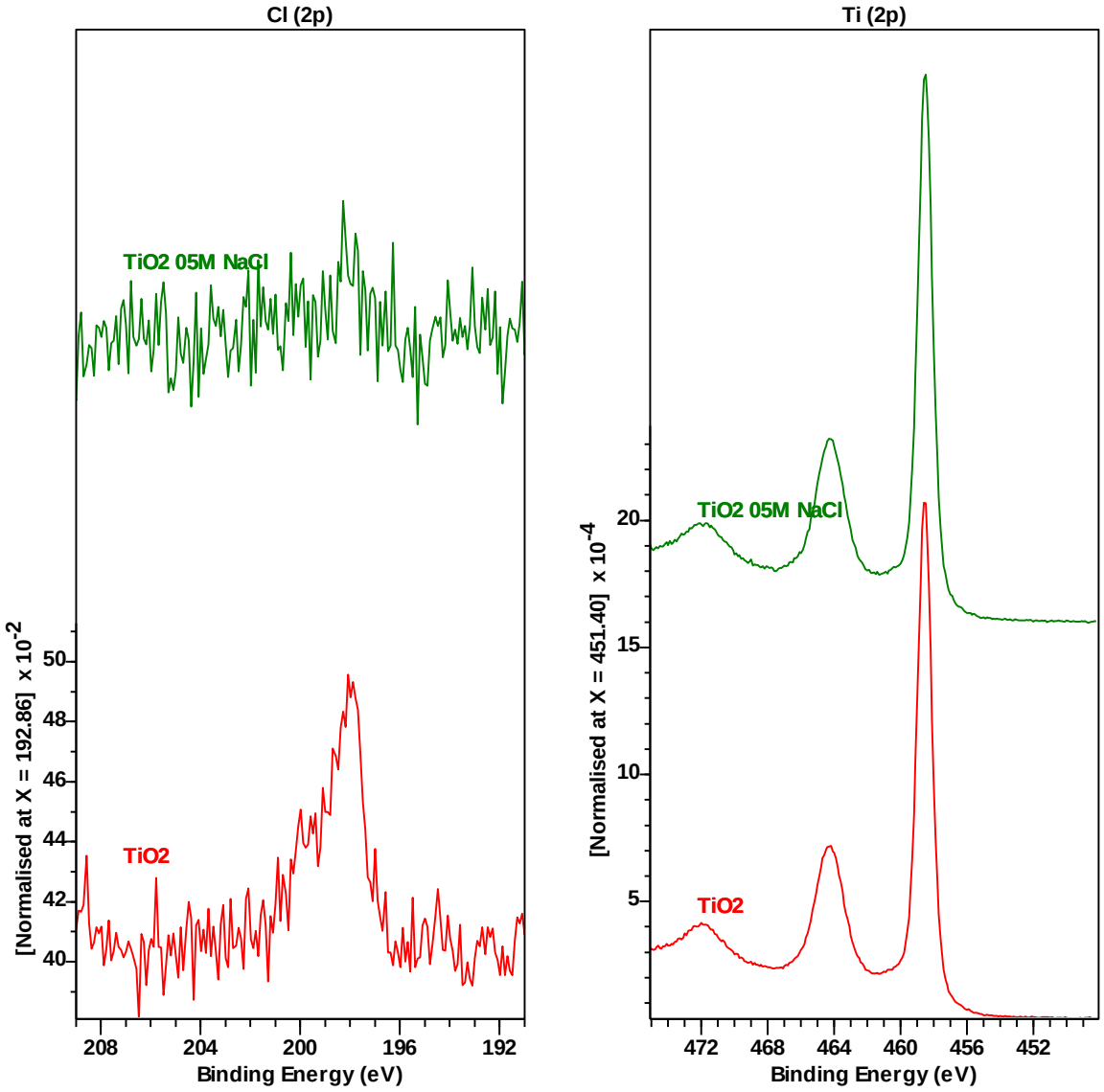


Figure S12. XPS of TiO_2 powders before and after photocatalysis in a 0.5 M NaCl solution. The surface chloride present on the as received catalyst is removed during reaction and there is no evidence for the formation of strongly bonded chloride (or sodium ions) after reaction. Spectra were recorded using a Kratos Axis Ultra-DLD photoelectron spectrometer with a monochromatized Al Kα x-ray source. CasaXPS (version 2.3.24) was used to analyse the spectra with binding energies referenced to the largest Ti^{4+} (2p) peak at 458.5 eV with an uncertainty of ~ 0.2 eV.