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Single oxygen vacancies of $(TiO_2)_{35}$ as a prototype of reduced nanoparticle: Implication to photocatalytic activity

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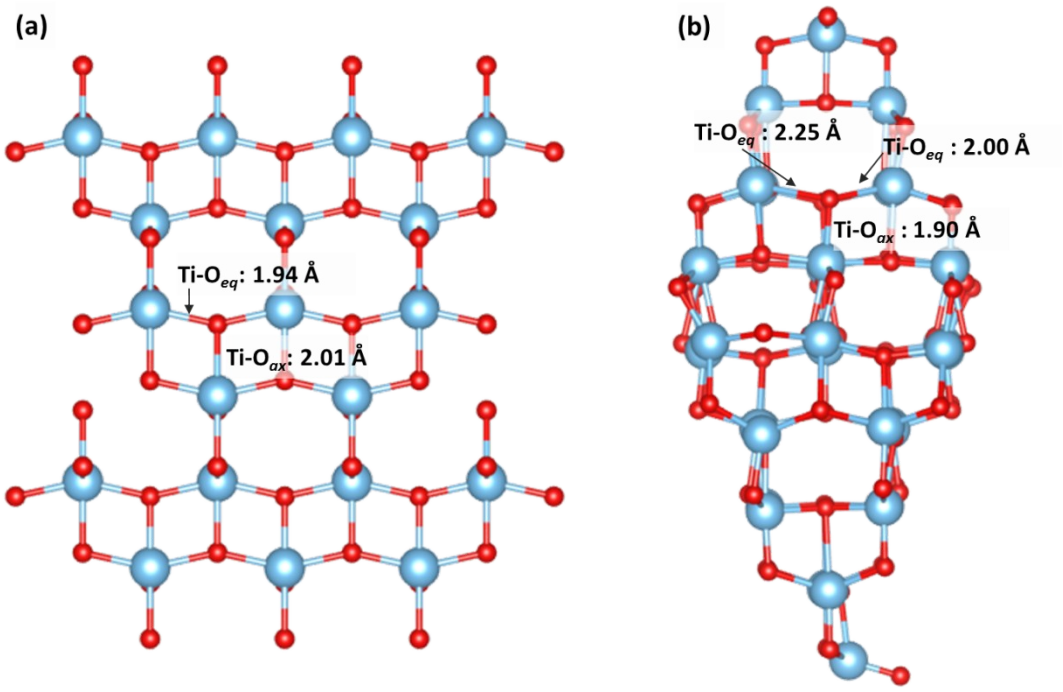
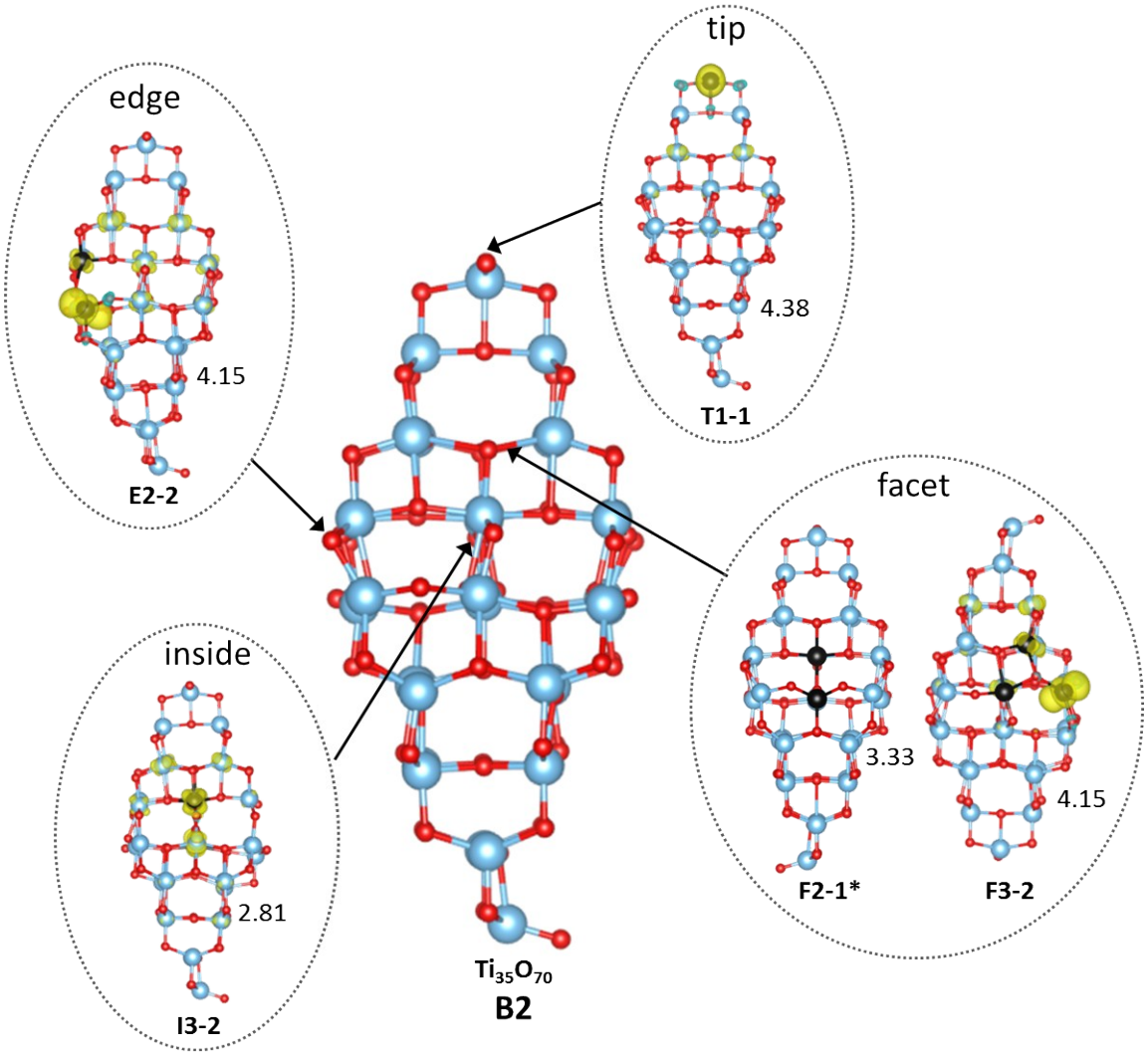


Fig. S1 Structures of TiO_2 anatase bulk and NP are presented. Ti-O lengths in bulk are from the previous paper.[7, 27]

Table S1 Calculated band gap energy (E_g), O_{vac} defect state from conduction band minimum (CBM) and oxygen vacancy formation energy (E_f^O) in bulk anatase TiO_2 (in eV) are given. Results are summarized according to the ratio of HF exchange from the previous studies.

Functional (%Fock)	E_g	O_{vac} defect state from CBM	E_f^O
PBE (0)[34]	2.14	0.10	3.68
PBEx (12.5)[34]	3.22	0.41 ~ 0.64	4.21 ~ 4.65
B3LYP (20)[28]	3.92	0.59	4.78
HSE (20)[66]	3.37	0.54	4.78
HSE06 (25)[39]	3.6	1.3	4.81*

* Calculated under extreme O-rich conditions.



*At F2-1 site, closed-shell singlet state was more stable than open-shell triplet one.

Fig. S2 Calculated structure of B2 and five representative structures for single oxygen vacant $Ti_{35}O_{69}$ NP (**D**) at various O_v sites. Yellow color shows the spin density in isosurface of 0.025 $e \cdot au^{-3}$. Blue, red, and black spheres denote titanium, oxygen and first neighbored titanium atoms to the O_v site, respectively. E_f^O is in eV. All structures and values are calculated in PBE functional.

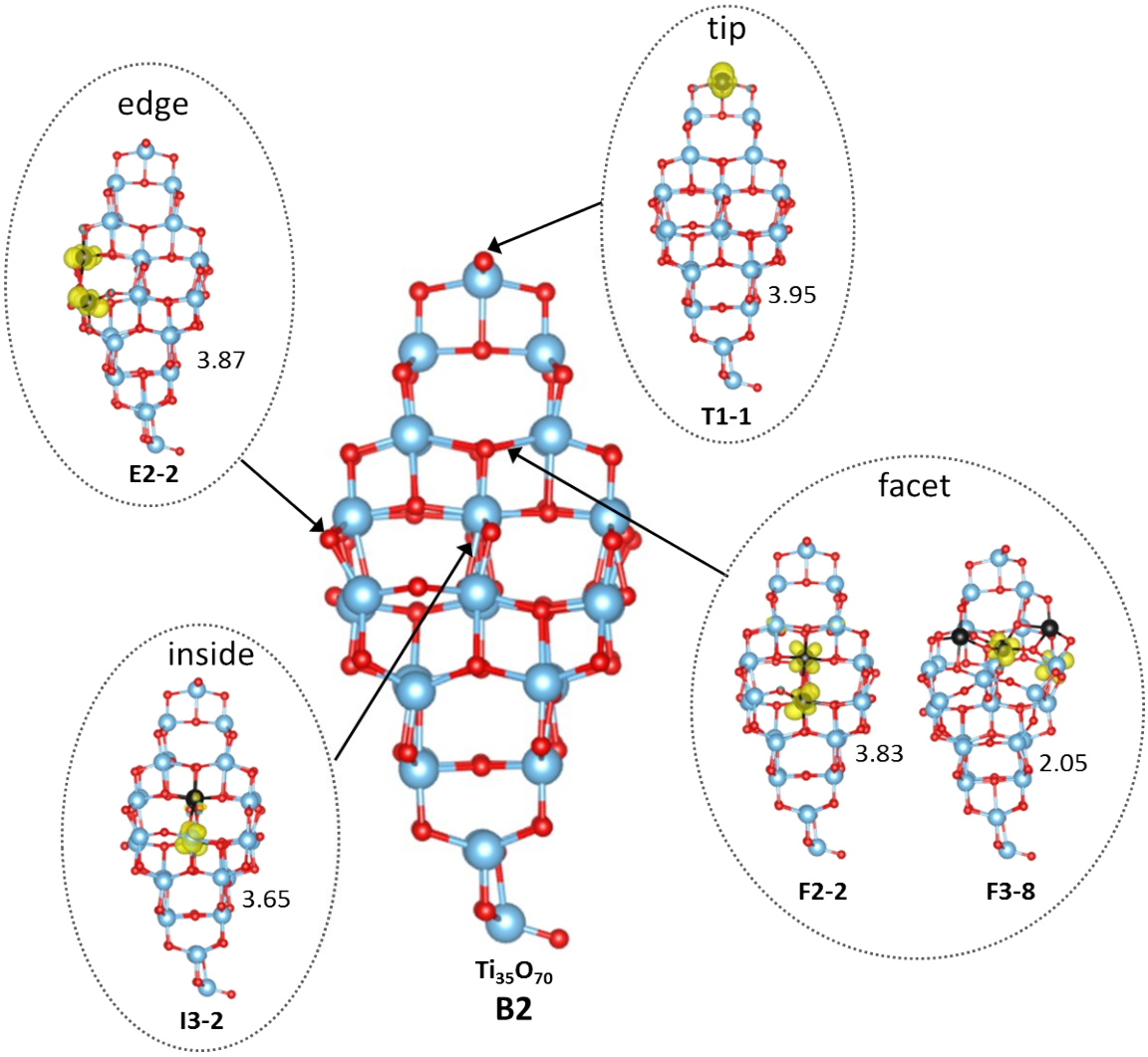


Fig. S3 Calculated structure of B2 and five representative structures for single oxygen vacant $Ti_{35}O_{69}$ NP (**D**) at various O_v sites. Yellow color shows the spin density in isosurface of 0.05 e·au^{-3}. E_f^O is in eV. All structures and values are calculated in PBE0 functional.

Table S2 The values (in eV) of vertical energy (E_v), relaxation energy (E_{rel}), oxygen vacancy formation energy (E_f^O), and energy level of oxygen vacancy defect state below LUMO (S_v**-1** and S_v**-2**) calculated using PBE and PBE0 functionals are given. All values are lined up in order of vacant oxygen atom distance from center of mass within each classification to compare functional effect at the same site. In each classification, the lowest E_f^O value words in bold type.

position	CN[a]	site[b]	PBE					PBE0				
			E_v	E_{rel}	E_f^O	S_v-1	S_v-2	E_v	E_{rel}	E_f^O	S_v-1	S_v-2
tip	1	T1-1	4.74	0.36	**4.38**	0.01	0.62	4.23	0.29	**3.95**	1.60	2.08
edge	2	E2-1	5.89	1.53	4.36	0.09	0.51	5.72	1.52	4.20	2.40	3.08
		E2-2	5.92	1.78	**4.15**	0.07	0.61	5.87	1.99	**3.87**	2.54	3.16
		E2-3	5.97	1.71	4.26	0.08	0.56	5.81	1.31	4.50	2.26	3.21
		E2-4	5.71	1.49	4.22	0.12	0.19	5.73	1.62	4.10	2.47	2.77
		E2-5	5.96	1.52	4.45	0.34		6.23	1.68	4.56	2.20	3.01
		E2-6	5.94	1.36	4.58	0.09	0.64	5.67	1.63	4.04	2.40	2.88
		E2-7	5.88	1.44	4.44	0.13		5.90	0.94	4.96	1.42	2.95
facet	2	F2-1	5.40	2.07	**3.33**	0.08		5.30	1.36	3.93	1.92	2.62
		F2-2	5.21	1.84	3.37	0.08		5.11	1.28	**3.83**	1.91	2.66
		F2-3	5.87	1.52	4.34	0.10	0.51	5.99	1.79	4.20	2.44	3.11
	3	F3-1	5.80	1.54	4.26	0.08	0.56	5.94	1.75	4.19	2.25	3.32
		F3-2	6.07	1.93	**4.15**	0.07	0.61	6.07	1.86	4.21	2.39	3.12
		F3-3	5.89	1.56	4.33	0.13	0.50	6.06	1.71	4.35	2.36	3.06
		F3-4	6.07	1.86	4.22	0.12	0.19	6.26	2.33	3.93	2.48	2.95
		F3-5	5.93	1.42	4.51	0.07		7.08	2.50	4.57	2.56	2.65
		F3-6	6.18	1.66	4.52	0.07	0.35	6.47	2.25	4.22	2.44	3.13
		F3-7	5.79	0.67	5.12	0.13		6.78	1.93	4.85	2.68	2.85
		F3-8	6.35	1.63	4.72	0.12	0.17	6.63	4.58	**2.05**	2.48	2.58
		F3-9	5.06	0.67	4.39	0.83		6.33	1.98	4.35	2.80	3.24
		F3-10	5.54	0.82	4.73	0.73		5.72	0.87	4.85	2.66	
inside	3	I3-1	5.95	1.83	4.13	0.07	0.48	5.57	1.14	4.42	2.55	
		I3-2	5.59	2.77	**2.81**	0.04	0.11	5.92	2.27	**3.65**	2.35	2.56
		I3-3	5.90	3.05	2.85	0.03	0.11	6.18	2.40	3.79	1.94	2.83
		I3-4	5.88	1.75	4.13	0.09	0.75	5.55	1.17	4.38	2.47	

[a] **CN** is number of first neighboring titanium atoms to removed oxygen atom.

[b] **site** is designated as combination of position, CN, and the order of vacant oxygen atom distant from center of mass.

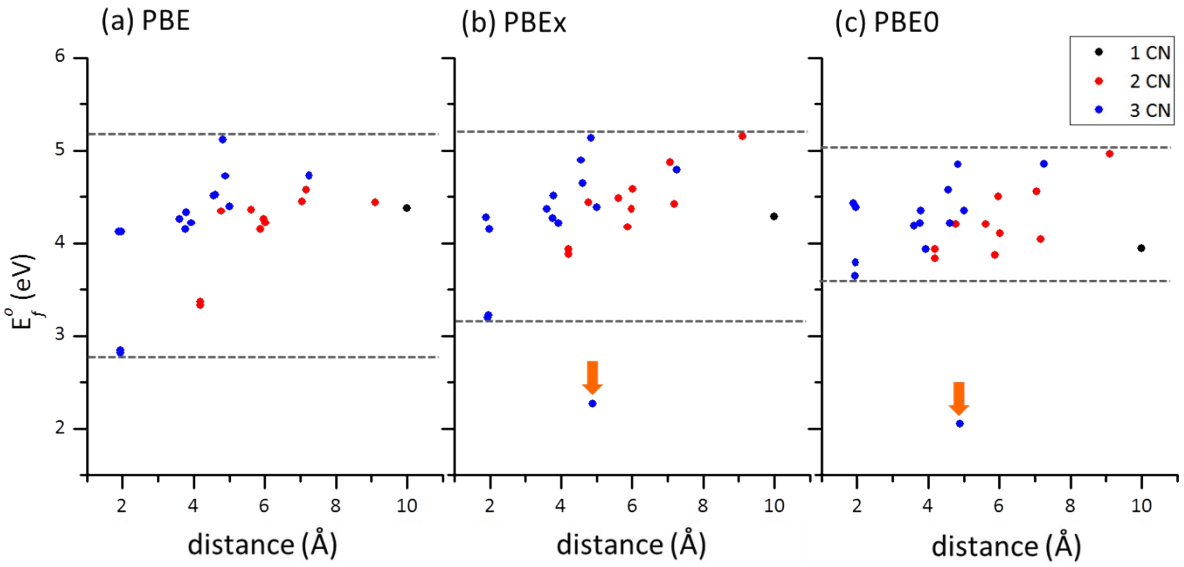
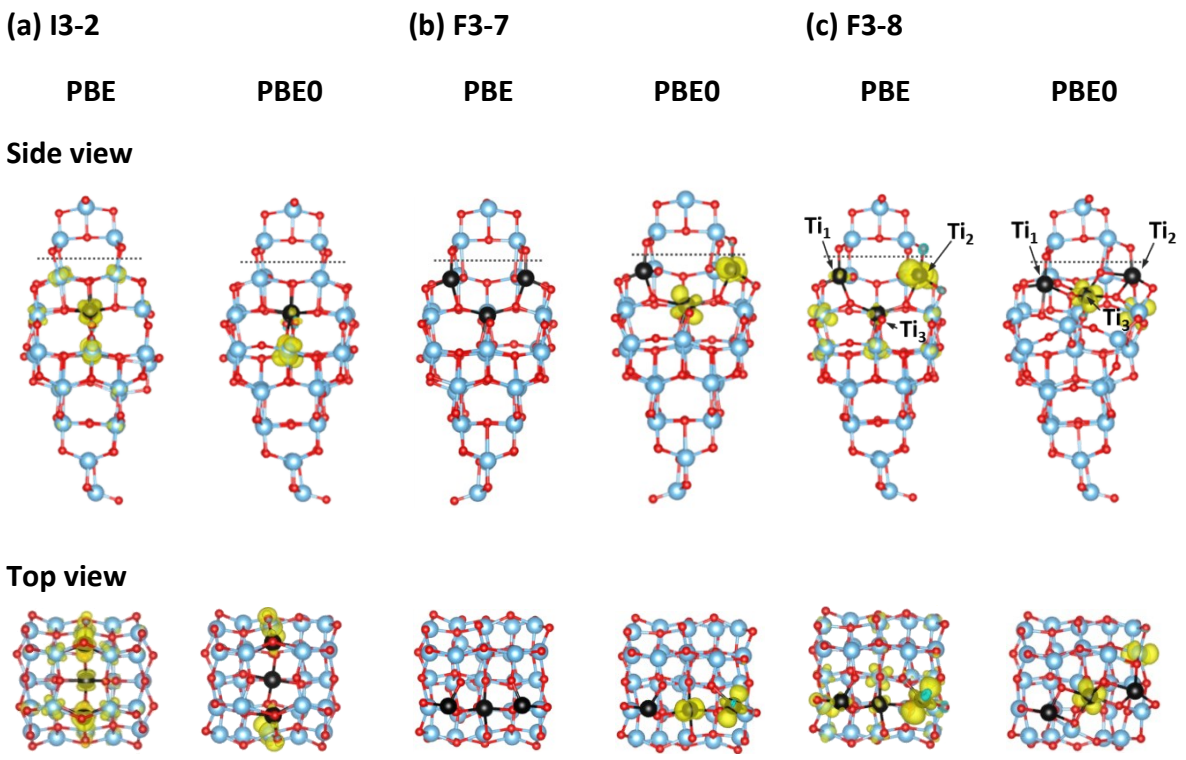


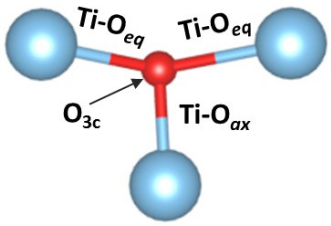
Fig. S4 E_f^O against vacant oxygen atom distance from center of mass is calculated using (a) PBE, (b) PBEx, and (c) PBE0. Dotted lines are marked at highest and lowest E_f^O in each graph, except particularly low points (F3-8 site) indicated by orange arrow.



*At F3-7 site in PBE result, closed-shell singlet state was more stable than open-shell triplet one.

Fig. S5 Calculated structures of $Ti_{35}O_{69}$ NP that oxygen removed at three O_{3c} sites that Ti-O_{ax} is shorter than two Ti-O_{eq} are presented depending on functionals. Isosurface of spin density are 0.025 in PBE and 0.05 e·au^{-3} in PBE0. For clarity, atoms above the dotted line were removed in top view structures.

Table S3 Interatomic distances (in Å) in optimized pristine TiO_2 NP are listed according to type of O_{3c} site that Ti-O_{ax} is shorter than two TiO_{eq} and DFT functional.



site	functional	Ti-O_{ax}	Ti-O_{eq}	Ti-O_{eq}
	PBE	1.955	2.036	2.043
I3-2	PBEx	1.941	2.020	2.027
	PBE0	1.930	2.005	2.013
	PBE	1.945	1.986	2.143
F3-7	PBEx	1.935	1.976	2.122
	PBE0	1.927	1.971	2.100
	PBE	1.906	2.009	2.276
F3-8	PBEx	1.896	1.999	2.251
	PBE0	1.894	1.994	2.206

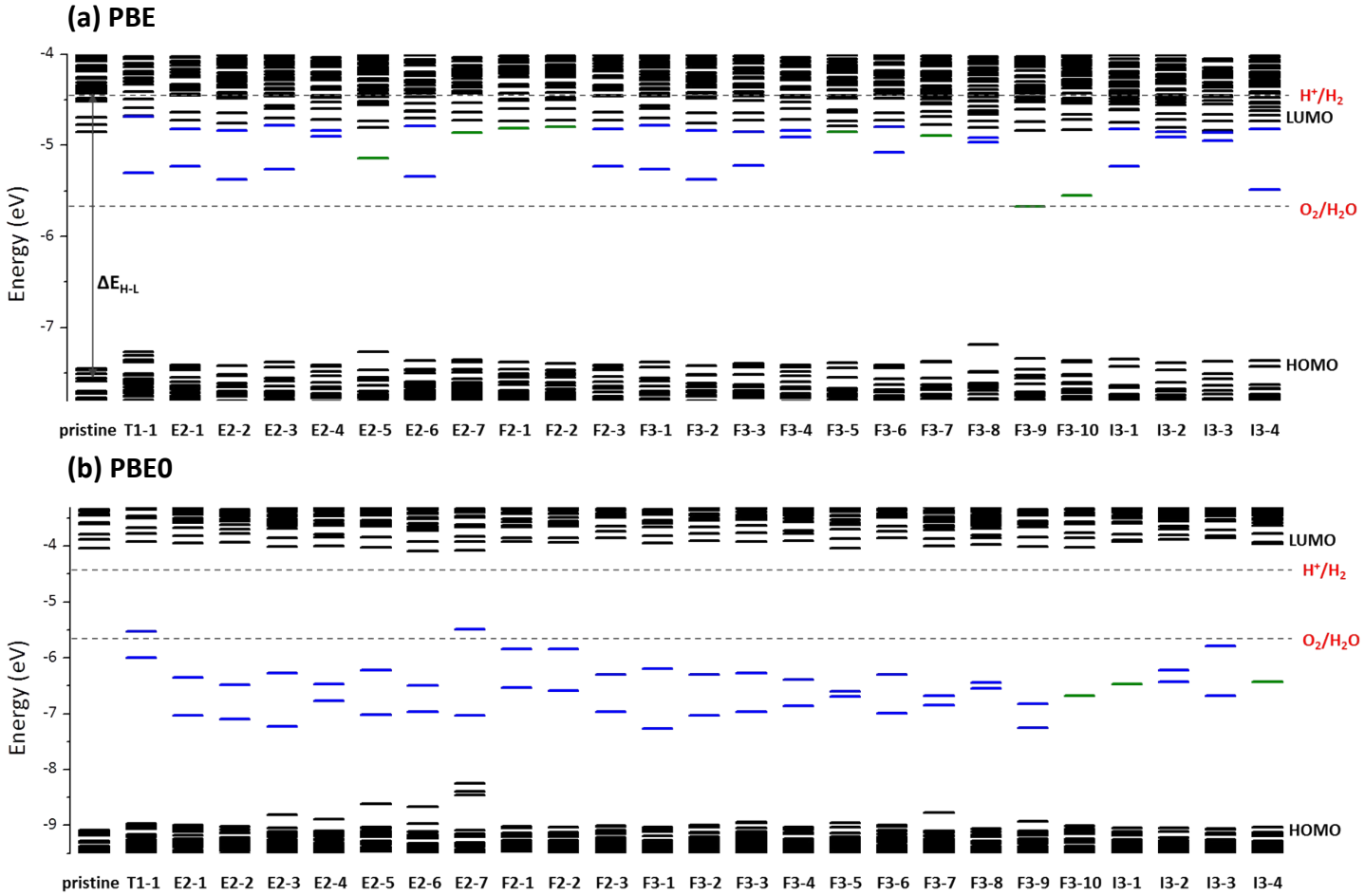


Fig. S6 Molecular orbitals energy level diagrams of $Ti_{35}O_{69}$ NP are given depending on functionals. The triplet state energy level is up spin eigenvalues. The dotted lines indicate the standard redox potentials for water splitting at pH = 0. The singly and doubly occupied defect states are denoted in blue and green, respectively. Other occupied and unoccupied molecular orbitals are shown in black.