

Supporting Information

Surface Structure and Reactivity of Anatase TiO₂ with Dominant {001} Facets

Sencer Selcuk and Annabella Selloni*

Department of Chemistry, Princeton University, Frick Laboratory, Princeton, New Jersey 08544, USA

Methods and Models. All calculations are based on Density Functional Theory (DFT) in the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE)¹ and the plane wave pseudopotential scheme as implemented in the QUANTUM ESPRESSO package². We used ultrasoft pseudopotentials³ and expanded the electronic states in plane waves using a kinetic energy cut-off of 25.0 (200) Ry for the smooth part of the wavefunction (augmented charge density). We used a convergence threshold of 10^{-6} Ry for self-consistency and $1 \cdot 10^{-4}$ Ry for ionic minimizations.

To study the convergence with respect to k-point sampling, we compared water adsorption energies on the bulk-terminated (001) surface using a $2 \times 1 \times 1$ mesh and the Γ point only. As shown in **Table S1**, differences are rather small. Therefore we chose to perform extensive scan of possible structures with Γ -only calculations, and then repeat the calculations using a $2 \times 1 \times 1$ mesh for the most stable configuration at each adsorbate coverage. Coverages are referred to the total number of exposed undercoordinated Ti sites. Thus 1ML coverage corresponds to 8 (10) adsorbed molecules per 2×4 unit cell for the bulk-terminated (reconstructed) surface.

Table S1. Comparison of water adsorption on the bulk-terminated surface, calculated with different numbers of k-points

k-points	E _{ads} /water (eV)	
	0.125 ML	0.5 ML
$2 \times 1 \times 1$	2.241	1.359
gamma	2.426	1.393

Both unreconstructed and 1×4 reconstructed slabs were generated with a vacuum layer of about 12 Å between slabs, and relaxed with the same convergence criteria while keeping the atoms in the bottom surface tri-layer fixed at their bulk positions. For better consistency, we used 2×4 supercells for both the reconstructed and unreconstructed surfaces. For the bulk-terminated structure, surface energies of slabs with different numbers of layers are compared in Table S2. It appears that a slab with 4 layers

provides a reasonable choice. Relevant structural parameters for the bulk-terminated and reconstructed surfaces are shown in Figure S1.

Table S2. Surface energies vs number of layers for the bulk-terminated (001) surface

# layers	θ (eV/Å ²)
4	$5.92 \cdot 10^{-2}$
5	$5.86 \cdot 10^{-2}$
6	$5.82 \cdot 10^{-2}$
7	$5.69 \cdot 10^{-2}$
8	$5.62 \cdot 10^{-2}$

Free energy diagrams. The definition of surface free energy (γ) is

$$A \cdot \gamma = G_{slab} - G_{bulk} - \sum n_i \mu_i \quad (I)$$

where A stands for the surface area, G for the Gibbs free energy, and μ_i for the chemical potential of a single molecule of species i . This expression can be rewritten by adding and subtracting the Gibbs free energy of the clean surface:

$$\begin{aligned} A \cdot \gamma &= (G_{slab} - G_{clean_slab} - \sum n_i \mu_i) + G_{clean_slab} - G_{bulk} \\ &= \Delta G_{ads} + A \cdot \gamma^0 \end{aligned} \quad (II)$$

Here, γ^0 is the surface energy of the clean slab. As a first approximation, assuming that the entropic and pV contributions to the free energies do not vary significantly throughout the condensed phase species, one can use differences between DFT energies instead of the differences between Gibbs free energies. Chemical potentials of the adsorbate species can be written as $\mu_i = h_i - Ts_i + RT \ln \left(\frac{p_i}{p_i^0} \right) = E_i^{DFT} + \Delta\mu_i(T, p)$ with the definition of $\Delta\mu_i = (h_i(T) - h_i(0\text{ K})) - Ts_i + RT \ln \left(\frac{p_i}{p_i^0} \right)$. Small letters are used to indicate potentials for single molecules. Then, one obtains a simple relation (III) for the surface energy, in which E_{ads} and γ^0 can be calculated from the DFT, and $\Delta\mu_i$ can be obtained from tabulated⁴ NIST-JANAF data.

$$A \cdot \gamma = E_{ads} + A \cdot \gamma^0 - \sum n_i \cdot \Delta\mu_i \quad (III)$$

First Principles Molecular Dynamics simulations. FPMD simulations were performed using the Car-Parrinello method⁵ as implemented in the QUANTUM ESPRESSO package. We used symmetric bulk-terminated and 1x4 reconstructed slabs with 4 layers in the (001) direction and 2x4 supercells in the xy plane. 8 HF molecules were adsorbed on each of the two surfaces of the slab and 34 water molecules were introduced to fill the region between adjacent slabs, so that the resulting water density was equal to the experimental density at STP. After an equilibration of 2 picoseconds at 350 K, simulations were continued for additional 10 ps. For bulk TiO₂, a 3x3 supercell with 4 layers is used. The structure was equilibrated for 2 ps and continued for additional 8 ps.

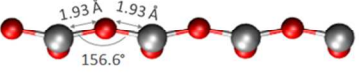
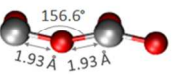
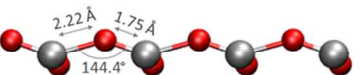
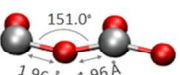
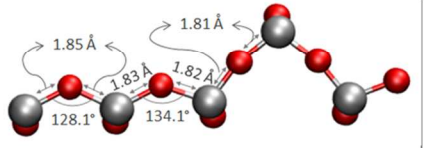
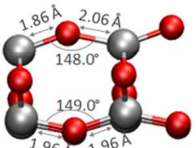
	-[100] Direction→	-[010] Direction→
Before Relaxation		
After Relaxation		
1x4 Reconstruction		

Figure S1. Structural parameters for the bulk-terminated surface before (top) and after (middle) relaxation, and for the 1x4 reconstructed surface (bottom).

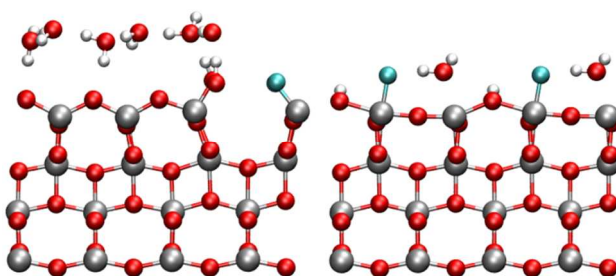


Figure S2. Adsorption of one monolayer of HF/Water mixture always occurs with dissociative adsorption of HF while water is only physisorbed or not adsorbed at all.

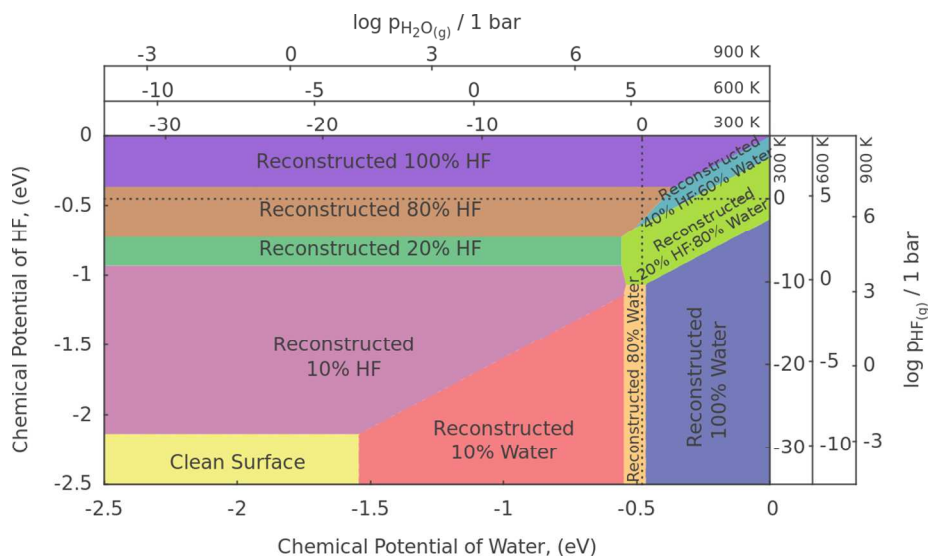


Figure S3. Surface phase diagram for anatase (001) in contact with a gaseous water-HF mixture. Dashed lines indicate 1 bar-300K for the corresponding species.

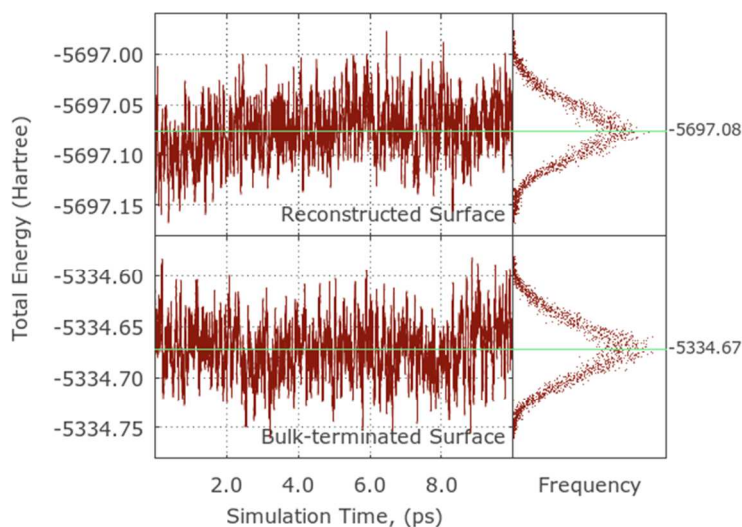


Figure S4. Total potential energy evolutions and corresponding probability distributions for the bulk terminated and 1x4 reconstructed anatase (001) surfaces over a 10 ps FPMD simulation at 350 K. The values on the right are the average energies in Hartrees; note that the reconstructed slab has 4 additional TiO_2 units relative to the bulk-terminated slab. The difference between these average values, -362.41 Hartree, can be compared to the energy of 4 bulk TiO_2 units at the same temperature, see Figure S5.

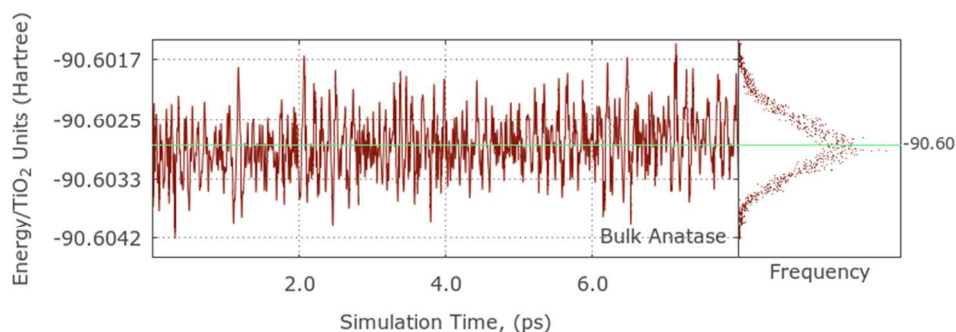


Figure S5. Total potential energy evolution and corresponding probability distribution for a TiO_2 unit in bulk anatase, from a 8 ps FPMD simulation at 350K. The average energy per TiO_2 unit is -90.60 a.u.

References

- (1) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865-3868.
- (2) Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Chiarotti, G. L.; Cococcioni, M.; Dabo, I. *et. al.* Quantum Espresso: A Modular and Open-Source Software Project for Quantum Simulations of Materials. *J. Phys.: Condens. Matter* **2009**, *21*, 395502.
- (3) Vanderbilt, D. Soft Self-Consistent Pseudopotentials in a Generalized Eigenvalue Formalism. *Phys. Rev. B* **1990**, *41*, 7892-7895.
- (4) Nist Chemistry Webbook. <http://webbook.nist.gov/chemistry/> (accessed on 22 September 2013)
- (5) Car, R.; Parrinello, M. Unified Approach for Molecular Dynamics and Density-Functional Theory. *Phys. Rev. Lett.* **1985**, *55*, 2471-2474.