Electronic Structures of Hydroxyled Low Index Surfaces of Rutile and Anatase-Type Titanium Dioxide

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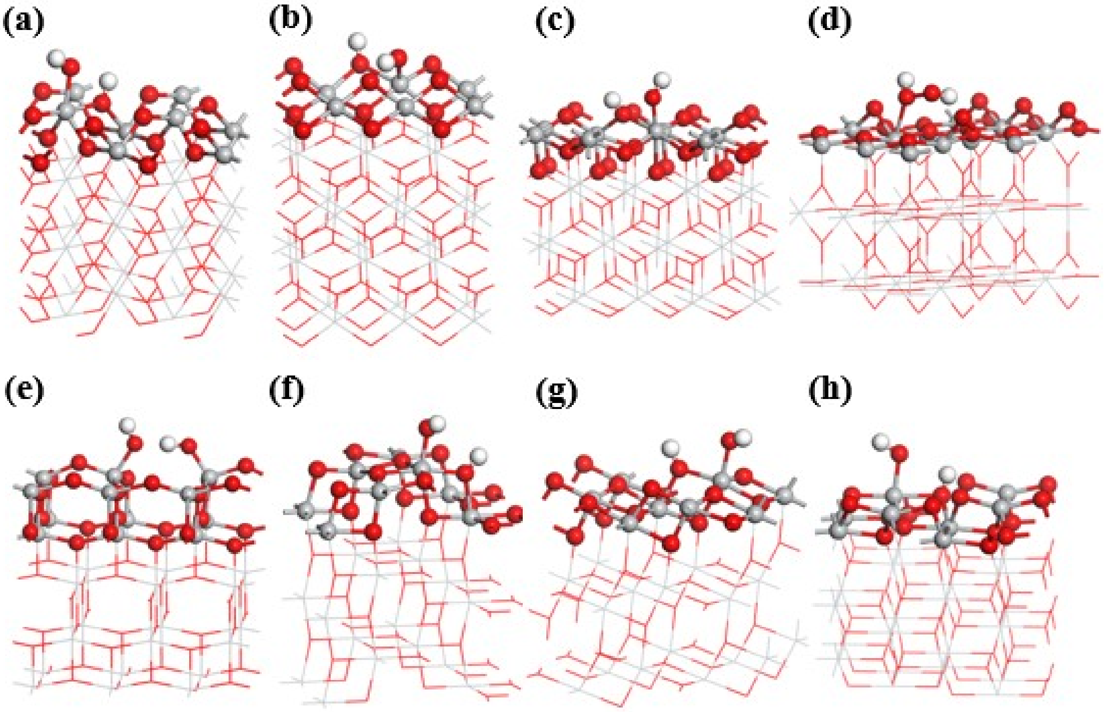

Fig. S1. Optimized structure of the OH1-type hydroxylated (001), (100), (101), and (110) surfaces of rutile (a, R-001-OH1; b, R-100-OH1; c, R-101-OH1; d, R-110-OH1) and anatase (e, A-001-OH1; f, A-100-OH1; g, A-101-OH1; h, A-110-OH1). The gray, red, and white balls represent titanium, oxygen, and hydrogen atoms, respectively.

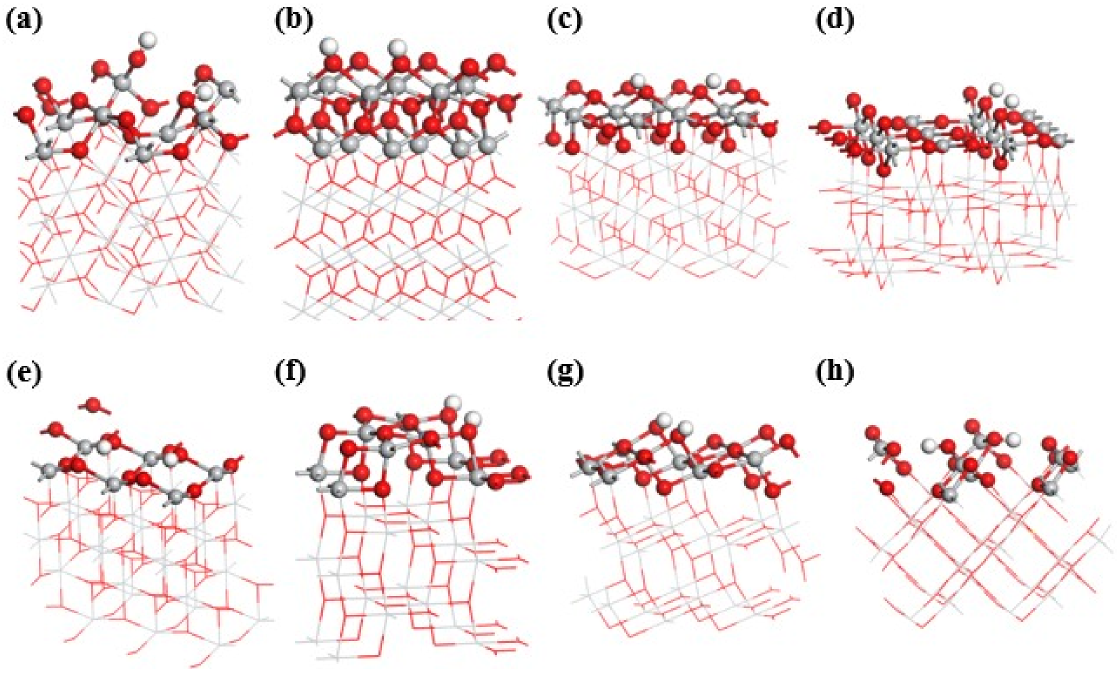

Fig. S2. Optimized structure of the OH2-type hydroxylated (001), (100), (101), and (110) surfaces of rutile (a, R-001-OH2; b, R-100-OH2; c, R-101-OH2; d, R-110-OH2) and anatase (e, A-001-OH2; f, A-100-OH2; g, A-101-OH2; h, A-110-OH2). The gray, red, and white balls represent titanium, oxygen, and hydrogen atoms, respectively.

Surface energy calculation

Surface energy is used to assess the stability of surfaces and is defined as follows:

$$\gamma_s = \frac{1}{2A}\left(E_s^{unrelax} - NE_b\right) + \frac{1}{A}\left(E_s^{relax} - E_s^{unrelax}\right) \tag{S1}$$

A is the considered surface area, E_s^{relax} and $E_s^{unrelax}$ are the relaxed energies and the unrelaxed surface, respectively. N is the number of TiO_2 units in the structure, and E_b is the energy of each TiO_2 unit. The calculated surface energies are listed in Table S1.

Table S1: Surface energies of eight TiO_2 rutile and anatase surfaces.

Structure	$E_{unrelax}$/eV	E_{relax}/eV	A/Å2	NEb/eV	γ_s/J·m^{-2}
R-001	-576.289	-578.961	9.238×9.238	28 ×(-21.378)	1.591
R-100	-628.547	-630.654	9.238×8.965	30 ×(-21.378)	0.830
R-101	-665.724	-667.635	9.238×11.003	32 ×(-21.378)	1.147
R-110	-751.182	-754.540	8.966×13.064	36 ×(-21.378)	0.801
A-001	-627.191	-628.061	7.668×11.502	30 ×(-21.308)	0.936
A-100	-498.735	-501.991	7.668×9.473	24 ×(-21.308)	0.678
A-101	-500.954	-503.350	7.668×10.220	24 ×(-21.308)	0.532
A-110	-572.156	-575.834	9.473×10.844	28 ×(-21.308)	1.330

Formation energy calculation

Formation energy was used to evaluate the stability of the surface hydroxyl groups, which is defined as:

$$E_f = E_T - E_{OH} - E_S \qquad (S2)$$

E_{OH} is the energy of water or hydrogen that is dissociated when hydroxyl groups are formed on the surface of TiO_2, E_S is the energy of pure TiO_2 surface, and E_T is the total energy of hydroxyl-containing TiO_2 surface.

Table S2: Formation energy and detailed data during formation energy calculation (all in eV).

Structure	E_T	E_S	E_{OH}	E_f
A-001-OH1	-643.633	-625.862	-11.015	-6.756
A-100-OH1	-517.201	-500.737	-8.845	-7.619
A-101-OH1	-518.351	-502.202	-8.752	-7.397
A-110-OH1	-591.495	-575.019	-8.729	-7.747
R-001-OH1	-594.617	-578.252	-8.733	-7.632
R-100-OH1	-645.610	-629.225	-8.753	-7.632
R-101-OH1	-682.812	-666.405	-8.839	-7.568
R-110-OH1	-766.223	-750.654	-9.694	-5.875
A-001-OH2	-635.990	-626.438	-2.233	-7.319
A-100-OH2	-510.006	-500.168	-2.234	-7.604
A-101-OH2	-511.031	-501.485	-2.234	-7.312
A-110-OH2	-584.950	-574.161	-2.233	-8.556
R-001-OH2	-586.672	-575.896	-2.233	-8.543
R-100-OH2	-638.404	-628.379	-2.218	-7.807
R-101-OH2	-675.955	-665.860	-2.233	-7.862
R-110-OH2	-763.740	-752.442	-2.217	-9.081

The data of formation energy show that the hydroxyl group is stable on the surface of TiO2, and the formation energy is mostly around -7.0~-8.0 eV. The most stable hydroxyl TiO2 surface is R-110-OH2 with a formation energy of -9.081, and the less stable A-001-OH1 and R-110-OH1, which are consistent with the results of structural optimization. Considering the effect of surface hydroxyl zero-point energy on stability, we proceeded to analyze the Gibbs free energy of the hydroxylated surface reverting to pure surface.

Free energy calculation for H_2O/H_2 dissociate from TiO_2 surface

To assess the stability of the surface hydroxyl group at room temperature (T=298.15K), the Gibbs free energy variation of the hydroxyl group dissociating from the surface was calculated. The dissociation of hydroxyl from the surface is as follows:

$$Ti_xO_{2x-1}\text{—}2OH \rightleftharpoons Ti_xO_{2x} + 2H_2O$$

$$Ti_xO_{2x-2}\text{—}2OH \rightleftharpoons Ti_xO_{2x} + 2H_2$$

$\Delta G = \Delta E + \Delta ZPE - T\Delta S$ is calculated as follows: ΔE is reaction energy and ΔZPE is the difference in zero-point energies that we get from density functional theory (DFT). ΔS is the change in entropy, which we get from Computational Chemistry Comparison and Benchmark DataBase (CCCBDB)[1]. No correction was applied to the surface entropy, so the stability of hydroxyl groups would be underestimated [2].

Table S3: Pure surface, water and hydrogen energy calculated by DFT; ZPE and TS for water and hydrogen.

Structure	E (eV)	ZPE (eV)	TS (eV)
H_2O	-14.226	0.566	0.586
H_2	-6.759	0.267	0.406
A-001	-628.060	---	---
A-100	-501.991	---	---
A-101	-503.350	---	---
A-110	-575.834	---	---
R-001	-578.907	---	---
R-100	-630.654	---	---
R-101	-667.635	---	---
R-110	-754.540	---	---

Table S4: Total energy and ZPE of the hydroxylated surface by DFT; Gibbs free energy change of hydroxylated surface dissociation water or hydrogen.

Structure	E (eV)	ZPE (eV)	ΔG (eV)
A-001-OH1	-643.633	0.693	0.634
A-100-OH1	-517.201	0.714	0.249
A-101-OH1	-518.351	0.708	0.046
A-110-OH1	-591.495	0.725	0.688
R-001-OH1	-594.617	0.721	0.743
R-100-OH1	-645.610	0.729	-0.020
R-101-OH1	-682.812	0.728	0.202
R-110-OH1	-766.223	0.761	-3.324
A-001-OH2	-635.990	0.759	0.273
A-100-OH2	-510.006	0.749	0.368
A-101-OH2	-511.031	0.754	0.029
A-110-OH2	-584.950	0.751	1.466
R-001-OH2	-586.672	0.689	0.177
R-100-OH2	-638.404	0.728	0.123
R-101-OH2	-675.955	0.744	0.677
R-110-OH2	-763.740	0.736	1.565

Table S5: Band gap values and their corresponding frequencies on the hydroxy R-101, R-001, A-110, A-100 and A-001 surfaces. Values in parentheses and brackets were calculated using the GGA-PBESol+U and HSE06 methods, respectively.

Structure	Band gap/eV	Frequency/cm^{-1}	Structure	Band gap/eV	Frequency/ cm^{-1}
R-101	1.608	12968.353	A-110	1.830	14758.760
R-101-OH1	1.631	13153.845	A-110-OH1	1.831	14766.824
R-101-OH2	1.583	12766.730	A-110-OH2	1.865	15038.589
				(1.206)	(9727.837)
R-001	1.860	15000.706	A-100	1.730	13952.270
				[2.531]	[20413.848]
R-001-OH1	1.860	15000.706	A-100-OH1	1.723	13895.816
				[2.507]	[20217.871]
R-001-OH2	0.556	4484.082	A-100-OH2	0.320	2580.767
	(0.488)	(3939.700)		(0.242)	(1952.510)
				[1.650]	[13308.707]
---	---	---	A-001	1.600	12903.833
---	---	---	A-001-OH1	1.710	13790.972
---	---	---	A-001-OH2	1.414	11403.763

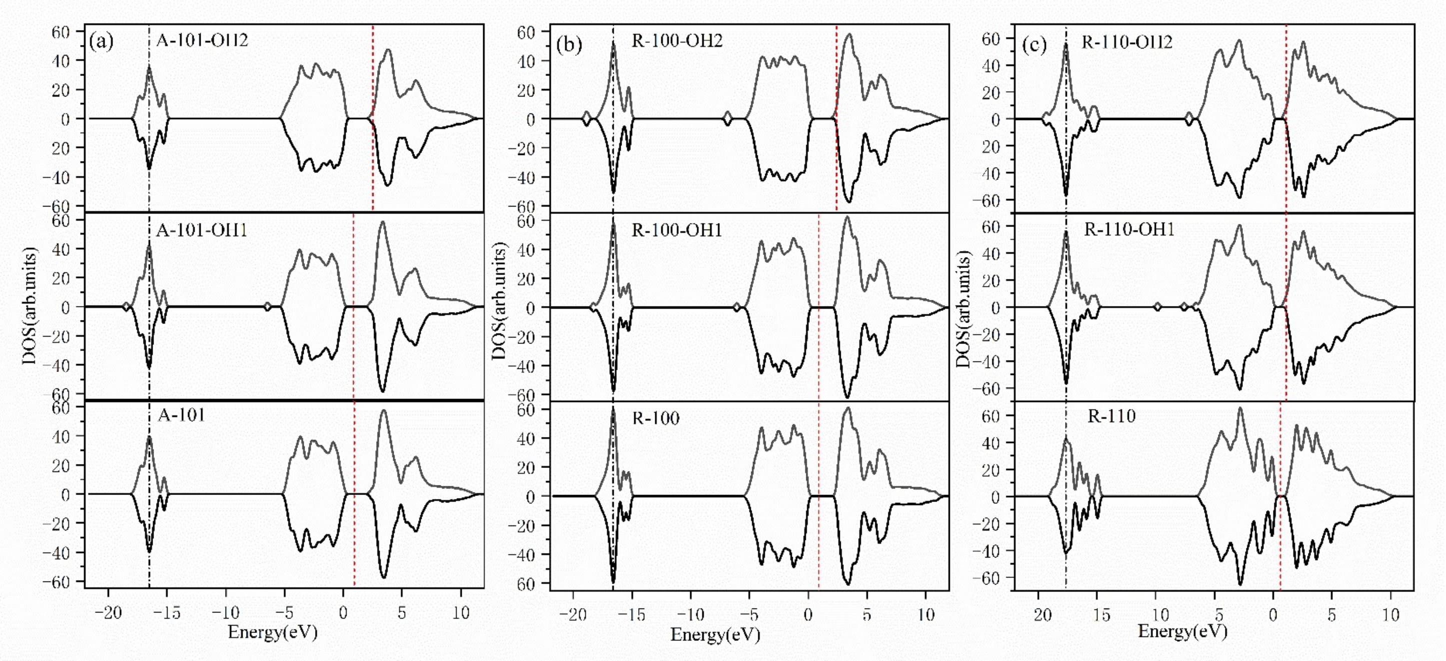

Fig. S3. TDOS of the A-101 (a bottom), R-100 (b bottom), and R-110 (c bottom) surfaces as well as their OH1- (middle of a-c) and OH2-type (top of a-c) hydroxylated surfaces. The energy of top of the valence band of the pure surface is set to zero. The black dotted line aligns the strongest low energy DOS peaks of OH1- and OH2- types hydroxylated surfaces with that of the pure surface. The red dotted line represents the Fermi level (E_F).

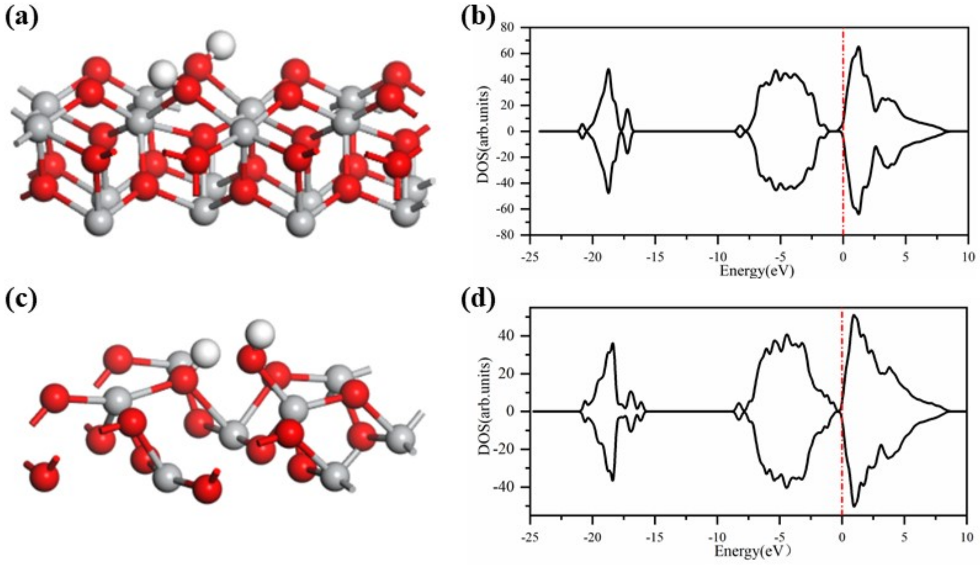

Fig. S4. Structure and TDOS of OH2-type hydroxylated TiO_2 surfaces with adjusted hydroxyl distances. a and e are the structures of R-101-OH2 and R-001-OH2, respectively; b and d are the corresponding TDOS, respectively.

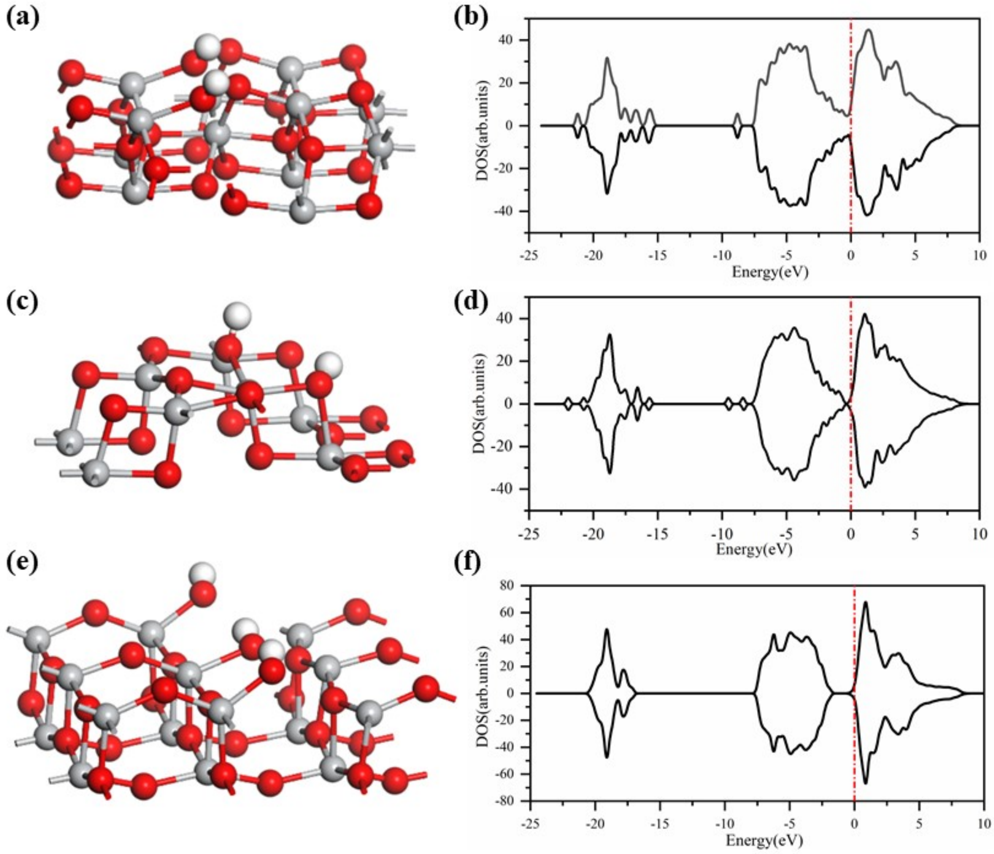

Fig. S5. Structure and TDOS of OH2-type hydroxylated TiO_2 surfaces with adjusted hydroxyl distances. a, c and e are the structures of A-110-OH2, A-100-OH2 and A-001-OH2, respectively; b, d and f are the corresponding TDOS, respectively.

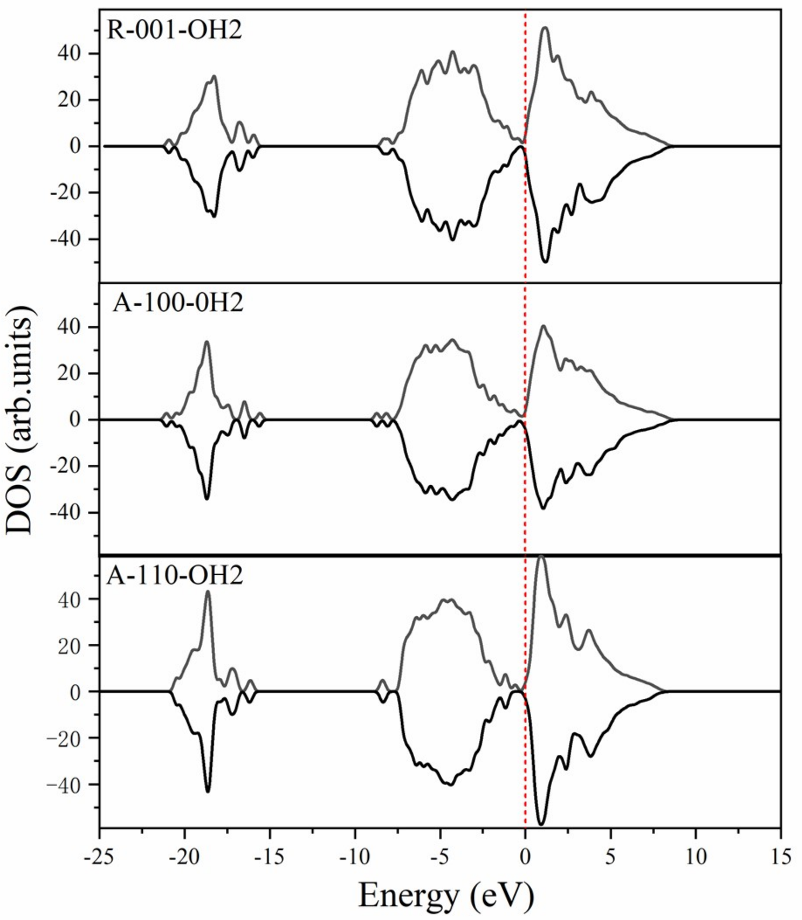

Fig. S6. TDOS of R-001-OH2, A-100-OH2, and A-110-OH2 surfaces obtained by GGA-PBESol+U method.

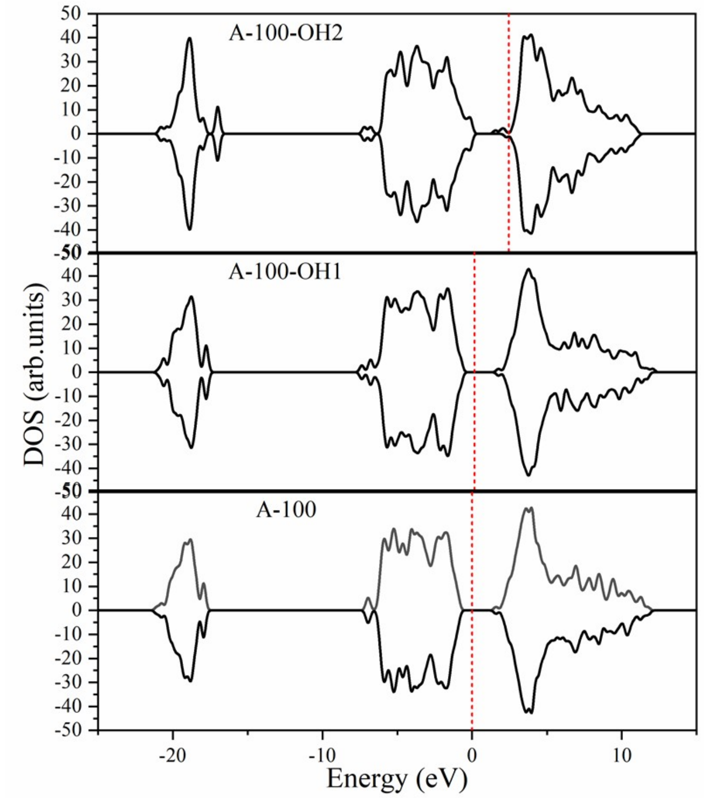

Fig. S7. TDOS of A-100, A-100-OH1, and A-100-OH2 surfaces obtained by HSE06 method.

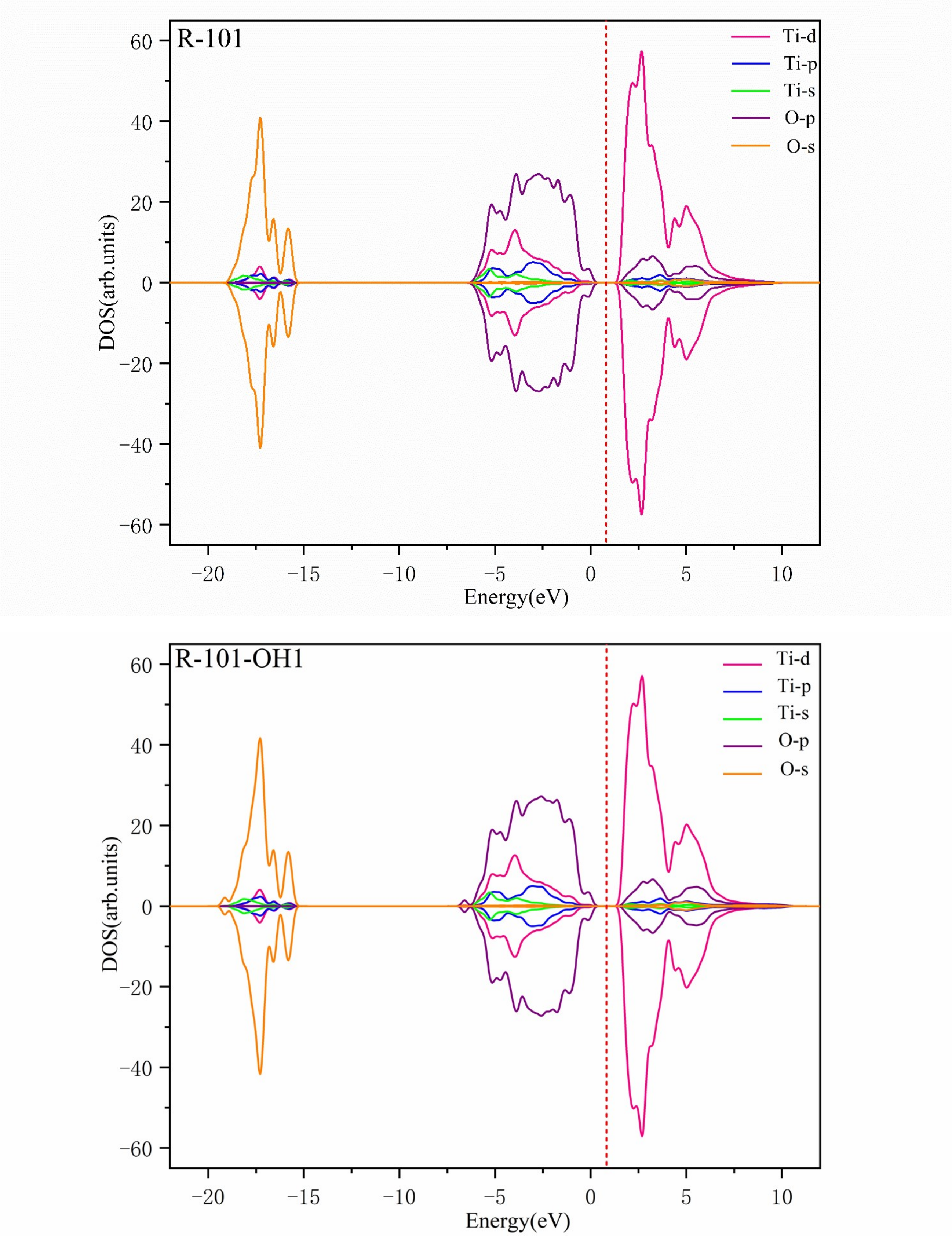

Fig. S8. Projected density of states (PDOS) of R-101 and R-101-OH1 surfaces.

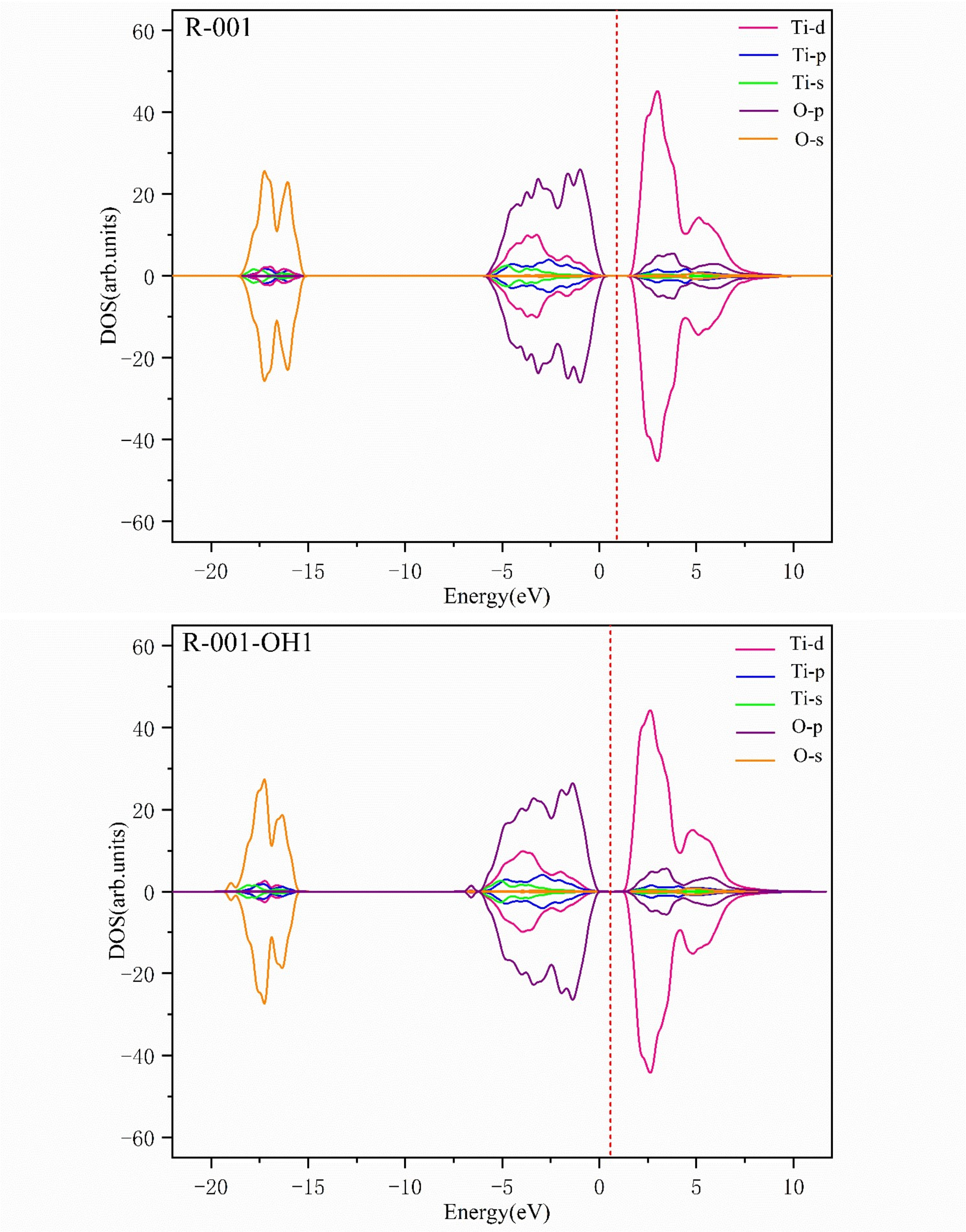

Fig. S9. Projected density of states (PDOS) of R-001 and R-001-OH1 surfaces.

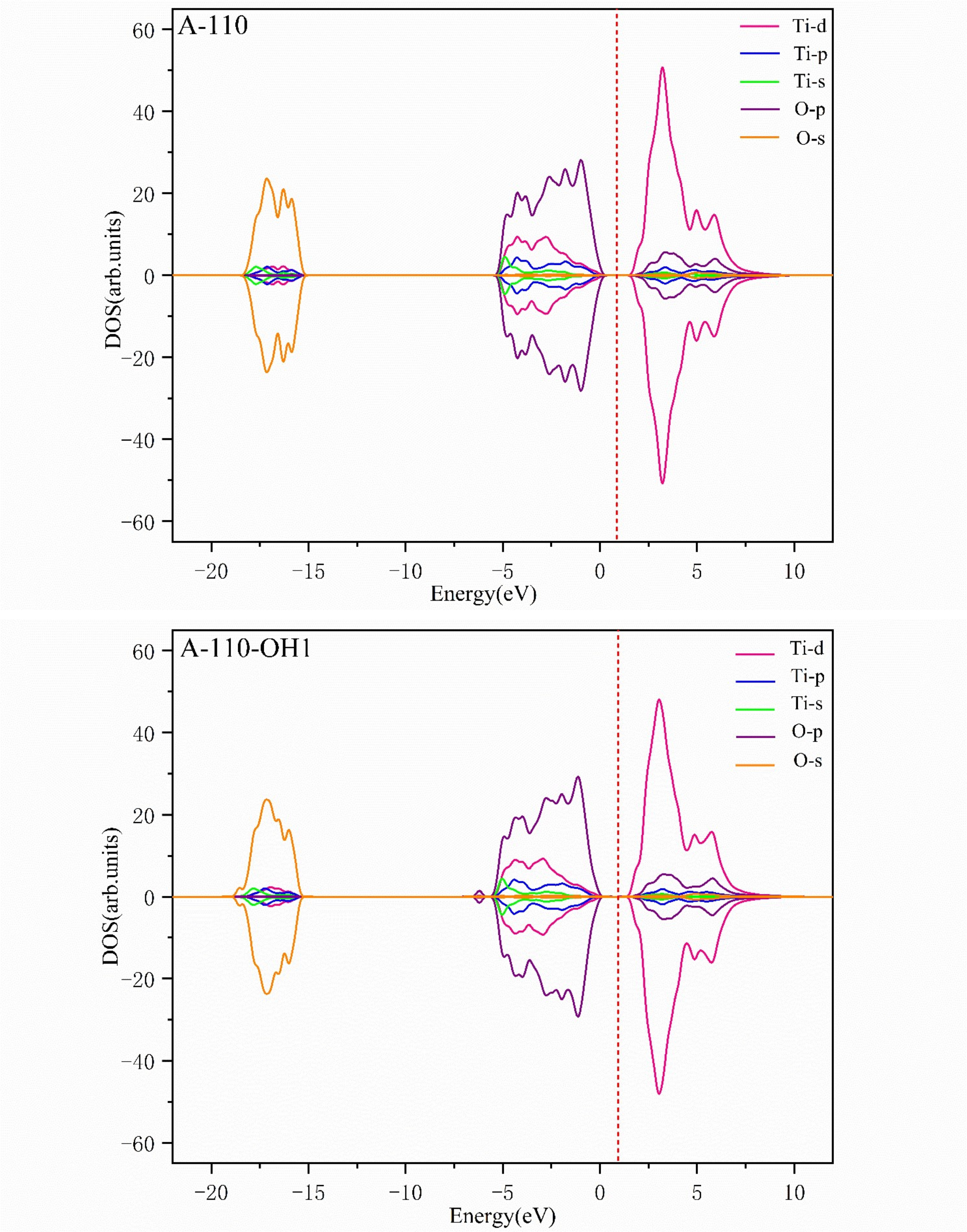

Fig. S10. Projected density of states (PDOS) of A-110 and A-110-OH1 surfaces.

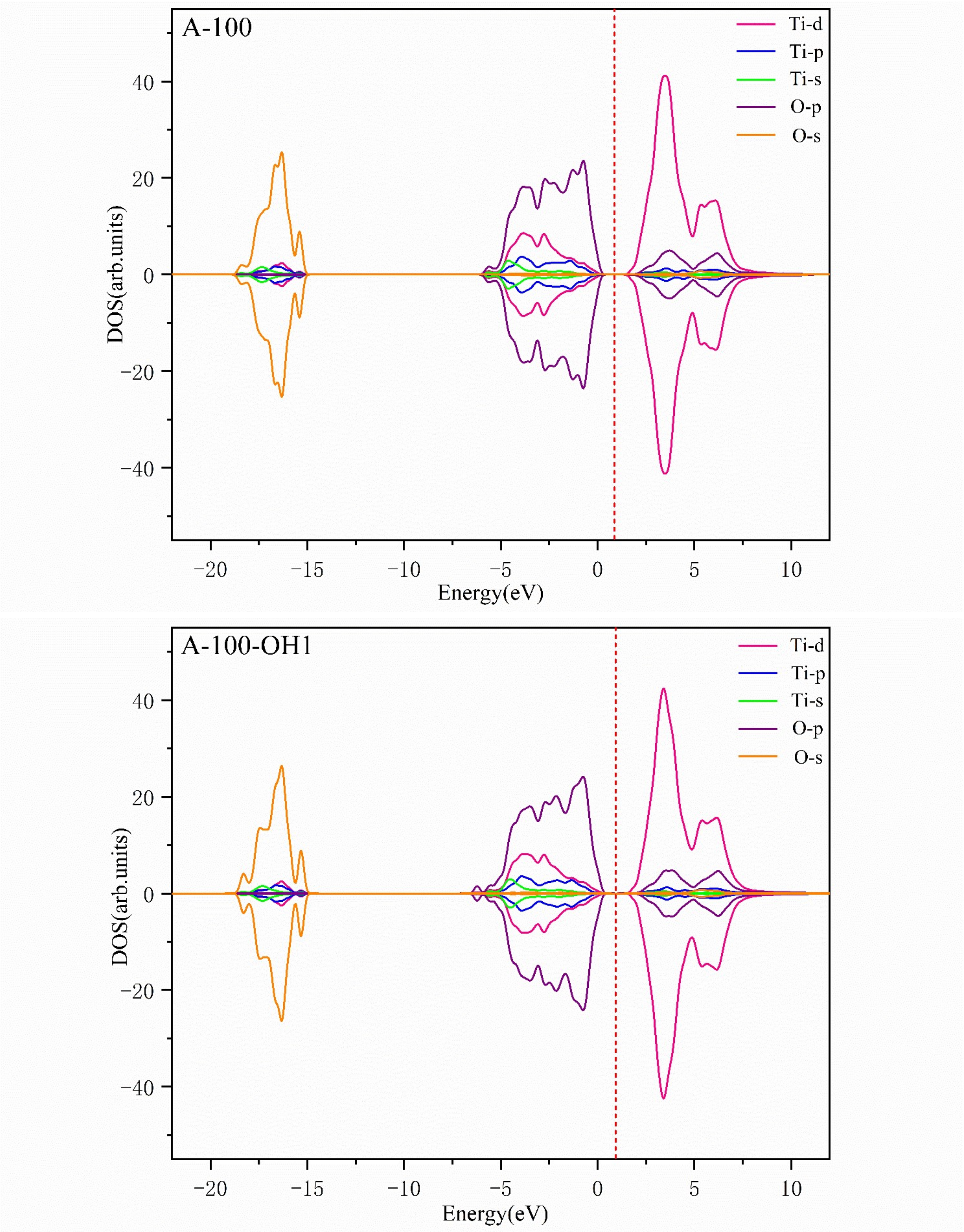

Fig. S11. Projected density of states (PDOS) of A-100 and A-100-OH1 surfaces.

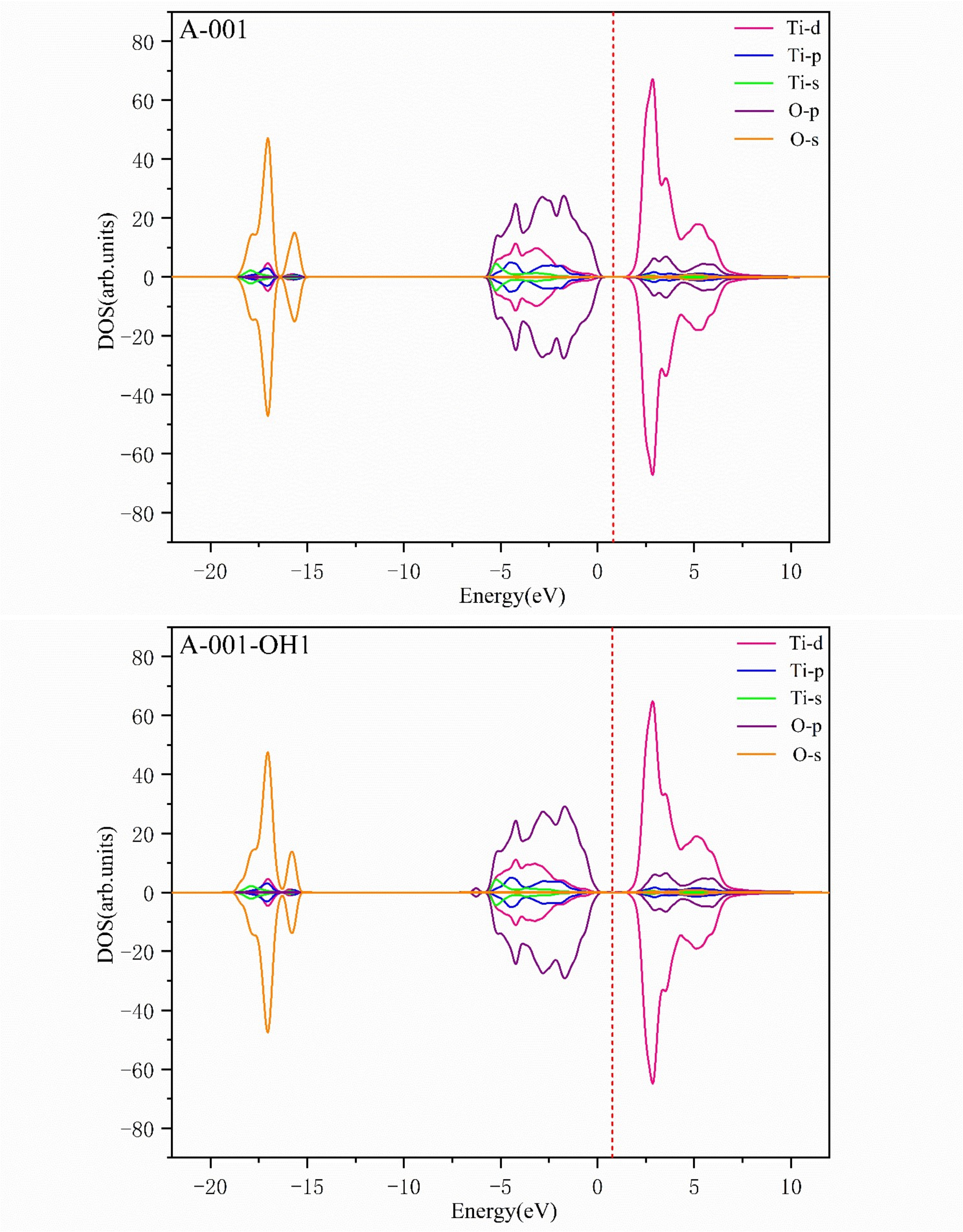

Fig. S12. Projected density of states (PDOS) of A-001 and A-001-OH1 surfaces.

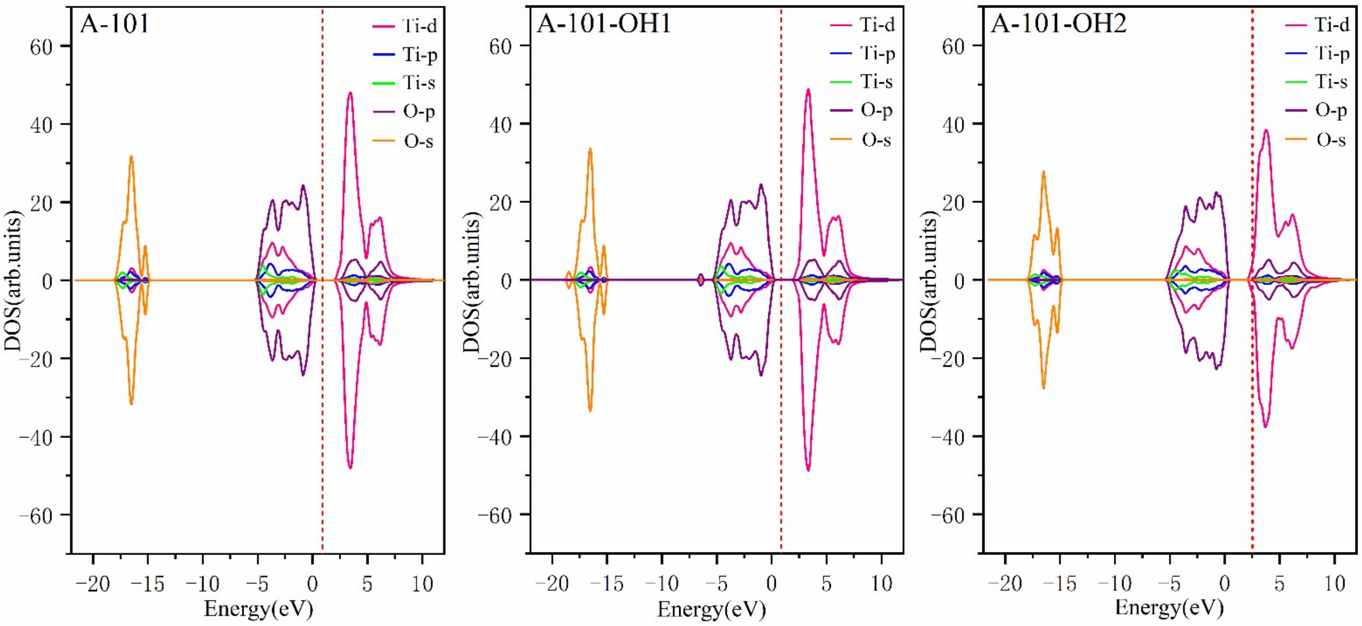

Fig. S13. Projected density of states (PDOS) of A-101, A-101-OH1, and A-101-OH2 surfaces.

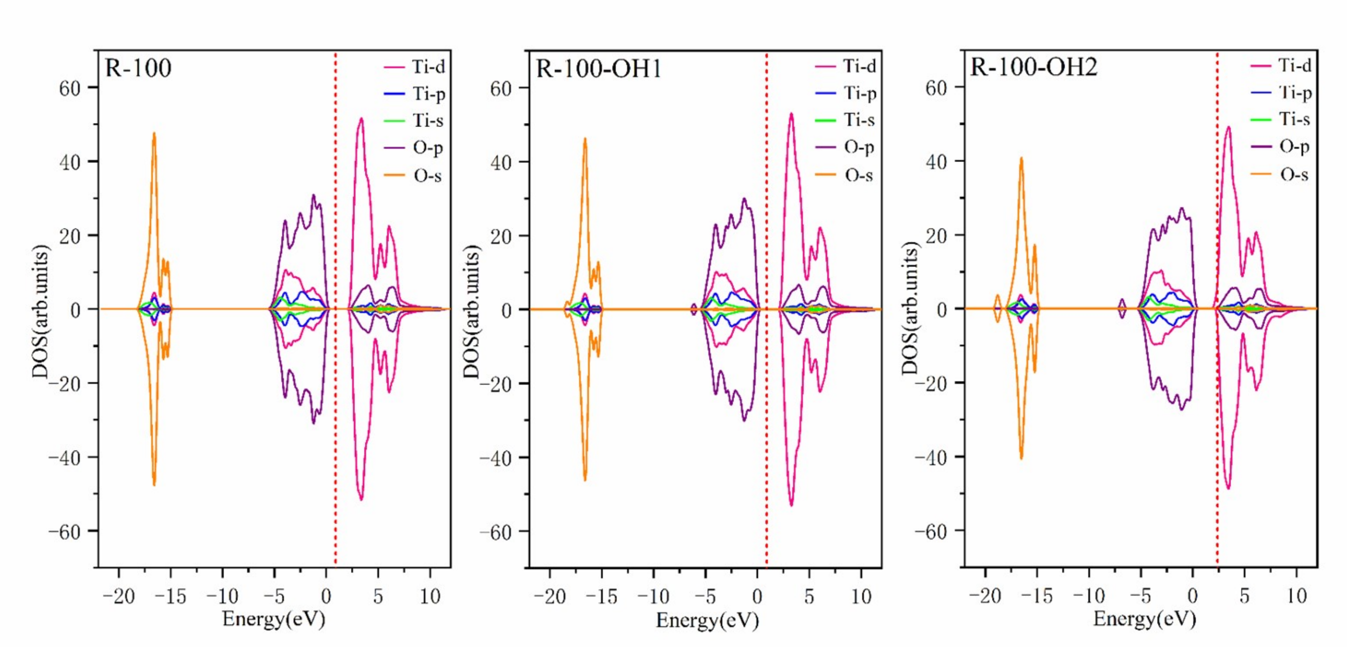

Fig. S14. Projected density of states (PDOS) of R-100, R-100-OH1, and R-100-OH2 surfaces.

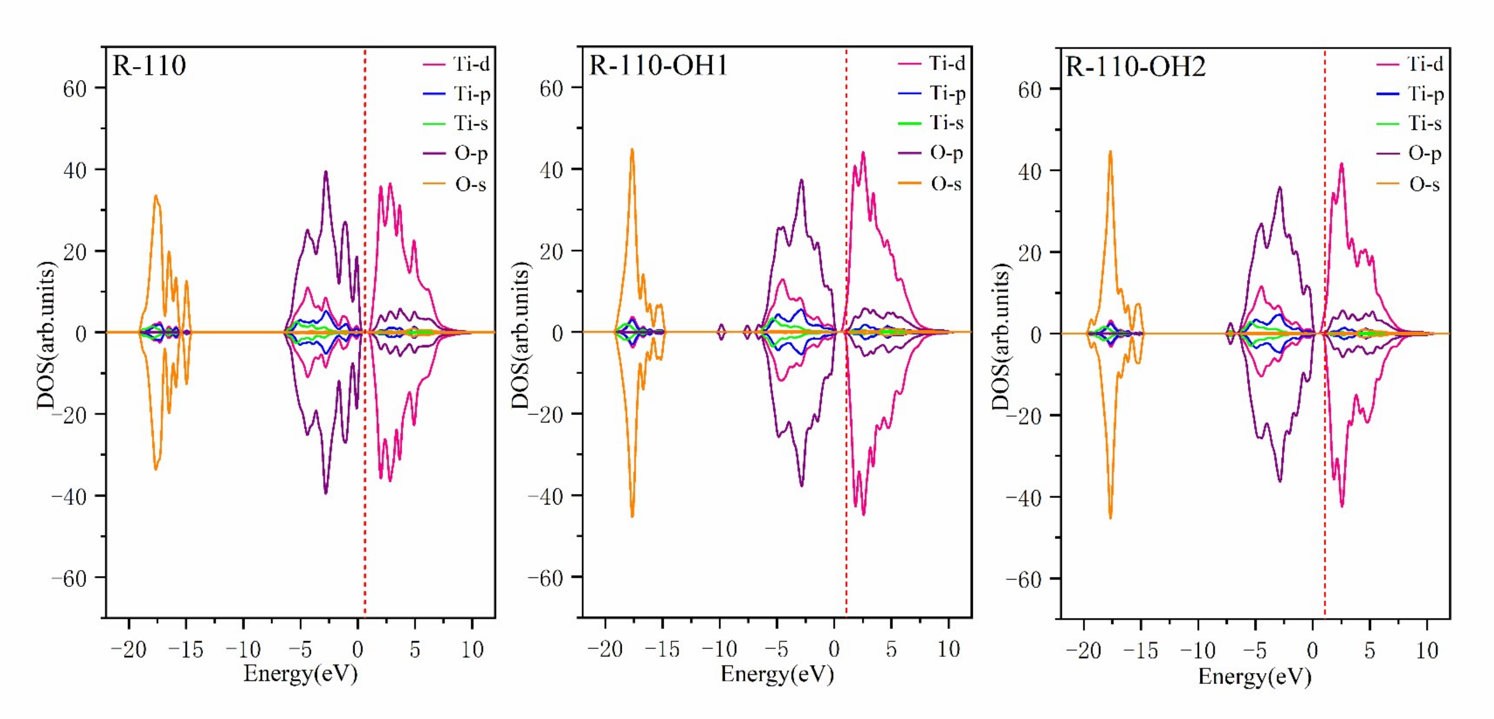

Fig. S15. Projected density of states (PDOS) of R-110, R-110-OH1, and R-110-OH2 surfaces.

Bader charge analysis

Table S6: Bader charge analysis of R-101-OH1/OH2.

Structure	Atom	X	Y	Z	Bader charge
R-101-OH1	H (terminal hydroxyl)	6.515	2.663	10.963	-0.696
	O (terminal hydroxyl)	6.134	2.234	10.175	1.178
	Ti (Hydroxyl-linked Ti)	6.216	3.171	8.557	-2.117
	H (bridged hydroxyl)	4.100	3.742	9.932	-0.609
	O (bridged hydroxyl)	4.556	4.272	9.252	1.171
	Ti (Hydroxyl-linked Ti)	3.221	5.372	8.209	-2.073
	O (inner layer O)	1.033	1.750	5.027	1.055
	Ti (inner layer Ti)	2.236	3.054	5.831	-2.115
R-101-OH2	H (bridged hydroxyl)	3.981	3.744	9.989	-0.630
	O (bridged hydroxyl)	4.544	4.227	9.356	1.234
	Ti (Hydroxyl-linked Ti)	3.232	5.378	8.234	-2.070
	Ti (Ti between two hydroxyl groups)	6.049	3.215	8.288	-1.877
	H (bridged hydroxyl)	7.981	3.956	9.928	-0.591
	O (bridged hydroxyl)	7.414	4.477	9.323	1.202
	Ti (Hydroxyl-linked Ti)	8.910	5.381	8.210	-2.063
	Ti (Ti between two hydroxyl groups)	6.049	3.215	8.288	-1.877
	O (inner layer O)	1.043	1.747	5.038	1.052
	Ti (inner layer Ti)	2.235	3.065	5.835	-2.117

Table S7: Bader charge analysis of R-001-OH1/OH2.

Structure	Atom	X	Y	Z	Bader charge
R-001-OH1	H (terminal hydroxyl)	3.143	7.775	11.356	-0.606
	O (terminal hydroxyl)	3.755	7.198	10.864	1.138
	Ti (Surface Ti connected to terminal hydroxyl）	3.614	7.382	8.977	-2.066
	H (bridged hydroxyl)	5.317	5.676	9.948	-0.647
	O (bridged hydroxyl)	5.092	5.921	9.033	1.196
	Ti (Surface Ti connected to terminal hydroxyl）	3.614	7.382	8.977	-2.066
	Ti (Subsurface Ti linked by bridging hydroxyl）	6.101	4.901	7.584	-2.115
	O (inner layer O)	0.000	3.575	4.483	1.038
	Ti (inner layer Ti)	1.404	4.979	4.483	-2.108
R-001-OH2	H (terminal hydroxyl)	4.874	6.966	11.093	-0.660
	O (terminal hydroxyl)	4.447	6.573	10.314	1.212
	Ti (Surface Ti connected to terminal hydroxyl）	3.537	7.451	8.927	-1.999
	H (bridged hydroxyl)	7.870	4.878	9.361	-0.672
	O (bridged hydroxyl)	7.153	4.200	9.206	1.297
	Ti (Surface Ti connected to terminal hydroxyl）	8.349	2.605	8.784	-1.986
	Ti (Subsurface Ti linked by bridging hydroxyl）	6.128	4.897	7.381	-2.061
	O (inner layer O)	0.000	3.575	4.483	1.036
	Ti (inner layer Ti)	1.404	4.979	4.483	-2.112

Table S8: Bader charge analysis of A-110-OH1/OH2.

Structure	Atom	X	Y	Z	Bader charge
A-110-OH1	H (terminal hydroxyl)	7.473	4.141	10.506	-0.669
	O (terminal hydroxyl)	6.638	4.135	10.004	1.188
	Ti (Surface Ti connected to terminal hydroxyl）	6.877	4.097	8.125	-2.011
	H (bridged hydroxyl)	4.519	4.056	9.086	-0.675
	O (bridged hydroxyl)	4.772	3.940	8.150	1.183
	Ti (Surface Ti connected to terminal hydroxyl）	6.877	4.097	8.125	-2.011
	Ti (Subsurface Ti linked by bridging hydroxyl）	4.363	5.460	6.910	-2.061
	O (inner layer O)	1.642	5.419	4.067	1.033
	Ti (inner layer Ti)	4.384	2.708	4.067	-2.085
A-110-OH2	H (bridged hydroxyl)	4.238	7.745	8.490	-0.699
	O (bridged hydroxyl)	3.822	6.837	8.511	1.293
	Ti (Surface Ti connected to terminal hydroxyl）	1.933	6.723	7.962	-1.991
	Ti (Subsurface Ti linked by bridging hydroxyl）	4.406	5.391	6.871	-1.861
	H (bridged hydroxyl)	4.563	3.038	8.554	-0.719
	O (bridged hydroxyl)	4.984	3.944	8.561	1.306
	Ti (Surface Ti connected to terminal hydroxyl）	6.843	4.106	7.976	-1.991
	Ti (Subsurface Ti linked by bridging hydroxyl）	4.406	5.391	6.871	-1.861
	O (inner layer O)	1.642	5.419	4.067	1.038
	Ti (inner layer Ti)	4.384	2.708	4.067	-2.083

Table S9: Bader charge analysis of A-100-OH1/OH2.

Structure	Atom	X	Y	Z	Bader charge
A-100-OH1	H (terminal hydroxyl)	2.032	3.941	12.245	-0.599
	O (terminal hydroxyl)	2.900	4.136	11.847	1.079
	Ti (Surface Ti connected to terminal hydroxyl）	2.891	4.366	9.989	-2.103
	H (bridged hydroxyl)	3.082	1.710	10.412	-0.662
	O (bridged hydroxyl)	2.882	2.370	9.726	1.174
	Ti (Surface Ti connected to terminal hydroxyl）	2.891	4.366	9.989	-2.103
	Ti (Subsurface Ti linked by bridging hydroxyl）	2.878	2.053	7.717	-2.081
	O (inner layer O)	2.878	0.021	3.834	1.044
	Ti (inner layer Ti)	2.878	2.016	3.834	-2.077
A-100-OH2	H (bridged hydroxyl)	3.723	2.057	10.226	-0.712
	O (bridged hydroxyl)	2.924	2.466	9.839	1.242
	Ti (Surface Ti connected to terminal hydroxyl）	2.876	4.458	9.591	-2.040
	Ti (Subsurface Ti linked by bridging hydroxyl）	2.878	2.022	7.721	-2.087
	H (bridged hydroxyl)	7.530	2.015	10.213	-0.623
	O (bridged hydroxyl)	6.736	2.436	9.828	1.189
	Ti (Surface Ti connected to terminal hydroxyl）	6.710	4.453	9.604	-1.825
	Ti (Subsurface Ti linked by bridging hydroxyl）	6.711	2.033	7.726	-2.087
	O (inner layer O)	2.878	0.021	3.834	1.043
	Ti (inner layer Ti)	2.878	2.016	3.834	-2.067

Table S10: Bader charge analysis of A-001-OH1/OH2.

Structure	Atom	X	Y	Z	Bader charge
A-001-OH1	H (terminal hydroxyl)	4.173	6.416	12.471	-0.629
	O (terminal hydroxyl)	3.797	6.005	11.672	1.152
	Ti (Hydroxyl-linked Ti)	3.834	7.029	10.062	-2.067
	H (terminal hydroxyl)	3.812	4.400	11.681	-0.653
	O (terminal hydroxyl)	3.835	3.392	11.597	1.086
	Ti (Hydroxyl-linked Ti)	3.841	2.394	10.090	-2.064
	O (inner layer O)	1.916	2.848	5.553	1.045
	Ti (inner layer Ti)	5.751	0.927	5.110	-2.069
A-001-OH2	H (bridged hydroxyl)	5.061	4.632	10.672	-0.617
	O (bridged hydroxyl)	4.076	4.611	10.610	1.252
	Ti (Hydroxyl-linked Ti)	3.818	2.675	9.876	-2.011
	Ti (Ti between two hydroxyl groups)	3.797	6.667	9.978	-1.851
	H (bridged hydroxyl)	5.041	8.651	10.730	-0.621
	O (bridged hydroxyl)	4.057	8.643	10.654	1.265
	Ti (Hydroxyl-linked Ti)	3.809	10.632	9.885	-2.017
	Ti (Ti between two hydroxyl groups)	3.797	6.667	9.978	-1.851
	O (inner layer O)	1.916	2.844	5.556	1.046
	Ti (inner layer Ti)	5.751	0.927	5.110	-2.061

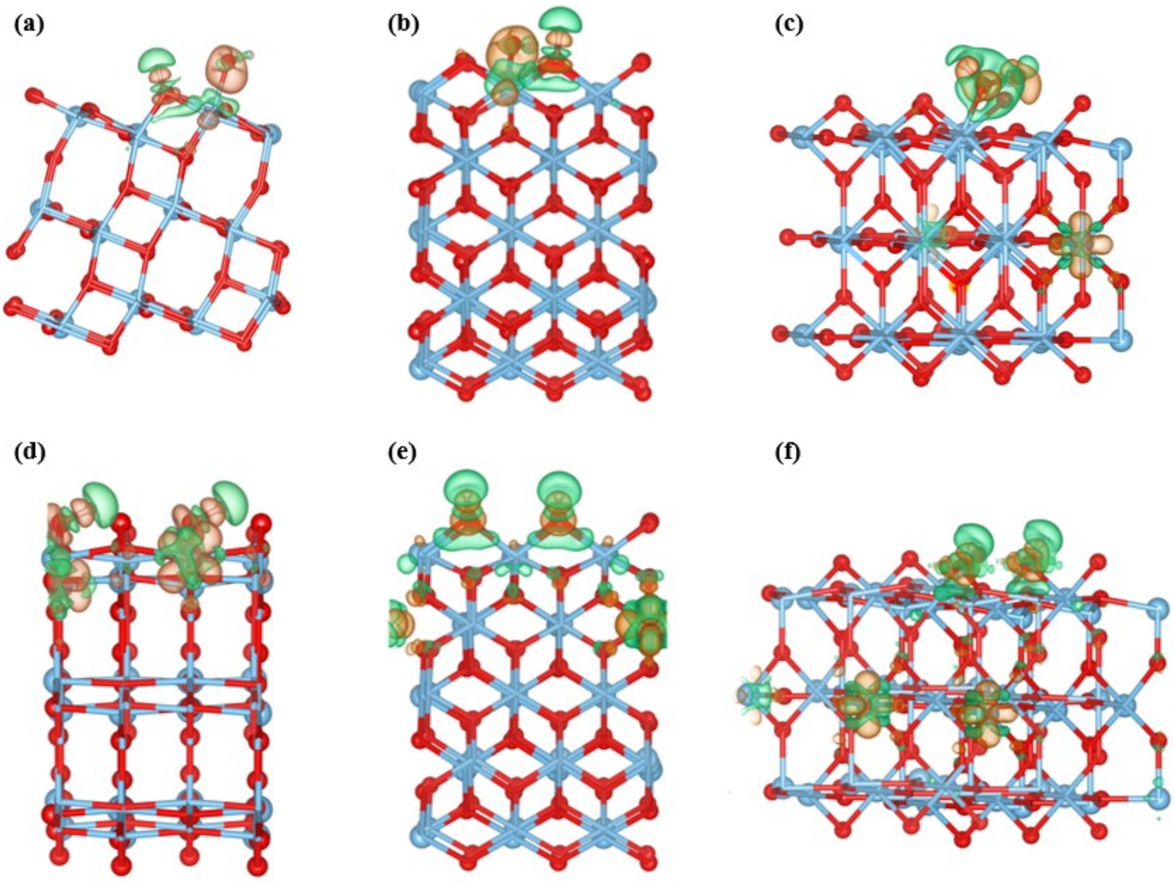

Fig. S16. The differential charge densities of OH1- (a-c) and OH2-type (d-f) hydroxylated surfaces of A-101 (a,d), R-100 (b, e), and R-110 (c, f). The isosurface value is taken as 0.009 e/bohr^3. The brown and green regions represent positive (electron accumulation) and negative (electron depletion) values, respectively.

Reference:

[1] R. Johnson, NIST Computational Chemistry Comparison and Benchmark Database NIST Standard Reference Database Number 101 Release 21, August 2020, http://cccbdb.nist.gov.

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