

SURFACE RECONSTRUCTIONS OF PEROVSKITE-TYPE OXIDES: THEIR
EXOTIC STRUCTURES AND MODIFIED CHEMISTRY

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John Mark. P. Martirez

*To my parents, Helen and Jess; teachers; mentors; fiancé', Brian; and friends
for their patience, encouragements, knowledge, wisdom, and for enriching my life.*

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ABSTRACT

SURFACE RECONSTRUCTIONS OF PEROVSKITE-TYPE OXIDES: THEIR EXOTIC STRUCTURES AND MODIFIED CHEMISTRY

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The ability to manipulate the atomic and electronic structures and stoichiometry of surfaces is of utmost importance in optimizing heterogeneous catalysts. A critical requirement in this endeavor is a deep thermodynamic and kinetic understanding of surface reconstruction behavior, under various thermal and chemical constraints. We explore the reconstruction behaviors (structure and chemistry) of Ti-based perovskite type oxides: BaTiO_3 , PbTiO_3 and SrTiO_3 . The former two exhibit ferroelectricity. We find that these oxides undergo surface reconstruction transformations that generally result in enrichment of their catalytically active component: Ti. These reconstructions show rich bonding and structural motifs that affect the active sites' reactivity and accessibility. In addition to the thermodynamic understanding of the surface reconstructions, we introduce the kinetic tunability of the surface reconstruction. We demonstrate this from a particular surface phase coexistence observed in BaTiO_3 , namely the $c(2\times 2)$ and $c(4\times 4)$, where the diffusion behavior of the TiO units that compose both surfaces strongly dictate their degree of agglomeration. This work emphasizes that employing kinetics in addition to thermodynamics is sometimes needed in explaining surface phase transformations. We also explore the unique chemistry that these reconstructions enable, specifically the reduced Ti-rich reconstruction of BaTiO_3 and the oxidized TiO_2 -rich double-layer reconstructions of SrTiO_3 . In the

former, a promising route for hydrogen production is found upon reaction with water. In the latter, low thermodynamic barriers for the oxidation of water to O_2 has been found on the reconstructed surface relative to the typical native termination and the surface of rutile-phase TiO_2 . Finally, we show that in ferroelectrics, BaTiO_3 and PbTiO_3 , these surface transformations can be tuned with the help of an electric field. An applied electric field changes the material's polarization, which then alters the surface electronic properties, and thereby also affects their sensitivity towards stoichiometric changes.

TABLE OF CONTENTS

ACKNOWLEDGEMENT	iv
ABSTRACT	v
LIST OF TABLES	xii
LIST OF ILLUSTRATIONS	xv
PREFACE	xlvi
CHAPTER 1 : Introduction	1
CHAPTER 2 : General methodology: theory and simulations	10
2.1 Density functional theory	10
2.2 The Kohn-Sham density functional theory	10
2.3 Exchange-correlation functionals	12
2.3.1 Local density approximation	12
2.3.2 Generalized gradient approximation	13
2.4 Effective Hubbard U corrections	15
2.5 The Bloch theorem and the plane wave basis	21
2.6 Pseudopotentials	23
2.7 Density functional theory and thermodynamics	27
2.7.1 Integration of thermodynamic potentials in isothermal conditions	27
2.7.2 Integration of thermodynamic potentials in isobaric conditions	28
2.7.3 Approximation of vibrational energies	30
2.8 Surface phase diagrams	32

2.8.1	ATiO_3 surface free energies	33
2.8.2	ATiO_3 bulk stability boundaries	34
2.9	Reduction and oxidation potentials calculated from DFT	37
2.10	Guiding principles for modeling surface structures and chemistry of ionic compounds	41
2.10.1	Pauling's rules	41
2.10.2	Polyhedral motifs, and crystal and ligand field theories	45
2.10.3	Potential divergence and excess charges on surfaces	49
2.10.4	Acid-base chemistry on surfaces	52
2.11	STS and STM simulations.	55
 CHAPTER 3 : The Ti-rich ($\sqrt{5} \times \sqrt{5}$)$R26.6^\circ$ surface reconstruction of $\text{BaTiO}_3(001)$		
3.1	Introduction	56
3.2	Methodology	57
3.2.1	Experimental	57
3.2.2	Computational	58
3.3	Results and discussion	60
3.3.1	Surface's spatial and electronic profile	60
3.3.2	Predicted atomic and electronic structure	64
3.3.3	Comparison with the ($\sqrt{5} \times \sqrt{5}$) $R26.6^\circ$ $\text{SrTiO}_3(001)$ reconstruc- tion	69
 CHAPTER 4 : The thermodynamic and kinetic aspects of the coex- istence of the $c(2 \times 2)$ and $c(4 \times 4)$ reconstructions on $\text{BaTiO}_3(001)$ surface		
4.1	Introduction	71

4.2	Methodology	73
4.2.1	Experimental	73
4.2.2	Computational	73
4.3	Results and Discussion	76
4.3.1	Surface Atomic Structures	76
4.3.2	Coexistence of the Two Phases	85
	The thermodynamics of coexistence	85
	The kinetics of coexistence	88
4.3.3	Domains and 1D interfaces	89
4.3.4	Other Coexisting Structures in Transition Metal Oxides	93
4.4	Conclusion	94
CHAPTER 5 : Oxidative adsorption of water on the highly reduced		
	$(\sqrt{5} \times \sqrt{5})R26.6^\circ$ surface reconstruction of $\text{BaTiO}_3(001)$	96
5.1	Introduction	96
5.2	Computational methods	98
5.3	Results and discussion	98
5.3.1	Different modes of water adsorption	98
5.3.2	Mechanisms of formation of hydride/hydrogen molecule from adsorbed water	109
5.3.3	Catalytic applications	113
CHAPTER 6 : Synergistic oxygen evolving activity of a TiO_2-rich re-		
	constructed $\text{SrTiO}_3(001)$ surface	115
6.1	Introduction	115
6.2	Results and discussion	118
6.2.1	(Photo)electrochemical measurements	118

6.2.2	Computational framework	121
6.2.3	Surface hydration and oxidation	121
6.2.4	Catalytic mechanism	125
6.2.5	Comparison of the mechanism with biological and molecular systems	131
6.3	Materials and methods	131
6.3.1	Surface reconstruction	131
6.3.2	Electrode preparation and (photo)electrochemical measurements	132
6.3.3	Resistivity and optical properties	135
6.3.4	Density Functional Theory	135
 CHAPTER 7 : Tunable surface stoichiometry in oxide ferroelectrics		
	via the switchable bulk-polarization	137
7.1	Introduction	137
7.2	Methodology	139
7.3	Results and Discussion	140
7.3.1	Atomic structures of the reconstructions	140
	BaO/PbO-derived surfaces	140
	Ti _x O _y -derived surfaces	143
	Ti/Pb-rich surfaces	144
7.3.2	Polarization-dependent phase diagrams	144
7.3.3	Effects of surface stoichiometry on bulk polarization in thin-films	149
7.4	Summary	153
 CHAPTER 8 : Future Prospects		
8.1	New heterogeneous catalyst design paradigm: bifunctional active sites on “uniform” surfaces	155

APPENDIX	157
CHAPTER A : Wood’s notation for reconstructions of square lattices	157
CHAPTER B : Supplemental: The Ti-rich $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ surface reconstruction of $\text{BaTiO}_3(001)$	159
CHAPTER C : Supplemental: The thermodynamic and kinetic aspects of the coexistence of the $c(2 \times 2)$ and $c(4 \times 4)$ reconstructions on $\text{BaTiO}_3(001)$ surface	165
CHAPTER D : Supplemental: Oxidative adsorption of water on the highly reduced $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ surface reconstruction of $\text{BaTiO}_3(001)$	186
CHAPTER E : Supplemental: Synergistic oxygen evolving activity of a TiO_2-rich reconstructed $\text{SrTiO}_3(001)$ surface	192
CHAPTER F : Supplemental: Tunable surface stoichiometry in oxide ferroelectrics via the switchable bulk-polarization . . .	209
BIBLIOGRAPHY	233

LIST OF TABLES

TABLE 2.1 : Coordination numbers predicted from the ratio of the cation and the anion radii	44
TABLE 2.2 : Hard-soft classification of acids and bases	54
TABLE 5.1 : Löwdin charges (in electron charge, e) of select surface species after reaction of water with the $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ $\text{TiO}_2\text{-Ti}_{3/5}$ reconstruction. The structures are found in Fig. 5.1.	107
TABLE 5.2 : Reaction energetics of the different water adsorption types for when Ti_A and Ti_B are the main reaction sites.	112
TABLE 6.1 : Calculated Löwdin charges, bond lengths, and stretching fre- quencies of the O_2 moieties in the structures in the catalytic cycle of the reconstructed surfaces.	124
TABLE 6.2 : The minimum required applied potentials, U (vs. SHE) pre- dicted to make the elementary steps of the catalytic cycles spontaneous.	130
TABLE 7.1 : Comparison of the stability region of the reconstructions in the surface phase diagram of the different types of surfaces. .	146
TABLE D.1 : Löwdin charges ^a of select surface species after reaction of wa- ter with the $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ $\text{TiO}_2\text{-Ti}_{3/5}$ reconstruction with $\text{Ti}_\text{B'}$ as the main reaction site. ^b	190
TABLE E.1 : Sample resistivities.	192

TABLE E.2 : Tafel slopes (A) and apparent exchange current densities (j_0) obtained from the Tafel plots shown in Fig. 6.2d in chapter 6.	194
TABLE E.3 : Gas phase zero point energies and entropies ($T=298$ K).	203
TABLE E.4 : Reaction energies (ΔE) and zero point energy changes (ΔZPE) of the surface hydration-oxidation reaction: $A0 + jH_2O \rightarrow$ $X + (k/2)H_2(g)$, where $A0$ is the adsorbate-free bulk-like $TiO_2(001)$ termination.	204
TABLE E.5 : Reaction energies (ΔE) and zero point energy changes (ΔZPE) of the surface hydration-oxidation reaction: $B0 + jH_2O \rightarrow X$ $+ (k/2)H_2(g)$, where $B0$ is the adsorbate-free 2×1 TiO_2 -rich double layer reconstruction.	205
TABLE F.1 : Relative surface energy, $(\phi^i - \phi^{BaO})$, eV per 1×1 surface cell), for different slab models (I–V) defined in the text, and bulk polarization (P^+, P^0, P^-).	211
TABLE F.2 : Change in the relative surface energy $(\phi^i - \phi^{BaO})$ with and without spin-relaxation.	214
TABLE F.3 : Formation enthalpies obtained from the present GGA calcu- lations and from published thermodynamic data (1).	215

TABLE F.4 : Calculated Bader charges for the surface and sub-surface atoms for some of the stable surface reconstructions. Atoms are ordered starting from the adatoms/ad-layers then to deeper sublayers (up to two sub-layers). Total surface charges are per 1×1 surface. For comparison, bulk charges for Ba, Ti, O_{Ba} , O_{Ti} are 1.60 (1.56), 1.98 (2.00), -1.15 (-1.19), and -1.21 (-1.19) electron for FE (PE) phases. The correspond- ing charges in PTO are 1.37 (1.41), 2.09 (2.09), -1.10 (-1.15) and -1.18 (-1.18) electron.	216
TABLE F.5 : Table F.4 continued	217
TABLE F.6 : Table F.4 continued	218
TABLE F.7 : Table F.4 continued	219

LIST OF ILLUSTRATIONS

FIGURE 1.1 : The perovskite (ABO_3) cubic structure.	3
FIGURE 1.2 : Two types of (001) termination of ABO_3: AO and BO_2.	4
FIGURE 1.3 : A schematic of the ferroelectric phase transition (cubic to tetragonal), with the corresponding energy diagram, of a perovskite.	5
FIGURE 2.1 : Calculation of U value for Ti in $BaTiO_3$ from linear response method. (2) Red line corresponds to n_i^{Ti} vs. $\alpha^{Ti,KS}$ with a slope $\chi_0^{Ti} = -0.519 \text{ eV}^{-1}$, whereas the blue line corresponds to n_i^{Ti} vs. α^{Ti} with a slope $\chi^{Ti} = -0.147 \text{ eV}^{-1}$. $U = (\chi_0^{-1} - \chi^{-1})$ is therefore 4.9 eV.	20
FIGURE 2.2 : Stability domain for BTO(left) and PTO(right) at 300 K relative to their respective secondary phases.	36
FIGURE 2.3 : Free energy diagram of a hypothetical four-electron oxidation of R to O showing the relative energies of the elementary steps. The standard free energy changes for each step at zero applied potential ($U=0$) in orange. Applying a positive U lowers the free of all the steps. The blue bars show the energy steps when applying the minimum U that make all steps spontaneous, free energy ≤ 0 , and yellow bars show when applied U is in excess of the aforementioned minimum potential.	40

FIGURE 2.4 : Crystal field splitting diagrams for common polyhedral motifs. The electronic structure evolution can be predicted by the change in coordination number of the metal (M) surrounded by ligands (L), or from the distortion of the polyhedra leading to a different type of polyhedral motif.(3)	47
FIGURE 2.5 : Ligand field molecular orbital splitting diagram for octahedral complexes. Left diagram shows σ only interactions between the metal M and ligand L. Right diagram shows the effect of a π -donor L (t_{2g} filled) to the non-bonding ML_6 t_{2g} orbitals. π donors lower the octahedral gap (Δ_O). Adapted from reference (4) Figs. 8-6 and 8-12.	48
FIGURE 2.6 : Different charge (q) stacking cases with planes parallel to the surface. Case 1: neutral layers; 1': "neutral" layers with ferroelectric displacements; 2: charged layers with zero dipole moment; 3: alternating charge with non-zero dipole moment; 3': charge-passivated case 3 with opposite half charges on each termination.	51

FIGURE 3.1 : Experimental and calculated STM images of BaTiO₃ (001) ($\sqrt{5} \times \sqrt{5}$)*R*26.6° surface. (a) Empty-state image at bias - 3.02 V and 0.17 nA, 30 nm × 10 nm, (b) Filled-state image at bias 2.09 V and 0.17 nA, 30 nm × 10 nm. Simulated STM (5); (c) and (d) are the empty (3 eV above E_F) and filled (2 eV below E_F) state images for TiO₂-Ti _{$\frac{3}{5}$} , respectively. (e) and (f) are the empty and filled state images for TiO₂-Ti _{$\frac{4}{5}$} , respectively. The white dash-lined squares denote the ($\sqrt{5} \times \sqrt{5}$)*R*26.6° unit, while the lower left insets are the raw images prior to computational smearing to mimic the finite tip resolution. (g) and (h) are the ball-and-stick models of ($\sqrt{5} \times \sqrt{5}$)*R*26.6° TiO₂-Ti _{$\frac{3}{5}$} and TiO₂-Ti _{$\frac{4}{5}$} reconstructions, with dashed lines denoting the $\sqrt{5} \times \sqrt{5}$ super cell. Yellow, purple, and pink: Ti adatoms, blue: sub-surface Ti, red: O, and pale green: Ba. 62

FIGURE 3.2 : Experimental and calculated LDOS of BaTiO₃ (001) ($\sqrt{5} \times \sqrt{5}$)*R*26.6° surface. (a) Experimental surface-LDOS and calculated z-scaled projected densities of states (PDOS) (6) of ($\sqrt{5} \times \sqrt{5}$)*R*26.6° TiO₂-Ti_{3/5} and TiO₂-Ti_{4/5}. The valance band maxima (VBM) of the experimental and calculated LDOS are aligned. (b) and (c) PDOS for Ti species found on the surface. The sets of three lines for each Ti adatom (Ti_A, Ti_B, and Ti_C) correspond to $d_{x^2-y^2} + d_{xy}$, $d_{xz} + d_{yz}$, and d_{z^2} , from top to bottom (lightest to darkest shade). For sub-surface Ti (found on the underlying TiO₂), the sum of the contribution of all sub-surface Ti states are shown. Some of the spectra are shifted along the *y*-axis for clarity. 63

FIGURE 3.3 : (a) Phase diagram generated from first-principles thermodynamic calculations as a function of the relative chemical potential of Ba and O. The white solid lines bound the stability region of BaTiO₃ relative to the secondary phases(7) at 1300 K. DL and V_O refer to the double layer structure and surface oxygen vacancy, respectively. (b) Surface phase population where we count the number of surface phases whose energies are within 0.10 eV/primitive unit cell of the lowest energy structure. Regions I to III correspond to log[*p*_{O₂} (torr)] in the range of -9 to -17, -17 to -20, and -20 to -24, respectively. The experiment is believed to be between log[*p*_{O₂} (torr)]=-10 to -27 (8). 66

FIGURE 3.4 : A perspective view of the surface structure of $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ $\text{TiO}_2\text{-Ti}_{\frac{3}{5}}$ (a) and $\text{TiO}_2\text{-Ti}_{\frac{4}{5}}$ (b) showcasing the oxygen cage geometry of the Ti adatoms, see Figs. 3.1g and h for legend. (c) Crystal field splitting profile for square-planar (left) and distorted square-planar (right) geometries. 70

FIGURE 4.1 : **Experimental and simulated STM images of the $c(2 \times 2)$ and $c(4 \times 4)$ surface reconstructions on $\text{BaTiO}_3(001)$.** The experimental STM parameters are: **a** (0.929 V, 0.15 nA) and **b** (1.008 V, 0.18 nA). Inset in **a** indicates crystallographic directions, that also apply to **b-d**. Upper left portion shows $c(2 \times 2)$, while the rest shows $c(4 \times 4)$. DFT simulated STM for $c(2 \times 2)$, **c**, and $c(4 \times 4)$, **d**. Red squares indicate supercells of the reconstructions. 78

FIGURE 4.2 : **Experimental and calculated surface electronic structures.** The measured LDOS spectra show narrowed surface band gaps and states near and below the Fermi level for both **a**, $c(2 \times 2)$, and **b**, $c(4 \times 4)$. These states indicate that the reconstructions are reduced, and DFT PDOS shows that they are due to occupied $3d$ orbitals of both sub-surface and surface Ti, as well as O $2p$ orbitals of the O adatoms. 79

FIGURE 4.3 : **Calculated atomic structures of the BaTiO₃ reconstructions.** Ball and stick models for the **a** bulk-like TiO₂ termination, **b** $c(2\times 2)$ and **c** $c(4\times 4)$ surfaces. The reconstructions exhibit TiO units adsorbed on a bulk-like TiO₂ surface. The TiO units are either isolated or in a cluster. Dark blue and red balls represent Ti and O adatoms respectively. The dash-dotted lines mark the 1×1 , $\sqrt{2}\times\sqrt{2}$ and $2\sqrt{2}\times 2\sqrt{2}$ surface supercell in **a-c**, respectively. Angled views for both **b** and **c** are provided in the same viewing direction as shown in **b**. 81

FIGURE 4.4 : **Surfaces' relative free energy and adatomic vibrational DOS.** **a**, surface free energy of $c(2\times 2)$ TiO₂-(TiO)_{1/2} *vs.* $c(4\times 4)$ TiO₂-(Ti₃O₃)_{1/8}(TiO)_{1/8} ($\Delta\Omega$ in energy per (1×1) surface cell, black curve) as a function of temperature. Also shown in the upper axis is thermal energy ($k_B T$) in wavenumbers. Surface TiO units' vibrational DOS (number of modes per (1×1) surface cell) for, **b**, $c(2\times 2)$ TiO₂-(TiO)_{1/2} (simulation size $2\sqrt{2}\times 2\sqrt{2}$); **c**, $c(4\times 4)$ TiO₂-(Ti₃O₃)_{1/8}(TiO)_{1/8}. 86

FIGURE 4.5 : **Surface transformation diagram and kinetics.** **a** Starting from a clean TiO_2 surface, progressive addition of a TiO unit on the surface leads to different reconstructions leading to the proposed $c(2\times 2)$ and $c(4\times 4)$ reconstructions with half monolayer TiO coverages. Energies from GGA (black) and/or GGA+ U (blue), in $\text{eV}/2\sqrt{2} \times 2\sqrt{2}$ surface cell are given relative to the lowest energy structure of each tier. **b**, Predicted GGA reaction barriers for the transformation of a transitional structure (0 reaction coordinate) to $c(2\times 2)$, path towards left, and $c(4\times 4)$, towards right. The energy barriers are shown for each pathway, where the numbers in parenthesis are the barriers for the reverse of the paths. The thick arrows in **a** mark the kinetically relevant structures as described in the text. 87

FIGURE 4.6 : **Proposed interfacial structures and their simulated STM images.** **a**, Experimental STM image showing two distinct interfaces between the $c(2\times 2)$ and $c(4\times 4)$ that run along $[\bar{1}10]$ and $[110]$ directions. Lower panel shows the composite of the simulated STM images for the reconstructions and the interfaces between them. Predicted atomic structures of the interfaces that run along $[\bar{1}10]$, **b**, and $[110]$, **c**. Regions marked by dashed squares in the STM and structural models correspond to each other. An angled view is shown for structure **c** which emphasizes the Ti_3O_3 cluster closely adjacent to a TiO unit at the interface (compare with Fig.. 4.3c). 90

FIGURE 4.7 : **Domain growth and interface formation.** Schematic diagram for how domains of each reconstruction can grow, eventually leading to the interfaces shown in Fig. 4.6 . Dashed squares show precursors of $c(2\times 2)$ and $c(4\times 4)$ in different stages of completion. 92

FIGURE 5.1 : **Different adsorption products of a water molecule on the Ti adatom rich reconstruction of BaTiO₃.** **a**, Bare $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ TiO₂-Ti_{3/5} reconstruction, showing four-fold coordinated Ti adatoms (Ti_A and Ti_B) on the TiO₂ (001) termination. **b–f**, different adsorption products of H₂O on Ti_A: **b**, molecular; **c**, dissociative with H on a lattice O (O_l); **d**, dissociative with H on Ti_B; **e**, oxidative with surface OH as the product; and **f**, oxidative with surface O as the product. Viewing direction for the angled-view structures is shown in **a**. 101

FIGURE 5.2 : **Electronic PDOS of the adsorption products of a water molecule on the $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ reconstruction.** **a**, Bare $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ $\text{TiO}_2\text{-Ti}_{3/5}$ reconstruction. Resulting PDOS after: **b**, molecular; **c**, dissociative with H on a lattice O (O_l); and **d**, dissociative with H on $\text{Ti}_{\text{B}'}$. For Ti adatoms (A and B (B')), the DOS contribution is resolved to show orbital types: d_{z^2} , $d_{xz} + d_{yz}$ and $d_{x^2-y^2} + d_{xy}$ from bottom to top. See Fig. 5.1 a-d for the corresponding atomic structures. **e**, Spin resolved 1s orbital projection of the H on $\text{Ti}_{\text{B}'}$ showing hydride orbital occupation in **d**. By contrast, the H in OH does not have occupied 1s orbital (cationic). Lower panel in **e** shows the surface $\text{Ti}_\text{A}\text{-OH}$ and the adjacent $\text{Ti}_{\text{B}'}\text{-H}$ structure (see Fig. 5.1d for legend). For the PDOS, the valence band maxima were aligned, which are set to -0.7 eV (9) for ease of comparison. 103

FIGURE 5.3 : **Electronic PDOS of the oxidative adsorption products of a water molecule on the $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ reconstruction.** **a**, oxidative adsorption with surface OH as the product; and **b**, with surface O as the product. For Ti adatoms (A and B), the DOS contribution is resolved to show orbital types: d_{z^2} , $d_{xz} + d_{yz}$ and $d_{x^2-y^2} + d_{xy}$ from bottom to top. See Fig. 5.1e and f for the corresponding atomic structures. **c**, orbital resolved projection of the O adsorbates $2p$ orbitals in **b**, where the p_z orbital overlaps with the d_{z^2} (Ti_A –O σ bonding), and p_x and p_y orbital overlap with the d_{xz} and d_{yz} orbitals (Ti_A –O π bonding). Lower panel in **c** shows the surface Ti_A –O structure (see Fig. 5.1 for legend). For the PDOS, the valence band maxima were aligned, which are set to -0.7 eV (9) for ease of comparison. 105

FIGURE 5.4 : **Hydrogen producing reaction scheme from dissociated water.** The hydride at the $\text{Ti}_\text{B'}$ site can react **(a)** with a proton that hops to an adjacent lattice O (O_l) site from an O_l site associated with an OH on a Ti_A site, reaction (6), or **(b)** directly with the proton from an OH on the adjacent Ti_A site, reaction (7). 111

FIGURE 6.1 : **Structure of the $\text{SrTiO}_3(001)$ bulk-like and double-layer (DL) reconstructed surfaces.** (a) The bulk-like TiO_2 and (b) the 2×1 -DL surfaces.(93) (c) Top-down view of the 2×1 -DL surface, which shows the surface Ti arranged in a zigzag pattern (traced by the blue dot-dashed line). The 2×1 supercell is marked by the red dashed line. (d) Upper panel: Ti_4O_6 subunit of the surface reconstruction exhibiting cubane-like structure. Lower panel: Structure of Mn_4CaO_5 cluster found in the OEC of Photosystem II.(11; 12) (e) A typical LEED pattern of a double-domain 2×1 reconstruction measured at 38 eV, a 2×1 pattern is marked. (f) Highly oxidized derivative of the 21-DL, predicted to be stable under catalytic conditions (B5 in Fig. 6.3, R4 in Fig. 6.4b). The 2×2 supercell simulation size is marked by the red dashed lines. (g) Angled view of the structure in (f). 117

FIGURE 6.2 : **Electrochemical measurements** . (a) I - V (vs. standard hydrogen electrode, SHE, at 10 mV/s, average five anodic-cathodic scan cycles), colored lines, and I - t (at 1.2 V vs. SHE with UV-Vis illumination), black lines, plots for the surface reconstructed samples. Shaded regions correspond to the current standard deviation and surface area uncertainty. m1 and m2 denote measurements from fresh samples and after the 14-hr constant voltage electrolysis, respectively. Insets show m2-type measurement averaged over 25 anodic-cathodic scan cycles at 10 mV/s. (b) and (c), I - V for reconstructed and control samples (1 mV/s, averaged over 2 anodic-cathodic scan cycles), respectively, with and without illumination. Thick arrows mark the onset voltages (≈ 0.75 V). (d) Tafel plots. I - V curves were taken from 1mV/s data acquisition (averaged over 2 cycles) from 0.9 to 1.2 V vs. SHE ($\eta = 0.5$ to 0.8 V). Solid line, surface reconstructed samples; broken line, control. The colors correspond to the same sample color designations in a and c and Fig. E.1 in Appendix E. Tafel parameters are summarized in Table E.2 in Appendix E. 120

FIGURE 6.3 : **Reverse Latimer (Hydration and oxidation) diagram**

for the 2×1 TiO_2 -DL surface. (a) The diagram shows a series of hydration and deprotonation reactions leading to O-enrichment of the reconstructed surface. It shows the transformation of the adsorbate-free surface (B0) into the most oxidized form of the surface (B5), passing through the most stable intermediates (B1, B2, B3, and B4). A single bond between two O atoms indicates a peroxo while a one-and-a-half bond indicates a superoxo species. The schematics show only the top basis atoms of the 2×2 supercell (simulation size). The species experiencing chemical changes are in color. The Gibbs free energies of the reactions are indicated next to the arrows (*vs.* SHE, pH=14). B4 and B5 are R3 and R4 of Fig. 6.4b, respectively. The corresponding relative surface free energy at pH=14 as a function of applied potential (B0 + $4\text{H}_2\text{O}$ are chosen as the zero energy) and the Pourbaix diagram are shown in (b) and (c), respectively. 123

FIGURE 6.4 : **Catalytic mechanisms** (a) Oxygen evolving reaction cycle on the bulk-like TiO_2 termination, and, (b), on the 2×1 -DL reconstruction. A single bond between two O atoms indicates a peroxo while a one-and-a-half bond indicates a superoxo species. Schematics show only the basis units of the top TiO_2 layer for the 2×2 supercells. For a complete cycle, two water molecules are consumed, and an O_2 molecule and 4H^+ ions are produced. The species experiencing chemical changes are in color. See Table 6.2 for the required applied potential for each reaction step to be driven to spontaneity. 127

FIGURE 6.5 : **Atomic orbital projected density of states (PDOS) of the O species in the intermediates of the catalytic cycle for the 2×1 TiO_2 -DL surface.** Orbital projections of the O $2s$ and $2p$ states of the oxygen species on the active site in Fig. 6.4b. Broken line: majority spin states, solid line: minority spin states. E_F is the Fermi level. The orbital occupation is consistent with oxo, oxo radical, peroxo, and superoxo orbital occupation schemes, from top to bottom. The splitting of the O_2 π^* orbitals is due to the sigma bonding interaction between one of these orbitals and some of the $^a\text{Ti } t_{2g}$ orbitals. 128

FIGURE 6.6 : **Proton-coupled electron transfer step involving both ^aTi and ^bTi simultaneously in step 3 of Fig. 6.4b.** . . . 129

FIGURE 6.7 : **Sample (working) electrode.** Electrode preparation for single crystals. The upper panel shows the schematic of the metallic contact on the backside of the SrTiO_3 crystals. Ga-In is painted first, then a thin layer of Ag paint is coated on it before a flattened head of a Cu wire is attached via Ag paint. Insulation of the backside is achieved with a water-proof epoxy, while a heat shrink tube is used to cover the Cu wire. See Fig. E.11 in Appendix E. 133

FIGURE 6.8 : **(Photo)electrolysis set-up.** A custom-built electrolysis cell is constructed with a quartz window to allow UV-Vis illumination onto the sample surface. A Pt coil is used as an auxiliary electrode, while a Ag/AgCl (4M KCl) was used as a reference. Upper left, top-view, and upper right, birds-eye view, shows the relative positions of the electrodes. Lower left: front view. Note that the Pt coil is behind to the right of the sample, while the reference is on the left side of the sample. The Pt electrode and the porous tip of the Ag/AgCl electrode are ≈ 2.5 cm and ≈ 1 cm away from the sample, respectively. The cell is an open system where the sample is in contact with an aqueous solution of 1M NaOH. Lower right shows the bubble formation on the surface of the crystal.134

FIGURE 7.1 : Surface phase diagram for BTO (a-c) and PTO (d-f). First column, a and d, FE cases with polarization directed toward the surface (P^+), second column, b and e, PE cases, and third column, c and f, FE cases with P^- . The white lines show ABO_3 stability regions with respect to the secondary bulk phases (see Fig. 2.2 in General methodology for the definition of the lines) for $T \leq T_C$ for FE cases, and $T \geq T_C$ for PE where the Curie temperature $T_C = 403$ K (BTO) and 763 K (PTO). White solid (300 K), fine dash-dotted (500 K), dashed (700 K), dash-dotted (800 K), and dotted (1000 K) lines show the stability region at different temperatures. The black arrows indicate the trajectory for the changes of the phase boundaries from the PE case (shown as black-dashed lines). For (e), $\Delta\mu_{Pb}$ for different $PbO(g)$ pressures are marked for the $\Delta\mu_O$ value corresponding to the experimental conditions in Ref. (13). Legend: first two columns are for (a-c), final two columns are for (d-f). . . . 141

FIGURE 7.2 : Ball-and-stick models for important surfaces that are affected by bulk polarization: (a) (1×1) BaO/PbO and (b) TiO_2 . Top and side views for (c) 3×1 BaO- $\text{O}_{2/3}$, (d) $c(2 \times 2)$ PbO- $\text{O}_{1/2}$, (e) $c(2 \times 2)$ TiO_2 double-layer, (f) 3×1 TiO_2 - $\text{TiO}_{5/3}$, (g) 3×1 TiO_2 -(TiO) $_{1/3}$, (h) 2×1 TiO_2 -(TiO) $_{1/2}$, (i) 3×1 TiO_2 - $\text{Ti}_{2/3}$, and (j) 2×1 TiO_2 - $\text{Pb}_{1/2}$. Large red spheres: O; small green, yellow, and blue spheres are Ba, Pb, and Ti, respectively. The arrows in (d), (e) and (f) are to help identify the same atoms in the top and side views. Dashed lines in (d) and (e) mark the $(\sqrt{2} \times \sqrt{2})$ $R45^\circ$ supercell. For (c) and (d), the ^AO atoms are lattice oxygen atoms, while ^aO are O adsorbates. In both cases ^AO atoms remain in the same sites as in the bulk termination. For (d), the Pb atoms are displaced away from their original positions defined as in the bulk termination (marked by circular broken lines), where half of these abandoned sites are occupied by the ^aO atoms. 142

FIGURE 7.3 : The computed surface phase diagram for BTO (a) and PTO (b) combining corresponding P^+ and P^- phase diagrams. See Fig. 7.1 for legend. The labels P^+ and P^- indicate whether the substrate polarization is up- or down-polarized, respectively. (c)-(d) Preferred bulk phase polarization for BTO (c) and PTO (d), where blue and red regions indicate, respectively that P^+ and P^- are stable, and gray indicates regions where both P^+ and P^- are stable. Dashed vertical lines mark the $\Delta\mu_{\text{O}}$ range where $P^+ \leftrightarrow P^-$ transition may occur within the bulk stability regions. 150

FIGURE A.1 : **Wood's notation for common reconstructions of square**

lattices. The dots represent the original identical lattice points. The red shaded regions are the reconstructions. The names characterize the sizes and orientations of the new smallest repeat cells relative to the original lattice. In the cases of $(\sqrt{2} \times \sqrt{2})R45^\circ$ and $(2\sqrt{2} \times 2\sqrt{2})R45^\circ$, they are also commonly referred to as $c(2 \times 2)$ and $c(4 \times 4)$. c stands for "centered" since, for example, $(\sqrt{2} \times \sqrt{2})R45^\circ$ is simply a (2×2) (square outlined by broken lines next to the $(2\sqrt{2} \times 2\sqrt{2})R45^\circ$ supercell) with an additional repeat unit at its center. 158

FIGURE B.1 : Experimental I-V on BaTiO_3 (001) $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ surface covering four orders of magnitude in log-scale. 160

FIGURE B.2 : Ball-and-stick models of some of the $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ reconstructions considered in the study. The dashed lines denotes the $\sqrt{5} \times \sqrt{5}$ supercell, which matches the position in their corresponding STM images (Fig. B.3). Large spheres (red): O, medium spheres (pale green): Ba, and small spheres (Blue, yellow, purple, pink): Ti. 162

FIGURE B.3 : Simulated empty (3 eV above E_F , first column) and filled state (2 eV below E_F , second column) STM images (5) of the structures found in Fig. B.2. The dashed lines denote the $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ unit, while the lower left insets are the raw images prior to computational smearing to mimic the finite tip resolution. 163

FIGURE B.4 : Calculated z-scaled PDOS (6) from spin-polarized DFT+ U calculations of the structures in Fig. B.2. E_F is the Fermi energy, defined as being midway between the valence band maximum and conduction band minimum of the whole slab. Majority spin above $y = 0$, minority spin below $y = 0$. Atomic projections to the LDOS of the adatoms, and sub-surface Ti and O atoms are shown on the right of each LDOS. Blue and red lines correspond to the majority and minority spin-states. 164

FIGURE C.1 : **Structures of the candidate $c(2 \times 2)$ reconstructions of BaTiO_3 (001).** Ball-and-stick models showing top-down and angled views of the structures. Red: O, light-blue/dark-blue: Ti. Dashed orange boxes mark the $\sqrt{2} \times \sqrt{2}$ supercell. Angled views: the view point and angle are demonstrated by the eye and line symbols. 167

FIGURE C.2 : **The isothermal phase diagrams for the $c(2\times 2)$ reconstruction.** Isothermal surface phase diagrams as functions of oxygen chemical potential ($\Delta\mu_{\text{O}}$). Different approximations are used in the two phase diagrams: (1) the surfaces' free energies of vibration are negligible (left) and (2) all the condensed phases' (surface and bulk) free energies of vibration are negligible (right). The real case is between these two approximations. The blue broken vertical lines mark the range of oxygen chemical potentials relevant in the experiment. Red: $\text{TiO}_2\text{-TiO}_2$, green: $\text{TiO}_2\text{-TiO}_{3/2}$, blue: $\text{TiO}_2\text{-(TiO)}_{1/2}$, pink: $\text{TiO}_2\text{-(TiO)}_{1/2}\text{-}\beta$, light blue: $\text{TiO}_2\text{-Ti}_{1/2}$, and yellow: $\text{TiO}_2\text{-(TiO)}_{1/2}\text{Ti}_{1/2}$. Energies are in eV per primitive surface unit cell or (1×1) surface cell. 168

FIGURE C.3 : **Simulated STM.** Red dashed lines mark the supercell corresponding to the structures shown in Figure S1 (first and second columns) and S4 (third and fourth columns). Sample bias: -1 eV (equivalent to +1 eV tip bias as is done in the experiment), except for $\text{TiO}_2\text{-TiO}_2$ which is biased at -1.5 eV to get an image contrast. 169

FIGURE C.4 : **Simulated surface PDOS.** The valence band maximum (VBM) are aligned to the experimental VBM. The left column is for the $c(2\times 2)$ structures while the right column is for the $c(4\times 4)$. States on the valence band edges are predominantly Ti-derived in cases where surface Ti:O (defined in the main text) is greater than 1:2 (reduced surfaces), while they are purely surface O-derived for when surface Ti:O is 1:2 (oxidized surface). 170

FIGURE C.5 : **Surface free energy diagram and surface vibrational DOS for the two $c(2\times 2)$ $\text{TiO}_2\text{-(TiO)}_{1/2}$ structures A,** surface free energy of $c(2\times 2)$ $\text{TiO}_2\text{-(TiO)}_{1/2-\beta}$ vs. $c(2\times 2)$ $\text{TiO}_2\text{-(TiO)}_{1/2}$, $\Delta\Omega = \Delta E_{\text{DFT}} + \Delta A_{\text{vib}}$, black curve. The temperature dependence of the adatomic (TiO units) vibrational contribution to the Helmholtz free energy, A_{vib} , for the different reconstructions, pink and blue curves, respectively. Energies are in eV/(1 $\times$ 1) surface cell. TiO units vibrational DOS of **B**, $c(2\times 2)$ $\text{TiO}_2\text{-(TiO)}_{1/2-\beta}$; and **C**, $c(2\times 2)$ $\text{TiO}_2\text{-(TiO)}_{1/2}$ (simulation size $\sqrt{2} \times \sqrt{2}$). 171

FIGURE C.6 : **Candidate $c(4\times 4)$ structures.** All structures have net surface stoichiometry of $\text{TiO}_2\text{-(TiO)}_{1/2}$, except for the structures in the last row, which both have effective surface stoichiometry of $\text{TiO}_2\text{-(TiO)}_{3/8}\text{Ti}_{1/2}$ (slightly more reduced). Red: O, light-blue/dark-blue: Ti. Dashed orange boxes mark the $2\sqrt{2} \times 2\sqrt{2}$ supercell. Angled views (lower right insets): the view point and angle are demonstrated by the eye and line symbols. 174

FIGURE C.7 : Surface transformation diagram. Extension of Fig. 4.5a in chapter 4 showing other $c(4\times 4)$ reconstructions investigated. Energies from GGA (black) and/or GGA+ U (blue), in eV/ $2\sqrt{2}\times 2\sqrt{2}$ surface supercell, are given relative to the lowest energy structure of each tier. The table below shows the special name designations for some of the structures in the diagram and are found in Fig. C.6. 175

FIGURE C.8 : Candidate structures of the surface reconstruction interfaces and their simulated STM. **A-B**, candidate $[\bar{1}10]$ interfaces, **C-D**, candidate $[110]$ interfaces. Dashed orange boxes mark the structurally relevant region associated with the interfaces ($2\sqrt{2}\times 2\sqrt{2}$ cell), while the dash-dotted light blue boxes mark the actual simulation cells ($2\sqrt{2}\times 5\sqrt{2}$ for **A** and **B**, while $2\sqrt{2}\times 4\sqrt{2}$ for **C** and **D**). Ball-and-stick models, Red: O, light-blue/dark-blue: Ti. Angled views (lower right insets): the view point and angle are demonstrated by the eye and line symbols. 179

FIGURE C.9 : **Reconstruction transformation trajectory and energetics.** **A**, transformation leading to the formation of the $c(2\times 2)$ $\text{TiO}_2\text{-(TiO)}_{1/2}$ reconstruction from the transitional state showing two likely paths (green and the lower energy barrier orange path). **B**, transformation leading to the formation of the $c(4\times 4)$ $\text{TiO}_2\text{-(Ti}_3\text{O}_3)_{1/8}(\text{TiO})_{1/8}$. Ball-and-stick models, Red: O, light-blue/dark-blue: Ti. See Fig. 4.3 for structural references. The thick black arrows mark the relevant structural components undergoing transitions. **C**, reaction energetics for the transformations shown in **A** and **B**; green and orange, and purple paths; respectively. See Fig. 4.5 in chapter 4 for reference. 183

FIGURE C.10 : **Experimental surface line profiles for $c(2\times 2)$, **A**, and $c(4\times 4)$, **B**.** The distance between the peaks correspond to $\sqrt{2}a$ and $2\sqrt{2}a$ in **A** and **B**, respectively. 184

FIGURE C.11 :Lattice constant dependence of the surface energies.

Effect of lattice constant compression (DFT+ U relaxed bulk paraelectric phase lattice constant $a=4.05\text{ \AA}$) to the surface free energy, $\Delta\Omega^i$. Experimental $a=4.00\text{ \AA}$ (1.3% compressive strain) is used in this study. Shown are two points in the oxygen chemical potential space ($\Delta\mu_{\text{O}}$), see Figure S1B. Red: $\text{TiO}_2\text{-TiO}_2$, blue: $\text{TiO}_2\text{-(TiO)}_{1/2}$, and light blue: $\text{TiO}_2\text{-Ti}_{1/2}$. The magnitude of change are quite similar for the different reconstructions ($\approx 0.10\text{ eV/u.c.}$ at $a=4.05\text{ \AA}$) that their relative energies are unaffected by the strain. $\Delta\Omega^i$ here is for when $G(T)_{\text{surf}} - G(T)_{\text{bulk}} = 0$ (chapter 2 section 2.8.1). Energies are in eV per primitive surface unit cell or (1 $\times$ 1) surface cell. 185

FIGURE D.1 :Layer-by-layer PDOS (LDOS) of the Ti_A centered water adsorption/oxidative adsorption products. a, Bare ($\sqrt{5}\times\sqrt{5}$) $R26.6^\circ$ $\text{TiO}_2\text{-Ti}_{3/5}$ reconstruction; **b,** molecular; **c,** dissociative with H on a lattice O (O_I); **d,** dissociative with H on $\text{Ti}_{B'}$; **e,** oxidative adsorption with surface OH as the product; and **f,** with surface O as the product. The corresponding atomic structures are shown in Figure 1 of the main text. The plots are shifted along the y -axes for clarity, top to bottom: top layer (reconstructed TiO_2 layer) to bottom layer (BaO). The valence band maxima are aligned at 0 eV. 187

FIGURE D.2 : **Different adsorption products of H_2O on $\text{Ti}_{\text{B}'}$.** **a**, molecular; **b**, dissociative with H on a lattice O (O_1); **c**, dissociative with H on Ti_{A} ; **d**, oxidative with surface OH as the product; and **e**, oxidative with surface O as the product.

Viewing direction for the angled-view structures is shown in **a**. 189

FIGURE D.3 : **Electronic PDOS of the adsorption products shown**

in Fig. D.2. **a**, molecular; **b**, dissociative with H on a lattice O (O_1); and **c**, dissociative with H on Ti_{A} . outset: spin resolved $1s$ orbital projection of the H on Ti_{A} showing hydride orbital occupation. In contrast, the H in OH do not have occupied $1s$ orbital (cationic). **d**, oxidative adsorption with surface OH as the product; and **e**, with surface O as the product. outset: orbital resolved projection of the O adsorbates $2p$ orbitals, where the p_z orbital overlaps with the d_{z^2} ($\text{Ti}_{\text{B}'}-\text{O}$ σ bonding), and p_x and p_y orbital overlap with the d_{xz} and d_{yz} orbitals ($\text{Ti}_{\text{B}'}-\text{O}$ π bonding). For Ti adatoms (A, B' and B), the DOS contribution is resolved to show orbital types: d_{z^2} , $d_{xz} + d_{yz}$ and $d_{x^2-y^2} + d_{xy}$ from bottom to top. The valence band maxima are aligned at -0.7 eV. 191

FIGURE E.1 : **Additional (photo)electrochemical measurements.** I - V (blue and grey) curves and I - t (black, at 1.2 V with illumination) curves for two other trials of the 2×1 reconstructed $\text{SrTiO}_3(001)$ surface. I - V plots are from average of 5 anodic and cathodic cycles. m1 and m2 correspond to measurements from fresh samples and after the 14-hr constant voltage electrolysis, respectively. 193

FIGURE E.2 : **Optical Spectrum.** (a) Indices of refraction: n and k , real and imaginary components, respectively. (b) Reflectivity. Samples do not show significant variation in their spectra. Solid line, surface reconstructed samples; broken line, control. The colors correspond to the same sample color designations in Fig. 6.2d. Also plotted in (a) are the measured refraction indices for pure SrTiO_3 (14) (black line). Note that the k is nonzero even in the higher wavelengths with energy below SrTiO_3 gap, $3.2\text{eV} = 390\text{nm}$, (15) due to free charge carriers in the highly Nb-doped oxides. About 20% of the entire spectrum is being reflected off by the samples (averaged over different polarization). 195

FIGURE E.3 : **Reverse Latimer (Hydration and oxidation) diagram**

for the bulk-like TiO_2 surface. The diagram shows a series of hydration and deprotonation reactions leading to O-enrichment of the surface. The colored path corresponds to the transformation of the adsorbate-free surface (A0) into the most oxidized form of the surface (A4), passing through the most stable intermediates (A1, A2, and A3). Black paths are alternative paths leading to less stable structures. The schematic show the basis atoms of the 2×2 supercell (simulation size). The Gibbs free energies of the reactions are indicated next to the arrows (*vs.* SHE, $p\text{H}=14$). A2 and A3 are L2 and L3 of Fig. 6.4a in chapter 6, respectively. The corresponding free energy *vs.* potential at $p\text{H}=14$ plot and the Pourbaix diagram are shown in Fig. E.5 196

FIGURE E.4 : **Complete reverse Latimer (Hydration and oxidation)**

diagram for the 21 TiO₂-DL surface. The diagram shows a series of hydration and deprotonation reactions leading to O-enrichment of the surface. The colored path corresponds to the transformation of the adsorbate-free surface (B0) into the most oxidized form of the surface (B5), passing through the most stable intermediates (B1, B2, B3, and B4), as is shown in Fig. 6.3a in chapter 6. Black paths are alternative paths leading to less stable structures. A single bond between two O atoms indicates a peroxo while a one-and-a-half bond indicates a superoxo species. The schematics show only the top basis atoms of the 2×2 supercell (simulation size). The Gibbs free energies of the reactions are indicated next to the arrows (*vs.* SHE, *pH*=14). B4 and B5 are R3 and R4 of Fig. 6.4b in chapter 6, respectively. 197

FIGURE E.5 : **pH and potential dependence of surface structure of the bulk-like TiO_2 .** (a), the relative free energy diagram ($\text{pH}=14$) of the most stable structures found for each surface oxygen and hydrogen content for the bulk-like TiO_2 . Energy of each surface is plotted relative to that of TiO_2 (A0) + $4\text{H}_2\text{O}$. Structures A0, A2, A3, and A4 are found to be stable reconstructions of bulk-like TiO_2 under aqueous oxidation; where A2 persists a little above the reversible potential for O_2 evolution half reaction ($\varepsilon_{\text{eq}}=0.4\text{ V}$, $\text{pH}=14$). (b) Pourbaix diagrams for the bulk-like TiO_2 . A0, red line or region; A1, green; A2, orange; A3, pink; and A4 blue. See Fig. E.3 and Fig. 6.4a (chapter 6) for the corresponding schematics of the structures. 198

FIGURE E.6 : **Structure of some oxidation derivatives of the 2×1 TiO_2 -rich DL reconstruction.** (a)-(c) Ball-and-stick models of structure B1, B3, and B5(R4), respectively (see Fig. 6.3 in chapter 6). Red spheres: O; blue: Ti; white: H; yellow: Sr. B1 is the maximally hydrated form, beyond which addition of more H_2O becomes unfavorable, while B3 and B5 show the resulting surfaces after oxidation. The surfaces show various combinations of Ti-OH and side-on Ti- O_2 ($\eta^2\text{-O}_2$) structures. The $\eta^2\text{-O}_2$ could either be a peroxo or a superoxo, depending on the extent of oxidation of the surfaces. These can be distinguished by their charge, bond length and stretching frequencies (see Table 6.1 in chapter 6). 199

FIGURE E.7 : Catalytic cycles involving other derivatives of the bulk-like TiO_2 surface. Cycles involve surfaces A0 and A3/A4 defined in Fig. E.3. Reactions involve formation of hydroxo, oxo(peroxo) and hydroperoxo intermediates. The energies within the cycles are the Gibbs free energy of the step and for the proton and electron producing steps, the required potential to drive the designated step to spontaneity is of the same magnitude and sign in V. (a) At low potentials where A0 prevails, the rate limiting reaction is predicted to be the hydroperoxo formation (step 3), (b), while at high potentials, where A3 and/or A4 prevail, the second oxidation step, hydroxo to oxo(peroxo-like) step, is rate-limiting. Both involve large overpotential ($\Delta\varepsilon_{\text{max}}$) requirements of 0.68 and 1.41 V, respectively. In the case of the A0 cycle, the A0 surface is no longer the stable surface at the required potential (1.08 V). 200

FIGURE E.8 : **Catalytic cycles involving other derivatives of the 2×1 TiO_2 -DL surface.** Catalytic cycles involve surfaces B1, (a), and B3, (b) and (c), defined in Fig. 6.3 in chapter 6 and Fig. E.4. Just like on surface B5 (defined as R4 in chapter 6, Fig. 6.4b), the "Ti sites are the oxidation/ O_2 generation sites. The energies within the cycles are the Gibbs free energy of the step and for the proton and electron producing steps, the required potential to drive the designated step to spontaneity is of the same magnitude and sign in V. At the potentials where all the steps of these reactions will be spontaneous, B5 (R4) will be the preferred surface, and therefore making these cycles become kinetically irrelevant. 201

FIGURE E.9 : **Bulk-like TiO_2 (a) and TiO_2 -DL (b) reconstruction barriers, similarity of GGA (solid) and GGA+ U (dotted lines) barriers.** (a) and (b) illustrate the calculated barriers (step heights) for the reaction cycles in Fig. 6.4a (bulk-like TiO_2) and 6.4b (2×1 -DL TiO_2 -rich reconstruction), respectively. GGA and GGA+ U (Ti 3d at 4.72 eV) predicted values, solid and broken lines, respectively. Zero point energies in both are taken from GGA vibrational spectra. Each step (1-5) corresponds to the relative free energy of the surfaces and molecules as shown in (c). (1) is set as the zero energy. S corresponds to L in (a), while it is R in (b). The numbers in the parentheses are the differences in the GGA+ U and GGA calculated barriers in eV. Note that the differences are generally small and inconsequential to the identity of the ratelimiting step. The GGA+ U predicted difference in the thermodynamic overpotential ($\Delta\varepsilon_{\text{max}}$) between the bulk-like TiO_2 and the 2×1 TiO_2 -rich reconstruction is 0.51 V, nearly equal to the 0.50 V predicted by GGA. . . . 202

FIGURE E.10 :**Ti-site designation for the naming conventions of the surfaces followed in Tables E.4 and E.5.** 206

FIGURE E.11 :**Step-by-step preparation of the sample (working) electrode.** See section E.2 for the accompanying text. 208

FIGURE F.1 : The surface phase diagrams for the (1×1) reconstructions for different slab models (I–V), defined in the text, and bulk polarization (P^+ , P^0 , P^-). 212

FIGURE F.2 : Density of states (DOS) and projected density of states (PDOS)

from spin-relaxed calculations for P^+ $c(2\times 2)$ PbO-O_{1/2}, (a), P^0 and P^- 3×1 BaO-O_{2/3}, (b) and (c), respectively. Energies are relative to the Fermi level (E_F). Broken line: total DOS, grey shaded line: sum of the atomic PDOS of the O adatoms and the atoms of the two outer most surface layers, red and blue shaded lines: sum of the atomic PDOS of the O adatom or O₂ moieties on the surfaces. For (a) and (b), the O and O₂ moiety don't have net electronic spin. For (c), the two O₂ moieties have opposite non-zero net electronic spins. The corresponding real space spin-density difference isosurface plot (± 0.01 a.u.) is shown in (d) (red: excess up-spin, blue: excess down-spin). See Fig. 7.2(c) of the main document for the legend of the ball-and-stick model. 213

FIGURE F.3 : Surface phase population diagrams, where the surfaces with energies within 0.10 eV/ 1×1 surface cell of the lowest energy structure are counted. a–d BTO(001): P^+ , P^0 , P^- , and P^+/P^- , e–h: PTO(001): same order. 221

PREFACE

Data analysis and interpretation, and the writing of the published works, where the materials presented in this document are derived, were combined efforts from all the authors involved. The ideas presented in these works were borne out of the discussion between the authors.

The materials in chapter 3 appeared in J. M. P. Martirez, E. H. Morales, W. A. Saidi, D. A. Bonnell, and A. M. Rappe, "Atomic and Electronic Structure of the $\text{BaTiO}_3(001)$ ($\sqrt{5}\sqrt{5}$) $R26.6^\circ$ Surface Reconstruction", *Phys. Rev. Lett.* **2012**, *109* 256802 (1-5). Copyright © 2012 American Physical Society.

The materials in chapter 4 appeared in E.H. Morales, J. M. P. Martirez, W. A. Saidi, A. M. Rappe, and D. A. Bonnell "Coexisting surface phases and coherent one-dimensional interfaces on $\text{BaTiO}_3(001)$ ", *ACS Nano* **2014**, *8*, 4465. Copyright © 2014 American Chemical Society.

In both chapters 3 and 4, the experimental section was performed by E. H. Morales with the supervision of D. A. Bonnell of the Department of Materials Science and Engineering at the University of Pennsylvania. Theoretical calculations were designed and performed by myself, with the supervision of W. A. Saidi and A. M. Rappe.

The materials in chapter 5 appeared in N. Z. Koocher, J. M. P. Martirez, and A. M. Rappe, "Theoretical Model of Oxidative Adsorption of Water on a Highly Reduced Reconstructed Oxide Surface", *J. Phys. Chem. Lett.* **2014**, *5*, 3408. Copyright © 2014 American Chemical Society. In this chapter, the calculations were designed by N. Z. Koocher and by myself, and performed by N. Z. Koocher. The data were analyzed and processed by all the aforementioned authors.

The materials in chapter 6 has been submitted as J. M. P. Martirez, S. Kim, E. H. Morales, B. T. Diroll, M. Cargnello, T. R. Gordon, C. B. Murray, D. A. Bonnell, and A. M. Rappe, "Synergistic Oxygen Evolving Activity of a TiO_2 rich Reconstructed $\text{SrTiO}_3(001)$ Surface", to the *Journal of the American Chemical Society* **2014**, which is currently under review. A.M.R. initiated the project. J.M.P.M. conceptualized the mechanism. Both S.K. and J.M.P.M. performed the calculations. J.M.P.M. and E.H.M. prepared the samples. E.H.M. performed the UHV annealing and LEED analysis. T.R.G. M.C., and J.M.P.M. designed the photoelectrochemical set-up. J.M.P.M prepared the sample electrodes and performed the electrochemical measurements. B.T.D. performed the resistivity and ellipsometry measurements. A.M.R., D.A.B., and C.B.M. advised on the calculations, crystal preparation procedure, and electrochemical measurements, respectively.

The materials in chapter 7 appeared in W. A. Saidi, J. M. P. Martirez, and A. M. Rappe, "Strong Reciprocal Interaction between Polarization and Surface Stoichiometry in Oxide Ferroelectrics" *Nano Lett.* **2014**, 14, 6711. Copyright © 2014 American Chemical Society. In this chapter, the calculations were performed by myself and W. A. Saidi. A. M. Rappe supervised the project.

CHAPTER 1 : Introduction

The last decade has seen a resurgence of interest in ferroelectric (FE) compounds, due in a large part to recent developments in materials processing that enable new materials properties. Examples include strain controlled ferroelectric coupling (16), polarization controlled surface reactions (17; 18), surface chemical control of polarization (19; 20), and multi-ferroic behavior (21). Surface atomic and electronic structures are crucial parameters that influence these phenomena, and although the surface science of transition metal oxides is a long standing field, its application to ferroelectric compounds has been limited.

Ferroelectricity is characterized by coordinated ionic displacements from nominal high-symmetry lattice sites that cause a macroscopic electric polarization (22). Consequently, electric charge appears at the surfaces or interfaces due to the polar discontinuity. This produces an electrostatic surface instability that is similar to the situation of polar surfaces (23; 24; 25; 26; 27). Stabilization can be achieved by charge passivation of electronic or ionic origin. In the first case, the surface electronic structure is modified, perhaps leading to metallic surfaces (28). In the second case, the surface stoichiometry is altered from that of the bulk. Both cases lead to surfaces that are very different from the bulk or from the non-polar terminations. The surface conductivity and catalytic chemistry of these surfaces are of prime interest for practical as well as fundamental purposes.

The reorientable polarization of FE oxides holds the promise for immense control of surface composition and properties. The interest in FE perovskites has been continuously increasing, due to their widespread use in a wide range of applications including catalysis, sensing devices, actuators, high storage capacitors and non-volatile

memories (22; 29). BaTiO_3 (BTO) and PbTiO_3 (PTO) of the ABO_3 perovskite family (cubic phase structure shown in Fig. 1.1), perhaps the most prominent and well studied FE oxides, have divalent A -cations (Ba^{2+} and Pb^{2+}) and tetravalent B -cations (Ti^{4+}). Because of their cationic charges, BTO and PTO are sometimes referred to as 2-4 type perovskites.

The importance of surfaces and their structures have long been recognized because of the drastic electronic and compositional changes that may arise that is strongly dependent on the processing and operational conditions. ABO_3 perovskite-type oxides, have alternating layers of AO and BO_2 along its $[100]$, $[010]$, $[001]$ crystallographic axes, and therefore can be terminated by either layers along these directions. Fig. 1.2 shows the AO and BO_2 exposed (001) terminations with rock-salt type (rotated 45°) AO termination and the corner-shared square planar BO_4 composing the BO_2 termination. For 2-4 type perovskites, in the cubic phase, the (100), (010), and the (001) surfaces are the most stable surfaces from the electrostatic stand point since they don't carry excess charge. However, PTO has a single phase transition from the cubic to tetragonal phase at (Currie temperature T_C) 763 K (22), while BTO undergoes three phase transitions: cubic centrosymmetric to polar tetragonal at $T_C = 403$ K, tetragonal to orthorhombic at 278 K, and orthorhombic to rhombohedral at 183 K.(22) Fig. 1.3 shows the characteristic structural transformation for a cubic to tetragonal (ferroelectric) phase transition and the associated energy diagram below the material's T_C . For ferroelectrics, the expansion of the lattice in one direction has associated ionic displacements in the same direction where cations displace one way, while the anions displace the opposite way. Due to the ferroelectric displacements perpendicular to the surface, the surface is destabilized with the appearance of the polarization charges.

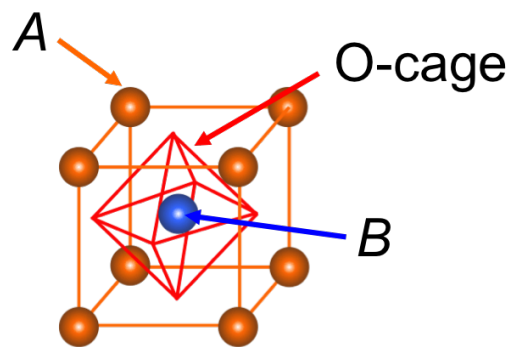


Figure 1.1: The perovskite (ABO_3) cubic structure.

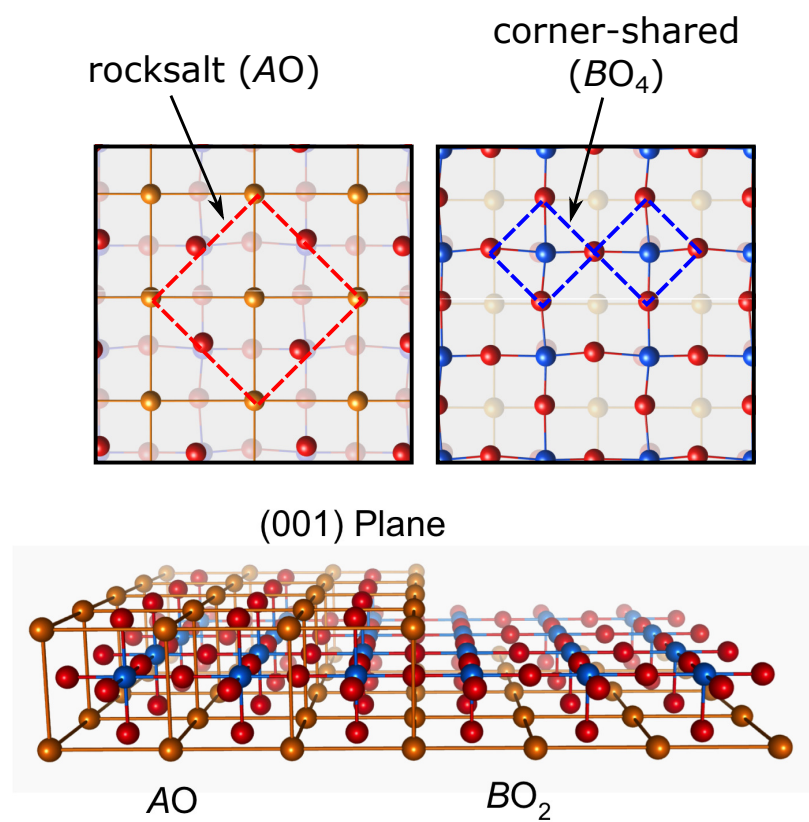


Figure 1.2: Two types of (001) termination of ABO_3 : AO and BO_2 .

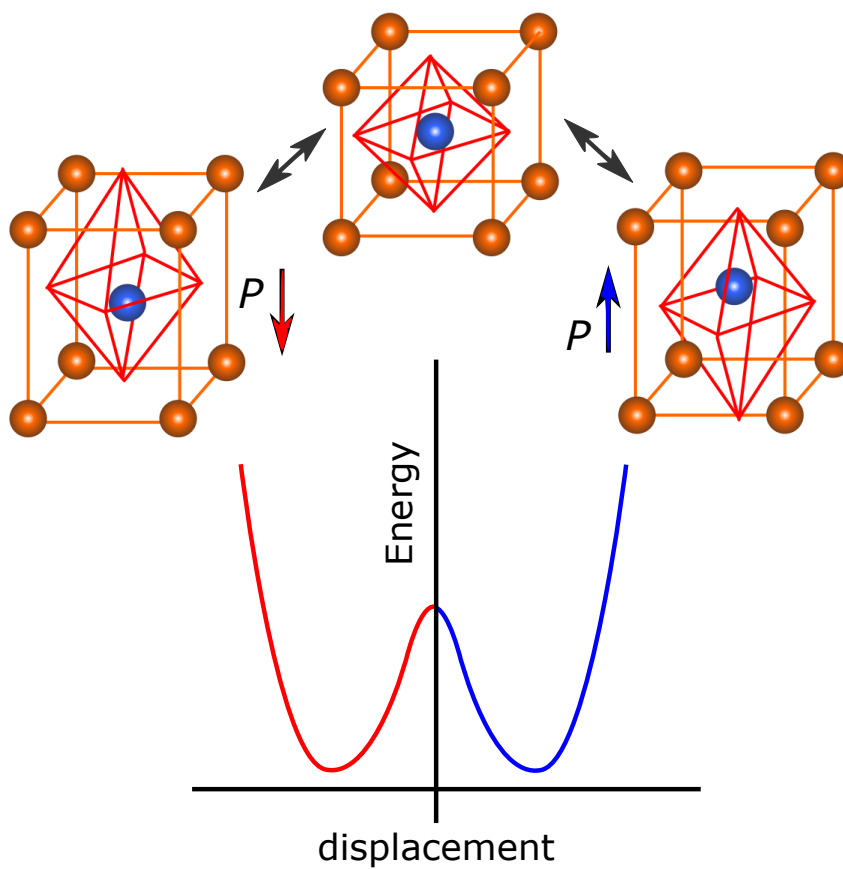


Figure 1.3: A schematic of the ferroelectric phase transition (cubic to tetragonal), with the corresponding energy diagram, of a perovskite.

In this work, we explore the reconstruction behavior of paraelectric (cubic) phase ATiO_3 ($[\text{BaTiO}_3]$ chapters 3 and 4), and their chemistry (chapters 5 $[\text{BaTiO}_3]$ and 6 $[\text{SrTiO}_3]$). Since BTO and PTO are ferroelectric oxides, we also study the effects of ferroelectric polarization on their surface reconstruction behaviors (chapter 7).

Chapter 3 presents a study of the atomic and electronic structure of the $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ surface reconstruction on BaTiO_3 (001) formed by annealing in ultra high vacuum (UHV) at 1300 K. Through density functional theory (DFT) calculations in concert with thermodynamic analysis, we assess the stability of several BaTiO_3 surface reconstructions and construct a phase diagram as a function of the chemical potential of the constituent elements. Using both experimental scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) measurements, we were able to further narrow down the candidate structures, and conclude that the surface is either $\text{TiO}_2\text{-Ti}_{\frac{3}{5}}$, $\text{TiO}_2\text{-Ti}_{\frac{4}{5}}$, or some combination, where Ti adatoms occupy hollow sites of the TiO_2 surface. DFT indicates that the defect states close to the valence band are from Ti adatom $3d$ orbitals (≈ 1.4 eV below the conduction band edge) in agreement with STS measurements showing defect states 1.56 ± 0.11 eV below the conduction band minimum (1.03 ± 0.09 eV below E_F). STM measurements show electronic contrast between empty and filled states images. The calculated local density of states at the surface shows that Ti $3d$ states below and above E_F explain the difference in electronic contrast in the experimental STM images by the presence of electronically distinctive arrangements of Ti adatoms. This work provides an interesting contrast with the related oxide SrTiO_3 , for which the (001) surface $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ reconstruction is reported to be the TiO_2 surface with Sr adatoms.

In chapter 4, we illustrate the importance of coexistence of surface reconstructions due to the diversity in kinetic and thermodynamic processes involved. We identify

the coexistence of kinetically accessible phases that are chemically identical and form coherent interfaces. Here, we establish the coexistence of two phases, $c(2\times 2)$ and $c(4\times 4)$, in $\text{BaTiO}_3(001)$ with atomically-resolved Scanning Tunneling Microscopy (STM). First principles thermodynamic calculations determine that TiO adunits and clusters compose the surfaces. We show that TiO diffusion results in a kinetically accessible $c(2\times 2)$ phase, while TiO clustering results in a kinetically and thermodynamically stable $c(4\times 4)$ phase. We explain the formation of domains based on the diffusion of TiO units. The diffusion direction determines the observed 1D coherent interfaces between $c(2\times 2)$ and $c(4\times 4)$ reconstructions. We propose atomic models for the $c(2\times 2)$, $c(4\times 4)$, and 1D interfaces.

In chapter 5, we predict the reactivity of the highly oxophilic and reduced surface Ti species found in the highly reduced surface reconstruction of $\text{BaTiO}_3(001)$ presented in chapter 3. Through density functional theory, we calculate the adsorption of H_2O on the $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ $\text{TiO}_2\text{-Ti}_{3/5}$ reconstruction. H_2O serves as the primary O source and oxidizing agent. We demonstrate that H_2O oxidizes some of the Ti adatoms, shifting their occupied $3d$ states to the surface conduction band edge. We find that, due to the high concentration of reduced Ti species on the surface, a dissociative adsorption of water on the reconstructed surface can also lead to the formation of surface hydrides, which serve as a precursor for H_2 evolution. This suggests that the reconstructed surface may be an attractive single phase hydrogen evolution catalyst.

Transition-metal based oxides attract significant attention for their ability to catalyze the highly complex four-electron oxidation of water to molecular oxygen, the pair reaction to the reduction of water to hydrogen gas (water splitting). Researchers have focused on a few well-studied transition metals, such as Mn, Co, and Ni, in-

incorporating new synthetic techniques and/or crystallographic structures. A topic of lively discussion is the value of mimicking the cubane-like structure adopted by the Mn_4CaO_5 cluster found in the oxygen evolving complex (OEC) of Photosystem II for the design of new catalysts. Recently, anomalous Ti oxide-rich surface phases of ternary oxides have been stabilized as non-stoichiometric epitaxial overlayers exhibiting cubane-like motifs.

In chapter 6, through an *ab initio* investigation, we predict that preannealing to form a TiO_2 overlayer will enhance the oxygen evolving activity of SrTiO_3 , and we confirm this through annealing and (photo)electrochemical measurements. Our theoretical work suggests that similar to the oxygen-evolving complex, a crucial aspect for catalytic dioxygen synthesis is cooperation between electronically distinct Ti sites of this reconstruction that bind and make available electron-deficient and electron-rich O species. In this regard, the parallelism between the Mn-cluster and the Ti-rich reconstruction is also chemical. We predict the reduction of the overpotential requirement as $\approx 0.5\text{V}$ relative to the bulk-like surface. Experimentally we find an order of magnitude increase in the current density and a three-fold decrease in the dependence of the overpotential with $\log(\text{current})$, in line with the predicted overpotential lowering. This work also demonstrates the possibility of introducing cooperative catalytic active sites based on a single element.

Finally in chapter 7, we present a systematic evaluation of the effects of polarization switchability on surface structure and stoichiometry in ferroelectric (FE) oxides. We show that charge passivation, mostly by ionic surface reconstructions, is the driving force for the stability of the different surface compositions in the FE oxides BaTiO_3 and PbTiO_3 . This suggests that in addition to chemical-environmental changes, varying the substrate polarization offers a new mechanism for controlling

surface reconstructions in polar systems. We found that most of the paraelectric (PE) surface reconstructions are also found in the phase diagrams of the FE surfaces, however the ranges of chemical potential where they are stable are shifted due to the coupling between FE polarization and surface charges. The FE polarization can enhance or reduce stability of surfaces found in the PE case, while also induce highly non-stoichiometric structures. Our calculated value of the oxygen partial pressure for the positive-to-negative ($P^+ \leftrightarrow P^-$) polar transition is in good agreement with the recent experimental value for thin-film PTO. For BTO we predict that it would be more challenging to drive the $P^+ \rightarrow P^-$ via oxygen control, mostly due to the lack of oxygen-deficient stable surface compositions in BTO. This study opens up the possibility of real-time control of structure and composition, and therefore chemical activities, of oxide surfaces.

CHAPTER 2 : General methodology: theory and simulations

2.1. Density functional theory

The pioneering work by P. Hohenberg and W. Kohn in describing the energy of interacting inhomogeneous electron gas (30) provided the foundation of a simple way to describe systems composed of interacting electrons, such as atoms, molecules, and extended periodic systems. They have shown that the energy E of a system can be expressed as a unique functional of the electron density, $n(\mathbf{r})$:

$$E = \int v(\mathbf{r})n(\mathbf{r})d\mathbf{r} + F[n(\mathbf{r})], \quad (2.1)$$

and that $F[n(\mathbf{r})]$ exists, which is a functional of $n(\mathbf{r})$ and independent of the external potential $v(\mathbf{r})$ where the electron propagates, such that the ground-state density $n(\mathbf{r})$ gives the minimum value of E (corresponding to the ground-state energy) associated with $v(\mathbf{r})$.

This leads to the variational treatment of the problem, where one simply needs to find the unique solution (charge density) that minimizes the energy. The method is now known as density functional theory or DFT.

2.2. The Kohn-Sham density functional theory

The Kohn-Sham (KS) treatment of the density functional theory (31) to describe multi-electronic systems is perhaps the most implemented. It simplifies the time-independent, non-relativistic, many-electron problem into an equivalent set of self-

consistent one-electron differential equations. The KS wave equation is of the form:

$$\left\{-\frac{1}{2}\nabla^2 + [\varphi(\mathbf{r}) + \mu_{xc}(n(\mathbf{r}))]\right\}\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r}) \quad (2.2)$$

where,

$$\varphi(\mathbf{r}) = v(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (2.3)$$

the sum of the total electron-ion and Hartree potential, and

$$\mu_{xc}(n) = d(n\epsilon_{xc})/dn \quad (2.4)$$

the exchange-correlation potential, where $\epsilon_{xc}(n)$ can be the exchange-correlation energy per electron of a uniform electron gas, as in the local density approximation (see section 2.3 Exchange-correlation functionals).

The total charge density,

$$n(\mathbf{r}) = 2 \sum_i^{N/2} |\psi_i(\mathbf{r})|^2 \quad (2.5)$$

(where N is the total number of electrons) that minimizes the total energy of the system

$$\begin{aligned} E = & 2 \sum_i^{N/2} \epsilon_i - \frac{1}{2} \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \\ & + \int n(\mathbf{r})[\epsilon_{xc}(n(\mathbf{r})) - \mu_{xc}(n(\mathbf{r}))] d\mathbf{r} + E_{ion}(\{\mathbf{R}\}) \end{aligned} \quad (2.6)$$

$E_{ion}(\{\mathbf{R}\})$ is the total Coulomb energy from the interaction among nuclei with nuclear spatial configuration $\{\mathbf{R}\}$ must be the ground state energy, as is prescribed in the inherent variational nature of the method.

The ground-state $n(\mathbf{r})$ can be found by solving Equations 2.2–2.6 self-consistently starting with an initial guess of $n(\mathbf{r})$. In the succeeding iterations, either the new $\varphi(\mathbf{r}) + \mu_{xc}(n(\mathbf{r}))$ or an arbitrary mixture of both old and new $\varphi(\mathbf{r}) + \mu_{xc}(n(\mathbf{r}))$ is used, and continued until E no longer changes within a given tolerance.

2.3. Exchange-correlation functionals

A complete *ab-initio* picture can't be achieved without the knowledge of the exact forms of the exchange and correlation (EXC) potentials (Eq. 2.4). To some extent, this has been one of the short comings of the DFT method. Currently, there are two widely used flavors of EXC potential approximations for slowly varying densities: the local (spin) density approximation (L(S)DA) and the generalized gradient approximation (GGA).

2.3.1. Local density approximation

L(S)DA EXC energy has the general form:

$$E_{xc}^{LDA}(n(\mathbf{r})) = \int n(\mathbf{r}) \epsilon_{xc}^{hom}(n(\mathbf{r})) d\mathbf{r} \quad (2.7)$$

where $\epsilon_{xc}^{hom}(n(\mathbf{r}))$ is the exchange-correlation energy per electron of a homogeneous electron gas. Although other variants of this approximation exist, such as the Perdew-Zunger (32) and Perdew-Wang (33), where some form of self-interaction correction was introduced, as in the former, or a simple analytical expression for the correlation energy of a homogeneous electron gas was proposed, as in the later.

2.3.2. Generalized gradient approximation

A functional form for both exchange and correlation interactions can be expressed as a function of both the density and the gradient of the density. This method of approximation is known as the generalized gradient approximation or GGA. GGA EXC energy has the general form:

$$E_{xc}^{\text{GGA}}(n(\mathbf{r})) = \int f(n(\mathbf{r}), \nabla n(\mathbf{r})) d\mathbf{r} \quad (2.8)$$

It has been demonstrated that GGA generally improves total energies, atomization energies, relative energies, and reaction energy barriers, compared to LDA (34; 35).

One notable variant of this approximation is the Perdew-Burke-Ernzerhof (PBE) form (34). The PBE form of GGA is used throughout as we are interested in the thermodynamic and kinetic barriers in the studies herein. J. P. Perdew, K. Burke, and M. Ernzerhof expressed the correlation energy E_C as:

$$E_C^{\text{GGA}}[n_{\uparrow}, n_{\downarrow}] = \int d\mathbf{r} n [\epsilon_C^{\text{hom}}(r_s, \zeta) + H(r_s, \zeta, t)] \quad (2.9)$$

where $n_{\uparrow}$ and $n_{\downarrow}$ denote up and down spin density, respectively; $\epsilon_C^{\text{hom}}(r_s, \zeta)$ is the correlation energy per electron of a homogeneous electron gas, which is a function of $r_s = (3/4\pi n)^{1/3}$, $n = k_F^3/3\pi^2$ (local Seitz radius) and $\zeta = (n_{\uparrow} - n_{\downarrow})/n$ (relative spin polarization); and

$$H = (e^2/a_0)\gamma\phi^3 \ln\{1 + \frac{\beta}{\gamma}t^2[\frac{1 + At^2}{1 + At^2 + A^2t^4}]\}, \quad (2.10)$$

where $A = \frac{\beta}{\gamma}[\exp \frac{\{-\epsilon_C^{\text{hom}}\}}{(\gamma\phi^3 e^2/a_0)} - 1]^{-1}$, $a_0 = \hbar^2/me^2$, $\beta \simeq 0.0066725$, $\phi(\zeta) = [(1 + \zeta)^{2/3} + (1 - \zeta)^{2/3}]/2$, $t = |\nabla n|/2_s n$, $k_s = \sqrt{4k_F/\pi a_0}$, and $\gamma = (1 - \ln 2)/\pi^2$.

H was derived by satisfying the following limits: (a) for slowly varying density ($t \rightarrow 0$): $H \rightarrow (e^2/a_0)\beta\phi^3 t^2$, (b) for rapidly varying density ($t \rightarrow \infty$): $H \rightarrow -\epsilon_C^{\text{hom}}$, and (c) under uniform scaling at high-density limit, the correlation energy must scale to a constant: $H \rightarrow (e^2/a_0)\gamma\phi^3 \ln[t^2]$.

On the other hand, the exchange energy is expressed as:

$$E_X^{\text{GGA}}[n_\uparrow, n_\downarrow] = (E_X^{\text{GGA}}[2n_\uparrow] + E_X^{\text{GGA}}[2n_\downarrow])/2 \quad (2.11)$$

and

$$E_X^{\text{GGA}} = \int d\mathbf{r} n \epsilon_X^{\text{hom}} F_X(s), \quad (2.12)$$

where $\epsilon_X^{\text{hom}} = -3e^2 k_F / 4\pi$,

$$F_X(s) = 1 + \kappa - \frac{\kappa}{1 + \mu s^2 / \kappa}, \quad (2.13)$$

with $\kappa = 0.804$, $\mu = \beta\pi^2/3 \simeq 0.21951$, and $s = |\nabla n|/2k_F n$.

Eq. 2.12 obeys the following limits: (a) for the spin unpolarized case, $\zeta = 0$, $F_X(0) = 1$, (b) for $\zeta = 0$ and small density variation around uniform density, LDA EXC is recovered:

$$F_X(s) \rightarrow 1 + \mu s^2, \quad (2.14)$$

and (c) $E_X^{\text{GGA}}[n_\uparrow, n_\downarrow] \geq E_X^{\text{GGA}}[n_\uparrow, n_\downarrow]$ or $E_X^{\text{GGA}}[n_\uparrow, n_\downarrow] \geq -1.679e^2 \int d\mathbf{r} n^{4/3}$

2.4. Effective Hubbard U corrections

Constrained LDA was proposed to address the shortcoming of LDA in predicting Mott insulators, as in strongly correlated materials such as transition metal oxides (36). It is based on the multiband Hubbard model, where for strongly correlated d or f electron, the Coulomb energy penalty to localize two electrons at one site is:

$$U = E(d^{n_i+1}) + E(d^{n_i-1}) - 2E(d^{n_i}), \quad (2.15)$$

known as the Hubbard parameter. LDA assumes weak interactions (U) compared to the bandwidth (W). Note that in the atomic limit, $U \gg W$. For Mott insulators, U is large enough to open a gap. V. I. Anisimov, J. Zaanen, and O. K. Andersen pointed out that the problem with LSDA lies in the homogeneous electron gas approximation where the spin dependence originates from the Hund's rule exchange (J), whereas for a Mott insulator, the Hubbard parameter U dominates (36). J is an order of magnitude smaller than U . Therefore, they proposed that a Hubbard-like interaction should be added in the total energy expression:

$$\begin{aligned} E = E^{\text{LDA}} &+ \frac{1}{2} \sum_{m,m',\sigma} U (n_{im\sigma} - n_i^0)(n_{im'-\sigma} - n_i^0) \\ &+ \frac{1}{2} \sum_{m,m' \neq m,\sigma} (U - J)(n_{im\sigma} - n_i^0)(n_{im'\sigma} - n_i^0) \end{aligned} \quad (2.16)$$

for occupation n_i of orbital m with spin σ , and average orbital occupation n_i^0 , e.g. $n_i^0 = \sum_{m,\sigma} n_{im\sigma}/10$ for d orbitals. The single-electron expression of the potential is:

$$V_{m\sigma} = V^{\text{LDA}} + U \sum_{m'} (n_{m'-\sigma} - n_i^0) + (U - J) \sum_{m' \neq m} (n_{m'\sigma} - n_i^0), \quad (2.17)$$

which may be used to solve Eq. 2.2. Note that here, n_i^0 occupation is used as a reference point.

Later, V. I. Anisimov *et al.* (37) modified Eq. 2.16, and therefore also Eq. 2.17, into

$$E = E^{\text{LDA}} - [UN(N-1)/2 - JN(N-2)/4] + \frac{1}{2} \sum_{m,m',\sigma} U_{mm'} n_{im\sigma} n_{im'-\sigma} + \frac{1}{2} \sum_{m,m' \neq m,\sigma} (U_{mm'} - J_{mm'}) n_{im\sigma} n_{im'\sigma}, \quad (2.18)$$

and

$$V_{m\sigma} = V^{\text{LDA}} + \sum_{m'} (U_{mm'} - U_{\text{eff}}) n_{im-\sigma} + \sum_{m' \neq m} (U_{mm'} - J_{mm'} - U_{\text{eff}}) n_{im\sigma} + U_{\text{eff}} \left(\frac{1}{2} - n_{im\sigma} \right) - \frac{1}{4} J, \quad (2.19)$$

respectively, where N is the number of electrons and $U_{\text{eff}} = U - \frac{1}{2}J$. The determination of $U_{mm'}$ and $J_{mm'}$ matrices, and U and J are described therein (37). It is clear from comparing 2.18 and 2.19 to 2.16 and 2.17, that the n^0 reference point is

abandoned, since the original assumption that LDA maps into a homogeneous solution of the Hartree-Fock equation with averaged orbital occupancy (as is shown in 2.16 and 2.17) does not describe well the difference between LDA and the exact density functional. Rather it is that the potential jumps discontinuously in the later, whereas the potential varies continuously in the former as N increases through integer values (37).

Following the work described above, M. Cococcioni and S. de Gironcoli proposed a simplified, rotationally invariant scheme of LDA+ U (2). In their approximation, they defined U_{eff} , or simply U , as $U - J$, or equivalently, assumed J to be negligible. Moreover, they used the rotationally invariant form that was later introduced (38). Eq. 2.18 was simplified into

$$\begin{aligned}
E &= E^{\text{LDA}} + \frac{1}{2}U \sum_I [\sum_{m,\sigma} (n_{imm\sigma}^I - \sum_{m',\sigma} n_{imm'\sigma}^I n_{im'm\sigma}^I)] \\
&= E^{\text{LDA}} + \frac{1}{2}U \sum_{I,m,\sigma} (n_{imm\sigma}^I)(1 - n_{imm\sigma}^I) \\
&= E^{\text{LDA}} + \frac{1}{2}U \sum_{I,\sigma} \text{Tr}[(n_{imm'\sigma}^I)(1 - n_{imm'\sigma}^I)] \tag{2.20}
\end{aligned}$$

with a matrix representation of the occupation on atom I given by

$$n_{imm'\sigma}^I = \sum_{\mathbf{k},v} f_{\mathbf{k}v\sigma} \langle \psi_{\mathbf{k}v\sigma} | P_{mm'}^I | \psi_{\mathbf{k}v\sigma} \rangle \tag{2.21}$$

where $\psi_{\mathbf{k}v\sigma}$ is the valence wave function of state $\mathbf{k}v$ with occupation number $f_{\mathbf{k}v\sigma}$, $P_{mm'}^I$ is a projection operator defined by the localized atomic orbitals of atom I ($P_{mm'}^I = |\varphi_m^I\rangle\langle\varphi_{m'}^I|$). Here I is introduced to include the contributions of all atom I subject to the Hubbard-like correction and we assume the same U for all atomic site I .

It follows from Eq. 2.20 and 2.21, that the eigenvalue for the valence state $\mathbf{k}v$, by differentiating Eq. 2.20 with respect to $f_{\mathbf{k}v\sigma}$, is:

$$\epsilon_{\mathbf{k}v\sigma} = \epsilon_{\mathbf{k}v\sigma}^{\text{LDA}} + U \sum_{I,m} \left(\frac{1}{2} - n_{imm\sigma}^I \right) \langle \psi_{\mathbf{k}v\sigma} | P_{mm}^I | \psi_{\mathbf{k}v\sigma} \rangle \quad (2.22)$$

Eq. 2.20 indicates that E is simply E^{LDA} for fully occupied or fully empty localized m orbital with spin σ of atomic site I , whereas the energy penalty is maximum at half occupation ($\frac{1}{8}U$). Eq. 2.22 stipulates that the orbital energy is shifted down at $> \frac{1}{2}$ occupation (favoring a response of adding electrons to the orbital), and shifted up at $< \frac{1}{2}$ (favoring a response of removing electrons from the orbital).

Further, they propose a method of calculating U through a linear-response approach (2). The Legendre transform of $E[n(\mathbf{r})]$ to $E[\{\alpha^I\}]$ is

$$\begin{aligned} E[\{\alpha^I\}] &= E[n(\mathbf{r})] + \sum_I \alpha^I n_i^I, \\ E^{\text{KS}}[\{\alpha^I\}] &= E^{\text{KS}}[n(\mathbf{r})] + \sum_I \alpha^{I,\text{KS}} n_i^I, \end{aligned} \quad (2.23)$$

where, $n_i^I = \sum_{\sigma} \mathbf{Tr}[n_{imm'\sigma}^I]$, and α^I and $\alpha^{I,\text{KS}}$ are localized perturbations at atom site I . The interacting and noninteracting density response functions relative to α are

$$\begin{aligned} \frac{\partial n_i^I}{\partial \alpha^J} &= \frac{\partial^2 E}{\partial \alpha^I \partial \alpha^J} = \chi^{IJ}, \\ \frac{\partial n_i^I}{\partial \alpha^{J,\text{KS}}} &= \frac{\partial^2 E^{\text{KS}}}{\partial \alpha^{I,\text{KS}} \partial \alpha^{J,\text{KS}}} = \chi_0^{IJ}. \end{aligned} \quad (2.24)$$

Thus, the effective parameter U (2) at atom site I using Eqs. 2.20 and 2.24 is

$$U = (\chi_0^{-1} - \chi^{-1})^{II}. \quad (2.25)$$

Thus from Eq. 2.24 and 2.25, one can find U at atom site I from a plot of n_i^I vs. α . In the linear regime, χ and χ_0 are the slope of the linear n_i^I vs. α plot from the resulting population after self-consistent calculation of the charge density in response to the perturbation and from a non-self-consistent calculation using the KS ground state density (2). This U can be used in solving Eq. 2.20

Note that the Hubbard-like parameter U method presented above can be employed for any EXC, *e.g.* PBE-GGA which is also limited to slowly varying densities and thus can benefit from the correction.

We implemented Eqs. 2.24 and 2.25 to find a suitable U value for Ti in BaTiO₃, which we used herein in describing the bulk and surface Ti. Fig. 2.1 shows the plot of n_i^{Ti} vs. α (eV) for a 2×2×2 supercell of BaTiO₃ (8 unit cells). The perturbation α is applied to one of the Ti sites (all Ti sites are equivalent) with a projection operator ($P_{mm'}^I$) built from the atomic Ti 3d orbitals. The KS equation is evaluated using the PBE-GGA approximation. A U value of 4.9 eV is calculated. This U parameter is used in chapters 3 to 5.

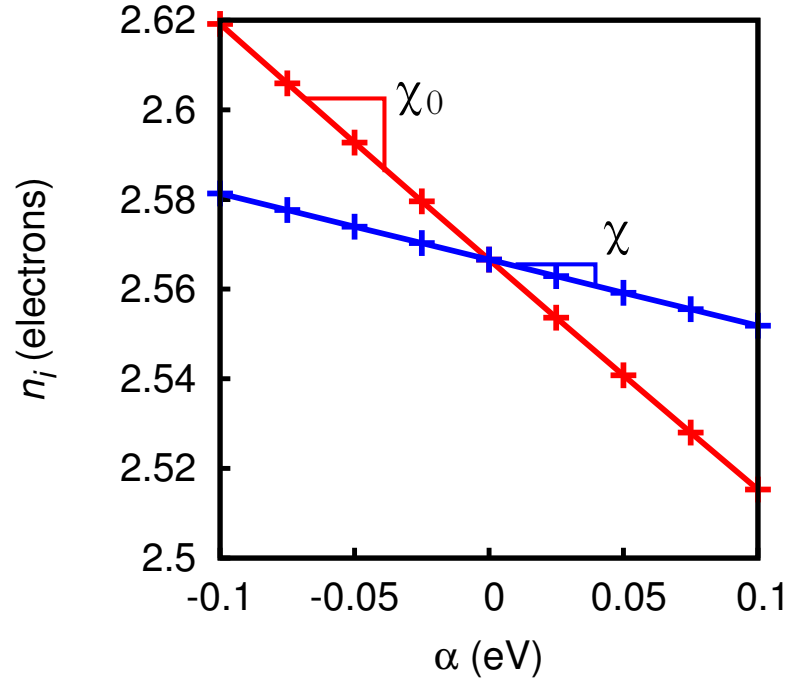


Figure 2.1: **Calculation of U value for Ti in BaTiO₃ from linear response method. (2)** Red line corresponds to n_i^{Ti} vs. $\alpha^{\text{Ti,KS}}$ with a slope $\chi_0^{\text{Ti}} = -0.519 \text{ eV}^{-1}$, whereas the blue line corresponds to n_i^{Ti} vs. α^{Ti} with a slope $\chi^{\text{Ti}} = -0.147 \text{ eV}^{-1}$. $U = (\chi_0^{-1} - \chi^{-1})$ is therefore 4.9 eV.

2.5. The Bloch theorem and the plane wave basis

An extended system (crystals) has an infinite number of electrons moving through an infinite number of nuclei. Bloch's theorem can be implemented to handle periodic systems which then makes the problem solvable.

According to the Bloch theorem, the wavefunction for an electron in a periodic potential has a generic form:

$$\psi_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}} \quad (2.26)$$

where, $u_{\mathbf{k}}(\mathbf{r})$ represents the cell periodic part, with the following property: $u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r}+\mathbf{l})$, where $\mathbf{l}$ is the translation vector of the lattice (39). Thus, $u_{\mathbf{k}}(\mathbf{r})$ can be represented as a Fourier series over the reciprocal lattice vectors $\mathbf{G}$ ($\mathbf{G}\cdot\mathbf{l}=2\pi m$, m is an integer).

$$u_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} e^{-i\mathbf{G}\cdot\mathbf{r}} \quad (2.27)$$

Therefore, Eq. 2.26 can be written as a sum of plane waves:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{G}} c_{\mathbf{k}-\mathbf{G}} e^{[i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}]} \quad (2.28)$$

The Bloch wavefunction (Eq. 2.28) maybe substituted to the KS equation (Eq. 2.2), where integration over $\mathbf{r}$ gives the central equation:

$$\sum_{\mathbf{G}'} \left[\frac{1}{2} |\mathbf{k} - \mathbf{G}|^2 \delta_{\mathbf{G}\mathbf{G}'} + \varphi(\mathbf{G}' - \mathbf{G}) + \mu_{xc}(n(\mathbf{G}' - \mathbf{G})) \right] c_{i,\mathbf{k}-\mathbf{G}'} = \epsilon_i c_{i,\mathbf{k}-\mathbf{G}} \quad (2.29)$$

where, $\varphi(\mathbf{G}' - \mathbf{G}) + \mu_{xc}(n(\mathbf{G}' - \mathbf{G}))$ is the Fourier transform of $\varphi(\mathbf{r}) + \mu_{xc}(n(\mathbf{r}))$. Note that i in the superscript refers to the imaginary number, while the subscript i refers to the index of the parameters corresponding to i th electron in the KS equation.

Eq. 2.29 can be solved by diagonalizing the equivalent matrix whose elements are given by the equation. The size of the aforementioned matrix depends on the choice of the plane wave energy cutoff ($E_{\text{cut}} = \frac{1}{2}|\mathbf{k} - \mathbf{G}_{\text{cut}}|^2$ in units of energy), which can be unreasonably large. This shortcoming may be amended by the use of pseudopotentials (see section 2.6 Pseudopotentials)

In principle, Eq. 2.29 needs to be solved for each $\mathbf{k}$ in the Brillouin zone, since each $\mathbf{k}$ contributes to the electronic potential in the periodic solid (40). However, there are an infinite number of $\mathbf{k}$, making it impossible to do so. To some approximation, however, the wavefunctions at $\mathbf{k}$ that are very close to each other are almost identical. Therefore, the solution at one $\mathbf{k}$ may represent the solutions in a region of $\mathbf{k}$ space. (40) In this work, the Monkhorst-Pack method (41) is employed to sample the Brillouin zone.

2.6. Pseudopotentials

To limit the number of planewave basis sets used to describe the wavefunctions (therefore make the resulting matrix from Eq. 2.29 manageable), artificial softening of the wavefunction in regions where atomic interactions, as in chemical bonding, is negligible maybe employed. Moreover, the core electronic structure maybe approximated to be constant. Therefore an effective screened potential maybe defined and constructed to represent the nuclear-and-core-electron and core-electron-core-electron interactions. Thus Eq. 2.28 is replaced by a set of pseudo valence wavefunctions and the potentials in Eq. 2.2 are replaced by pseudopotentials (PPs).

A pseudopotential (PP) is derived by inverting the radial KS equation (see Eq. 2.2), starting by solving for the screened (scr) potential using a pseudo(radial)wavefunction ($\mathbf{R}_{i,l}^P(\mathbf{r})$) (42):

$$[\varphi(\mathbf{r}) + \mu_{xc}(n(\mathbf{r}))]_{scr}^P = V_{scr,i,l}^P(r) = \epsilon_{i,l} - \frac{l(l+1)}{2r^2} + \frac{1}{2r\mathbf{R}_{i,l}^P(\mathbf{r})} \nabla^2 r \mathbf{R}_{i,l}^P(\mathbf{r}) \quad (2.30)$$

$\mathbf{R}_{i,l}^P(\mathbf{r})$ have the following properties (some criteria are conditional depending on the method used):

- (1) $\mathbf{R}_{i,l}^P(\mathbf{r}) = \mathbf{R}_{i,l}^{AE}(\mathbf{r})$ for $r \geq r_c$, here $\mathbf{R}_{i,l}^{AE}(\mathbf{r})$ is the all electron radial wavefunction and r_c is an arbitrary radial cut-off, where for $r < r_c$, $\mathbf{R}_{i,l}^{AE}(\mathbf{r})$ is replaced by a smoother and nodeless curve.
- (2) $\partial \mathbf{R}_{i,l}^P(\mathbf{r}) / \partial r = \partial \mathbf{R}_{i,l}^{AE}(\mathbf{r}) / \partial r$, $\partial^2 \mathbf{R}_{i,l}^P(\mathbf{r}) / \partial r^2 = \partial^2 \mathbf{R}_{i,l}^{AE}(\mathbf{r}) / \partial r^2$, for $r \geq r_c$.
- (3) $\int_0^\infty r^2 \mathbf{R}_{i,l}^{P*}(\mathbf{r}) \mathbf{R}_{i,l}^P(\mathbf{r}) d\mathbf{r} = \int_0^\infty r^2 \mathbf{R}_{i,l}^{AE*}(\mathbf{r}) \mathbf{R}_{i,l}^{AE}(\mathbf{r}) d\mathbf{r}$ (norm-conserving).
- (4) $\epsilon_{i,l}^P = \epsilon_{i,l}^{AE}$.

From the screened potential ($V_{scr,i,l}^P(r)$), an ionic pseudopotential ($V_{ion,i,l}^P(r)$) is calculated by subtracting the Hartree $[\varphi(\mathbf{r}) - v(\mathbf{r})]^P$ and exchange-correlation potential

$\mu_{xc}^P(\mathbf{r})$ of the pseudowavefunction from the $V_{scr,i,l}^P(r)$:

$$V_{ion,i,l}^P(r) = V_{scr,i,l}^P(r) - [\varphi(\mathbf{r}) - v(\mathbf{r})]^P - \mu_{xc}^P(\mathbf{r}) \quad (2.31)$$

The above equation suggests that each angular momentum component of the wave function will experience a distinct potential. Therefore, the ionic pseudopotential operator should be defined as (42):

$$\hat{V}_{ion}^P(r) = V_{ion,local}^P(r) + \sum_l V_{semilocal,l}(r) \hat{P} \quad (2.32)$$

where,

$$V_{semilocal,l}(r) = V_{ion,l}^P(r) - V_{ion,local}^P(r) \quad (2.33)$$

and $\hat{P}$ projects the l angular momentum component from the wavefunction. An arbitrary local potential (in principle, the pseudopotential associated with any of the angular momentum components) may be used.

To create a fully separable nonlocal pseudopotential from the semilocal potential Eq. 2.33, the method suggested by Kleinman and Bylander (KB) is employed (43):

$$\hat{V}_{nonlocal,l}^{KB}(r) = \frac{V_{semilocal,l}(r) |\mathbf{R}_{i,l}^P(\mathbf{r})\rangle \langle \mathbf{R}_{i,l}^P(\mathbf{r})| V_{semilocal,l}(r)}{\langle \mathbf{R}_{i,l}^P(\mathbf{r}) | V_{semilocal,l}(r) | \mathbf{R}_{i,l}^P(\mathbf{r}) \rangle}. \quad (2.34)$$

N. J. Ramer and A. M. Rappe then introduced a modified Eq. 2.34 referred to as designed nonlocal (DNL) pseudopotential (44):

$$\hat{V}_{nonlocal,l}^{DNL}(r) = \frac{(V_{semilocal,l}(r) - A) |\mathbf{R}_{i,l}^P(\mathbf{r})\rangle \langle \mathbf{R}_{i,l}^P(\mathbf{r})| (V_{semilocal,l}(r) - A)}{\langle \mathbf{R}_{i,l}^P(\mathbf{r}) | (V_{semilocal,l}(r) - A) | \mathbf{R}_{i,l}^P(\mathbf{r}) \rangle}. \quad (2.35)$$

and

$$\hat{V}_{ion}^P(r) = (V_{ion,local}^P(r) + A) + \sum_l \hat{V}_{nonlocal,l}^{DNL}(r) \quad (2.36)$$

where, A is an arbitrary function that may be designed to improve transferability of the pseudopotential.

There are several methods available to generate pseudo valence wavefunctions and pseudopotentials. In our work we employ the norm-conserving designed non-local PPs (45; 44; 46). The pseudowavefunctions were constructed following the Rappe-Rabe-Kaxiras-Joannopoulos (RRKJ) method (45).

In the RRKJ method, the pseudowavefunctions are expressed as sums of Bessel functions:

$$\begin{aligned} \mathbf{R}_l^P(r) &= F(r) + C(r) \\ F(r) &= \sum_{i=1}^4 \alpha_i j_l(q'_i r); \quad \frac{\partial j_l(q'_i r_c)/\partial r}{j_l(q'_i r_c)} = \frac{\partial \mathbf{R}_l^{AE}(r_c)/\partial r}{\mathbf{R}_l^{AE}(r_c)} \\ C(r) &= \sum_{i=1}^N \beta_i j_l(q_i r); \quad j_l(q_i r_c) = 0, \end{aligned} \quad (2.37)$$

where q'_i are wave vectors chosen such that the natural logarithmic derivative of the Bessel functions, $j_l(q'_i r)$, match that of the all-electron wavefunction, $\mathbf{R}_l^{AE}(r)$, at r_c . Wave vectors q_i , on the other hand, are chosen such that the Bessel functions, $j_l(q_i r)$, in $C(r)$ have nodes at r_c . The coefficients α_i s are chosen to normalize $\mathbf{R}_l^P(r)$ and make its first and second derivatives equal to that of $\mathbf{R}_l^{AE}(r)$ at r_c . The coefficients β_i s are constrained to minimize the kinetic energy beyond a chosen cutoff wave vector q_c , *i.e.* the following equation is minimized

$$- \int_0^\infty \mathbf{R}_l^{P*}(r) \nabla^2 \mathbf{R}_l^P(r) d^3r - \int_0^{q_c} q^2 |\mathbf{R}_l^P(q)|^2 d^3q. \quad (2.38)$$

Using the RRKJ scheme for the generation of PPs, r_c and q_c may be carefully chosen so that the transferability (by tuning r_c) and the kinetic energy error (by tuning r_c and q_c) are within the desired quality and tolerance.⁽⁴⁵⁾ Finally, the number of Bessel functions in $C(r)$ is chosen to be 10, *i.e.* $N = 10$ in Eq. 2.37, for good convergence.

2.7. Density functional theory and thermodynamics

At constant temperature T (isothermal) and pressure p (isobaric), the relevant thermodynamic potential is the Gibbs free energy G , which is the Legendre transform of the internal energy $E(S, V, N)$

$$G(T, P, N) = E - TS + pV \quad (2.39)$$

$$dG = dE - d(TS) + d(pV) = -SdT + Vdp + \mu dN \quad (2.40)$$

S , V , N , and μ are entropy, volume, number of moles/particles, and chemical potential, respectively.

The Gibbs-Duhem equation relates the chemical potential of component elements i (μ_i), T , and partial pressures (p_i):

$$\sum_i N_i d\mu_i = -SdT + V \sum_i dp_i, \quad (2.41)$$

It follows that $G = \sum_i \mu_i N_i$. Eq. 2.41 relates the intensive parameters μ , T , and p . For an element, μ_i could very well represent conditions that can be described by a combination of T and p_i (p) (which are usually experimentally measured).

2.7.1. Integration of thermodynamic potentials in isothermal conditions

For an ideal gas,

$$p_i V = N_i k_B T \quad (2.42)$$

where k_B is the Boltzmann constant. Substituting Eq. 2.42 into Eq. 2.41 and integrating over p at constant T yields

$$\begin{aligned}\int_{\mu_{i0}}^{\mu_i} N_i d\mu_i &= \int_{p_{i0}}^{p_i} V dp_i \\ \mu_i - \mu_{i0} &= \int_{p_{i0}}^{p_i} \frac{k_B T}{p_i} dp_i \\ &= k_B T \ln\left(\frac{p_i}{p_{i0}}\right)\end{aligned}\tag{2.43}$$

We use Eq. 2.43 to calculate the chemical potential of gas phase system i at a given T and p_i .

For condensed phases (liquid and solid), equations of state, such as Eq. 2.42 for an ideal gas, are not always available. However, for these systems, the term $\int_{p_0}^p V dp$ is usually small (≈ 0). This is due to their small isothermal compressibility $\beta = -1/V(\partial V/\partial p)_T$, and thus, $V(p_i) \approx V(p_0)$,

$$\mu_i - \mu_{i0} = \frac{V_i}{N_i} \int_{p_{i0}}^{p_i} dp_i = \frac{V_i}{N_i} (p_i - p_{i0}) = \frac{1}{\rho_i} (p_i - p_{i0})\tag{2.44}$$

where, ρ_i is the molar density of substance i . For example, for water with a molar density of about 0.056 mol/cm³, a change of +1 bar in pressure corresponds to 2 J/mol or 2×10^{-5} eV/particle of work at 298 K. Therefore, $\mu_i - \mu_{i0} = 0$ or $\mu_i = \mu_{i0}$ at any external pressure p at a given T for when β is small and ρ_i is large, as in liquids and solids.

2.7.2. Integration of thermodynamic potentials in isobaric conditions

At constant p , integration of Eq. 2.41 over T yields

$$\int_{\mu_{i0}}^{\mu_i} N_i d\mu_i = - \int_{T_0}^T S dT.\tag{2.45}$$

Eq. 2.45 requires an equation of state that relates S and T . Alternatively, we may begin with the relevant thermodynamic potential at constant pressure, which is the enthalpy H

$$H(S, P, N) = E + pV \quad (2.46)$$

$$dH = dE + d(pV) = TdS + Vdp + \mu dN \quad (2.47)$$

Eq. 2.46 may be integrated over T at constant p and N , using the isobaric heat capacity ($c_p = T(\partial S/\partial T)_p$), assuming no phase change:

$$\int_{H_0}^H dH = \Delta H = \int_{S_0}^S TdS = \int_{T_0}^T c_p dT \quad (2.48)$$

Isobaric heat capacities and integrated isobaric heat capacities are usually supplied in thermodynamic tables. Since

$$G = H - TS \quad (2.49)$$

$$\Delta G = N\Delta\mu = \Delta H - \Delta(TS) \quad (2.50)$$

then Eq. 2.48, together with known T -dependent S , will enable us to calculate $\Delta\mu$ as T varies.

To extend the DFT calculated energies in describing equilibrium conditions at well defined temperatures and pressures, we use Eq. 2.43 and 2.49 relying on experimental thermochemical tables, *e.g.* NIST-JANAF thermochemical tables (47; 48) as used herein.

In chapters 3 and 7, we calculated the Gibbs free energies of formation from DFT energies (reference states at 0K), and experimental entropies and integrated isobaric

heat capacities (1; 47) using

$$\Delta G_f = \Delta H_f - TS + \sum_{i=1}^n c_i [H_i(T) - H_i(0 \text{ K})] \quad (2.51)$$

for a substance composed of n type(s) of element(s). Here c_i and $[H_i(T) - H_i(0 \text{ K})]$ are the stoichiometric coefficient and the integrated isobaric heat capacity of reference element i , and ΔH_f and S are the enthalpy of formation (approximated by the DFT calculated formation energy) and entropy (obtained from the thermodynamic tables) at T , respectively. The calculated and experimental formation enthalpies of the relevant compounds herein are shown in Table F.3. These values are used for when GGA is used as in chapters 3 and 7.

2.7.3. Approximation of vibrational energies

The Helmholtz free energy due to adatom vibrations, F_{vib} , is given by:

$$F_{\text{vib}} = \sum_i^{\text{surface modes}} \left[\frac{\hbar\omega_i}{2} + k_B T \ln(1 - e^{-\frac{\hbar\omega_i}{k_B T}}) \right], \quad (2.52)$$

where the first term is the zero point energy (ZPE) while the second term is the resulting expression from the combined internal energy and entropy of vibration which bears the temperature dependence. k_B is the Boltzmann constant and T is temperature. The energy of these vibrational modes maybe approximated using the harmonic approximation and DFT. In chapters 4 and 6, the adatom vibrational normal modes were calculated via the diagonalization of the $3N_{\text{adatom}} \times 3N_{\text{adatom}}$ mass-weighted Hessian matrices (49). In chapter 4, the elements of the matrices were obtained from the linear equation fits to the Hellmann-Feynman forces *vs.* adatom displacements in the range between $[-0.01, +0.01]$ Å from the equilibrium position, with increments of 0.005 Å. Moreover, the ground state structures were further relaxed with a lower

force threshold of $0.002 \text{ eV/\AA}$ prior to these calculations. In chapter 3, a linear response method, based on random ionic displacements is performed, which is build into the Quantum Espresso (QE) code.(50)

2.8. Surface phase diagrams

The Gibbs free energy of surface I relative to the chemical reservoir(51) (which includes the bulk) is given by

$$\Omega^I = \frac{1}{A^I} [G^I - \sum_i N_i \mu_i], \quad (2.53)$$

where A^I is the surface area, and N_i is the number and μ_i is the chemical potential of compound or element i . Here surface I is composed of element(s) i .

Eq. 2.53 defines the energy of the surface relative to the prevailing chemical species. The chemical potential of each species are fixed due to the negligible size of the surface relative to the reservoirs. In the following section, the definition of the surface energies relative to arbitrarily chosen references will be first described. In this manner a universal surface phase diagram may be constructed independent of the chosen reservoir (except for the bulk that brings about the surface, which is assumed to be stable). In the next section, we independently define the stability domains of the chemical reservoirs relative to the references chosen in the construction of the surface diagram. Ultimately, combining the universal surface phase diagram and stability domains provides a complete picture of the surface phase transformation of a given material under well defined chemical conditions. We demonstrate this in the construction of the surface diagrams of perovskite-type $ATiO_3$ oxides using DFT-calculated energies.

2.8.1. ATiO_3 surface free energies

The surface Gibbs free energy Ω^I for the I th termination of $\text{PbTiO}_3/\text{BaTiO}_3$ is defined as

$$\Omega^I = \frac{1}{A^I} [\Delta E^I - n_{\text{Ba/Pb}}^I \mu_{\text{Ba}} - n_{\text{Ti}}^I \mu_{\text{Ti}} - n_{\text{O}}^I \mu_{\text{O}}], \quad (2.54)$$

where ΔE^I is the DFT total energy which may be computed with respect to the fixed base of the slab (*i.e.* Pt + BTO/PTO layers which are fixed during the structural optimization as in chapter 7), $n_{\text{Ba/Pb}}^I$, n_{Ti}^I , n_{O}^I denote the number of Ba/Pb, Ti, and O atoms in the slab (excluding those in the fixed base), and $\mu_{\text{Ba/Pb}}$, μ_{Ti} , and μ_{O} are their corresponding chemical potentials. It is convenient to measure the chemical potentials for each atomic species with respect to their standard states at 0K, corresponding to zero thermal vibrations (as in DFT), *i.e.* $\Delta\mu_a = \mu_a - E_a^{\text{std}}$. The reference state for oxygen is O_2 gas with $E_a^{\text{std}} = E_{\text{O}_2}^{\text{gas}}/2$ (52), while for the cations, it is their respective bulk elemental phases (bcc for Ba, fcc for Pb, and hcp for Ti). To emphasize, these are arbitrarily chosen phases, but conveniently chosen for being these elements' standard states, of which standard thermodynamic data are available.

The chemical potentials from Eq. 2.54 are not completely independent because we assume the bulk oxide is in equilibrium with the oxide surface (a reasonable assumption since without a stable bulk, the surface would not exist), imposing the following constraint:

$$\Delta\mu_{\text{Ba/Pb}} + \Delta\mu_{\text{Ti}} + 3\Delta\mu_{\text{O}} = \Delta G_f(\text{BTO/PTO}), \quad (2.55)$$

where $\Delta G_f(\text{BTO/PTO})$ is the formation energy of BTO/PTO relative to the 0K references (see section 2.7.2). Choosing the chemical potentials of O and Ba/Pb as

independent variables, we re-write Ω^I as,

$$\Omega^I = \phi^I + \Gamma_{\text{Ba/Pb}}^I \Delta\mu_{\text{Ba/Pb}} + \Gamma_{\text{O}}^I \Delta\mu_{\text{O}}, \quad (2.56)$$

where $\phi^I = [\Delta E^I - n_{\text{Ti}}^I E_{\text{PTO/BTO}}^{\text{bulk}}]/A^I + \Gamma_{\text{O}}^I (\frac{1}{2} E_{\text{O}_2}^{\text{gas}}) + \Gamma_{\text{Ba/Pb}}^I (E_{\text{Ba/Pb}}^{\text{bulk}})$, $\Gamma_{\text{Ba/Pb}}^I = -(n_{\text{Ba/Pb}}^I - n_{\text{Ti}}^I)/A^I$, and $\Gamma_{\text{O}}^I = -(n_{\text{O}}^I - 3n_{\text{Ti}}^I)/A^I$ are all intrinsic properties for each surface termination that are independent of the chemical environment.(17)

2.8.2. $ATiO_3$ bulk stability boundaries

The stability range of the ABO_3 phase is restricted due to the formation of other competing phases such as $\text{Ti}^{\text{bulk}}(\text{hcp})$, $\text{Ti}_2\text{O}_3(\text{corundum})$ and $\text{TiO}_2(\text{rutile})$ for both BTO and PTO, $\text{Ba}^{\text{bulk}}(\text{bcc})$, $\text{BaO}(\text{rock-salt})$ and $\text{BaO}_2(\text{tetragonal})$ for BTO, and $\text{Pb}^{\text{bulk}}(\text{fcc/liquid})$, $\text{PbO}(\text{tetragonal/orthorhombic})$, and $\text{PbO}_2(\text{rutile})$ for PTO. If we assume that during annealing there is no precipitation on the surface of these secondary phases, then the A -cation and oxygen chemical potentials have to satisfy the following inequalities:

$$\Delta\mu_A < \Delta G_f(A); \quad (2.57)$$

$$\Delta\mu_A + 3\Delta\mu_O > \Delta G_f(ATiO_3) - \Delta G_f(\text{Ti}); \quad (2.58)$$

$$\Delta\mu_A + \Delta\mu_O < \Delta G_f(AO); \quad (2.59)$$

$$\Delta\mu_A + 2\Delta\mu_O < \Delta G_f(AO_2); \quad (2.60)$$

$$\Delta\mu_A + 1.5\Delta\mu_O > \Delta G_f(ATiO_3) - 0.5\Delta G_f(\text{Ti}_2\text{O}_3); \quad (2.61)$$

$$\Delta\mu_A + \Delta\mu_O > \Delta G_f(ATiO_3) - \Delta G_f(\text{TiO}_2), \quad (2.62)$$

where $\Delta G_f(A)$, $\Delta G_f(AO)$, $\Delta G_f(AO_2)$, $\Delta G_f(\text{Ti})$, $\Delta G_f(\text{Ti}_2\text{O}_3)$ and $\Delta G_f(\text{TiO}_2)$ are the Gibbs formation energies of A , AO , AO_2 , Ti , Ti_2O_3 , and TiO_2 , respectively,

relative to the 0K reference states (see section 2.7.2). The above inequalities are used to define the temperature dependent stability region of $ATiO_3$ in the chemical potential space.

We calculated the Gibbs free energies of formation needed in Eqs. 2.57-2.62 using Eq. 2.51. Fig. 2.2 shows the boundary lines for BTO and PTO at 300 K corresponding to the same phase boundary lines shown in Fig. 3.3 in chapter 3 and Fig. 7.1 in chapter 7 at different temperatures, unless otherwise specified.

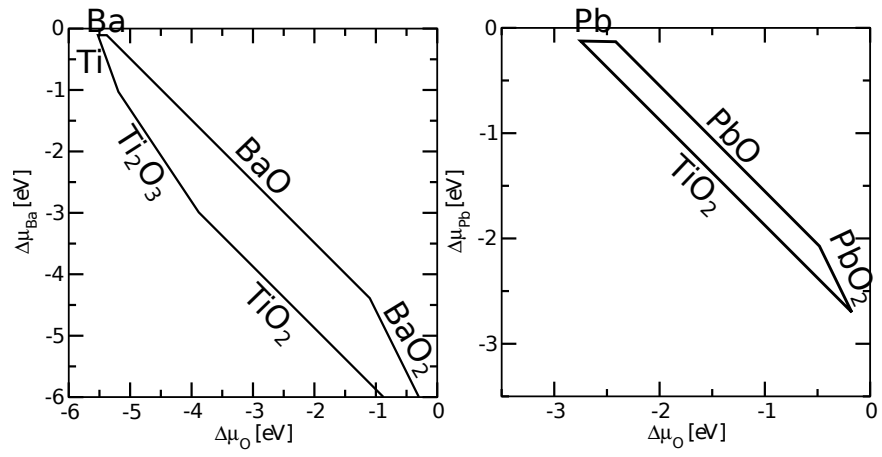
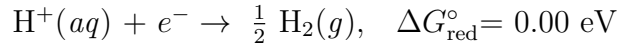


Figure 2.2: Stability domain for BTO(left) and PTO(right) at 300 K relative to their respective secondary phases.

2.9. Reduction and oxidation potentials calculated from DFT

We implement the method of evaluating redox catalysts employed in refs. (53; 54; 55; 56; 57). We employ density functional theory (DFT) and calculate the equilibrium reduction potential, $\varepsilon(i)$, for each elementary step i involved in the evolution of O_2 from water.(53; 54; 55; 56; 57) For a reaction consisting of n single-electron steps: $\eta = U - \varepsilon_{\text{eq}} = 1/n \sum_i^n [U - \varepsilon(i)]$. We can define the minimum $|\eta|$ at which all $[U - \varepsilon(i)]$ are ≥ 0 to favor oxidation, thus $\eta \geq \max[\varepsilon(i) - \varepsilon_{\text{eq}}] = \Delta\varepsilon_{\text{max}}$. Several *ab initio* studies of water splitting on oxide catalysts have shown that oxides with exceptional oxygen evolving activity have low predicted $\Delta\varepsilon_{\text{max}}$.(53; 54; 55; 56; 57)

To determine the reduction potentials of half-reactions we employ the method where no explicit modeling of proton or electron is necessary. The free energy of a standard hydrogen electrode (SHE), composed of 1M of aqueous H^+ in contact with 1 atm of H_2 gas, is usually used as a reference. The standard Gibbs free energy changes of the oxidation reactions, $\Delta G_{\text{ox}}^\circ$, are thus calculated relative to the SHE:



Given this, we may define the standard Gibbs free energy of $(\text{H}^+ + e^-)$, $G_{(\text{H}^+ + e^-)}^\circ$, as:

$$G_{(\text{H}^+ + e^-)}^\circ = \frac{1}{2} G_{\text{H}_2}^\circ. \quad (2.63)$$

$G_{\text{H}_2}^\circ$ is calculated from DFT and tabulated standard entropy data (see Table E.3 in Appendix E).

To avoid the calculation of the DFT energy of O_2 , the bonding energy of which is severely overestimated by DFT, we used the standard Gibbs free energy change of the reaction:



to get the expression for the standard Gibbs free energy of O_2 (56). At 298 K, the liquid phase H_2O is in equilibrium with 0.035 bar of vapor phase H_2O , the Gibbs free energy of liquid H_2O can be expressed as:

$$G_{\text{H}_2\text{O}(l)}^\circ = E_{\text{H}_2\text{O}(g)}^\circ + \text{ZPE}_{\text{H}_2\text{O}} + \text{TS}_{\text{H}_2\text{O}(g)}^\circ + kT \ln(0.035 \text{ bar}). \quad (2.64)$$

Therefore, we have:

$$\begin{aligned} \frac{1}{2}G_{\text{O}_2}^\circ &= 4.92 \text{ eV} + 2[E_{\text{H}_2\text{O}}^{\text{DFT}} - E_{\text{H}_2}^{\text{DFT}} + \Delta\text{ZPE}_{\text{H}_2\text{O}-\text{H}_2} \\ &\quad - T(S_{\text{H}_2\text{O}(g)}^\circ - S_{\text{H}_2}^\circ) + kT \ln(0.035 \text{ bar})] \end{aligned} \quad (2.65)$$

The Gibb's free energies, ΔG_{ox} , (in eV) for the oxidative conversion of hypothetical surface X to X' :



is given by:

$$\Delta G_{\text{ox}} = \Delta G_{\text{ox}}^\circ + \Delta G_{\text{SHE}}^\circ - n \cdot e \cdot U - 0.0592 \cdot n \cdot \text{pH} \quad (2.67)$$

where,

$$\Delta G_{\text{ox}} = E_{X'}^{\text{DFT}} - E_X^{\text{DFT}} + \Delta\text{ZPE}_{X'-X} + \frac{n}{2}G_{\text{H}_2}^\circ + rG_{\text{O}_2}^\circ - mG_{\text{H}_2\text{O}(l)}^\circ, \quad (2.68)$$

while the third term includes the effect of the applied potential U (e is the electron charge), and the fourth term shows the effect of the pH of the solution in contact with the oxidation reaction.

Given that the combined entropy of adsorbed species and the substrates are negligible relative to the entropy of the gas phase reactants and products (O_2 , H_2O , and H_2), we assume that the entropy contribution to the ΔG_{rxn} is solely associated with the latter species. Possible effects of a water overlayer on the surface were not considered here, and are presumed to be negligible considering that the degree of hydration of each adsorbate species is likely to be similar(56).

We also checked the binding energy overestimation errors when dealing with peroxo and superoxo ligands by calculating the formation energies of hydrogen peroxide and hydroperoxy radical. We found that the errors are small and change neither the identity of the rate-limiting step nor the overpotential.

In Fig. 2.3, the free energy diagram of a hypothetical four-electron($n = 4$) oxidation process:



is shown relative to the energy of R . The orange steps are the standard free energy reactions of the elementary processes. With an applied positive potential U , each step is lowered by $n \cdot e \cdot U$. Blue steps describe a situation when $U = \varepsilon_{\text{max}}$, where therefore $\eta = \max[\varepsilon(i) - \varepsilon_{\text{eq}}]$. This is when the minimum U required to make all steps spontaneous ($\Delta G_{\text{ox}}(i) \leq 0$) is applied. The yellow steps is for when $U > \varepsilon_{\text{max}}$.

The method described above is used in chapter 6 to evaluate the relative catalytic efficiency of the TiO_2 termination and a TiO_2 -rich reconstruction of the (001) surface of SrTiO_3 .

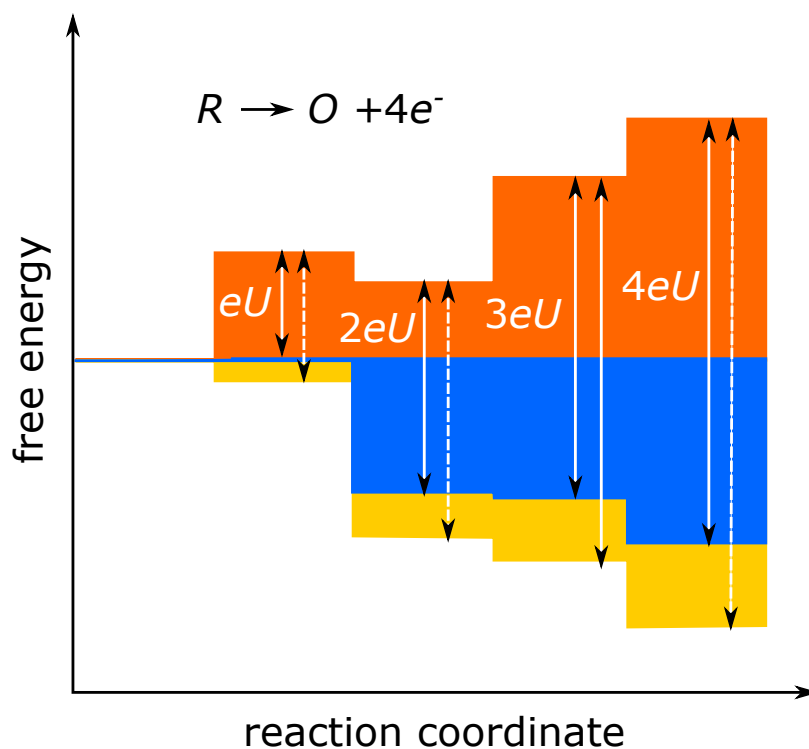


Figure 2.3: **Free energy diagram of a hypothetical four-electron oxidation of R to O showing the relative energies of the elementary steps.** The standard free energy changes for each step at zero applied potential ($U=0$) in orange. Applying a positive U lowers the free of all the steps. The blue bars show the energy steps when applying the minimum U that make all steps spontaneous, free energy ≤ 0 , and yellow bars show when applied U is in excess of the aforementioned minimum potential.

2.10. Guiding principles for modeling surface structures and chemistry of ionic compounds

Perhaps the most rigorous method of sampling the phase space is through a wide search of all possible configurations. This is ideal, but not always feasible. General chemical guiding principles are, fundamentally, the best tool a theoretical chemist/material scientist can have in narrowing chemical and configurational possibilities, although caution should be taken as not to overly bias the set. In the following sections, I discuss the basic guiding principle one can use to create an initial set of guess structures when dealing with structures and chemistry of ionic surfaces .

2.10.1. Pauling's rules

Although originally meant to explain structures of ionic crystals in the bulk (58), Pauling's rules have been successfully applied on surfaces as well.(59) The following is a summary of Pauling's rules (58):

Rule 1: The nature of the coordinated polyhedra -*for a cation surrounded by a polyhedron of anions, the bond distance between the cations and anions, and the coordination number of the cation, may be predicted by the sum and ratio of their ionic radii, respectively.*

Perhaps the most useful in defining the coordination motif of the polyhedral unit, this rule derived its physical meaning from the strong attractive Coulomb interactions between nearest neighbor cations and anions, the repulsive interactions between the anions, and the balance between the two. Table 2.1 summarizes the preferred polyhedron, derived from purely geometric arguments, given the ratios of the univalent cation to anion radii.(58)

Rule 2: The electrostatic valence principle -the charge of the anion is $-\zeta$, where ζ is the sum of the ratio of the charge (ez_i) and the coordination number (v_i) of the cations it is coordinated to ($\zeta = e \sum_i z_i/v_i$).

The $s = z_i/v_i$ defines the strength of the electrostatic valence bond. Here, anions with large negative charges would tend to occupy corners of shared polyhedra with large s . It is mentioned that the summation need not be complied to by all crystals exactly, but satisfied approximately. This is a powerful tool in deciding where to place an anion to accommodate its preferred charge. Additionally, if the chemical condition is fixed for the anion to retain its charge, the equation may reveal differences and changes in cations' oxidation states.

Rule 3: *Edge and face sharing between coordination polyhedra tend to distabilize the structure, especially for large cations with large valence charge and small coordination number, and even more so for structures that approach the minimum stability of their polyhedron (Rule 1).*

Rule 3 covers the extent of sharing permitted among cations/polyhedra. The sharing could be between corners (one anion shared), edges (two anions), or faces (three or more anions) of the polyhedra. The physical origin of this rule is the Coulombic repulsion between the cation centers, therefore larger cationic charges lead to more unfavorable sharing. Furthermore, the cation-cation distances decrease more between tetrahedrons than between octahedrons, thus sharing is less favorable for small coordination spheres. Deformation of the structure may alleviate this effect. Polyhedra with radii ratios closer to the minimum stability requirement (Table 2.1) will be less susceptible to deformation and thus less likely to break the rule.

Rule 4: The nature of contiguous polyhedra-for a crystal composed of

multiple types of cations, cations with large valence and small coordination tend to avoid sharing polyhedron with each other.

An extension of rule 3, the structure would tend to maximize the distances between high-charge, low-coordination cations to reduce repulsion.

Rule 5: The rule of parsimony-*the diversity in the types of constituent motifs tends to be small.*

This rule generalizes the tendency of most structures to homogenize ionic interactions. Chemically identical anions would want an identical electrostatic field, although not necessarily in identical sites. Additionally, cations of the same type would prefer a similar extent of polyhedral sharing.

Table 2.1: Coordination numbers predicted from the ratio of the cation and the anion radii

Polyhedron	Coordination no.	Minimum radius ratio
Tetrahedral	4	$(\sqrt{3}/\sqrt{2}) - 1 = 0.225$
Octahedral	6	$\sqrt{2} - 1 = 0.414$
Cubic	8	$\sqrt{3} - 1 = 0.732$

Taken from Pauling, L., *J. Am. Chem. Soc.* 1929, 51, p 1010 (Ref. (58)). Here L. Pauling suggested the use of univalent cation and anion radii.

2.10.2. Polyhedral motifs, and crystal and ligand field theories

Some of the common transition metal (M) cation-centered anionic (L=ligand) polyhedron motifs found in ionic solids are shown in Fig. 2.4. In the same figure, the corresponding crystal field splitting diagrams for each motif for d -block metals are also shown. Crystal field theory is an electrostatic approach that is commonly used to describe the energy splitting between the d orbitals of a transition metal cation as ligands (for example anions) surround it. In this approximation, the ligands are viewed as negative point charges approaching a positive metal center. Since the d orbitals are directional, electrons of orbitals along the direction of the ligands are electrostatically destabilized (repelled) by the electrons of the ligand and therefore raised in energy.⁽⁴⁾ Using this model, a rough estimate of how the electronic structure evolves as the coordination number of the metal and/or the spatial arrangement of the anions surrounding it changes. In chapter 3, we illustrate the utility of this model in predicting the electronic structure of the Ti adatoms on the $\text{TiO}_2(001)$ surface of reduced BaTiO_3 . Although it provides a highly intuitive picture, the theory lacks the ability to describe the nature of the metal-ligand bonding beyond an electrostatic picture.⁽³⁾

Ligand field theory is a molecular orbital approach that enables understanding of the bonding and energy levels in coordination compounds.⁽⁴⁾ The theory is based on the overlap between the atomic orbitals of the metals and of the ligands that depends on the orbital symmetry and energy. The resulting molecular orbital is thus a combination of the appropriate atomic orbitals.

The corresponding ligand field molecular orbital diagram for an octahedral complex is shown in Fig. 2.5. The designation of the orbitals depends on their degeneracies

(t = triplet, e = doublet, a/b= singlet symmetric/anti-symmetric with respect to the principal axis) and symmetries (g =gerade [even parity], u =ungerade [odd parity]). The corresponding octahedral splitting (Δ_O) ($d_{xy}, d_{xz}, d_{yz} \rightarrow d_{z^2}, d_{x^2-y^2}$ as in crystal field theory) is $t_{2g}(\text{non-bonding}) \rightarrow e_g$. This gap is narrowed by π -donor ligands ($t_{2g}(\pi^*) \rightarrow e_g$) and widened by π -acceptor ligands ($t_{2g}(\pi) \rightarrow e_g$, not shown) .

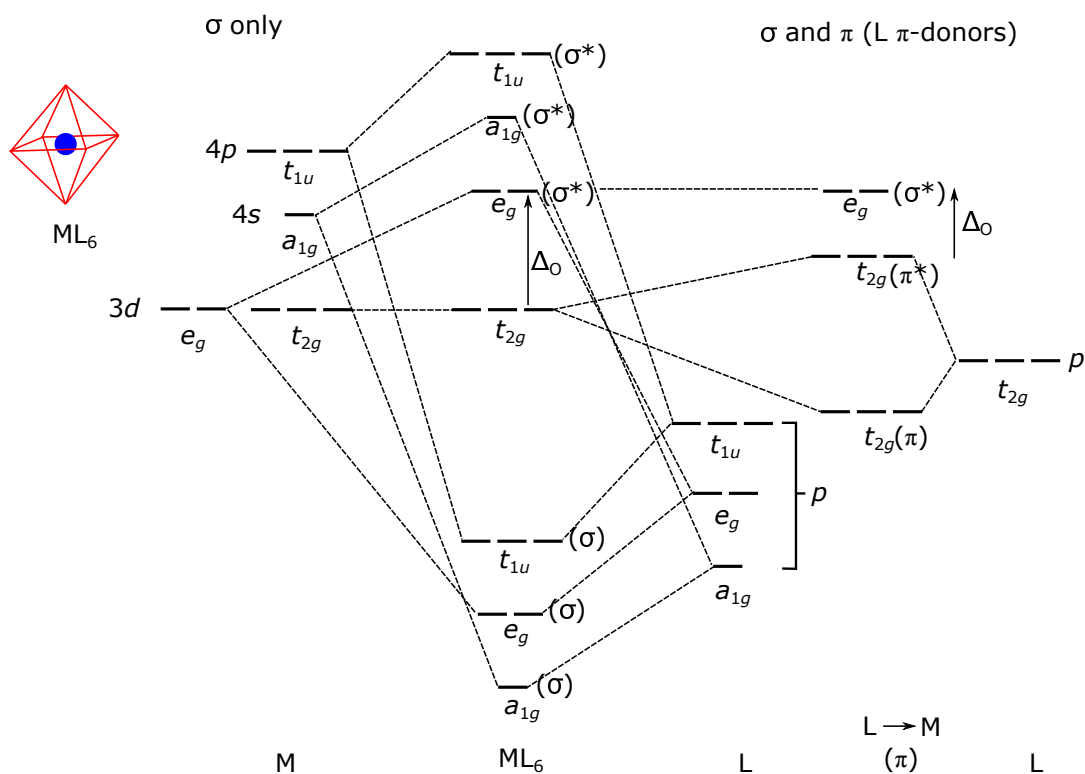


Figure 2.5: **Ligand field molecular orbital splitting diagram for octahedral complexes.** Left diagram shows σ only interactions between the metal M and ligand L. Right diagram shows the effect of a π -donor L (t_{2g} filled) to the non-bonding ML_6 t_{2g} orbitals. π donors lower the octahedral gap (Δ_O). Adapted from reference (4) Figs. 8-6 and 8-12.

2.10.3. Potential divergence and excess charges on surfaces

For surfaces, additional criteria exist for their stability. The electrostatic energy convergence criterion, proposed by P.W. Tasker in 1979 for ionic crystalline surfaces(60), is typically initially considered and satisfied. It has been demonstrated that when a net dipole moment points perpendicular to the surface, the potential diverges to infinity. Those surfaces with nominal perpendicular dipole moments are then subject to stabilization mechanisms, such as molecular adsorption, roughening, or more generally, reconstruction.(60)

To illustrate this schematically, we can define each atomic layers of the ionic lattice as either neutral or charged layers as in Fig. 2.6. According to Tasker's classification scheme, cases 1, 2 and 3 in Fig. 2.6 are the basic surface types (Types 1 to 3) for ionic crystals. (60) Their stability maybe derived from the resulting spatial electrostatic potential, where divergence means instability. The average potential along the direction perpendicular to the plane (z direction) is given by:

$$V_{av}(z) = \frac{2\pi qz}{A}. \quad (2.70)$$

Eq. 2.70 corresponds to the potential of a plane with in-plane charge density q/A with electric field $E = 2\pi q/A$. The potential does not converge with increasing distance z .

In case 1 of Fig. 2.6, each plane consists of an equal amount of positively and negatively charged ions, which has net zero charge q . In case 2, the system is composed of symmetric sets of charged planes $(-q, +2q, -q)$, where each set has net zero charge. In case 3, since the system is composed of alternating stacks of $+q$ and $-q$, each pair contributes a potential $V = 2\pi qd/A$, where d is the inter-planar distance. The potential then diverges outside the slab. Case 3' illustrates a stabilization scheme for

case 3. Addition of half q charge of opposite charge on each side cancels the average internal electric field.

Case 3' can be realized by introducing charge defects on both surfaces, which includes cationic and anionic vacancies and adunits, or via a hole or electron (surface metalization), producing surface states.

Case 1' considers the coordinated displacements of the ions on each layer (ferroelectric displacements) leading to a non-zero dipole directed towards the surface as in ferroelectric materials (see Introduction). In this case, the polarization charge per unit surface area is given by:

$$\frac{q}{A} = |\mathbf{P}_z| \quad (2.71)$$

where $\mathbf{P}_z$ is the net polarization perpendicular (z direction) to the surface. We explore the charge passivation mechanism due to bulk ferroelectric polarization in chapter 7 for BaTiO_3 and PbTiO_3 (001) surfaces.

It should be noted that the model here assumes fixed charges for the cations and anions. As we show in chapters 3, 4 and 7, this is not necessarily true when the cations and anions are capable of changing their oxidation states to accommodate excesses or deficiencies of any components, therefore reducing electrostatic instabilities.

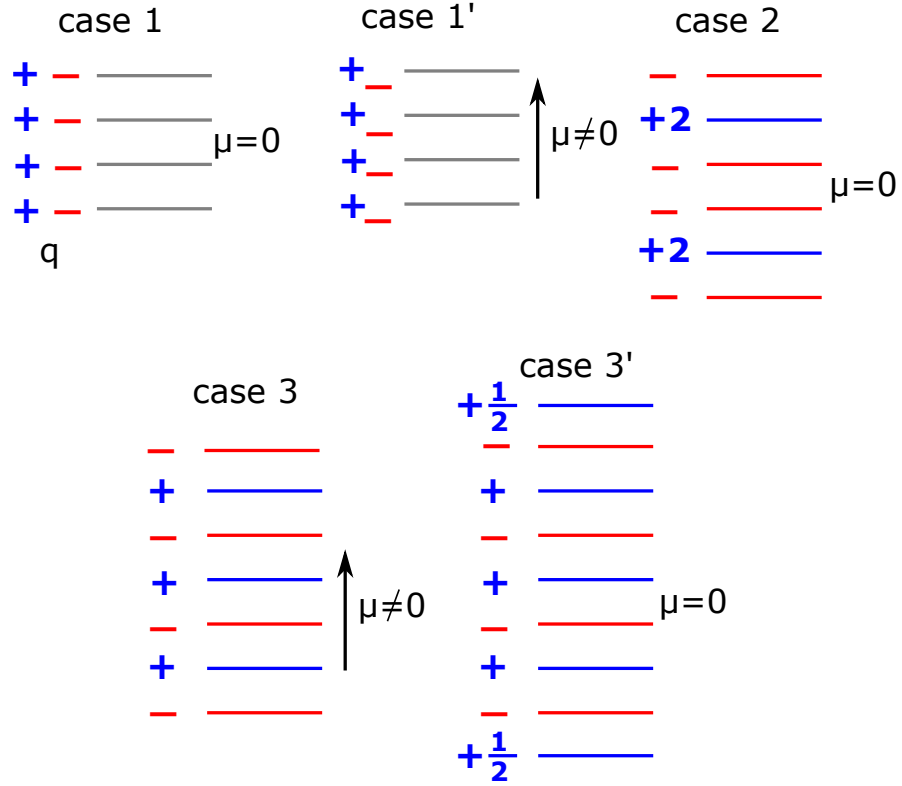


Figure 2.6: **Different charge (q) stacking cases with planes parallel to the surface.** Case 1: neutral layers; 1': "neutral" layers with ferroelectric displacements; 2: charged layers with zero dipole moment; 3: alternating charge with non-zero dipole moment; 3': charge-passivated case 3 with opposite half charges on each termination.

2.10.4. Acid-base chemistry on surfaces

It has been recognized that the reactivity of surfaces stems from presence of coordinatively unsaturated sites due to truncation of the continuity of interactions in the surface that are otherwise present in the bulk. There are perhaps a few widely recognized simple rules when it comes to determining potential acid and base sites on a surface:

- (1) exposed cations are potential Lewis acid sites
- (2) exposed anions are potential Lewis base sites
- (3) Protonated sites are potential Brønsted acid sites

The difficulty comes when determining the sites' acid and base strengths, and the list above is no where near complete. There are, however, empirically-derived qualitative characterizations of acid-base reactivity, one of which is the concept of hard and soft acids and bases (HSAB).

HSAB was conceptualized to explain reactions between metals and anions.⁽⁴⁾ With this scheme, cations (with some neutral species) are classified as either hard, borderline, and soft acids, while anions (including some neutral species) are classified as hard, borderline, and soft bases. However, these classifications should not be mistaken for their relative strengths as acids and bases, which should be considered in conjunction and is sometimes more important.⁽⁴⁾ However it has a very simple rule: hard-hard and soft-soft interactions are favorable and lead to insoluble salts where hard-hard interactions are more favorable.⁽⁴⁾ The classification is generally based on the polarizability of the species. The less polarizable (smaller ions), the harder. For a more thorough insight on nature of the interaction leading to these classifications, see Refs. (61; 62; 4). Table 2.2 shows the species according to the HSAB classification scheme. Naturally, this classification scheme is not without limitations.

It is tempting to apply this HSAB concept to surfaces, with one obvious caveat that on surfaces both acid and base may be equally present and exposed, forming acid-base pair sites.(63) In such a situation, the reactivity of one may affect the reactivity of the other. Indeed, it has been demonstrated that adsorption of both acid and base on adjacent sites (on basic and acid sites, respectively) of a surface is more favorable than the combined individual stability of exclusive adsorption of acid and base on the same surface.(63)

In chapter 5 we explore adsorption behavior of water (an acid, H^+ , and base, OH^- , source) on the reduced surface of $BaTiO_3$ with Ti adatoms composing the surface, acting as Lewis acids and water dissociation sites.

Table 2.2: Hard-soft classification of acids and bases

Hard	Soft	Borderline
Bases		
H ₂ O, OH ⁻ , F ⁻ CH ₃ CO ₂ ⁻ , PO ₄ ³⁻ , SO ₄ ²⁻ , Cl ⁻ , CO ₃ ²⁻ , ClO ₄ ⁻ , NO ₃ ⁻ , ROH, RO ⁻ , R ₂ O NH ₃ , RNH ₂ , N ₂ H ₄	R ₂ S, RSH, RS ⁻ , I ⁻ , SCN ⁻ , S ₂ O ₃ ²⁻ , R ₃ P, R ₃ As, (RO) ₃ P, CN ⁻ , RNC, CO C ₂ H ₄ , C ₆ H ₆ , H ⁻ , R ⁻	C ₆ H ₅ NH ₂ , C ₃ H ₅ N, N ₃ ⁻ , Br ⁻ , NO ₂ ⁻ , SO ₃ ²⁻ , N ₂
Lewis acids		
H ⁺ , Li ⁺ , Na ⁺ , K ⁺ , Be ²⁺ , Mg ²⁺ , Ca ²⁺ , Sr ²⁺ , Mn ²⁺ , Al ³⁺ , Sc ³⁺ , Ga ³⁺ , In ³⁺ , La ³⁺ , N ³⁺ , Cl ³⁺ , Gd ³⁺ , Lu ³⁺ , Cr ³⁺ , Co ³⁺ , Fe ³⁺ , As ³⁺ , CH ₃ Sn ³⁺ , Si ⁴⁺ , Ti ⁴⁺ , Zr ⁴⁺ , Th ⁴⁺ , U ⁴⁺ , Pu ⁴⁺ , Ce ³⁺ , Hf ⁴⁺ , WO ⁴⁺ Sn ⁴⁺ , UO ₂ ²⁺ , (CH ₃) ₂ Sn ²⁺ , VO ²⁺ , MoO ³⁺ , BeMe ₂ , BF ₃ , B(OR) ₃ Al(CH ₃) ₃ , AlCl ₃ , AlH ₃ , RPO ₂ ⁺ , ROPO ₂ ⁺ , RSO ₂ ⁺ , ROSO ₂ ⁺ , SO ₃ , I ⁷⁺ , I ⁵⁺ , Cl ⁷⁺ , Cr ⁶⁺ RCO ⁺ , CO ₂ , NC ⁺ HX (hydrogen bonding molecules)	Cu ⁺ , Ag ⁺ , Au ⁺ , Tl ⁺ , Hg ⁺ , Pd ²⁺ , Cd ²⁺ , Pt ²⁺ , Hg ²⁺ , CH ₃ Hg ⁺ , Co(CN) ₅ ²⁻ , Pt ⁴⁺ , Te ⁴⁺ Tl ³⁺ , Tl(CH ₃) ₃ , BH ₃ , Ga(CH ₃) ₃ , GaCl ₃ , GaI ₃ , InCl ₃ , RS ⁺ , RSe ⁺ , RTe ⁺ , I ⁺ Br ⁺ , HO ⁺ , RO ⁺ , I ₂ , Br ₂ , ICN, trinitrobenzene tetracyanoethylene chloranil, quinones, O, Cl, Br, I, N RO [·] , RO ₂ [·] , metal atoms bulk metals CH ₂ , carbenes	Fe ²⁺ , Co ²⁺ , Ni ²⁺ , Cu ²⁺ , Zn ²⁺ , Pb ²⁺ , Sn ²⁺ , Sb ³⁺ , Bi ³⁺ , Rh ³⁺ , Ir ³⁺ , B(CH ₃) ₃ , SO ₂ , NO ⁺ , Ru ²⁺ , Os ²⁺ , R ₃ C ⁺ , C ₆ H ₅ ⁺ , GaH ₃

Taken from Table 3 and 4 of R. G. Pearson, *J. Chem. Educ.*, 1968, 45 (9), p 581 (Ref. (61)); R means alkyl or aryl group.

2.11. STS and STM simulations.

The surface local density of states (LDOS) were simulated by summing the atomic orbital projected density of states (PDOS) of the atoms in the surface overlayer or adatoms, and the sub-surface layer (first bulk-like TiO₂ layer). The constant current STM images were simulated using,

$$STM(x, y) = \sum_{j=-y_{\max}}^{2y_{\max}} \sum_{i=-x_{\max}}^{2x_{\max}} g(i-x, j-y) \frac{f(i, j) - f_{\min}}{f_{\max} - f_{\min}} \quad (2.72)$$

$$g(a, b) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{a^2+b^2}{2\sigma^2}} \quad (2.73)$$

Eq. 2.72 describes a convolution of a Gaussian function, $g(a, b)$, with $\sigma = 1\text{\AA}$, and a linearly scaled function, $f(i, j)$, which is the discrete isosurface contour map (10^{-5} a.u.) of the tunneling current. Following the Tersoff-Hamann approximation (64) as implemented in Quantum espresso (QE) (50), the tunneling current is proportional to the charge density for bands within $[E_F - 1, E_F]$ where E_F is the Fermi energy (in eV). x and y refer to the in-plane grid coordinates. Eq. 2.72 is summed over 9 supercells, although the Gaussian decays with a full-width-at-tenth-maximum of about a unit cell lattice constant, $\approx 4\text{\AA}$.

CHAPTER 3 : The Ti-rich $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ surface reconstruction of $\text{BaTiO}_3(001)$

3.1. Introduction

The last decade has seen a resurgence of interest in ferroelectric compounds, due in a large part to recent developments in materials processing that enable new materials properties. Examples include strain controlled ferroelectric coupling (16), polarization controlled surface reactions (17; 18), surface chemical control of polarization (19; 20), and multi-ferroic behavior (21). Surface atomic and electronic structure is a crucial parameter that influences these phenomena, and although the surface science of transition metal oxides is a long standing field, its application to ferroelectric compounds has been limited. BaTiO_3 is considered the prototypical ferroelectric perovskite compound and a model system on which to examine ferroelectric interactions, yet, it is only recently that surface reconstructions have been observed on the (001) surface (65; 8; 66; 67). The determination of the detailed geometric and electronic structure of $\text{BaTiO}_3(001)$ is a precursor to understanding interactions at the surface of this compound and of ferroelectric materials in general.

Experimental evidence shows that BaTiO_3 undergoes a series of surface reconstructions with (1×1) , (2×1) , $c(2 \times 2)$, $(\sqrt{5} \times \sqrt{5})R26.6^\circ$, (3×1) , (3×2) , and (6×1) periodicity at increasing annealing temperatures in highly reducing conditions (8) (see Appendix A for an explanation of the naming convention). The identity of the $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ is also believed to be of the $\text{TiO}_2\text{-Ti}_x$ -type, because experimentally the (3×1) $\text{TiO}_2\text{-Ti}_{\frac{2}{3}}$ forms under similar experimental conditions (8). However, the $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ reconstruction has not been investigated theoretically

or experimentally in detail.

The present contribution explores the atomic and electronic structure of the ($\sqrt{5} \times \sqrt{5}$) $R26.6^\circ$ surface theoretically and experimentally using *ab initio* density functional theory (DFT) and scanning tunnelling techniques (STM and STS). We examine many structures and compositions with the same periodicity to identify the experimentally observed surface structures. Our DFT results explain the electronic contrast in STM images, and the surface atomic state contributions to the valence and conduction bands, which are corroborated by STS measurements. The surface model, consistent with thermodynamic stability analysis, confirms a TiO_2 with Ti adatom surface.

3.2. Methodology

3.2.1. Experimental

BaTiO_3 single crystals that are (001) oriented, one side polished with size $10 \times 10 \text{ mm}^2$ and 0.5 mm thick, are purchased at MTI Corporation. The UHV system (Omicron VT-AFT-STM) maintains a pressure of 2×10^{-10} Torr. After cutting, a $2.5 \times 10 \text{ mm}^2$ sample is mounted on a standard Omicron Ta sample plate (with hole) and held in place by spot welded Ta strips. The plate allows radiative heating in UHV carried out at 1100 K for 13 minutes, causing the crystal color to change from clear yellow to either dark blue or black (68). The as-received electrical resistance is nearly infinite and annealing creates donor states due to oxygen vacancies (69) lowering the resistance to approximately 100 M Ω . The crystal is then mounted in a double-stage standard sample plate that allows passage of current through the crystal, to achieve the high temperatures necessary for the present experiments. The sample is re-introduced to the UHV chamber and radiatively outgassed for 20 min at about 700 K, followed by sputtering at 1 KV and 1 μA for 20 minutes (70). To

obtain the desired surface structure the crystal was annealed at 1000 K for four minutes and then at 1300 K for five minutes. In this step the pressure increases temporarily to 1×10^{-8} Torr and afterwards rapidly decreases to the UHV working pressure. STM measurements were carried out using electrochemically etched W tips. The single crystal is grounded, and the tip has been biased at positive and negative electrostatic potential effectively probing filled and empty BaTiO_3 states, respectively. STS measurements are performed by measuring I - V curves from -3 to 3 V, with feedback loop turned off in UHV conditions. The analysis follows the procedure outlined by Feenstra (71) to obtain surface-LDOS from I - V curves.

3.2.2. Computational

Calculations are done using a planewave cutoff of 50 Ry. $4 \times 4 \times 1$ and $10 \times 10 \times 1$ Monkhorst-Pack(41) k -point mesh was used to sample the Brillouin zone, for structure relaxations and densities of state determination, respectively. We relaxed the atomic positions until the forces are less than 0.01 eV/Å in all directions for the atoms found at the top 3-4 atomic layers. The bottom 3 layers were fixed to a cubic structure. We used more than 15 Å of vacuum in the direction perpendicular to our slabs' surfaces to prevent artificial electric field interactions between images. The molecular oxygen energy is calculated from the experimental atomization energy of O_2 (48) at 0K and the DFT-calculated isolated O atom energy. The U value used in GGA+ U to correct the localization of the Ti 3d states, was found by employing the method proposed by Cococcioni *et al.* (2) using a bulk $2 \times 2 \times 2$ cubic BaTiO_3 supercell. Spin-polarized calculations are considered for calculating projected density of states (PDOS) and simulating scanning tunneling microscopy (STM) images.

The surface phase diagram is defined by determining the surface that minimizes

the following equation:

$$\Omega^i = \frac{1}{A^i} [G^i - n_{\text{Ba}}^i \mu_{\text{Ba}} - n_{\text{Ti}}^i \mu_{\text{Ti}} - n_{\text{O}}^i \mu_{\text{O}}], \quad (3.1)$$

where n_X^i denotes the number of X atom in the slab, and μ_X is its respective chemical potential. G^i is the Gibbs free energy of the slab, approximated by the computed DFT total energy, and A^i is the surface area. The number of degrees of freedom was reduced to two (μ_{Ba} and μ_{O}) by assuming that the surface is in equilibrium with the bulk BaTiO_3 . Furthermore, the chemical potential of each element is expressed relative to its 0 K standard state, denoted as $\Delta\mu_X$. See General methodology for further details. The surfaces are simulated using slabs with 6-7 atomic layers with the in-plane supercell periodicity fixed at $4.00 \times \sqrt{5}$ Å, where 4.00 Å is the BaTiO_3 experimental lattice constant, a . The DFT calculations are performed using Quantum ESPRESSO (QE) (50) package and the Perdew-Burke-Ernzerhof (PBE) form of the generalized gradient approximation (GGA). The core electronic states of the elements were described using norm-conserving pseudopotentials (45; 44; 46), generated using the OPIUM code (72). We did spin-polarized DFT+ U (2) ($U=4.9$ eV) calculations for the electronic structure studies.

Approximately 50 surface structures with $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ symmetry, resulting from introduction of oxygen vacancies on both BaO and TiO_2 surfaces, and adatoms (Ba/Ti) and Ti_xO_y -layers on the TiO_2 surface, were studied.

3.3. Results and discussion

3.3.1. Surface's spatial and electronic profile

STM empty state (Fig. 3.1a) and filled state (Fig. 3.1 b) images have atomically resolved features corresponding to the periodicity of the $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ surface reconstruction previously observed in BaTiO₃ (001) single crystals (8). Both Figs. 3.1a and b show white agglomerates that could be composed of BaO-like, BaO₂, or BaTiO₃ (73). Additionally, both figures have the same periodicity; however, the latter exhibits contrast that resembles a mesh whereas the former presents sharper circular atomic features. A representative experimental local density of states (LDOS) obtained from an I - V curve (Fig. B.1, Appendix B) in Fig. 3.2a was measured on a $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ surface. The values shown are average values drawn from several x - y measurements. The onset of the conduction band minimum (CBM) is located 0.59 eV above E_F , and thus the bulk gap is roughly estimated to be from -2.6 to 0.59 eV since the bulk band gap energy is 3.2 eV (74; 75). The I - V curve has negative static conductance that produces an extra gap from 1.51 to 1.86 eV above E_F in Fig. 3.2a which is not an artifact and will be analyzed in context with other BaTiO₃ surface reconstructions in a future publication (76). The energy between the top of the defect states and the CBM is 1.56 ± 0.11 eV, which is less than the bulk band gap. STS measures the local electronic structure, thus, having states below E_F and in the gap indicates that surface Ti atoms are indeed reduced. The surface states located 1.03 ± 0.09 eV below E_F are attributed to Ti $3d^{3+}$ and also are observed 0.9 eV below E_F in ultraviolet photoelectron spectroscopy measurements (77). The Ti $3d^{3+}$ surface states seen in our study are in close agreement with previous STS measurements on a surface addressed as multiple of $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ where defect states located at 0.8 and 1.2 eV below E_F have also been observed (78; 65). The Ti $3d$ -derived states

are a common constituent of the electronic structures of titanates. They are, for example, observed in TiO_2 (79; 80) approximately 1 eV below E_F . Additionally, the $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ reconstruction occurs in SrTiO_3 and shows similar defect states at approximately 1.2 eV below E_F , see for example Ref. (81).

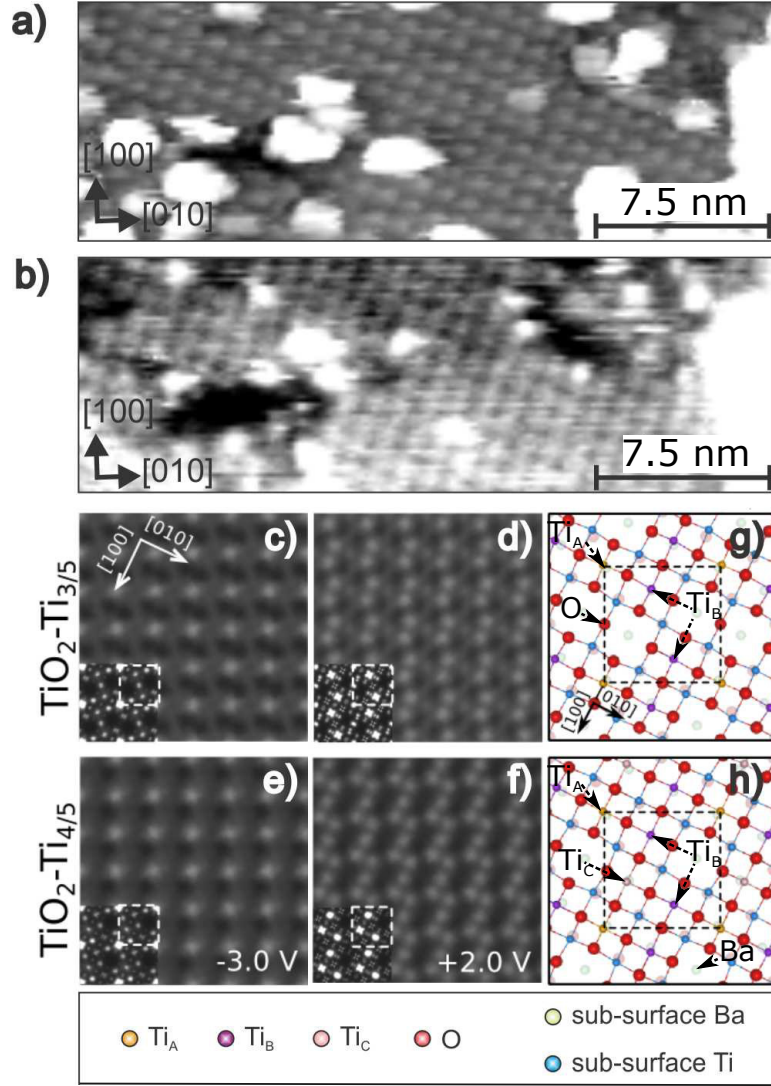


Figure 3.1: Experimental and calculated STM images of BaTiO_3 (001) $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ surface. (a) Empty-state image at bias -3.02 V and 0.17 nA, 30 nm $\times$ 10 nm, (b) Filled-state image at bias 2.09 V and 0.17 nA, 30 nm $\times$ 10 nm. Simulated STM (5); (c) and (d) are the empty (3 eV above E_F) and filled (2 eV below E_F) state images for $\text{TiO}_2\text{-Ti}_{3/5}$, respectively. (e) and (f) are the empty and filled state images for $\text{TiO}_2\text{-Ti}_{4/5}$, respectively. The white dash-lined squares denote the $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ unit, while the lower left insets are the raw images prior to computational smearing to mimic the finite tip resolution. (g) and (h) are the ball-and-stick models of $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ $\text{TiO}_2\text{-Ti}_{3/5}$ and $\text{TiO}_2\text{-Ti}_{4/5}$ reconstructions, with dashed lines denoting the $\sqrt{5} \times \sqrt{5}$ super cell. Yellow, purple, and pink: Ti adatoms, blue: sub-surface Ti, red: O, and pale green: Ba.

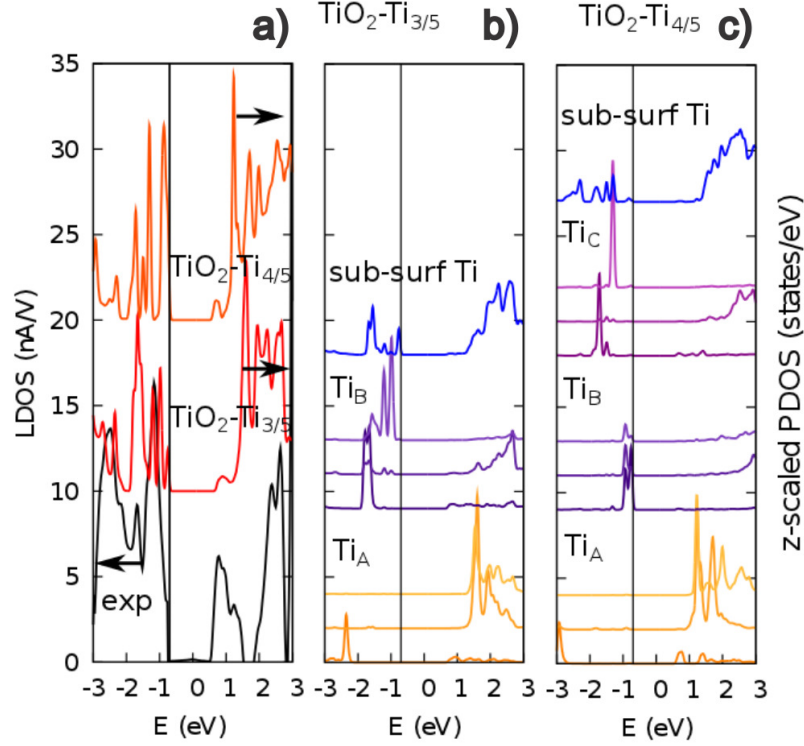


Figure 3.2: Experimental and calculated LDOS of BaTiO₃ (001) ($\sqrt{5} \times \sqrt{5}$) $R26.6^\circ$ surface. (a) Experimental surface-LDOS and calculated z-scaled projected densities of states (PDOS) (6) of ($\sqrt{5} \times \sqrt{5}$) $R26.6^\circ$ $\text{TiO}_2\text{-Ti}_{3/5}$ and $\text{TiO}_2\text{-Ti}_{4/5}$. The valence band maxima (VBM) of the experimental and calculated LDOS are aligned. (b) and (c) PDOS for Ti species found on the surface. The sets of three lines for each Ti adatom (Ti_A , Ti_B , and Ti_C) correspond to $d_{x^2-y^2} + d_{xy}$, $d_{xz} + d_{yz}$, and d_{z^2} , from top to bottom (lightest to darkest shade). For sub-surface Ti (found on the underlying TiO_2), the sum of the contribution of all sub-surface Ti states are shown. Some of the spectra are shifted along the y -axis for clarity.

3.3.2. Predicted atomic and electronic structure

The first principles surface phase diagram for surfaces with $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ symmetry is shown in Fig. 3.3a. The upper right corner is dominated by BaO and BaO-derived (BaO with O vacancy) surfaces, while the lower left corner contains TiO₂-derived surfaces: the TiO₂ double layer structure (TiO₂-DL), partially reduced TiO₂-DL (TiO₂-TiO _{$\frac{9}{5}$}), and Ti and TiO covered TiO₂ surfaces. The region of stability of BaTiO₃ at 1300 K with respect to other secondary phases (7), bordered by the white solid line, runs across the TiO₂-derived surfaces. Given the high temperature conditions of the experiment and the small free energy error due to neglect of entropic contributions from the surface, Fig. 3.3b shows the number of surface phases whose energies are within 0.10 eV per primitive unit cell ($\approx k_B T$) of the lowest energy surface, at any Ba and O chemical potentials.

Within the bulk stability boundary at 1300 K, several surface phases are possible as suggested by the stability analysis represented in Figs. 3.3a and b (see Appendix B for complete list). We calculated the surface LDOS, and empty and filled state STM images for TiO₂-DL, TiO₂-TiO _{$\frac{9}{5}$} (owing to their wide range of stability), TiO₂-Ti _{$\frac{1}{5}$} to TiO₂-Ti _{$\frac{4}{5}$} , and TiO₂-Ba _{$\frac{1}{5}$} and TiO₂-Ba _{$\frac{2}{5}$} (TiO₂-Sr _{$\frac{1}{5}$} having being proposed for the SrTiO₃(001) $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ reconstruction). The TiO₂-Ti _{$\frac{3}{5}$} and TiO₂-Ti _{$\frac{4}{5}$} proved to be most consistent with both the experimental LDOS spectrum and the STM images, and are identified as stable and close in energy by the DFT-thermodynamic calculations, and thus will be discussed here in more detail. For the structure, calculated LDOS and STM images of other phases, see Appendix B.

The ball-and-stick models for $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ TiO₂-Ti _{$\frac{3}{5}$} (hereafter TiO₂-Ti _{$\frac{3}{5}$}) and $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ TiO₂-Ti _{$\frac{4}{5}$} (hereafter TiO₂-Ti _{$\frac{4}{5}$}) are shown in Fig. 3.1g and h.

In both surfaces, Ti adatoms are situated at the hollow sites of the TiO_2 surface. For $\text{TiO}_2\text{-Ti}_{\frac{3}{5}}$, each Ti adatom has two Ti adatom neighbors and are arranged in a zigzag pattern where one type (Ti_A , yellow spheres) has its neighbors in a straight line, while the other (Ti_B , purple spheres) has its neighbors 90° to each other. In the case of $\text{TiO}_2\text{-Ti}_{\frac{4}{5}}$, all Ti-adatoms have the same number of Ti-adatom neighbors and neighbors' orientation. However, their electronic structures are different, thus resulting in different appearance in the empty and filled STM images, we annotate them as Ti_A (yellow spheres), Ti_B (purple spheres), and Ti_C (pink spheres).

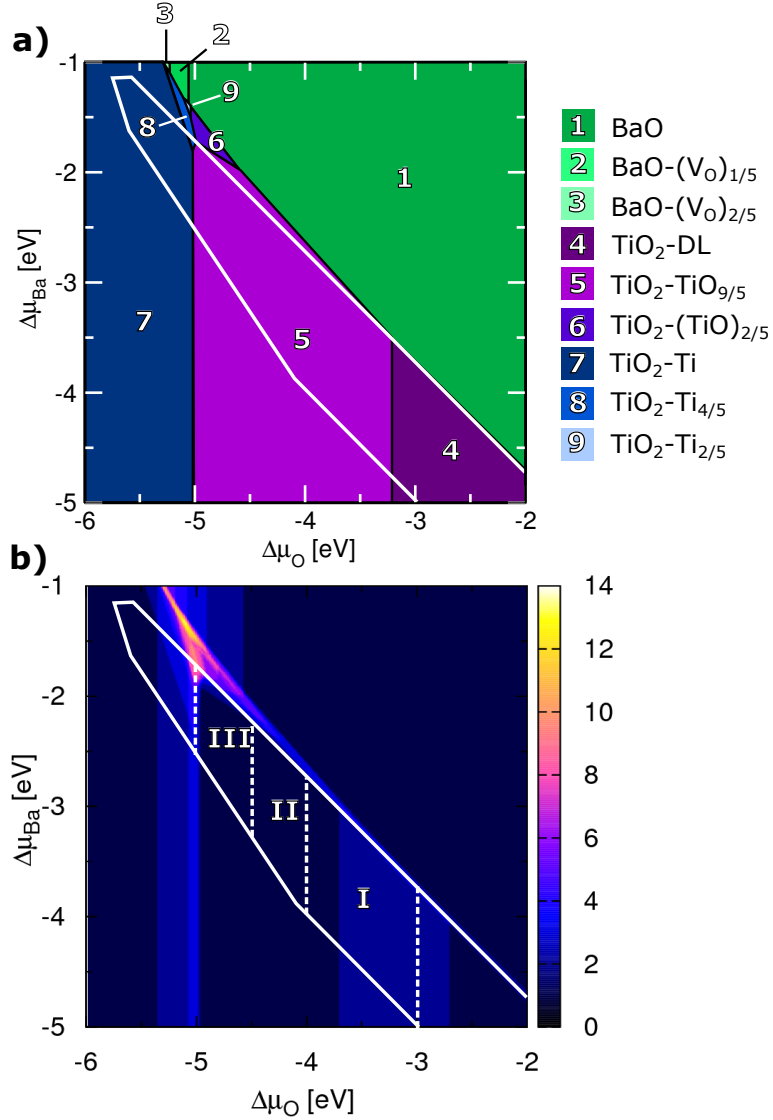


Figure 3.3: (a) Phase diagram generated from first-principles thermodynamic calculations as a function of the relative chemical potential of Ba and O. The white solid lines bound the stability region of BaTiO₃ relative to the secondary phases(7) at 1300 K. DL and V_O refer to the double layer structure and surface oxygen vacancy, respectively. (b) Surface phase population where we count the number of surface phases whose energies are within 0.10 eV/primitive unit cell of the lowest energy structure. Regions I to III correspond to $\log[p_{\text{O}_2}$ (torr)] in the range of -9 to -17, -17 to -20, and -20 to -24, respectively. The experiment is believed to be between $\log[p_{\text{O}_2}$ (torr)]=-10 to -27 (8).

Calculated empty and filled state STM images (5) of $\text{TiO}_2\text{-Ti}_{\frac{3}{5}}$ and $\text{TiO}_2\text{-Ti}_{\frac{4}{5}}$ are shown in Fig. 3.1 c-d and Fig. 3.1 e-f, respectively. For $\text{TiO}_2\text{-Ti}_{\frac{3}{5}}$, the empty state image has bright spots spaced $\sqrt{5}a$ from each other, corresponding to Ti_A adatoms. In the filled state image, a pair of bright spots corresponding to the Ti_B adatoms gives a columnar feature, where the columns are spaced $\sqrt{5}a$ apart. For $\text{TiO}_2\text{-Ti}_{\frac{4}{5}}$, the empty state image also has bright spots spaced $\sqrt{5}a$ from each other, associated with Ti_A . The filled state image shows three prominent continuous spots per unit-cell associated with Ti_B and Ti_C , with slight distinction between the shape of their contribution as shown in its inset STM.

The calculated local and projected densities of states (6) for the surfaces indicate that most of the states near E_F (above and below) are derived from d states of Ti adatoms, as shown in Figs. 3.2b and c. Ti_A adatoms compose most of the conduction band while Ti_B and Ti_C adatoms are mostly filled and are found in the energy gap. The LDOS for $\text{TiO}_2\text{-Ti}_{\frac{3}{5}}$ and $\text{TiO}_2\text{-Ti}_{\frac{4}{5}}$ have peaks at $\approx 1.44 \pm 0.01$ eV and $\approx 1.45 \pm 0.01$ eV below the surface conduction band, respectively, within the experimental uncertainty. The projected density of states explain the contrast between filled and empty state images, where Ti_A adatoms show in the empty state image while Ti_B and Ti_C show more prominently in the filled state image.

Annealing at extremely high temperature and UHV conditions is a reducing environment, increasing the metal cation-to-oxygen ratio at the surface and changing the Ba:Ti cation ratio as well. The experimental conditions are believed to be such that BaO forms surface agglomerates, which manifest as white cloud-like features in the STM images. Further, the experiment is estimated to be between $\log[p_{\text{O}_2} \text{ (torr)}] = -10$ and -27 , where the UHV base pressure serves as the upper limit, while the water partial pressure defines the lower limit (8). The phase diagram (Fig. 3.3a) predicts

the stability of $\text{TiO}_2\text{-Ti}_{\frac{4}{5}}$ at a point where BaO precipitates and at about $\Delta\mu_{\text{O}} = -5$ eV ($\log[p_{\text{O}_2} \text{ (torr)}] = -24$), where, according to Fig. 3.3b, a wide variety of phases may coexist at a 0.10 eV/primitive-unit-cell surface energy window. Despite possible coexistence, we assign the consistency of the $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ surface reconstruction to be of the $\text{TiO}_2\text{-Ti}_x$ type, based on the experimental STM and STS and computed STM images and LDOS spectra.

In both $\text{TiO}_2\text{-Ti}_{\frac{3}{5}}$ and $\text{TiO}_2\text{-Ti}_{\frac{4}{5}}$, the Ti adatoms have distorted square planar geometries, where adatoms are relaxed away from the bulk relative to the coordinating O atoms (Figs. 3.4a and b). Due to this distortion, the crystal field splitting is found to resemble a compromise between the splitting in a square-planar and in a square-antiprismatic geometry. The crystal field splitting profiles are shown in Fig. 3.4c, where the distortion leads to the stabilization of the d_{z^2} , d_{xy} and $d_{x^2-y^2}$ orbitals and destabilization of the d_{yz} and d_{xz} orbitals.

The occupied states for both surfaces are mostly derived from the d_{z^2} orbitals of Ti_A and Ti_B (and Ti_C in the case of $\text{TiO}_2\text{-Ti}_{\frac{4}{5}}$); and d_{xy} and $d_{x^2-y^2}$ orbitals of Ti_B (Ti_C in the case of $\text{TiO}_2\text{-Ti}_{\frac{4}{5}}$). In the calculated STM images, Ti_B and Ti_C adatoms exhibit the most intense signal in the +2 V tip bias image, where the d_{z^2} , d_{xy} and $d_{x^2-y^2}$ derived states are sampled. In the -3 V tip bias, the strongest response comes from Ti_A since most of the bands above E_F are derived from d orbitals of Ti_A . Although Ti_A has its d_{z^2} state partially occupied, Ti_B and Ti_C have more occupied d -states below E_F , making them more prominent in the filled state images. Therefore, the STM image of empty states shows the distinctive atomic features which are due to Ti_A , and the filled state image is better described by a mesh/columnar feature produced by Ti_B and Ti_C as described above. The compelling resemblance of the experimental and calculated STM images is the consequence of the different

electronic structure of the Ti adatoms producing filled and empty defect states in the gap.

3.3.3. Comparison with the $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ $\text{SrTiO}_3(001)$ reconstruction

$\text{SrTiO}_3(001)$ is chemically similar to $\text{BaTiO}_3(001)$ and also reconstructs into $(\sqrt{5} \times \sqrt{5})R26.6^\circ$. The surface has been proposed to be TiO_2 terminated with ordered Sr-adatoms at 0.20 atoms per unit cell coverage ($\theta = 0.20$, $\text{TiO}_2\text{-Sr}_{\frac{1}{5}}$) (82; 83; 84). Due to the common perovskite crystal structure and cationic oxidation state of BaTiO_3 and $\text{SrTiO}_3(001)$ we anticipate that our results are similar for both oxides at the $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ surface. The work of Kubo *et al.* presents DFT calculations with LDOS (82; 83; 84) but does not explore the thermodynamic stability of a Sr adatom surface relative to other surfaces. Our calculations, on the other hand, explore systematically several $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ surface phases. In view of similarities between BaTiO_3 and SrTiO_3 , we suggest further study of the composition and structure of the $\text{SrTiO}_3(001)$ $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ surface reconstruction.

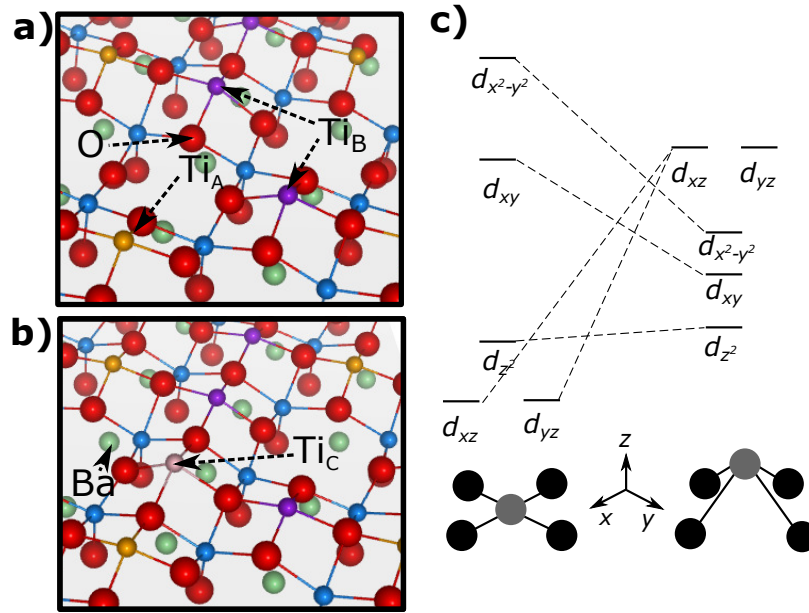


Figure 3.4: A perspective view of the surface structure of $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ $\text{TiO}_2\text{-Ti}_{\frac{3}{5}}$ (a) and $\text{TiO}_2\text{-Ti}_{\frac{4}{5}}$ (b) showcasing the oxygen cage geometry of the Ti adatoms, see Figs. 3.1g and h for legend. (c) Crystal field splitting profile for square-planar (left) and distorted square-planar (right) geometries.

CHAPTER 4 : The thermodynamic and kinetic aspects of the coexistence of the $c(2\times 2)$ and $c(4\times 4)$ reconstructions on $\text{BaTiO}_3(001)$ surface

4.1. Introduction

There is renewed interest in BaTiO_3 and related oxides due to recent demonstrations of their versatile surface properties. *In-situ* ferroelectric poling has been shown to control surface reactions, (18) as well as the converse effect in which adsorbates control the polarization. (85; 86; 87) Complex metal oxide surfaces are interesting both from a fundamental perspective and for the promise they hold for practical applications. Compelling interest stems from the ability of transition metal cations to induce structural complexity and functional properties. (88; 89; 90; 91; 92; 93; 94; 95; 96; 97; 98; 99; 100; 101; 102; 103; 104; 105) Nevertheless, this family of materials represents an experimental and theoretical challenge. In perovskites the coexistence of different surface structures has been shown using STM, (88; 89; 90; 91; 92; 93; 94; 95) but the origin of such coexistence has not been mechanistically considered. In this study, we use electronic structure measurements in tandem with first principles density functional theory (DFT) to obtain the most precise atomistic model of the coexisting phases that we experimentally observe on BaTiO_3 . Additionally, we elucidate the atomic and electronic structures of two new phases, the $c(2\times 2)$ and $c(4\times 4)$ reconstructions of BaTiO_3 . We conclude that TiO and TiO-clusters allow the kinetic coexistence of the two reconstructions. We show that the $c(2\times 2)$ surface is a trapped kinetic phase while the $c(4\times 4)$ is the equilibrium thermodynamic phase, and explain their domain formation. Furthermore, we observe that at the meeting of these phases 1D coherent interfaces form. We precisely address the atomic details of the 1D coherent interfaces

between the phases.

Depending on thermochemical processing, BaTiO_3 develops a range of surface reconstructions; (1×1) , (2×1) , $c(2 \times 2)$, (3×2) , (6×1) (106), (3×1) , $(\sqrt{5} \times \sqrt{5})R26.6^\circ$, and $(\sqrt{13} \times \sqrt{13})R33.6^\circ$. (8; 107; 9) Each surface must be carefully considered in order to successfully model its composition. Here, determining the correct atomic structure involves the interplay of experimental and theoretical results where we employ the following four criteria; (1) DFT: from first principles thermodynamics we calculate the surface compositions with low free energy, (2) STM images: we compare STM simulations with experiment to find matching contrast variations, (3) electronic structure: from projected density of states (PDOS) we identify electronic spectral features of candidate structures, (4) Ti:O ratio: our previous studies (8; 9) provide an upper limit for the expected reduction of the structures in consideration.

The above mentioned criteria were employed to evaluate the structure of the smaller reconstruction ($c(2 \times 2)$), where the reasonable simulation size enabled us to explore a wide range in the chemical phase space (various compositions) in our DFT calculations. Based on chemical constraints, the established $c(2 \times 2)$ composition will point to the potential candidates for the coexisting $c(4 \times 4)$ phase as we illustrate below. This allowed us to limit the variations in the chemical composition of the $c(4 \times 4)$ structures, and we concentrated instead on structural permutations. To solve for the $c(4 \times 4)$ structure, we rely on (1), (2), and (3) as discussed above. In the present study, we elucidate the atomic and electronic structures of two new phases, the $c(2 \times 2)$ and $c(4 \times 4)$ reconstructions of BaTiO_3 , and measure and calculate that they can coexist. We determine the thermodynamic and kinetic factors that lead to this stabilization and precisely address the atomic details of coherent interfaces between the phases.

4.2. Methodology

4.2.1. Experimental

BaTiO₃ single crystals are (001) oriented and one side polished. The UHV system (Omicron VT-AFM-STM) operates at a pressure of 2×10^{-10} Torr, and at room temperature. The single crystal is radiatively heated in UHV, effectively reducing it. (68) After sputtering at 600 V and 0.5 μ A for 15 minutes (107) and two UHV annealing steps at 1100 K, we obtain the desired reconstruction. STS measurements are performed by measuring I - V curves from -2 to 3 V, with feedback loop turned off. To obtain surface-LDOS from I - V curves we follow the procedure outlined by Feenstra. (71)

4.2.2. Computational

The surfaces were simulated using slabs with six or seven atomic layers with the in-plane supercell periodicity fixed at $0.4 \times \sqrt{2}$ nm for $c(2 \times 2)$ and $0.4 \times 2 \times \sqrt{2}$ nm for $c(4 \times 4)$, where 0.40 nm is the BaTiO₃ experimental lattice constant (relaxed bulk lattice constant is 0.405 nm, $\approx 1\%$ compressive strain is introduced). Spin-polarized DFT calculations using a planewave basis set are performed using the Quantum ESPRESSO (QE) (50) package. Calculations are done using a planewave cutoff of 50 Ry. Exchange and correlation interactions were described using the Perdew-Burke-Ernzerhof (PBE) (34) form of the generalized gradient approximation (GGA) plus Hubbard-like effective U correction to the Ti 3d states (2) ($U=4.9$ eV (9)), unless otherwise stated. The core electronic states of the elements were described using norm-conserving pseudopotentials, (45; 44; 46) generated using the OPIUM code (72), and tested previously. (108) We relaxed the atomic positions until the forces are less than 0.03 eV/Å in all directions for the atoms in the top three or four atomic

layers while we fix the bottom three layers to a bulk cubic non-polar structure. We used ≈ 20 Å of vacuum in the direction perpendicular to the surface of the slab to prevent artificial interactions between images. The climbing image nudged elastic band method (109) was employed to calculate reaction barriers using GGA. We used $6 \times 6 \times 1$ and $14 \times 14 \times 1$ Monkhorst-Pack(41) k -point meshes to sample respectively the Brillouin zone for structure relaxations and DOS determination with $\sqrt{2} \times \sqrt{2}$ supercells. Appropriately scaled down k -point meshes are used for larger supercells. Calculations involving 10 atomic layers for $\sqrt{2} \times \sqrt{2}$ supercells confirmed convergence of the electronic structure at the surface.

The one dimensional isothermal phase diagrams, see Fig. C.2, as a function of the chemical potential of O, μ_{O} , were constructed starting from Eq. 2.54 (chapter 2, section 2.8). The Ti-enriching processes (Ar^+ sputtering plus annealing (110) and BaO vaporization) in addition to the more flexible oxidation state of Ti compared to Ba, suggest the preference for Ti-rich reconstructions in reducing environments. We thus assume that the surface is in equilibrium with the bulk BaTiO_3 and an oxide of Ti (TiO_2 or Ti_2O_3) due to the enrichment. We can then express the chemical potential of O with respect to $\text{O}_2(g)$ at 0 K as:

$$\mu_{\text{O}} = \Delta\mu_{\text{O}} + \frac{1}{2}E_{\text{O}_2(g)} \quad (4.1)$$

$$\mu_{\text{Ti}} = \frac{1}{x}\Delta G_{\text{Ti}_x\text{O}_y}^f + E_{\text{Ti}} - \frac{y}{x}\Delta\mu_{\text{O}} \quad (4.2)$$

$$\mu_{\text{Ba}} = \Delta G_{\text{BaTiO}_3}^f - \frac{1}{x}\Delta G_{\text{Ti}_x\text{O}_y}^f + E_{\text{Ba}} - \left(3 - \frac{y}{x}\right)\Delta\mu_{\text{O}} \quad (4.3)$$

$\Delta G_{\text{BaTiO}_3}^f$ and $\Delta G_{\text{Ti}_x\text{O}_y}^f$ are the formation energies of BaTiO_3 and Ti_xO_y , respectively, against the standard elemental reference states at 0 K: Ba (cubic fcc), Ti (hcp), and

$O_2(g)$. $\Delta\mu_O$ is evaluated as follows:

$$\Delta\mu_O = \frac{1}{2}[H_{O_2}(T) - H_{O_2}(0 \text{ K}) - TS_{O_2} + k_B T \ln(\frac{p}{p^\circ})] \quad (4.4)$$

where $H(T) - H(0 \text{ K})$ and S denote integrated isobaric heat capacity and entropy, respectively. k_B is the Boltzmann constant, T is the temperature, and p/p° is the ratio of the partial pressure and the standard pressure (1 bar) of O_2 . The O_2 energy, $E_{O_2(g)}$, has large errors when computed using PBE. To rectify this, we used instead the total energy of O_2 as computed from the experimental atomization energy of O_2 (48) and atomic O PBE energy. $\Delta G_{Ti_xO_y}^f$ can be extrapolated to finite temperatures using published entropy and integrated isobaric heat capacity of the oxides (47):

$$\Delta G_{Ti_xO_y}^f = \Delta E^f(\text{DFT}) + [H_{Ti_xO_y}(T) - H_{Ti_xO_y}(0 \text{ K})] - TS_{Ti_xO_y}. \quad (4.5)$$

It should be noted that the formation energy is always relative to the elemental reference states at 0 K. Consequently the enthalpy, entropy, and terms involving the reference states are not included in the expression.

Also, we express the surface energy of surface I relative to the bulk-like TiO_2 surface, which reduces the surface energy expression to:

$$\begin{aligned} \Delta\Omega^I = \frac{1}{A^I} [& (E^I - n_{Ti-\text{adatom}}^I E_{Ti} - n_{O-\text{adatom}}^I \frac{1}{2} E_{O_2(g)} - E^{TiO_2}) - n_{Ti-\text{adatom}}^I \frac{1}{x} \Delta G_{Ti_xO_y}^f \\ & - (n_{O-\text{adatom}}^I - \frac{y}{x} n_{Ti-\text{adatom}}^I) \Delta\mu_O] \end{aligned} \quad (4.6)$$

which is a function of $\Delta\mu_O$ alone. The free energy of the slab does not include the finite temperature enthalpy and entropy terms, $G(T)$. There are two extreme scenarios that can be drawn out. The first case is when $G(T)$ term of the surface is negligible thus

Eq. 4.6 holds, while the second case is when the difference between the $G(T)$ terms of the condensed phases (surfaces and bulk oxides) is negligible. The resulting phase diagrams for the two cases are shown in Fig Fig. C.2 in the main text, left and right respectively. Since $G(T)$ is largely governed by the vibrational internal energy and entropy in condensed phases, the real case is believed to be between the two aforementioned cases, *i.e.* $0 < G(T)_{\text{surf}} - G(T)_{\text{bulk}} < -G(T)_{\text{bulk}}$. This is because bonds are generally stiffer in the surface than in the bulk due to the reduced coordination, resulting in a less negative $G(T)$.

4.3. Results and Discussion

4.3.1. Surface Atomic Structures

Using DFT, we explore six structures of $\text{BaTiO}_3(001)$ surfaces exhibiting $c(2 \times 2)$ superstructures. These were selected in light of the results of past calculations involving a thorough investigation of the $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ reconstruction under reducing conditions. (9) We previously demonstrated that Ti-rich derivatives of the $\text{TiO}_2(001)$ surface have low surface free energies and produce electronic structure profiles consistent with experiment, whereas O vacancy or adatomic Ba models do not.

The experimental STM images of coexisting $c(2 \times 2)$ and $c(4 \times 4)$ phases are presented in Fig. 4.1a and b. Both phases are in registry with the substrate, with bright features that have periodicities of 0.57 and 1.16 nm for the $c(2 \times 2)$ and $c(4 \times 4)$, respectively. The $c(2 \times 2)$ atomic structures are the result of either the formation of a TiO_x overlayer [$\text{TiO}_2\text{-TiO}_2$ and $\text{TiO}_2\text{-TiO}_{3/2}$]; or the addition of TiO units [$\text{TiO}_2\text{-(TiO)}_{1/2}$], Ti adatoms [$\text{TiO}_2\text{-Ti}_{1/2}$], or both [$\text{TiO}_2\text{-Ti}_{1/2}(\text{TiO})_{1/2}$]; on a bulk-like TiO_2 surface. These structures are described in Appendix C, Fig. C.1, while the corresponding calculated STM images are shown in Fig. C.3. From comparison to the simulated STM

images alone, the $c(2\times 2)$ TiO_2 - TiO_2 surface can be disregarded since the spatial contrast variations are not consistent with the experiment. Though the calculations of the structurally related double-layer reconstruction TiO_2 - $\text{TiO}_{3/2}$ is similar to the experimental STM images, this composition is predicted to have a high surface energy within the experimental oxygen chemical potential range, μ_{O} [-2.63, -3.88 eV], see Appendix C Fig. C.2.

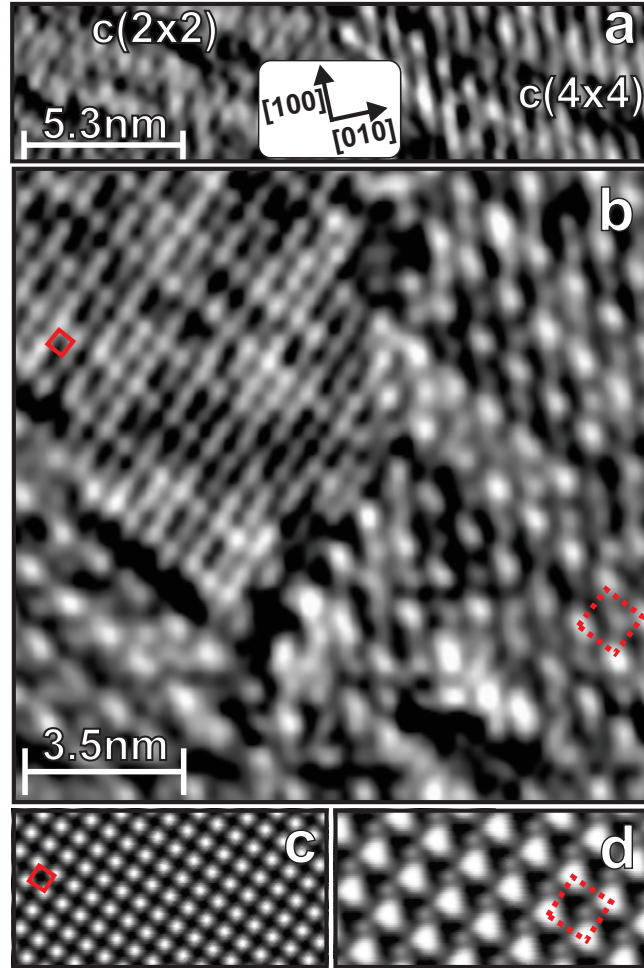


Figure 4.1: **Experimental and simulated STM images of the $c(2\times 2)$ and $c(4\times 4)$ surface reconstructions on $\text{BaTiO}_3(001)$.** The experimental STM parameters are: **a** (0.929 V, 0.15 nA) and **b** (1.008 V, 0.18 nA). Inset in **a** indicates crystallographic directions, that also apply to **b-d**. Upper left portion shows $c(2\times 2)$, while the rest shows $c(4\times 4)$. DFT simulated STM for $c(2\times 2)$, **c**, and $c(4\times 4)$, **d**. Red squares indicate supercells of the reconstructions.

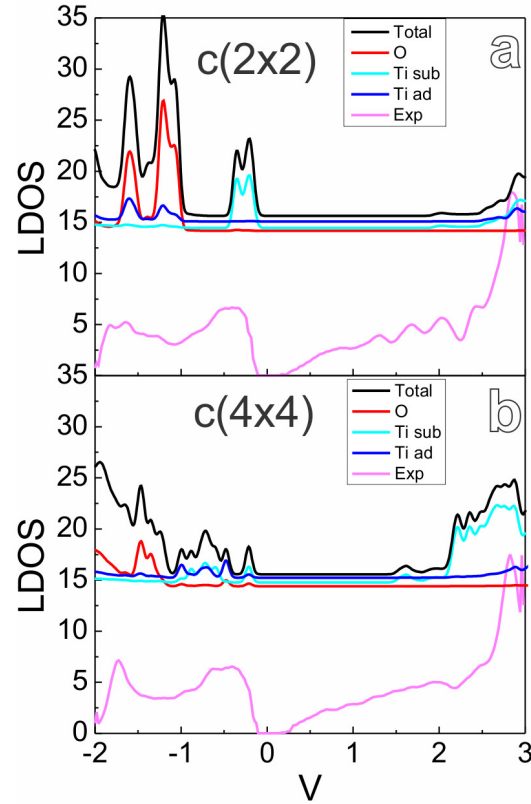


Figure 4.2: **Experimental and calculated surface electronic structures.** The measured LDOS spectra show narrowed surface band gaps and states near and below the Fermi level for both **a**, $c(2 \times 2)$, and **b**, $c(4 \times 4)$. These states indicate that the reconstructions are reduced, and DFT PDOS shows that they are due to occupied $3d$ orbitals of both sub-surface and surface Ti, as well as O $2p$ orbitals of the O adatoms.

To determine the atomic structure of the reconstructions, we measure the local density of states (LDOS) to obtain electronic signatures that indicate the extent of the surface reduction. Calculations of atomic projected density of states (PDOS) for the surface Ti, Ti sub-surface, and O adatoms provide further comparison with experiment. The LDOS of the reconstructions are presented in Fig. 4.2 **a** and **b**. The measured LDOS for both reconstructions have identical band gaps of 0.25 eV, with broad peaks associated with surface states below the Fermi level (0 V). These states are attributed to the occupied $3d$ states of reduced Ti species on the surface, narrowing the gap from 3.2 eV. (74; 75) Aside from the clear indication of surface reduction, the similarity of the two surface electronic structures suggests a similar or identical chemical composition. From the simulated PDOS (Appendix C, Fig. C.4), one can point out that excess Ti on the surface (*i.e.* higher Ti:O ratios) results in occupied Ti $3d$ -orbital derived states close to the valence band edge. Additionally, O adsorbates give rise to O $2p$ states that are higher in energy than the “bulk” O $2p$ states comprising the valence band. Incidentally, the lack of occupied Ti $3d$ orbitals in the TiO_2 - TiO_2 , and TiO_2 - $\text{TiO}_{3/2}$ supports our previous conclusion, in which we discarded these as candidate structures. Thus, these fully oxidized or lightly reduced surfaces, can not account for the significant density of states near the Fermi level observed in the experiment.

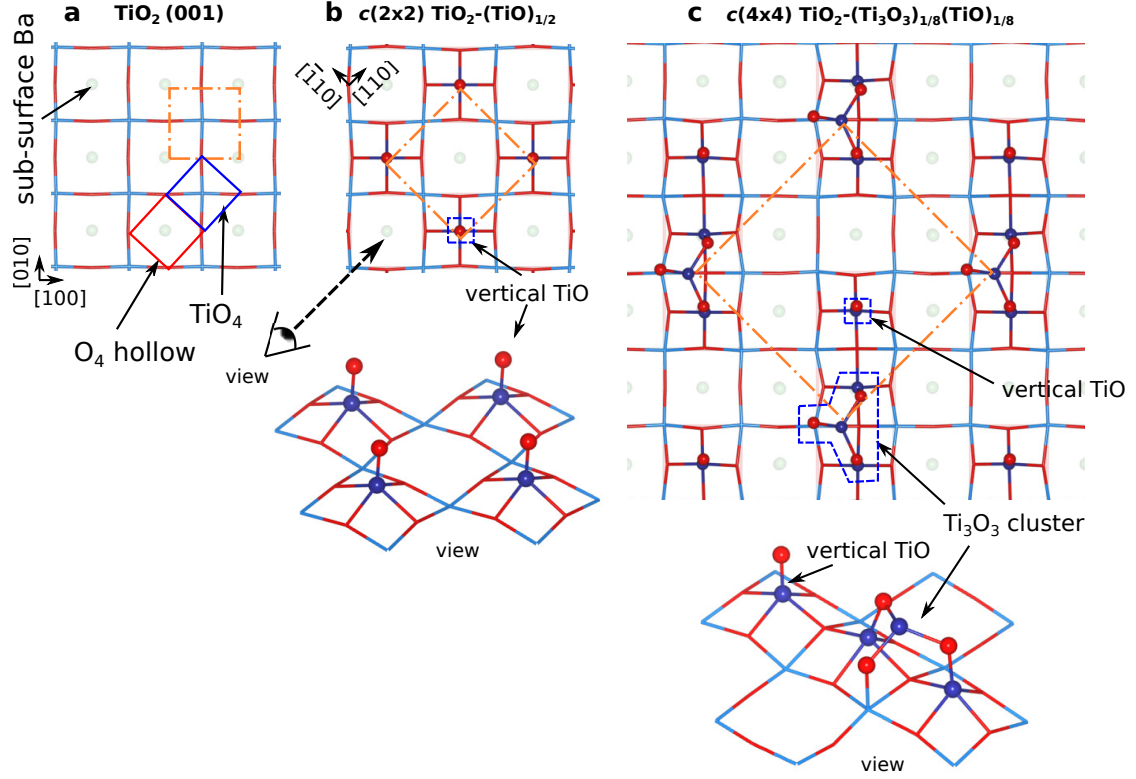


Figure 4.3: **Calculated atomic structures of the BaTiO_3 reconstructions.** Ball and stick models for the **a** bulk-like TiO_2 termination, **b** $c(2 \times 2)$ and **c** $c(4 \times 4)$ surfaces. The reconstructions exhibit TiO units adsorbed on a bulk-like TiO_2 surface. The TiO units are either isolated or in a cluster. Dark blue and red balls represent Ti and O atoms respectively. The dash-dotted lines mark the 1×1 , $\sqrt{2} \times \sqrt{2}$ and $2\sqrt{2} \times 2\sqrt{2}$ surface supercell in **a-c**, respectively. Angled views for both **b** and **c** are provided in the same viewing direction as shown in **b**.

The temperature at which the crystal is treated (1100 K) to form $c(2\times 2)$ and $c(4\times 4)$ is less than that used for the $(\sqrt{5}\times\sqrt{5})R26.6^\circ$ reconstruction (1300 K). (8; 107; 9) This indicates a less reduced surface in the present case. We can define the surface Ti:O ratio from the Ti and O content of the reconstruction, and the underlying bulk-like layer. Ti:O relates directly to the degree of surface reduction. More precisely, we determined the $(\sqrt{5}\times\sqrt{5})R26.6^\circ$ to be $\text{TiO}_2\text{-Ti}_{3/5}$, with Ti content of $1+3/5=8/5$, and O content of 2, giving a Ti:O ratio of 4:5. Thus, 4:5 defines the upper limit ratio of the reconstructions found below 1300 K. The Ti:O ratios for the candidates vary from fully oxidized 1:2 [bulk-like TiO_2 , $\text{TiO}_2\text{-TiO}_2$]; to moderately reduced 4:7 [$\text{TiO}_2\text{-TiO}_{3/2}$] and 3:5 [$\text{TiO}_2\text{-(TiO)}_{1/2}$]; to highly reduced 3:4 [$\text{TiO}_2\text{-Ti}_{1/2}$] and 4:5 [$\text{TiO}_2\text{-Ti}_{1/2}(\text{TiO})_{1/2}$]. In consequence, we disregard the [$\text{TiO}_2\text{-Ti}_{1/2}(\text{TiO})_{1/2}$] which has a 4:5 Ti:O ratio, inconsistent with the Ti:O progression: $c(2\times 2) < \sqrt{5}\times\sqrt{5}R26.6^\circ$ (4:5). (9)

The clustering behavior of the defects, as demonstrated by the $c(4\times 4)$, requires a defect unit that is energetically favorable to aggregate. TiO units demonstrate such capability, in contrast to Ti adatoms as further discussed below. Therefore, a Ti adatom model ($\text{TiO}_2\text{-Ti}_{1/2}$) is less well able to explain the $c(4\times 4)$ surface than a TiO adunit model, and its coexistence with $c(2\times 2)$ strongly implies a similar extent of oxidation for both reconstructions. The factors described above lead to the proposed $c(2\times 2)$ model, see Fig. 4.3**b**, with a surface stoichiometry of $\text{TiO}_2\text{-(TiO)}_{1/2}$, a TiO_2 surface with half TiO coverage. Although, the TiO adunit model has two structural variations, the calculated surface energies favors one (structure discussed here) over the other, see Appendix C. Fig. 4.3**a** shows the bulk-like (001) TiO_2 termination which serves as the underlying structure (“sub-surface”) of the reconstruction. This sub-surface layer is composed of corner shared TiO_4 units with O_4 hollow sites. The

$c(2\times 2)$ reconstruction is composed of vertically oriented TiO units, where each Ti is coordinated to four O atoms in the sub-surface (O_4 hollow as defined in Fig. 4.3a). The TiO units have nearest neighbors along $[110]$ and $[1\bar{1}0]$. These TiO units are observed as bright contrast in the simulated STM $c(2\times 2)$ image in Fig. 4.1c. We propose that in the experimental STM $c(2\times 2)$ image the bright features correspond to TiO units, upper left in Fig. 4.1b. The surface, LDOS spectrum shown in Fig. 4.2a, exhibits occupied Ti $3d$ -orbital derived states associated with the sub-surface Ti (light blue) and Ti adatoms (dark blue). The high energy O $2p$ peaks (red), between -2.0 and -1.0 eV can be ascribed to π bonding orbitals between the Ti and O adatoms in the vertical TiO units. High covalency in these bonds is indicated by the overlapping Ti $3d$ and O $2p$ projections in this energy range. The match between the simulation and measurement strongly supports this assignment of the $c(2\times 2)$ atomic structure.

From the similarity between the LDOS of the two reconstructions and their co-existence, we conclude that the $c(4\times 4)$ is a derivative of $c(2\times 2)$ resulting from some degree of agglomeration. The TiO units and Ti adatoms are positively charged defects that have partially donated their electrons to the sub-surface Ti atoms *via* their bonds with the sub-surface O atoms. Strong coulombic repulsion between ions of the same charge discourages clustering of Ti^{n+} defects. However, surface O atoms, as in the TiO units, provide an avenue for agglomeration, as they mediate interactions between these Ti^{n+} ions while simultaneously satisfying their divalent nature by forming more bonds. A variety of structures with different TiO unit orderings and a net stoichiometry of $TiO_2-(TiO)_{1/2}$ which lead to $c(4\times 4)$ periodicity have been explored, see Appendix C Fig. C.6. Among these structures, the surface $TiO_2-(Ti_3O_3)_{1/8}(TiO)_{1/8}$, whose structure is shown in Fig. 4.3c, exhibits the lowest surface energy, and its simulated STM images is the most consistent with experiment (Fig. 4.1d). The $c(4\times 4)$

is composed of Ti_3O_3 clusters and isolated vertically-oriented TiO units. The Ti_3O_3 cluster is formed by two vertical and one horizontal TiO units, arranged such that the cluster top has a TiO_3 subunit in a trigonal pyramidal geometry, and two Ti adatoms and one sub-surface Ti support the three O adatoms, Fig. 4.3c. It should be noted that the atomic features in the $c(4\times 4)$ surface are larger and brighter than those of the $c(2\times 2)$, and that the $c(4\times 4)$ contains an additional fainter off-center feature. The off-center vertical TiO unit and the Ti_3O_3 cluster are observed with bright contrast in the simulated STM image in Fig. 4.1d, with the Ti_3O_3 being the brighter of the two (compare with experimental STM image in Fig. 4.1b). The electronic spectrum of the $c(4\times 4)$ structure, Fig. 4.2b, exhibits similar occupied Ti $3d$ gap states as in $c(2\times 2)$, however with less overlap with the O adsorbate $2p$ states, indicative of reduced TiO bond covalency due to clustering.

Despite having similar electronic structure and the same composition in the two phases, the TiO unit and TiO clustering introduce significant chemical differences. The Ti atoms in the vertically oriented TiO units, as in the $c(2\times 2)$ structure is relatively inaccessible. Further, the O adatoms are unsaturated, subject to electrophilic attack to adopt a preferred two-fold coordination. The clustering of the TiO units into Ti_3O_3 , as in the $c(4\times 4)$ structure, results in an exposed three-fold coordinated Ti, that is ready for nucleophilic attack (reduced Ti species are oxophilic.) Conversely, the O adatoms in the cluster are less susceptible to reaction, having satisfied two-fold coordination. Considering the similarities and differences presented above, it is necessary to address the mechanisms that lead to the coexistence of the $c(2\times 2)$ and $c(4\times 4)$ reconstructions.

4.3.2. Coexistence of the Two Phases

The thermodynamics of coexistence

Since both $c(2\times 2)$ and $c(4\times 4)$ reconstructions have the same TiO coverage, there is no chemical driving force for inter-conversion. The relative energies are, therefore, a function of the Helmholtz free energy content associated with surface bond vibrations, see General methodology section 2.7.3. In Fig. 4.4a we show the temperature dependent relative surface energy of the two reconstructions. The $c(4\times 4)$ is approximately 0.16 eV/(1×1) surface cell, which is 0.32 eV/TiO, lower in energy than the $c(2\times 2)$ across all temperatures. The vibrational contribution to the Helmholtz free energy provides insight into surface stability. Vibrational density of states indicates that the $c(4\times 4)$ has a broader energy distribution in the low energy regime, than does the $c(2\times 2)$, see Fig. 4.4b and c. Consequently, the $c(4\times 4)$ has a more negative Helmholtz free energy of vibration. The $c(4\times 4)$ is more stable than $c(2\times 2)$ due to clustering that results in the valency increase of the O adatoms and softening of the surface vibrational modes. These considerations indicate that thermodynamic principles alone do not explain the experimentally observed coexistence of the $c(2\times 2)$ and $c(4\times 4)$ reconstructions, in thus pointing to the role of kinetic considerations.

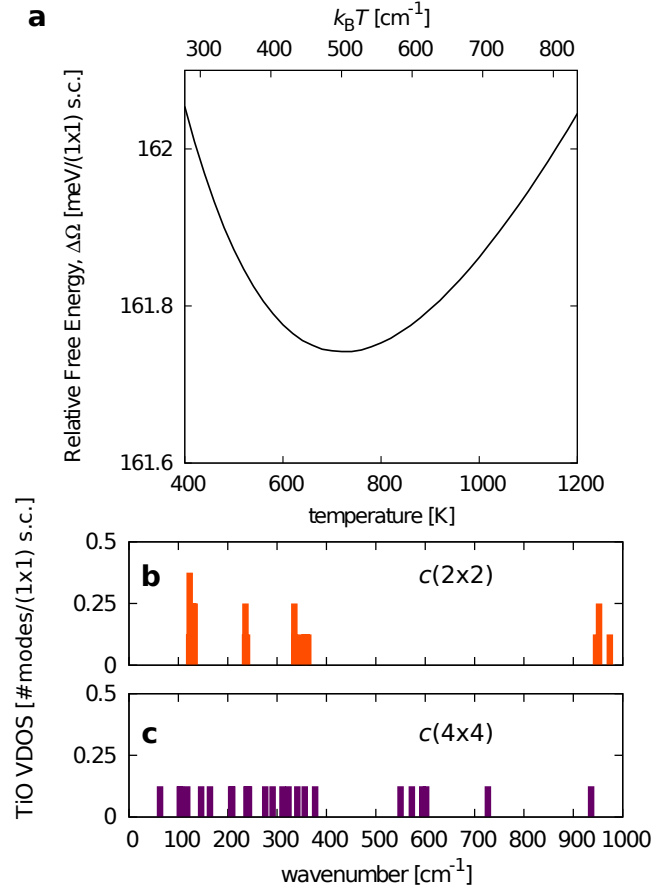


Figure 4.4: **Surfaces' relative free energy and adatomic vibrational DOS.** **a**, surface free energy of $c(2 \times 2)$ $\text{TiO}_2\text{-(TiO)}_{1/2}$ vs. $c(4 \times 4)$ $\text{TiO}_2\text{-(Ti}_3\text{O}_3)_{1/8}\text{(TiO)}_{1/8}$ ($\Delta\Omega$ in energy per (1x1) surface cell, black curve) as a function of temperature. Also shown in the upper axis is thermal energy ($k_B T$) in wavenumbers. Surface TiO units' vibrational DOS (number of modes per (1x1) surface cell) for, **b**, $c(2 \times 2)$ $\text{TiO}_2\text{-(TiO)}_{1/2}$ (simulation size $2\sqrt{2} \times 2\sqrt{2}$); **c**, $c(4 \times 4)$ $\text{TiO}_2\text{-(Ti}_3\text{O}_3)_{1/8}\text{(TiO)}_{1/8}$.

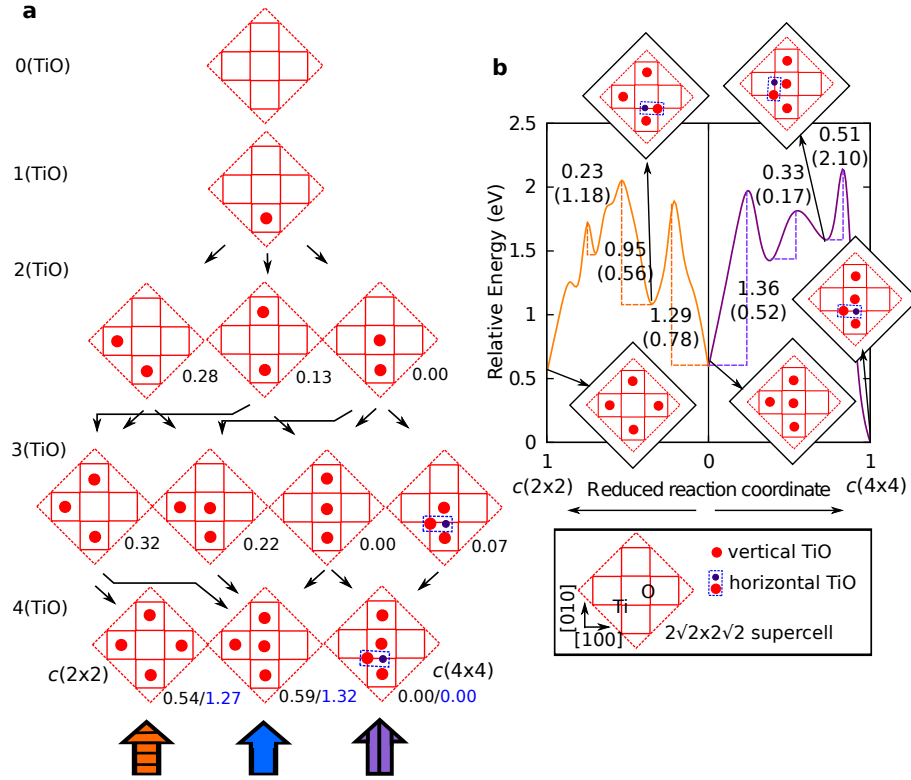


Figure 4.5: **Surface transformation diagram and kinetics.** **a** Starting from a clean TiO_2 surface, progressive addition of a TiO unit on the surface leads to different reconstructions leading to the proposed $c(2 \times 2)$ and $c(4 \times 4)$ reconstructions with half monolayer TiO coverages. Energies from GGA (black) and/or GGA+ U (blue), in $\text{eV}/2\sqrt{2} \times 2\sqrt{2}$ surface cell are given relative to the lowest energy structure of each tier. **b**, Predicted GGA reaction barriers for the transformation of a transitional structure (0 reaction coordinate) to $c(2 \times 2)$, path towards left, and $c(4 \times 4)$, towards right. The energy barriers are shown for each pathway, where the numbers in parenthesis are the barriers for the reverse of the paths. The thick arrows in **a** mark the kinetically relevant structures as described in the text.

The kinetics of coexistence

The formation of these reconstructions can be viewed as a gradual increase of TiO at the surface, with TiO units diffusing until an optimum concentration is reached. Fig. 4.5a shows the coverage cascade, from bare TiO_2 surface to the optimum 4 TiO units per 8 unit cells coverage (in a $2\sqrt{2} \times 2\sqrt{2}$ surface super cell) with energies measured relative to the lowest energy structure in each tier. The propensity of the surface to transform into either one of the two reconstructions depends on the accessibility of the paths leading to them. Specifically, it depends on the relative rates for TiO to diffuse away from each other (favouring the $c(2 \times 2)$ structure) or to form small clusters (favouring the $c(4 \times 4)$ structure). The mere addition of TiO on the surface, without a preconceived notion of defect diffusion, would not exclusively form the $c(2 \times 2)$ $\text{TiO}_2\text{-(TiO)}_{1/2}$ and $c(4 \times 4)$ $\text{TiO}_2\text{-(Ti}_3\text{O}_3)_{1/8}\text{(TiO)}_{1/8}$, indicated with horizontally-hatched and vertically-hatched arrows in Fig. 4.5a, respectively. It is interesting to note that the transitional structure (thick solid arrow, in Fig. 4.5a) satisfies the following: (1) it is a precursor of both $c(2 \times 2)$ and $c(4 \times 4)$, (2) it is on the minimum-energy pathway from one reconstruction to the other, (3) it is energetically downhill for this phase to transform into either of the other phases, and (4) the two transformation paths are mutually exclusive. Fig. 4.5b shows the calculated energy barriers of the transformation paths of the transitional phase into the $c(2 \times 2)$ and the $c(4 \times 4)$ (more details in Appendix C).

To explain the coexistence of the two phases we can analyze the forward and reverse transformation paths in Fig. 4.5b. a) The forward path starts at the center, the barrier heights of the two paths that lead to the $c(2 \times 2)$ *vs* $c(4 \times 4)$ are almost equal 1.29 *vs.* 1.36 eV/migrating TiO unit. This illustrates that at this surface coverage, dispersion and clustering have almost equivalent kinetic probabilities. b)

The reverse path starts at the end, the barrier heights from the $c(2\times 2)$ *vs* $c(4\times 4)$ are different 1.18 *vs.* 2.10 eV/migrating TiO. This illustrates that the $c(2\times 2)$ is more likely to reverse its path back to the center. The TiO units are mobile at high temperatures, and free to diffuse and reorganize until three TiO units form a cluster, at which point breaking free from the cluster is both thermodynamically discouraged and kinetically improbable. Thus, while a $c(2\times 2)$ can transform with relative ease, the $c(4\times 4)$ clusters are very stable, thus terminating the process.

4.3.3. Domains and 1D interfaces

The coexistence of $c(2\times 2)$ and $c(4\times 4)$ implies the presence of interfaces between them. The experimental STM images reveal two distinct interfaces that run along the $[\bar{1}10]$ (left side) and the $[110]$ (right side) directions, shown in Fig. 4.1b, also 6a upper panel. The $[\bar{1}10]$ interface can be characterized as a dark trench that is ≈ 1.1 nm ($2\sqrt{2}$ times the primitive cell) wide. The $[110]$ interface on the other hand is atomically sharp and narrower. In both cases, the reconstructions on either side of the interfaces have the bright spots of the $c(4\times 4)$ aligned with every other row of the smaller spots of the $c(2\times 2)$. Furthermore, the bright spots border the edge of the $c(4\times 4)$.

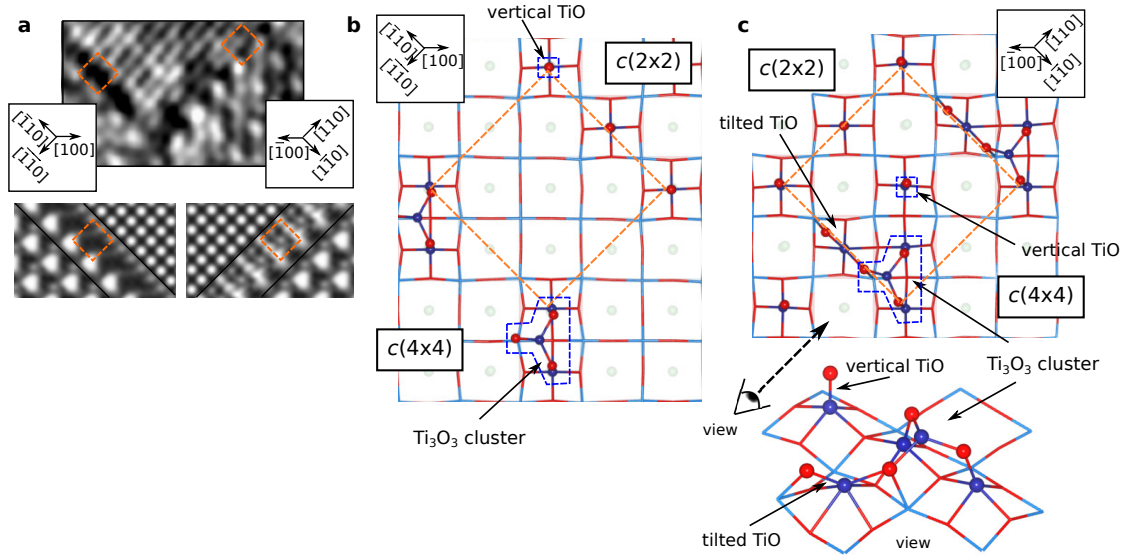


Figure 4.6: **Proposed interfacial structures and their simulated STM images.** **a**, Experimental STM image showing two distinct interfaces between the $c(2 \times 2)$ and $c(4 \times 4)$ that run along $[\bar{1}10]$ and $[110]$ directions. Lower panel shows the composite of the simulated STM images for the reconstructions and the interfaces between them. Predicted atomic structures of the interfaces that run along $[\bar{1}10]$, **b**, and $[110]$, **c**. Regions marked by dashed squares in the STM and structural models correspond to each other. An angled view is shown for structure **c** which emphasizes the Ti_3O_3 cluster closely adjacent to a TiO unit at the interface (compare with Fig.. 4.3c).

The lack of four-fold symmetry in the $c(4\times 4)$ reconstruction helps us to determine the relative positions of the reconstructions and define probable candidate structures of the interfaces. The faint off-center STM image feature in the $c(4\times 4)$ is towards the $[\bar{1}\bar{1}0]$ direction, and therefore this surface could only be oriented as is shown in Fig. 4.3c. The structures shown in Fig. 4.6b and c result in the best agreement between the simulated and experimental STM contrast for the $[\bar{1}\bar{1}0]$ and $[110]$ interfaces, respectively. See Appendix C for other structures explored. Fig. 4.6 a lower panels show the composite calculated STM images of the interfaces and the two reconstructions. The dark trench in the $[\bar{1}\bar{1}0]$ interface (Fig. 4.6 a lower left) is due to the absence of a TiO unit in the region that is 1.1 nm wide, indicated in Fig. 4.6 b. As a result, this interface has locally lower TiO coverage than the parent reconstructions. The $[110]$ interface (Fig. 4.6 a lower right) is characterized as having a row of Ti_3O_3 clusters that is adjacent to a row of TiO. The proximity of the clusters to the TiO units induces a conformational change on every other TiO. The structure shows two types of geometries for the TiO units on the edge of $c(2\times 2)$: the typical vertical orientation and a tilted geometry. The tilted geometry is a consequence of the repulsion between the O adatom adsorbed on a sub-surface Ti, belonging to the cluster, and the O adatom of the now tilted TiO. The interfaces are believed to be the result of the meeting of the growth edges of the domains of the $c(2\times 2)$ and $c(4\times 4)$ reconstructions. The prevalence of both the $[\bar{1}\bar{1}0]$ and $[110]$ interfaces, therefore, indicates preference for 45° growth edges in both reconstructions.

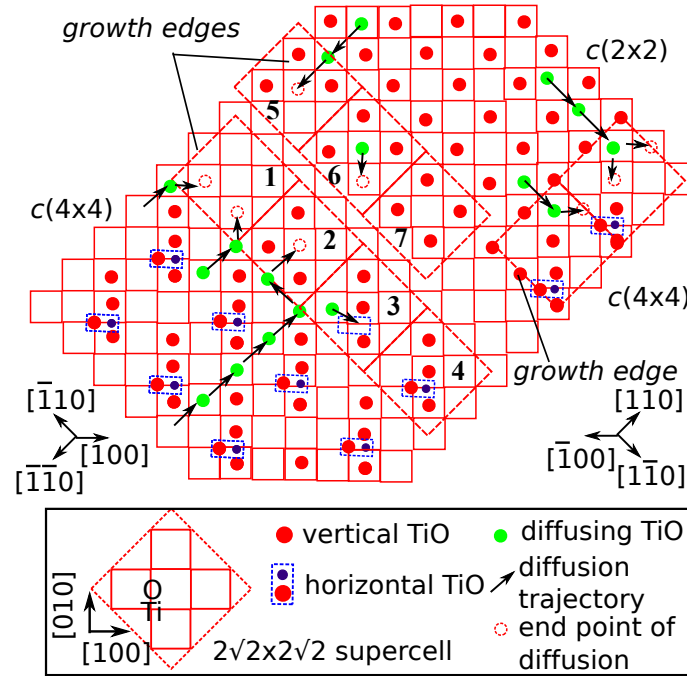


Figure 4.7: **Domain growth and interface formation.** Schematic diagram for how domains of each reconstruction can grow, eventually leading to the interfaces shown in Fig. 4.6 . Dashed squares show precursors of $c(2 \times 2)$ and $c(4 \times 4)$ in different stages of completion.

The preference for a 45° growth edge is closely related to the manner in which TiO migrates on the surface. The barrier for diffusion of a TiO unit unaided by a neighboring TiO unit is prohibitively large, 2.5 eV (see Appendix C). Thus TiO has a limited diffusion length of only one unit cell to remain adjacent to another TiO. However, the diffusion length along $[110]$ (diagonal diffusion) could be extended by a row of TiO adunits along this direction, thus effectively creating growth edges along the lattice diagonal. The growth of domains is schematically shown in Fig. 4.7. Domain growth is achieved through the extension of the TiO chain along $[110]$ or $[\bar{1}10]$ for both reconstructions. Growth is achieved by a combination of two types of TiO diffusion; (1) toward the edge, and (2) at the edge. (1) TiO is delivered near the edge *via* the low barrier diagonal diffusion (green circles with diagonal arrows). (2) The domain is extended by one unit cell through horizontal or vertical diffusion at the growth edge (green circles with horizontal/vertical arrows). The growth of the $c(4\times 4)$ and $c(2\times 2)$ domains are shown at different stages of completion box 1-4 and box 5-7, respectively, see Fig. 4.7. The transitional structures form, box 1-3 and box 5-6, that transform into either $c(4\times 4)$ or $c(2\times 2)$, box 4 and box 7, respectively.

4.3.4. Other Coexisting Structures in Transition Metal Oxides

The coexistence of surface phases observed on oxides to date reside in two categories. In the case of $\text{SrTiO}_3(110)$, $\text{ZnO}(0001)$, and $\text{Fe}_2\text{O}_3(0001)$, reconstructed terraces are attributed to the polar character of the surface. The surface neutrality and charge balance is accomplished through the termination at an anion or cation atomic layer with terraces constituting long range defect patterns (adatoms or vacancies) (104; 89) or in a periodic surface phase containing a large number of coordinated vacancies forming novel surface structures. (99; 101) Enterkin *et al.* (105) presented STM and DFT data on the $\text{SrTiO}_3(110)$ surface where a (3×1) reconstruction contains

an intergrowth of the (4×1) phase. The thermodynamic stability of both surfaces was ascribed to TiO_4 surface tetrahedral complexes but the kinetics of the phases was not explored. In all these polar systems where coexistence of phases has been found, the ability to accommodate charge imbalance to restore chemical stability is presumably the main driving force. STM of $\text{Fe}_3\text{O}_4(001)$ thin films indicated the presence of coexisting domains due to stacking faults (100), and the coexistence of a stable and a metastable surface with the presence of Fe dimers (111; 112). The domain growth of the dimer structure is not understood at present.

The case of non polar $\text{SrTiO}_3(001)$ is structurally similar to $\text{BaTiO}_3(001)$. Co-existing domains (103; 91) and nanostructures (90; 95; 113) in SrTiO_3 have been observed using STM. Studies indicate the presence of a TiO_x terminated surface on top of a TiO_2 layer, and surface DFT models presented therein account for the experimental observations. The relevance of the Ti:O ratio are acknowledged by these and other SrTiO_3 studies (89; 114) as a factor in determining the surface reconstruction.

In none of these studies is the relative roles of thermodynamic and kinetic factors quantified, is the relation of the atomic structure of the reconstruction and the interfaces between them determined, nor are the transition mechanisms contemplated. Our results accomplish this with two reconstructions not previously observed on BaTiO_3 and on a non polar surface such that the principles that might be generalized to a wider range of oxide materials.

4.4. Conclusion

Our thermodynamic and kinetic calculations suggest that both $c(2\times 2)$ and $c(4\times 4)$ will likely coexist as shown in the experimental STM. Prolonged heating or higher temperatures will favor the $c(4\times 4)$ surface, as illustrated in previous studies. (8)

The coexistence of the $c(2\times 2)$ and $c(4\times 4)$ phase is in essence different from the cases mentioned for other transition metal oxides due to the diffusion of a TiO unit. The coexistence of these two surface reconstructions and the atomic scale structural analysis yield two important implications. First, these results demonstrate that it is possible to produce surfaces with a combination of thermodynamically stable and kinetically trapped structures which, along with the connecting interfaces, possess different and known atomic structures. Because the structures have inherently different chemical properties, this points to a strategy to engineer surface reactivity. For example, the difference in the structures between the two phases gives rise to different chemical properties of the two reconstructions, *i.e.* differences in the accessibility of the Ti and O adatoms toward nucleophilic and electrophilic attack, respectively, between the vertically oriented TiO and the Ti_3O_3 cluster. Second, the interface between a thermodynamically stable and a kinetically trapped metastable surface is a transitional state between two phases. These results provide an atomistic mechanism of the phase transition between the $c(2\times 2)$ and $c(4\times 4)$ reconstructions.

CHAPTER 5 : Oxidative adsorption of water on the highly reduced ($\sqrt{5} \times \sqrt{5}$) $R26.6^\circ$ surface reconstruction of $\text{BaTiO}_3(001)$

5.1. Introduction

Water can interact with surfaces in many ways. For example, on metallic surfaces water can form an ordered monolayer upon adsorption (physical adsorption) (115; 116; 117); on metal oxide surfaces, water can simultaneously hydroxylate and protonate a surface (chemisorption, acid-base reaction) (118), or act as an oxidizing agent, for example, by filling surface oxygen vacancies (redox reaction) (119). Interaction of metal oxides with water has been, and still is, of great interest due to the diversity of applications of this type of compound, from electronics, to sensing devices, to catalysis, where water directly or indirectly contributes to the demise or success of a device. (120; 121; 122; 123)

With recent advances in material synthesis and surface structure manipulation, interesting surface structures with little known or unknown chemistry have been created and identified. Among the particularly well studied oxides is the perovskite family. Two types of theoretical studies populate the literature of water interacting with perovskite-type oxide surfaces: those that deal with ideal surfaces and those that deal with reconstructed surfaces. Of the surfaces surveyed, emphasis is placed on SrTiO_3 (STO), with fewer studies addressing BaTiO_3 (BTO). To the best of our knowledge, furthermore, there are no reports of surface reconstructions of BTO interacting with water. Regarding STO surfaces, molecular and dissociative adsorption to the perfect surface (both SrO - and TiO_2 -terminations) has been modeled. (124; 125; 126) More

recently, reconstructed STO surfaces have also been investigated. (127; 128; 129; 130) Regarding BTO surfaces, it was recently found that water dissociatively adsorbs on the BTO (001) surface. (131) H_2O was also found to reverse the surface layer buckling on the (001) surface of BTO (122; 120), while surface hydroxyls were found to stabilize out-of-plane polarization in BTO nanowires due to its effective positive polarization charge screening (87). Despite these studies, the reactivity of BTO surface reconstructions has not been examined.

BaTiO_3 , a prototypical perovskite, has been shown to exhibit various surface reconstructions in reducing environments (8; 9; 132). These reconstructions are Ti enriched surfaces, where surface reduction is achieved not exclusively through formation of surface O vacancies, but through excess surface Ti adatoms (8; 9) or TiO ad-units (132), analogous to Ti interstitials in bulk. One particular example is the $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ reconstruction of BaTiO_3 (001) surface, the structure of which has been characterized as having a Ti adatom coverage of three-fifths, four-fifths, or some combination of the two on a TiO_2 termination. (9)

Here we report the effect of water adsorption on the aforementioned $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ BaTiO_3 surface reconstruction. Through density functional theory (DFT) we demonstrate enhanced water reactivity of a metal oxide due to a surface reconstruction enabling adsorption channels that are otherwise inaccessible on the bulk-like stoichiometric surface. These adsorption channels lead to formation of stable surface hydrides that may be used to do various useful reductive chemistries. The dual nature of the surface investigated offers both a Lewis acid site for the usual water dissociation and a redox active site for hydride formation. This is a quality that is rare for a homogeneous surface. Mechanisms for H_2 generation on the reconstructed surface are also presented.

5.2. Computational methods

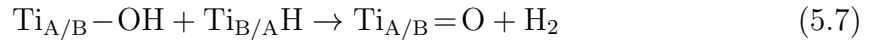
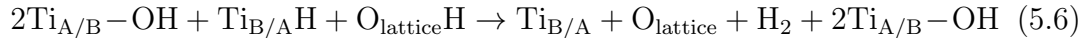
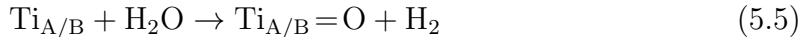
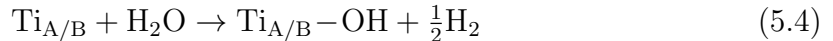
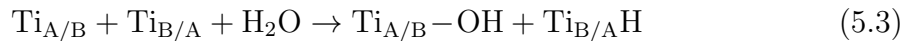
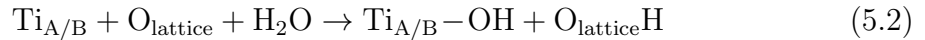
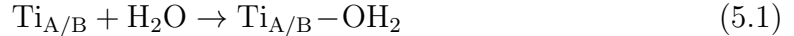
The spin-polarized, effective U -corrected (2) density functional theory calculations were performed with the Quantum ESPRESSO DFT package (50), with a 50 Ry plane-wave cutoff and the PBE-GGA functional (34). The U correction was applied to the Ti $3d$ states ($U=4.9$ eV) (9) and the core states of all elements were described using norm-conserving pseudopotentials generated with the OPIUM code (72). A $4 \times 4 \times 1$ Monkhorst-Pack (41) k-point mesh was used for relaxation calculations and a $10 \times 10 \times 1$ mesh was used for the density of states calculations. The surface calculations were performed using a slab model containing 6 atomic layers, with the in-plane periodicity of the supercell fixed at $4.00 \times \sqrt{5}$ Å. During relaxation calculations, the atomic positions of the top three layers, adatoms, and adsorbates were relaxed until the forces on atoms were less than 0.01 eV/Å in all directions, while the bottom three layers were fixed to a cubic structure. Approximately 20 Å of vacuum separate the slabs in order to prevent artificial electric field interactions between images. A molecule in a box, where images are separated by a vacuum, was used to simulate the H_2 and H_2O molecules. Calculations were then performed at the Γ -point of the Brillouin zone.

5.3. Results and discussion

5.3.1. Different modes of water adsorption

Starting from the reconstructed atomic structure (9), we explore various water adsorption configurations and coverages, paying particular attention to the interaction of water with the undercoordinated Ti adatoms. Shown in Fig. 5.1a is the $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ TiO_2 - $Ti_{3/5}$ reconstruction (without H_2O). The structure shows two

types of Ti adatoms, Ti_A (yellow) and Ti_B (purple) on O_4 hollow sites of the TiO_2 (001) termination. The Ti adatoms are differentiated according to their Ti-adatom neighbors. Ti_A has two Ti adatom neighbors (two Ti_B) along the [100] direction, while Ti_B has its two Ti adatom neighbors (Ti_A and another Ti_B) along [001] and [010] directions. These atoms are shown to have different electronic structures, where Ti_A has its d_{z^2} orbital occupied, while Ti_B has its d_{z^2} , d_{xy} , and $d_{x^2-y^2}$ orbitals occupied, indicating that these adatoms are highly reduced (9). Shown in Fig. 5.2 is the orbital projected density of states (PDOS) of these surfaces. Water can interact with the surface via molecular, dissociative, or oxidative adsorption. In all cases, the oxygen of the H_2O would bond to either Ti_A or Ti_B . When water breaks the symmetry between the two Ti_B adatoms, one will be referred to as B and the other B'. Since the surface is highly reduced, with combined adatomic and sub-layer (TiO_2) Ti:O ratio of $(1+3/5):2 = 4:5$, we explored physical and dissociative, as well as oxidative adsorption of H_2O , described by the following reactions:



Reaction (1) describes molecular adsorption, reactions (2) and (3) describe different dissociative adsorption channels, reactions (4) and (5) describe different oxidative

adsorption channels (which will be further discussed below), and reactions (6) and (7) describe required reactions for H_2 evolution. We model low coverage situations where a single adsorbate per $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ supercell on the $\text{Ti}_{3/5}$ coverage is explored. We do so to attain fundamental understanding of water interacting with a highly reduced surface, without the complexity of intermolecular water effects leading to additional electronic structure changes or structural rearrangements. The maximum interaction between a water molecule and the surface occurs at this low coverage.

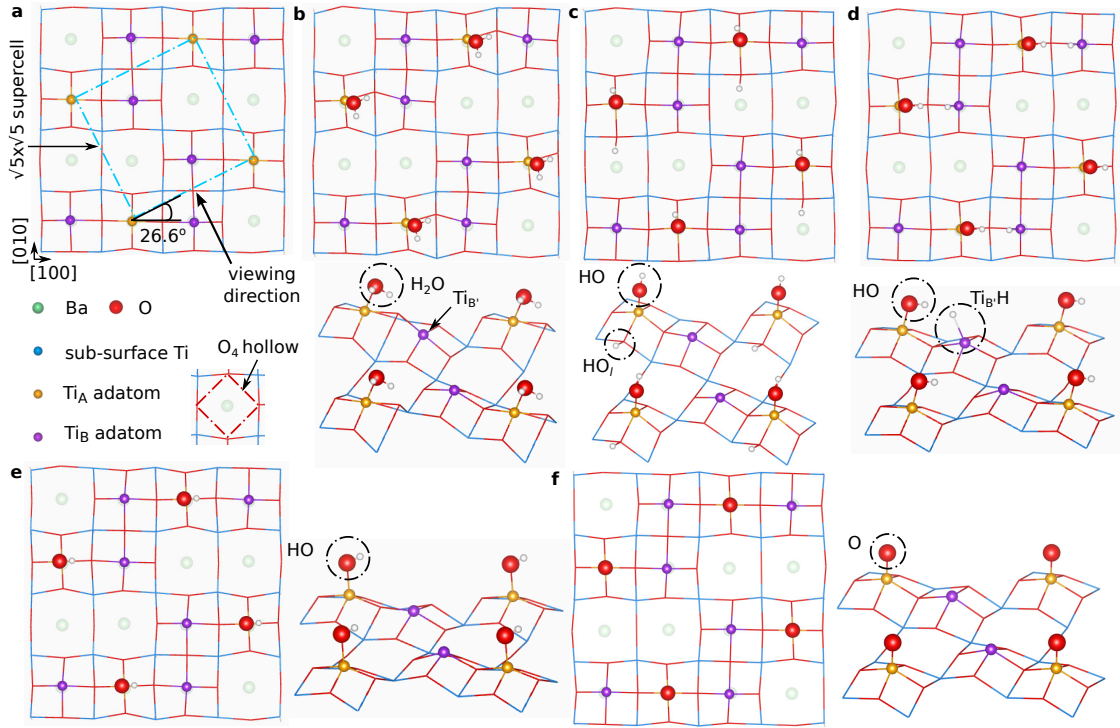


Figure 5.1: **Different adsorption products of a water molecule on the Ti adatom rich reconstruction of BaTiO₃.** **a**, Bare $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ TiO₂-Ti_{3/5} reconstruction, showing four-fold coordinated Ti adatoms (Ti_A and Ti_B) on the TiO₂ (001) termination. **b–f**, different adsorption products of H₂O on Ti_A: **b**, molecular; **c**, dissociative with H on a lattice O (O_l); **d**, dissociative with H on Ti_B; **e**, oxidative with surface OH as the product; and **f**, oxidative with surface O as the product. Viewing direction for the angled-view structures is shown in **a**.

Fig. 5.1 shows the structure of the bare surface and the range of structures corresponding to reactions (1)-(5). Adsorption is modeled by saturating one inequivalent binding site (Ti_A or Ti_B) at a time. Fig. 5.1b shows the product of reaction (1), in which molecular water interacts with the surface. The $\text{Ti}_\text{A}-\text{O}_\text{w}$ (water oxygen) bond length is 2.30 Å and makes an angle of 15° relative to the surface normal. The water molecule is tilted with respect to the surface, with one $\text{Ti}_\text{A}-\text{O}_\text{w}-\text{H}$ bond angle at 75° (OH pointing down) and the other at 119° (OH pointing horizontally). The $\text{H}-\text{O}_\text{w}-\text{H}$ angle is 108° . One hydrogen atom of the molecule makes a 1.60 Å hydrogen bond with a surface lattice oxygen. By contrasting the electronic structures of the bare and molecular adsorption configurations, we can conclude that molecular adsorption is a physisorbed state. The projected densities of states for the two surfaces (Fig. 5.2a and b) shows that the electronic structure of the surface is not perturbed very much by the presence of H_2O . The d_{xz} and d_{yz} orbitals of Ti_A , however, now become filled, while the d_{z^2} orbital moves up in energy and empties. This is an expected electronic response due to repulsion between the water molecule (along z) and the non-bonding electron.

Dissociative adsorption reactions (2) and (3) are seen in Fig. 5.1c and d, respectively. The OH would most likely adsorb to a Ti adatom while the H atom would adsorb to an adjacent lattice oxygen or another Ti adatom. Fig. 5.1c shows the Ti_A as the OH binding site while H attaches to the least coordinated lattice O adjacent to Ti_A , henceforth referred to as $\text{Ti}_\text{A}(\text{OH})(\text{O}_\text{l}\text{H})$. Fig. 5.1d, on the other hand, shows the H bonded to the nearest Ti_B site, henceforth referred to as $\text{Ti}_\text{A}(\text{OH})\text{Ti}_\text{B}'\text{H}$. $\text{Ti}_\text{A}(\text{OH})(\text{O}_\text{l}\text{H})$ is 2.1 kJ/ H_2O mol more stable than the $\text{Ti}_\text{A}(\text{OH})\text{Ti}_\text{B}'\text{H}$. Given that this is the case, it is very likely that the H atom could diffuse on the surface and access both configurations at finite temperatures (thermal energy : $k_\text{B}T = 2.5$ kJ/mol at

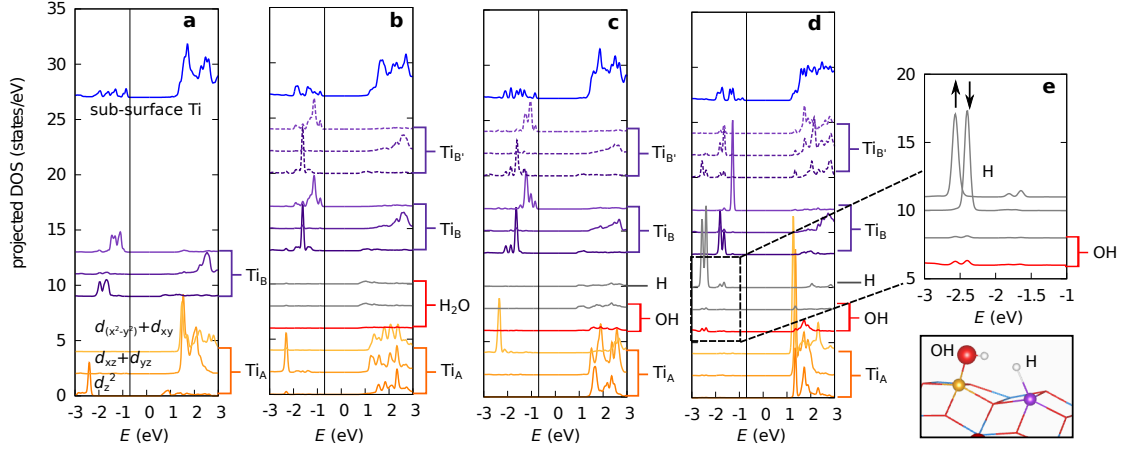


Figure 5.2: **Electronic PDOS of the adsorption products of a water molecule on the $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ reconstruction.** **a**, Bare $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ $\text{TiO}_2\text{-Ti}_{3/5}$ reconstruction. Resulting PDOS after: **b**, molecular; **c**, dissociative with H on a lattice O (O_l); and **d**, dissociative with H on $\text{Ti}_{B'}$. For Ti adatoms (A and B (B')), the DOS contribution is resolved to show orbital types: d_{z^2} , $d_{xz} + d_{yz}$ and $d_{x^2-y^2} + d_{xy}$ from bottom to top. See Fig. 5.1 a-d for the corresponding atomic structures. **e**, Spin resolved 1s orbital projection of the H on $\text{Ti}_{B'}$ showing hydride orbital occupation in **d**. By contrast, the H in OH does not have occupied 1s orbital (cationic). Lower panel in **e** shows the surface $\text{Ti}_A\text{-OH}$ and the adjacent $\text{Ti}_{B'}\text{-H}$ structure (see Fig. 5.1d for legend). For the PDOS, the valence band maxima were aligned, which are set to -0.7 eV (9) for ease of comparison.

298 K). In $\text{Ti}_\text{A}(\text{OH})(\text{O}_\text{l}\text{H})$, Ti_A acts as a Lewis acid and O_l as a Bronsted base. The $\text{Ti}-\text{O}_\text{w}$ bond length is 1.92 Å and the $\text{Ti}-\text{O}_\text{w}-\text{H}$ angle is 129°. The $\text{O}_\text{l}-\text{H}$ bond length is 0.98 Å and is at a 66° angle with respect to the surface normal. By contrast, in the $\text{Ti}_\text{A}(\text{OH})\text{Ti}_\text{B'}\text{H}$ configuration, Ti_A and $\text{Ti}_\text{B'}$ function as reducing species, and both become oxidized. This produces a hydride from a proton of water, which adsorbs to $\text{Ti}_\text{B'}$ (electronic structure discussed below). Ti_A and $\text{Ti}_\text{B'}$ also perform as Lewis acid sites after proton reduction in this case.

$\text{Ti}_\text{A}(\text{OH})\text{Ti}_\text{B'}\text{H}$ also differs from $\text{Ti}_\text{A}(\text{OH})(\text{O}_\text{l}\text{H})$ in terms of bond lengths and bond angles. In $\text{Ti}_\text{A}(\text{OH})\text{Ti}_\text{B'}\text{H}$, the $\text{Ti}_\text{A}-\text{O}_\text{w}$ bond length is 1.85 Å and the $\text{Ti}_\text{A}-\text{O}_\text{w}-\text{H}$ angle is 113°. The $\text{Ti}_\text{B'}-\text{H}$ bond is 1.867 Å and is tilted toward the OH at 23° with respect to the surface normal. The $\text{Ti}_\text{A}-\text{O}_\text{w}$ bond lengths are in reasonable agreement with a previous quantum chemical calculation of the $\text{Ti}-\text{OH}$ bond length in the $\text{Ti}(\text{OH})_4$ molecule (1.81 Å) (133). Furthermore, various quantum chemical calculations have given a $\text{Ti}-\text{H}$ bond length of about 1.7 Å for organic Ti hydrides (134) and DFT-GGA predicted the bond length for the TiH dimer to be 1.8 Å (135), which are in reasonable agreement with the $\text{Ti}-\text{H}$ bond length herein.

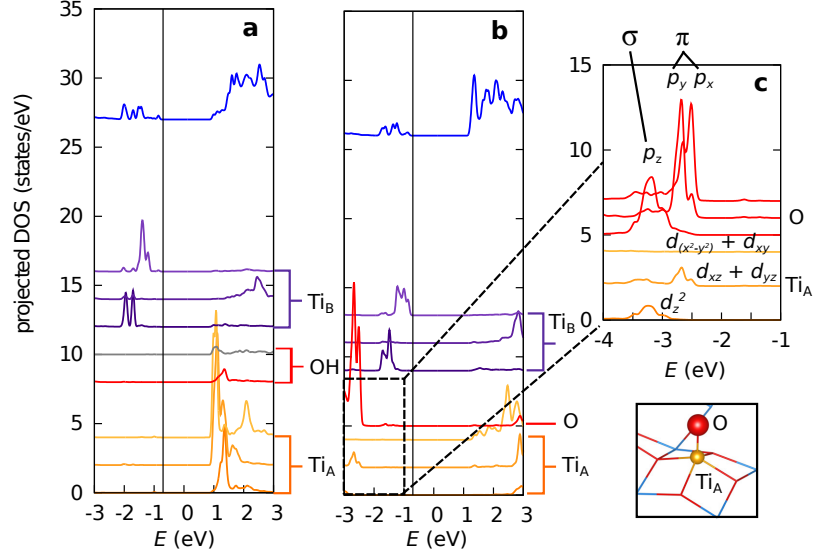


Figure 5.3: **Electronic PDOS of the oxidative adsorption products of a water molecule on the $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ reconstruction.** **a**, oxidative adsorption with surface OH as the product; and **b**, with surface O as the product. For Ti adatoms (A and B), the DOS contribution is resolved to show orbital types: d_{z^2} , $d_{xz} + d_{yz}$ and $d_{x^2-y^2} + d_{xy}$ from bottom to top. See Fig. 5.1e and f for the corresponding atomic structures. **c**, orbital resolved projection of the O adsorbates 2p orbitals in **b**, where the p_z orbital overlaps with the d_{z^2} ($\text{Ti}_A\text{--O}$ σ bonding), and p_x and p_y orbital overlap with the d_{xz} and d_{yz} orbitals ($\text{Ti}_A\text{--O}$ π bonding). Lower panel in **c** shows the surface $\text{Ti}_A\text{--O}$ structure (see Fig. 5.1 for legend). For the PDOS, the valence band maxima were aligned, which are set to -0.7 eV (9) for ease of comparison.

Comparing the electronic structures of the two dissociative configurations (Fig. 5.2c and d) with the molecular adsorption and bare surface cases, we see that either the occupied Ti_A $3d$ state(s) changed valence orbital character (remaining occupied) similar to the physisorption case, as in $\text{Ti}_\text{A}(\text{OH})(\text{O}_\text{I}\text{H})$, or moved to the conduction band (becoming less occupied), as in $\text{Ti}_\text{A}(\text{OH})\text{Ti}_\text{B'}\text{H}$. It is clear that the electronic population profiles, and therefore the oxidation states, of the Ti adatoms are unchanged in $\text{Ti}_\text{A}(\text{OH})(\text{O}_\text{I}\text{H})$. In $\text{Ti}_\text{A}(\text{OH})\text{Ti}_\text{B'}\text{H}$, however, both Ti_A and $\text{Ti}_\text{B'}$ were oxidized, while the H from water that moves to $\text{Ti}_\text{B'}$ is greatly reduced. Fig. 5.2e shows the protonic profile of the H on O and a hydridic electronic profile for H on $\text{Ti}_\text{B'}$, where the two occupied H $1s$ PDOS peaks (spin up and down, zoomed-in and spin-resolved in Fig. 5.2e) are hybridized with the $\text{Ti}_\text{B'}$ $3d_{z^2}$ orbital. Table 5.1 shows the calculated Löwdin charges of pertinent surface species for structures found in Fig. 5.1 a-d. These charges further illustrate that water may react with the surface in an acid-base type reaction as in $\text{Ti}_\text{A}(\text{OH})(\text{O}_\text{I}\text{H})$, where the Löwdin charges on the Ti adatoms remain the same, or in a redox type reaction as in $\text{Ti}_\text{A}(\text{OH})\text{Ti}_\text{B'}\text{H}$, where the Löwdin charges on the Ti adatoms increase. Also shown is the very negative Löwdin charge on H on top of $\text{Ti}_\text{B'}$ ($-0.67e$ vs. $+0.4e$ in protonic H).

Table 5.1: Löwdin charges (in electron charge, e) of select surface species after reaction of water with the $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ TiO_2 - $\text{Ti}_{3/5}$ reconstruction. The structures are found in Fig. 5.1.

Structure	Adsorption type	Ti _A	Ti _B	Ti _{B'}	O _w	H _{h_{xy}l}	H _{diss}
1a	none	+2.07	+1.80	+1.80			
1b	physisorption	+2.08	+1.80	+1.82	-0.79	+0.42	+0.36
1c	dissociative	+2.12	+1.79	+1.79	-1.01	+0.41	+0.39
1d	dissociative	+2.27	+1.79	+2.11	-0.88	+0.37	-0.67
1e	oxidative	+2.28	+1.79	+1.80	-0.94	+0.41	
1f	oxidative	+2.14*	+1.79	+1.79	-0.87		

Bulk Ti: +2.33 e ; bulk O: -1.02 e . O_w is O from water; H_{h_{xy}l} is H in hydroxyl; H_{diss} is H-bonded to a surface O, or dissociated H on a lattice O (O_l) or Ti_{B'}.

*less positive due to the very covalent bond between Ti_A and O_w, leading also to less negative charge on O_w.

Reduced Ti–H species on oxide surfaces are rare, but have been observed. A recent study found that Ti–H hydrides were the photoactive species on the defective (via oxygen vacancy) rutile TiO₂(110) surface (136). Various spectroscopic techniques confirmed the existence of the hydride-type species, and DFT calculations identified O vacancies at the O-bridging sites and basal five-fold coordinated Ti sites (coordinately unsaturated sites) as stable hydride adsorption sites. Notably, the Ti–H species are stable because of excess electrons on the surface due to the oxygen vacancies, which is analogous to our case, in which the nonstoichiometric surface reconstruction is Ti-rich. The existence and stability of these Ti–H species on a reduced TiO₂ (110) surface is further supported by scanning tunneling microscopy (STM) and electron stimulated desorption (ESD) studies (137) in which an H atom is shown to form a hydride when it gets trapped at an oxygen vacancy site. Titanium hydrides were also observed in low energy ion scattering (LEIS) measurements of H₂⁺ ions adsorbing on a highly oxygen deficient TiO₂ (110) surface (138). These studies show an O-vacancy-mediated hydride-type species formation as opposed to being excess-Ti-mediated.

Oxidative adsorption reaction (reactions (4) and (5)) products are seen in Fig. 5.1e and f, respectively. They are the oxidized surface structures that result from surface H₂ generation and desorption. In the Ti_A–OH configuration, the Ti_A–O_w bond length is 1.89 Å and the bond is oriented perpendicular to the surface. In Ti_A=O, the Ti_A–O_w is shorter (1.68 Å). Fig. 5.3a and b show the atomic PDOS of select surface species for Ti_A–OH and Ti_A–O, respectively. It is clear that the Ti_A in both cases is oxidized, as seen by the absence of significantly occupied 3*d* orbitals and the increased positive Löwdin charges (Table 5.1). The calculated charge on Ti_A for Ti_A=O is less positive however, which may seem counterintuitive, but it is due to the very covalent bond between Ti_A and O_w. The high energy oxygen 2*p* peaks (red)

located between -2.0 and -4.0 eV in the density of states of $\text{Ti}_\text{A}=\text{O}$ (see also Fig. 5.3c) are due to sigma and pi bonding between the oxygen and Ti_A . The high covalency of the interaction can be seen from the overlapping Ti 3d and O 2p projections in this energy window, wherein the p_z orbital of O overlaps the $3d_{z^2}$ orbital of the Ti_A , and the p_x and p_y orbitals of O overlap the d_{xz} and d_{yz} orbitals of the Ti_A . This type of surface defect (TiO unit) has been shown to organize into ordered structures on the (001) surface of BaTiO_3 , producing either a $c(2 \times 2)$ or $c(4 \times 4)$ reconstruction (132). Similar calculations have been done for Ti_B as the oxidation site, and their atomic and electronic structures are shown, respectively, in Fig. D.2 and Fig. D.3 in Appendix D, showing similar properties.

5.3.2. Mechanisms of formation of hydride/hydrogen molecule from adsorbed water

To produce either $\text{Ti}_\text{A}-\text{OH}$ or $\text{Ti}_\text{A}-\text{O}$, a mechanism to stably produce and desorb H_2 from the surface must be in operation. Fig. 5.4a and b illustrate stepwise mechanisms for how equations (6) and (7) may occur to produce H_2 after dissociative adsorption of H_2O on the surface. Fig. 5.4a shows a reaction leading to surface hydroxyls and liberation of $\text{H}_2(\text{gas})$. A proton from an O_l site (coming from $\text{Ti}_\text{A}(\text{OH})(\text{O}_\text{l}\text{H})$) may hop to another lattice O site adjacent to a Ti_B' with a hydride adsorbed. Then a nucleophilic attack onto the proton from the hydride produces H_2 . Fig. 5.4b, on the other hand, shows production of $\text{Ti}_\text{A}=\text{O}$ and $\text{H}_2(\text{gas})$, where starting from a $\text{Ti}_\text{A}(\text{OH})\text{Ti}_\text{B}'\text{H}$ configuration, a nucleophilic attack by the hydride onto the proton of the hydroxyl produces H_2 .

The mechanism of water reduction with concomitant release of hydrogen gas has been explored extensively in metal and metal oxide clusters (139; 140; 141; 142; 143) where active sites are more available and accessible. Indeed, surfaces have a tendency to restrict access to active sites due to the rigidity of the underlying structures and

reduced dimensionality of the architecture. (144; 145) We have shown, however, that on the Ti covered TiO_2 surface of BaTiO_3 , the multiple active sites are sufficiently exposed to alleviate structural restrictions in catalyzing reactions requiring multiple reaction sites.

The energetics for hydrogen production as outlined in Fig. 5.4 (reactions (6) and (7) in Table 5.2) is comparable to that of known H_2 catalysts. In Fig. 5.4a, the reaction energy can be approximated by the energies of twice reaction (4) minus the sum of reactions (2) and (3), yielding an energy cost of +67 kJ/mol. In Fig. 5.4b, the reaction energy is approximated by the energy of reaction (5) minus the energy of reaction (3), yielding an energy cost of +54 kJ/mol. For the former reaction, the Ti_B centered reaction is found to be exothermic, -25 kJ/mol, while for the latter reaction, the Ti_B centered reaction has a higher barrier of +77 kJ/mol (see Table 5.2). These are less than or comparable to the calculated barriers for the rate-limiting dimerization of H to H_2 on known H_2 producing catalysts, such as Pt (111), +73 kJ/mol, Ni (111), +103.2 kJ/mol, and Ni_2P (001), +43.4 kJ/mol, in low surface coverage (146).

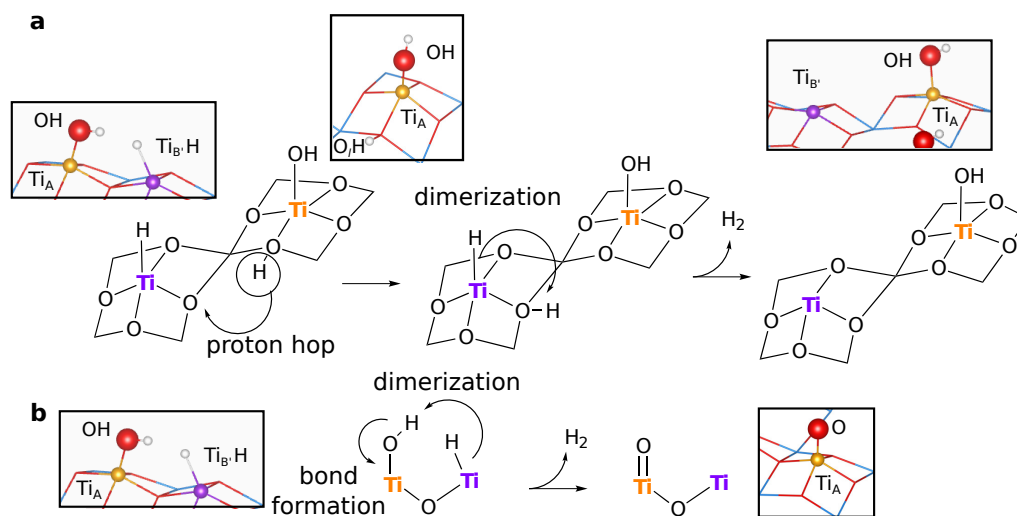


Figure 5.4: **Hydrogen producing reaction scheme from dissociated water.** The hydride at the $\text{Ti}_{B'}$ site can react **(a)** with a proton that hops to an adjacent lattice O (O_l) site from an O_l site associated with an OH on a Ti_A site, reaction (6), or **(b)** directly with the proton from an OH on the adjacent Ti_A site, reaction (7).

Table 5.2: Reaction energetics of the different water adsorption types for when Ti_A and Ti_B are the main reaction sites.

Reaction	ΔE (DFT-GGA+ U [4.9eV]) [kJ/mol]	
	Ti_A	Ti_B
(1) $\text{Ti}_{\text{A/B}} + \text{H}_2\text{O} \rightarrow \text{Ti}_{\text{A/B}} - \text{OH}_2$	-61.8	-62.3
(2) $\text{Ti}_{\text{A/B}} + \text{O}_{\text{lattice}} + \text{H}_2\text{O} \rightarrow \text{Ti}_{\text{A/B}} - \text{OH} + \text{O}_{\text{lattice}}\text{H}$	-129.7	-106.7
(3) $\text{Ti}_{\text{A/B}} + \text{Ti}_{\text{B/A}} + \text{H}_2\text{O} \rightarrow \text{Ti}_{\text{A/B}} - \text{OH} + \text{Ti}_{\text{B/A}}\text{H}$	-127.6	-131.9
(4) $\text{Ti}_{\text{A/B}} + \text{H}_2\text{O} \rightarrow \text{Ti}_{\text{A/B}} - \text{OH} + \frac{1}{2}\text{H}_2$	-95.0	-131.7
(5) $\text{Ti}_{\text{A/B}} + \text{H}_2\text{O} \rightarrow \text{Ti}_{\text{A/B}} = \text{O} + \text{H}_2$	-73.6	-55.3
(6) $\text{Ti}_{\text{B/A}}\text{H} + \text{O}_{\text{lattice}}\text{H} \rightarrow \text{Ti}_{\text{B/A}} + \text{O}_{\text{lattice}} + \text{H}_2$	+67.3	-24.8
(7) $\text{Ti}_{\text{A/B}} - \text{OH} + \text{Ti}_{\text{B/A}}\text{H} \rightarrow \text{Ti}_{\text{A/B}} = \text{O} + \text{H}_2$	+54.0	+76.6

The difference between the reaction energies of the two sites indicate that they are chemically distinct from each other, especially in the proton transfer: (2) to (3), and towards oxidation: (4) and (5).

The catalytic efficiency can be linearly correlated to certain thermodynamic parameters, known as descriptors (*e.g.* adsorption energies), which are effective in finding candidate catalysts. (147; 53; 146; 148; 54; 149) However, further exploration into the effect of adsorbate concentration and environmental chemical constraints on the barriers will enhance the understanding of this class of catalytic surfaces in realistic operational conditions. We have clearly demonstrated, nonetheless, the ability of the surface to stabilize a hydride on the surface essential for H₂ production or hydride-dependent chemistries, *e.g.* the water-gas shift reaction.

Oxidation of the surface with water leads to production of hydrides and ultimately to H₂ gas (water reduction). We explore a pathway of H₂ production by explicitly showing a possible path for hydride formation from water. Furthermore, we find that the direct reaction of H₂O with a Ti adatom does not spontaneously lead to a H₂ bond formation between the hydrogen atoms of the incoming water molecule. Therefore, we propose an initial dissociative adsorption state where OH is adsorbed on a Ti adatom, while the H bonds with the least coordinated surface O or another Ti adatom. In the former case, the H carries a net positive charge, while in the latter case H carries a net negative charge. The reaction of an electron-rich and an electron-deficient H then forms an H₂ gas molecule, ultimately oxidizing the surface Ti adatoms.

5.3.3. Catalytic applications

Water reduction is of great interest because it is a method to generate hydrogen gas, which is an attractive alternative fuel resulting in no pollutants. Water reduction often is conducted in the presence of a catalyst, as in the electrocatalytic hydrogen production from water: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$ (146; 150), the water-gas shift reaction: $\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$, (151; 152) and the steam reforming of ethanol:

$\text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 6\text{H}_2$ (151). In the first reaction, Pt, Ni_2P (146; 150), and MoS_2 (153; 154; 155) have been shown to be good catalysts, while the latter two reactions are commonly catalyzed by a combination of a metal and a metal oxide, such as Au/CeO_2 (156), Ni/CeO_2 (151) and Cu/ZnO . (152) In these reactions, hydrides are important reaction intermediates. It is plausible that the $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ reconstruction of BaTiO_3 (001) could catalyze a hydrogen generating reaction without the need for a metal co-catalyst, as there is an equilibrium between the two dissociative adsorption states as shown earlier. The equilibrium, moreover, is characterized by an energy barrier that can be surmounted via thermal energy. In water reduction, eventual protonation of Ti-OH and Ti=O and electroreduction of the Ti sites would lead to a reversible water desorption, leaving behind the hydrides and thus leading to H-enrichment of the surface. In the water gas shift and steam reforming, CO and/or other small reduced hydrocarbons may be used to sequester the O species left behind from H_2 formation which will then re-expose the reduced Ti.

CHAPTER 6 : Synergistic oxygen evolving activity of a TiO₂-rich reconstructed SrTiO₃(001) surface

6.1. Introduction

Transition-metal based oxides attract significant attention for their ability to catalyze the highly complex four-electron oxidation of water to molecular oxygen, the pair reaction to the reduction of water to hydrogen gas (water splitting). A topic of lively discussion is the value of mimicking the cubane-like structure adopted by the Mn₄CaO₅ cluster found in the oxygen evolving complex (OEC) of Photosystem II (11; 12) for the design of new catalysts. Researchers have focused on a few well-studied transition metals, such as Ti, Mn, Co, and Ni, incorporating new synthetic techniques and/or crystallographic structures.(157; 158; 159; 160; 161) Through synthetic variations, they have observed different catalytic activities for compositionally similar compounds.

Significant work has been dedicated to studying surface structural modification on SrTiO₃, a known water-splitting photocatalyst,(15) leading to the discovery of diverse and chemically distinct surface structures.(162) SrTiO₃, a perovskite-type oxide, has alternating layers of SrO and TiO₂ along its [001] crystallographic axis. Fig. 6.1 a shows the TiO₂ exposed (001) termination with the corner-shared square planar TiO₄ units on the surface layer. This surface can reconstruct into TiO₂ double-layer structures, with the bulk-like TiO₂ layer supporting a TiO₂ over-layer.(162; 93; 163) The 2×1 TiO₂ double-layer (DL) reconstruction (Fig. 6.1b) was reported to form,(161) where the over-layer is composed of edge-shared TiO₄ units distributed in a zigzag ladder pattern, and each over-layer Ti sits atop a surface layer oxygen.(93) The laterally

unshared O atoms are either one- or two-fold coordinated, ^aO and ^bO , respectively, while the laterally shared O atoms are either three- or four-fold coordinated, ^cO and ^dO , respectively (^bO and ^dO sit atop surface layer Ti, see Fig. 6.1c). The bonding between over-layer ^aTi and ^aO is quite covalent, since O is divalent and ^aO is singly coordinated. Fig. 6.1d shows the cubane-like Ti_4O_6 subunit of the surface, illustrating its structural congruence with the Mn_4CaO_5 cluster found in the OEC of Photosystem II. Later we show that the parallelism between the two structures is not only structural but also chemical, leading to enhanced catalytic properties.

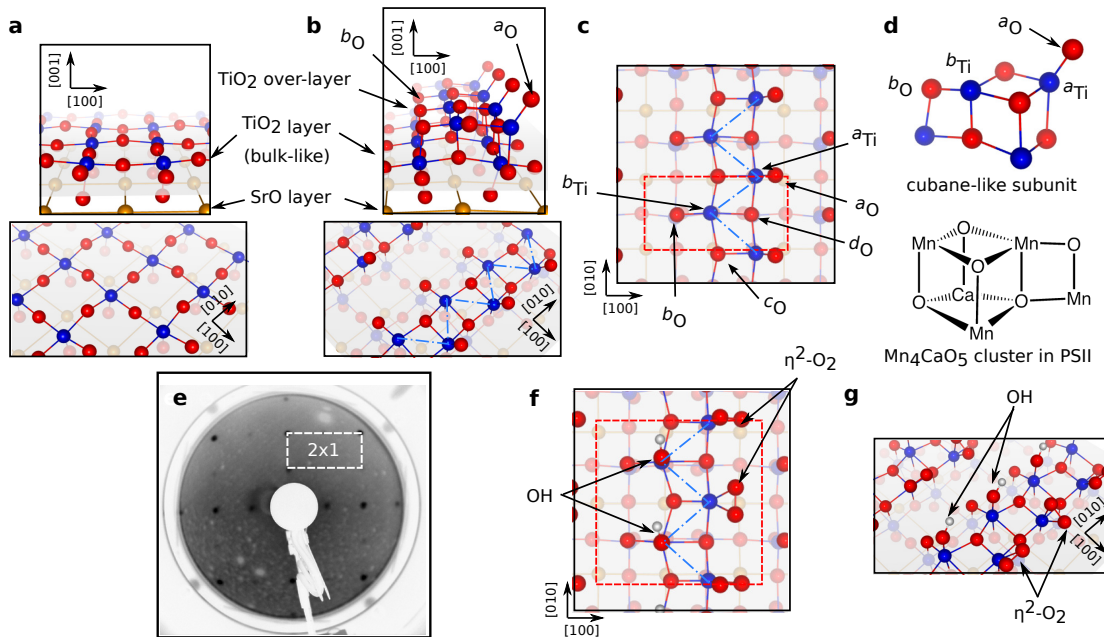


Figure 6.1: **Structure of the $\text{SrTiO}_3(001)$ bulk-like and double-layer (DL) reconstructed surfaces.** (a) The bulk-like TiO_2 and (b) the 2×1 -DL surfaces.(93) (c) Top-down view of the 2×1 -DL surface, which shows the surface Ti arranged in a zigzag pattern (traced by the blue dot-dashed line). The 2×1 supercell is marked by the red dashed line. (d) Upper panel: Ti_4O_6 subunit of the surface reconstruction exhibiting cubane-like structure. Lower panel: Structure of Mn_4CaO_5 cluster found in the OEC of Photosystem II.(11; 12) (e) A typical LEED pattern of a double-domain 2×1 reconstruction measured at 38 eV, a 2×1 pattern is marked. (f) Highly oxidized derivative of the 21-DL, predicted to be stable under catalytic conditions (B5 in Fig. 6.3, R4 in Fig. 6.4b). The 2×2 supercell simulation size is marked by the red dashed lines. (g) Angled view of the structure in (f).

6.2. Results and discussion

6.2.1. (Photo)electrochemical measurements

Four 2×1 surface reconstructed Nb-doped (1.4 mol %) SrTiO_3 single crystals were prepared, and the appearance of the reconstruction was confirmed via low energy electron diffraction (LEED), as shown in Fig. 6.1e. Heavily doped samples were chosen to decouple variation in the bulk conductivity from surface reconstruction due to processing. Indeed, resistivity measurements indicate that none of the processing required to create the reconstruction significantly alters the bulk electrical properties (see Table E.1 in Appendix chapter E). (Photo)electrochemical measurements were performed on these reconstructed samples. Fig. 6.2a shows the current vs. voltage (I - V) curves of the surface reconstructed samples (see also Fig. E.1 in Appendix chapter E) with onset voltages of ≈ 0.75 V *vs.* the standard hydrogen electrode (SHE). Along with the I - V curves, the current vs. time (I - t) curves (black lines), at constant potential and UV-Vis illumination, are plotted. Stable current densities of about 0.1-1 mA/cm² at 1.2 V were obtained corresponding to turnover numbers of ≈ 1 -10 $\mu\text{molO}_2/\text{hr}\cdot\text{cm}^2$ assuming Faradic efficiency of unity. The contribution of the photo-excitation to the catalytic activity in all cases is found to be minimal (≈ 0.02 -0.04 mA/cm² shift in the current density at low potentials), Fig. 6.2b; this is as expected for heavily doped semiconductors, where the free carriers effectively screen or reflect incident photons. Ellipsometric measurements show that the optical properties of the samples are unperturbed by their history (see Fig. E.2). I - V curves for control samples (with no reconstruction) with and without UV-Vis illumination were also obtained, Fig. 6.2c. Much lower current densities were obtained from these samples and are at least an order of magnitude less than the surface-reconstructed samples at potentials greater than 0.9 V.

The anodic current density, j , is known to increase exponentially with overpotential, the difference between the applied potential, U , and the equilibrium reduction potential, $\varepsilon_{\text{eq}} = 0.40 \text{ V vs. SHE at pH=14}$). This is expressed in the Tafel relation: $j = j_o \exp(\eta/A)$, where j_o is the exchange current density and A is the temperature-dependent Tafel slope.(164) η is usually plotted against $\log_{10}(j)$, $\eta = 2.303A \log(j/j_o)$ which are shown in Fig. 6.2d.(164) Tafel slopes $\approx 0.20 \text{ V}$ with exchange current densities of $0.003\text{-}0.05 \text{ mA/cm}^2$ (see Table E.2 in Appendix E) were obtained from the reconstructed samples at $0.9\text{-}1.2 \text{ V}$ potential window. Much higher Tafel slopes ($0.5\text{-}1 \text{ V}$) and lower exchange current densities ($0.001\text{-}0.003 \text{ mA/cm}^2$) were found for the control samples, although the UHV annealed sample showed a better Tafel slope (0.20 V) but much lower j_o (0.0006 mA/cm^2). Exclusively annealing SrTiO_3 in UHV had been previously shown to produce the 2×1 reconstruction,(165) however we have found that the surface Ti-enrichment processes (sputtering and chemical etching) and calcination in furnace in O_2 are essential in producing very sharp LEED images (indicating large areas of the reconstruction). Thus, the observed enhancement of slope for the UHV annealed control sample is likely due to some surface reconstruction that is undetectable in LEED. Samples exhibiting similar Tafel slopes likely indicate similar catalytic mechanism; however varying the effective catalytic surface area will lead to changes in their j_o .

Although in most cases, decay in the activity is observed over prolonged use (compare curves m1 and m2 in Fig. 6.2a), the enhancement is still better than the controls. Also a sharp 2×1 LEED pattern can be reobtained from the used samples by simply reannealing the samples in UHV (necessary to remove adsorbates and restore long range order on the surface to get a sharp LEED), which does not occur in as received samples.

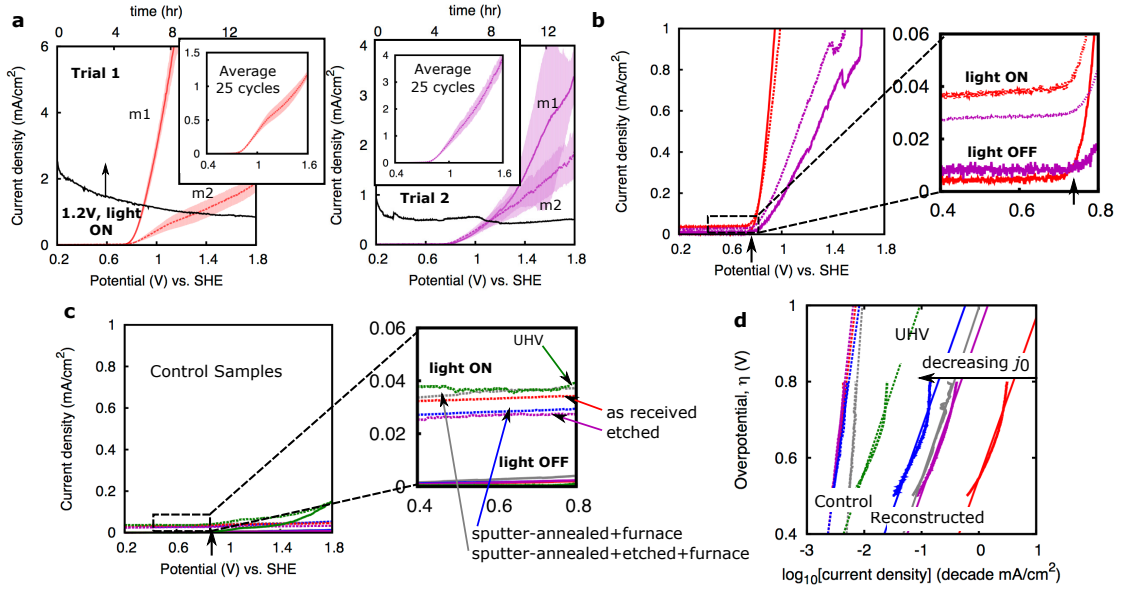


Figure 6.2: **Electrochemical measurements** . (a) I - V (vs. standard hydrogen electrode, SHE, at 10 mV/s, average five anodic-cathodic scan cycles), colored lines, and I - t (at 1.2 V vs. SHE with UV-Vis illumination), black lines, plots for the surface reconstructed samples. Shaded regions correspond to the current standard deviation and surface area uncertainty. m1 and m2 denote measurements from fresh samples and after the 14-hr constant voltage electrolysis, respectively. Insets show m2-type measurement averaged over 25 anodic-cathodic scan cycles at 10 mV/s. (b) and (c), I - V for reconstructed and control samples (1 mV/s, averaged over 2 anodic-cathodic scan cycles), respectively, with and without illumination. Thick arrows mark the onset voltages (≈ 0.75 V). (d) Tafel plots. I - V curves were taken from 1mV/s data acquisition (averaged over 2 cycles) from 0.9 to 1.2 V vs. SHE ($\eta = 0.5$ to 0.8 V). Solid line, surface reconstructed samples; broken line, control. The colors correspond to the same sample color designations in a and c and Fig. E.1 in Appendix E. Tafel parameters are summarized in Table E.2 in Appendix E.

6.2.2. Computational framework

We have found that this enhancement may be ascribed to the acquired efficiency due to the reconstruction, which enable thermodynamically balanced chemical routes. We employ density functional theory (DFT) and calculating the equilibrium reduction potential, $\varepsilon(i)$, for each elementary step i involved in the evolution of O_2 from water.(53; 54; 55; 56; 57) For a reaction consisting of n single-electron steps: $\eta = U - \varepsilon_{\text{eq}} = 1/n \sum_i^n [U - \varepsilon(i)]$. We can define the minimum $|\eta|$ at which all $[U - \varepsilon(i)]$ are ≥ 0 to favor oxidation, thus $\eta \geq \max[\varepsilon(i) - \varepsilon_{\text{eq}}] = \Delta\varepsilon_{\text{max}}$. Several ab initio studies of water splitting on oxide catalysts have shown that oxides with exceptional oxygen evolving activity have low predicted $\Delta\varepsilon_{\text{max}}$.(53; 54; 55; 56; 57) Other thermodynamic and electronic property-based descriptors, either experimentally or theoretically determined, have been successfully used to relate and predict the kinetic behavior of transition metal oxides toward water splitting.(166; 167; 168; 169; 170)

6.2.3. Surface hydration and oxidation

Before proceeding with evaluating the energetics of the catalytic mechanisms, we first find the equilibrium surface structure in highly oxidizing conditions for both surfaces. Specifically, the relative stability of the 1×1 and the 2×1 -DL surfaces with respect to their hydrated and more oxidized forms were determined. Surface stability of various reconstructions has been evaluated under realistic electrochemical conditions (298 K, equilibrium with an aqueous environment, pH=14, and subjected to an anodic (oxidizing) potential). To find the most stable surfaces, H_2O molecules have been added to the aforementioned surfaces, and then H atoms have been progressively removed. This is because it is expected that the surface becomes more O-rich as the potential bias becomes increasingly anodic. The complete hydration and oxidation

diagrams are constructed for the bulk-like TiO_2 and the 2×1 -DL surfaces, and are shown in Fig. E.3 and E.4, respectively, in Appendix E. Fig. 6.3a shows the most stable path to hydration and oxidation (reverse Latimer diagram) for the 2×1 -DL surface (2×2 surface cell). Starting from the pristine 2×1 -DL (B0), the surface is hydrated, preferentially on the ^aTi sites first then on a ^bTi site, leading to B1 (net hydration process is the red path). From this hydrated form, oxidation occurs by taking out electrons with the release of protons from the surface hydroxyls: total of $2(\text{H}^+ + e^-)$ leading to B2 (green path), $3(\text{H}^+ + e^-)$ leading to B3 (yellow), $5(\text{H}^+ + e^-)$ leading to B4 (pink), and finally, $6(\text{H}^+ + e^-)$ with the addition of water leading to B5 (blue). The oxidized structures feature side-on coordinated O_2 ($\eta^2\text{-O}_2$) molecules that are linked to the ^aTi atoms, either horizontally or vertically oriented, while hydroxide ions are adsorbed on the ^bTi atoms. Moreover these surface $\eta^2\text{-O}_2$ are either peroxo (single bond) or superoxo (one-and-a-half bond) as demonstrated by their charges, bond-lengths, and vibrational frequencies as shown in Table 6.1. Shown in Fig. 6.1f and g is the predicted highly oxidized form of the 2×1 -DL reconstruction (B5). The relative stability of the hydrated and oxidized surfaces vary with the applied potential and pH as shown in Fig. 6.3 b and c. In Fig. 6.3b, it shows the surface undergoes spontaneous hydration to B1 (red region), and then subsequently oxidized at 0.46 V ($=[1.26+0.13]\text{eV}/3e^-$) to B3 (orange region). At 0.63 V ($=[1.55+0.33]\text{eV}/3e^-$), the surface is further oxidized to B5 (blue region). Fig. 6.3c shows the corresponding Pourbaix diagram from pH=7 to 14. It illustrates how the coexistence potential varies with pH. The water splitting chemistry is done in excess of the equilibrium potential (0.40 V at pH=14) and each individual elementary step requires much larger potential to be spontaneous, as later shown. And thus, at these realistic kinetically permissive potentials (much >0.4 V), the most relevant surface would be B5.

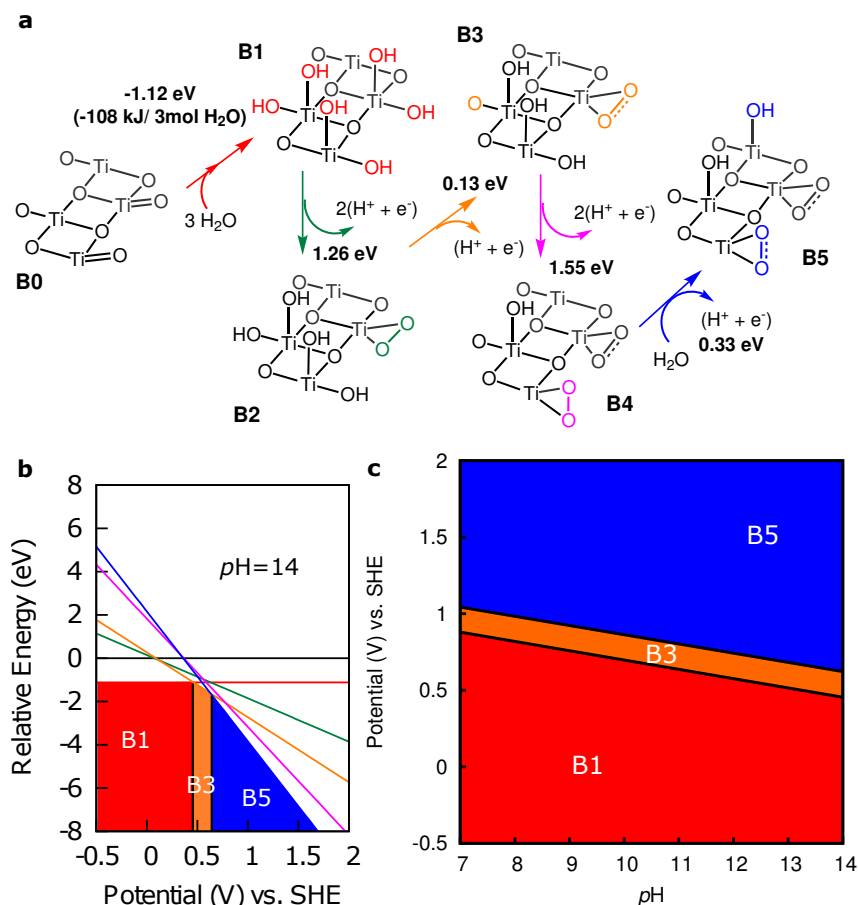


Figure 6.3: **Reverse Latimer (Hydration and oxidation) diagram for the 2×1 TiO_2 -DL surface.** (a) The diagram shows a series of hydration and deprotonation reactions leading to O-enrichment of the reconstructed surface. It shows the transformation of the adsorbate-free surface (B0) into the most oxidized form of the surface (B5), passing through the most stable intermediates (B1, B2, B3, and B4). A single bond between two O atoms indicates a peroxo while a one-and-a-half bond indicates a superoxo species. The schematics show only the top basis atoms of the 2×2 supercell (simulation size). The species experiencing chemical changes are in color. The Gibbs free energies of the reactions are indicated next to the arrows (*vs.* SHE, pH=14). B4 and B5 are R3 and R4 of Fig. 6.4b, respectively. The corresponding relative surface free energy at pH=14 as a function of applied potential ($\text{B0} + 4\text{H}_2\text{O}$ are chosen as the zero energy) and the Pourbaix diagram are shown in (b) and (c), respectively.

Table 6.1: Calculated Löwdin charges, bond lengths, and stretching frequencies of the O₂ moieties in the structures in the catalytic cycle of the reconstructed surfaces.

structure	orientation	charge (<i>e</i> /molecule)	bond length (Å)	stretching <i>v</i> (cm ⁻¹)
B2	horizontal	-0.75	1.40	971
B3	horizontal	-0.35	1.29	1174
R1	horizontal	-0.32	1.29	1173
R2	horizontal	-0.34	1.29	1173
R3 (B4)	horizontal	-0.72	1.41	961
	vertical	-0.36	1.30	1133
R4 (B5)	horizontal	-0.37	1.30	1156
	vertical	-0.33	1.29	1179
bulk O [†]		-1.05		
[‡] H ₂ O ₂ (<i>g</i>)			1.475	877
[‡] ¹⁶ O ₂ ^{•-}			1.35	1090

Structures are shown in Fig. 6.3 and in the catalytic cycle in Fig. 6.4b. The high-charge and the low-charge species show the lengths and vibrational frequencies of peroxo and superoxo ligands. [†]bulk lattice O charge is shown for comparison.

[‡]Experimental constants taken from NIST chemistry WebBook. (48)

6.2.4. Catalytic mechanism

The O₂ evolution catalytic cycles on the relevant highly oxidized bulk-like TiO₂ and 2×1-DL surfaces (B5 or R4) are shown in Fig. 6.4a and b, respectively. Here we discuss the 2×1-DL in more detail. O₂ evolution on the 2×1-DL surface is achieved as follows. (1) Beginning with surface R1, ^aTi=O is oxidized by adding H₂O and losing a proton, resulting in an O radical. (2) Further oxidation of the ^aTi site generates a peroxo-type O–O ligand. (3) After another single electron oxidation at the ^aTi site, coupled with the adsorption of a hydroxo at the ^bTi site, the R4 (B5) structure (Fig. 6.1g) is generated. The O₂ bond contracts, its stretching frequency rises, and the Lwdin charge decreases, consistent with forming a superoxo (Table 6.1, see also Fig. 6.5). These changes are accompanied by the removal of a proton from a water molecule at the ^bTi site, as summarized by the reactions in Fig. 6.6. (4) Finally, deprotonation at the ^bTi site creates an O²⁻ that replaces the desorbed dioxygen molecule at the ^aTi, regenerating R1. The mechanism proposed is of the Mars-van Krevelen type,⁽¹⁷¹⁾ where a lattice oxygen (^aO) participates directly as a reactant and is then replenished by a fully deprotonated water. Another defining characteristic of the mechanism is that the positive charge is accumulated on the O species and not on the Ti; the Ti charges remain at +4 through out the cycle.

Table 6.2 shows the calculated potential bias, U vs. SHE, required to make each step in the mechanisms shown in Fig. 6.4 reversible at $pH=14$. The largest biases are 1.45 V ($\Delta\varepsilon_{\max}=1.05$ V) and 0.92 V ($\Delta\varepsilon_{\max}=0.52$ V) for the bulk-like TiO₂ and the 2×1-DL reconstruction, respectively. The overpotential ($\Delta\varepsilon_{\max}$) lowering found in the 2×1-DL reconstruction agrees with the experimentally found increase in its catalytic activity. Although it is difficult to quantitatively ascribe the 0.5 V reduction in the theoretical thermodynamic overpotential $\Delta\varepsilon_{\max}$ to any of the Tafel parameters, this

lowering corresponds to barrier reduction in the rate-limiting step,.(53; 54; 55; 56; 57) leading to an enhanced rate. This could potentially explain the difference between the oxygen evolution rates experimentally found for the two surfaces.

Comparable DFT calculations involving the (110) surface of rutile phase TiO_2 reported an overpotential of $\Delta\varepsilon_{\text{max}}=0.78$ V.(57) This further illustrates that the cubane-like structure of the 2×1 -DL, which is not present on either the rutile (110) surface or the bulk-like TiO_2 termination of SrTiO_3 , is the key component in the reconstructions reactivity.

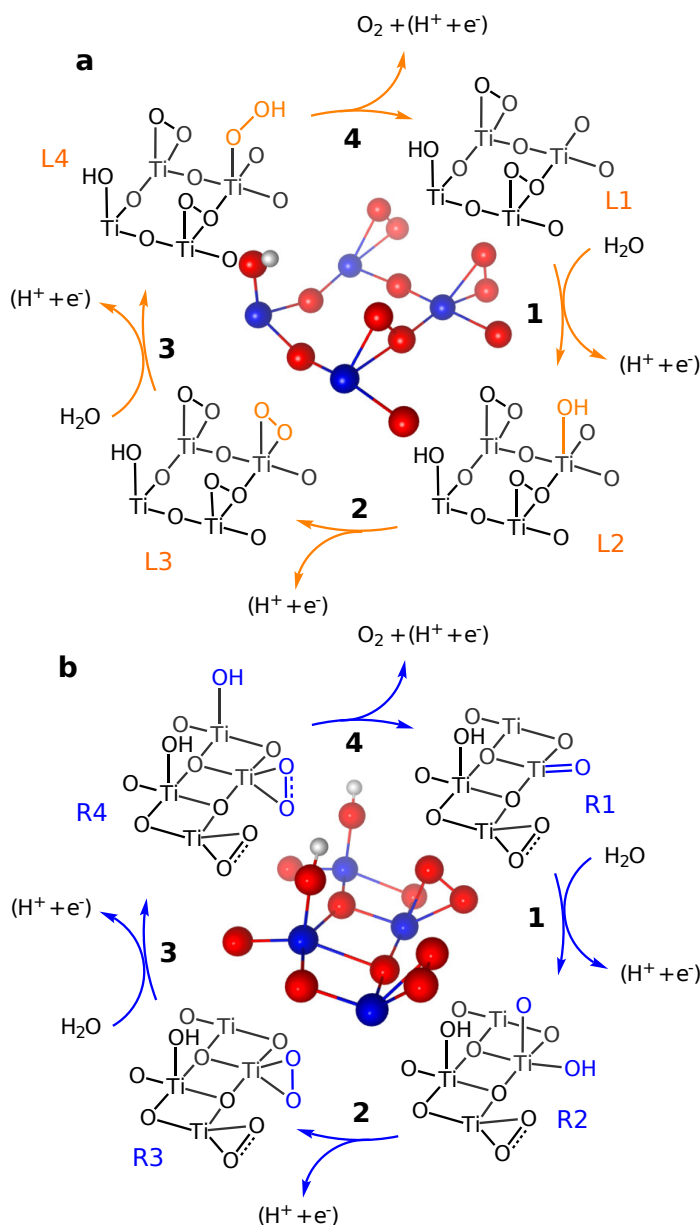


Figure 6.4: **Catalytic mechanisms** (a) Oxygen evolving reaction cycle on the bulk-like TiO_2 termination, and, (b), on the 2×1 -DL reconstruction. A single bond between two O atoms indicates a peroxo while a one-and-a-half bond indicates a superoxo species. Schematics show only the basis units of the top TiO_2 layer for the 2×2 supercells. For a complete cycle, two water molecules are consumed, and an O_2 molecule and 4H^+ ions are produced. The species experiencing chemical changes are in color. See Table 6.2 for the required applied potential for each reaction step to be driven to spontaneity.

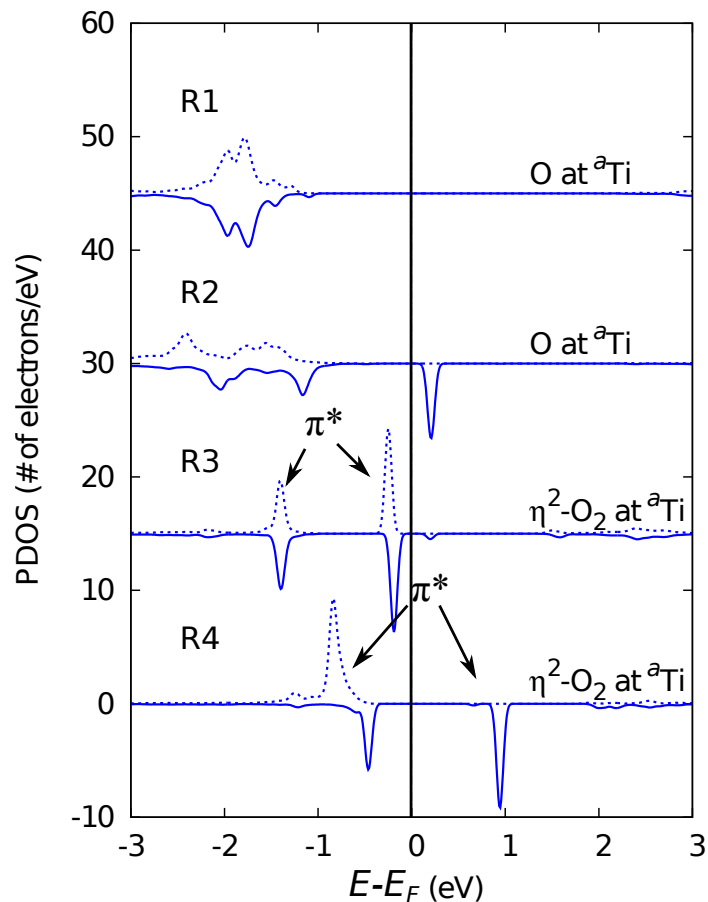


Figure 6.5: **Atomic orbital projected density of states (PDOS) of the O species in the intermediates of the catalytic cycle for the 2×1 TiO_2 -DL surface.** Orbital projections of the O 2s and 2p states of the oxygen species on the active site in Fig. 6.4b. Broken line: majority spin states, solid line: minority spin states. E_F is the Fermi level. The orbital occupation is consistent with oxo, oxo radical, peroxy, and superoxo orbital occupation schemes, from top to bottom. The splitting of the O_2 π^* orbitals is due to the sigma bonding interaction between one of these orbitals and some of the ^aTi t_{2g} orbitals.

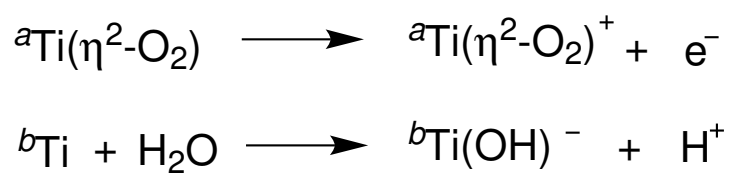


Figure 6.6: Proton-coupled electron transfer step involving both ${}^a\text{Ti}$ and ${}^b\text{Ti}$ simultaneously in step 3 of Fig. 6.4b.

Table 6.2: The minimum required applied potentials, U (vs. SHE) predicted to make the elementary steps of the catalytic cycles spontaneous.

step	Potential (V)	
	(1×1)TiO ₂	(2×1)TiO ₂ -DL
1	0.25	0.92
2	1.45	0.05
3	0.44	0.33
4	-0.53	0.30

The catalytic cycles are shown in Fig. 6.4.

6.2.5. Comparison of the mechanism with biological and molecular systems

Although several mechanisms have been proposed involving the Mn_4CaO_5 cluster,(172) some propose production of a highly electron-deficient O species on the terminal Mn not belonging to the Mn_3CaO_4 cube, while the Ca^{2+} acts as binding site for nucleophilic $\text{OH}^-/\text{H}_2\text{O}$, which reacts with the electron-deficient O to form O_2 .(12; 173; 174; 175) The two sites therefore perform different but complementary roles, while in this case, Ti atoms play both roles. Mechanism requiring dual active site has been proposed for some dinuclear Ru-based molecular water-oxidation catalysts.(175; 176) The two strongly electronically coupled Ru sites perform distinct roles, where only one Ru supports and produces the O_2 .(175; 176) The central mechanistic feature of complementarity, as has been demonstrated here theoretically and experimentally, is also present on the reconstructed SrTiO_3 surface, leading to enhanced activity.

6.3. Materials and methods

6.3.1. Surface reconstruction

To obtain the 2×1 surface we process the as-received single crystals (0.7 % Nb w/w or 1.4 mol %, MTI Corp.) as follows; (1) UHV outgassing at 600 °C for 30 min, (2) UHV Sputter with Ar^+ for 10 minutes at 1 kV and 1.1 μA ion current, followed by UHV (2×10^{-10} torr) annealing at 600 °C for 20 min, this sputter-anneal cycle is performed twice, (3) ultrasonication in water bath (177) at room temp for 1 hr in air, (4) etch for 90 s in a commercial buffered hydrofluoric acid etchant (178; 179) ($\text{NH}_4\text{F}:\text{HF} = 6:1$ by volume) in air, rinse with water and dry with N_2 stream, (5) furnace treatment at 980 °C for 2 hours with 5 °C/min ramp rate,(93) and O_2 flow (ultra high purity) at 2.5 L/min, (6) UHV anneal at 1020°C for 10 minutes or more as needed to obtain sharp and intense 2×1 surface reconstruction measured by LEED.

After electrolysis single crystals were annealed in UHV at 930°C for 7 min to observe the 2×1 with LEED. Control samples were generated using incomplete combinations of these processes, namely, as received, etched=(3)+(4), sputterannealed + furnace= (1)+(2)+(5), sputterannealed + etched + furnace=(1)+(2)+(3)+(4)+(5), and UHV=(6) for 10 min. LEED images were obtained at 38, 48, 61, 76 and 98 eV. 38 eV was found to be most suitable to get sharp 2×1 patterns.

6.3.2. *Electrode preparation and (photo)electrochemical measurements*

The $(2.5 \text{ or } 5)\times 5\times 0.5 \text{ mm}^3$ sized crystals were painted with Ga-In eutectic (99.99%) on the unpolished side to serve as the ohmic contact. Copper wires were then attached to this side of the crystals using Ag paint. Heat-shrink tubes were used to insulate the entire lengths of the Cu wires, while waterproof epoxy was used to insulate the back of the crystals (Fig. 6.7 and Fig. E.11 in Appendix E). A three-electrode setup was constructed and a custom-built glass photoelectrochemical cell equipped with a quartz window was used for all electrochemical measurements, shown in Fig. 6.8. The Epsilon Electrochemical workstation from BASi Analytical instruments was used as the potentiostat. A 23 cm Pt coil was used as the auxiliary electrode while a single-junction Ag/AgCl electrode (in 4M KCl electrolyte saturated with AgCl, Fisher Scientific Accumet) was used as the reference (+0.20 V *vs.* SHE). Prior to electrochemical measurements, the sample electrode is soaked in 1M NaOH for ≈ 1 hr. Electrochemical measurements were recorded in 1M NaOH aqueous solution, with and without UV-Vis light illumination from a 200 W Hg(Xe) lamp. The I - V and I - t curves were measured with acquisition frequencies of 1 Hz and 0.1 Hz, respectively.

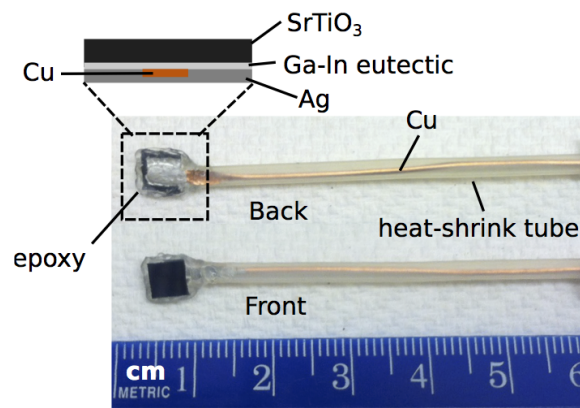


Figure 6.7: **Sample (working) electrode.** Electrode preparation for single crystals. The upper panel shows the schematic of the metallic contact on the backside of the SrTiO_3 crystals. Ga-In is painted first, then a thin layer of Ag paint is coated on it before a flattened head of a Cu wire is attached via Ag paint. Insulation of the backside is achieved with a waterproof epoxy, while a heat shrink tube is used to cover the Cu wire. See Fig. E.11 in Appendix E.

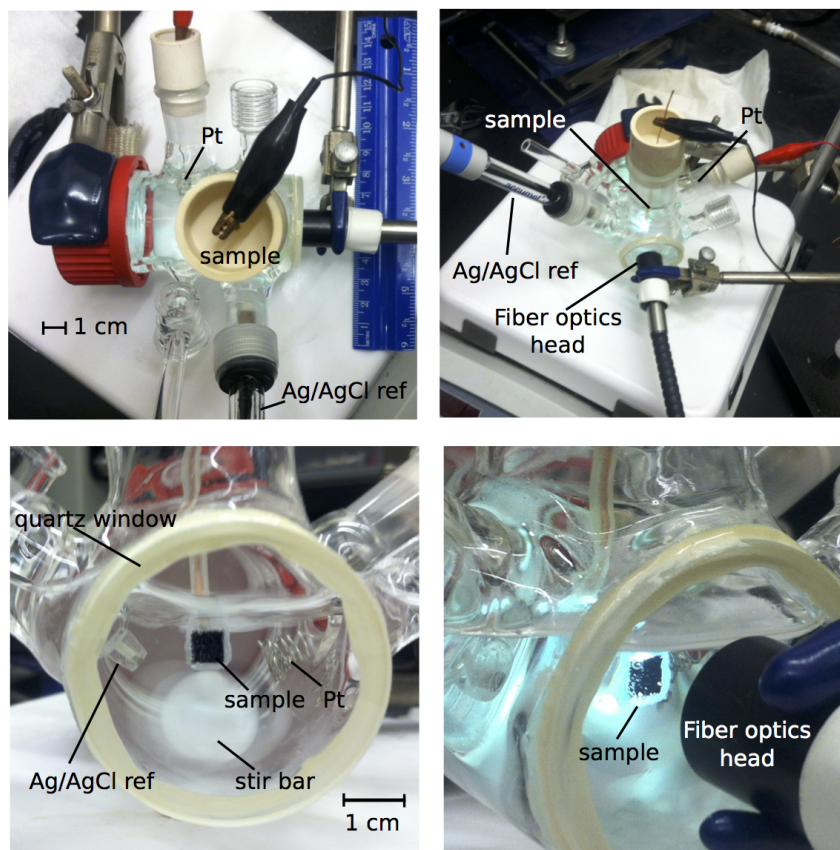


Figure 6.8: **(Photo)electrolysis set-up.** A custom-built electrolysis cell is constructed with a quartz window to allow UV-Vis illumination onto the sample surface. A Pt coil is used as an auxiliary electrode, while a Ag/AgCl (4M KCl) was used as a reference. Upper left, top-view, and upper right, birds-eye view, shows the relative positions of the electrodes. Lower left: front view. Note that the Pt coil is behind to the right of the sample, while the reference is on the left side of the sample. The Pt electrode and the porous tip of the Ag/AgCl electrode are ≈ 2.5 cm and ≈ 1 cm away from the sample, respectively. The cell is an open system where the sample is in contact with an aqueous solution of 1M NaOH. Lower right shows the bubble formation on the surface of the crystal.

6.3.3. Resistivity and optical properties

The resistivities of the samples were measured via the four-point probe method using a Cascade Microtech prober with 1.25 mm probe spacings. Using a J.A. Woollam M-2000 ellipsometer, dielectric properties, n and k , were extracted from raw data using an empirical spline fit. Reflectivities were taken at 65° angle averaged over different light polarizations.

6.3.4. Density Functional Theory

DFT calculations were performed with the Perdew-Burke-Ernzerhof (PBE) (34) generalized gradient approximation (GGA) for the exchange-correlation functional as implemented in the Quantum ESPRESSO package. (50) The effect of applying an effective Hubbard- U correction (2) onto the Ti $3d$ orbitals on the reaction energies in the catalytic cycles was checked and is shown in Fig. E.9 in Appendix E. The effective U was determined to be 4.72 eV from a linear-response calculation (2) involving a $2 \times 2 \times 2$ SrTiO₃ supercell. Norm-conserving optimized designed non-local pseudopotentials (45; 44; 46) were generated using the OPIUM package.(72) Four-unit-cell thick slabs with 2×2 surface supercells and in-plane lattice constant of 3.95 Å, were used to simulate the surfaces. A vacuum separation of ≈ 16 Å in the direction normal to the slab has been included, with a dipole correction (180) in the same direction to eliminate artificial electrostatic interactions. The Brillouin zone was sampled via the Monkhorst-Pack (41) method with a 3×31 mesh. As for the molecules (H₂ and H₂O), the total energy of a gas phase molecule was approximated by calculating the energy of an isolated molecule that is separated from its repeat image by 12 Å along three orthogonal directions. In the H₂O case, a dipole correction was also employed along the direction of the molecule’s dipole. We performed spin-unrestricted calculations

when deemed necessary. Structural relaxation has been carried out until the force on each atom is below 0.01 eVÅ. Zero point energy corrections to the total energy were calculated using linear response Γ -point phonon calculations for the surfaces and molecules (see General methodology). For the surface phonon calculations, only motions of the TiO₂ overlayer or bulk layer were considered. This was done because we assume that the zero point energy contribution of the bottom layers would simply cancel each other out in the Gibbs free energy change calculations.

CHAPTER 7 : Tunable surface stoichiometry in oxide ferroelectrics via the switchable bulk-polarization

7.1. Introduction

Ferroelectricity (FE) is characterized by coordinated ionic displacements from nominal high-symmetry lattice sites that cause a macroscopic electric polarization (22). Consequently, electric charge appears at the surfaces or interfaces due to the polar discontinuity. This produces an electrostatic surface instability that is similar to the situation of polar surfaces (23; 24; 25; 26; 27). Stabilization can be achieved by charge passivation of electronic or ionic origin. In the first case, the surface electronic structure is modified, perhaps leading to metallic surfaces (28). In the second case, the surface stoichiometry is altered from that of the bulk. Both cases lead to surfaces that are very different from the bulk or from the non-polar terminations. The surface conductivity and catalytic chemistry of these surfaces are of prime interest for practical as well as fundamental purposes.

The reorientable polarization of FE oxides holds the promise for immense control of surface composition and properties. The interest in FE perovskites has been continuously increasing over the past decade due to their widespread use in a wide range of applications including catalysis, sensing devices, actuators, high-storage capacitors and nonvolatile memories (22; 29). BaTiO_3 (BTO) and PbTiO_3 (PTO) of the ABO_3 perovskite family, perhaps the most prominent and well studied FE oxides, have divalent A -cations (Ba^{2+} and Pb^{2+}) and tetravalent B -cations (Ti^{4+}). There are only a few studies of reconstructions on FE surfaces (26; 27) despite their practical

importance in many applications. Adsorption studies of molecules on FE surfaces have shown unambiguously that the positive-polar (P^+), negative-polar (P^-), and nonpolar surfaces interact differently with molecules (87; 19; 17; 18; 85; 121; 181), and thus it can be anticipated that the stability of different surface compositions on FE surfaces would be highly polarization-dependent. Indeed, this was found the case in LiNbO_3 which has an intrinsically polar (0001) termination and is ferroelectric. The equilibrium stoichiometry on the P^+ surface contains more oxygen than on the P^- surface at similar chemical conditions (26).

To date, the systematic changes of surface composition with FE polarization have not been explored. In this Letter, we demonstrate the paradigm of polarization-controlled surface composition and structure. Because we are primarily interested in the effect of the polarization component perpendicular to the surface, we select the tetragonal phases of BTO and PTO for study. We use a thermodynamic approach in conjunction with density functional theory (DFT) energies to map out the stability regions of various surface compositions under different experimental boundary conditions. The tetragonal phases of BTO and PTO, both belonging to the perovskite family and sharing similar properties, are expected to have similar surface phase diagrams. We find that this is generally true, but there are several notable differences between them that stem from the stronger FE polarization of PTO compared to BTO, as well as from the greater reducibility and oxidizability of Pb^{2+} compared to Ba^{2+} . The current study highlights the significant and systematic impact that polarization can have on the reconstruction of polar surfaces, especially with structural and compositional changes beyond the formation of oxygen vacancies. We provide the general principles of how ionic nonstoichiometry enables compensation for bound polarization charge, and we give definite maps showing how to control reconstruction

type with temperature, pressure, and polarization.

7.2. Methodology

Density functional theory (DFT) calculations are performed using the Perdew-Burke-Ernzerhof functional (34) as implemented in the Quantum ESPRESSO package (50). We used norm-conserving RRKJ pseudopotentials (45) generated with OPIUM (72) which were shown previously (108) to be of good quality. The Kohn-Sham orbitals are expanded using plane waves with a cut-off energy of 25 Ha. The reciprocal space integration was performed using a $4 \times 4 \times 1$ Monkhorst-Pack (41) k -point mesh. Slabs are modeled using a supercell approach with seven to eight oxide layers capped on one end by three layers of Pt metal.(8) The bottom four oxide layers and the Pt layers are fixed during the optimization, while all other atomic coordinates are allowed to relax until the maximum component of the residual force is less than 0.4 mHa/ÅBy imposing the paraelectric (PE) or ferroelectric (FE) bulk distortions on the fixed oxide layers, finite-size effects that can be severe in FE slabs due to the depolarization field (182; 183) are suppressed. To prevent interactions between the periodic images, we included 12–20 Å of vacuum between the slabs. The validity of the computational model including effects of spin-polarization is extensively investigated as detailed in section F.1 of Appendix F.

We include a large variety of surface compositions and reconstructions including (1×1) , $c(2 \times 2)$, (2×1) , and (3×1) in addition to the (1×1) bulk-like terminations. We have also included a small set of (2×2) reconstructions to reproduce previous results for PE BTO (8). For each reconstruction, we examined BaO/PbO and TiO₂ terminations, as well as surface compositions that have adatoms (cations or oxygen), vacancies (cations or oxygen), and adlayers (BaO/PbO, TiO, or TiO₂).

The construction of the surface phase diagram is described in detail in chapter 3: General methodology, sections 2.7 Density functional theory and thermodynamics and 2.8 Surface phase diagrams.

7.3. Results and Discussion

The BTO and PTO phase diagrams in Figure 7.1 show a rich proliferation of surface reconstructions with a variety of stoichiometries. The range of chemical potentials for which the surfaces are in equilibrium with the corresponding bulk phase and with no precipitation of secondary phases is also drawn (described and defined General methodology). The surface compositions found can be grouped into three categories, namely (i) BaO/PbO-derived [BaO/PbO double layer (DL), BaO/PbO, BaO-(V_O)_x and BaO/PbO-O_x]; (ii) Ti_xO_y-derived [TiO₂-DL, TiO₂-TiO_x, and TiO₂-(TiO)_x]; and (iii) Ti-rich (TiO₂-Ti_x) for BTO(001) and Pb-rich (TiO₂-Pb_x) for PTO (001). The structures of some of the prominent reconstructions are shown in Fig. 7.2.

7.3.1. Atomic structures of the reconstructions

BaO/PbO-derived surfaces

In the BaO/PbO-DL termination, the BaO/PbO overlayer is shifted by half a unit cell along [110] with respect to the BaO/PbO layer underneath (two-layer rock salt structure). Modification of the stoichiometric BaO/PbO surface via the formation of O (Ba/Pb) vacancies is accompanied by downward (upward) displacement of the Ti atom below the vacancy but otherwise leaves most of the structure nearly unchanged. Excess oxygen adatoms interact with BaO and PbO terminated slabs differently. On BaO, oxygen binds with a surface oxygen to form an O₂ moiety (see Fig. 7.2(c)). On the other hand, on the PbO terminated slabs, O reacts with the surface Pb

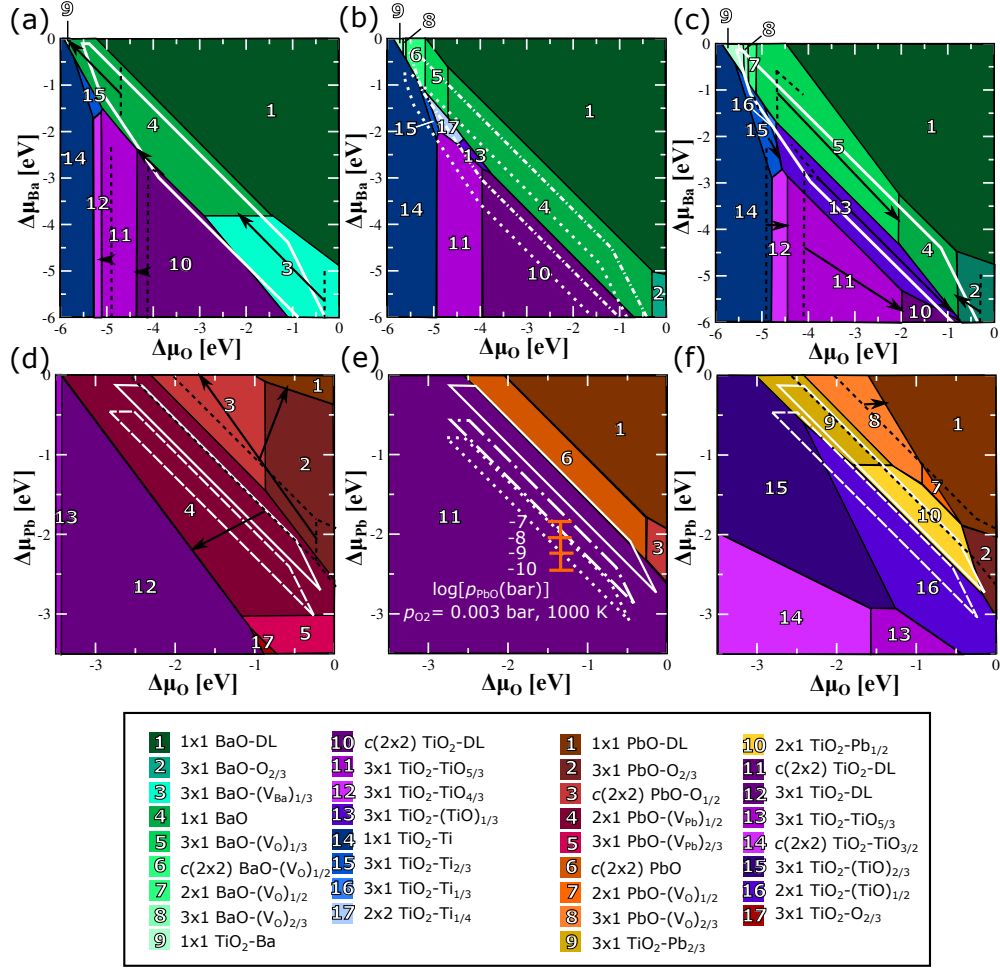


Figure 7.1: Surface phase diagram for BTO (a-c) and PTO (d-f). First column, a and d, FE cases with polarization directed toward the surface (P^+), second column, b and e, PE cases, and third column, c and f, FE cases with P^- . The white lines show ABO_3 stability regions with respect to the secondary bulk phases (see Fig. 2.2 in General methodology for the definition of the lines) for $T \leq T_C$ for FE cases, and $T \geq T_C$ for PE where the Curie temperature $T_C = 403$ K (BTO) and 763 K (PTO). White solid (300 K), fine dash-dotted (500 K), dashed (700 K), dash-dotted (800 K), and dotted (1000 K) lines show the stability region at different temperatures. The black arrows indicate the trajectory for the changes of the phase boundaries from the PE case (shown as black-dashed lines). For (e), $\Delta\mu_{Pb}$ for different $PbO(g)$ pressures are marked for the $\Delta\mu_O$ value corresponding to the experimental conditions in Ref. (13). Legend: first two columns are for (a-c), final two columns are for (d-f).

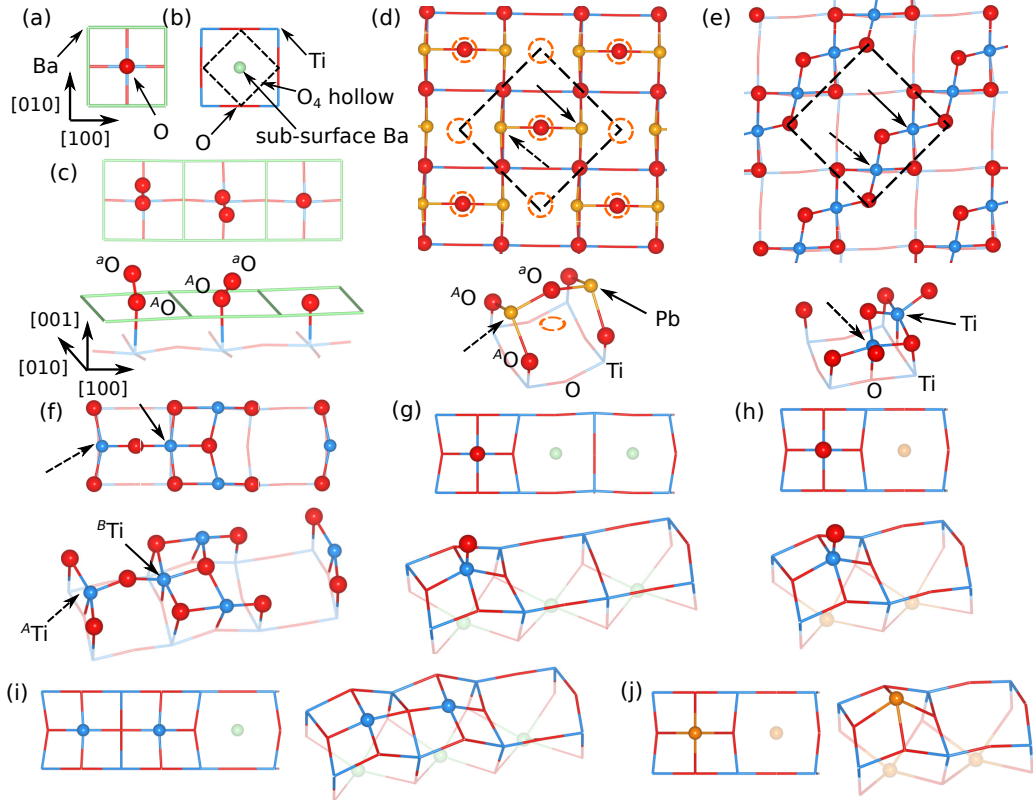


Figure 7.2: Ball-and-stick models for important surfaces that are affected by bulk polarization: (a) (1×1) BaO/PbO and (b) TiO_2 . Top and side views for (c) 3×1 BaO- $\text{O}_{2/3}$, (d) $c(2 \times 2)$ PbO- $\text{O}_{1/2}$, (e) $c(2 \times 2)$ TiO_2 double-layer, (f) 3×1 TiO_2 - $\text{TiO}_{5/3}$, (g) 3×1 TiO_2 -(TiO) $_{1/3}$, (h) 2×1 TiO_2 -(TiO) $_{1/2}$, (i) 3×1 TiO_2 - $\text{Ti}_{2/3}$, and (j) 2×1 TiO_2 - $\text{Pb}_{1/2}$. Large red spheres: O; small green, yellow, and blue spheres are Ba, Pb, and Ti, respectively. The arrows in (d), (e) and (f) are to help identify the same atoms in the top and side views. Dashed lines in (d) and (e) mark the $(\sqrt{2} \times \sqrt{2})$ $R45^\circ$ supercell. For (c) and (d), the ^AO atoms are lattice oxygen atoms, while ^aO are O adsorbates. In both cases ^AO atoms remain in the same sites as in the bulk termination. For (d), the Pb atoms are displaced away from their original positions defined as in the bulk termination (marked by circular broken lines), where half of these abandoned sites are occupied by the ^aO atoms.

that results in a more subtle reconstruction, where the Pb atoms rearrange on the surface to maximize Pb–O bonds while also minimizing O-to-O repulsion (showing propensity of Pb^{2+} to be further oxidized). For example in the $c(2\times 2)\text{PbO-O}_{1/2}$ case, Pb ions migrate on top of subsurface O atoms while also forming bonds with the O adatom (^aO), occupying half of the O_4 hollow sites previously occupied by Pb, see Fig. 7.2(d). This reconstruction is similar to forming a partially reduced TiO_2 double layer (discussed below) where instead the overlayer is composed of $\text{PbO}_{3/2}$ (or $\text{PbO-O}_{1/2}$). This striking similarity is not surprising if put in the context of the ability of PbO_2 to form similar structures as TiO_2 (for example rutile).

Ti_xO_y -derived surfaces

The TiO_2 -DL and its partially reduced forms have been extensively studied on the $\text{SrTiO}_3(001)$ surface (93; 94). The $c(2\times 2)$ TiO_2 -DL, see Fig. 7.2(e), which is the most stable among the investigated TiO_2 -DL structures, has its edge-shared TiO_5 polyhedra arranged in rows along the $[110]$ direction. The reduced forms of TiO_2 -DL such as 3×1 $\text{TiO}_2\text{-TiO}_{5/3}$ (see Fig. 7.2(f)) preserve these edge-shared TiO_5 units. However, some corner-shared TiO_5 polyhedra are also now present (see O-sharing in ^ATi - and ^BTi -centered polyhedra in Fig. 7.2(f)). Unlike in the TiO_2 -DL structures, excess TiO on TiO_2 terminations prefers the Ti adatoms to be in O_4 hollow sites with the O adatom directly on top of Ti, maximizing the Ti coordination (maintaining a five-fold coordination) despite the very low O concentration on the surface relative to Ti, see Fig. 7.2(g) and (h). This type of reconstruction has been thoroughly investigated recently by Morales *et al.* (132).

Ti/Pb-rich surfaces

The Ti adatom on the Ti-rich TiO_2 surfaces prefers to sit on an O_4 hollow site, a 4-fold coordination site. Increasing Ti coverage on the surface draws the O of the TiO_2 more out of plane, which further reduces the TiO_2 layer (see Fig. 7.2(i)). Analogous to this system are the Pb-rich TiO_2 terminations found in PTO. A Pb adatom adsorbs at the same site on a TiO_2 surface, although situated more out-of-plane than a Ti adatom, owing to its larger ionic radius (see Fig.

7.3.2. Polarization-dependent phase diagrams

PE BTO and PTO surfaces have distinctly different phase diagrams, as seen by comparing Fig. 7.1(b) and (e). The PE BTO phase diagram is in excellent agreement with previous theoretical and experimental studies (8; 9). For PE PTO, the oxidized $c(2\times 2)$ TiO_2 -DL and the $c(2\times 2)$ PbO termination are the most stable at high (800–1000 K) and room temperature, respectively. This is consistent with previous $T = 0$ DFT calculations which concluded that only PbO and not TiO_2 surface is stable for thin film PTO with an in-plane polarization (184). A number of experimental studies are available for PTO as well (19; 13).

It has been found that epitaxial PTO thin-films grown on STO substrate exhibited a $c(2\times 2)$ surface reconstruction in a wide range of temperature 875–1025 K, and with different oxygen partial pressure p_{O_2} conditions.(13) For very low PbO pressures, *e.g.* $p_{\text{PbO}} = 4\times 10^{-10}$ bar at 1000 K, this study found the surface to reconstruct into a disordered (1×6) superstructure that is more TiO_2 -rich than the $c(2\times 2)$ phase. We show in Fig. 7.1(e) the region corresponding to the oxygen chemical potential in these experiments at 1000 K. Our phase diagram explains the $c(2\times 2)$ -PbO seen, and additionally suggest that a $c(2\times 2)$ TiO_2 -DL layer can also be stable under these

chemical conditions. We note that a $c(6\times 2)$ reconstruction phase was found for $\text{SrTiO}_3(001)$ between 1323 and 1373 K and under high-purity O_2 . This reconstruction exhibits short-range order, prominently showing microscopic domains composed of more than one TiO_x overlayer on a bulk-like TiO_2 layer (94). Thus, it is likely that the disordered (1×6) phase found in PTO for very low p_{PbO} in Ref. (13) is similarly composed of multiple TiO_x overlayers.

We now examine how FE polarization influences the surface phase diagram. Most of the PE surface reconstructions are also found in the phase diagrams of the FE surfaces, but under different ranges of chemical potential. In fact, the FE polarization can stabilize or eliminate surface compositions with stoichiometry similar to the most stable reconstructions in the PE case, and polarization can also induce highly non-stoichiometric structures. This is explained schematically in Fig. 7.1, and described in Table 7.1.

The most significant differences between the surfaces of PE and FE slabs can be understood from charge passivation, which is of paramount importance for the stabilization of polar surfaces (25; 26). To illustrate this, it is useful to regard the different surface terminations as arising from the formation of defects on the stoichiometric surface, which then organize into stable reconstructions. We define neutral reconstructions as those with surface compositions where the layer A/O and Ti/O ratios are 1:1 and 1:2, respectively. Using a simple ionic-charge representation, we can refer to nonstoichiometric surface compositions as positive if the A/O or Ti/O ratios are greater than the neutral ones, and negative if they are smaller than the neutral ratios (with a few exceptions such as O on BaO as discussed below). We illustrate this further for BTO. Starting from the neutral TiO_2 -DL reconstruction ($\text{Ti}/\text{O} = 1:2$), abstraction of O from the top layer creates positive reconstructions such as

Table 7.1: Comparison of the stability region of the reconstructions in the surface phase diagram of the different types of surfaces.

<i>Charge</i> Reconstruction	Description of the stability region					
	BaTiO ₃			PbTiO ₃		
	P^+	P^0	P^-	P^+	P^0	P^-
<i>Neutral</i>						
AO-DL	p	p	p	p	p	p
TiO ₂ -DL	$\Delta\mu_{\text{O}}^-$	p	$\Delta\mu_{\text{O}}^+$	$\Delta\mu_{\text{O}}^-$	p	$\Delta\mu_{\text{O}}^+$
AO-O _x (peroxo)	a	p	a	na	na	na
<i>Positive</i>						
AO-O _x (superoxo)	a	a	p	na	na	na
AO-(V _O) _x	p	a	b	a	a	p
TiO ₂ -TiO _x	$\Delta\mu_{\text{O}}^-$	p	b, $\Delta\mu_{\text{O}}^+$	p	i	$\Delta\mu_{\text{O}}^+$
TiO ₂ -(TiO) _x	a	p	b	a	a	p
TiO ₂ -Ti _x	n	p	b	na	na	na
<i>Negative</i>						
AO-(V _{Ba}) _x	p	a	a	p	a	a
AO-O _x (oxo)	na	na	na	b, $\Delta\mu_{\text{O}}^-$	p	p
$\Delta\mu_{\text{O}}^-$ ($\Delta\mu_{\text{O}}^+$) indicates that the range of $\Delta\mu_{\text{O}}$ under which the reconstruction is stable is shifted to lower (higher) values of $\Delta\mu_{\text{O}}$. p: present, a: absent, b: broader, n: narrower, i: inaccessible, na: not applicable.						

$\text{TiO}_2\text{-TiO}_x$ ($\text{Ti/O} = 1:[1+\frac{x}{2}] > 1 : 2$ for all $x < 2$), and in extreme cases this may be accompanied by removal of some TiO_2 units as well as O, yielding $\text{TiO}_2\text{-(TiO)}_x$ ($\text{Ti/O} = [1+x]:[2+x] > 1 : 2$ for all $x > 0$) or $\text{TiO}_2\text{-Ti}_x$ ($\text{Ti/O} = [1+x]:2 > 1 : 2$ for all $x > 0$).

The FE polarization decreases the net surface charge of the PE surface for the P^+ case, while it increases the charge for the P^- surface. In turn, this coupling creates a mechanism to passivate the polarization charges. This can be seen from a charge partitioning scheme, for example, as provided by Bader charges (185). For illustration purposes, we consider Bader charges for 3×1 $\text{TiO}_2\text{-TiO}_{5/3}$ and 3×1 $\text{TiO}_2\text{-Ti}_{2/3}$ reconstructions shown in Figs. 7.2f and 7.2i (more Bader charge analysis is provided in Table F.4 in Appendix F). For the PE surface, the net surface charges per unit cell of these two reconstructions are respectively $0.25e$ and $0.52e$, which decrease to $0.10e$ and $0.43e$ for P^+ , and increase to $0.39e$ and $0.60e$ for P^- . This shows that on the P^+ surface, it is more difficult to abstract O from the surface, and much less desirable to have positive reconstructions. This accordingly shifts the region of stability of the 3×1 $\text{TiO}_2\text{-TiO}_{5/3}$ and 3×1 $\text{TiO}_2\text{-Ti}_{2/3}$, as well as other positive reconstructions to a lower $\Delta\mu_{\text{O}}$. The reverse is true for the P^- surface, where the stable regions in the phase diagram for positive reconstructions are shifted to higher $\Delta\mu_{\text{O}}$; an indication for the propensity of the P^- surface to stabilize positive reconstructions. Additional examples include $\text{BaO-(V}_\text{O})_{1/3}$ that has a broader stability range on P^-/BTO , and $\text{PbO-(V}_\text{O})_{2/3,1/2}$ that appears only on P^-/PTO . Additionally, $\text{BaO-(V}_\text{Ba})_{1/3}$ for BTO, and $\text{PbO-(V}_\text{Pb})_{2/3,1/2}$ and $\text{PbO-O}_{2/3,1/2}$ for PTO have larger stability regions on, or appear exclusively on the P^+ surface (see Table 7.1).

It is, however, still possible that relatively severe environmental conditions could impose reconstructions that are apparently of the wrong charge type on the FE surfaces. We find that in this case, the polar surface would alleviate the polar instability

by localizing a hole or electron around the defect to reduce the effective charge of the surface, as can be seen from inspecting bond lengths or from Bader charge decomposition. One notable example of this is the BaO-O_x surface termination, where the O-adatoms bond to the surface O rather than to the Ba cations. On the PE surface, the O₂ bond length is ≈ 1.44 Å as in BaO-O_{2/3} (see Figure 7.2c), consistent with the formation of a peroxo-like (O₂²⁻) surface species, thus maintaining a low surface charge (the Bader charge for O₂ = ^aO+^AO is $-1.42e$ while the charge of O atom in ATiO₃ is $\approx -1.2e$). On the other hand, on the negative surface, the O₂ bond length is ≈ 1.37 Å indicating the formation of a superoxo-like (O₂¹⁻) surface species. The charge of the surface O₂ is then lowered ($-1.12e$). This mechanism enables stabilization of the *P*⁻ surface despite the presence of high amounts of O, which explains why, in Fig. 7.1(c) the 3×1 BaO-O_{2/3} (phase # 2, shown in Fig. 7.2(c)) expands its stability at the expense of the 1×1 BaO (phase # 4). These show that O on BaO may be regarded as a neutral, negative or positive reconstruction, in response to the bulk polarization. The formation of the surface peroxo and superoxo species is similar to what has been seen before on other oxide surfaces such as LiNbO₃ (26), CeO₂ (186) and V₂O₃ (187). Interestingly, we find that another mechanism is operative on PTO where the oxygen adatom interacts with the Pb cations rather than the surface O. This is because Pb²⁺ can be oxidized to Pb⁴⁺, thereby stabilizing an additional surface oxo (O²⁻) group (see Fig. 7.2(d) for the structure).

Although, both BTO and PTO have similar structural characteristics (with their A cations in the same oxidation state), they show drastic differences in their surface stability, which can be attributed mostly to the significant differences between the affinities of Ba and Pb to oxygen. The PbO-derived surface is more reducible than the BaO-derived one, and Pb is more likely to precipitate out as Pb(*s*) or vaporize

into $\text{Pb}(g)$. This is directly related to the existence of $\text{TiO}_2\text{-Pb}_x$ phases on P^- /PTO while a $\text{TiO}_2\text{-Ba}_x$ reconstruction is found to be unstable. Also, $\text{PbO-(V}_\text{O})_x$ is stable at a less negative $\Delta\mu_\text{O}$ compared to $\text{BaO-(V}_\text{O})_x$. Additionally, PbO is more volatile than BaO or TiO_2 making the formation of the PbO surface less favorable compared to BaO or TiO_2 . Thus PbO -derived surfaces are found only near the $\Delta\mu_\text{Pb} = 0$ boundary. Moreover, because TiO_2 is also less reducible than PbO , Ti -rich phases are inaccessible in the region where PTO is stable. This means that moderately negative $\Delta\mu_\text{O}$ is enough to reduce Pb^{2+} and destroy the perovskite structure. The most reduced TiO_2 -derived surface that is accessible for PTO is $\text{TiO}_2\text{-(TiO)}_x$ in the P^- case. These effects combine to make the stability region of PTO a narrower slice of the phase diagram compared to BTO , and closer to the $\Delta\mu_\text{Pb} = 0$ and $\Delta\mu_\text{O} = 0$ boundaries.

It is also apparent that the highest accessible nonstoichiometry is higher for PTO than for BTO . For example, compare their respective $\text{AO-(V}_\text{A})_x$ or $\text{TiO}_2\text{-(TiO)}_x$ phases where the maximum value of x that is stable is greater for PTO ($x = 2/3$) than in BTO ($x = 1/3$). This is consistent with the nature of the charge passivation mechanism. Because PTO has higher polarization than BTO (calculated polarization: (108) 0.89 versus 0.46 C/m²), more charged species on the surface are required to stabilize the surface of FE PTO .

7.3.3. Effects of surface stoichiometry on bulk polarization in thin-films

In thin films, surface effects are closely coupled to the substrate polarization (188; 17; 18), and thus it is important to predict the polarization direction that is favored by different surface stoichiometries. Figures 7.3(a) and 7.3(b) show the combined phase diagrams of the P^+ and P^- polarizations for both BTO and PTO . A region is indicated as P^+ (P^-) if the stable surface compositions have all P^+ (P^-) bulk

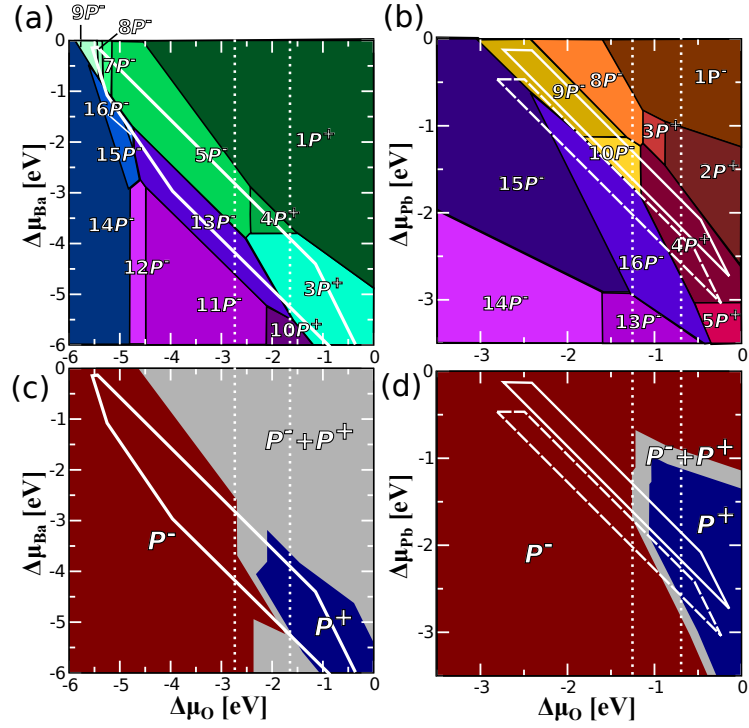


Figure 7.3: The computed surface phase diagram for BTO (a) and PTO (b) combining corresponding P^+ and P^- phase diagrams. See Fig. 7.1 for legend. The labels P^+ and P^- indicate whether the substrate polarization is up- or down-polarized, respectively. (c)-(d) Preferred bulk phase polarization for BTO (c) and PTO (d), where blue and red regions indicate, respectively that P^+ and P^- are stable, and gray indicates regions where both P^+ and P^- are stable. Dashed vertical lines mark the $\Delta\mu_O$ range where $P^+ \leftrightarrow P^-$ transition may occur within the bulk stability regions.

polarizations, and is indicated as $P^- + P^+$ if the surfaces have both P^- and P^+ stable compositions. However, instead of defining a sharp phase boundary, we consider the surface compositions that are within a small region δ from the lowest energy structure. We chose $\delta = \pm 0.1$ eV/primitive unit cell as a measure of an average error in the DFT energy differences. As can be seen from Figure 7.3, oxygen-poor and metal-rich conditions favor P^- , while oxygen-rich and metal-poor conditions favor P^+ . The $P^+ \leftrightarrow P^-$ transition can be approximated from the boundaries between surface phases that favor P^+ and P^- within the bulk stability boundary.

The region in the phase diagrams where P^+ and P^- may coexist according to the defined energy window approximates the chemical potential range where the $P^+ \leftrightarrow P^-$ transition will occur [see Figures 7.3(c) and 7.3(d)]. For BTO, the transition takes place at $\Delta\mu_{\text{O}} \approx -2.75$ to -1.5 eV at 300 K, while for PTO the transition happens at $\Delta\mu_{\text{O}} \approx -1.25$ to -1 eV at 300 K and $\Delta\mu_{\text{O}} \approx -1.25$ to -0.75 eV at 700 K. The approximate range of O_2 pressure corresponding to these chemical potentials can be obtained using

$$\Delta\mu_{\text{O}}(0 \text{ K} \rightarrow T, p_{\text{O}_2}) = \Delta\mu_{\text{O}}(0 \text{ K} \rightarrow T, p_{\text{O}_2}^0) + \frac{1}{2}kT \ln[p_{\text{O}_2}/p_{\text{O}_2}^0], \quad (7.1)$$

where $\Delta\mu_{\text{O}}(0 \text{ K} \rightarrow T, p_{\text{O}_2})$ and $\Delta\mu_{\text{O}}(0 \text{ K} \rightarrow T, p_{\text{O}_2}^0)$ are respectively the relative chemical potential of O at temperature T and O_2 partial pressures p_{O_2} and $p_{\text{O}_2}^0$, measured with respect to O_2 at 0 K and $p_{\text{O}_2}^0 = 1$ bar, and k is the Boltzmann constant. $\Delta\mu_{\text{O}}(0 \text{ K} \rightarrow T, p_{\text{O}_2}^0)$ can be calculated using tabulated entropies and integrated isobaric heat capacities for O_2 (1; 47). $\Delta\mu_{\text{O}} = -2.5$ eV corresponds to $p_{\text{O}_2} \approx 10^{-7.5}$ bar at 300 K, while $\Delta\mu_{\text{O}} = -1$ eV corresponds to $\approx 10^{-7} - 10^{-4}$ bar at 600 – 700 K. For PTO, this value of p_{O_2} is consistent with experiments on thin-film PTO at 644 K, where $p_{\text{O}_2} = 10^{-7}$ and 10^{-4} bar were found for a $P^+ \rightarrow P^-$ and $P^- \rightarrow P^+$ switching

that is induced by changing p_{O_2} .⁽⁸⁵⁾ On the other hand, for BTO, the low calculated switching value of p_{O_2} indicates that it will be challenging to switch BTO at low temperatures from a P^+ state via the control of oxygen partial pressure (starting from high p_{O_2}). It may be difficult to form sufficiently oxygen-deficient conditions at low T , although it should be accessible electrochemically via coulometric titration (189; 190).

To some extent, the limited number of sizes of supercells investigated imposes limitations on our ability to predict exact symmetries and sizes of the reconstructions that can be found experimentally. Nevertheless, the investigated wide range of defect concentrations and symmetries are excellent representatives of larger surface reconstructions of similar nonstoichiometry. The uncertainty in the predictive ability of the phase diagrams stemming from the neglect of the small contribution of the vibrational entropy to the total energy of the surface, inherent DFT errors, and possible coexistence due to thermal effects, does not change our findings significantly, as we discuss in Appendix F (see Fig. F.3 in Appendix F). We conclude that despite the modest uncertainty, the stable surface phases shown in the phase diagrams are close representatives of the likely stoichiometry and structure in a given environmental condition. Thus, the phase diagrams presented here enable the prediction of compositional phase transitions on the PE and FE BTO (001) and PTO (001) surfaces.

For polar surfaces, where the Curie temperature T_C serves as the upper bound for FE stability, severe reduction of oxygen partial pressure cannot be achieved by thermal means. Nevertheless, surface reduction could be carried out at fixed temperature by using reducing agents (for example, H_2 annealing) (191) or solid-state coulometric titration with gas-phase O_2 as the ambient gas in the sample chamber (189; 190). Furthermore, for these perovskites, their Curie temperatures can be raised and their

polarization can be enhanced by imposing an epitaxial strain (192; 193; 194; 195).

7.4. Summary

Different avenues to modify the stoichiometry of transition metal oxide surfaces are highly coveted in the field of catalysis. Here we demonstrate the strong interaction between the ferroelectric polarization and surface stoichiometry, which give the surface structure tunable sensitivity to changes in the ambient environment. Specifically, by altering the bulk P , the bound charge changes, altering the stability of various nonstoichiometric compositions and reconstructions. The possibility of systematically and reversibly tailoring the surface composition and pattern by accessing a switchable property of the bulk is clearly demonstrated by this investigation.

CHAPTER 8 : Future Prospects

Surface reconstructions may be highly reduced or oxidized derivatives of the bulk phase that may only exist in the presence of the bulk. These surfaces are therefore in equilibrium with the bulk phase and also with the atmosphere or the solvent. The surface undergoes structural and compositional changes that may result in changes in oxidation state and coordination number of the elements composing the surface. Such changes affect the chemistry and therefore may influence the catalytic activity of the surface. Thus, understanding the reconstruction behaviors of surfaces may pave the way to custom designing them for specific surface-sensitive applications. In addition, possible creation of unique surface active sites due to the reconstruction could enhance specificity of the type of molecules that may adsorb on them. This could then lead to interesting ways to functionalize surfaces.

Although we can tune reactivity of materials through reconstructions, which is of course an essential aspect of catalysis design, the real time thermodynamic flexibility of the surface towards oxidation state changes is not directly addressed in this manner. A catalyst should ideally be able to change easily between states throughout the reaction process as to not serve as an energy liability. Ideally one would be to identify conditions where different surface reconstructions may coexist, since in these conditions an interface between different reconstructions may serve as a dynamic phase that could easily change its chemical identity.

These reconstruction boundaries may be structurally or chemically distinct from the parent reconstructions, which would bring about chemical flexibility in being able to transition between the different coexisting reconstructions. We are at the stage where we can now identify the structure and composition of reconstructions through

the help of *ab initio*-thermodynamics and surface sensitive experimental methods such as low energy electron diffraction (LEED), scanning tunneling microscopy (STM), tunneling electron microscopy (TEM), and many others, as demonstrated in chapters 3, 4, 6, and 7. Thus, studying synthesis of multiple reconstructions and the interfaces between them would be an interesting addition to the field. This has been studied to some extent in chapter 4 for the BaTiO₃(001) surface, and could be explored further for other compounds.

8.1. New heterogeneous catalyst design paradigm: bifunctional active sites on “uniform” surfaces

In chapter 6, we showed that the presence of chemically distinct dual active sites (Ti sites) on the TiO₂ double-layer reconstruction on SrTiO₃ led to a favorable path for O₂ production from H₂O. Such bifunctionality in catalytic systems may be desired in other reactions as well. For example, having Lewis acid and base active sites in proximity in one catalytic system could enable catalysis of both nucleophilic and electrophilic reactions in tandem. For molecular catalysts, this is easily achieved by strategically attaching two functional groups, one being nucleophilic and the other electrophilic. In heterogeneous catalysts, this is usually achieved at interfaces of two different materials, for example at metal - metal oxide interfaces, which are regarded as the most active sites, where the metal may serve as the electron donor while the metal cation from the oxide may serve as the electron acceptor. For example, it has been demonstrated that the Au-TiO₂ interface is very important in catalyzing the water-mediated CO oxidation with O₂.⁽¹⁹⁶⁾ CO₂ reduction for methanol synthesis has also been demonstrated to be efficiently catalyzed by Cu-CeO_x and Cu-CeO_x-TiO₂ systems because of complementary sites located at the metal-metal oxide interfaces.⁽¹⁹⁷⁾

A very rewarding task in heterogeneous catalysis therefore lies in increasing the availability of such interfaces, which can be achieved by reducing cluster sizes, which could be challenging. It is therefore much better to design a catalyst that exhibits such properties in its entire surface: a “uniform” surface that exhibits bifunctionality. This is analogous to having monodispersed bifunctional molecular species on the surface.

Another prominent reaction that requires bifunctional catalysts is the methanation of CO. $\text{C}\equiv\text{O}$ dissociation is found to be the rate-limiting step for this reaction.⁽¹⁹⁸⁾ The dissociation of $\text{C}\equiv\text{O}$ requires an electrophile to lock in the position of O, while a nucleophile is required to hold onto the C in place ready for a nucleophilic attack by hydrogen atoms. Therefore such a reaction might be optimally catalyzed if both functionalities are present in close proximity.

Ultimately, the design will be based on finding surface reconstructions with surface cations or adatoms exhibiting mixed coordination numbers and oxidation states. Cations having lower oxidation state, anions, or species with available electron pairs may act as electron pair donors while cations having higher oxidation states will serve as electron pair acceptors. Cations likely to exhibit mixed valence, and therefore of interest, are Ti, Mn, Fe, Co, Ni, Nb, W, and Ce.

APPENDIX A : Wood's notation for reconstructions of square lattices

Wood's notation refers to the change in the size and orientation of the smallest repeat surface cell relative to the original lattice due to the reconstruction. The notation is of the form:

$$(p \times q)R\theta. \tag{A.1}$$

$p = |a|/|v_1|$ and $q = |b|/|v_2|$, where a and b are the new surface lattice vectors, v_1 and v_2 are the original surface vectors. R means the new cell is "rotated" by θ relative to the original cell.

Wood's notation for common reconstructions of square lattices, for example, surfaces of cubic and tetragonal (with out-of-plane polarization) ABO_3 perovskites, are shown in Fig. A.1.

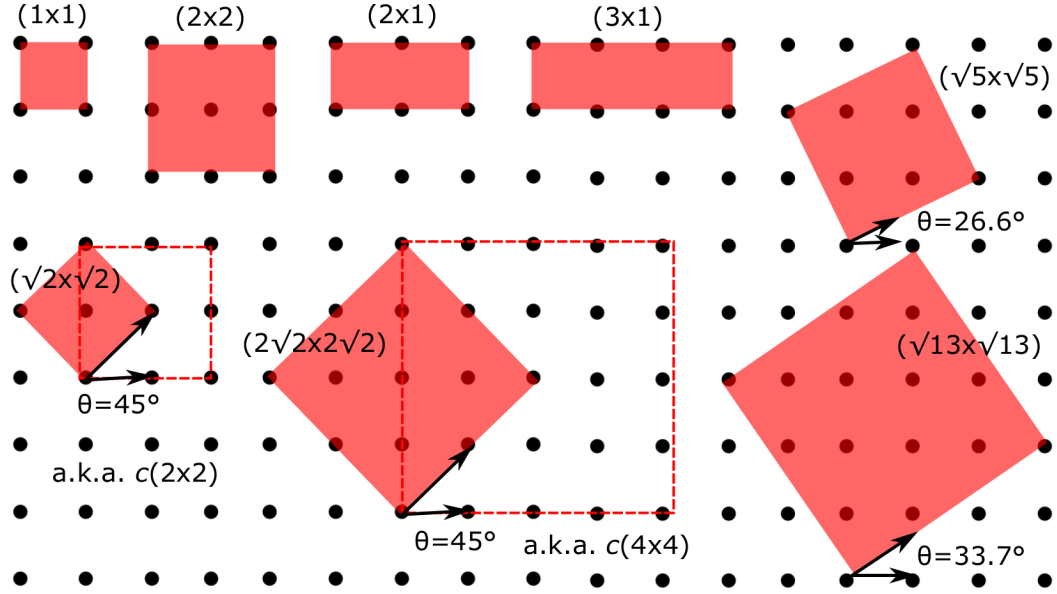


Figure A.1: **Wood's notation for common reconstructions of square lattices.** The dots represent the original identical lattice points. The red shaded regions are the reconstructions. The names characterize the sizes and orientations of the new smallest repeat cells relative to the original lattice. In the cases of $(\sqrt{2} \times \sqrt{2})R45^\circ$ and $(2\sqrt{2} \times 2\sqrt{2})R45^\circ$, they are also commonly referred to as $c(2 \times 2)$ and $c(4 \times 4)$. c stands for "centered" since, for example, $(\sqrt{2} \times \sqrt{2})R45^\circ$ is simply a (2×2) (square outlined by broken lines next to the $(2\sqrt{2} \times 2\sqrt{2})R45^\circ$ supercell) with an additional repeat unit at its center.

APPENDIX B : Supplemental: The Ti-rich $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ surface reconstruction of BaTiO₃(001)

B.1. Experimental STS I - V curve

Fig. B.1 shows the I - V curve for the $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ reconstruction. The arrow indicates the region in the conduction band where a negative static conductance leads to an apparent gap between 1.51 and 1.86 eV. This is not an artifact and it will be analyzed in context with other BaTiO₃ surface reconstructions in a future publication. If we consider the position of the conduction band minimum (CBM) to be our reference, at 0.59 eV, then the bulk valance band onset should be at around -2.6 eV. This was determined from published bulk band gap of BaTiO₃, which is 3.2 eV. The reason why the $\log(I)$ is still dropping between -3 and -2 eV is because of the presence of in-gap states, which we proved to be Ti 3*d*-state derived. Thus, the existence of the in-gap states leads to a new band gap that is smaller than the bulks.

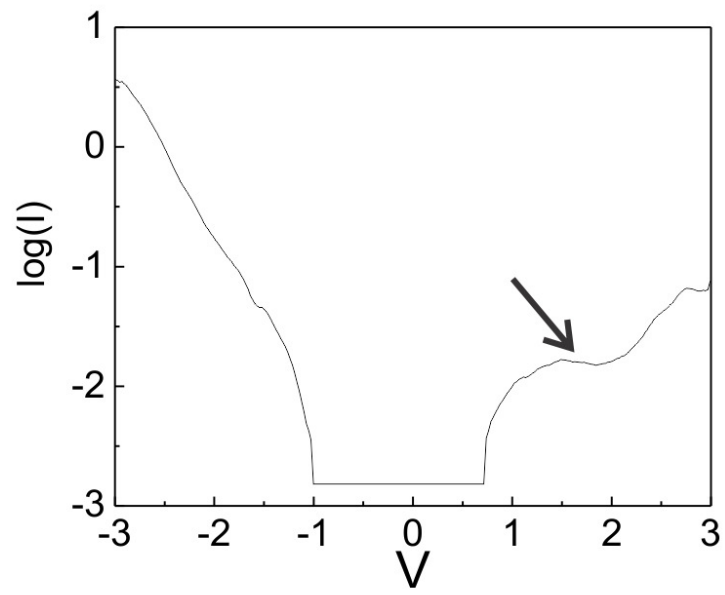


Figure B.1: Experimental I-V on BaTiO_3 (001) $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ surface covering four orders of magnitude in log-scale.

B.2. Theoretical phase diagram and other candidate phases

In Fig. 3.3b in chapter 3, most of the chemical potential space shown is straightforward, with one preferred surface phase for each region of stability, and two at or close to the phase boundaries. The region defined by $\Delta\mu_{\text{Ba}} = -2$ to -1 eV and $\Delta\mu_{\text{O}} = -5.5$ to -4.5 eV is much more complicated, with 6 to 14 phases close in energy to each other.

The surface phases that could possibly coexist within the 1300 K bulk stability boundary described in the main text are the following (see chapter 3 Figs. 3.3a and 3.3b): Region I (high p_{O_2}): BaO, TiO₂-DL, and TiO₂-TiO _{$\frac{9}{5}$} ; Region II (moderate p_{O_2}): TiO₂-TiO _{$\frac{9}{5}$} ; and Region III (low p_{O_2}): TiO₂-TiO _{$\frac{9}{5}$} , TiO₂-(TiO) _{$\frac{2}{5}$} , TiO₂-TiO _{$\frac{1}{5}$} , TiO₂-Ti _{$\frac{2}{5}$} O _{$\frac{1}{5}$} , TiO₂-Ti _{$\frac{1}{5}$} , TiO₂-Ti _{$\frac{2}{5}$} , TiO₂-Ti _{$\frac{3}{5}$} , TiO₂-Ti _{$\frac{4}{5}$} , and TiO₂-Ti. Fig. B.2 shows the ball-and-stick models of most of these surfaces, which are considered for electronic structure studies. The surfaces are of the type TiO₂-Ba _{x} , TiO₂-Ti _{x} , and TiO₂-TiO _{x} . Fig. B.3 and Fig. B.4 present the calculated STM and z-scaled LDOS of the structures shown in Fig. B.2, respectively. Fig. B.4 indicates that states near the Fermi energy are coming from either/both Ti 3*d*-states or/and O-2*p*-states, which makes either/both atoms visible in the STM images. Different electronic contrast are achieved between the STM empty and filled state images due to difference in the contribution of the surface atoms to the states found near E_F .

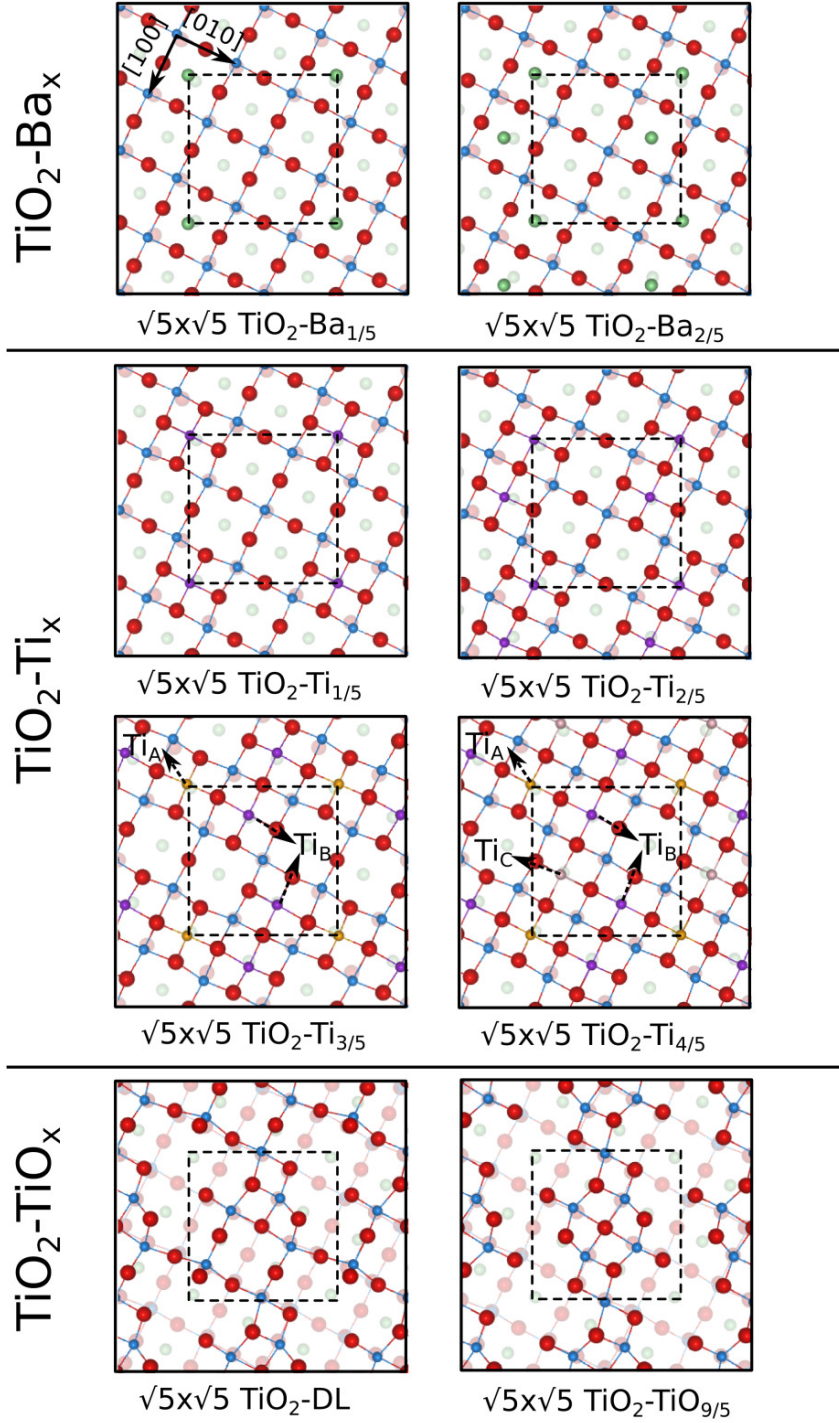


Figure B.2: Ball-and-stick models of some of the $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ reconstructions considered in the study. The dashed lines denotes the $\sqrt{5} \times \sqrt{5}$ supercell, which matches the position in their corresponding STM images (Fig. B.3). Large spheres (red): O, medium spheres (pale green): Ba, and small spheres (Blue, yellow, purple, pink): Ti.

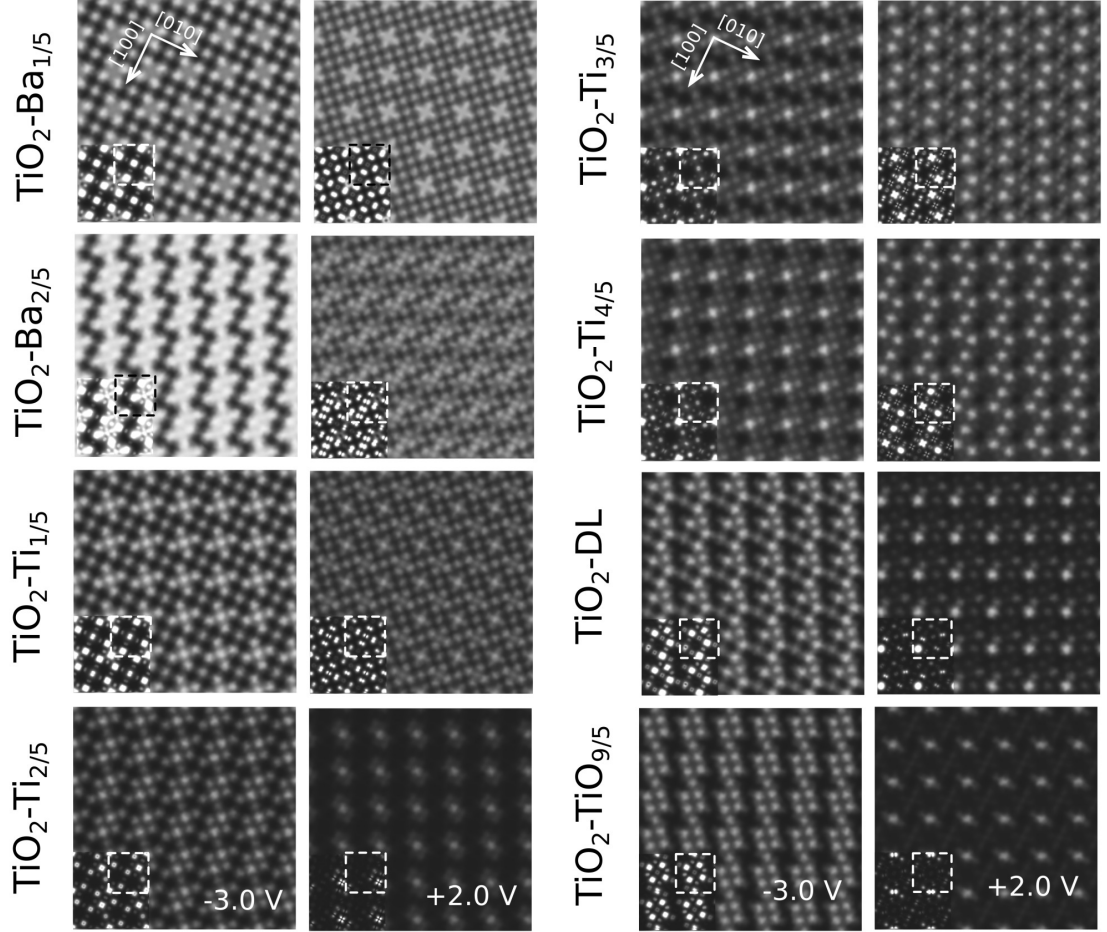


Figure B.3: Simulated empty (3 eV above E_F , first column) and filled state (2 eV below E_F , second column) STM images (5) of the structures found in Fig. B.2. The dashed lines denote the $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ unit, while the lower left insets are the raw images prior to computational smearing to mimic the finite tip resolution.

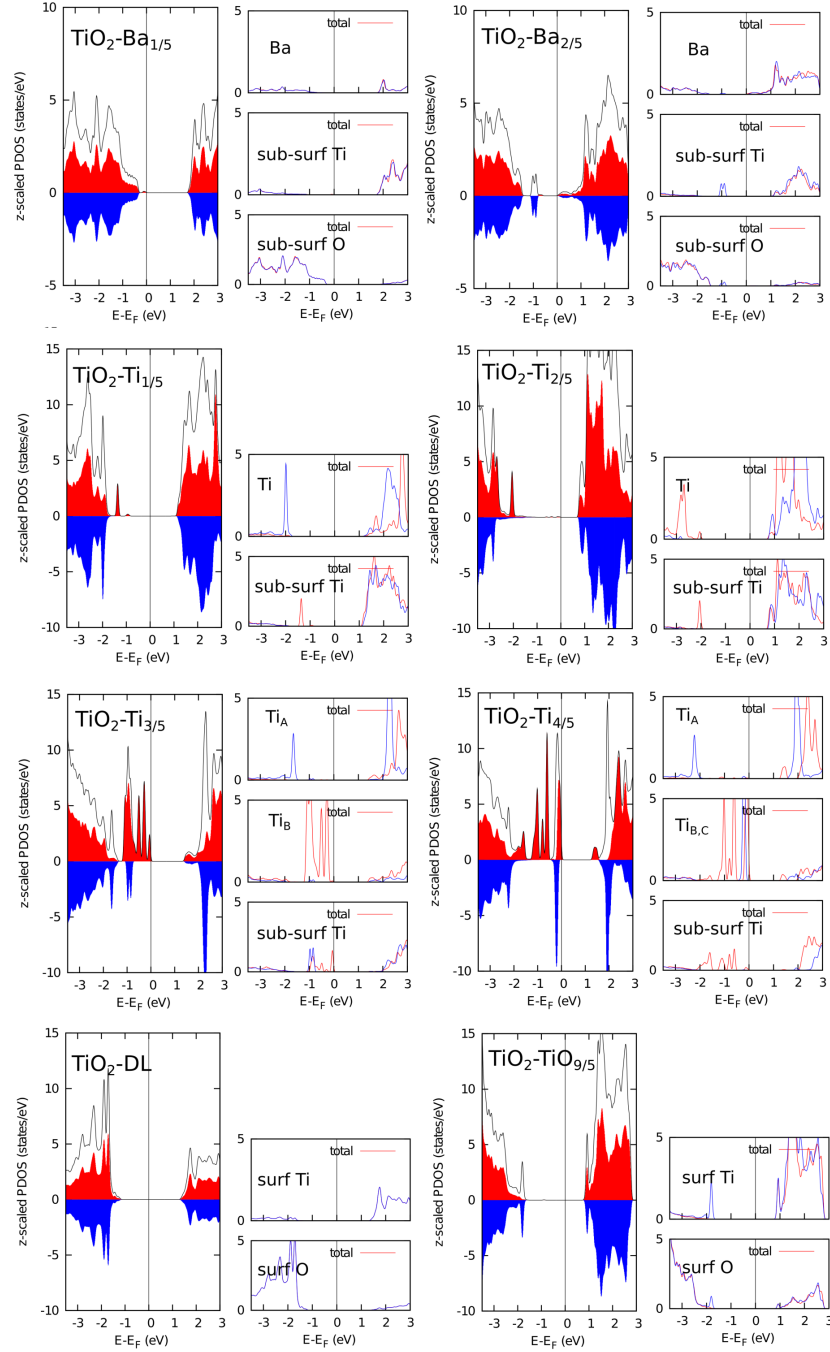


Figure B.4: Calculated z-scaled PDOS (6) from spin-polarized DFT+ U calculations of the structures in Fig. B.2. E_F is the Fermi energy, defined as being midway between the valence band maximum and conduction band minimum of the whole slab. Majority spin above $y = 0$, minority spin below $y = 0$. Atomic projections to the LDOS of the adatoms, and sub-surface Ti and O atoms are shown on the right of each LDOS. Blue and red lines correspond to the majority and minority spin-states.

APPENDIX C : Supplemental: The thermodynamic and kinetic aspects of the coexistence of the $c(2\times 2)$ and $c(4\times 4)$ reconstructions on $\text{BaTiO}_3(001)$ surface

C.1. Additional Information on the determination of the structure of the $c(2\times 2)$ reconstruction

We show in Fig. C.1 the structures of the $c(2\times 2)$ candidate phases while Fig. C.2 shows the approximate surface phase diagrams at 1100 K. The range of O_2 partial pressure in the experiment is believed to be from 10^{-27} torr to 10^{-10} torr(8), corresponding to the relative chemical potential of oxygen, $\Delta\mu_{\text{O}}$, of -3.87 to -2.63 eV. The phases that are likely to persist in the chemical condition of interest includes all the phases investigated except for the $\text{TiO}_2\text{-TiO}_{3/2}$, and only to some extent $\text{TiO}_2\text{-Ti}_{1/2}(\text{TiO})_{1/2}$. Because of the uncertainty inherent in the calculations and approximations, the relevance of each phase cannot be judged directly. Thus, there is a need for the proposed structure to have a strong consistency with experimentally observed electronic structure and suggested atomic arrangements, as discussed in the main text. First and second columns of Fig. C.3 and first column of Fig. C.4 show the DFT+ U simulated STM images and surface PDOS, respectively.

We also explored the temperature effects on the relative energies of the two possible $c(2\times 2)$ $\text{TiO}_2\text{-(TiO)}_{1/2}$ reconstructions. The alternative structure denoted in Fig. C.1 as $c(2\times 2)$ $\text{TiO}_2\text{-(TiO)}_{1/2}\text{-}\beta$. For the purpose of discussion, the surface with vertically oriented TiO units will be referred to as the α phase while the alternative structure, with tilted TiO units, as the β phase. Fig. C.5A shows the free energy

of the β phase relative to the α phase and the Helmholtz free energy of vibration (A_{vib}) contribution of the surface adatoms as functions of temperature. Fig. C.5 **B** and **C** show the DOS of the adatomic vibrations of the two structures, see General methodology section 2.7.3 for theoretical details. The 974 cm^{-1} vibrational mode in the α phase is softened in the β structure due to the coordination of the O adatom to the subsurface Ti, which weakens its bond with the Ti adatom. The difference in the surface energies between the two phases is $0.16\text{ eV}/(1\times 1)$ surface cell based only on DFT energies, with the β phase as being less favorable. Introducing the Helmholtz free energy of vibration (A_{vib}) correction does not change the structural preference, where the surface free energy difference becomes $0.17\text{ eV}/(1\times 1)$ surface cell at 300 K and $0.21\text{ eV}/(1\times 1)$ surface cell at 1100 K. Despite the mode softening in the β phase, the energy distribution of the adatomic vibrational modes are generally shifted to higher energies resulting to less negative A_{vib} contribution. It is clear from both DFT energies and the A_{vib} contributions that the vertically oriented TiO is favored over the tilted geometry, the former having lower DFT energy and more negative A_{vib} .

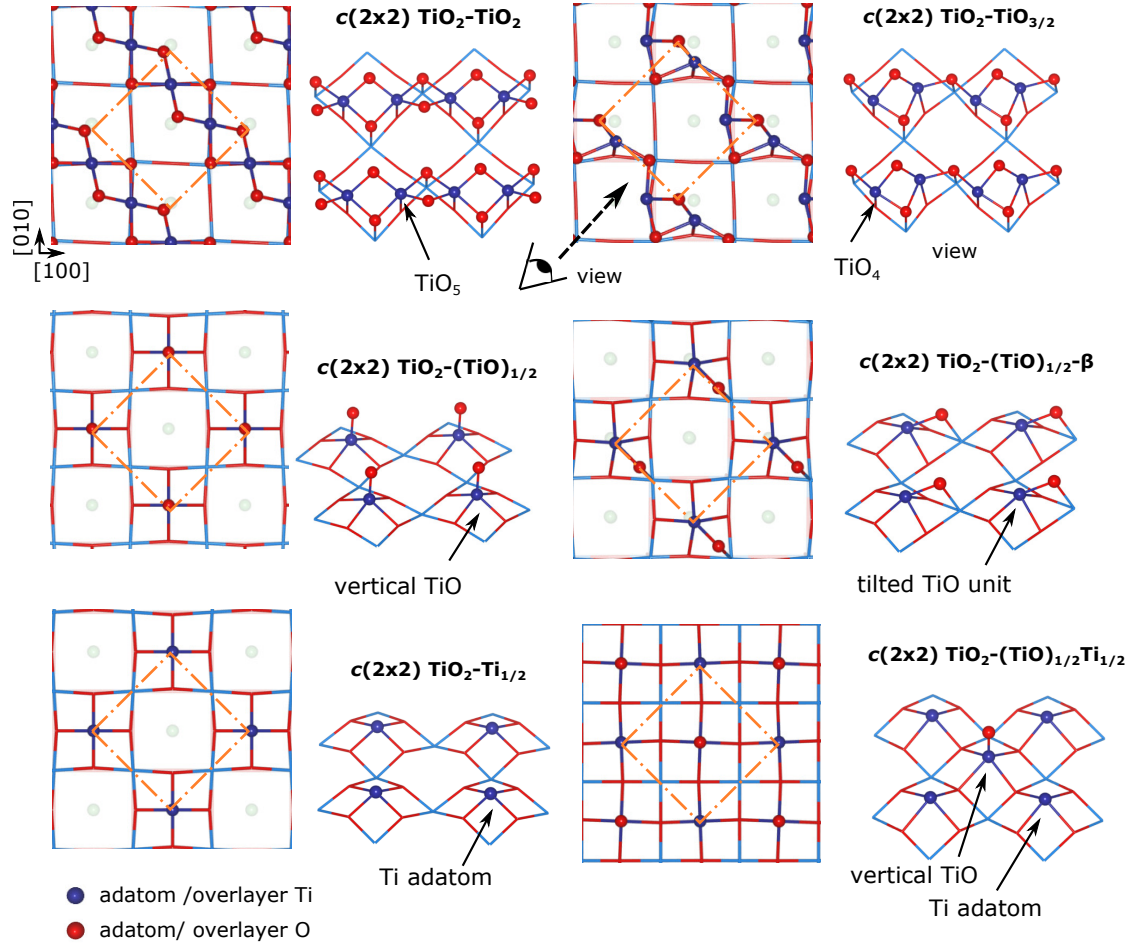


Figure C.1: **Structures of the candidate $c(2 \times 2)$ reconstructions of BaTiO_3 (001).** Ball-and-stick models showing top-down and angled views of the structures. Red: O, light-blue/dark-blue: Ti. Dashed orange boxes mark the $\sqrt{2} \times \sqrt{2}$ supercell. Angled views: the view point and angle are demonstrated by the eye and line symbols.

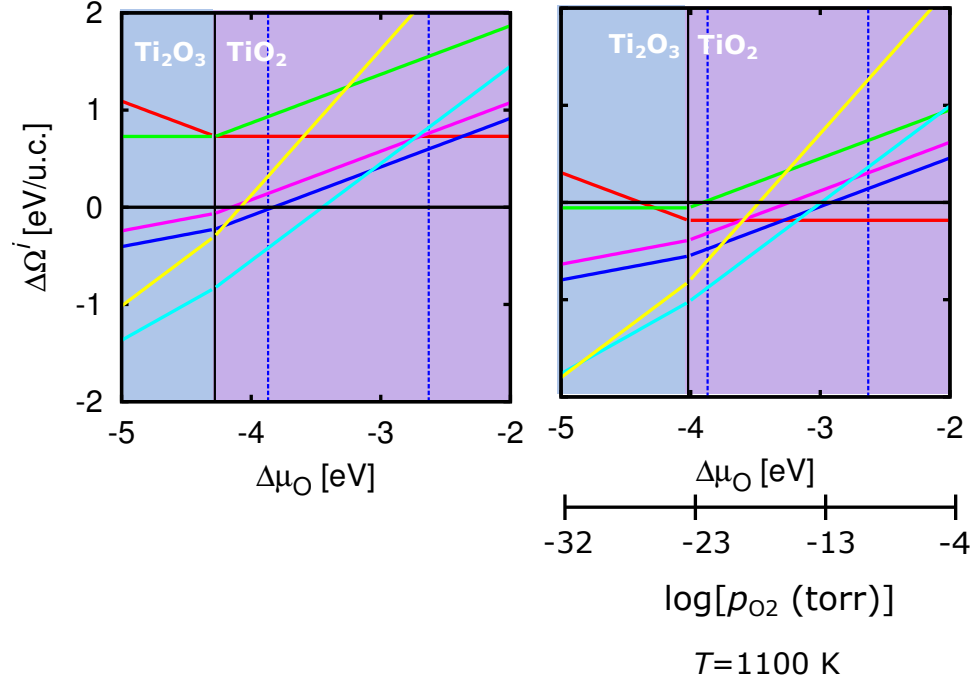


Figure C.2: **The isothermal phase diagrams for the $c(2\times 2)$ reconstruction.** Isothermal surface phase diagrams as functions of oxygen chemical potential ($\Delta\mu_O$). Different approximations are used in the two phase diagrams: (1) the surfaces' free energies of vibration are negligible (left) and (2) all the condensed phases' (surface and bulk) free energies of vibration are negligible (right). The real case is between these two approximations. The blue broken vertical lines mark the range of oxygen chemical potentials relevant in the experiment. Red: $\text{TiO}_2\text{-TiO}_2$, green: $\text{TiO}_2\text{-TiO}_{3/2}$, blue: $\text{TiO}_2\text{-(TiO)}_{1/2}$, pink: $\text{TiO}_2\text{-(TiO)}_{1/2-\beta}$, light blue: $\text{TiO}_2\text{-Ti}_{1/2}$, and yellow: $\text{TiO}_2\text{-(TiO)}_{1/2}\text{Ti}_{1/2}$. Energies are in eV per primitive surface unit cell or (1×1) surface cell.

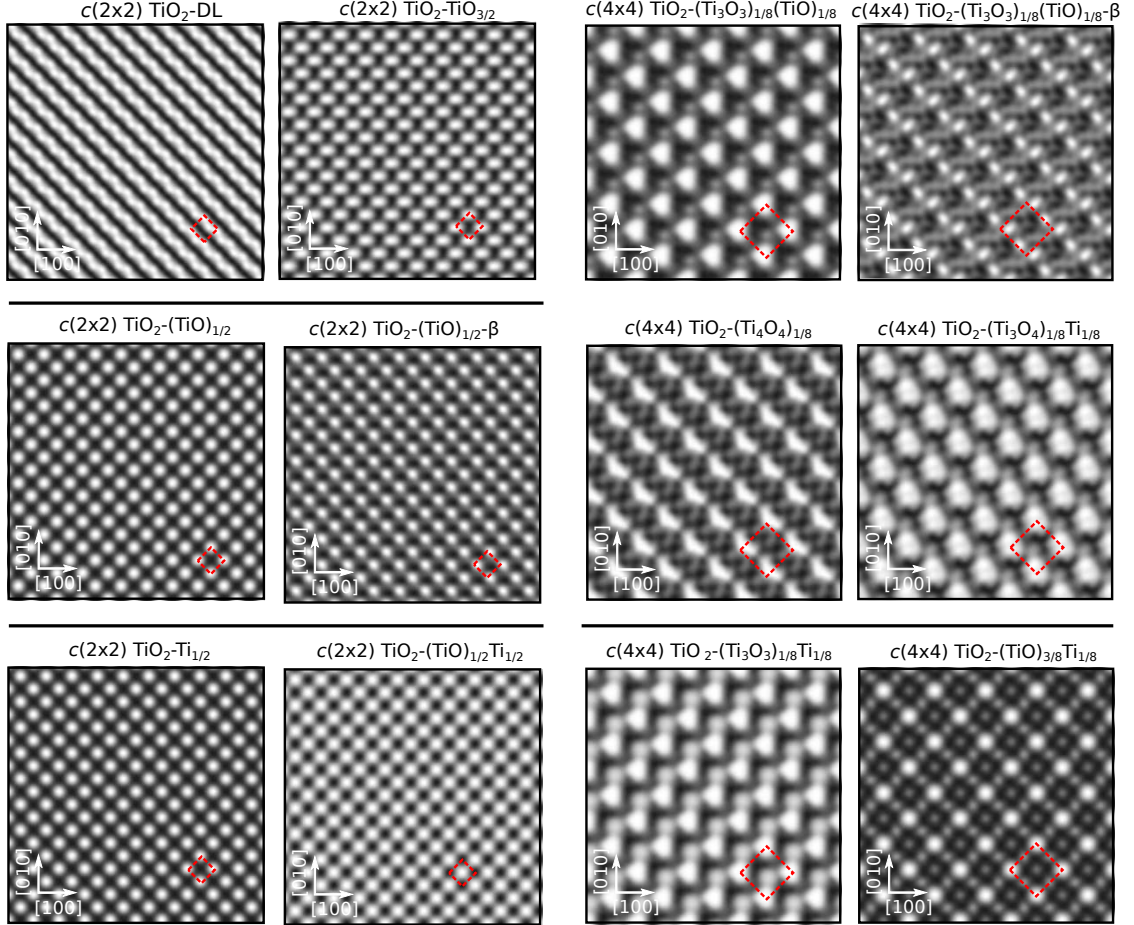


Figure C.3: **Simulated STM.** Red dashed lines mark the supercell corresponding to the structures shown in Figure S1 (first and second columns) and S4 (third and fourth columns). Sample bias: -1 eV (equivalent to +1 eV tip bias as is done in the experiment), except for $\text{TiO}_2\text{-TiO}_2$ which is biased at -1.5 eV to get an image contrast.

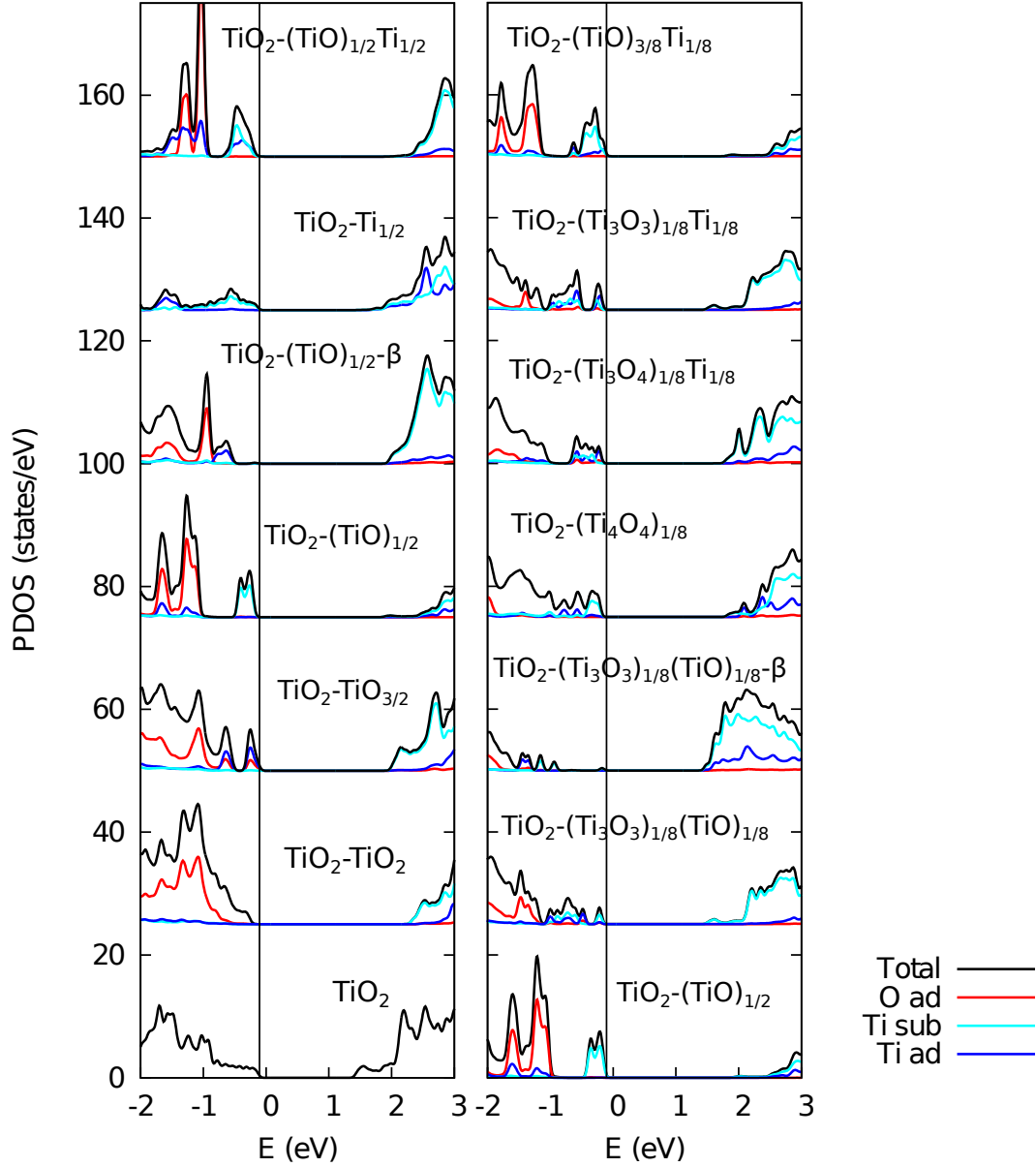


Figure C.4: **Simulated surface PDOS.** The valence band maximum (VBM) are aligned to the experimental VBM. The left column is for the $c(2\times 2)$ structures while the right column is for the $c(4\times 4)$. States on the valence band edges are predominantly Ti-derived in cases where surface Ti:O (defined in the main text) is greater than 1:2 (reduced surfaces), while they are purely surface O-derived for when surface Ti:O is 1:2 (oxidized surface).

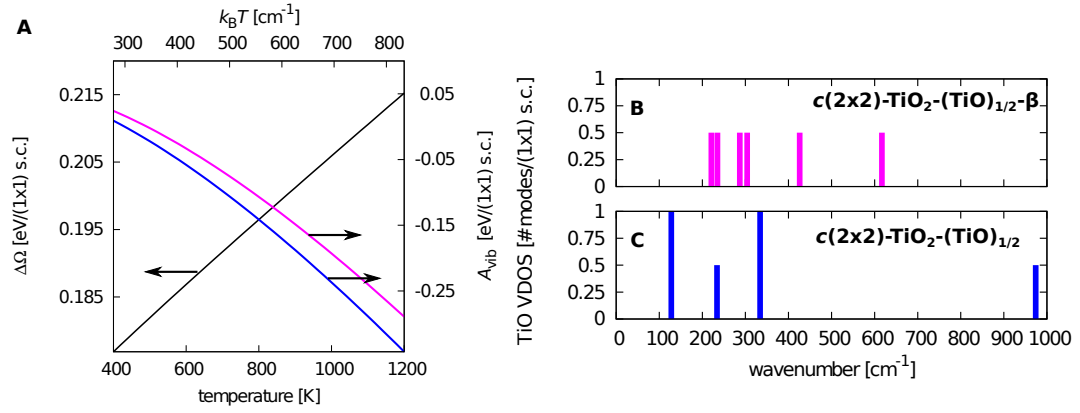


Figure C.5: **Surface free energy diagram and surface vibrational DOS for the two $c(2 \times 2)$ TiO₂-(TiO)_{1/2} structures A**, surface free energy of $c(2 \times 2)$ TiO₂-(TiO)_{1/2}-β vs. $c(2 \times 2)$ TiO₂-(TiO)_{1/2}, $\Delta\Omega = \Delta E_{\text{DFT}} + \Delta A_{\text{vib}}$, black curve. The temperature dependence of the adatomic (TiO units) vibrational contribution to the Helmholtz free energy, A_{vib} , for the different reconstructions, pink and blue curves, respectively. Energies are in eV/(1x1) surface cell. TiO units vibrational DOS of **B**, $c(2 \times 2)$ TiO₂-(TiO)_{1/2}-β; and **C**, $c(2 \times 2)$ TiO₂-(TiO)_{1/2} (simulation size $\sqrt{2} \times \sqrt{2}$).

C.2. Additional Information on the determination of the structure of the $c(4\times 4)$

We explored variations in the TiO unit arrangements that bring about the $c(4\times 4)$ order. Additionally, few structures that are slightly more reduced, *i.e.* an O adatom is removed for every $2\sqrt{2} \times 2\sqrt{2}$ surface supercell, were considered.

Fig. C.6 shows the atomic structures of the $c(4\times 4)$ reconstructions considered, which are derivatives of the $c(2\times 2)$ $\text{TiO}_2\text{-(TiO)}_{1/2}$ reconstruction. Their relative energies according to GGA and GGA+ U are shown in Fig. C.7 and Fig. 4.5a. Calculations for $c(2\times 2)$ $\text{TiO}_2\text{-(TiO)}_{1/2}$ using a $2\sqrt{2} \times 2\sqrt{2}$ instead of a $\sqrt{2} \times \sqrt{2}$ were also performed to eliminate supercell size dependence when comparing the energy and electronic properties of the $c(2\times 2)$ reconstruction against the $c(4\times 4)$ structures. The lowest energy $c(4\times 4)$ structure is $\text{TiO}_2\text{-(Ti}_3\text{O}_3)_{1/8}\text{(TiO)}_{1/8}$ whose structural and electronic properties are discussed in chapter 4. The $c(4\times 4)$ structures considered have different degrees of TiO clustering: Ti_3O_3 , Ti_3O_4 , and Ti_4O_4 . These clusters are composed of TiO units where a Ti adatom is either in a O_4 subsurface hollow site, in which case it is coordinated to an O adatom above it; or on top of a subsurface O, in which case it is additionally coordinated to three O adatoms found laterally. The O adatoms on the other hand, are either on top of a Ti adatom (as in a vertical TiO unit), a sub-surface Ti (as in a horizontal TiO unit), or an empty O_4 subsurface hollow site (as in a horizontal TiO unit found in the Ti_4O_4 cluster).

To form a Ti_3O_4 cluster and maintain the same stoichiometry, the Ti adatom outside the cluster has to be free of an O adatom. Among the “4(TiO)” structures studied shown in Fig. C.7 (see also Fig. C.6 for the ball-and-stick models), this is the least favorable phase, 2.10 eV per $2\sqrt{2} \times 2\sqrt{2}$ surface supercell (GGA+ U) relative to

the most stable phase. This indicates that the reduction of a TiO unit (by losing an O adatom) is not energetically compensated enough by the oxidation of the cluster: $\text{Ti}_3\text{O}_3 + \text{TiO} \rightarrow \text{Ti}_3\text{O}_4(\text{restructured}) + \text{Ti}$. Although such process will maximize O coordination, *i.e.* all O adatoms will have two-fold coordination. The Ti_4O_4 cluster, structure V in Fig. C.7, also maximizes the O coordination but without sacrificing a Ti adatom to O adatom bond, which is thus more favorable. However, this also results in an unfavorable increase in the local TiO coverage. The $\text{TiO}_2-(\text{Ti}_3\text{O}_3)_{1/8}(\text{TiO})_{1/8}$ strikes a balance between maximization of the O adatom coordination and defect distribution.

Partially more reduced $c(4\times 4)$ structures were also investigated, the structures of which are shown on the last row of Fig. C.6. These two structures are derivatives of the $\text{TiO}_2-(\text{Ti}_3\text{O}_3)_{1/8}(\text{TiO})_{1/8}$ and $\text{TiO}_2-(\text{TiO})_{1/2}$, left and right, respectively. These structures result from taking away an O adatom from a vertical TiO unit outside the cluster, in their respective parent reconstructions, for every $2\sqrt{2} \times 2\sqrt{2}$ surface supercell.

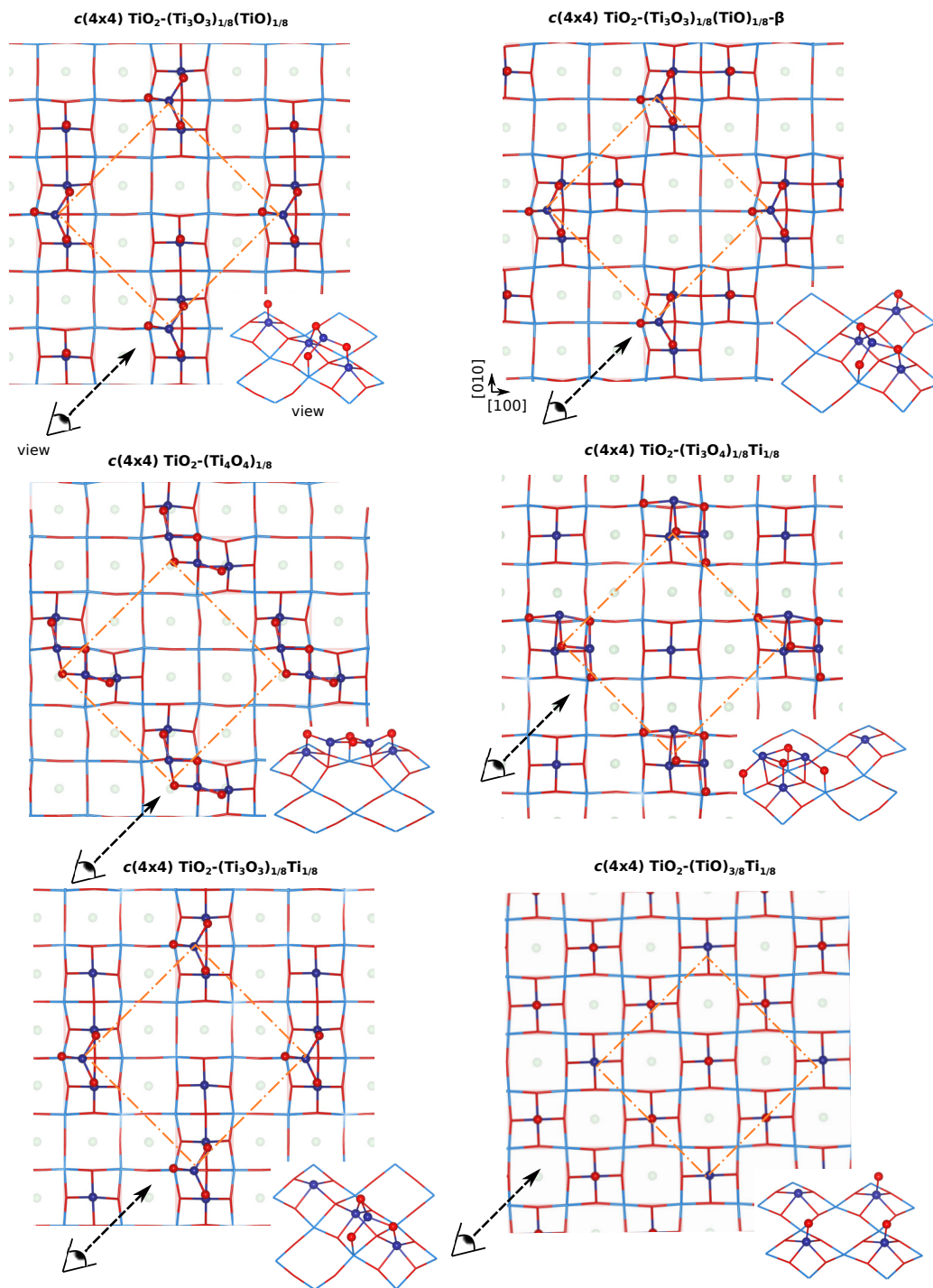


Figure C.6: **Candidate $c(4 \times 4)$ structures.** All structures have net surface stoichiometry of $\text{TiO}_2-(\text{TiO})_{1/2}$, except for the structures in the last row, which both have effective surface stoichiometry of $\text{TiO}_2-(\text{TiO})_{3/8}\text{Ti}_{1/2}$ (slightly more reduced). Red: O, light-blue/dark-blue: Ti. Dashed orange boxes mark the $2\sqrt{2} \times 2\sqrt{2}$ supercell. Angled views (lower right insets): the view point and angle are demonstrated by the eye and line symbols.

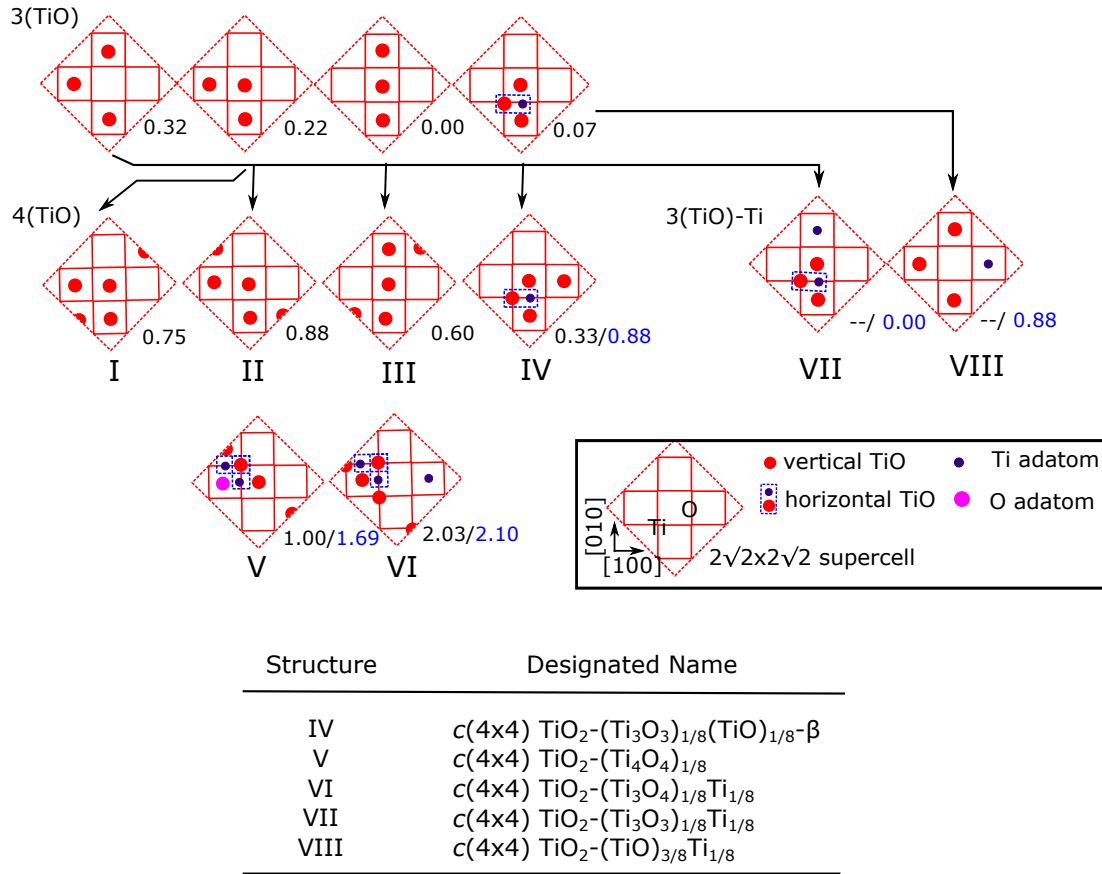


Figure C.7: **Surface transformation diagram.** Extension of Fig. 4.5a in chapter 4 showing other $c(4 \times 4)$ reconstructions investigated. Energies from GGA (black) and/or GGA+ U (blue), in eV/ $2\sqrt{2} \times 2\sqrt{2}$ surface supercell, are given relative to the lowest energy structure of each tier. The table below shows the special name designations for some of the structures in the diagram and are found in Fig. C.6.

The simulated STM and surface PDOS for the $c(4\times 4)$ surfaces are shown in the third and fourth columns of Fig. C.3, and second column of Fig. C.4, respectively. The surface PDOS cannot clearly distinguish against any of the phases, largely due to the similarity or close proximity in the surfaces' stoichiometry. The simulated STM however supports the existence of either $\text{TiO}_2\text{-(Ti}_3\text{O}_3)_{1/8}(\text{TiO})_{1/8}$, $\text{TiO}_2\text{-(Ti}_3\text{O}_4)_{1/8}\text{Ti}_{1/8}$, or $\text{TiO}_2\text{-(Ti}_3\text{O}_3)_{1/8}\text{Ti}_{1/8}$. However, the $\text{TiO}_2\text{-(Ti}_3\text{O}_4)_{1/8}\text{Ti}_{1/8}$ structure is found to be thermodynamically unfavorable (see relative energies in Fig. C.7).

The surface energy difference between the $\text{TiO}_2\text{-(Ti}_3\text{O}_3)_{1/8}(\text{TiO})_{1/8}$ and $\text{TiO}_2\text{-(Ti}_3\text{O}_3)_{1/8}\text{Ti}_{1/8}$ is a function of $\Delta\mu_{\text{O}}$ (see chapter 2, section 2.8.1):

$$\Delta\Omega = 0.43 \text{ eV}/(1 \times 1) \text{ surface cell} + \frac{1}{8}[\Delta\mu_{\text{O}} - A_{\text{vib}}^{\text{O-atom}}] \quad (\text{C.1})$$

where $A_{\text{vib}}^{\text{O-atom}}$ is the Helmholtz free energy contribution of the the vibrational mode of an O adatom in a vertically oriented TiO unit. To a good approximation $A_{\text{vib}}^{\text{O-atom}} \approx -0.31 \text{ eV}$ at 1100 K, see section C.1. The approximation is based on the vibrational distribution of the TiO units in the $c(2\times 2)$ $\text{TiO}_2\text{-(TiO)}_{1/2}$ reconstruction, where the O adatom has associated vibrational frequencies of 974, 128 and 128 cm^{-1} , corresponding to the Ti=O stretching and two bending modes (see Fig. C.5C). Eq. C.1 translates to an equilibrium point at $\Delta\mu_{\text{O}} = -3.75 \text{ eV}$ for the aforementioned surfaces at 1100 K, which is on the lower end of the chemical potential range of interest (see Fig. C.2). We explored $\text{TiO}_2\text{-(Ti}_3\text{O}_3)_{1/8}(\text{TiO})_{1/8}$ in our modeling of reconstruction interfaces and kinetic studies, which can represent both. This is because the TiO unit or Ti adatom outside the Ti_3O_3 cluster does not participate in the mechanism explored in our kinetic studies nor do they show perceivable difference in their STM profiles.

C.3. Modeling of the interfacial structures

The compositions and the structures of the interface region between the $c(2\times 2)$ and the $c(4\times 4)$ were guided by the experimental STM images. The STM images show how the two reconstructions are aligned with respect to each other as discussed in the main text. Also the images show interfaces that run 45° relative to the in-plane primitive crystal axes. We looked at four possible boundary structures, two of which are shown to be consistent with the two types of interfacial structures found in the experiment, as discussed in the main text.

We simulated the interfaces with $5\sqrt{2} \times 2\sqrt{2}$ and $4\sqrt{2} \times 2\sqrt{2}$ surface supercells for the possible interfaces that run along $[\bar{1}10]$ and $[110]$, respectively, with the longer in-plane side of the simulation supercells perpendicular to the interface. The structure and the corresponding STM images for the candidate interfaces are shown in Fig. C.8. The most consistent STM images among the structures studied are found for structures shown in Fig. C.8**A** and **C**, also shown in Fig. 4.6 in chapter 4 and discussed therein.

Fig. C.8**B** shows an alternative case for the $[\bar{1}10]$ interface. This structure has an extra row of TiO units, where the units are $8\sqrt{2}$ Å apart, between the row of Ti_3O_3 clusters on the edge of $c(4\times 4)$ and the row of TiO units on the edge of $c(2\times 2)$. Due to these extra TiO units, the interface shows bright spots in the interfacial region in the simulated STM image. It also follows that this interface locally has higher TiO concentration than the structure in Fig. C.8**A** (Fig. 4.6**b** in chapter 4). On the other hand, Fig. C.8**D** shows an alternative case for the $[110]$ interface. In this interface, the tilted TiO that is present in Fig. C.8**C** is absent. This interface locally has a lower TiO concentration compared to the structure in Fig. C.8**C** (Fig. 4.6**c** in chapter

4). This structure does not render a simulated STM image with a sharp interface between the two reconstructions.

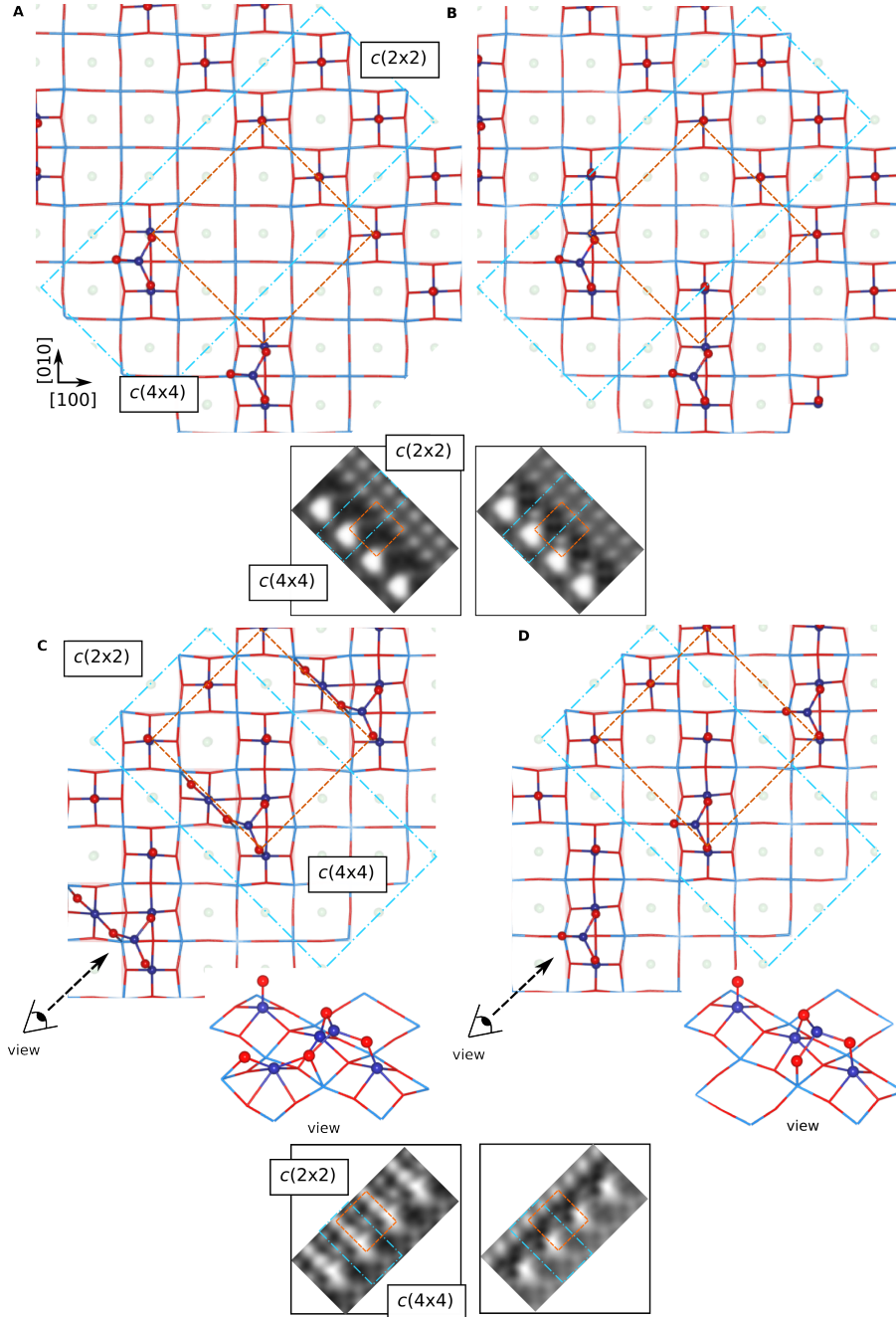


Figure C.8: **Candidate structures of the surface reconstruction interfaces and their simulated STM.** **A-B**, candidate $[\bar{1}10]$ interfaces, **C-D**, candidate $[110]$ interfaces. Dashed orange boxes mark the structurally relevant region associated with the interfaces ($2\sqrt{2} \times 2\sqrt{2}$ cell), while the dash-dotted light blue boxes mark the actual simulation cells ($2\sqrt{2} \times 5\sqrt{2}$ for **A** and **B**, while $2\sqrt{2} \times 4\sqrt{2}$ for **C** and **D**). Ball-and-stick models, Red: O, light-blue/dark-blue: Ti. Angled views (lower right insets): the view point and angle are demonstrated by the eye and line symbols.

C.4. Diffusion kinetics and trajectories

The transitional structure is defined as the meta-stable phase that could transform into either the $c(2\times 2)$ or the $c(4\times 4)$ (see subsection in chapter 4: *Coexistence of the Two Phases*). This structure consists of four vertically oriented TiO units on a $2\sqrt{2}\times 2\sqrt{2}$ TiO₂ (001) termination as in $c(2\times 2)$, see Fig. 4.3b of chapter 4, however instead it has them arranged such that they form the letter T, see Fig. C.9, first row structures. To transform into either of the two reconstructions, a TiO unit diffuses in either manner described in Fig. C.9A or Fig. C.9B, forming either the $c(2\times 2)$ or the $c(4\times 4)$, respectively.

C.4.1. The kinetics of the formation of $c(2\times 2)$

A TiO unit can effectively migrate in two ways to give the $c(2\times 2)$ reconstruction. The first path, the green path (first column Fig. C.9A) starting from the transitional structure, involves the TiO unit, marked by a thick arrow, hopping to an adjacent empty sub-surface O₄ hollow site. The O adatom anchors itself first to a sub-surface Ti. Distinctively, the TiO unit swings while O-anchored, where the Ti adatom hops to the adjacent O₄ hollow site. The transition state, structure c2_ii', has the hopping Ti adatom and the anchored O adatom sitting directly on top of a sub-surface O and Ti, respectively. Upon creation of the transition state, the Ti adatom lost three of its four bonds with the sub-surface O in the O₄ hollow site, while the O adatom gained a bond with a subsurface Ti. The Ti adatom then relaxes down to the adjacent O₄ hollow site, while concurrently, the O adatom detaches itself from the sub-surface Ti. Finally it forms the $c(2\times 2)$ structure. This path has a very large barrier of 2.46 eV associated with the formation of c2_ii' (see Fig. C.9C green curve) however, as it happens, a low-energy alternative path is available. The second path, the orange

path (second column Fig. C.9A) ultimately involves the displacement of a sub-surface Ti by a Ti adatom of a vertical TiO unit, while also transferring the associated O adatom to the aforementioned sub-surface Ti. First, the TiO unit (marked by a thick arrow) swings while O-anchored, where the Ti adatom moves toward an adjacent vertical TiO unit rather than an empty O_4 hollow site, see c2.ii and c2.iii. This leads to the coordination of the Ti adatom with the O adatom of the adjacent TiO unit, forming a Ti_2O_2 cluster, structure c2.iii. The Ti adatom then moves toward the sub-surface Ti, which it pushes toward the center of an adjacent empty subsurface O_4 cage (structures c2.iii to c2.v). The O adatom that was directly above the sub-surface Ti migrates with the aforementioned sub-surface Ti. This step finally creates a new TiO unit composed of the displaced sub-surface Ti and the migrating O adatom, resulting in the $c(2\times 2)$ reconstruction. The highest barrier in the orange path (1.26 eV, from the transitional structure to c2.iii) is significantly lower than the barrier for the green path (see Fig. C.9C orange curve). The concerted steps in the orange path enabled to simultaneously create new TiO bonds while breaking old TiO bonds, which effectively lowered the barrier compared to the green path.

C.4.2. The kinetics of the formation of $c(4\times 4)$

The purple path, Fig. C.9B, shows the transformation of the transitional structure into the $c(4\times 4)$ reconstruction. The TiO unit (marked with a thick arrow) not belonging to the three TiO units in a row, undergoes an O-anchored swinging motion mentioned above, towards the nearest TiO neighbor, similarly forming a Ti_2O_2 cluster (structures c4.ii to c4.iv). The diffusing Ti adatom then hops between the two O adatoms belonging to the two adjacent vertical TiO units, structures c4.iv to $c(4\times 4)$, forming the Ti_3O_3 cluster. This process has the highest energy barrier associated with the formation of c4.ii (1.36 eV) (see Fig. C.9C purple curve). Although the

paths of formation of the $c(2\times 2)$ and $c(4\times 4)$ structures are mechanistically different, the resemblance between their high-barrier step, which are the O-anchored swinging motion of the TiO units to form Ti_2O_2 clusters, prompted an almost equivalent energy barrier.

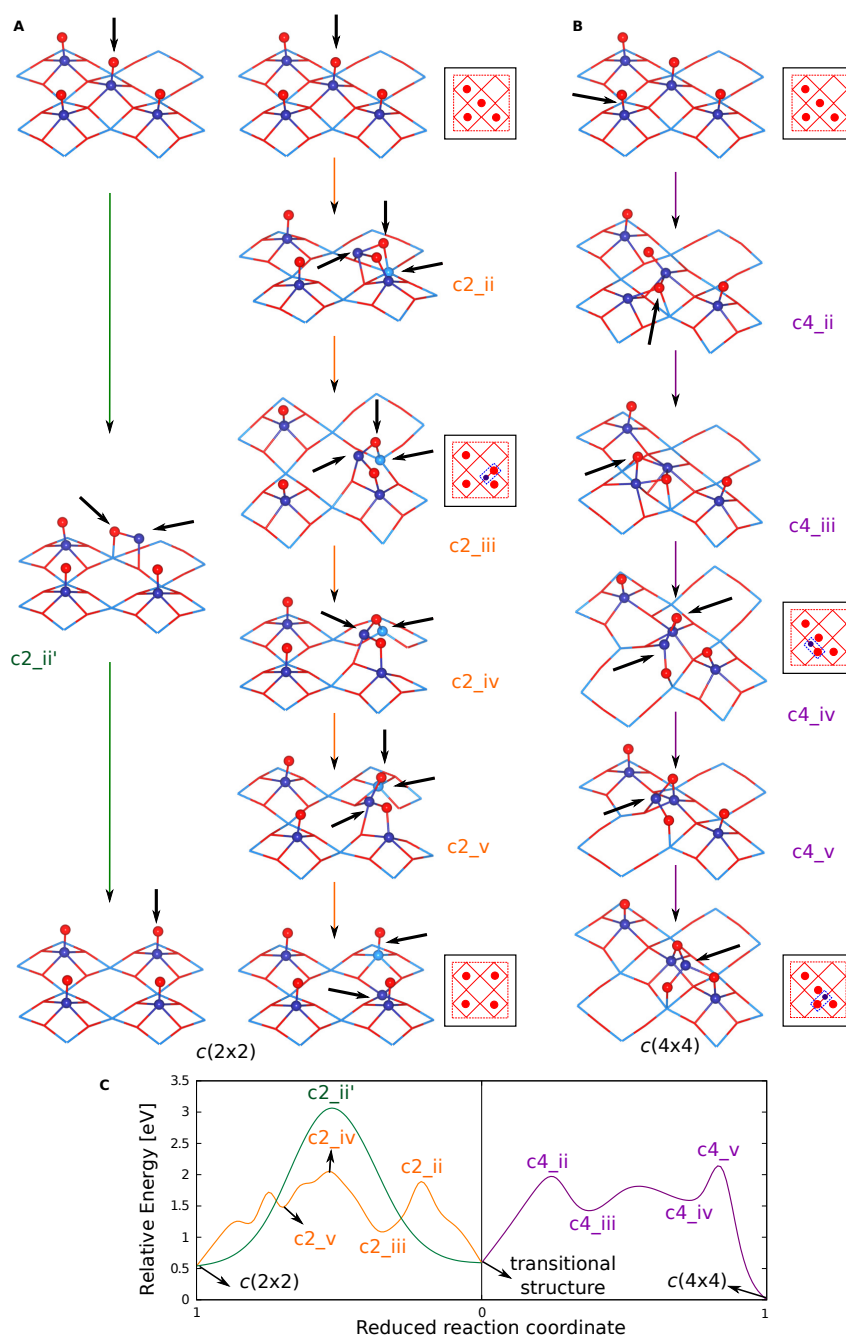


Figure C.9: **Reconstruction transformation trajectory and energetics.** **A**, transformation leading to the formation of the $c(2 \times 2)$ $\text{TiO}_2\text{-(TiO)}_{1/2}$ reconstruction from the transitional state showing two likely paths (green and the lower energy barrier orange path). **B**, transformation leading to the formation of the $c(4 \times 4)$ $\text{TiO}_2\text{-(Ti}_3\text{O}_3)_{1/8}(\text{TiO})_{1/8}$. Ball-and-stick models, Red: O, light-blue/dark-blue: Ti. See Fig. 4.3 for structural references. The thick black arrows mark the relevant structural components undergoing transitions. **C**, reaction energetics for the transformations shown in **A** and **B**; green and orange, and purple paths; respectively. See Fig. 4.5 in chapter 4 for reference.

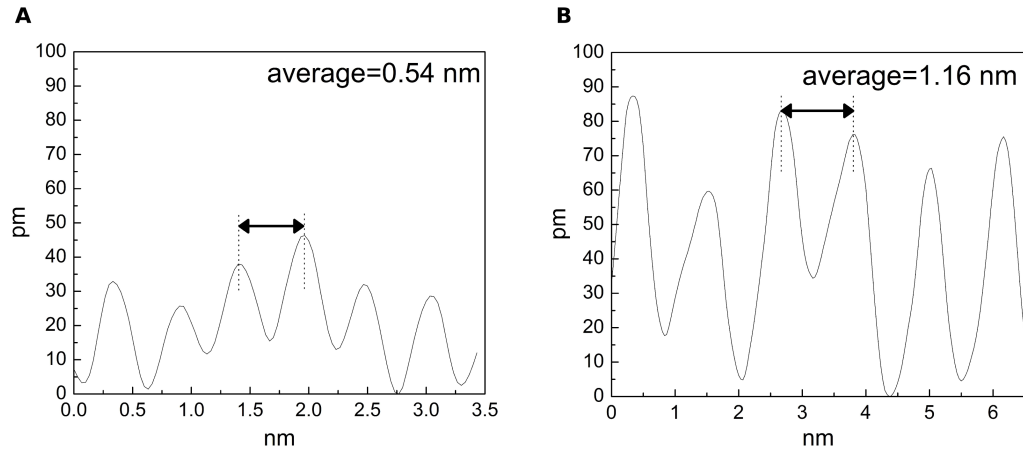


Figure C.10: **Experimental surface line profiles for $c(2 \times 2)$, A, and $c(4 \times 4)$, B.** The distance between the peaks correspond to $\sqrt{2}a$ and $2\sqrt{2}a$ in **A** and **B**, respectively.

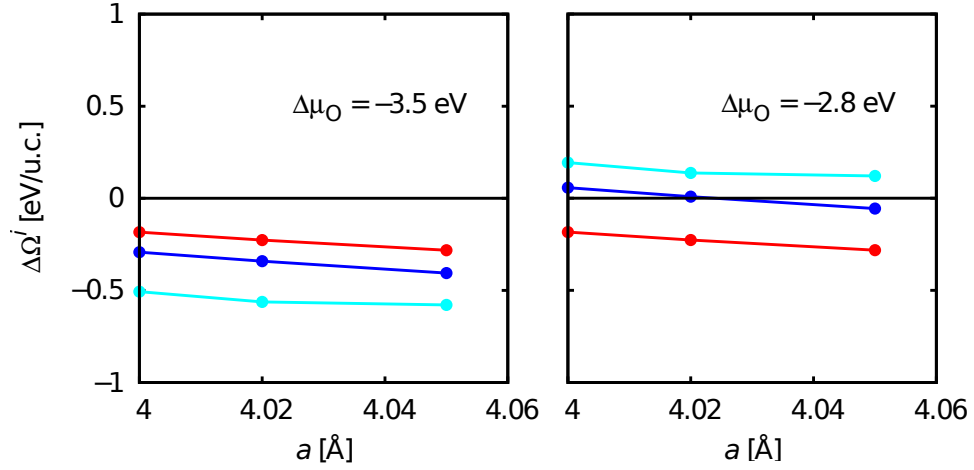


Figure C.11: **Lattice constant dependence of the surface energies.** Effect of lattice constant compression (DFT+ U relaxed bulk paraelectric phase lattice constant $a = 4.05 \text{ \AA}$) to the surface free energy, $\Delta\Omega^i$. Experimental $a = 4.00 \text{ \AA}$ (1.3% compressive strain) is used in this study. Shown are two points in the oxygen chemical potential space ($\Delta\mu_O$), see Figure S1B. Red: TiO₂-TiO₂, blue: TiO₂-(TiO)_{1/2}, and light blue: TiO₂-Ti_{1/2}. The magnitude of change are quite similar for the different reconstructions (≈ 0.10 eV/u.c. at $a = 4.05 \text{ \AA}$) that their relative energies are unaffected by the strain. $\Delta\Omega^i$ here is for when $G(T)_{\text{surf}} - G(T)_{\text{bulk}} = 0$ (chapter 2 section 2.8.1). Energies are in eV per primitive surface unit cell or (1×1) surface cell.

APPENDIX D : Supplemental: Oxidative adsorption of water on the highly reduced $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ surface reconstruction of $\text{BaTiO}_3(001)$

D.1. Layer-by-Layer electronic structure of Ti_A -centered water adsorption modes

In situations where the oxidation states of the molecules and adatoms are of interest, it is important to determine whether any artificial charge transfer occurs between the two surfaces in a slab model. In Fig. D.1, the layer-by-layer LDOS of the different Ti_A -centered water adsorption modes are shown. They demonstrate that there is no unrealistic charge transfer that occurs between the bottom and top layers of the slabs to facilitate charge compensation. Furthermore, the effects of the reconstruction and adsorbate on the electronic structures are limited up to only about the first bulk TiO_2 layer. This validates that the charge states of the species on the surface of interest (Ti-rich reconstruction with water) is solely due to the local non-stoichiometry on the reconstructed surface, and not due to unrealistic interaction between the two terminations.

D.2. Atomic and electronic structures of the Ti_B -centered water adsorption modes

Fig. D.2 shows the range of structures corresponding to reactions (1)-(5) described in chapter 5 with $\text{Ti}_\text{B'}$ as the main oxidation site (see Table 5.2 in chapter 5 for the energetics associated with the reactions). Fig. D.2a shows the product of reaction (1), wherein molecular water interacts with $\text{Ti}_\text{B'}$. This is a physisorption configura-

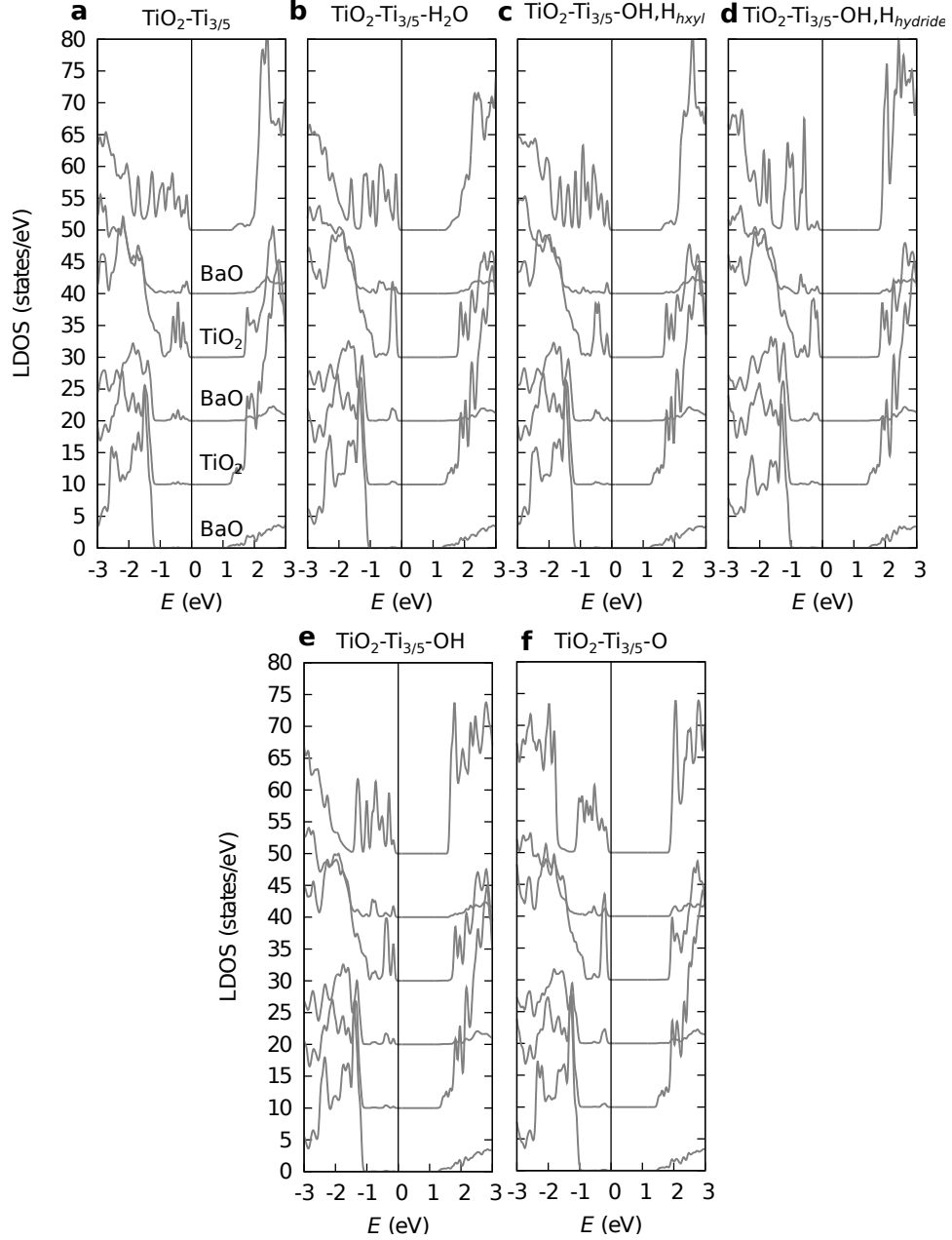


Figure D.1: **Layer-by-layer PDOS (LDOS) of the Ti_A centered water adsorption/oxidative adsorption products.** **a**, Bare $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ $\text{TiO}_2\text{-Ti}_{3/5}$ reconstruction; **b**, molecular; **c**, dissociative with H on a lattice O (O_1); **d**, dissociative with H on $\text{Ti}_{B'}$; **e**, oxidative adsorption with surface OH as the product; and **f**, with surface O as the product. The corresponding atomic structures are shown in Figure 1 of the main text. The plots are shifted along the y -axes for clarity, top to bottom: top layer (reconstructed TiO_2 layer) to bottom layer (BaO). The valence band maxima are aligned at 0 eV.

tion, as seen from the weak change in the density of states (Fig. D.3a). Fig. D.2b and c correspond to the products of dissociative reactions (2) and (3), respectively. Fig. D.2b shows OH bonding to $\text{Ti}_{\text{B}'}$ and H bonding to a nearby lattice oxygen, forming the so-called $\text{Ti}_{\text{B}'}(\text{OH})(\text{O}_\text{l}\text{H})$ structure. Fig. D.2c shows OH bonding to $\text{Ti}_{\text{B}'}$ and H bonding to Ti_A , forming the so-called $\text{Ti}_{\text{B}'}(\text{OH})\text{Ti}_\text{A}\text{H}$ structure. It is likely that the hydrogen could diffuse and access different O_l sites, thereby forming H_2 once adjacent to a H on Ti_A or $\text{Ti}_{\text{B}'}$ site. This could occur through a scheme similar to what is shown in Fig. 5.4a of the main paper. Analysis of the Löwdin charges of the two configurations (Table D.1) shows that the H in $\text{Ti}_{\text{B}'}(\text{OH})(\text{O}_\text{l}\text{H})$ is protonic ($+0.38e$) while the H in $\text{Ti}_{\text{B}'}(\text{OH})\text{Ti}_\text{A}\text{H}$ is hydridic ($-0.55e$). The hydridic nature of the hydrogen atom is highlighted in Fig. D.3c, where the outset shows orbital contribution from the hydridic hydrogen onto a states near the valence band edge (-4.5 to -3 eV). The products of oxidative adsorption reactions (4) and (5) on $\text{Ti}_{\text{B}'}$ are shown in Figs. D.2d and e, respectively. In both cases, the $\text{Ti}_{\text{B}'}$ is oxidized, but in the case of $\text{Ti}_{\text{B}'}=\text{O}$, the interaction between the oxygen and titanium is more covalent. This is seen from the overlap of the O p_x and p_y orbitals with the $\text{Ti}_{\text{B}'}$ d_{xz} and d_{yz} orbitals (Fig. D.3e).

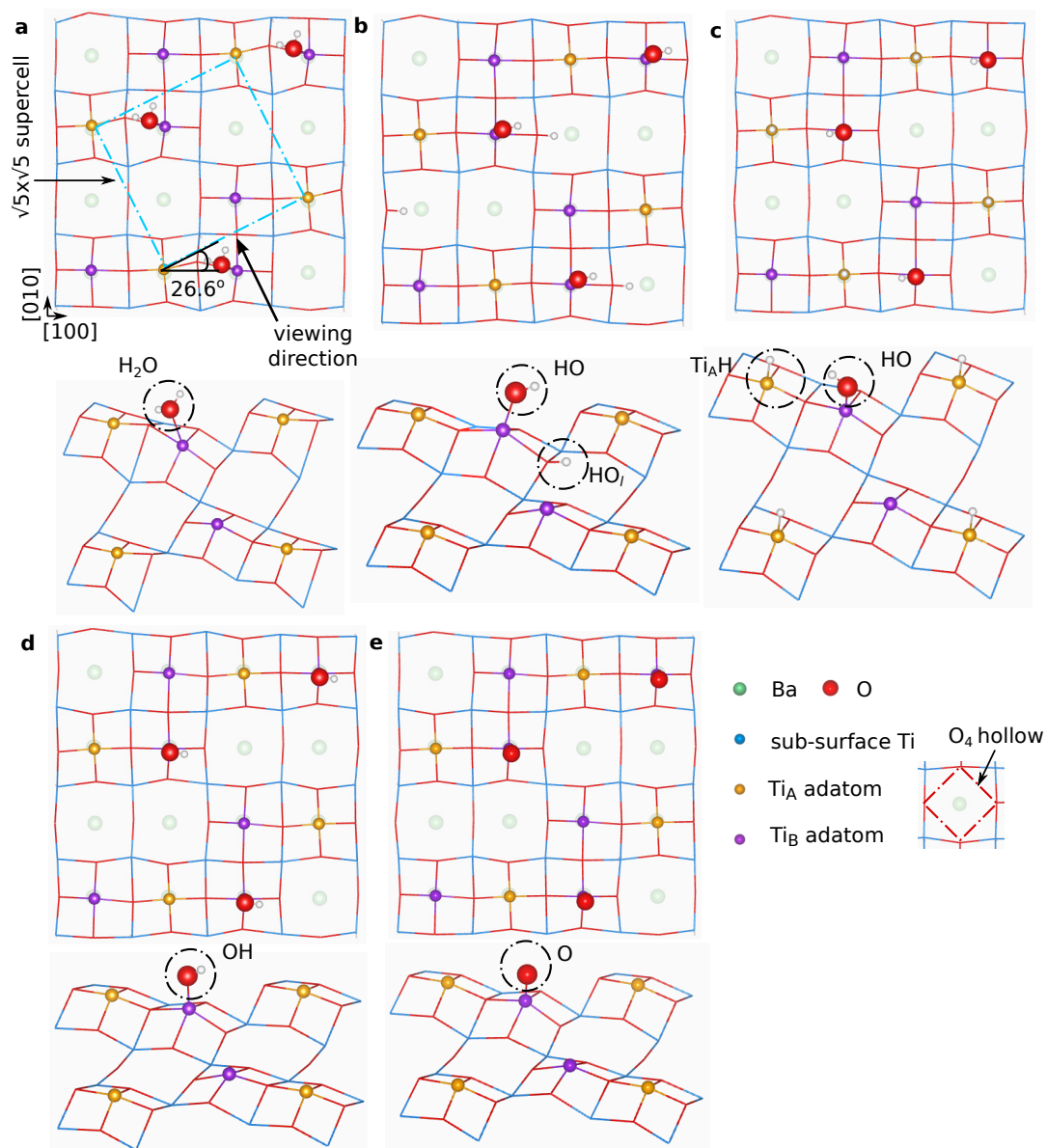


Figure D.2: **Different adsorption products of H_2O on TiB' .** a, molecular; b, dissociative with H on a lattice O (O_1); c, dissociative with H on Ti_A ; d, oxidative with surface OH as the product; and e, oxidative with surface O as the product. Viewing direction for the angled-view structures is shown in a.

Table D.1: Löwdin charges^a of select surface species after reaction of water with the $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ TiO₂-Ti_{3/5} reconstruction with Ti_{B'} as the main reaction site.^b

Structure	Adsorption type	Ti _A	Ti _B	Ti _{B'}	O _w	H _{h_{xy}l}	H _{diss}
S1a	physisorption	+2.07	+1.80	+1.79	-0.79	+0.41	+0.35
S1b	dissociative	+2.08	+1.79	+1.79	-1.09	+0.39	+0.38
S1c	dissociative	+2.23	+1.79	+2.11	-0.99	+0.41	-0.55
S1d	oxidative	+2.08	+1.84	+2.11	-1.00	+0.41	
S1e	oxidative	+2.09	+1.82	+2.13	-0.84		

^ain electron charge, e . ^b The structures are found in Fig. D.2. Bulk Ti: +2.33 e ; bulk O: -1.02 e . O_w is O from water; H_{h_{xy}l} is H in the hydroxyl; H_{diss} is H-bonded to a surface O, or dissociated H on a lattice O (O_l) or Ti_A.

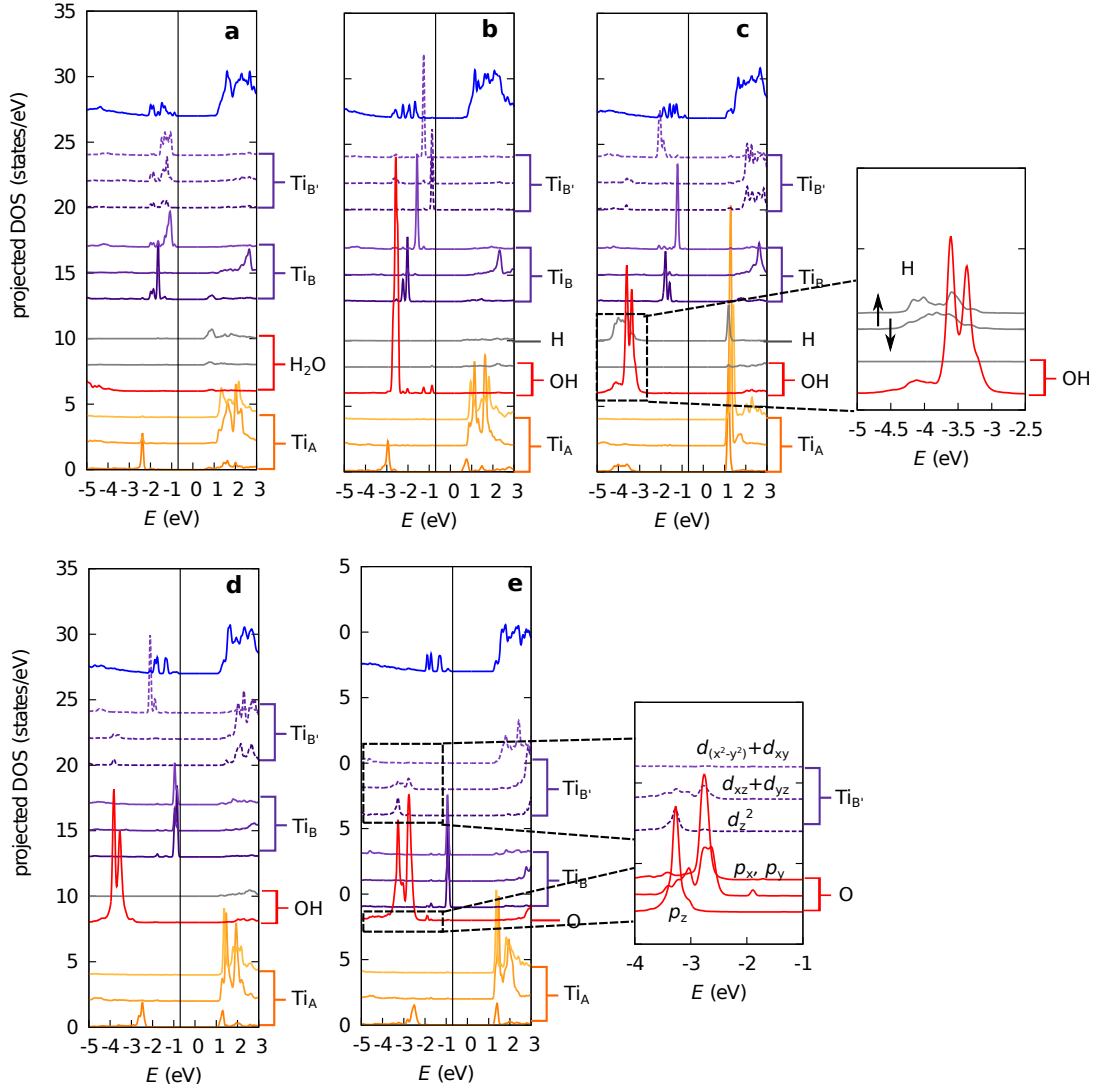


Figure D.3: **Electronic PDOS of the adsorption products shown in Fig. D.2.** **a**, molecular; **b**, dissociative with H on a lattice O (O_1); and **c**, dissociative with H on Ti_A . outset: spin resolved $1s$ orbital projection of the H on Ti_A showing hydride orbital occupation. In contrast, the H in OH do not have occupied $1s$ orbital (cationic). **d**, oxidative adsorption with surface OH as the product; and **e**, with surface O as the product. outset: orbital resolved projection of the O adsorbates $2p$ orbitals, where the p_z orbital overlaps with the d_{z^2} ($Ti_{B'}-O$ σ bonding), and p_x and p_y orbital overlap with the d_{xz} and d_{yz} orbitals ($Ti_{B'}-O$ π bonding). For Ti adatoms (A, B' and B), the DOS contribution is resolved to show orbital types: d_{z^2} , $d_{xz} + d_{yz}$ and $d_{x^2-y^2} + d_{xy}$ from bottom to top. The valence band maxima are aligned at -0.7 eV.

APPENDIX E : Supplemental: Synergistic oxygen evolving activity of a TiO_2 -rich reconstructed $\text{SrTiO}_3(001)$ surface

E.1. Miscellaneous data

Table E.1: Sample resistivities.

sample	resistivity ($\text{m}\Omega\text{-cm}$)
Reconstructed	
Trial 1	8.7
Trial 2	13.5
Trial 3	7.6
Trial 4	8.1
Control	
As received	7.1
Etched	7.9
Sputter-annealed + furnace calcined	11.0
Sputter-annealed + etched + furnace calcined	10.0
UHV annealed (10 min)	7.6
Spinelli et al. (199)	6.90
Manufacturer	7

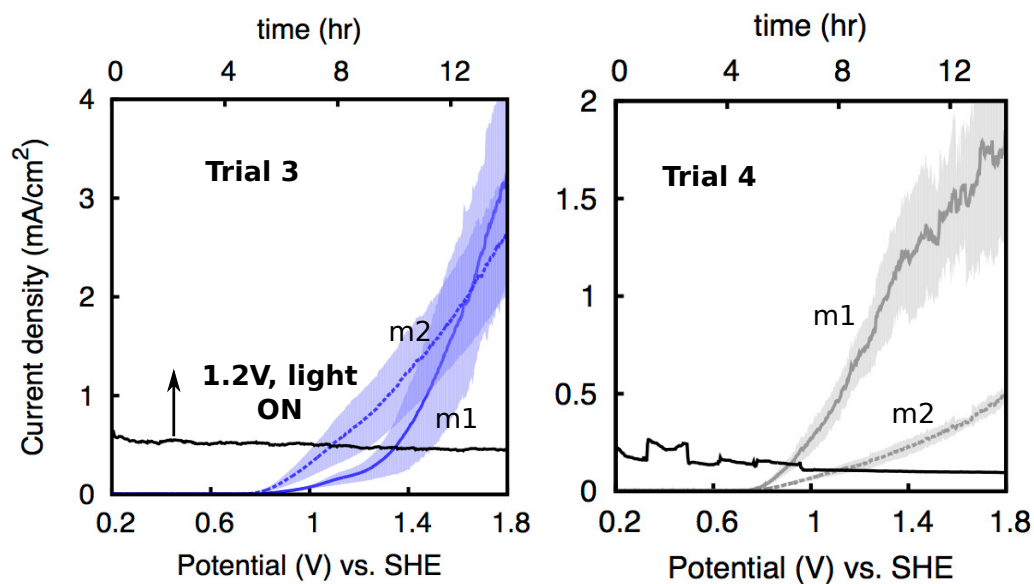


Figure E.1: **Additional (photo)electrochemical measurements.** I - V (blue and grey) curves and I - t (black, at 1.2 V with illumination) curves for two other trials of the 2×1 reconstructed $\text{SrTiO}_3(001)$ surface. I - V plots are from average of 5 anodic and cathodic cycles. m1 and m2 correspond to measurements from fresh samples and after the 14-hr constant voltage electrolysis, respectively.

Table E.2: Tafel slopes (A) and apparent exchange current densities (j_o) obtained from the Tafel plots shown in Fig. 6.2d in chapter 6.

sample	A (V)	j_o (mA/cm ²)
Reconstructed		
Trial 1	0.183±0.002	0.0504±0.0021
Trial 2	0.185±0.002	0.0065±0.0003
Trial 3	0.184±0.003	0.0026±0.0003
Trial 4	0.196±0.002	0.0062±0.0003
Control		
As received	0.542±0.009	0.00112±0.00016
Etched	0.593±0.002	0.00119±0.00003
Sputter-annealed + furnace calcined	0.476±0.004	0.00100±0.00008
Sputter-annealed + etched + furnace calcined	0.949±0.017	0.00323±0.00044
UHV annealed (10 min)	0.195±0.003	0.00056±0.00008

Uncertainties derived from the standard error of the fit from $I - V$ curves that were averaged over two continuous cyclic voltammetry cycles at 1 mV/s scan rate.

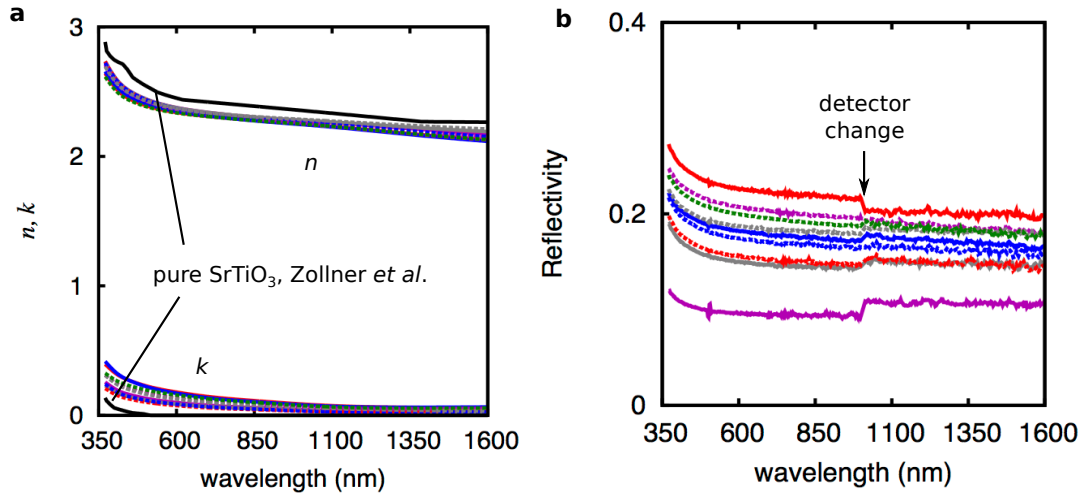


Figure E.2: **Optical Spectrum.** (a) Indices of refraction: n and k , real and imaginary components, respectively. (b) Reflectivity. Samples do not show significant variation in their spectra. Solid line, surface reconstructed samples; broken line, control. The colors correspond to the same sample color designations in Fig. 6.2d. Also plotted in (a) are the measured refraction indices for pure SrTiO_3 (14) (black line). Note that the k is nonzero even in the higher wavelengths with energy below SrTiO_3 gap, $3.2\text{eV} = 390\text{nm}$, (15) due to free charge carriers in the highly Nb-doped oxides. About 20% of the entire spectrum is being reflected off by the samples (averaged over different polarization).

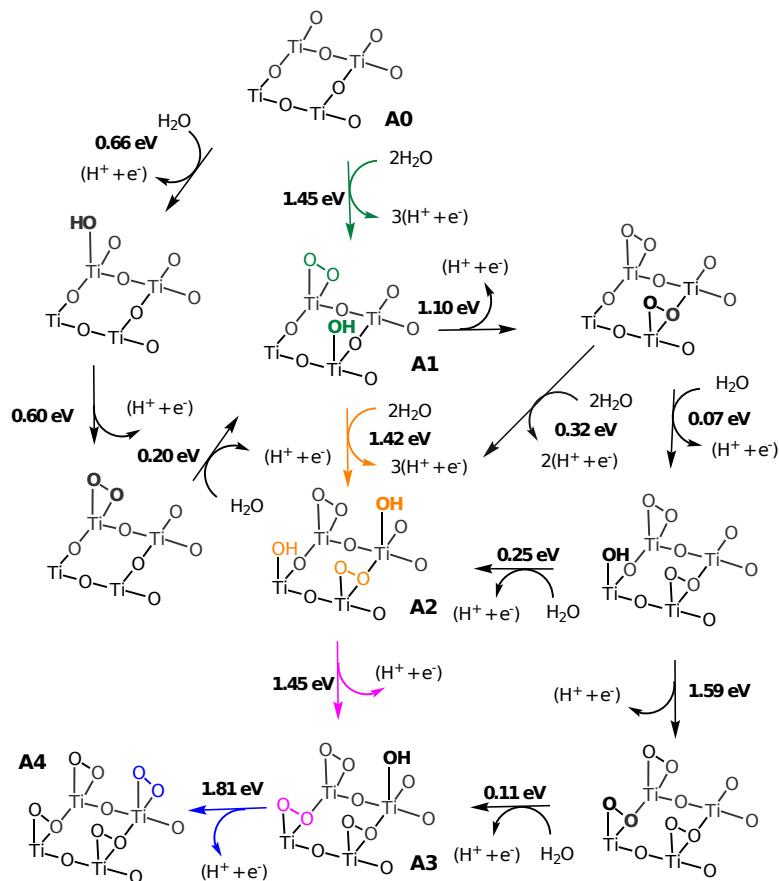


Figure E.3: **Reverse Latimer (Hydration and oxidation) diagram for the bulk-like TiO_2 surface.** The diagram shows a series of hydration and deprotonation reactions leading to O-enrichment of the surface. The colored path corresponds to the transformation of the adsorbate-free surface (A0) into the most oxidized form of the surface (A4), passing through the most stable intermediates (A1, A2, and A3). Black paths are alternative paths leading to less stable structures. The schematic shows the basis atoms of the 2×2 supercell (simulation size). The Gibbs free energies of the reactions are indicated next to the arrows (*vs.* SHE, $\text{pH}=14$). A2 and A3 are L2 and L3 of Fig. 6.4a in chapter 6, respectively. The corresponding free energy *vs.* potential at $\text{pH}=14$ plot and the Pourbaix diagram are shown in Fig. E.5

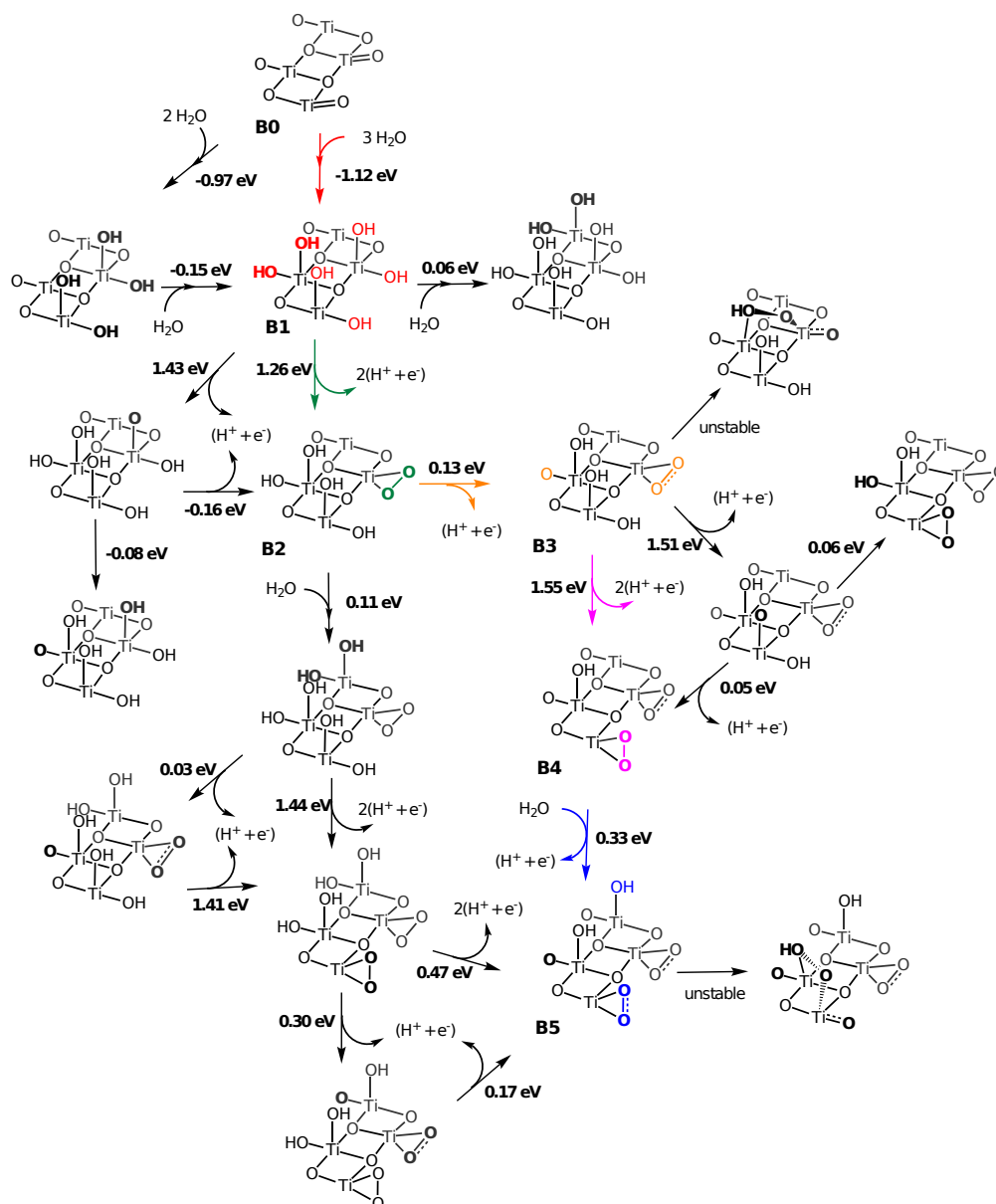


Figure E.4: **Complete reverse Latimer (Hydration and oxidation) diagram for the 21 TiO₂-DL surface.** The diagram shows a series of hydration and deprotonation reactions leading to O-enrichment of the surface. The colored path corresponds to the transformation of the adsorbate-free surface (B0) into the most oxidized form of the surface (B5), passing through the most stable intermediates (B1, B2, B3, and B4), as is shown in Fig. 6.3a in chapter 6. Black paths are alternative paths leading to less stable structures. A single bond between two O atoms indicates a peroxo while a one-and-a-half bond indicates a superoxo species. The schematics show only the top basis atoms of the 2×2 supercell (simulation size). The Gibbs free energies of the reactions are indicated next to the arrows (*vs.* SHE, *pH*=14). B4 and B5 are R3 and R4 of Fig. 6.4b in chapter 6, respectively.

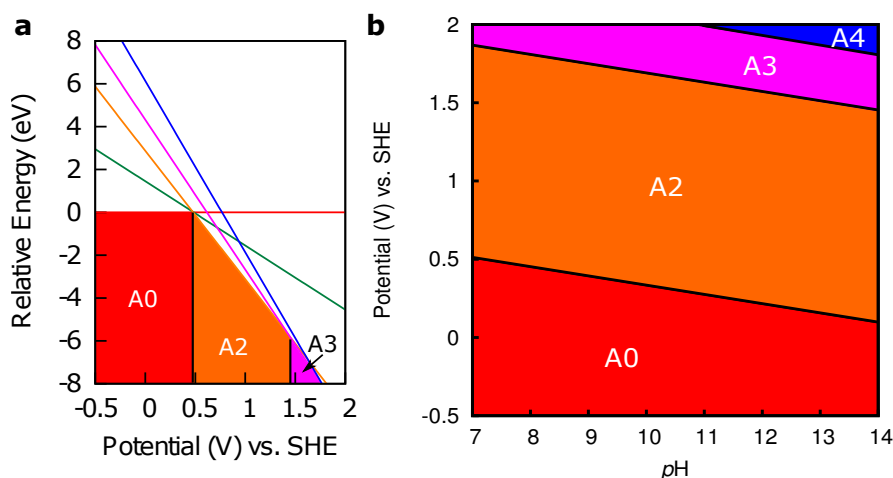


Figure E.5: **pH and potential dependence of surface structure of the bulk-like TiO_2 .** (a), the relative free energy diagram ($p\text{H}=14$) of the most stable structures found for each surface oxygen and hydrogen content for the bulk-like TiO_2 . Energy of each surface is plotted relative to that of TiO_2 (A0) + $4\text{H}_2\text{O}$. Structures A0, A2, A3, and A4 are found to be stable reconstructions of bulk-like TiO_2 under aqueous oxidation; where A2 persists a little above the reversible potential for O_2 evolution half reaction ($\varepsilon_{\text{eq}}=0.4\text{ V}$, $p\text{H}=14$). (b) Pourbaix diagrams for the bulk-like TiO_2 . A0, red line or region; A1, green; A2, orange; A3, pink; and A4 blue. See Fig. E.3 and Fig. 6.4a (chapter 6) for the corresponding schematics of the structures.

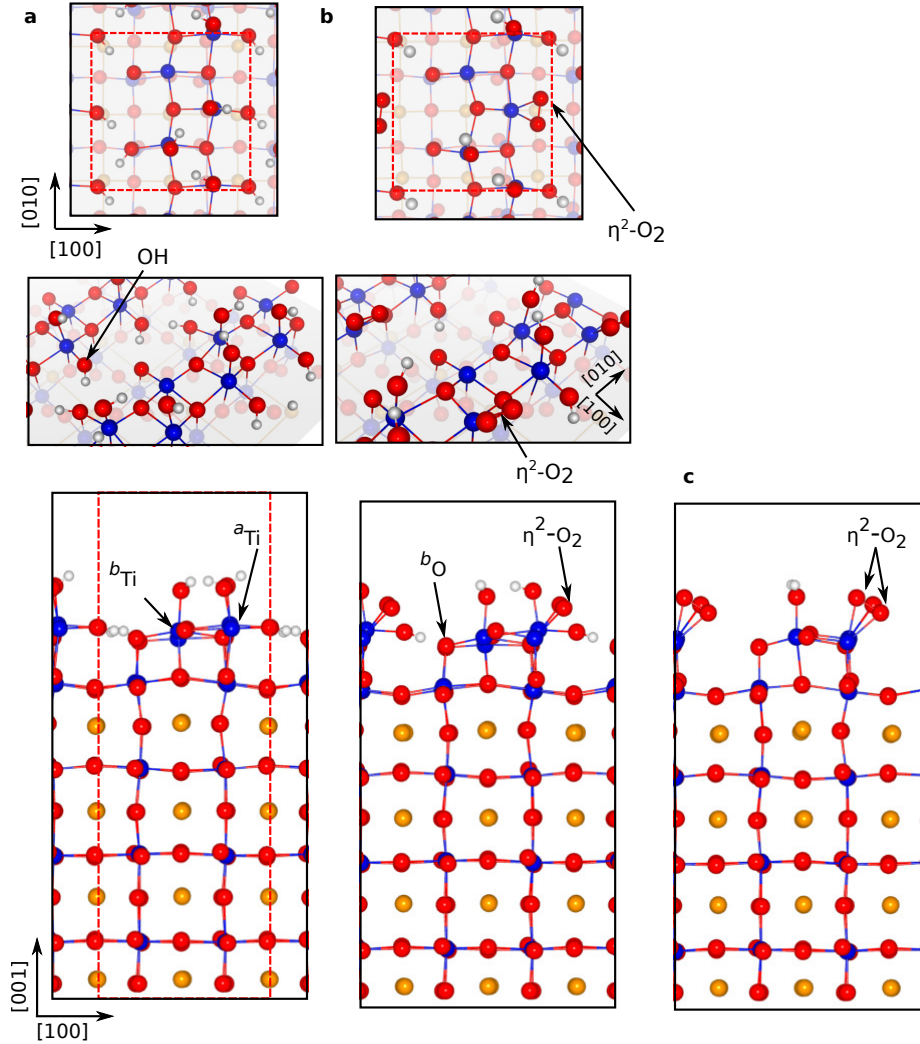


Figure E.6: **Structure of some oxidation derivatives of the 2×1 TiO₂-rich DL reconstruction.** (a)-(c) Ball-and-stick models of structure B1, B3, and B5(R4), respectively (see Fig. 6.3 in chapter 6). Red spheres: O; blue: Ti; white: H; yellow: Sr. B1 is the maximally hydrated form, beyond which addition of more H₂O becomes unfavorable, while B3 and B5 show the resulting surfaces after oxidation. The surfaces show various combinations of Ti-OH and side-on Ti-O₂ ($\eta^2\text{-O}_2$) structures. The $\eta^2\text{-O}_2$ could either be a peroxo or a superoxo, depending on the extent of oxidation of the surfaces. These can be distinguished by their charge, bond length and stretching frequencies (see Table 6.1 in chapter 6).

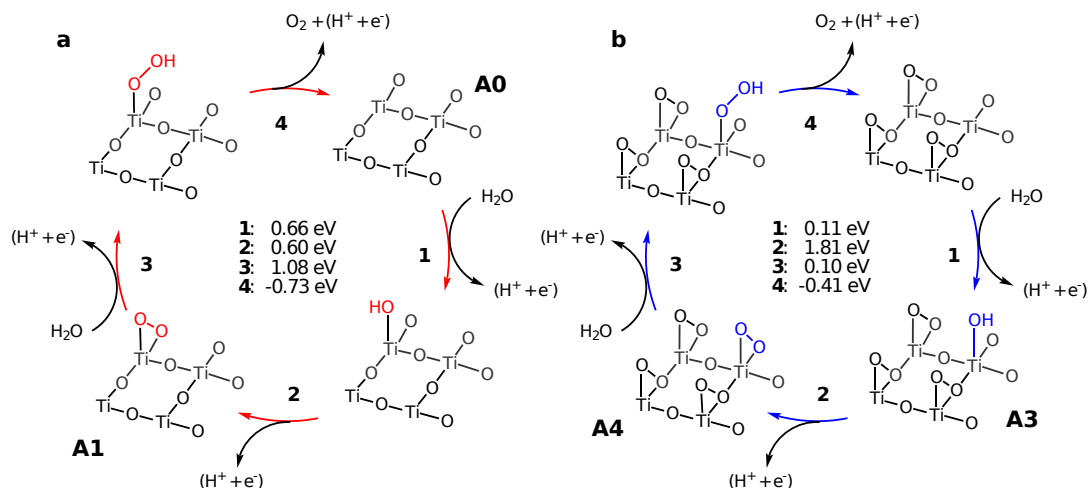


Figure E.7: **Catalytic cycles involving other derivatives of the bulk-like TiO_2 surface.** Cycles involve surfaces A0 and A3/A4 defined in Fig. E.3. Reactions involve formation of hydroxo, oxo(peroxo) and hydroperoxo intermediates. The energies within the cycles are the Gibbs free energy of the step and for the proton and electron producing steps, the required potential to drive the designated step to spontaneity is of the same magnitude and sign in V. (a) At low potentials where A0 prevails, the rate limiting reaction is predicted to be the hydroperoxo formation (step 3), (b), while at high potentials, where A3 and/or A4 prevail, the second oxidation step, hydroxo to oxo(peroxo-like) step, is rate-limiting. Both involve large overpotential ($\Delta\varepsilon_{\text{max}}$) requirements of 0.68 and 1.41 V, respectively. In the case of the A0 cycle, the A0 surface is no longer the stable surface at the required potential (1.08 V).

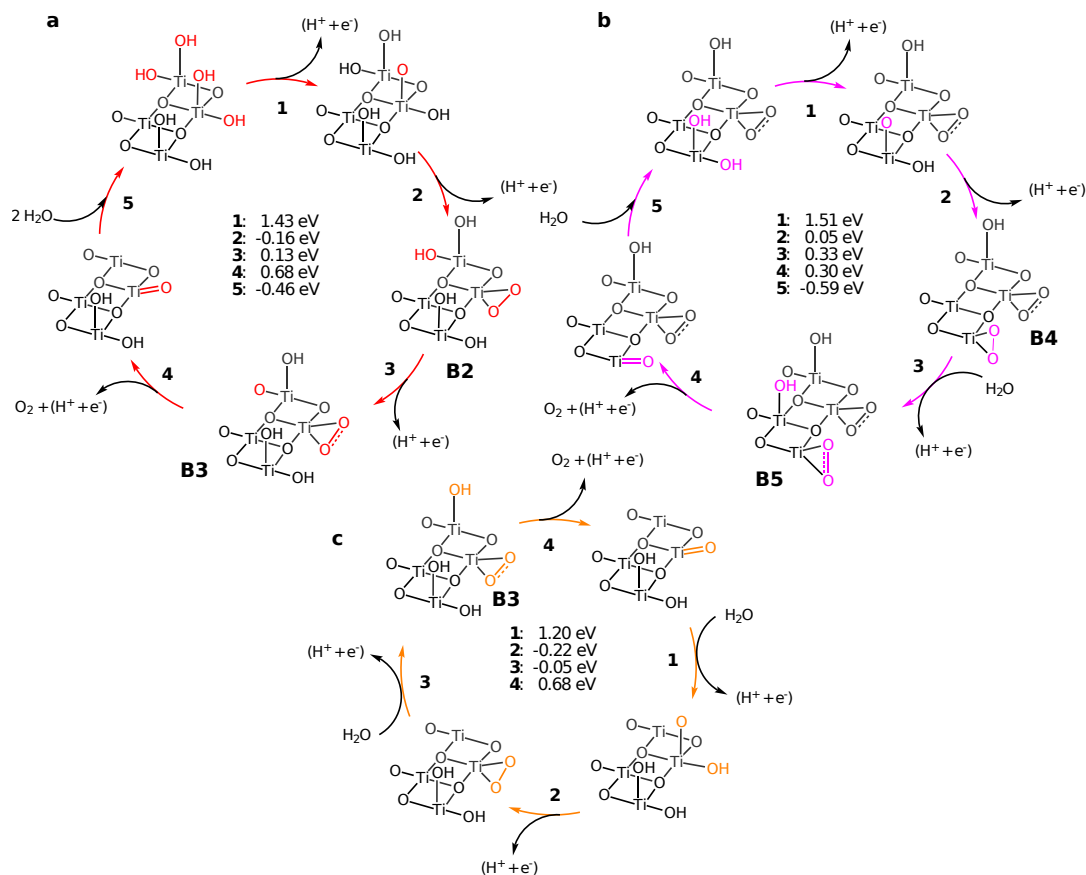


Figure E.8: **Catalytic cycles involving other derivatives of the 2×1 TiO_2 -DL surface.** Catalytic cycles involve surfaces B1, (a), and B3, (b) and (c), defined in Fig. 6.3 in chapter 6 and Fig. E.4. Just like on surface B5 (defined as R4 in chapter 6, Fig. 6.4b), the "Ti sites are the oxidation/ O_2 generation sites. The energies within the cycles are the Gibbs free energy of the step and for the proton and electron producing steps, the required potential to drive the designated step to spontaneity is of the same magnitude and sign in V. At the potentials where all the steps of these reactions will be spontaneous, B5 (R4) will be the preferred surface, and therefore making these cycles become kinetically irrelevant.

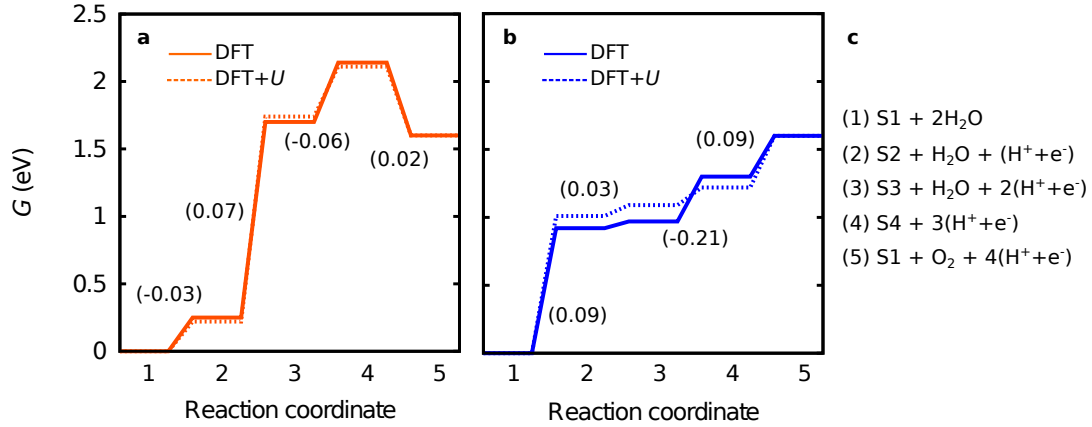


Figure E.9: **Bulk-like TiO₂ (a) and TiO₂-DL (b) reconstruction barriers, similarity of GGA (solid) and GGA+*U* (dotted lines) barriers.** (a) and (b) illustrate the calculated barriers (step heights) for the reaction cycles in Fig. 6.4a (bulk-like TiO₂) and 6.4b (2×1-DL TiO₂-rich reconstruction), respectively. GGA and GGA+*U* (Ti 3d at 4.72 eV) predicted values, solid and broken lines, respectively. Zero point energies in both are taken from GGA vibrational spectra. Each step (1-5) corresponds to the relative free energy of the surfaces and molecules as shown in (c). (1) is set as the zero energy. S corresponds to L in (a), while it is R in (b). The numbers in the parentheses are the differences in the GGA+*U* and GGA calculated barriers in eV. Note that the differences are generally small and inconsequential to the identity of the ratelimiting step. The GGA+*U* predicted difference in the thermodynamic overpotential ($\Delta\varepsilon_{\text{max}}$) between the bulk-like TiO₂ and the 2×1 TiO₂-rich reconstruction is 0.51 V, nearly equal to the 0.50 V predicted by GGA.

Table E.3: Gas phase zero point energies and entropies ($T=298$ K).

Molecule	ZPE (eV)	$TS^\circ(eV)$
H ₂	0.268	0.404
H ₂ O	0.561	0.583

Taken from the NIST Chemistry WebBook database. (48)

Table E.4: Reaction energies (ΔE) and zero point energy changes (ΔZPE) of the surface hydration-oxidation reaction: $A0 + jH_2O \rightarrow X + (k/2)H_2(g)$, where A0 is the adsorbate-free bulk-like $TiO_2(001)$ termination.

surface*	Special Name	Figure no.	j, k	ΔE (eV)	ΔZPE (eV)
$H_2O_x_x_x$			1, 0	-0.73	0.11
$H_2O_x_H_2O_x$			2, 0	-1.34	0.22
$H_2O_H_2O_H_2O_x$			3, 0	-2.29	0.30
$H_2O_H_2O_H_2O_H_2O$			4, 0	-2.92	0.41
$OH_x_x_x$		E.3, E.7	1, 1	1.20	-0.18
$O_x_x_x$		E.3, E.7a	1, 2	2.86	-0.21
$vO_x_x_x^\dagger$			1, 2	4.06	
$O_x_OH_x$	A1	E.3	2, 3	3.51	-0.31
$O_x_O_x$		E.3	2, 4	5.76	-0.42
$O_x_O_OH$	L1	6.4a, E.3	3, 5	6.26	-0.50
$O_OH_O_OH$	A2, L2	6.4a, E.3	4, 6	6.95	-0.58
$O_x_O_O$		E.3, E.7b	3, 6	9.02	-0.63
$O_OH_O_O$	A3, L3	6.4a, E.3, E.7b	4, 7	9.57	-0.71
$O_O_O_O$	A4	E.3, E.7b	4, 8	12.51	-0.81
$O_OOH_O_OH$	L4	6.4a	5, 8	10.42	-0.76
$x_OOH_x_x$		E.7a	2, 3	4.42	-0.33
$O_OOH_O_O$		E.7b	5, 9	13.06	-0.90

* The surfaces are named according to the type of adsorbate on the four Ti sites separated by “_”, where x means an adsorbate-free site. See Fig E.10 for the ordering scheme of the Ti sites. $^\dagger v$ means vertically oriented Ti-O bond, as found by Man et al. (54) which is less stable than the tilted geometry considered here.

Table E.5: Reaction energies (ΔE) and zero point energy changes (ΔZPE) of the surface hydration-oxidation reaction: $B0 + jH_2O \rightarrow X + (k/2)H_2(g)$, where B0 is the adsorbate-free 2×1 TiO_2 -rich double layer reconstruction.

surface*	Special Name	Figure no.	j, k	ΔE (eV)	ΔZPE (eV)
OHOH_OHOH_OHOH_O	B1	6.3, E.4, E.8a	3, 0	-3.35	0.22
OHOH_pOO_OHOH_O	B2	6.3, E.4, E.8a	3, 2	0.26	-0.07
OHOH_sOO_OH,O_O	B3	6.3, E.4, E.8a-c	3, 3	1.56	-0.21
pOO_sOO_OH,O_O	B4, R3	6.3, E.4, 6.4b, E.8b	3, 5	5.50	-0.53
sOO_sOO_OH,O_OH,O	B5, R4	6.3, E.4, 6.4b, E.8b	4, 6	6.23	-0.56
sOO_O_OH,O_O	R1	6.4b, E.8b	2, 3	2.89	-0.28
sOO_O_OH_OH,O_O	R2	E.4, 6.4b, E.8b	3, 4	4.29	-0.40
OHOH_OHOH_O_O		E.4	2, 0	-2.43	0.12
OHOH_OHOH_OHOH_OHOH		E.4	4, 0	-4.03	0.30
OHOH_O_OH_OHOH_O		E.4, E.8a	3, 1	-0.74	0.07
OHOH_OHOH_OH,O_O		E.4	3, 1	-0.83	0.08
pOO_pOO_OHOH_O		E.4	3, 4	4.33	-0.37
OHOH_pOO_OHOH_OHOH		E.4	4, 2	-0.37	0.00
OHOH_sOO_OH,O_OHOH		E.4	4, 3	0.85	-0.15
pOO_pOO_OHOH_OHOH		E.4	4, 4	3.44	-0.30
pOO_sOO_OHOH_OH,O		E.4	4, 5	4.89	-0.42
OHOH_O_O_O		E.8a and c	1, 0	-1.39	0.07
OHOH_O_OH_O_O		E.8c	2, 1	0.25	-0.02
OHOH_pOO_O_O		E.8c	2, 2	1.18	-0.14

* The surfaces are named according to the type of adsorbate on the four Ti sites, including ^aO and ^bO, separated by “_”. See Fig E.10 for the ordering scheme of the Ti sites. pOO and sOO stand for peroxo and superoxo, respectively.

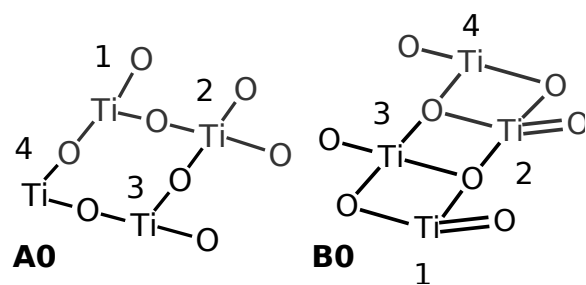


Figure E.10: **Ti-site designation** for the naming conventions of the surfaces followed in Tables E.4 and E.5.

E.2. Sample (working) electrode preparation

Preparation of the working electrode from pieces of single crystal Nb-doped SrTiO_3 for electrochemical testing is shown in Fig. E.11. (a) First, flatten the head of a Cu wire that is about 12 cm in length. (b) Tape the single crystal sample on the edge of a glass slide covered with low-lint wiper, with polished side facing down. Make sure you expose the back side as much as possible. This is to keep the sample in place before treatment with the conductive contacts and prevent the polished side (surface of interest) from being contaminated with the conductive paste. Paint the exposed back with Ga-In (99.99%) eutectic. Rubbing the eutectic with the end of a copper wire will help make it adhere to the surface evenly. (c) Slide the copper wire in the heat-shrink tube insulation (≈ 7 cm long, radially shrunken to fit Cu wire snugly). Paint a thin layer of Ag paste/paint on the Ga-In painted back of the crystal. Place the flattened head of the copper wire on top of it. You may tape the wire onto the benchtop to hold it in place. Apply additional Ag paint to cover the copper wire in contact with the crystal until a desired coverage is achieved. Wait for the Ag contact to set (≈ 24 hrs in ambient condition). (d) Cut the sample out of the glass slide using a thin blade, cutting the tape about 1 cm away from the edge of the crystal. (e-f) Carefully pull the tape off the sample with a pair of forceps. The Ag paint should remain intact and the crystal remains securely attached to the wire. (g-h) Carefully apply epoxy over the entire back and edge of the sample. Make sure none of the epoxy touches the polished surface. Add an extra amount of epoxy on the Cu wire near the edge of the sample. (i) This will seal the tip of the heat-shrink tube near the sample once the heat-shrink tube is slid near the edge of the sample. Make sure no epoxy gets pushed toward the polished surface of the sample. Seal the other end of the heat-shrink tube with an epoxy.

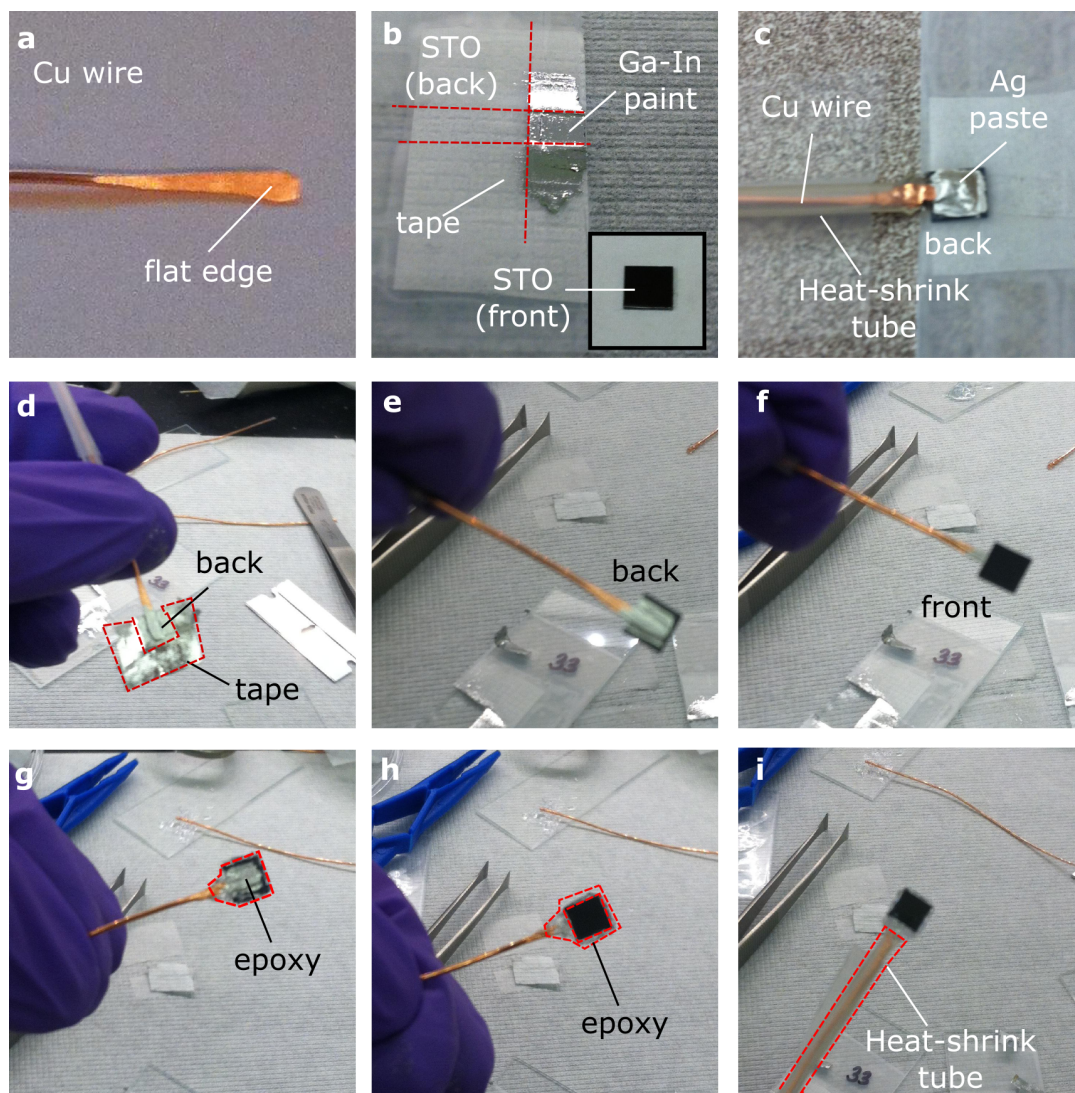


Figure E.11: **Step-by-step preparation of the sample (working) electrode.** See section E.2 for the accompanying text.

APPENDIX F : Supplemental: Tunable surface stoichiometry in oxide ferroelectrics via the switchable bulk-polarization

F.1. Validation of the slab model

We have done several convergence studies to validate our computational setup such as convergence on k -grid and planewave cutoff. Additionally, to validate the slab model for the paraelectric and ferroelectric slabs adapted in our investigations, we have computed the phase diagram for the competing (1×1) surface compositions using 4 different slab models in addition to the model defined in previous section, and applied for all of the surface reconstructions. Due to computational demands of these investigations, we limited our validation to the (1×1) surface compositions only. However, this should give us a very good indication of the fidelity of the slab model, as the list of structures includes paraelectric and ferroelectric cases with different surface compositions similar to the larger reconstructions.

Table F.1 summarizes the relative surface energy of the thermodynamically relevant surfaces, $(\phi^i - \phi^{\text{BaO}}, \text{ eV per primitive unit cell})$ measured with respect the (1×1) -BaO surface composition. The slab models are set as defined in previous section indicated by (I), and additionally 4 sets obtained by starting from slab model (I) and, adding one ABO_3 unit cell to simulate the substrate which is kept fixed (II); adding one ABO_3 unit cell that is relaxed (III); increasing the vacuum thickness by 10 Å(IV); and increasing vacuum thickness and including a dipole correction (180) perpendicular to the slab (V). Table F.1 shows that majority of the differences are less than 0.1 eV which is the margin of error normally expected in DFT calculations,

which validate slab model (I). Later in Section VII, we will analyze the implications of this error on the overall phase diagram. Fig. F.1 shows the (1×1) phase diagram for different slab models. As can be seen, the global features of the phase diagrams for I–V are the same, and for some, only minor changes in the phase boundaries are observed.

Table F.1: Relative surface energy, $(\phi^i - \phi^{\text{BaO}}, \text{eV per } 1 \times 1 \text{ surface cell})$, for different slab models (I–V) defined in the text, and bulk polarization (P^+, P^0, P^-).

Pol	Reconstruction	I	II	III	IV	V
P^+	BaO-DL	-5.28	-5.36	-5.13	-5.28	-5.28
	BaO-Ba	–	–	–	–	–
	TiO ₂ -Ba	5.81	5.79	5.63	5.78	5.77
	TiO ₂	7.06	7.01	7.12	7.00	6.96
	TiO ₂ -DL	14.02	13.97	14.18	13.95	13.91
	TiO ₂ -TiO	–	–	–	–	–
	TiO ₂ -Ti	23.68	23.64	23.47	23.62	23.60
P^0	BaO-DL	-5.29	-5.28	-5.28	-5.28	-5.28
	BaO-Ba	–	–	–	–	–
	TiO ₂ -Ba	5.24	5.39	5.14	5.25	5.25
	TiO ₂	6.95	6.94	6.93	6.92	6.90
	TiO ₂ -DL	13.97	13.98	13.98	13.97	13.95
	TiO ₂ -TiO	–	–	–	–	–
	TiO ₂ -Ti	22.88	22.71	22.37	22.88	22.87
P^-	BaO-DL	-5.30	-5.31	-5.27	-5.30	-5.30
	BaO-Ba	-0.85	-0.92	-0.85	-0.83	-0.81
	TiO ₂ -Ba	4.23	4.16	4.22	4.25	4.27
	TiO ₂	6.69	6.65	6.69	6.68	6.67
	TiO ₂ -DL	13.92	13.89	13.93	13.90	13.89
	TiO ₂ -TiO	17.62	17.52	17.58	17.60	17.59
	TiO ₂ -Ti	21.96	21.87	21.92	21.96	21.96

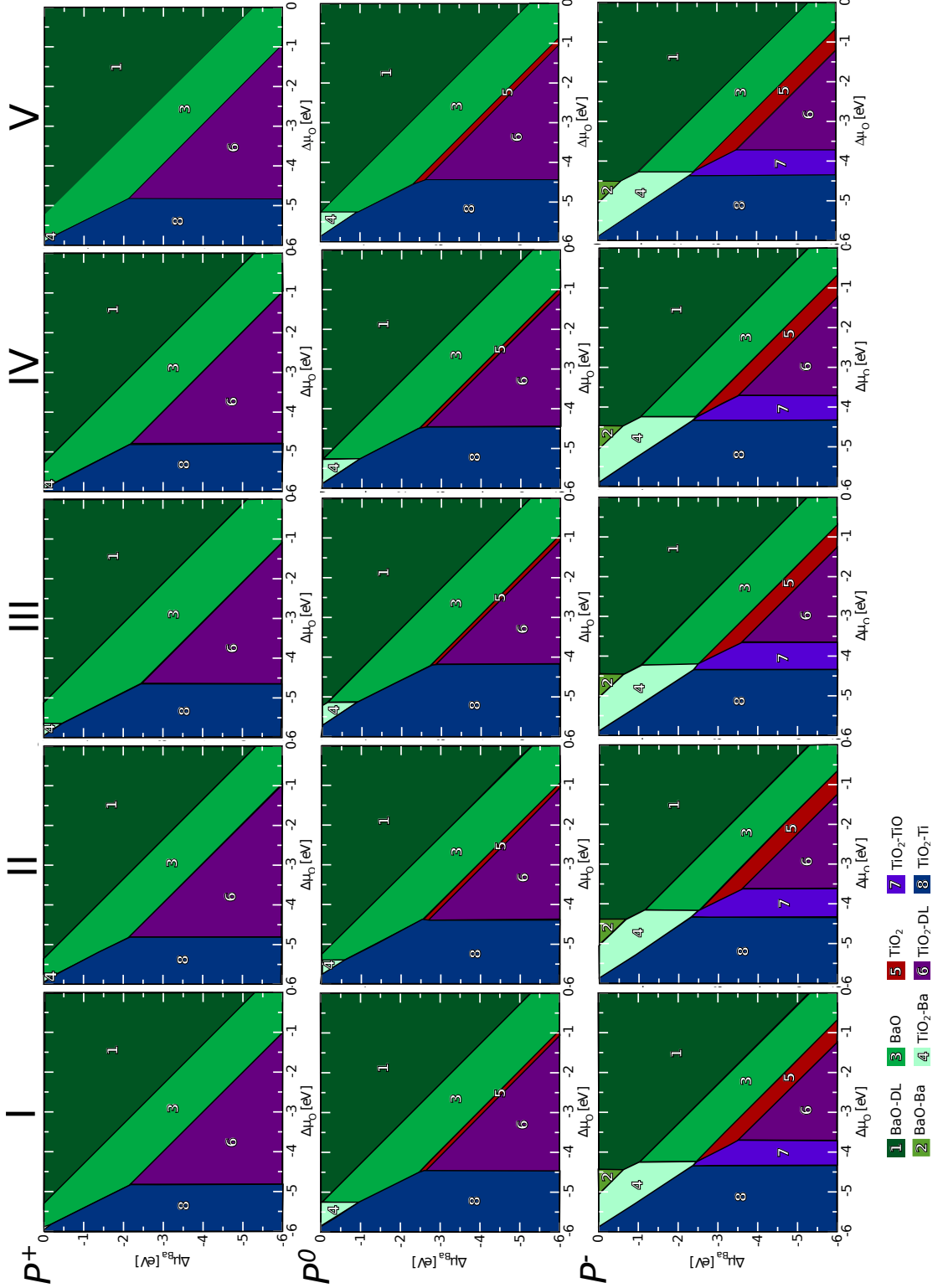


Figure F.1: The surface phase diagrams for the (1×1) reconstructions for different slab models (I–V), defined in the text, and bulk polarization (P^+ , P^0 , P^-).

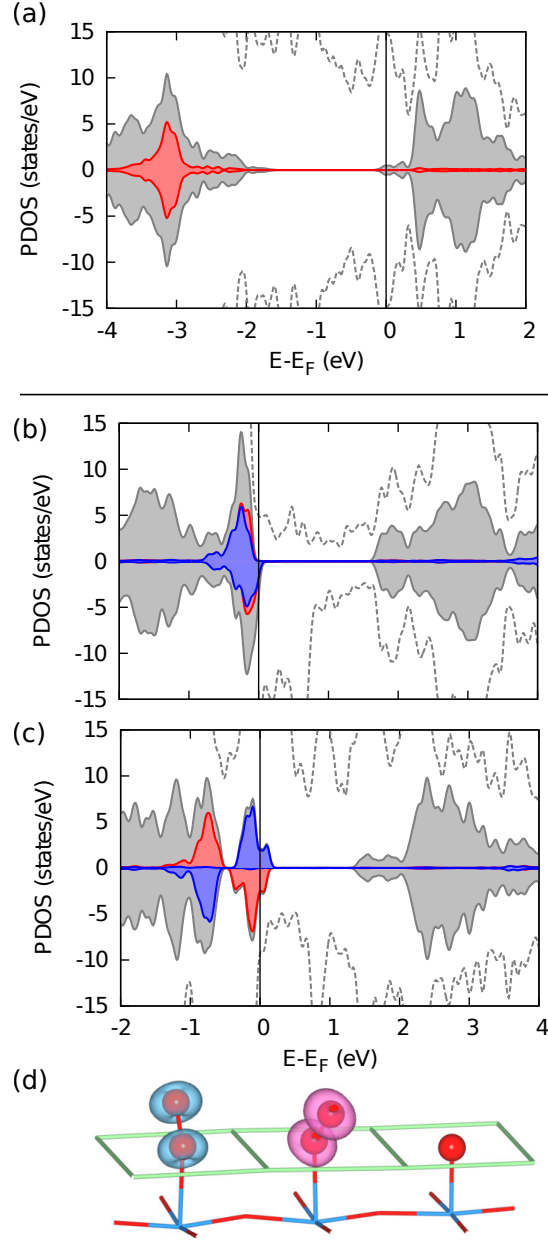


Figure F.2: Density of states (DOS) and projected density of states (PDOS) from spin-relaxed calculations for P^+ $c(2 \times 2)$ PbO-O_{1/2}, (a), P^0 and P^- 3×1 BaO-O_{2/3}, (b) and (c), respectively. Energies are relative to the Fermi level (E_F). Broken line: total DOS, grey shaded line: sum of the atomic PDOS of the O adatoms and the atoms of the two outer most surface layers, red and blue shaded lines: sum of the atomic PDOS of the O adatom or O₂ moieties on the surfaces. For (a) and (b), the O and O₂ moiety don't have net electronic spin. For (c), the two O₂ moieties have opposite non-zero net electronic spins. The corresponding real space spin-density difference isosurface plot (± 0.01 a.u.) is shown in (d) (red: excess up-spin, blue: excess down-spin). See Fig. 7.2(c) of the main document for the legend of the ball-and-stick model.

Table F.2: Change in the relative surface energy ($\phi^i - \phi^{\text{BaO}}$) with and without spin-relaxation.

Reconstruction	P^+		P^0		P^-	
	sp	sp/strx	sp	sp/strx	sp	sp/strx
BaO-DL	-0.03	-0.03	0.00	0.00	-0.02	-0.02
BaO-Ba	—	—	—	—	0.00	0.00
TiO ₂ -Ba	0.00	0.00	-0.08	-0.07	0.00	0.00
TiO ₂	0.00	0.00	-0.02	-0.02	0.00	0.00
TiO ₂ -DL	0.00	0.00	-0.01	0.00	-0.02	-0.02
TiO ₂ -TiO	—	—	—	—	0.00	0.00
TiO ₂ -Ti	0.00	0.00	-0.07	-0.06	-0.01	-0.01

sp: spin relaxed with structure fixed to spin-restricted calculations, strx: spin and structure relaxed.

Energies are in eV per 1×1 surface cell and are relative to spin-restricted relaxation.

Table F.3: Formation enthalpies obtained from the present GGA calculations and from published thermodynamic data (1).

	GGA-PBE	Exp
BTO(cubic)	-16.58	-17.19 (400K)
BTO(tetragonal)	-16.61	-17.20
BaO(rock-salt)	-5.41	-5.74
BaO ₂ (tetragonal)	-6.47	-6.57
PTO(cubic)	-12.40	-12.33 (800K)
PTO(tetragonal)	-12.59	-12.42
PbO(tetragonal)	-2.47	-2.27
PbO(orthorhombic)	-2.41	-2.26
PbO ₂ (rutile)	-2.98	-2.84
Ti ₂ O ₃ (corundum)	-15.68	-15.76
TiO ₂ (rutile)	-9.78	-9.79

Formation energies are in eV/formula unit. For experiments the values correspond to 298 K, unless otherwise stated.

Table F.4: Calculated Bader charges for the surface and sub-surface atoms for some of the stable surface reconstructions. Atoms are ordered starting from the adatoms/ad-layers then to deeper sublayers (up to two sub-layers). Total surface charges are per 1×1 surface. For comparison, bulk charges for Ba, Ti, O_{Ba} , O_{Ti} are 1.60 (1.56), 1.98 (2.00), -1.15 (-1.19), and -1.21 (-1.19) electron for FE (PE) phases. The corresponding charges in PTO are 1.37 (1.41), 2.09 (2.09), -1.10 (-1.15) and -1.18 (-1.18) electron.

Reconstruction	Atom	Charge [e]	
		P^+	P^-
3×1 BaO- $O_{2/3}$ (BaTiO ₃)	O	-0.69	-0.51
	O	-0.68	-0.51
	Ba	1.56	1.58
	Ba	1.57	1.56
	Ba	1.59	1.59
	O	-0.74	-0.61
	O	-1.24	-1.32
	O	-0.75	-0.61
	Ti	2.09	2.08
	Ti	2.12	2.07
	Ti	2.03	2.07
	O	-1.22	-1.25
	O	-1.20	-1.24
	O	-1.16	-1.22
	O	-1.16	-1.28
	O	-1.21	-1.23
	O	-1.23	-1.23
	total	-0.11	-0.02
$c(2 \times 2)$ PbO- $O_{1/2}$ (PbTiO ₃)	O	-1.15	
	Pb	1.24	
	Pb	1.26	
	O	-1.11	
	O	-1.11	
	Ti	2.14	
	Ti	2.14	
	O	-1.16	
	O	-1.17	
	O	-1.16	
	O	-1.17	
	total	-0.62	

Table F.5: Table F.4 continued

Reconstruction	Atom	Charge [e]		
		P^+	P^0	P^-
3×1 BaO-(V _{Ba}) _{1/3}	Ba	1.56	1.55	
	Ba	1.55	1.55	
	O	-1.18	-1.17	
	O	-1.08	-1.08	
	O	-1.08	-1.08	
	Ti	2.13	2.12	
	Ti	2.13	2.13	
	Ti	2.03	2.08	
	O	-1.24	-1.20	
	O	-1.22	-1.15	
	O	-1.20	-1.12	
	O	-1.24	-1.19	
	O	-1.18	-1.09	
	O	-1.20	-1.12	
	total	-0.41	-0.26	
3×1 BaO-(V _O) _{1/3} (BaTiO ₃)	Ba		1.30	1.37
	Ba		1.30	1.38
	Ba		1.54	1.49
	O		-1.33	-1.31
	O		-1.33	-1.31
	Ti		1.97	2.02
	Ti		1.97	2.02
	Ti		1.86	2.00
	O		-1.33	-1.32
	O		-1.28	-1.28
	O		-1.28	-1.28
	O		-1.16	-1.15
	O		-1.22	-1.21
	O		-1.22	-1.21
	total		-0.06	0.07
3×1 TiO ₂ -TiO _{5/3} (BaTiO ₃)	Ti	2.03	2.02	2.04
	Ti	2.03	2.02	2.05
	Ti	1.85	1.93	1.98
	O	-0.95	-0.90	-0.89
	O	-0.95	-0.90	-0.90
	O	-1.21	-1.21	-1.19
	O	-1.21	-1.21	-1.20
	O	-1.38	-1.27	-1.27

Table F.6: Table F.4 continued

Reconstruction	Atom	Charge [e]		
		P^+	P^0	P^-
	Ti	2.14	2.13	2.10
	Ti	2.14	2.16	2.13
	Ti	1.92	1.94	2.07
	O	-1.21	-1.16	-1.15
	O	-1.22	-1.25	-1.12
	O	-1.14	-1.10	-1.14
	O	-1.14	-1.11	-1.14
	O	-1.19	-1.17	-1.15
	O	-1.13	-1.12	-1.12
	Ba	1.56	1.58	1.57
	Ba	1.55	1.55	1.56
	Ba	1.55	1.55	1.55
	O	-1.26	-1.27	-1.26
	O	-1.26	-1.27	-1.25
	O	-1.21	-1.17	-1.10
	total	0.10	0.25	0.39
3×1 TiO ₂ -(TiO) _{1/3} (BaTiO ₃)	Ti		2.01	2.01
	O		-0.81	-0.79
	Ti		2.01	2.03
	Ti		2.05	2.07
	Ti		2.03	2.06
	O		-1.31	-1.33
	O		-1.26	-1.26
	O		-1.12	-1.10
	O		-1.26	-1.26
	O		-1.10	-1.13
	O		-1.13	-1.14
	Ba		1.55	1.57
	Ba		1.53	1.57
	Ba		1.55	1.60
	O		-1.19	-1.18
	O		-1.16	-1.16
	O		-1.16	-1.17
	total		0.41	0.46

Table F.7: Table F.4 continued

Reconstruction	Atom	Charge [e]		
		P^+	P^0	P^-
3×1 TiO ₂ -Ti _{2/3} (BaTiO ₃)	Ti	1.42	1.38	1.42
	Ti	1.43	1.39	1.42
	Ti	1.93	1.99	1.97
	Ti	1.93	1.98	1.97
	Ti	1.59	1.61	1.66
	O	-1.33	-1.34	-1.31
	O	-1.31	-1.29	-1.28
	O	-1.29	-1.27	-1.27
	O	-1.29	-1.28	-1.27
	O	-1.32	-1.33	-1.31
	O	-1.13	-1.13	-1.13
	Ba	1.56	1.57	1.57
	Ba	1.45	1.44	1.46
	Ba	1.45	1.45	1.46
	O	-1.26	-1.21	-1.18
	O	-1.26	-1.21	-1.18
	O	-1.26	-1.18	-1.21
	total	0.43	0.52	0.60
1×1 TiO ₂ -Ti (BaTiO ₃)	Ti	1.30	1.33	1.32
	Ti	1.66	1.67	1.76
	O	-1.31	-1.32	-1.32
	O	-1.31	-1.32	-1.32
	Ba	1.42	1.49	1.48
	O	-1.22	-1.20	-1.25
	total	0.55	0.66	0.67

F.2. Phase coexistence analysis

Difference in the surface energies between surface structures can be small enough to be within the level of uncertainty in our calculations and may also suggest possible coexistence. Fig. F.3 shows the number of phases with energies within 0.1 eV per unit cell from the lowest energy structures as a function of the chemical potentials. The number of competing phases ranges from one to twelve within the chosen energy window. The highest incidence of coexistence are mostly found at or near the phase boundaries. However, despite the large number of phases in some regions, it is important to note that the structures that are likely to coexist are stoichiometrically related. For example for the paraelectric case of BTO at $\Delta\mu_{\text{O}} = -4.9$ eV and $\Delta\mu_{\text{Ba}} = -2$ eV, nine structures are likely to exist in equilibrium. These structures include two configurations of $\text{TiO}_2\text{-TiO}_{5/3}$, $\text{TiO}_2\text{-(TiO)}_{1/2,1/3}$, and $\text{TiO}_2\text{-Ti}_{1/4,1/2,2/3,3/4,1}$. The surfaces are all TiO_2 -derived with varying degree of Ti_xO_y adatom/ad-layer coverages. The same is true for the down polarized case for PTO at $\Delta\mu_{\text{O}} = -1$ eV and $\Delta\mu_{\text{Pb}} = -1.5$ eV, where about five structures that are energetically close to each other are stoichiometrically related: $\text{PbO-(VO)}_{1/2,2/3}$, two $\text{TiO}_2\text{-Pb}_{1/2}$ ($c(2 \times 2)$ and 2×1), and $\text{TiO}_2\text{-Pb}_{2/3}$, which are PbO -derived surfaces of varying degree of oxygen and Pb deficiency. Thus, despite the uncertainty or possible coexistence in some regions, the surface phase diagrams in the main text present excellent predictive ability on the likely stoichiometry and structure of the surface reconstructions for these oxides.

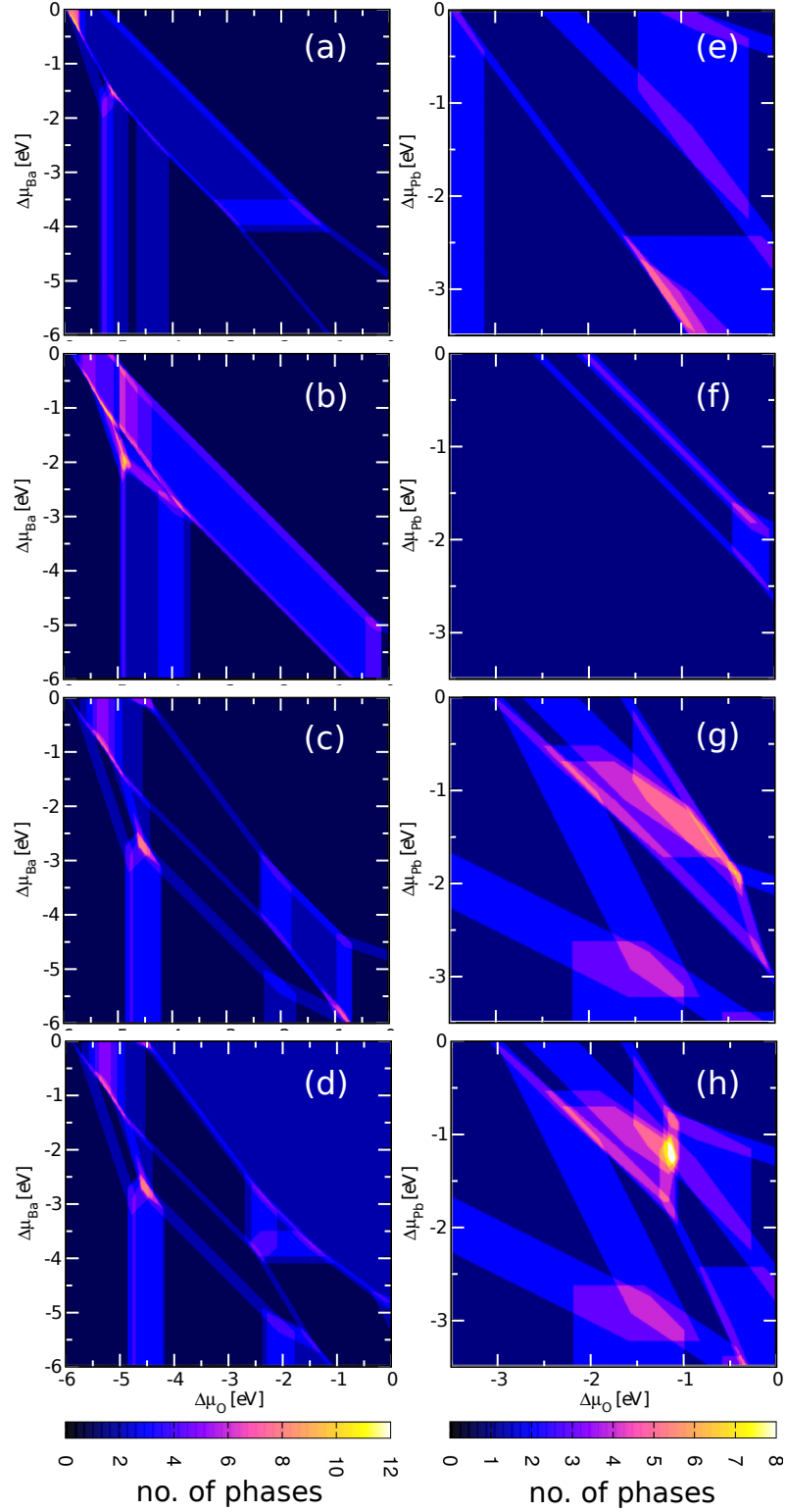


Figure F.3: Surface phase population diagrams, where the surfaces with energies within 0.10 eV/1×1 surface cell of the lowest energy structure are counted. a–d BTO(001): P^+ , P^0 , P^- , and P^+/P^- , e–h: PTO(001): same order.

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- [6] The contribution of atom i to the PDOS is multiplied by an exponential decay function, $\exp(z^i - z^0)$, where z^i and z^0 are the the z-coordinate of atom i and of the top most atom on the surface, respectively.
- [7] Secondary phases considered are BaO₂(tetragonal), BaO(rock-salt), Ba(*liquid*), TiO₂(rutile), Ti₂O₃(corundum), and Ti(hexagonal close-packed).
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