

## Electronic Supplementary Information

### **A first-principles computational comparison of defect-free and disordered, fluorinated anatase TiO<sub>2</sub> (001) interfaces with water**

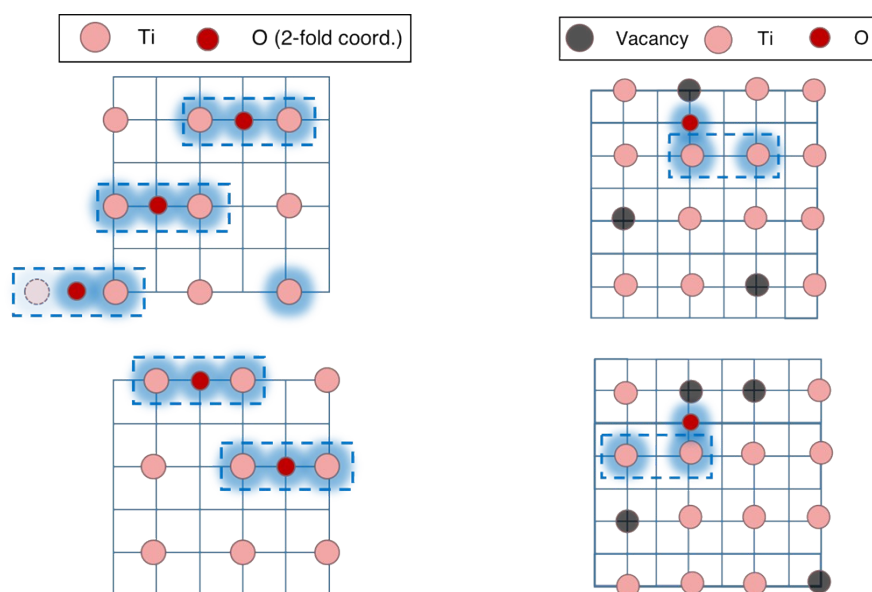
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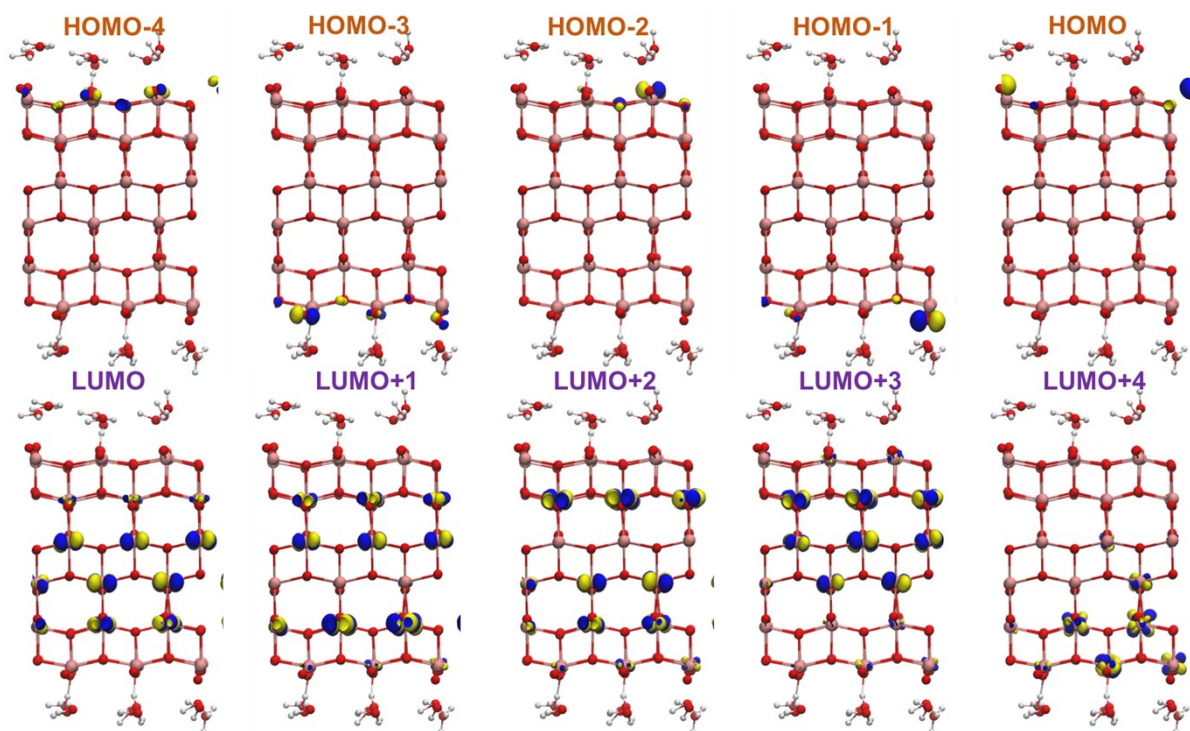
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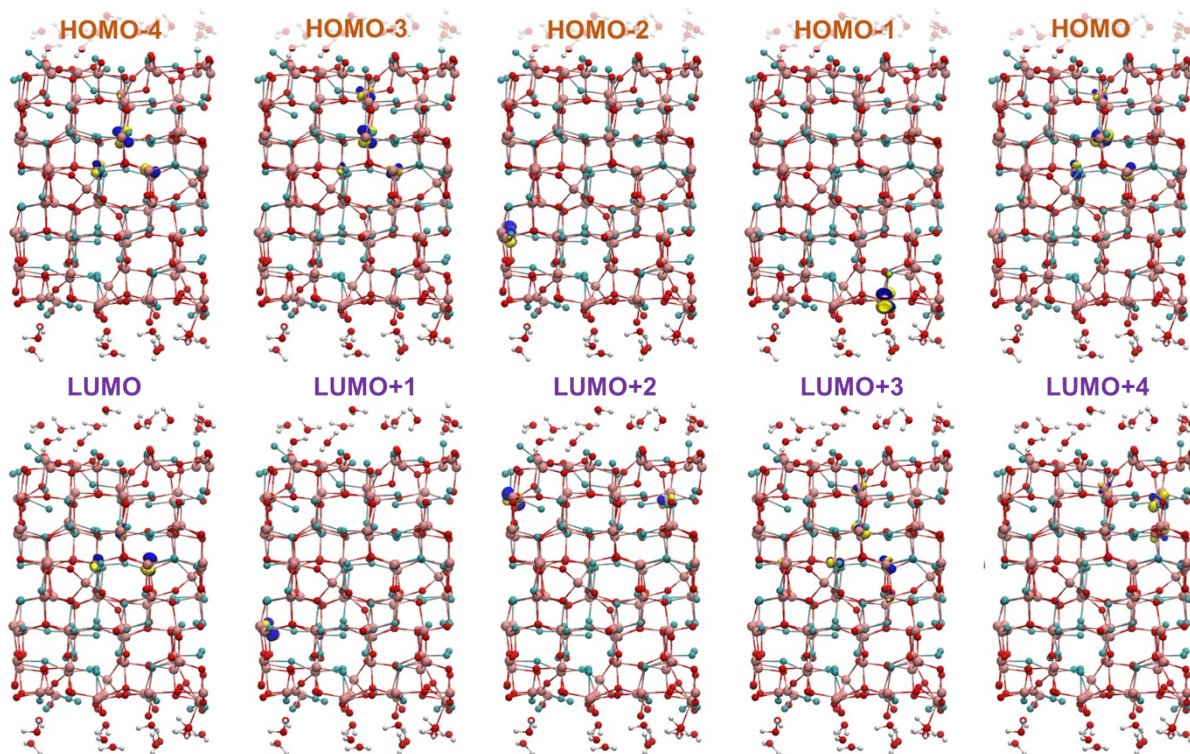
**Figure S1** | The locations of the dissociation of water at the titanate (001) surface in the pure anatase (left) and the fluorinated system (right). The two surfaces represent the top and bottom of the slab. Atoms indicated in blue represent participate directly in the dissociation and in the end become part of the hydroxyl group that is formed at the surface.

As shown in the schematic in [Figure S1](#), the surface hydroxylation is not 100% in either of the systems. Between the two anatase surfaces, neither results in 100% coverage in hydroxyl groups. Moreover, the mechanism by which each system undergoes hydrolysis is different. In the case of the anatase, a bridging oxygen is protonated by the incoming water followed by the breaking of the Ti-O bond farther from the adsorbed water molecule. Thus, the three atoms at the anatase surface are colinear. Alternatively, on fluorinated surface, a cationic vacancy plays its own role in facilitating the hydrolysis. The oxygen atom adjacent to the vacancy is undercoordinated and accepts a proton from the incoming water. The remaining hydroxyl group bonds to a titanium atom adjacent to the first, but in an orthogonal direction. Thus, while the two hydroxyl groups are on neighbouring titanium atoms, the source of the oxygen differs.



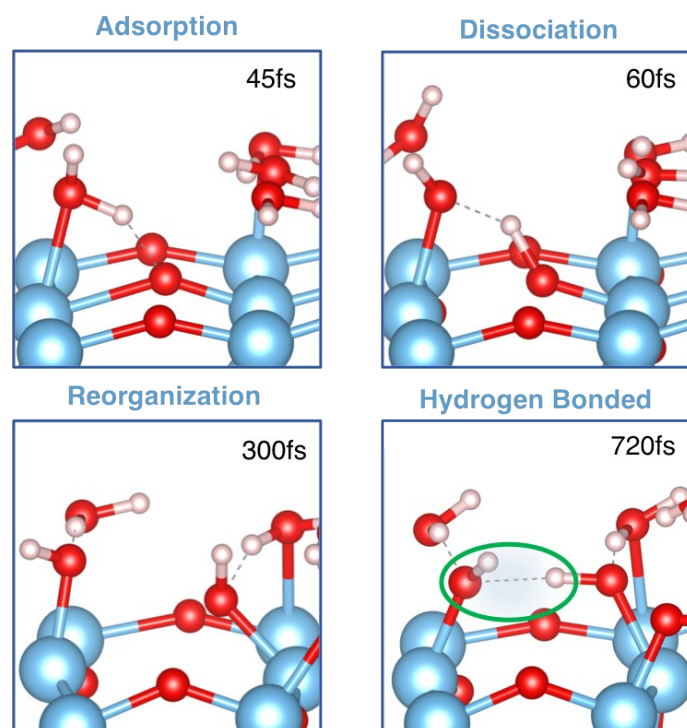
**Figure S2** | The five highest-occupied Kohn-Sham orbitals (HOMO-n) and the five lowest-occupied Kohn-Sham orbitals (LUMO+n) for the anatase  $\text{TiO}_2$  slab. Positive and negative values of the wavefunction are indicated in yellow and blue respectively.

In [Figure S2](#), we see that the valence electrons are all at the surface of the system, yet they are not localized at any one atom. Alternatively, the unoccupied states, especially those lowest in energy, are all localized in the interior of the slab. These unoccupied states are also non-localised states and contain contributions from atoms throughout the simulation cell.



**Figure S3** | The five highest-occupied Kohn-Sham orbitals (HOMO-n) and the five lowest-occupied Kohn-Sham orbitals (LUMO+n) for the fluorinated anatase  $\text{TiO}_2$  slab. Positive and negative values of the wavefunction are indicated in yellow and blue respectively.

The cationic vacancies throughout the structure to account for the difference in charge associated with the substitution of oxygen with fluorine. We observe that the HOMO and LUMO states are generally localized in the vicinity of these vacancies with only one of the five highest-occupied/lowest-unoccupied states being localized that the surface.



**Figure S4** | A dissociative event at the anatase titanate (001) surface. The process is observed in four phases: the adsorption of the water molecule (upper left), the dissociation of the water via proton transfer (upper right), the free movement and reorganization of the hydroxyl groups (bottom left), and finally the stabilization between the two hydroxyl groups via hydrogen bonding (bottom right). The corresponding time for each frame is noted in the upper-right of each frame.

The mechanism by which water is dissociated at the surface is shown in [Figure S4](#) and is consistent with all observed dissociation events. Initially, the water molecule adsorbs on the surface of the anatase with the oxygen nearest to the surface titanium atom ([Figure S4](#), adsorption). The water molecule then transfers a proton to a neighbouring two-fold coordinated bridging oxygen atom ([Figure S4](#), dissociation). The two resulting hydroxyl groups are then able to move freely out of the plane of the surface ([Figure S4](#), reorganization) but generally find locally stable configurations in which one hydroxyl group hydrogen bonds to the other ([Figure S4](#), hydrogen bonded). This process is generally a fast one occurring in less than 1 fs.