

Supporting Information for
Theoretical Model of Oxidative Adsorption of Water
on a Highly Reduced Reconstructed Oxide Surface

Nathan Z. Koocher, John Mark P. Martirez, and Andrew M. Rappe*

*The Makineni Theoretical Laboratories, Department of Chemistry, University of Pennsylvania,
Philadelphia, PA 19104–6323 USA*

E-mail: rappe@sas.upenn.edu

*To whom correspondence should be addressed

Figure S1 shows the range of structures corresponding to reactions (1)-(5) described in the main text with $\text{Ti}_{\text{B}'}$ as the main oxidation site (see Table 2 in the main text for the energetics associated with the reactions). Figure S1a shows the product of reaction (1), wherein molecular water interacts with $\text{Ti}_{\text{B}'}$. This is a physisorption configuration, as seen from the weak change in the density of states (Figure S2a). Figures S1b and S1c correspond to the products of dissociative reactions (2) and (3), respectively. Figure S1b 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. Figure S1c 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 Figure 4a of the main paper. Analysis of the Löwdin charges of the two configurations (Table S1) 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 Figure S2c, 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 Figures S1d and S1e, 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 (Figure S2e).

Table S1: Löwdin charges^a 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 with $\text{Ti}_{\text{B}'}$ as the main reaction site.^b

Structure	Adsorption type	Ti_A	Ti_B	$\text{Ti}_{\text{B}'}$	O_w	$\text{H}_{\text{hxy}}\text{l}$	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 Figure S1. Bulk Ti: $+2.33 e$; bulk O: $-1.02 e$. O_w is O from water; $\text{H}_{\text{hxy}}\text{l}$ 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 .

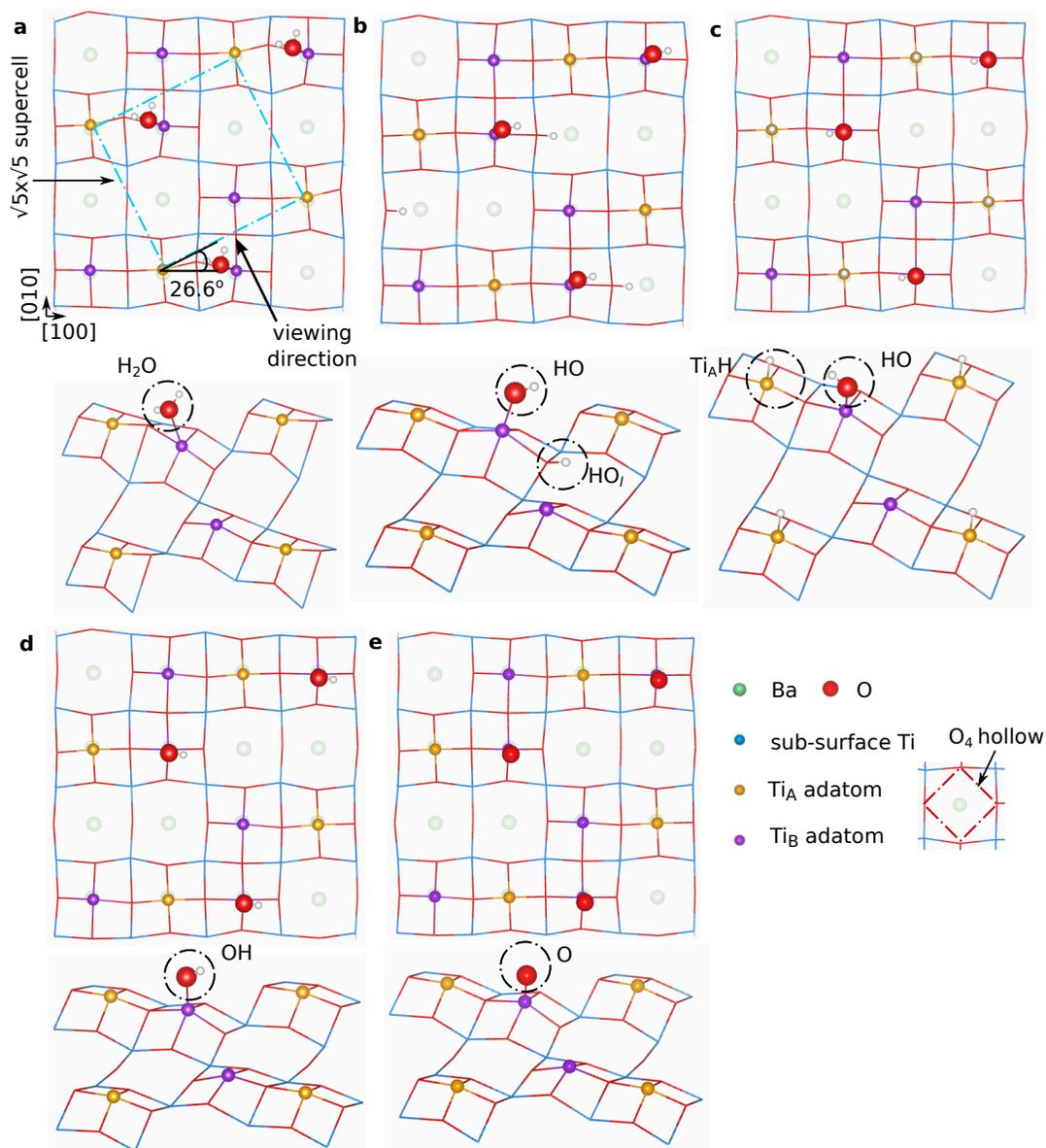


Figure S1: Different adsorption products of H₂O on Ti_B'. **a**, molecular; **b**, dissociative with H on a lattice O (O_l); **c**, dissociative with H on Ti_A; **d**, oxidative with surface OH as the product; and **e**, oxidative with surface O as the product. Viewing direction for the angled-view structures is shown in **a**.

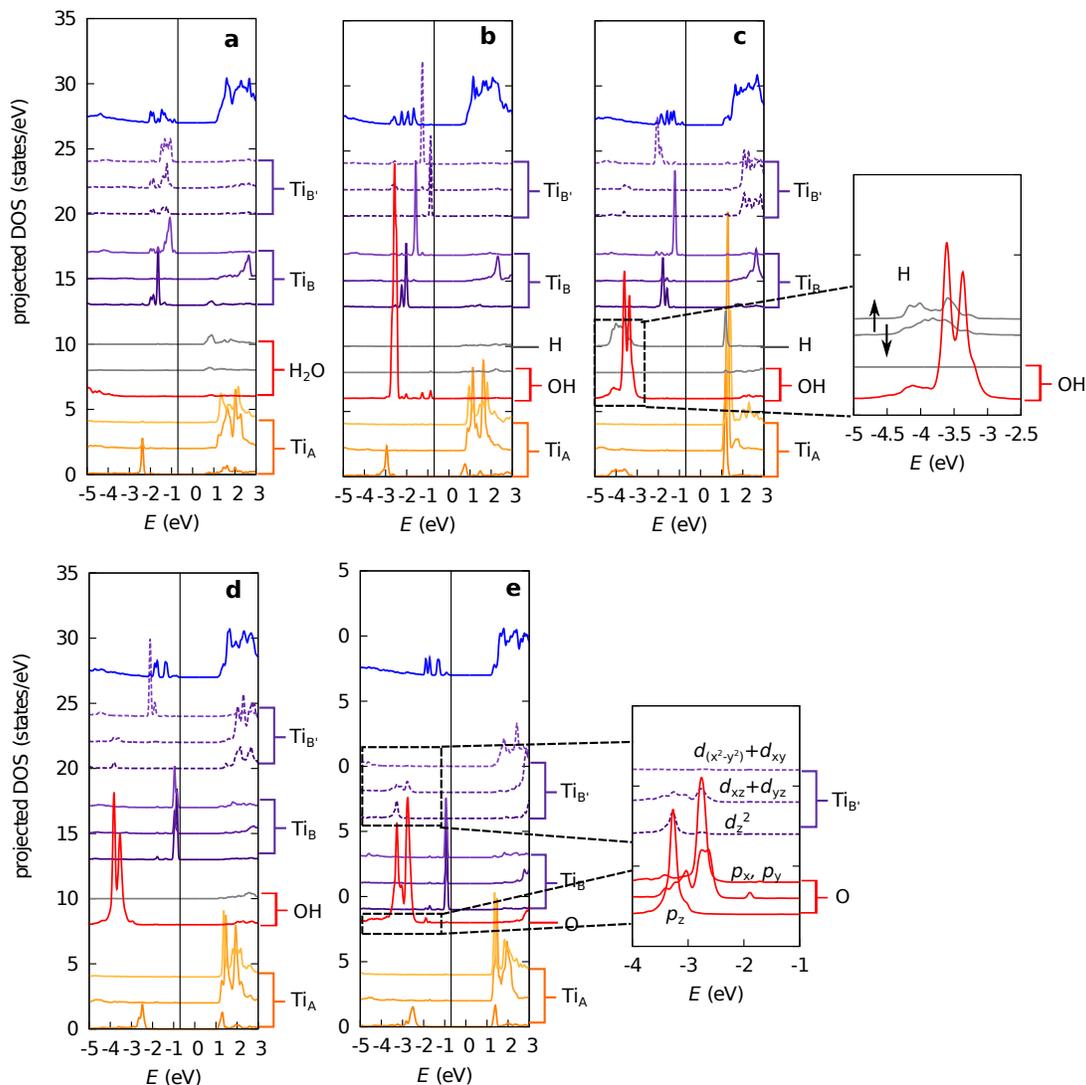


Figure S2: Electronic PDOS of the adsorption products shown in Figure S1. **a**, molecular; **b**, dissociative with H on a lattice O (O_1); and **c**, dissociative with H on Ti_A . outset: spin resolved $1s$ orbital projection of the H on Ti_A showing hydride orbital occupation. In contrast, the H in 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.

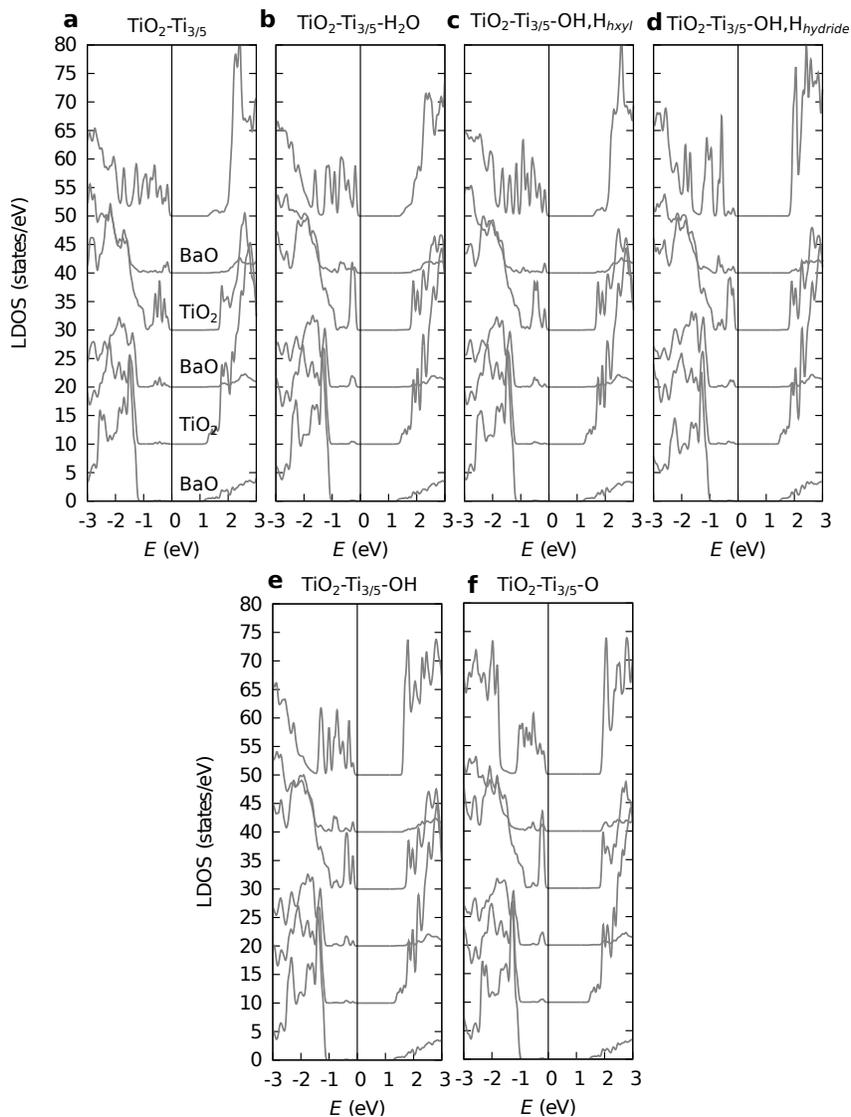


Figure S3: Layer-by-layer PDOS (LDOS) of the Ti_A centered water adsorption/oxidative adsorption products. **a**, Bare $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ $TiO_2-Ti_{3/5}$ reconstruction; **b**, molecular; **c**, dissociative with H on a lattice O (O_1); **d**, dissociative with H on Ti_B ; **e**, 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. The LDOS show that no unrealistic charge transfer occurs between the bottom and top layers 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.