Morphology of TiO_2 Nanoparticles as Fingerprint for the Transient Absorption Spectra: Implications for Photocatalysis

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Table S1. Features of TDDFT electronic excitations for the negatively charged $(TiO_2)_{35}^-$ NP.

Excited state number	Excitation energy / nm.	Oscillator strength x 10^{-3}	Main excitations	Percentage of electronic state / %
4	**1148.6**	**3.1**	SOMO → LUMO + 1	62.8
10	861.7	1.7	SOMO → LUMO + 7	28.9
11	**844.9**	**2.9**	SOMO → LUMO + 8	32.7
16	762.2	1.6	SOMO → LUMO + 15	24.4
17	756.8	1.4	SOMO → LUMO + 10	13.0
18	736.3	1.1	SOMO → LUMO + 11	37.2
19	**715.3**	**2.2**	SOMO → LUMO + 16 SOMO → LUMO + 14 SOMO → LUMO + 10 SOMO → LUMO + 15	14.4 14.2 13.0 11.8
21	693.7	1.2	SOMO → LUMO + 20	25.0
22	688.6	1.5	SOMO → LUMO + 17 SOMO → LUMO + 16 SOMO → LUMO + 15 SOMO → LUMO + 19	16.3 13.8 10.9 10.0
26	651.3	1.3	SOMO → LUMO + 24 SOMO → LUMO + 25 SOMO → LUMO + 27	16.8 13.9 10.9
27	636.5	1.2	SOMO → LUMO + 30	30.0
29	624.4	1.7	SOMO → LUMO + 34	16.3
31	614.5	1.2	SOMO → LUMO + 32	22.8
34	581.5	1.1	SOMO → LUMO + 33	34.3

Table S2. Features of TDDFT electronic excitations for the positively charged $(TiO_2)_{35}^+$ NP.

Excited state number	Excitation energy / nm.	Oscillator strength x 10^{-3}	Main excitations	Percentage of electronic state / %
4	**404.5**	**3.4**	HOMO – 3 → SUMO	64.2
8	**385.8**	**2.0**	HOMO – 5 → SUMO	30.4
11	382.1	1.6	HOMO – 11 → SUMO HOMO – 16 → SUMO	10.4 10.1
12	**376.4**	**7.0**	HOMO – 6 → SUMO HOMO – 25 → SUMO	17.7 16.3
62	293.4	1.5	HOMO – 5 → SUMO + 1	22.1

Table S3. Features of TDDFT electronic excitations for the negatively charged $(TiO_2)_{29}^-$ NP.

Excited state number.	Excitation energy / nm.	Oscillator strength x 10^{-3}	Main excitations	Percentage of electronic state / %
3	**895.1**	**3.2**	SOMO → LUMO + 9	28.8
4	**835.3**	**7.2**	SOMO → LUMO + 1	38.3
6	782.4	1.2	SOMO → LUMO + 2	33.6
7	722.3	1.6	SOMO → LUMO + 5	22.4
8	**706.4**	**5.7**	SOMO → LUMO	15.5
9	703.1	1.4	SOMO → LUMO	19.9
			SOMO → LUMO + 11	17.3
			SOMO → LUMO + 10	14.9
			SOMO → LUMO + 8	10.1
11	**672.5**	**4.2**	SOMO → LUMO + 12	18.3
			SOMO → LUMO + 15	11.3
15	622.5	1.2	SOMO → LUMO + 8	11.0
			SOMO → LUMO + 1	10.4
16	609.6	1.4	SOMO → LUMO + 5	21.3
18	**591.5**	**2.9**	SOMO → LUMO + 27	15.4
			SOMO → LUMO + 13	11.8
			SOMO → LUMO + 25	10.7
21	557.6	1.1	SOMO → LUMO + 8	15.6
			SOMO → LUMO + 16	11.0
23	**544.4**	**2.0**	SOMO → LUMO + 11	30.2
26	526.6	1.2	SOMO → LUMO + 16	27.4
40	452.1	1.2	SOMO → LUMO + 36	17.6
			SOMO → LUMO + 39	11.8
			SOMO → LUMO + 28	10.6
			SOMO → LUMO + 32	10.2
45	432.1	1.2	SOMO → LUMO + 38	17.4
			SOMO → LUMO + 32	11.5
82	314.4	1.3	SOMO → LUMO + 88	16.5
99	291.3	1.7	SOMO – 1 → LUMO	6.4

Table S4. Features of TDDFT electronic excitations for the positively charged $(TiO_2)_{29}^+$ NP.

Excited state number	Excitation energy / nm.	Oscillator strength x 10^{-3}	Main excitations	Percentage of electronic state / %
2	**507.0**	**6.8**	HOMO – 7 → SUMO HOMO – 16 → SUMO	19.2 10.2
3	**495.3**	**8.0**	HOMO – 10 → SUMO	21.4
4	**471.5**	**3.4**	HOMO – 7 → SUMO	17.0
10	**395.8**	**4.7**	HOMO – 10 → SUMO HOMO – 7 → SUMO	15.7 10.1
19	364.4	1.4	HOMO – 11 → SUMO	20.2
27	**345.6**	**2.1**	HOMO – 23 → SUMO	20.2
41	312.1	1.1	HOMO – 37 → SUMO HOMO – 31 → SUMO	13.1 10.0
64	292.3	1.2	HOMO – 3 → SUMO + 1	7.4
66	**291.9**	**4.5**	HOMO – 2 → SUMO + 1	8.2
84	**284.0**	**2.3**	HOMO – 6 → SUMO + 1	5.2
100	**279.8**	**4.1**	HOMO – 7 → SUMO + 1	4.1

Table S5. Features of TDDFT electronic excitations for the negatively charged $(TiO_2)_{43}^-$ NP.

Excited state number	Excitation energy / nm.	Oscillator strength x 10^{-3}	Main excitations	Percentage of electronic state / %
3	**768.5**	**7.2**	SOMO → LUMO	90.8
9	490.3	1.4	SOMO → LUMO + 3	38.3
12	**459.2**	**2.8**	SOMO → LUMO + 6	29.9
19	426.2	1.7	SOMO → LUMO + 10	50.3
20	**421.2**	**5.1**	SOMO → LUMO + 10	11.8
			SOMO → LUMO + 11	10.4
27	**392.9**	**2.5**	SOMO → LUMO + 27	13.2
			SOMO → LUMO + 23	11.9
			SOMO → LUMO + 19	11.9
			SOMO → LUMO + 21	10.2
29	385.4	1.6	SOMO → LUMO + 19	20.5
39	362.5	1.2	SOMO → LUMO + 36	13.7
			SOMO → LUMO + 33	10.4
42	357.1	1.2	SOMO → LUMO + 40	13.7
59	331.9	1.6	SOMO → LUMO + 52	17.4
			SOMO → LUMO + 57	12.8
63	**327.9**	**2.7**	SOMO → LUMO + 58	25.1
64	327.2	1.5	SOMO → LUMO + 47	17.3
			SOMO → LUMO + 57	12.2
65	**323.8**	**3.7**	SOMO → LUMO + 59	15.4
			SOMO → LUMO + 51	11.2
75	**315.6**	**2.8**	SOMO → LUMO + 56	22.3
83	**310.1**	**11.0**	SOMO → LUMO + 67	12.2
			SOMO → LUMO + 56	11.8
			SOMO → LUMO + 64	10.9
97	**302.8**	**7.8**	SOMO → LUMO + 63	16.2
			SOMO → LUMO + 66	12.1
99	301.3	1.7	HOMO – 12 → SOMO	8.6

Table S6. Features of TDDFT electronic excitations for the positively charged $(TiO_2)_{43}^+$ NP.

Excited state number	Excitation energy / nm.	Oscillator strength x 10^{-3}	Main excitations	Percentage of electronic state / %
7	**376.5**	**2.1**	HOMO – 16 → SUMO	39.3
10	**360.0**	**5.6**	HOMO – 10 → SUMO	17.9
			HOMO – 20 → SUMO	13.0
			HOMO – 26 → SUMO	10.5
14	347.5	1.2	HOMO – 27 → SUMO	13.2
			HOMO – 19 → SUMO	10.7
86	**296.0**	**3.0**	HOMO – 12 → SUMO + 2	4.0

Figure S1. Unrelaxed and relaxed SUMO and SOMO orbitals of $(TiO_2)_n$ (n = 29, 35, and 43) NPs. Such orbitals are energetically described in Figure 1. Green and blue isosurfaces correspond to positive and negative sign of the electron density, respectively.

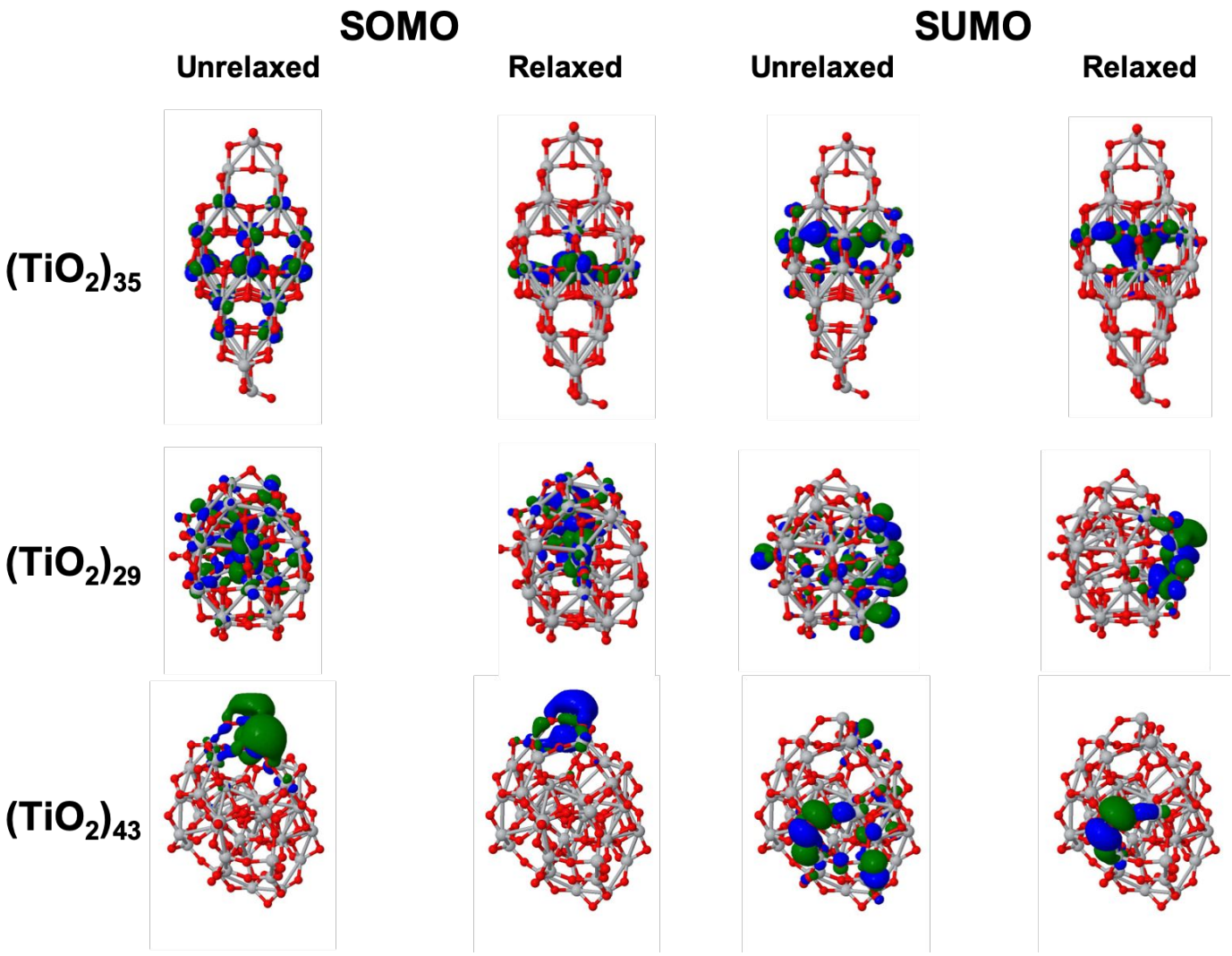

Figure S2. MOs of the negatively and positively charged $(TiO_2)_{35}$ NP involved in the electronic excitations listed in Tables S1 and S2. Green and blue isosurfaces correspond to positive and negative sign of the electron density, respectively.

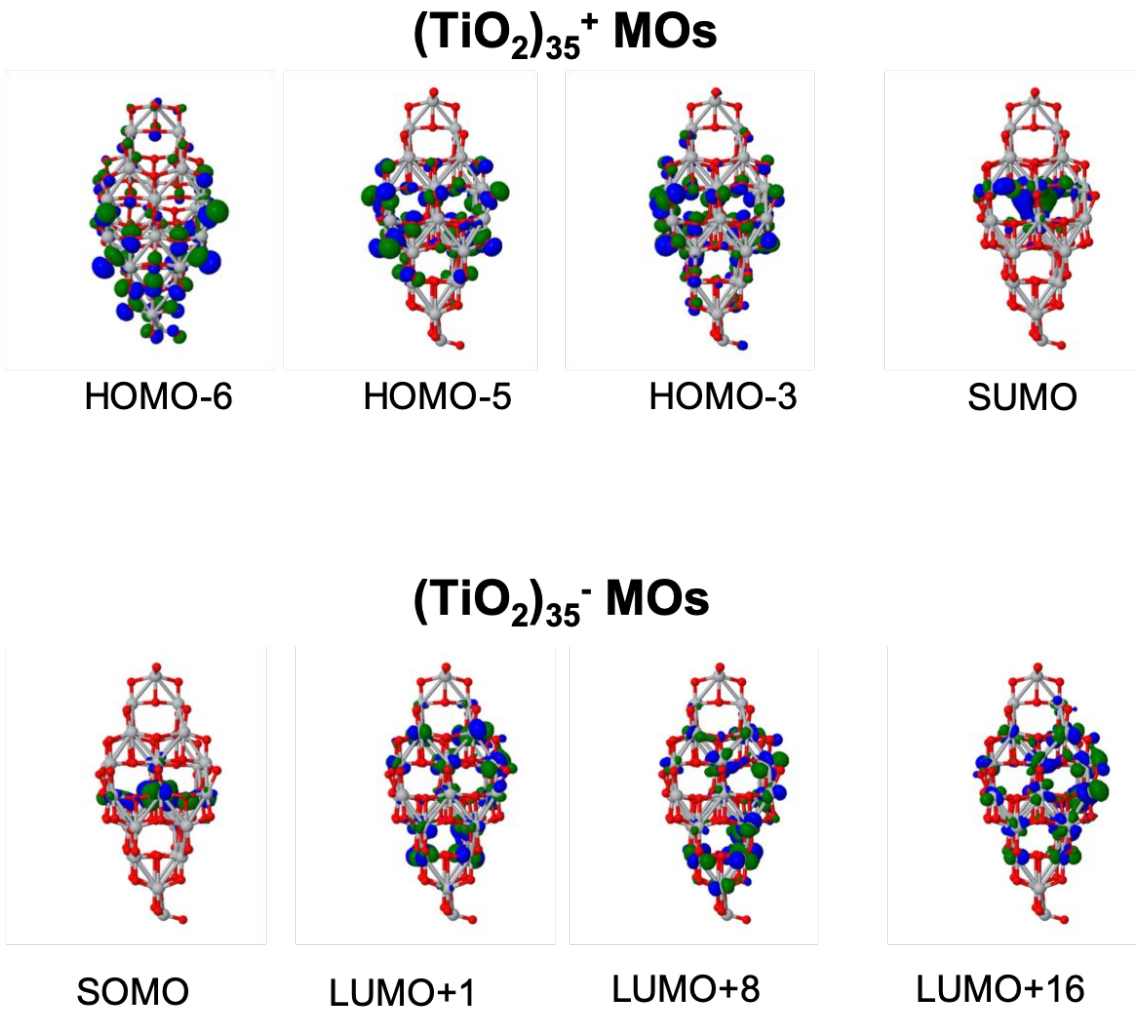

Figure S3. MOs of the negatively and positively charged $(TiO_2)_{29}$ NP involved in the electronic excitations listed in Tables S3 and S4. Green and blue isosurfaces correspond to positive and negative sign of the electron density, respectively.

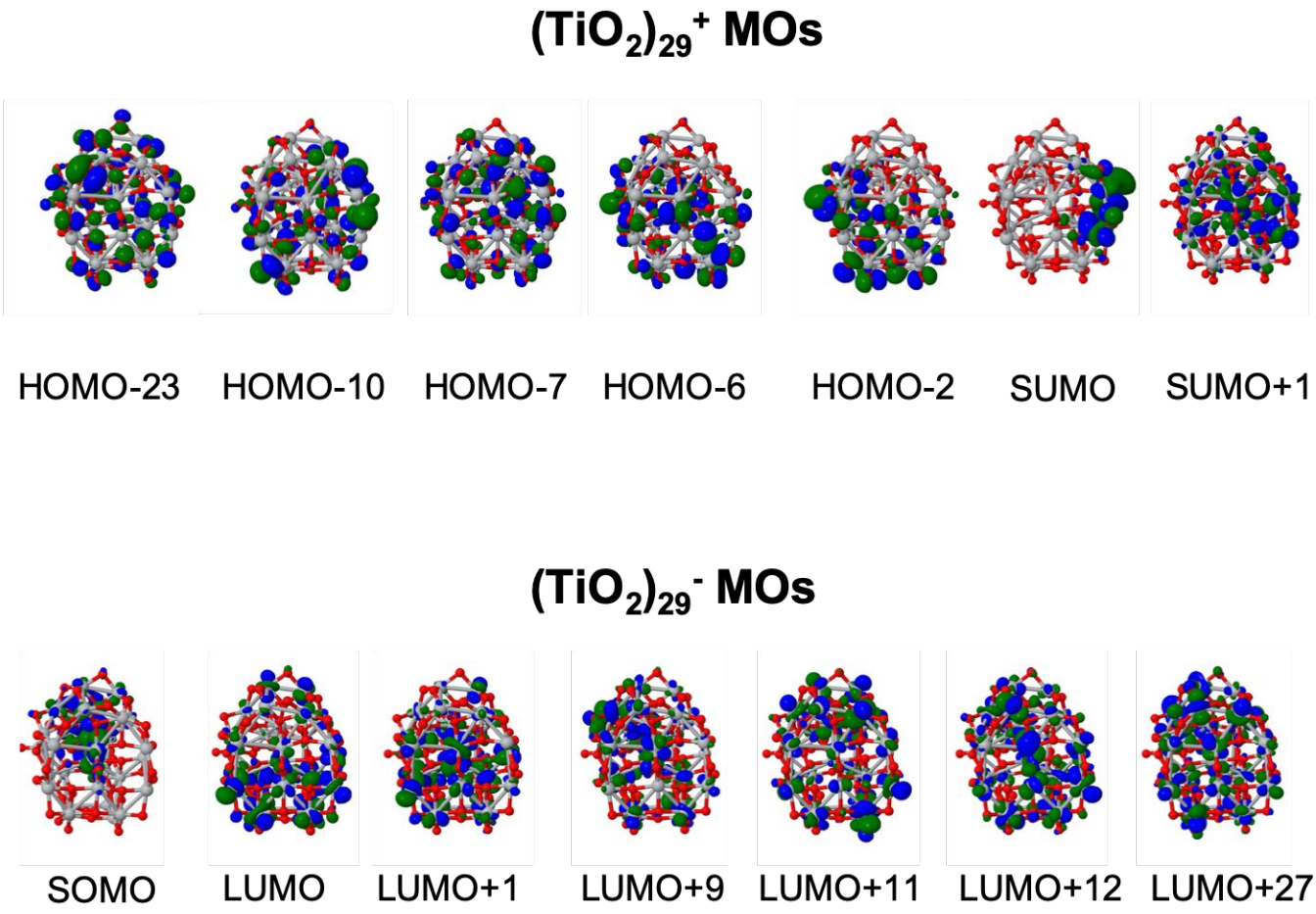

Figure S4. MOs of the negatively and positively charged $(TiO_2)_{43}$ NP involved in the electronic excitations listed in Tables S3 and S4 Green and blue isosurfaces correspond to positive and negative sign of the electron density, respectively.