

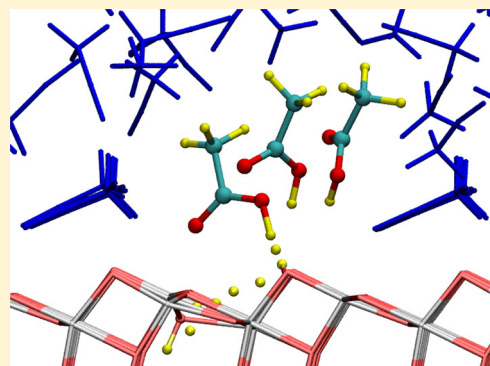
Structure and Mobility of Acetic Acid at the Anatase (101)/
Acetonitrile Interface

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S Supporting Information

ABSTRACT: Acetic acid is one of the simplest molecules containing a carboxylic moiety, a common anchoring groups used to functionalize TiO_2 -based devices. The behavior of acetic acid in proximity of the anatase (101) surface has been investigated by means of first-principles density functional theory (DFT) calculations, including explicit liquid solvent in the simulations. A novel acetic acid binding mode, characterized by proton insertion below the first layer of oxide atoms, has been found employing a sufficiently thick anatase slab model. Hybrid DFT calculations show that the subsurface proton insertion leads to a trap-state for excess electrons, favoring localization below the surface edge. Proton deintercalation represents the largest barrier for acid mobility and desorption. However, if the proton is adsorbed on top of the surface, the acid molecule can partially detach from the surface and easily move toward a thermodynamically more stable state. A series of consecutive changes in the adsorption mode can lead to long-range diffusion of the molecule along the [010] direction of the surface, with a barrier of only $E_{\text{act}} = 20.3$ kJ/mol. Similarly, the free energy barrier to completely detach an acetic acid molecule from the surface into the solvent has been computed to be $E_{\text{act}} = 51.0$ kJ/mol, if the proton is adsorbed on top of the anatase slab. Where significant, a comparison between the “explicit liquid” environment and the more often employed “solvent monolayer” environment has been carried out, highlighting the importance of solvent interactions.



■ INTRODUCTION

Titanium dioxide is a naturally occurring compound, widely employed for applications including catalysis,^{1–3} sensor,^{4,5} and solar cell⁶ technology. In many cases, the oxide properties are combined with functions provided by molecular subunits, anchored to the TiO_2 substrate via carboxylate, salicylate, or phosphonate groups.^{7,8} A prominent example of such a system is the dye sensitized solar cell (DSSC), in which a layer of anchored dyes is employed to absorb light, to inject electrons into the semiconducting nanocrystalline TiO_2 film that supports them. An important additional component of these devices is a hole transporting material, which is commonly a liquid electrolyte based on acetonitrile^{9,10} (CH_3CN), containing the I^-/I_3^- redox couple^{11–13} as a hole transporter. Further additives increase cell performance.¹⁴ Since the publication of a key paper by O'Regan and Grätzel at the beginning of the 1990s,⁶ various components of this system have been studied and optimized, and the progress in the field has been assessed by several review papers.^{15–17} Currently, the most efficient DSSCs have conversion efficiencies in the range 10–12%,^{18,19} which is still relatively far away from the approximately 30% Shockley–Queisser²⁰ limit attainable by single junction solar cells. Further room for directed optimization of this system is thus available, motivating the current study aimed at providing an improved understanding of the structure and dynamics of the functionalized interface. In this work, we aim at systematically improving the understanding of how anchoring

groups interact with the oxide surface in the presence of the solvent. Whereas several papers deal with the binding of small molecules to the oxide surface,^{21–33} only few address the role of the solvent.^{34,35} In particular, a quantitative study of the TiO_2 –adsorbate–acetonitrile interface that explicitly includes an atomistic representation of the solvent is still missing. Given the strong interaction between solvent and oxide,^{36,37} and likely with other adsorbed species, a detailed treatment might be important to provide further insight in the system, to provide benchmark results for other approaches. Our approach employs DFT-based molecular dynamics simulations in the presence of explicit solvent to quantitatively describe adsorption processes on the anatase (101) surface, including the computation of free energies for surface diffusion, dissociation.

The model adopted is based on a slab representation of the anatase (101) surface, which is a good approximation of the nanoparticles (>10 nm) that are commonly employed in DSSCs. Anatase is the stable phase for the nanoparticle sizes (tens of nanometers) employed in experimental devices: its optical band gap compares favorably with that of rutile (3.2 vs 3.0 eV), and a higher open-circuit potential for the same conduction band electron concentration is reported.¹⁵ On these nanoparticles, the (101) surface is dominant due to its lower

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surface energy.^{23,38} As mentioned above, acetonitrile (ACN) constitutes the basis of the most common electrolytic solutions employed in DSSCs, and has been chosen to represent the explicit liquid solvent. In this work, further additives have not been considered. An acetic acid molecule (acetic acid) has been introduced to model the binding group by which the sensitizing dye is anchored to the oxide surface. As illustrated in Figure 1,

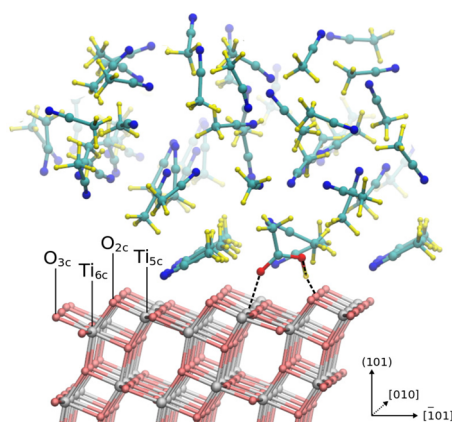


Figure 1. Representation of an acetic acid molecule adsorbed on the anatase (101) surface, in the presence of explicit liquid acetonitrile solvent. The ordered structure of the first solvent layer in contact with the surface is clearly visible. Coordination numbers for surface anatase ions are indicated. Color coding: silver = titanium, red = oxygen, blue = nitrogen, cyan = carbon, yellow = hydrogen.

ACN molecules preferentially bind to the anatase (101) surface with the carbonitrile group pointing toward the 5-fold coordinated Ti^{2+} cations,^{36,37} so that the first layer of solvent molecules in contact with the surface assumes a distinctive and ordered structure; on the other hand, carboxylic moieties can assume a range of different configurations^{24,28,33,39,40} that are to be discussed in this paper.

Results are organized as follows: At first, an investigation of the influence that slab size and the presence of the solvent have on the relative energy of the many possible acetic acid binding modes is carried out to determine which modes are most stable. A study on proton diffusion paths and on the interconversion between adsorption modes is then presented, followed by a detailed investigation of the desorption process. A brief summary and outlook is then presented in the concluding section.

METHODS

All density functional theory calculations were performed using the CP2K program package.⁴¹ DFT calculations are based on the hybrid Gaussian and plane wave (GPW) scheme,⁴² with the Perdew–Burke–Erzerhof (PBE)⁴³ exchange correlation functional and corresponding pseudo potentials.^{44,45} The plane wave density cutoff of 600 Ry and periodic boundary conditions have been employed. Dispersion interactions were included by means of an empirical analytical potential, using the Grimme D3 method,⁴⁶ within a range of 15 Å. Standard coefficients⁴⁷ and scaling factors for PBE and PBE0 functionals were adopted. Scaling factors for PBE are: $s_6 = 1.0$; $sr_6 = 1.217$; $s_8 = 0.722$. For PBE0: $s_6 = 1.0$; $sr_6 = 1.287$; $s_8 = 0.928$.

All the atomic species involved in the simulation were described with Gaussian basis sets of double- ζ quality.⁴⁸

Relative stabilities of the different binding modes have been computed for a variety of slab models to ensure size convergence of the slab and to test the effect of different environments. The parameters of the unit cell adopted for building the different slabs are: $x = 10.227$ Å; $y = 3.782$ Å; $z = 3.513$ Å. The (101) interface under study is perpendicular to the z axis. Each slab presented in the text is identified by a three digit code, reporting its size in terms of repetitions of the unit cell along the x, y and z direction. The tested slab sizes range from $10.227 \times 11.346 \times 10.540$ Å³ (slab 133) up to $20.454 \times 22.692 \times 17.570$ Å³ (slab 265). Three different environment models have been studied: the bare slab without any coadsorbed ACN molecules, and a four and a five ACN monolayer. As only certain adsorption modes can accommodate a perfect five ACN monolayer, an overall comparison of adsorption modes is only possible for the four ACN monolayer. Therefore, only the four ACN results are discussed in this paper while the five ACN results are reported in the Supporting Information (SI) for completeness.

An investigation of the electronic properties of the system in its most stable configuration was carried out by hybrid-DFT calculations. The truncated PBE0 functional^{49,50} with 25% of Hartree–Fock exchange and a cutoff radius of 6 Å has been employed. For computational efficiency, the auxiliary density matrix method⁵¹ was used. The cpFIT3 basis sets as provided by CP2K and a specially optimized basis (see SI) for Ti of similar quality⁵¹ have been used as auxiliary basis for this method.

Minimum energy paths have been computed using the climbing image nudged elastic band (CI-NEB) method, introduced by Jónsson and co-workers.^{52–54} The spring constant value for NEB calculations was set to 0.02 au.

Free energy profiles have been computed using the thermodynamic integration scheme based on molecular dynamics. All reaction coordinates have been defined as linear combinations of interatomic distances, and therefore, the computation of additional correction terms is not required.⁵⁵ The model in these calculations consisted out of the $20.454 \times 22.692 \times 17.570$ Å³ slab to avoid a bias due to missing k -points and to obtain a better description of the solvent structure. For efficiency reasons, four acid molecules have been included at each side of the slab. In this way, 8 points of the TI could be computed simultaneously. The slab was enclosed into an orthorhombic unit cell of dimension $20.454 \times 22.692 \times 38$ Å³ and surrounded by the explicit liquid environment, for a total of 1396 atoms. This setup was equilibrated at 300 K with a 50 ps (0.5 fs time step) NVT simulation using force fields from literature^{36,56,57} and fixed acid positions. The constrained MD runs were carried out in the NVT ensemble at 300 K, with a time step of 0.5 fs for a total of 20 000 steps (10 ps). The thermostatting scheme of NVT runs was canonical sampling through a velocity rescaling algorithm (CSVR), as implemented in the cp2k package.⁵⁸ Error bars were calculated from independent averages over the Lagrange multipliers during the first half of simulation (upper limit) and during the second half of the simulation (lower limit), equilibration period excluded. The asymmetry of the error bars along the reaction path is due to the integration procedure, which, by convention, fixes the first integration point to zero.

■ ADSORPTION MODES OF ACETIC ACID ON TiO_2

In the first part of this study, we perform a careful analysis of our computational model and present the energy landscape of

different adsorption modes of acetic acid to anatase TiO_2 . A schematic representation of the different identified minima are displayed in Figure 2. The sensitivity of the adsorption energies

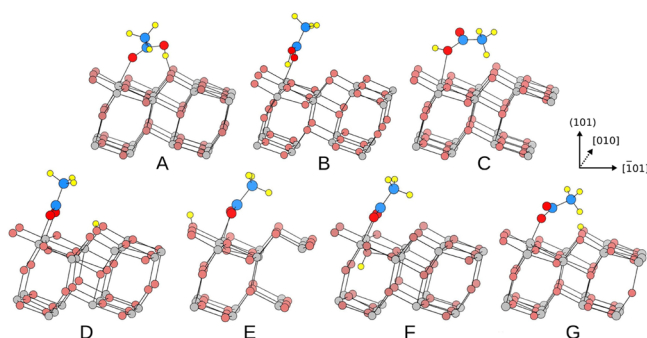


Figure 2. Most stable adsorption modes of the carboxylic moiety on the anatase (101) slab, from side view. (A, B) Molecular bridging with hydrogen interactions. (C) Molecular monodentate binding. (D, E) Dissociative bridging with proton adsorption on the anatase surface. (F) Dissociative bridging with proton insertion below the surface. Several possible locations for the proton have been tested (see the SI), and the most stable is reported. The proton is pointing inward and the 3-fold coordinated oxygen atom to which the proton is bound relaxes accordingly. (G) Dissociative ester linkage.

with respect to surface size and first layer solvation effects has been carefully tested using a variety of possible setups. The results show that the thickness of the slab employed in these calculation has a serious impact on the relative stabilities. Moreover, a stable adsorption mode including a subsurface proton has been identified which has not been predicted previously.

A common model to study adsorbents on anatase TiO_2 is based on a 108 atom slab with a thickness of 3 layers. Comparing the relative stabilities of the different adsorption modes for this model with the larger 5-layer and 7-layer slab models (Table 1), a noticeable change in energies can be seen.

Table 1. Comparison of the Gas Phase Adsorption Energies of Geometries A, D, and F of Figure 2, Establishing the Importance of Slab Thickness^a

	E_{ads} [kJ/mol]		
	slab 133	slab 135	slab 137
A	−114.3	−125.0	−122.9
D	−98.6	−119.5	−120.8
F	−105.8	−120.3	−119.7

^a $x = 10.227 \text{ \AA}$; $y = 3.782 \text{ \AA}$; $z = 3.513 \text{ \AA}$.

Between the 133 and 135 model, adsorption energies change up to about 20 kJ/mol. More importantly, this change is not a systematic shift of the energies but affects their relative stabilities as well. While the 3-layer model strongly favors A as most stable adsorption mode, the larger models predict almost the same stability for A, D, and F. This finding can be explained by the fact that a 3-layer model is not big enough to accommodate all lattice relaxations (see the SI) induced by acetic acid adsorbed on anatase. Increasing the slab thickness further to a 7-layer slab leads only to minor differences of about 2 kJ/mol. From these results, it is obvious that a 3-layer model gives qualitatively wrong results and a 5-layer model is needed

to obtain a reasonable compromise between accuracy and computational cost.

At the Γ -point, the size of the unit cell in the periodic directions could be important. Energy convergence tests (see the SI) did not show a significant size effect and therefore size, and thus, k-point, convergence in the periodic directions is assumed.

Next, we focus on the influence of coadsorbed ACN molecules on the adsorption energies. Again, size convergence of the model has been carefully tested to exclude artificial interactions (electrostatic or steric) induced by periodic boundary conditions. The effects we found were up to 7 kJ/mol from the smallest model to the biggest (Table 2). We find that the relative stabilities are converged employing the 255 model and thus these values are used in our further discussion.

A significant problem with the monolayer model arises because of the two different types of binding modes that the carboxyl groups can adopt. The monodentate modes (A–C, G) only occupy a single adsorption site in the monolayer, while the bidentate modes (D–F) occupy two. Therefore, two different definitions for the reference monolayer for the adsorption process are possible. The ideal monolayer with one ACN vacancy, which is only suitable for the monodentate binding modes, or a monolayer with two ACN vacancies. The latter model describes the bidentate modes well but leaves a vacant ACN adsorption site on the surface in case of monodentate binding. Hence, an energy penalty of the order of the binding energy of a ACN to the surface (about 90 kJ/mol) has to be added to the bidentate modes if the energies of the system in contact with ACN vapor are being discussed. In case an explicit solvent model is chosen, the energy alignment of the different binding types cannot be easily evaluated as the shift is a combination of the binding energy of an acetonitrile from the liquid and the solvation energy of the different structures. Therefore, deductions from the gas phase models to solvated system can only be made for sufficiently similar configurations (binding modes, dipoles, etc.). Even if the monolayer models are not perfect, they can give insight in the interactions of the acid with coadsorbed ACN molecules and can account for sizable stabilization effects. This is observed for configuration G, in which the carboxylate group is partially pointing away from the surface. This geometry is metastable in the gas phase, but is stabilized by hydrogen interactions with the surrounding molecules if a monolayer of ACN is introduced.

PROTON BINDING SITE ACCESSIBILITY AND MOBILITY

So far little attention has been paid to subsurface proton states due to the higher energy originally assigned to these configurations. In previous theoretical studies, subsurface hydrogen insertion has always been reported as less stable compared to surface adsorption.^{59,60} Configuration F presented here differs from the ones previously investigated by the presence of the above coadsorbed carboxylate moiety, that stabilizes the subsurface position. Although configuration F presents a stable adsorption mode, the formation depends on the accessibility of the subsurface proton site. A detailed investigation of possible intercalation pathways and proton diffusion pathways on and below the surface is therefore necessary.

Starting from an adsorption mode in which the proton is placed on top of the anatase surface, configuration F can be reached by proton migration via many possible paths. All

Table 2. Comparison of Adsorption Energies of the Geometries Illustrated in Figure 2 for Increasing Slab Width And Decreasing Acid Coverage

	E_{ads} [kJ/mol]					
	slab135		slab255		slab265	
	gas phase	solvent monolayer 4 ACN	gas phase	solvent monolayer 18 ACN	gas phase	solvent monolayer 22 ACN
A	−125.0	−118.7	−120.0	−122.1	−119.5	−121.7
A*		−133.7 ^b		−129.0 ^c		−129.9 ^d
B			−114.6	−100.7		
C			−72.1	−82.8		
D	−120.3	−127.6	−117.0	−122.1	−117.3	−119.9
E			−117.6	−103.5		
F	−120.5	−125.2	−117.9	−126.3	−122.0	−128.3
G			−52.8	−122.1		

^aA*: different monolayer model. ^b5 ACN monolayer. ^c19 ACN monolayer. ^d23 ACN monolayer.

proton intercalation and diffusion processes involve mainly interactions with the surface atoms and small contributions from molecules that are located close to the anatase surface. Hence, the role of the liquid solvent above the first layer is assumed to be small and the monolayer description of the interface is employed. Exploring all possible pathways is beyond the scope of this work; therefore, we restrict the simulations to the three pathways which we assume to require the smallest barriers. The pathways are illustrated in Figure 3, and reaction energies provided in Table 3.

Proton migration into the anatase surface is a stepwise process transferring the migrating proton from one oxygen site to a neighboring one. Due to the strength of the O–H bond and to the fact that the surrounding anatase lattice is heavily deformed by the presence of the migrating proton, a high activation energy is required for most of the proposed paths. Only those involving a short-range proton migration and a small lattice distortion present an activation energy around 100 kJ/mol (see Table 3), and thus, the reaction is likely to proceed on the hour time scale at room temperature. As this energy is significantly higher than the barrier for interconversion between molecular configurations (see the SI), the lowest energy path will be the same for all of the configurations. In addition, configuration F is most stable, and thus, the reverse process always occurs with a higher energy cost.

The lowest energy path for direct intercalation is found to proceed via configuration B (Path3, Figure 3). From the molecular adsorption mode B, the proton is transferred to the interacting surface oxygen and from there rotates into the surface and configuration F is formed. Interaction with the carboxylate moiety therefore assists intercalation, by allowing the proton to approach the final subsurface position without causing a big lattice distortion. The activation energy to reach that state from B is 72.3 kJ/mol. As mentioned earlier, the different configurations interconvert and hence the barrier for intercalation from, for example, the more stable configuration A has an activation energy of 93.5 kJ/mol and the reverse reaction 97.6 kJ/mol. To reach the initial state B from A, an initial barrier of 36.2 kJ/mol has to be overcome (see the SI). These findings indicate that proton intercalation will be the rate determining step the formation of the subsurface proton configuration F and that the carboxylate moiety is crucial for a low barrier intercalation process.

It is intuitive that the presence of a nearby coadsorbed carboxylate moiety has an influence not only on the relative stability of various proton adsorption or insertion sites, but also

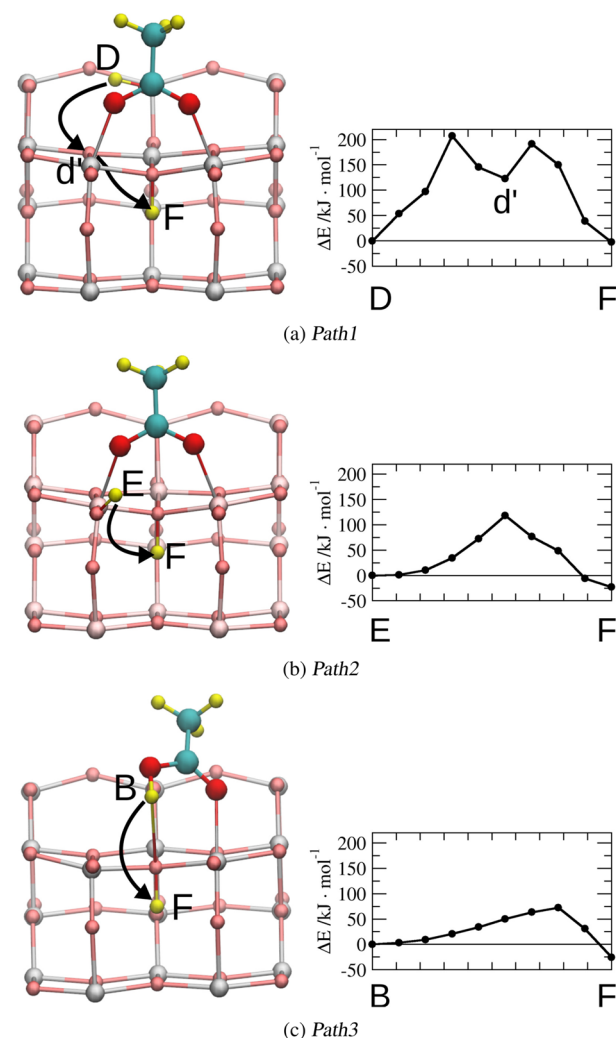


Figure 3. NEB profiles for subsurface proton insertion, starting from configuration D (Path1), E (Path2), and B (Path3), computed in the presence of a coadsorbed carboxylate moiety and of an acetonitrile monolayer. For clarity, ACN molecules are not shown. Positions D and B can be reached from position A, as discussed in the following sections.

the proton diffusion on top or below the anatase surface. For this reason, other possible proton migration paths have been investigated in presence of the coadsorbed carboxylate moiety (Figure 4). These paths focus on proton diffusion completely

Table 3. Starting Configurations and Activation Energies Relative to the Hydrogen Interpolation Paths Shown in Figure 3 Calculated for the “18ACN Monolayer” Environment, with the NEB Method

	starting configuration	E_{act} [kJ/mol]	ΔE [kJ/mol]
Path1	D	207.4	−4.2
Path2	E	118.3	−22.8
Path3	B	72.3	−25.6

above or below the surface edge, with no crossing between different layers.

Regarding subsurface proton migration, we note that the required E_{act} for proton migration is 84.8 kJ. This indicates that this type of subsurface diffusion should happen on a similar time scale as proton intercalation/deintercalation. However, the energy differences between initial and final position is about 20 kJ/mol. Further calculations on more distant sites show that this trend continues (see the SI). This can be easily understood from the electrostatic interaction between the positively charged proton and the negatively charged acetate. Due to this stability gradient, protons are likely to remain in the proximity of the corresponding acetate.

The other possible subsurface migration path (Path5) studied exhibits a significantly higher barrier of >150 kJ/mol and therefore should not play a significant role in this system. As these are the only two escape routes for the proton, we do not expect to see a noticeable subsurface proton diffusion in this system.

Contrary the subsurface migration, proton migration above the anatase surface should be facilitated as a nearby carboxylate moiety might stabilize the transition states for proton migration. In fact, Path7 shows that hydrogen bonds between the carboxylate group and the proton are formed during the migration process. The energy barrier for this process is found to be 19.4 kJ/mol. In case the carboxylate is turned away from the proton (Path6), no such stabilization is possible and the activation barrier is increased to about 50 kJ/mol, almost 2.5 times the value of the carboxyl assisted path. As there are almost no interactions with the acetate, this value should be close to the barrier for migration of a free proton on the surface.

■ ELECTRONIC PROPERTIES OF SUBSURFACE PROTONS

Several studies have shown that different binding modes and the presence of acidic protons affect important properties for a DSSC device (i.e., shift in the oxide electronic levels, increased electron injection/charge collection efficiency and increased amount of adsorbed dye molecules^{61–66}). Therefore, the electronic properties of the anatase slab in the presence of a subsurface proton in combination with an excess electron have been investigated by hybrid DFT calculations.

Results are shown in Figure 5. The excess electron tends to localize in proximity of the subsurface proton, on a Ti cation that acquires a formally (3+) valence. From the density of states calculations, it can be seen that the fully localized electron represents a trap state in the band gap, located 1.19 eV below the conduction band edge. Electron localization deeper in the slab is also possible, with a loss in stability of about 4 kJ/mol and no substantial change in the DOS distribution (see the SI). The presence of a coadsorbed carboxylate moiety does not alter the overall DOS distribution (see the SI), even if the most

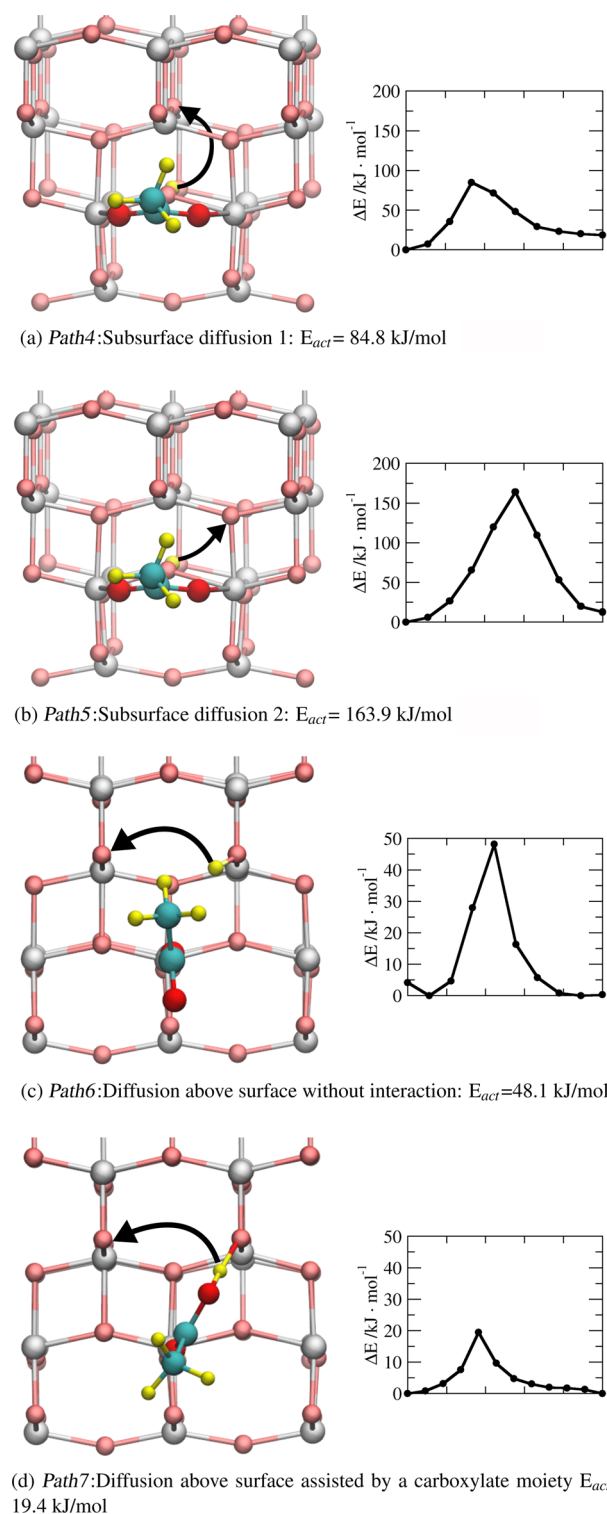


Figure 4. NEB profiles for proton migration in presence of a coadsorbed carboxylate moiety and of an acetonitrile monolayer, seen from top view.

stable position for the localized proton is found to be located deeper below the surface edge, probably because of the electrostatic repulsion and surface deformations due to the presence of the negatively charged carboxylate moiety.

A more extended polaron, with the excess charge delocalized over several Ti atoms, is also observed. Such partially delocalized state is located somewhat higher in the band gap,

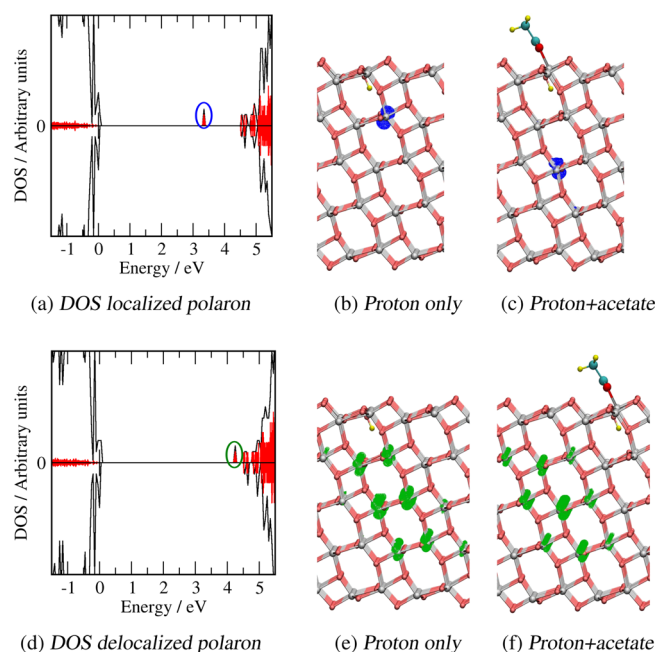


Figure 5. Total density of states for the fully localized polaron (upper panel, excess charge in blue) and for the partially delocalized polaron (lower panel, excess charge in green). The projected DOS on Ti d orbitals is painted in red.

0.25 eV below the CB edge (Figure 5d). This state is only metastable and nearly isoenergetic with the localized state, both in the presence and in the absence of a carboxylate moiety. Their relative stability may be significantly influenced by the nature of the exchange and correlation functional and on the amount of Hartree–Fock exchange,⁶⁷ but it appears that both solutions are possible.

Hence, it can be stated that the presence of a subsurface proton, stabilized by the coadsorbed carboxylate moiety, acts as a trap state for the excess electrons injected into the anatase slab, favoring localization below the surface edge. Such behavior may influence the electron injection dynamics and the overall device performance.

SURFACE MOBILITY OF ACETIC ACID

Following the activation energy computations for proton diffusion on the anatase surface, the possibility of acetic acid migration with the proton on top of the anatase slab has been investigated. In this case, solvent plays a fundamental role, by assisting partial detachment of the acid molecule, filling up vacant binding positions, and interacting with the molecule in its transition state. Hence, a monolayer model for the solvent is not sufficient anymore to describe the reaction path. Instead, we have adopted an explicit solvent model and used the thermodynamic integration scheme (TI) to explore the free energy surface. The details of the reaction coordinate (RC) used for these simulations are shown in Figure 6. The most likely molecular movement studied is a geometry switch from configuration A to configuration D (Path8).

During the MD run, a spontaneous exchange of protons takes place from the acid molecule adsorbed in configuration A (RC = −0.94 Å) to the surface and vice versa, so that the carboxylic moiety adsorbed in configuration A exists in both its protonated and deprotonated forms, as illustrated in the lower panel of Figure 7. We observe that with respect to the solvent

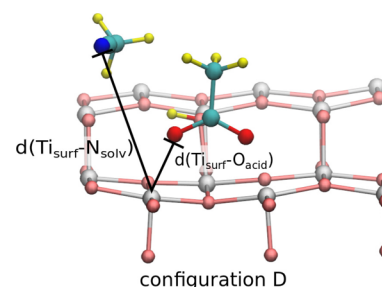


Figure 6. Representation of the two components of the reaction coordinate chosen for Path8 and relative to configuration D of Figure 2. $RC = d(Ti_{surf} - N_{solv}) - d(Ti_{surf} - O_{acid})$. For clarity, coadsorbed and surrounding solvent molecules are not shown.

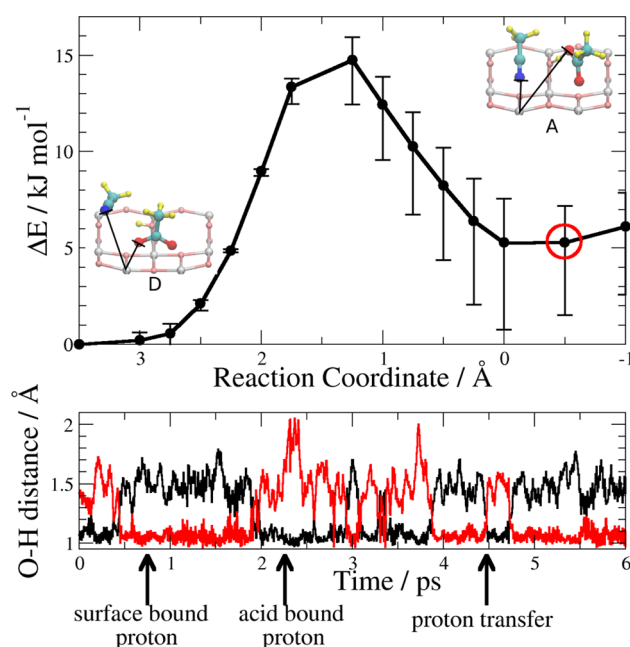


Figure 7. Upper panel: Free energy profile relative to Path8, obtained by thermodynamic integration. Lower panel: Plot of the distance between the acidic proton and the surface (red) and between the proton and the carboxylate moiety (black) as a function of simulation time (0.5 fs/step), for RC = −0.50 Å (circled in red on the free energy profile). Spontaneous proton transfer between the acid and the surface (black/red crossover) is observed.

monolayer environment the relative stability of the two modes is slightly altered, with the bidentate configuration D stabilized in the liquid environment with respect to the monodentate configuration A by $\Delta E = 5.3$ kJ/mol (Figure 7). The activation energy for moving from configuration D to A is lowered by 5.9 kJ/mol for the reaction compared to the monolayer simulation ($E_{act} = 14.7$ kJ/mol in the liquid environment vs 20.6 kJ/mol in the solvent monolayer environment; see the SI). This shows that the presence of solvent molecules facilitates the interconversion of the structures.

A continuous sequence of switches in adsorption geometry and hydrogen diffusion steps (as described in the previous section) leads to an overall migration of the acid molecule along the [010] direction of anatase (101), as pictured in detail in Figure 8. The highest barrier to overcome along the studied migration path is at most $E_{act} = 19.4$ kJ/mol, so that a stepwise molecular diffusion on the surface, without complete detach-

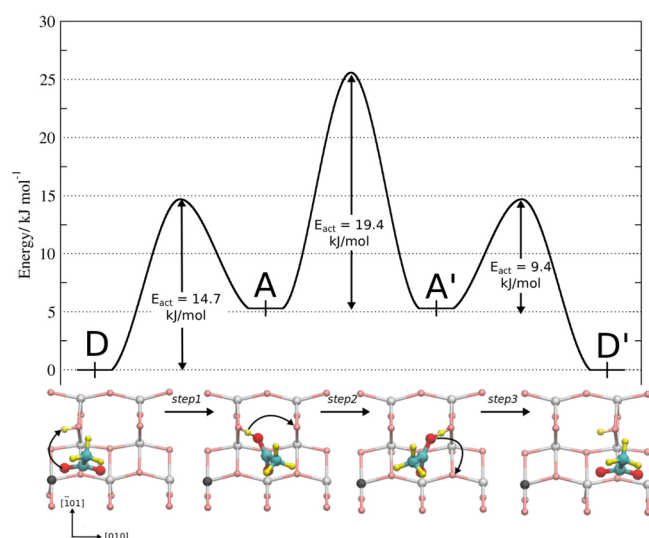


Figure 8. Upper panel: Energy diagram reporting the activation energies computed (in kJ/mol) for the stepwise migration of the acid molecule on anatase (101). Lower panel: Graphical representation of the migration process; for clarity, surrounding solvent molecules are not shown. As a reference, the initial detachment point is painted in black. Step1: movement from configuration D to configuration A. Step2: Proton transfer from the surface to the molecule and rearrangement in a symmetric position. Step3: movement from configuration A to configuration D. For each series of steps, the overall displacement of the molecule is 3.79 Å along the [010] direction.

ment of the adsorbed carboxylate moiety, is easily feasible if the proton does not intercalate below the surface edge.

■ ACETIC ACID DESORPTION

In this section, the desorption process in presence of a liquid solvent is studied, establishing the strength of the interaction. Configuration A depicted in Figure 2 was chosen as starting point for these simulations. As demonstrated in the previous sections, this geometry is energetically almost equivalent to the dissociative bridging configuration D and both modes can easily interconvert. The desorption process is necessarily associated with the adsorption of ACN molecules to fill the created vacancy in the monolayer. Therefore, an explicit solvent model is again needed in these simulations and the relative stabilities and barriers are obtained via TI. The reaction coordinate employed in these simulations is depicted in Figure 9 and accounts at the same time for acid desorption as well as ACN adsorption.

We note that, at the final point in the TI calculation, the acid molecule is fully detached from the anatase (101) surface, but a complete separation from the interface is not yet achieved. The acid can be involved in multiple hydrogen bonds with the nearby adsorbed acetonitrile molecules. Such interactions strongly influence the stability of the detached acid molecule, making it difficult to precisely obtain its adsorption energy, that is, the stability difference between the surface-adsorbed acid molecule and the solvated acid molecule. For the process studied, the obtained binding energy of acetic acid adsorbed in a molecular bridging configuration (configuration A of Figure 2.) is $E_{ads} = 37.5$ kJ/mol. From the dissociative bridging configuration D, this value increases to 42.8 kJ/mol considering the 5.3 kJ/mol stability difference between binding modes A and D derived earlier. The activation energies obtained for the

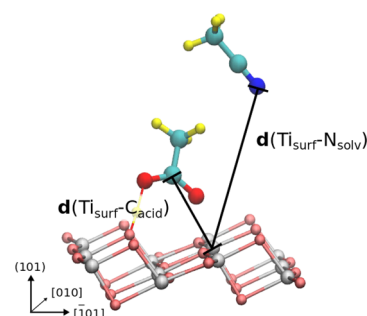


Figure 9. Representation of the two components of the reaction coordinate chosen for the desorption process. $RC = d(Ti_{surf} - N_{solv}) - d(Ti_{surf} - C_{acid})$. For clarity, coadsorbed and surrounding solvent molecules are not shown.

desorption from A and D are 52.2 and 57.3 kJ/mol, respectively.

It is important to note that the desorption mechanism presented requires the molecular acetic acid to be desorbed. As this requirement was not part of the reaction coordinate, this shows that a dissociative desorption has to have a higher barrier. As it can be seen in Figure 10, in the early stages of the reaction, proton transfer from the surface to the acid molecule and vice versa is possible, while this is not the case in the final state. This means that this mechanism can only occur in a configuration where the proton can be easily transferred to the acid. Therefore, the observation of a stable subsurface proton state can kinetically trap the acid on the surface and prevent desorption.

■ CONCLUSION AND OUTLOOK

In this work, first-principles DFT calculations were performed to investigate the behavior of acetic acid molecules adsorbed on the anatase (101) surface, in the presence of explicit acetonitrile liquid solvent. A systematic screening on different anatase slabs, with varying thickness and width, led to the conclusion that a slab thickness of at least 5 layers (about 17 Å) should be adopted to correctly evaluate the acid binding properties. A similar size dependence of the relative stability of different adsorption modes has been previously reported for water on the rutile (100) surface,⁶⁸ supporting the need of a fully converged slab thickness to perform calculations.

The use of such a thick slab allowed us to discover a novel, more stable binding mode, characterized by proton insertion below the first layer of oxide atoms. Hybrid DFT calculations show that the subsurface proton insertion slightly distorts the anatase lattice and favors localization of excess electrons below the surface edge.

NEB calculations show that the presence of the above coadsorbed acetate moiety assists proton intercalation, while subsurface proton migration remains limited. On the other hand, proton diffusion on top of the anatase surface is favored by the interaction with a nearby adsorbed carboxylate moiety.

Activation energies computed with the nudged elastic band and thermodynamic integration method also demonstrate that if the proton is adsorbed on top of the anatase slab, an acid molecule adsorbed on the surface in a less stable geometry can move toward the thermodynamically stable state, by partial detachment, rotation, and readsorption on the surface. A stepwise sequence of changes in the acetic acid adsorption geometry can take place, leading to an overall diffusion of the molecule along the [010] direction, with a maximum activation

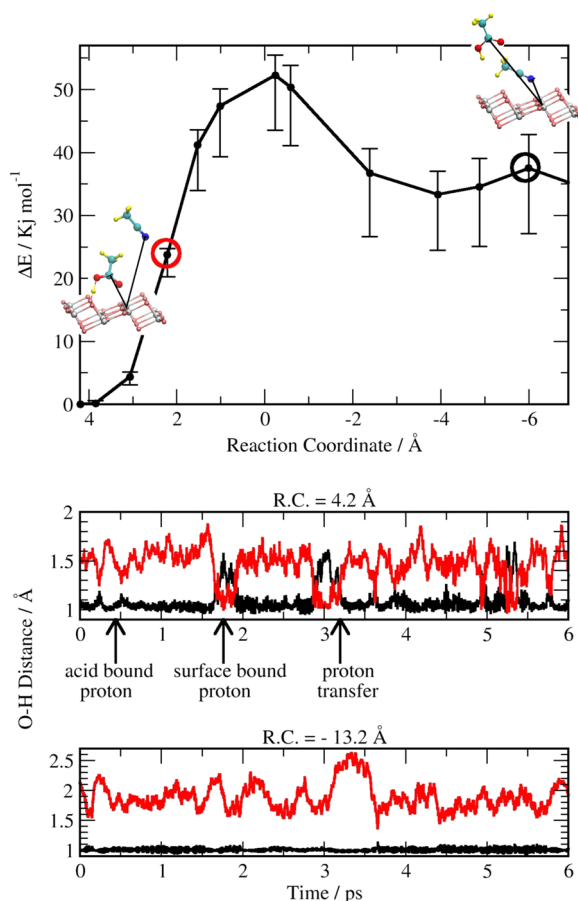


Figure 10. Upper panel: Free energy profile relative to the detachment of an acetic acid molecule from the anatase (101) surface, obtained by thermodynamic integration. Middle and lower panels: Plot of the distance between the acidic proton and the surface (red) and between the proton and the carboxylate moiety (black) as a function of simulation time, for a molecule partially attached to the surface (RC = 2.2 Å circled in red on the free energy profile) and for a completely detached molecule (RC = -6.0 Å circled in black on the free energy profile). Spontaneous proton transfer between the acid and the surface (black/red crossover) is observed only if the molecule is partially attached to the surface and, even in this case, a preponderance of the protonated acid form is evident.

energy of only $E_{\text{act}} = 19.4$ kJ/mol. The process of complete acetic acid desorption from the surface has been shown to require an activation energy, in the presence of explicit liquid solvent, of $E_{\text{act}} = 51.0$ kJ/mol. The protonated acid form is dominant during the desorption process, and, at the end, the molecule detaches from the slab in its protonated form. For this reason, proton deintercalation from the more stable subsurface state is essential for the acid detachment. Such process is characterized by an high activation barrier, so that the acetic acid molecule results effectively “pinned” to the surface if proton intercalation takes place. The performed simulations account for effects of the solvent explicitly, which might be overlooked or difficult to take into account in calculations adopting less advanced models. By direct comparison of the explicit solvent with “gas phase” and “solvent monolayer” environments, it was demonstrated that the adsorption energy differs by almost a factor of 2 between these models. Such quantitative results, which were obtained by ab initio MD calculations on a complex solid–liquid interface made up of 1400 atoms, could be used as a benchmark result to validate

more expedient computational approaches. Future work should extend these results, both toward more realistic dyes, including bulky organic ligands and organometallic compounds, as well as toward explicit electrolytic solutions that contain the additives commonly employed in high efficiency devices. Finally, experimental verification of the subsurface proton state and a characterization of its influence on electron injection would further contribute to rationalizing the performance of dye sensitized solar cells.

■ ASSOCIATED CONTENT

■ Supporting Information

S1: Adsorption energies computed for the 5 ACN monolayer environment. S2: Displacement of the TiO_2 ions for adsorption modes A and D. S3: Gasphase adsorption energies of geometry A, D, and F for increasing slab width and constant acid coverage. S4: Stability of various subsurface proton positions with respect to configuration F. S5: DOS for the fully localized polaron in two different sites of the anatase lattice. S6: DOS for the subsurface proton in the presence and in the absence of a coadsorbed carboxylate moiety. S7: Energy diagrams and E_{act} for paths 8–10. S8: Auxiliary basis set employed for the Ti atoms in hybrid calculations. S9: sample of a *cp2k* input file. S10: Coordinates of the NEB replicas for paths 1–10. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Hadjiivanov, K. I.; Klissurski, D. G. Surface Chemistry of Titania (Anatase) and Titania-Supported Catalysts. *Chem. Soc. Rev.* **1996**, *25*, 61–69.
- (2) Linsebigler, A. L.; Lu, G.; Yates, J. T. Photocatalysis on TiO_2 Surfaces: Principles, Mechanisms, and Selected Results. *Chem. Rev.* **1995**, *95*, 735–758.
- (3) Wold, A. Photocatalytic Properties of Titanium Dioxide (TiO_2). *Chem. Mater.* **1993**, *5*, 280–283.
- (4) Azad, A. M.; Akbar, S. A.; Mhaisalkar, S. G.; Birkefeld, L. D.; Goto, K. S. Solid-State Gas Sensors: A Review. *J. Electrochem. Soc.* **1992**, *139*, 3690–3704.
- (5) Brown, G. E.; Henrich, V. E.; Casey, W. H.; Clark, D. L.; Eggleston, C.; Felmy, A.; Goodman, D. W.; Grätzel, M.; Maciel, G.; McCarthy, M. I.; et al. Metal Oxide Surfaces and Their Interactions with Aqueous Solutions and Microbial Organisms. *Chem. Rev.* **1999**, *99*, 77–174.
- (6) O'Regan, B.; Grätzel, M. A Low-Cost, High-Efficiency Solar Cell Based on Dye-Sensitized Colloidal TiO_2 Films. *Nature* **1991**, *353*, 737–740.
- (7) Gerfin, T.; Grätzel, M.; Walder, L. *Progress in Inorganic Chemistry*; John Wiley and Sons, Inc.: New York, 2007; pp 345–393.
- (8) Diebold, U. The Surface Science of Titanium Dioxide. *Surf. Sci. Rep.* **2003**, *48*, 53–229.

- (9) Fukui, A.; Komiya, R.; Yamanaka, R.; Islam, A.; Han, L. Effect of a Redox Electrolyte in Mixed Solvents on the Photovoltaic Performance of a Dye-Sensitized Solar Cell. *Sol. Energy Mater. Sol. Cells* **2006**, *90*, 649–658.
- (10) Lee, K.-M.; Suryanarayanan, V.; Ho, K.-C. Influences of Different TiO₂ Morphologies and Solvents on the Photovoltaic Performance of Dye-Sensitized Solar Cells. *J. Power Sources* **2009**, *188*, 635–641.
- (11) Nazeeruddin, M.; Zakeeruddin, S.; Humphry-Baker, R.; Jirousek, M.; Liska, P.; Vlachopoulos, N.; Shklover, V.; Fischer, C.; Grätzel, M. Acid-Base Equilibria of (2,2'-bipyridyl-4,4'-dicarboxylic acid)Ruthenium(II) Complexes and the Effect of Protonation on Charge-Transfer Sensitization of Nanocrystalline Titania. *Inorg. Chem.* **1999**, *38*, 6298–6305.
- (12) Nazeeruddin, M. K.; Péchy, P.; Renouard, T.; Zakeeruddin, S. M.; Humphry-Baker, R.; Comte, P.; Liska, P.; Cevey, L.; Costa, E.; Shklover, V.; et al. Engineering of Efficient Panchromatic Sensitizers for Nanocrystalline TiO₂-Based Solar Cells. *J. Am. Chem. Soc.* **2001**, *123*, 1613–1624.
- (13) Nazeeruddin, M. K.; De Angelis, F.; Fantacci, S.; Selloni, A.; Viscardi, G.; Liska, P.; Ito, S.; Takeru, B.; Grätzel, M. Combined Experimental and DFT-TDDFT Computational Study of Photoelectrochemical Cell Ruthenium Sensitizers. *J. Am. Chem. Soc.* **2005**, *127*, 16835–16847.
- (14) Haque, S. A.; Palomares, E.; Cho, B. M.; Green, A. N. M.; Hirata, N.; Klug, D. R.; Durrant, J. R. Charge Separation versus Recombination in Dye-Sensitized Nanocrystalline Solar Cells: the Minimization of Kinetic Redundancy. *J. Am. Chem. Soc.* **2005**, *127*, 3456–3462.
- (15) Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H. Dye-Sensitized Solar Cells. *Chem. Rev.* **2010**, *110*, 6595–663.
- (16) Reynal, A.; Palomares, E. Ruthenium Polypyridyl Sensitizers in Dye Solar Cells Based on Mesoporous TiO₂. *Eur. J. Inorg. Chem.* **2011**, 4509–4526.
- (17) Hardin, B.; Snaith, H.; McGehee, M. The Renaissance of Dye-Sensitized Solar Cells. *Nat. Photonics* **2012**, *6*, 162–169.
- (18) Green, M. A.; Emery, K.; Hishikawa, Y.; Warta, W. Solar Cell Efficiency Tables (Version 32). *Prog. Photovoltaics* **2008**, *16*, 435–440.
- (19) Yella, A.; Lee, H.-W.; Tsao, H. N.; Yi, C.; Chandiran, A. K.; Nazeeruddin, M.; Diau, E. W.-G.; Yeh, C.-Y.; Zakeeruddin, S. M.; Grätzel, M. Porphyrin-Sensitized Solar Cells with Cobalt (II/III)-Based Redox Electrolyte Exceed 12% Efficiency. *Science* **2011**, *334*, 629–634.
- (20) Shockley, W.; Queisser, H. J. Detailed Balance Limit of Efficiency of p-n Junction Solar Cells. *J. Appl. Phys.* **1961**, *32*, 510–519.
- (21) Lindan, P. J. D.; Harrison, N. M.; Gillan, M. J. Mixed Dissociative and Molecular Adsorption of Water on the Rutile (110) Surface. *Phys. Rev. Lett.* **1998**, *80*, 762–765.
- (22) Bates, S. K. G.; Gillan, M. The Adsorption and Dissociation of ROH Molecules on TiO₂(110). *Surf. Sci.* **1998**, *409*, 336–349.
- (23) Vittadini, A.; Selloni, A.; Rotzinger, F.; Grätzel, M. Structure and Energetics of Water Adsorbed at TiO₂ Anatase (101) and (001) Surfaces. *Phys. Rev. Lett.* **1998**, *81*, 2954–2957.
- (24) Vittadini, A.; Selloni, A.; Rotzinger, F.; Grätzel, M. Formic Acid Adsorption on Dry and Hydrated TiO₂ Anatase (101) Surfaces by DFT Calculations. *J. Phys. Chem. B* **2000**, *104*, 1300–1306.
- (25) Tilocca, A.; Selloni, A. Structure and Reactivity of Water Layers on Defect-Free and Defective Anatase TiO₂(101) Surfaces. *J. Phys. Chem. B* **2004**, *108*, 4743–4751.
- (26) Tilocca, A.; Selloni, A. Vertical and Lateral Order in Adsorbed Water Layers on Anatase TiO₂(101). *Langmuir* **2004**, *20*, 8379–8384.
- (27) Tilocca, A.; Selloni, A. Methanol Adsorption and Reactivity on Clean and Hydroxylated Anatase (101) Surfaces. *J. Phys. Chem. B* **2004**, *108*, 19314–19319.
- (28) Nilsing, M.; Persson, P.; Ojamäe, L. Anchor Group Influence on Molecule-Metal Oxide Interfaces: Periodic Hybrid DFT Study of Pyridine Bound to TiO₂ via Carboxylic and Phosphonic Acid. *Chem. Phys. Lett.* **2005**, *415*, 375–380.
- (29) Nilsing, M.; Lunell, S.; Persson, P.; Ojamäe, L. Phosphonic Acid Adsorption at the TiO₂ Anatase (101) Surface Investigated by Periodic Hybrid HF-DFT Computations. *Surf. Sci.* **2005**, *582*, 49–60.
- (30) Gong, X.-Q.; Selloni, A.; Vittadini, A. Density Functional Theory Study of Formic Acid Adsorption on Anatase TiO₂(001): Geometries, Energetics, and Effects of Coverage, Hydration, and Reconstruction. *J. Phys. Chem. B* **2006**, *110*, 2804–2811.
- (31) Oviedo, J.; Sánchez-de Armas, R.; San Miguel, M. A.; Sanz, J. F. Methanol and Water Dissociation on TiO₂ (110): The Role of Surface Oxygen. *J. Phys. Chem. C* **2008**, *112*, 17737–17740.
- (32) Sánchez, V. M.; Cojulan, J. A.; Scherlis, D. A. Dissociation Free Energy Profiles for Water and Methanol on TiO₂ Surfaces. *J. Phys. Chem. C* **2010**, *114*, 11522–11526.
- (33) Sánchez, V.; de la Llave, E.; Scherlis, D. A. Adsorption of R-OH Molecules on TiO₂ Surfaces at the Solid–Liquid Interface. *Langmuir* **2011**, *27*, 2411–2419.
- (34) De Angelis, F.; Fantacci, S.; Gebauer, R. Simulating Dye-Sensitized TiO₂ Heterointerfaces in Explicit Solvent: Absorption Spectra, Energy Levels, and Dye Desorption. *J. Phys. Chem. Lett.* **2011**, *2*, 813–817.
- (35) Mosconi, E.; Selloni, A.; De Angelis, F. Solvent Effects on the Adsorption Geometry and Electronic Structure of Dye-Sensitized TiO₂: A First-Principles Investigation. *J. Phys. Chem. C* **2012**, *116*, 5932–5940.
- (36) Schiffrmann, F.; Hutter, J.; VandeVondele, J. Atomistic Simulations of a Solid/Liquid Interface: a Combined Force Field and First Principles Approach to the Structure and Dynamics of Acetonitrile near an Anatase Surface. *J. Phys.: Condens. Matter* **2008**, *20*, 064206.
- (37) Schiffrmann, F.; VandeVondele, J.; Hutter, J.; Urakawa, A.; Wirz, R.; Baiker, A. An Atomistic Picture of the Regeneration Process in Dye Sensitized Solar Cells. *Proc. Natl. Acad. Sci. U.S.A.* **2010**, *107*, 4830–4833.
- (38) Burnside, S. D.; Shklover, V.; Christophe, B.; Comte, P.; Arendse, F.; Brooks, K.; Grätzel, M. Self-Organization of TiO₂ Nanoparticles in Thin Films. *Chem. Mater.* **1998**, *10*, 2419–2425.
- (39) Persson, P.; Bergström, R.; Ojamäe, L.; Lunell, S. *Quantum-chemical Studies of Metal Oxides for Photoelectrochemical Applications*; Advances in Quantum Chemistry; Academic Press: New York, 2002; Vol. 41, pp 203–263.
- (40) Schiffrmann, F.; VandeVondele, J.; Hutter, J.; Wirz, R.; Urakawa, A.; Baiker, A. Protonation-Dependent Binding of Ruthenium Bipyridyl Complexes to the Anatase(101) Surface. *J. Phys. Chem. C* **2010**, *114*, 8398–8404.
- (41) The CP2K developers group, 2013; <http://www.cp2k.org>.
- (42) Lippert, G.; Hutter, J.; Parrinello, M. A Hybrid Gaussian and Plane Wave Density Functional Scheme. *Mol. Phys.* **1997**, *92*, 477–487.
- (43) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865.
- (44) Hartwigsen, C.; Goedecker, S.; Hutter, J. Relativistic Separable Dual-Space Gaussian Pseudopotentials from H to Rn. *Phys. Rev. B* **1998**, *58*, 3641.
- (45) Krack, M. Pseudopotentials for H to Kr Optimized for Gradient-Corrected Exchange-Correlation Functionals. *Theor. Chem. Acc.* **2005**, *114*, 145.
- (46) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 154104.
- (47) DFT-D3: A Dispersion Correction for Density Functionals, Hartree-Fock and Semi-Empirical Quantum Chemical Methods. <http://www.thch.uni-bonn.de/tc/index.php?section=downloads&subsection=DFT-D3&lang=english>.
- (48) VandeVondele, J.; Hutter, J. Gaussian Basis Sets for Accurate Calculations on Molecular Systems in Gas and Condensed Phases. *J. Chem. Phys.* **2007**, *127*, 114105.

- (49) Adamo, C.; Barone, V. Toward Reliable Density Functional Methods Without Adjustable Parameters: The PBE0 Model. *J. Chem. Phys.* **1999**, *110*, 6158–6170.
- (50) Guidon, M.; Hutter, J.; VandeVondele, J. Robust Periodic Hartree-Fock Exchange for Large-Scale Simulations Using Gaussian Basis Sets. *J. Chem. Theory Comput.* **2009**, *5*, 3010–3021.
- (51) Guidon, M.; Hutter, J.; VandeVondele, J. Auxiliary Density Matrix Methods for Hartree-Fock Exchange Calculations. *J. Chem. Theory Comput.* **2010**, *6*, 2348–2364.
- (52) Mills, G.; Jónsson, H.; Schenter, G. K. Reversible Work Transition State Theory: Application to Dissociative Adsorption of Hydrogen. *Surf. Sci.* **1995**, *324*, 305–337.
- (53) Henkelman, G.; Jónsson, H. Improved Tangent Estimate in the Nudged Elastic Band Method for Finding Minimum Energy Paths and Saddle Points. *J. Chem. Phys.* **2000**, *113*, 9978–9985.
- (54) Henkelman, G.; Uberuaga, B. P.; Jónsson, H. A Climbing Image Nudged Elastic Band Method for Finding Saddle Points and Minimum Energy Paths. *J. Chem. Phys.* **2000**, *113*, 9901–9904.
- (55) Sprik, M.; Ciccotti, G. Free Energy from Constrained Molecular Dynamics. *J. Chem. Phys.* **1998**, *109*, 7737–7744.
- (56) Grabuleda, X.; Jaime, C.; Kollman, P. A. Molecular Dynamics Simulation Studies of Liquid Acetonitrile: New Six-Site Model. *J. Comput. Chem.* **2000**, *21*, 901–908.
- (57) Bandura, A. V.; Sofo, J. O.; Kubicki, J. D. Derivation of Force Field Parameters for $\text{SnO}_2\text{-H}_2\text{O}$ Surface Systems from Plane-Wave Density Functional Theory Calculations. *J. Phys. Chem. B* **2006**, *110*, 8386–8397.
- (58) Bussi, G.; Donadio, D.; Parrinello, M. Canonical Sampling through Velocity Rescaling. *J. Chem. Phys.* **2007**, *126*, 014101.
- (59) Aschauer, U.; Selloni, A. Hydrogen Interaction with the Anatase $\text{TiO}_2(101)$ Surface. *Phys. Chem. Chem. Phys.* **2012**, *14*, 16595–16602.
- (60) Islam, M. M.; Calatayud, M.; Pacchioni, G. Hydrogen Adsorption and Diffusion on the Anatase $\text{TiO}_2(101)$ Surface: A First-Principles Investigation. *J. Phys. Chem. C* **2011**, *115*, 6809–6814.
- (61) De Angelis, F.; Fantacci, S.; Selloni, A.; Grätzel, M.; Nazeeruddin, M. K. Influence of the Sensitizer Adsorption Mode on the Open-Circuit Potential of Dye-Sensitized Solar Cells. *Nano Lett.* **2007**, *7*, 3189–3195.
- (62) Watson, D. F.; Meyer, G. J. Cation Effects in Nanocrystalline Solar Cells. *Coord. Chem. Rev.* **2004**, *248*, 1391–1406.
- (63) Wang, Z.-S.; Yamaguchi, T.; Sugihara, H.; Arakawa, H. Significant Efficiency Improvement of the Black Dye-Sensitized Solar Cell through Protonation of TiO_2 Films. *Langmuir* **2005**, *21*, 4272–4276.
- (64) Park, K.-H.; Jin, E. M.; Gu, H. B.; Shim, S. E.; Hong, C. K. Effects of HNO_3 Treatment of TiO_2 Nanoparticles on the Photo-voltaic Properties of Dye-sensitized Solar Cells. *Mater. Lett.* **2009**, *63*, 2208–2211.
- (65) Guai, G. H.; Song, Q. L.; Lu, Z. S.; Ng, C. M.; Li, C. M. Tailor and Functionalize TiO_2 Compact Layer by Acid Treatment for High Performance Dye-Sensitized Solar Cell and its Enhancement Mechanism. *Renewable Energy* **2013**, *51*, 29–35.
- (66) Hao, S.; Wu, J.; Fan, L.; Huang, Y.; Lin, J.; Wei, Y. The Influence of Acid Treatment of TiO_2 Porous Film Electrode on Photoelectric Performance of Dye-Sensitized Solar Cell. *Solar Energy* **2004**, *76*, 745–750.
- (67) Finazzi, E.; Valentin, C. D.; Pacchioni, G.; Selloni, A. Excess Electron States in Reduced Bulk Anatase TiO_2 : Comparison of Standard GGA, GGA + U, and Hybrid DFT Calculations. *J. Chem. Phys.* **2008**, *129*, 154113.
- (68) Liu, L.-M.; Zhang, C.; Thornton, G.; Michaelides, A. Structure and Dynamics of Liquid Water on Rutile $\text{TiO}_2(110)$. *Phys. Rev. B* **2010**, *82*, 161415.