

## Supporting information

# Reactivity of anatase TiO<sub>2</sub> nanoparticles: the role of the minority (001) surface

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## Computational details

- Structural optimizations and MD simulations have been performed within the Car-Parrinello (CP) approach. Electron-ion interactions are described by ultrasoft pseudopotentials,<sup>1</sup> with electrons from C and O 2s, 2p and Ti 3s, 3p, 3d and 4s shells explicitly included in the calculations. Plane-wave basis set cut offs for the smooth part of the wave functions and the augmented density were 25 and 200 Ry, respectively. *k*-point sampling was restricted to the  $\Gamma$  point. The anatase TiO<sub>2</sub>(001)-1×1 surface was modelled as a periodic slab with 4 layers of oxide (~8 Å thick), while the vacuum between slabs was ~10 Å wide. A p(3×2) surface supercell was used, with a surface area of 11.36×7.57 Å<sup>2</sup>. Water and methanol molecules were adsorbed on one side of the slab only. In all calculations, the atoms in the bottom layer were fixed to their bulk position, while all the other atoms were allowed to relax/move. Geometry optimizations were carried out through damped

molecular dynamics until the largest component in the forces on all mobile atoms was below 0.05 eV/Å. In the MD simulations, a time step of 0.145 fs and a fictitious electronic mass of 700 atomic units and a 2 amu hydrogen mass were used. Ionic temperature was controlled by means of a Nosè thermostat.<sup>2</sup>

- The surface energy ( $\gamma$ ) of the clean surface was computed using the PWSCF code,<sup>3</sup> which is part of the same (ESPRESSO) package that includes also the CP code. For clean anatase TiO<sub>2</sub>(001)-1×1 and 1×4 surfaces, we calculated  $\gamma$  with the expression  $\gamma = (E_{\text{slab}} - n \cdot E_{\text{TiO}_2})/A$ , where  $E_{\text{slab}}$  is the total energy of the slab,  $E_{\text{TiO}_2}$  is the energy of a TiO<sub>2</sub> unit in the bulk,  $n$  is the number of TiO<sub>2</sub> units in the slab and  $A$  is the total exposed area, including both surfaces of the slab. To determine the energy of the anatase bulk, we considered the primitive cell containing 4 TiO<sub>2</sub> units and used a 4×4×2 mesh of  $k$ -points to sample the Brillouin zone. The TiO<sub>2</sub>(001)-1×1 surface was modelled by a slab of 4 layers of oxide and a p(1×1) unit cell was used (4 TiO<sub>2</sub> units in a cell). The TiO<sub>2</sub>(001)-1×4 surface was modelled by 4 layers of oxide and a p(1×4) super cell was used with the ADM model<sup>4</sup> on both surfaces of the slab (18 TiO<sub>2</sub> unit in a cell). Meshes of 4×4×1 and 4×1×1  $k$ -points were used for the (001)-1×1 and (001)-1×4 surfaces, respectively. All the atoms were allowed to move (force threshold = 0.03 eV/Å). In this way we obtain  $\gamma = 0.98 \text{ J} \cdot \text{m}^{-2}$  for the clean anatase TiO<sub>2</sub>(001)-1×1 surface and  $\gamma = 0.48 \text{ J} \cdot \text{m}^{-2}$  for the reconstructed 1×4 surface, as reported in the paper. The estimated errors on these values, about  $\pm 0.05 \text{ J} \cdot \text{m}^{-2}$ , are due to both the strong dependence of  $\gamma$  on the value of the bulk energy  $E_{\text{TiO}_2}$  and to the rather small thickness of our slabs.
- To estimate the surface energy of the hydrated surface ( $\gamma'$ ), we used the expression  $\gamma' = \gamma - n \cdot E_d/A'$ , where  $\gamma$  is the surface energy of clean surface,  $E_d$  is the adsorption energy of dissociated water (Table 1),  $n$  is the number of adsorbed water molecules in a unit cell ( $n = 2$  and  $3$  at  $1/3$  ML and  $1/2$  ML coverage, respectively) and  $A'$  is the area of one surface of the slab ( $11.36 \times 7.57 \text{ Å}^2$ ,  $A' = 1/2A$ ). Using the values of  $E_d$  listed in Table 1, which are referred to a water molecule in the *gas phase*, we

obtain  $\gamma' = 0.33$  (0.57)  $\text{J}\cdot\text{m}^{-2}$  for the fully (1/2 ML) and partially (1/3 ML) hydrated anatase  $\text{TiO}_2(001)\text{-}1\times 1$  surface, respectively.

- We can also calculate the water adsorption energy by taking a water molecule in *liquid water* as the reference. For the surface energy of the hydrated surface ( $\gamma''$ ) we then use the expression  $\gamma'' = \gamma - (n\cdot E_d - n\cdot \Delta H)/A'$ , where  $\Delta H$  is the enthalpy of vaporization of water. From tabulated values, we estimate  $\Delta H \sim 0.45$  eV ( $43.5 \text{ KJ}\cdot\text{mol}^{-1}$ ) at room temperature.<sup>5</sup> Accordingly, we obtain  $\gamma'' = 0.58$  (0.73)  $\text{J}\cdot\text{m}^{-2}$  for the fully and partially hydrated anatase  $\text{TiO}_2(001)\text{-}1\times 1$  surface, respectively. It is still evident that hydration significantly stabilises the clean  $\text{TiO}_2(001)\text{-}1\times 1$  surface ( $\gamma = 0.98 \text{ J}\cdot\text{m}^{-2}$ ). Moreover, the  $1\times 4$  reconstructed surface ( $\gamma = 0.48 \text{ J}\cdot\text{m}^{-2}$ ) has very similar stability compared to the fully hydrated  $\text{TiO}_2(001)\text{-}1\times 1$ .

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