Diffusion and reaction pathways of water near fully hydrated TiO_2 surfaces from ab initio molecular dynamics

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Introduction

Ab initio molecular dynamics simulations (AIMD) are performed for water-embedded TiO_2 surfaces to determine the diffusion and reactive behaviour at full hydration. A three-domain model is developed for the six surfaces [rutile (110), (100), and (001), and anatase (101), (100), and (001)] that describes surface-bound waters in terms of "hard" (irreversibly bound), "soft" (with reduced mobility but orientation freedom) hydration layers, and bulk water. The model helps interpreting previous experimental data and gives a detailed and consistent picture of water diffusion near TiO_2 surfaces. In addition to direct water splitting, graph theoretical analysis reveals a number of water reaction pathways on TiO_2 that occur at full hydration. Hydronium H_3O^+ is identified to be the key intermediate state and facilitates water dissociation by proton hopping between (surface-adsorbed) intact and dissociated waters. These discoveries significantly improve the understanding of nanoscale water dynamics and reactivity near TiO_2 interfaces under ambient conditions.

a soft domain where the translational motion is restricted but no the rotational one; the bulk water domain where standard water diffusion is regained. This 3 domain model is in agreement with NMR experimental data[4].



Simulation Method and statistical analysis

AIMD simulations were performed with DFT in CP2K [1]. Each hydrated surface was simulated for 50 ps. The BLYP functional was augmented with the DFT-D3 dispersion corrections of Grimme. TiO_2 slabs consist of 3 to 5 layers and about 150 water molecules were used to fill the simulation box in order to reproduce the bulk water density at room temperature. The system temperature was kept slightly above room temperature (310 K) to avoid the overstructured liquid structure characteristic to DFT-GGA-simulated water.

The Surface Separation Distance (SSD),

$$s_i(t) = z_i(t) - z_0$$
, (1)

is defined as the difference between the z-coordinate of atom i at time t and the z-position of the outermost titanium layer of the slab (z_0) . The (free) self-diffusion coefficient must be defined for fluids confined by interfaces, where the particle motion is influenced by the z-dependent potential produced by the solid interface. When calculating diffusion coefficients, one must account for the probability that the water molecule diffuses out of the SSD-layer under consideration during the time interval. Hence, the diffusion coefficient in the lateral α -direction at SSD-value s is [2]

$$D_{\alpha}(s) = \frac{1}{2} \lim_{t \to \infty} \frac{\text{MSD}_{\alpha}(s, t)}{tP(s, t)}, \qquad (2)$$

P(t, s) is the ratio between the number of molecules in layer s at time t compared to that at the initial time and $MSD_{\alpha}(s,t)$ the mean square displacement of the particles that remain in the layer s at time t. To minimize the statistical errors a window function was used to weight the MSD_{α} . In order to discover and track complex reactions involving intermediates and/or co-reactants a timedependent graph theory-based method was developed following Ref.[3].

Figure 2: Lateral diffusion of water molecules as function of *s*

Reaction pathways

In Fig. 3 the time evolution of the number of bulk water, adsorbed water, and dissociated water molecules on the 6 TiO_2 surfaces is shown. Anatase 001 and Rutile 110 and 001 surfaces were found to be reactive at fully hydration. All the reactions occur by a proton donor-acceptor process mediated by a third water molecule that create a H_3O^+ intermediate state. The most reactive surface is the the Rutile 001 for which we observed a proton hopping mechanism (Fig. 4 B). Splitting water processes on Rutile 110 has been object of many studies, but none of them reported the formation of a H_3O^+ compound as possible dissociation path (Fig. 4 A).



Results

Layered water structure

Water molecules order in layers above the TiO_2 surfaces. The extension of this ordering effect strictly depends on the exposed surface. In Fig. 1 A a general overview of the simulated hydrated TiO_2 surfaces is shown, orange and green circles represent water covalently adsorbed on Ti sites or oxygen bridge O_{br} sites respectively. The density profiles of water oxygen in Fig. 1 B shed light on the variety of landscapes formed by water molecules on the TiO_2 surfaces. Up to 5 water layers can be generated for a maximum penetration of about 10 Å in the water bulk. In Fig.1 C the water dipole orientation is plotted as function of the SSD s parameter. A preferential orientation of the water molecule is observed for the first 2 absorbed layers.



Time [ps] Time [ps]

Figure 3: Time evolution of the number of bulk water, adsorbed water, and dissociated water molecules on the 6 TiO_2 surfaces. The number of water molecules are normalized with respect the surface area.



Figure 4: Reaction pathways on the Rutile surfaces.

Conclusions and Forthcoming Research

- Detail insights of water structure at the interface with TiO_2 surfaces were provided.
- Accurate analysis of water diffusion coefficients clarified the controversial [4] water motion on TiO_2 surfaces. A 3 domain model was developed and the results are in agreement with experimental data.[5]
- New reaction pathways were discovered. In particular has been shown the importance of consider-

Figure 1: A) Representative hydrated TiO_2 surfaces, B) water oxygen density profiles from the outermost surface Tiatoms, C) spatial water dipole distribution as function of s.

Diffusion coefficients

Gradually increasing diffusion coefficients were found for all the TiO_2 surfaces. The specific layered structure that each TiO_2 surface induced to water creates different diffusion regimes. in Fig. 2 we can distinguish a bound domain where water molecules are immobile (first and second adsorbed layers);

ing the H_3O^+ formation in order to describe splitting water reactions.

• Parametrization of classical force fields, able to reproduce the phenomena observed at the TiO_2 water interfaces, will be developed in order to create a solid model for large scale bio-inorganic simulations.

References

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