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# SUPPORTING INFORMATION

Electronic structures of the MoS<sub>2</sub>/TiO<sub>2</sub> (anatase) heterojunction:

influence of physical and chemical modifications of the interface.

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## SI 1. Slabs used for the TiO<sub>2</sub> (101) surface and hydrated (001) surface



Figure S1: Slab supercells of a)TiO<sub>2</sub> anatase (101) and b) TiO<sub>2</sub> anatase (001) hydrated



Figure S2: Slab supercells before and after multiplication for a) TiO<sub>2</sub> anatase (101), b) MoS<sub>2</sub> monolayer, c) TiO<sub>2</sub> anatase (001) hydrated and d) MoS<sub>2</sub> monolayer

### SI 2. Determination of the vacuum potential



Figure S3: Plot of the electrostatic potential as a function of the Z coordinate for a  $TiO_2$ anatase (101) surface

## SI 3. Case of TiO<sub>2</sub> anatase surfaces and bulk



Figure S4: DOS with element decomposition for TiO<sub>2</sub> anatase (101)



Figure S5: DOS with element decomposition for  $TiO_2$  anatase (001) bare



Figure S6: DOS with element decomposition for TiO<sub>2</sub> anatase (001) hydrated



*Figure S7: DOS with element decomposition for TiO*<sub>2</sub> *anatase Bulk* 



*Figure S8:* Evolution of the band position of TiO<sub>2</sub> anatase (101) and (001) with implicit and explicit water solvation

#### SI 4. Density of states (DOS) with element decomposition



Figure S9: DOS with element decomposition associated to  $MoS_2$  in physical interaction on  $TiO_2$  (101) on the left and  $TiO_2$  (001) hydrated on the right



Figure S10: DOS with element decomposition associated to  $MoS_2$  in physical interaction on  $TiO_2$  (101) sulfide on the left and  $TiO_2$  (001) hydrated-sulfided on the right



Figure S11: DOS with element decomposition associated to MoS<sub>2</sub> in chemical interaction on a) TiO<sub>2</sub> (101) b) TiO<sub>2</sub> (001) hydrated (interaction with S-edge) and c) TiO<sub>2</sub> (001) hydrated (interaction with Medge)



Figure S12: DOS with element decomposition associated to  $MoS_2$  in chemical interaction  $TiO_2$  anatase (101) with a) 2 rows instead of 4, b) sulfidation at the edge and c) oxygenation at the interface

### SI 5. Spin polarized calculations

Spin polarized calculations were performed in some epitaxial cases in order to describe better the electronic structure of the interface and in particular the localized states that appear.



Figure S13: DOS with spin differenciation for a)MoS<sub>2</sub>/TiO<sub>2</sub> (101) 4Mo rows, b) MoS<sub>2</sub>/TiO<sub>2</sub> (101) 2Mo rows and c) MoS<sub>2</sub>/TiO<sub>2</sub> (101) sulfided



## SI 6. Complementary density of states for MoS<sub>2</sub>/TiO<sub>2</sub> (001)

Figure S14: DOS with material decomposition and evolution of the band position for a)  $MoS_2/TiO_2$ (001) bare and b)  $MoS_2/TiO_2$  (001) sulfided

## SI 7. Spatial localization of the most relevant interfacial states



*Figure S15: Localization of the most relevant states for*  $MoS_2$  *in chemical interaction through the Mo-edge on*  $TiO_2$  *anatase (101)* 



Figure S16: Localization of the most relevant states for MoS<sub>2</sub> in chemical interaction through S-edge on TiO<sub>2</sub> anatase (001)



Figure S17: Localization of the most indicative states for  $MoS_2$  in chemical interaction through Moedge on TiO<sub>2</sub> anatase (001)



*Figure S18: Localization of the most indicative states for MoS*<sub>2</sub> *with 2Mo rows in chemical interaction through Mo-edge on TiO*<sub>2</sub> *anatase (101)* 



Figure S19: Localization of the most indicative states for  $MoS_2$  sulfided in chemical interaction through Mo-edge on  $TiO_2$  anatase (101)



Figure S20: Localization of the most indicative states for MoS<sub>2</sub> oxygenated in chemical interaction through Mo-edge on TiO<sub>2</sub> anatase (101)

#### SI 8. Convergence tests for the selection of computational parameters



Figure S21: (a) structure of the TiO<sub>2</sub>(101) and MoS<sub>2</sub> in physical interaction. Ti, Mo, O and S atoms are in blue, grey, red and yellow respectively. (a) convergence of the electronic energy as a function of the k-points mesh in the x direction. (b) convergence of the electronic energy as a function of the k-points mesh in the y direction. (c) convergence of the electronic energy as a function of the vacuum thickness. (d) convergence of the electronic energy as a function.



Figure S22: (a) structure of the TiO<sub>2</sub>(101) and MoS<sub>2</sub> in epytaxic interaction. Ti, Mo, O and S atoms are in blue, grey, red and yellow respectively. (a) convergence of the electronic energy as a function of the k-points mesh in the x direction. (b) convergence of the electronic energy as a function of the k-points mesh in the y direction. (c) convergence of the electronic energy as a function of the vacuum thickness. (d) convergence of the electronic energy as a function.



Figure S23: (a) structure of the hydrated TiO<sub>2</sub>(001) and MoS<sub>2</sub> in physical interaction. Ti, Mo, O, S and H atoms are in blue, grey, red, yellow and white respectively. (a) convergence of the electronic energy as a function of the k-points mesh in the x direction. (b) convergence of the electronic energy as a function of the k-points mesh in the y direction. (c) convergence of the electronic energy as a function of the vacuum thickness. (d) convergence of the electronic energy as a function.