

RESEARCH ARTICLE

Dissociation of liquid water on defective rutile TiO₂ (110) surfaces using *ab initio* molecular dynamics simulations

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In order to obtain a comprehensive understanding of both thermodynamics and kinetics of water dissociation on TiO₂, the reactions between liquid water and perfect and defective rutile TiO₂ (110) surfaces were investigated using *ab initio* molecular dynamics simulations. The results showed that the free-energy barrier (~4.4 kcal/mol) is too high for a spontaneous dissociation of water on the perfect rutile (110) surface at a low temperature. The most stable oxygen vacancy (Vo₁) on the rutile (110) surface cannot promote the dissociation of water, while other unstable oxygen vacancies can significantly enhance the water dissociation rate. This is opposite to the general understanding that Vo₁ defects are active sites for water dissociation. Furthermore, we reveal that water dissociation is an exothermic reaction, which demonstrates that the dissociated state of the adsorbed water is thermodynamically favorable for both perfect and defective rutile (110) surfaces. The dissociation adsorption of water can also increase the hydrophilicity of TiO₂.

Keywords *ab initio* molecular dynamics, rutile (110), free energy barrier, spontaneous reaction, exothermic reaction

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1 Introduction

Since the study by Fujishima *et al.* in 1972 on photocatalysis of titanium dioxide (TiO₂) with a photochemical production of hydrogen from water, extensive studies have been performed on photochemistry of TiO₂ owing to its applications in various fields, including photochemical water splitting, solar cells, and catalysis [1–4]. Oxygen vacancies are crucial in the reactions on the oxide's surface [5, 6]. As the rutile TiO₂ (110) surface is the most common and stable surface of this material [7, 8], the dissociation of water on a perfect and defective TiO₂ (110) surfaces with different kinds of oxygen vacancy defects has been intensively studied. However, a proper correlation between the experimental and theoretical studies has not been yet established.

According to scanning tunneling microscopy (STM) observations and first-principles calculations, it is generally accepted that at room temperature water can be trapped by bridging oxygen vacancies, accompanied by dissociative adsorption at the bridging oxygen vacancies and formation of two bridging hydroxyls (OH_b) [9–15]. Wendt *et al.* reported that the two OH_b are near neighbors and remain stable until they interact with the surrounding water, splitting to single hydroxyl groups [12]. However, several studies argued that the number of dissociative water molecules is larger than the number of bridging oxygen vacancies [16, 17]. For example, Kristoffersen *et al.* revealed a new water-dissociation channel, and showed that oxygen vacancies at the <111> step edges are active sites for water dissociation contributing with up to two hydrogen adatoms on the terraces [18]. It is not yet known whether other vacancy defects have similar effects on the water dissociation. In addition, there has been a controversy for many years whether water adsorbed at a five-fold coordinated titanium at a perfect

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TiO₂ (110) surface can dissociate [11, 12, 19–22]. Water dissociation attracts an increasing interest as the reaction is exothermic but the large barrier hinders water dissociation at a low temperature [17, 23–25]. Therefore, the *ab initio* molecular dynamics (AIMD) simulations at finite temperature is very necessary for the research of water dissociation on the perfect TiO₂ (110) surface. A possible reason for the contradiction between the different studies of water/TiO₂ (110) interfaces is that most of them considered water in the vapor phase or at a low coverage under ultrahigh-vacuum conditions, which significantly differs from the real situation where TiO₂ interacts with liquid water at ambient conditions. To the best of our knowledge, although many studies have been performed on liquid-water/rutile-(110) interfaces [26–29], there is no systematic study on dynamics of water dissociation at interfaces between liquid water and defective rutile TiO₂ (110) surfaces with different types of oxygen vacancies at ambient conditions.

In this study, we systematically investigate the interaction between liquid water and perfect and defective rutile TiO₂ (110) surfaces with different types of oxygen vacancies denoted as Vo₁, Vo₂, Vo₃, and Vo₄, as shown in Fig. 1. Using AIMD simulations, we reveal the dynamic process of water dissociation at different interfaces in an aqueous environment at room temperature. We show that Vo₁ and Vo₃ have higher stabilities, compared with the other defects on the rutile (110) surface; however, their catalytic activities for water dissociation are inferior with respect to those of Vo₂ and Vo₄. On the other hand, the 5-coordinated Ti_{5c} site exhibits an unexpectedly higher activity for water dissociation, which indicates that the water dissociation adsorption can occur on

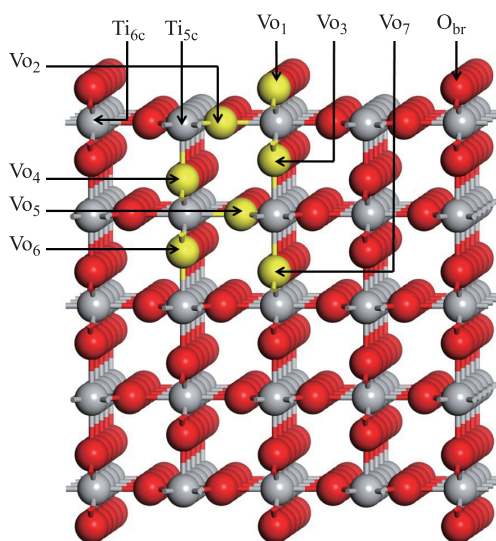


Fig. 1 Ball and stick model of the rutile TiO₂ (110) surface. Red and gray balls represent the O and Ti atoms. The yellow balls represent the different types of oxygen defects.

the ideal rutile (110) surface, without significant contributions from highly stable oxygen vacancies on the rutile surface. These results provide a detailed understanding of the water dissociation on rutile at the atomic scale in a real environment.

2 Computational methods

AIMD simulations are performed in the framework of density functional theory (DFT) using the QUICKSTEP code in the CP2K software [30], in order to not only reveal the interatomic interactions determined by the electronic structure, but also investigate the real-time dynamics and thermal fluctuations at a finite temperature. A mixed Gaussian and plane-wave basis set with an energy cutoff of 280 Ry was used for the expansion of the wave functions. The Becke–Lee–Yang–Parr (BLYP) functional was employed for the exchange correlation energy, combined with an empirical correction for the Van der Waals forces [31, 32]. All MD simulations are performed in a constant volume and temperature ensemble with a target temperature of 350 K controlled by a Nose–Hoover thermostat [33]. The simulation time for each MD trajectory is larger than 20 ps with a time step of 1.0 fs. We utilized a five-layer (4 × 2) periodic slab containing three planes with a composition of O–Ti₂O₂–O (see Fig. 1) with a vacuum space of 30.0 Å to model the rutile (110) surface. It has been demonstrated that the surface energy oscillates for a weak perturbation of the slab layers, and that a small odd number of slab layers leads to a rapid energy convergence; therefore, the five-layer slab is sufficiently thick for the TiO₂ calculations [7, 34, 35]. During the simulations, we fixed the last three layers. The liquid water film in contact with the surface had a thickness of approximately 5 Å, consisting of 32 molecules. The (110) surface consists of rows of five-coordinated Ti atoms (Ti_{5c}) and rows of two-coordinated O atoms (O_{br}) bridged to six-coordinated Ti atoms (Ti_{6c}), as shown in Fig. 1.

3 Results and discussion

First, we calculate the formation energies of different single oxygen vacancies in vacuum, as shown in Table 1. The vacancy formation energy is defined as the energy required to transfer an oxygen atom to the gap phase:

$$E_{vac} = E_{\text{Ti}_n\text{O}_{2n-1}} + \frac{1}{2}E_{\text{O}_2} - E_{\text{Ti}_n\text{O}_{2n}}, \quad (1)$$

where $E_{\text{Ti}_n\text{O}_{2n-1}}$ and $E_{\text{Ti}_n\text{O}_{2n}}$ are the total energies of the defective and perfect slab systems, respectively, and E_{O_2} is the total energy of an isolated O₂ molecule. Vo₁ has the lowest formation energy of 3.61 eV, which in-

Table 1 Formation energies of the different types of oxygen defects shown in Fig. 1.

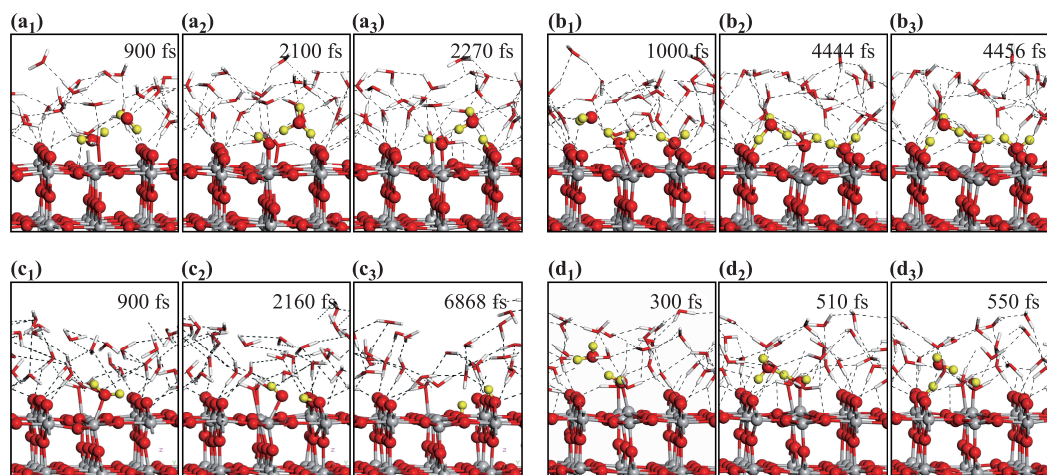
Defect	Vo ₁	Vo ₂	Vo ₃	Vo ₄	Vo ₅	Vo ₆	Vo ₇
E_{vac} (eV)	3.61	5.54	4.04	5.58	4.98	5.67	4.52

indicates that this is the most likely vacancy to form. In addition, the Vo₃ and Vo₇ defects form more easily, compared with the Vo₂ and Vo₄ defects. This result is in agreement with that of Oviedo *et al.* [34].

Using AIMD simulations, a spontaneous water dissociation is observed on a perfect, Vo₁, Vo₂, and Vo₄ rutile (110) surfaces. As shown in Figs. 2(a)–(d), identical dissociation processes are observed on the perfect and Vo₁ and Vo₄ defective surfaces. The water molecule adsorbed on a Ti_{5c} site gives its proton to another water molecule with a hydrogen bond to the lattice O_{br}, forming H₃O⁺. Another hydrogen-bonded proton of this intermediate structure transfers to the corresponding O_{br}, which leads to a formation of OH_b and terminal hydroxyl (OH_t). Therefore, our simulations show that intermolecular hydrogen bonds are important in water dissociation, consistent with results in previous studies [26, 27, 36]. At the interface between liquid water and Vo₁ TiO₂ (110) surface, a water molecule adsorbed on a Ti_{5c} site dissociates, while a water molecule adsorbed on the Vo₁ site remains unaffected throughout the simulations. This confirms that the Vo₁ defect is not an active site for water dissociation. The water dissociation at the Vo₂ TiO₂ (110) surface exhibits a different behavior, as shown in Fig. 2(c). A water molecule adsorbed on Ti_{5c} next to the Vo₂ gives its proton to O_{br} directly through a hydrogen-bonding interaction, and then the terminal hydroxyl populates the Vo₂ defect. In order to provide further insights into the dissociation process, we calcu-

late the distance variation between the bridge oxygen atom and attached proton, and that between the oxygen atom in the dissociative water molecule and its missing proton (Fig. A1, Supporting information). The results show that the O–H distance becomes larger than 1.0 Å after the water dissociation, and that all bridging hydroxyls can stably exist as the O_{br}–H distances remain ~1.0 Å after the water dissociation. A dissociation of only one water molecule is observed during each simulation without any recombination, which indicates that the dissociation of the water molecule can prevent other water molecules to split. It is worth noting that no water dissociation is observed on the Vo₃ defective surface during the simulation, which demonstrates that the Vo₃ can even make the rutile (110) surface more inert to water.

The average density profiles of water along the surface normal before and after the water dissociation are calculated, as shown in Fig. 3. An obvious stratification of water is observed. Regarding the location of the first (main) adsorption layer, the AIMD predicts a height of ~2.15 Å from the surface, which is in agreement with previous simulation results of 2.10 Å and 2.07 Å [28, 29]. The second layer is centered at a height of ~3.75 Å, consistent with other simulation and experimental results [28, 29]. For the perfect TiO₂-(110)/water interface, the first largest peak corresponds to a density of ~4.92 g/cm³ before the water dissociation, smaller than the value of 6.12 g/cm³ after the water dissociation, which indicates that TiO₂ is more strongly bonded to water after the water dissociation. A similar phenomenon is observed for the Vo₁ and Vo₂ defective surfaces; for example, the first peak of the water density increases from 5.13 g/cm³ to 6.08 g/cm³ after the water dissociation for the Vo₁ surface, and from 4.14 g/cm³ to 5.66 g/cm³ after the water dissociation for the Vo₂ surface. Therefore, the AIMD simulations demonstrate that the surface hydrophilicity

**Fig. 2** MD snapshots of water dissociation processes on a (a) perfect, (b) Vo₁, (c) Vo₂, and (d) Vo₄ rutile (110) surfaces. The dashed circles outline the locations of the oxygen vacancies.

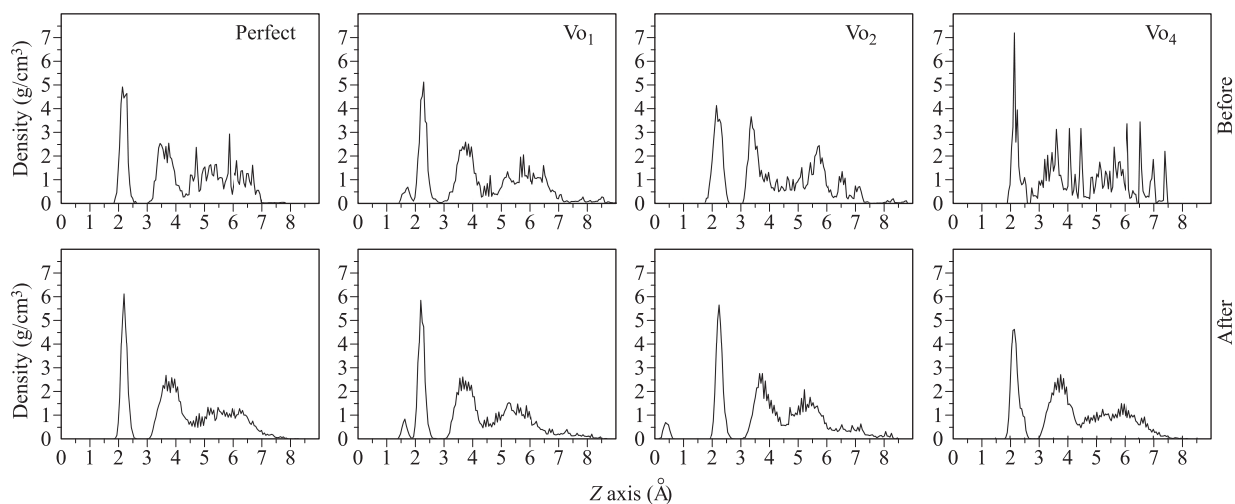


Fig. 3 Average densities of water along the surface normal before and after the water dissociation on a perfect, Vo_1 , Vo_2 , and Vo_4 TiO_2 (110) surfaces.

of TiO_2 is significantly enhanced by the water dissociation. We cannot make a definite conclusion owing to the too fast reaction rate on the Vo_4 interface.

Further, we study the thermodynamics of water splitting on the perfect and defective rutile (110) surfaces. According to the energy values before and after the water dissociation listed in Table 2, all of these reactions are exothermic, which indicates that the dissociative states are more stable than molecular adsorption states. The dissociation state on the Vo_2 interface is the most stable, followed by that on the Vo_1 rutile-(110)/water interface. The energy for the water dissociation on the Vo_4 defect is not provided, owing to the too fast dissociation reaction, which occurs before the system can be fully equilibrated and reach the target temperature.

In order to understand the kinetics of the water dissociation on the different TiO_2 surfaces, the free-energy surfaces for the reactions are studied using metadynamics [37, 38] with an appropriate collective variable (CV) as a function of the O–H bond length in the dissociative water. For a complete sampling, numerous Gaussian-type potentials are added to the free-energy surface to assist the system in overcoming a large free-energy barrier. The sum of the Gaussian potentials is opposite to the free-energy; therefore, we can obtain the free-energy of the water dissociation processes, as shown in Fig. 4. During these simulations, one Gaussian hill is spawned

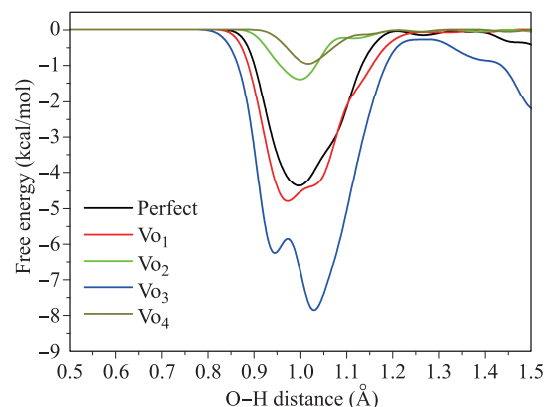


Fig. 4 Free energies for water dissociation at the different interfaces.

Table 2 Energy changes for the water dissociations at the different surfaces; $\Delta E = E_{\text{aft}} - E_{\text{bef}}$, where E_{bef} and E_{aft} denote the average energies before and after the water dissociation, respectively.

interface	perfect	Vo_1	Vo_2	Vo_3
$\Delta E/\text{eV}$	-0.16	-1.23	-2.09	-0.41

every 10 fs; the height of the hill is 10^{-4} Ha. The Vo_2 and Vo_4 defects exhibit extremely low free-energy barriers of 1.38 kcal/mol and 1.51 kcal/mol, respectively, which indicates that the water dissociation on these two defects can even occur at a very low temperature. On the other hand, at the perfect and Vo_1 interfaces, the dissociative water molecule adsorbs on the Ti_{5c} sites, so similar free energy barriers for water dissociation on the perfect (4.36 kcal/mol) and Vo_1 (4.79 kcal/mol) rutile (110) surfaces are obtained. These barriers are high for a reaction that spontaneously occurs at room temperature, which indicates that the dissociation adsorption rates for these two surfaces could be sensitive to temperature, consistent with previous experimental studies [39]. In order to check whether the Vo_1 defect is an active site, we considered five independent MD trajectories. Two trajectories show that the water molecule adsorbed on the Ti_{5c} site dissociates, while that in the Vo_1 site remained unaffected; no water dissociation was observed for the other three trajectories with the Vo_1 de-

fect. In the metadynamics simulation, a free barrier as high as 12.36 kcal/mol is obtained, which indicates that the dissociation of water on the Vo_1 site is kinetically unfavorable. Therefore, according to the MD simulation, the Ti_{5c} site, rather than the Vo_1 site, is the active site for water dissociation. The reaction rate is very sensitive to temperature. The free energy barrier of water dissociation on Vo_3 obtained from the metadynamics is as high as 7.85 kcal/mol, which reveals that the reaction is kinetically unfeasible at ambient conditions. This result also supports the conclusion that Vo_3 is inert to water dissociation.

4 Conclusion

Using AIMD simulations, we investigated water dissociation on rutile (110) surfaces. The water molecule adsorbed on the Ti_{5c} site of the perfect rutile (110) surface needed to overcome a free-energy barrier of 4.36 kcal/mol, which was too high for a spontaneous reaction at a low temperature; consequently, no dissociation was observed in some of the low-temperature experiments. In addition, the most common defect (Vo_1)

on the rutile (110) surface could not promote the dissociation of water, while other unstable oxygen vacancies such as Vo_2 and Vo_4 could significantly enhance the water dissociation rate. This is opposite to the established understanding that Vo_1 defects are active sites for water dissociation accompanied by two OH_b . In addition, the kinetics of water dissociation on the perfect and defective TiO_2 surfaces reveal that all dissociation states have higher thermodynamic stabilities than the molecular adsorption state. Furthermore, the dissociation adsorption of water can significantly increase the hydrophilicity of TiO_2 . Our findings provide a detailed understanding of the interactions between water and rutile surfaces, which is of importance for applications of TiO_2 materials.

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Appendix A Supporting information

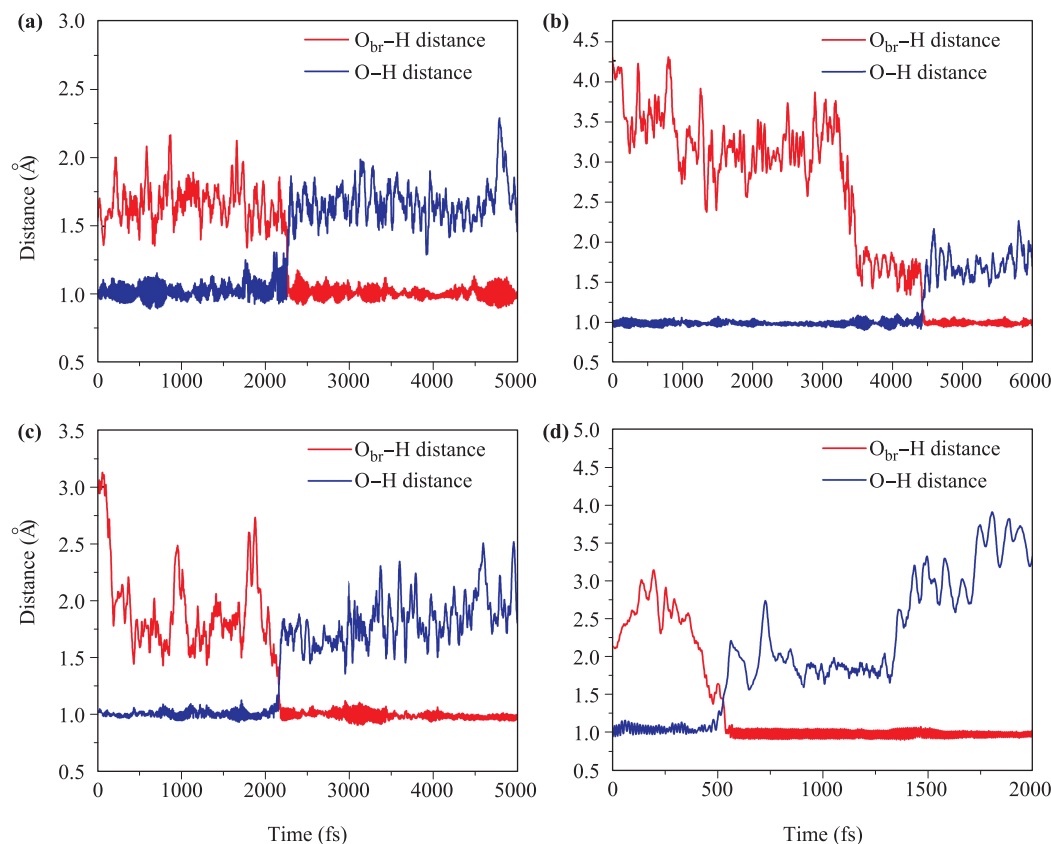


Fig. A1 The variation of OH distances before and after water dissociation on (a) perfect, (b) Vo_1 , (c) Vo_2 , and (d) Vo_4 rutile (110) surfaces, respectively. $\text{O}_{br}\text{-H}$ distance stands for the distance between the bridge oxygen atom and the attached hydrogen, and O-H distance is the distance between the oxygen atoms in the dissociative water and its missing protons.

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