

# WHAT CONTROLS PHOTOCATALYTIC WATER OXIDATION ON TiO<sub>2</sub>?

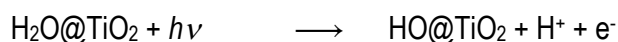
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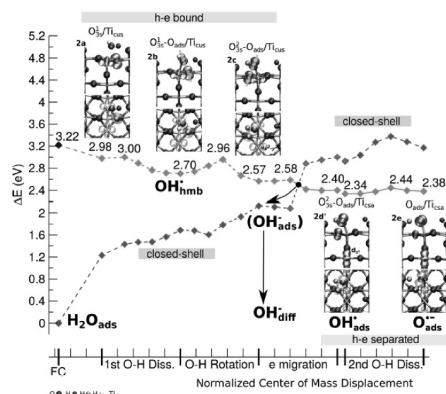
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In the photocatalytic oxidation of water by TiO<sub>2</sub>, excitation of the semiconductor generates a hole-electron pair that oxidizes and deprotonates adsorbed water molecules, leading to generation of oxygen. This process, also known as the oxygen evolution reaction (OER), is one of the main bottlenecks that prevents the use of water photoelectrolysis on TiO<sub>2</sub> for fuel generation, since it has a low efficiency. To determine the reasons behind this, we have studied the mechanism with theoretical methods.<sup>[1]</sup> Our approach considers the reactivity of the hole and electron as a correlated exciton pair. We center on the first step, where hydroxy radicals are generated after a coupled proton and electron transfer (PCET) step:



Our calculations show that the reaction is exothermic and almost barrierless. This is in contrast to previous studies which blame the low efficiency on the energy barriers for the PCET. In our model, the low efficiency is due to the high probability of charge recombination, which regenerates the reactant. In turn, the charge recombination is associated to crossings between electronic states with different charge configurations.



## References

- 1) L. Blancafort, A. Migani, *J. Am. Chem. Soc.* **2017**, 139, 11845.