

Supplementary Information

Water effect on band edges of anatase TiO₂ surfaces: Theoretical study on charge migration across surface heterojunctions and facet-dependent photoactivity

Jie-Qiong Li,^{a,b*} Jin-Yuan Hu,^b Jun Cheng^{b*}

^aState Henan Engineering Center of New Energy Battery Materials, Henan D&A Engineering Center of Advanced Battery Materials, College of Chemistry and Chemical Engineering, Shangqiu Normal University, Shangqiu 476000, China

^bState Key Laboratory of Physical Chemistry of Solid Surfaces, *i*ChEM, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

*Corresponding authors. E-mail: lijqchem@foxmail.com (J.-Q. Li)

chengjun@xmu.edu.cn (J. Cheng)

Details of TiO₂/water interface model construction

Construction of the initial configuration for the TiO₂/water interface consisted of the following steps: (i) we added one monolayer (1 ML) of water molecules on both sides of the TiO₂ slab; (ii) we constructed an orthorhombic box containing an appropriate number of water molecules with a surface area that matches that of the semiconductor slab using the PACKMOL package;¹ (iii) we performed classical molecular dynamics (MD) simulations for the water box using the Lennard-Jones potential with the CP2K package;² and (iv) after a pre-equilibrium with classical MD simulation, we inserted the water box into the 1 ML model to generate the full semiconductor/water interface. For more detailed parameter settings of the TiO₂/water interfaces models with anatase (101), (100) and (001) surfaces, one can refer the descriptions in ref 3.

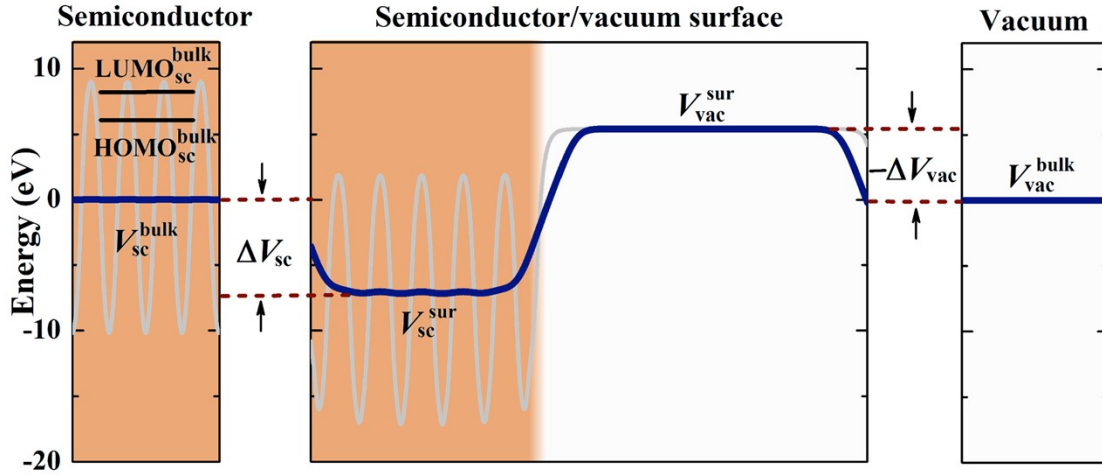


Fig. S1 Schematic representation of the band alignment at the semiconductor/vacuum surface. The gray curves are the electrostatic potential energies, the dark blue lines indicate the average electrostatic potential obtained by nanosmoothing the original potential profile with the MACROAVE code. ΔV_{sc} is the electrostatic potential shift of the semiconductor defined as $V_{sc}^{bulk} - V_{sc}^{sur}$ and ΔV_{vac} is the electrostatic potential shift of the vacuum defined as $V_{vac}^{bulk} - V_{vac}^{sur}$. V_{vac}^{bulk} is the electrostatic potential in bulk vacuum ($V_{vac}^{bulk} = 0$).

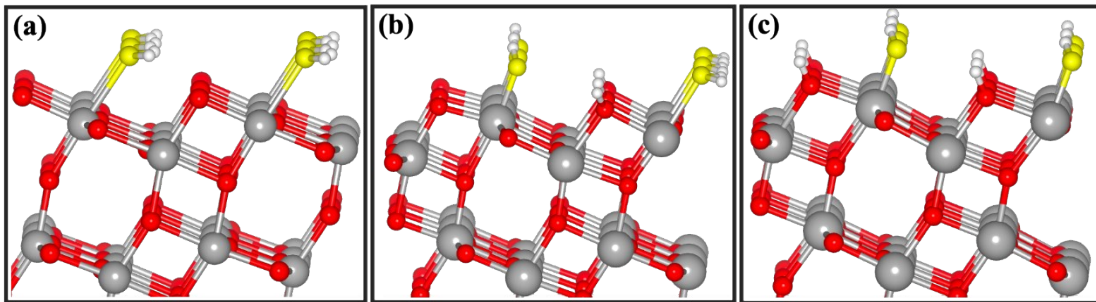


Fig. S2 Optimized structures (side view) of different water adsorption states on anatase (101) surface. (a) molecular state; (b) mixed molecular-dissociative state; (c) fully dissociative state. Ti, O atoms in TiO_2 and H, O atoms in H_2O are distinguished in grey, red, white and yellow, respectively.

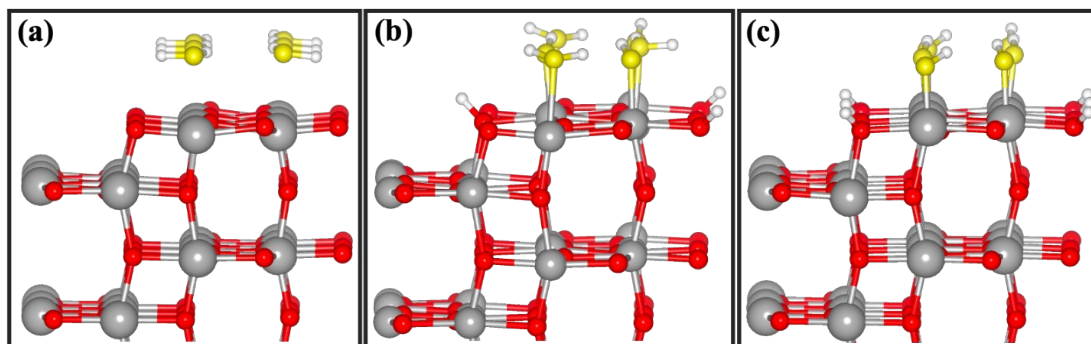


Fig. S3 Optimized structures (side view) of different water adsorption states on anatase (100) surface. (a) molecular state; (b) mixed molecular-dissociative state; (c) fully dissociative state. Ti, O atoms in TiO_2 and H, O atoms in H_2O are distinguished in grey, red, white and yellow, respectively.

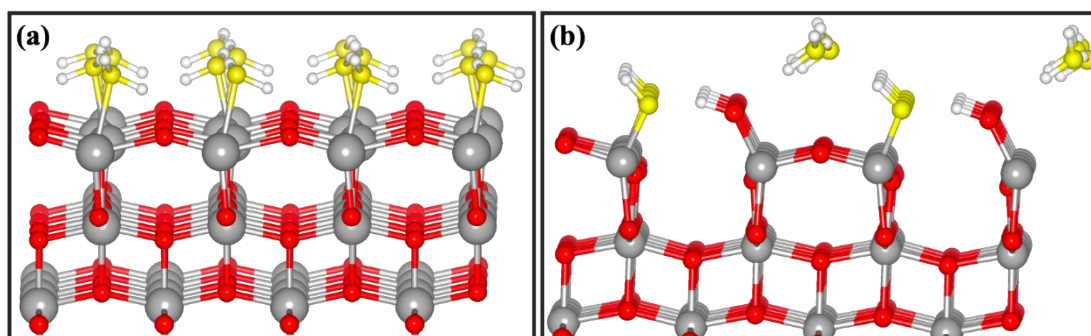


Fig. S4 Optimized structures (side view) of different water adsorption states on anatase (001) surface. (a) molecular state; (b) mixed molecular-dissociative state. Ti, O atoms in TiO_2 and H, O atoms in H_2O are distinguished in grey, red, white and yellow, respectively.

Table S1 Band edges relative to vacuum level of the bare anatase TiO_2 surfaces and surfaces with different water adsorption states computed with the GGA-PBE functional.

Surface	No water		1 ML $\text{H}_2\text{O}_{\text{mol}}$		1 ML $\text{H}_2\text{O}_{\text{dis}}$		1 ML $\text{H}_2\text{O}_{\text{mix}}$	
	VBM	CBM	VBM	CBM	VBM	CBM	VBM	CBM
(101)	-7.33	-5.27	-6.63	-4.57	-6.48	-4.42	-6.43	-4.37
(100)	-6.91	-4.85	-5.92	-3.86	-6.30	-4.24	-6.01	-3.95
(001)	-6.96	-4.90	-6.17	-4.11	*	*	-6.23	-4.17

Table S2 Band edges relative to vacuum level of the bare anatase TiO₂ surfaces (TiO₂/vac), the surfaces with the stable adsorption of one monolayer water molecules (TiO₂-1 ML water/vac) and the anatase TiO₂/water interfaces computed with the GGA-PBE functional.

Surface	TiO ₂ /vac		TiO ₂ -1 ML water /vac		TiO ₂ /water	
	VBM	CBM	VBM	CBM	VBM	CBM
(101)	-7.33	-5.27	-6.63	-4.57	-5.91	-3.85
(100)	-6.91	-4.85	-6.01	-3.95	-5.54	-3.48
(001)	-6.96	-4.90	-6.23	-4.17	-5.80	-3.74

Table S3 Band edges relative to vacuum level of the bare anatase TiO₂ surfaces (TiO₂/vac), the surfaces with the adsorption of one monolayer water molecules (TiO₂-1ML water/vac) and the anatase TiO₂/water interfaces computed with the hybrid HSE06 functional.

Surface	TiO ₂ /vac		TiO ₂ -1 ML water/vac		TiO ₂ /water	
	VBM	CBM	VBM	CBM	VBM	CBM
(101)	-8.34	-4.84	-7.64	-4.14	-6.92	-3.42
(100)	-7.92	-4.42	-7.02	-3.52	-6.55	-3.05
(001)	-7.97	-4.47	-7.24	-3.74	-6.81	-3.31

References

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