

SUPPORTING INFORMATION

Untangling product selectivity on clean low indexed rutile TiO₂ surfaces using first-principles calculations

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This SI is divided into three parts.

1. PCET mechanism/ Free energy profile calculation details.
2. Step-free free energies.
3. Optimized structures.

SECTION I

We characterized the OER mechanism on four TiO₂ low-index Miller surfaces (110), (101), (010), and (001) slabs. We considered the 4-step proton-coupled electron-transfer mechanism and the intermediates OH*, O*, and OOH*.¹ In what follows we use the O^(d) and O^(p) to represent the dangling and peroxo O* intermediate i.e. 2nd step of oxygen evolution reaction. The most stable form of O* intermediate species varies with the material.^{1,2} The structures of the TiO₂ (110), (101), (010), and (001) surfaces are shown in Figure S1 and in Figures S2-S5.

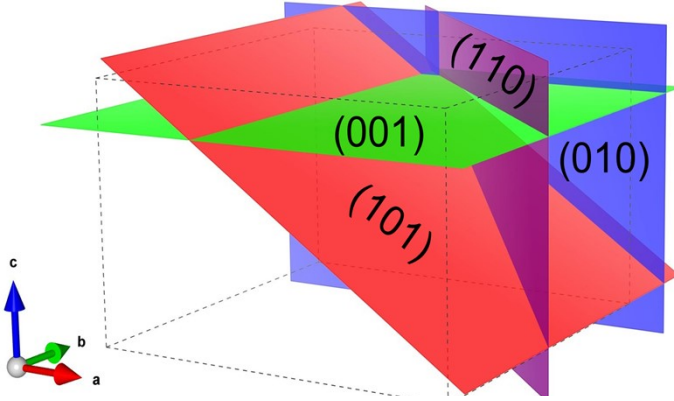
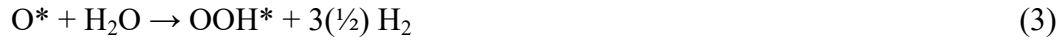


Figure S1. Rutile TiO₂ low-index Miller facets.

1. PCET mechanism

The four-step PCET mechanism starts with * + H₂O as the initial state of the catalysts.

The reaction steps are as follows:



2. Free energy calculation scheme for oxygen evolution reaction (OER)

The details of the determination of Gibbs's free energy changes for Steps 1-4 are given below.

$$\Delta G_1 = \Delta G_{\text{OH}^*} - eU + \Delta G_{\text{H}^+} (\text{pH}) \quad (5)$$

$$\Delta G_2 = \Delta G_{\text{O}^*} - \Delta G_{\text{OH}^*} - eU + \Delta G_{\text{H}^+} (\text{pH}) \quad (6)$$

$$\Delta G_3 = \Delta G_{\text{OOH}^*} - \Delta G_{\text{O}^*} - eU + \Delta G_{\text{H}^+} (\text{pH}) \quad (7)$$

$$\Delta G_4 = 4.92 (\text{eV}) - \Delta G_{\text{OOH}^*} - eU + \Delta G_{\text{H}^+} (\text{pH}) \quad (8)$$

Where U is the potential measured against normal hydrogen electrode (NHE) at standard conditions (T = 298.15 K, P = 1 bar, pH = 0). The free energy change of the protons relative to the above-specified electrode at non-zero pH is represented by Nernst equation as $\Delta G_{\text{H}^+} (\text{pH}) = -kT \ln(10) \times \text{pH}$. The sum of ΔG_{1-4} is fixed to the negative of experimental Gibbs free energy of formation of two water molecules -2Δ

$G_{OH_2} = 4 \times 1.23 = 4.92$ eV in order to avoid the calculation of the O_2 bond energy, which is difficult to determine accurately within GGA-DFT. The Gibbs free energies of eqs 5-8 depend on the adsorption energies of OH^* , O^* , and OOH^* . The Gibbs free energy differences of these intermediates include zero-point energy (ZPE) and entropy corrections accordingly, $\Delta G_i = \Delta E + \Delta ZPE - T\Delta S_i$ and energy differences ΔE_i considered relative to H_2O and H_2 (at $U = 0$ and $pH = 0$) as

$$\Delta E_{OH^*} = E(OH^*) - E(*) - [E(H_2O) - \frac{1}{2}E(H_2)] \quad (9)$$

$$\Delta E_{O^*} = E(O^*) - E(*) - [E(H_2O) - E(H_2)] \quad (10)$$

$$\Delta E_{OOH^*} = E(OOH^*) - E(*) - [2E(H_2O) - 3\frac{1}{2}E(H_2)] \quad (11)$$

The theoretical Overpotential is defined as:

$$\eta = \max[\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4] / e - 1.23 \text{ [V]} \quad (12)$$

$\Delta G = \Delta E + \Delta ZPE - T\Delta S$ is calculated as follows: ΔE is the reaction energy that we get from density functional theory (DFT). ΔZPE and ΔS are the differences in zero-point energies, and the change in entropy respectively, which we get from references ^{1,2}.

Table S1. Differences in Zero-Point Energies, ΔZPE , and the Change in Entropy ΔS for Intermediates.

$(\Delta ZPE - T\Delta S)_{OH^*}$	$(\Delta ZPE - T\Delta S)_{O^{(d)}/OOH^*}$	$(\Delta ZPE - T\Delta S)_{O^{(p)}/OOH^*}$
+0.40	- 0.30/+0.32	- 0.37/+0.39

SECTION II

1. Step Free energies of oxygen evolution reaction (OER) intermediates:

The standard hydrogen electrode potential at $pH = 0$ is equal to ~ 1.23 and ~ 0.40 V at $pH = 14$.¹ Accordingly, the threshold values for $1e^-$, $2e^-$, and $4e^-$ processes are as given in (Table S2) referenced from.² We used Nernst's equation,^{3,4} for the free energy correction at a given pH

$$\Delta G_{pH}(pH) = 2.30 \times pH \times k_B T \quad (13)$$

Table S2: Values of Standard Hydrogen Potential at $pH = 0/14$

pH	0	14
Product	Standard Hydrogen Potential in (V)	
$\bullet OH$	2.73	1.90
H_2O_2	1.76	0.93
O_2	1.23	0.40

Based on these pH values we calculated the step-free and free energies relative to the resting state ' $* + 2H_2O$ ' at $pH = 0$ the free energy data is provided in the main text in table 1 and step-free energies are shown in (Table S3) and at $pH = 14$ shown in (Table S4 and S5) respectively.

Table S3. Step-free energies relative to the resting state ‘* + 2H₂O’ for (ΔE^*), ‘OH*’ (ΔE_{OH^*}), O^(d) ($\Delta E_{\text{O}^{(d)}}$), O^(p) ($\Delta E_{\text{O}^{(p)}}$), OOH* (ΔE_{OOH^*}), and O₂ (ΔE_{O_2}) and overpotentials ‘ η ’ through four-, two- and one-electron (O₂/H₂O₂/•OH evolution) processes for all systems. The bold characters marked are rate-limiting steps.

Mechanism	ΔE_{OH^*}	$\Delta E_{\text{O}^{(d)}}$	$\Delta E_{\text{O}^{(p)}}$	ΔE_{OOH^*}	ΔE_{O_2}
001 ^(d)	2.59	2.50	–	0.51	–0.26
001 ^(p)	2.59	–	2.10	0.91	–0.26
101 ^(d)	1.73	2.83	–	0.49	–0.13
101 ^(p)	1.73	–	2.25	1.07	–0.13
110 ^(d)	1.59	2.86	–	–0.39	0.86
110 ^(p)	1.59	–	2.02	0.45	0.86
010 ^(d)	0.64	2.66	–	–0.56	2.18
010 ^(p)	0.64	–	1.09	1.01	2.18

Table S4. Step-free energies at pH=14 relative to the resting state ‘* + 2H₂O’

Mechanism pH (14)	ΔE_{OH^*}	$\Delta E_{\text{O}^{(d)}}$	$\Delta E_{\text{O}^{(p)}}$	ΔE_{OOH^*}	ΔE_{O_2}
001 ^(d)	1.76	1.67	–	–0.32	–1.09
001 ^(p)	1.76	–	1.27	0.08	–1.09
101 ^(d)	0.90	2.00	–	–0.34	–0.96
101 ^(p)	0.90	–	2.35	–0.34	–0.96
110 ^(d)	0.76	2.03	–	–1.22	0.03
110 ^(p)	0.76	–	1.19	–0.38	0.03
010 ^(d)	–0.19	1.83	–	–1.39	1.35
010 ^(p)	–0.19	–	0.26	0.18	1.35

Table S5: Free energies relative to the resting state ‘* + 2H₂O’ at pH= 14.

Mechanism pH (14)	ΔG_{OH^*}	$\Delta G_{\text{O}^{(d)}}$	$\Delta G_{\text{O}^{(p)}}$	ΔG_{OOH^*}	ΔG_{O_2}	Product	R.D.S	η (V) 1e [–]	η (V) 2e [–]	η (V) 4e [–]
001 ^(d)	2.16	3.53	–	3.53	1.60	•OH	OH*	1.76	–	–
001 ^(p)	2.16	–	3.06	3.53	1.60	•OH [–]	OH*	1.76	–	–
101 ^(d)	1.30	3.00	–	2.98	1.60	H ₂ O ₂	O*	–	0.77	1.30
101 ^(p)	1.30	–	2.35	2.98	1.60	H ₂ O ₂	OH*	–	0.37	0.90
110 ^(d)	1.16	2.89	–	1.99	1.60	H ₂ O ₂	O*	–	0.80	1.33
110 ^(p)	1.16	–	1.98	1.99	1.60	H ₂ O ₂	OH*	–	0.23	0.76
010 ^(d)	0.21	1.74	–	0.67	1.60	O ₂	O*	–	–	1.13
010 ^(p)	0.21	–	0.10	0.67	1.60	O ₂	O ₂	–	–	0.53

SECTION III

1. DoS Calculations for all the surfaces.

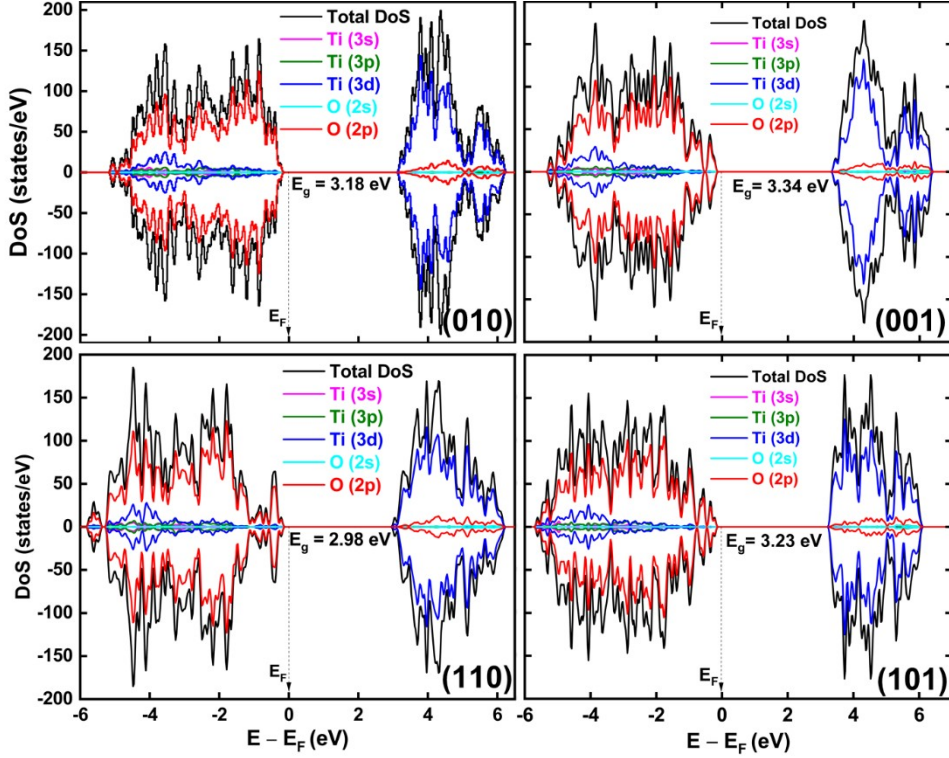


Figure S6. Plotted DoS for TiO₂ (010), (001), (110) and (101) surface. E_g represents the band gap value whereas Fermi energy level E_F lies at 0 eV.

Table S6: Bader charges of the OH*, dangling O^(d), peroxo O^(p), and OOH* intermediates. BC(OH*), BC(O^(d)), BC(O^(p)), and BC(OOH*) are the Bader charges (BC) of the OER intermediates; O^s is the charge on surface oxygen where O^(p) denotes adsorbed peroxo specie. Note that the O 1s core electrons are not included in the electron count as they are treated with pseudopotentials.

Intermediates / Surfaces	BC (OH*)			BC (O ^(d))		BC (O ^(p))			BC (OOH*)			
	Ti	O	H	Ti	O ^(d)	Ti	O ^s	O ^(p)	Ti	O	O	H
001	7.84	7.12	0.36	7.87	6.57	7.91	6.62	6.44	7.87	6.40	6.55	0.33
101	7.84	7.08	0.34	7.84	6.55	7.86	6.53	6.62	7.85	6.22	6.39	0.33
110	7.82	7.08	0.33	7.84	6.53	7.87	6.67	6.43	7.81	6.22	6.41	0.38
010	7.85	7.09	0.35	7.85	6.82	7.87	6.59	6.46	7.84	6.48	6.66	0.35

Table S7: Bond lengths of all optimized intermediates OH*, dangling O^(d), peroxo O^(p), and OOH* given in (Å).

Intermediates / Surfaces	OH*		O ^(d)		O ^(p)		OOH*		
	Ti-O	O-H	Ti-O ^(d)	Ti-O ^(p)	O ^(p) -O ^s	Ti-O	O-O	O-H	
001	1.847	0.973	1.835	1.917	1.425	2.039	1.406	0.984	
101	1.800	0.993	1.646	1.911	1.451	1.923	1.461	0.982	
110	1.790	0.976	1.654	1.905	1.467	2.264	1.353	0.989	
010	1.785	0.987	2.095	2.073	1.462	2.188	1.327	0.977	

2. Formation energies of oxygen evolution reaction (OER) intermediates:

We calculated the formation energies (Table S8) of all the studied systems and their intermediates. The formation of each unit cell structure from the constituent standard states of Ti, O₂, and H₂ were used. So that for each bare surface the formation energy is:

$$\Delta E_F^{(TiO_2)_n} = E_{(TiO_2)_n} - nE_{Ti} - \frac{n}{2}E_{O_2} \quad (14)$$

Where, E_{TiO_2} is the DFT total energy of the system TiO₂, E_{Ti} and E_{O_2} are DFT energies of metallic Ti and O₂ molecule.

Table S8: Formation energies of all the surfaces (ΔE_F^*) and intermediates OH* (ΔE_{OH}^{OH*}), dangling O^(d) ($\Delta E_{OH}^{O(d)}$), peroxo O^(p) ($\Delta E_{OH}^{O(p)}$), and OOH* (ΔE_{OH}^{OOH*}) given in eV/atom.

Intermediates / Surfaces	ΔE_F^* eV/atom	ΔE_{OH}^{OH*} eV/atom	$\Delta E_{OH}^{O(d)}$ eV/atom	$\Delta E_{OH}^{O(p)}$ eV/atom	ΔE_{OH}^{OOH*} eV/atom
001	-2.16	-2.14	-2.13	-2.13	-2.11
101	-2.16	-2.14	-2.13	-2.14	-2.12
110	-2.24	-2.21	-2.21	-2.21	-2.20
010	-2.24	-2.22	-2.21	-2.22	-2.20

References:

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