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The Reactivity of Anatase TiO₂ (211) Surface and the

Bond-Charge Counting Model

Jing Xu, Li-Fang Xu, Jian-Tao Wang and

Annabella Selloni

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Abstract

In this chapter, we intend to present a generic understanding of surface reactivity and water dissociation on TiO_2 surfaces through a study of anatase TiO_2 (211) surface—an idea model surface containing both four-coordinated Ti atom (Ti₄) and five-coordinated Ti atom (Ti₅). Our first-principles calculations show that the (211) surface is a high reactivity surface and reveal that water molecule can be easily dissociated on a Ti₄ site while it hardly dissociates on Ti₅ site. Furthermore, we introduce bond-charge counting model to clarify the mechanism. More generally, after an intensive investigation of literature, we found that the bond-charge counting model is applicable to all anatase and rutile TiO₂ surfaces including step edges and vacancies where the reactivity of surfaces enable to dissociate water attribute to the existence of Ti₄ atom or equivalent Ti₄ atom.

Keywords: TiO₂ surfaces, surface reactivity, water dissociation, first-principles calculations, bond-charge counting model

1. Introduction

Titanium dioxide is a semiconductor-based heterogeneous photocatalysis material which received more and more interest. In nature, TiO_2 crystallizes in three different structures: rutile, anatase, and brookite, all formed by TiO_6 octahedra connected by shared edges and/or corners; rutile is the thermodynamically most stable bulk phase, while anatase is very common and stable in nanomaterials. As a major polymorph of TiO_2 , anatase TiO_2 is the most widely studied phase and is extensively used in many industrial applications such as photovoltaic



© 2017 The Author(s). Licensee InTech. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. [cc] BY cells, photo and electrochromics, photocatalysis, photonic crystals, smart surface coatings, and sensors [1–9]. In all applications, the surface structure plays a key role, as the surface reactivity and physicochemical properties depend strongly on the exposed crystallographic facet. Therefore, the search for high reactivity TiO_2 surfaces is a topic of great interest and an area of intense activity.

The rutile (110) surface has been investigated early [10–12]. Anatase is less stable than rutile, but more efficient than rutile for applications. Many studies of the anatase TiO_2 surface focus on the (001) and (101) surfaces [13–20]. Theoretical studies [13–17] show that the (101) surface is the thermodynamically most stable surface with a small surface energy of 0.49 J/m², while the (001) surface is the highest reactivity surface with a high surface energy of 0.98 J/m². More recently, using different dopants, adsorbates, or solvated species, anatase TiO_2 nanocrystals exposing various crystalline facets have been prepared, including low-index facets such as (001) facets [18, 19], (100) [21–24], (010) [25, 26], (101) [27–32], (110) [33], and (111) [34], and high-index facets such as (103), (105), (106), (201), (301), and (401) [35–39]. Besides, many researchers have made extensive investigation on surface defects since those defects, e.g., step edges [40–42] and O vacancy [43, 44] are intrinsic on the surfaces of crystalline materials, which strongly influence the surface chemistry.

Since the discovery of photocatalytic splitting of water on a TiO_2 electrode in 1972 [1], the interaction of TiO_2 surfaces with water is of special interest. The structure of the hydrated surfaces is important not only because water is always present on TiO_2 surfaces, but also because it can help understand and control the catalytic and (photo) electrochemical properties of this material. In fact, different water adsorption states have been found; for example, water favors molecular adsorption on the anatase (101) surface and dissociative adsorption on the (001) surface [13].

There is still controversy for water adsorption on the TiO_2 surface based only on the DFT total energy calculations, e.g., on rutile (110). Despite numerous studies on this topic in literature, the mechanism of water dissociation on TiO_2 surfaces remains to be clarified. Moreover, there is still a lack of a generic understanding of different surfaces including surfaces with steps and vacancies.

Due to a recent experiment, a large percentage of exposed (211) facet has been prepared and it is found that the (211) surface can effectively improve the photocatalytic activity of TiO_2 for water dissociation reactions [45, 46]. Since the surface exposes both Ti_4 and Ti_5 atoms, the anatase (211) surface is studied in this work as an ideal model surface to illustrate the mechanism of water dissociation on TiO_2 surface [47]. The Ti_4 atom plays a critical role for splitting water molecule. Furthermore, we introduce a bond-charge counting model according to TiO_2 structure and conclude that two unsaturated Ti bonds are the necessary conditions for splitting water on the surface. Then, we examine as much as possible TiO_2 surfaces and find the model is applicable to all surfaces.

The paper is organized as follows: the reactivity of anatase TiO_2 (211) surface is briefly reviewed in Section 2; then, we propose the bond-charge counting model and give some typical examples in Section 3; finally, we present conclusion remakes in Section 4.

2. The reactivity of anatase TiO_2 (211) surface

2.1. Surface structure and stability

We begin with the experimental result. Recently, a large percentage of exposed (211) facet has been identified by X-ray diffraction (XRD) on N-doped TiO₂ film deposited using RF magnetron sputtering [45]. N-doped TiO₂ films were deposited on quartz glass substrates (2 cm × 4 cm) by RF reactive magnetron sputtering. The crystalline structure of the as-deposited N-doped TiO₂ films was identified by X-ray diffraction (XRD). **Figure 1** shows the XRD patterns of N-doped TiO₂ film. Diffraction peaks observed at $2\theta = 25.28^{\circ}$, 36.95°, 37.88°, 38.55°, 48.05°, 54.09°, 54.88°, 62.67°, and 68.76° correspond well with (101), (103), (004), (112), (200), (105), (211), (204), and (116) planes of anatase phase of TiO₂. It can be seen that N-doping can greatly influence the growth orientation of anatase TiO₂ particles. As shown in **Figure 1**, the intensities of the (004), (112), (200), and especially (211) peaks become stronger, while (101) peak become weaker for the N-doped TiO₂ film, compared with those of the undoped TiO₂ film. Especially, the increase of exposed (211) facets can effectively improve the photocatalytic activity of TiO₂ for water dissociation reactions [46], showing the high reactivity of exposed (211) facets.



Figure 1. The X-ray diffraction (XRD) on N-doped TiO_2 film.

Motivated by the above experimental findings, in a recent theoretical work [47], we have made a systematic study of the surface reactivity and water adsorption on anatase (211) using *ab initio* calculations. Calculations have been performed by the Vienna ab initio simulation package (VASP) [48–50] with all-electron projector augmented wave (PAW) method [51]. The generalized gradient approximation (GGA-PW91) [52] is set as the exchange and correlation functional. The valence states $3d^24s^2$ for Ti, $2s^22p^4$ for O, and $1s^1$ for H are used with an energy cutoff of 500 eV for the plane wave basis set. The calculated lattice constants for bulk anatase TiO₂ are used to construct the diverse facets listed in **Table 1**. The anatase (211) surface was modeled by a slab of six layers with a unit surface cell of 7.706 Å × 5.501Å × 27.677Å ($\gamma = 101.44^\circ$) comprising a total of 54 atoms separated by a vacuum region of 12 Å. The Monkhorst-Pack scheme [53] was adopted for the Brillouin zone integration with a 6 × 6 × 1 k-point mesh. All atoms are relaxed during geometry optimizations with the given surface cell. Convergence criteria employed for both the electronic self-consistent relaxation and the ionic relaxation were set to 10^{-6} eV and 0.01 eV/Å for the total energy and Hellmann-Feynman force, respectively.

We firstly discuss the surface stability. The stoichiometric unrelaxed termination of the (211) surface is shown in Figure 2(a) There are five under-coordinated and four fully-coordinated atoms exposed to the vacuum. The five under-coordinated atoms include three inequivalent twofold-coordinated oxygen atoms denoted by O₂₁, O₂₂, and O₂₃, a fourfoldcoordinated Ti₄ and a fivefold-coordinated Ti₅, respectively. The four fully-coordinated atoms are O₃₁, O₃₂, O₃₃, and Ti₆ [see Figure 2(a)]. Different from (001) and (101) surfaces [12], fourfold-coordinated Ti₄ atoms are present on the (211) surface. Figure 2(b) shows the optimized anatase (211) surface. After relaxation, the (211) surface shows a very corrugated structure, with a characteristic, saw tooth-like profile along the [1-31] direction. All under-coordinated oxygen (O_{2i}) atoms are displaced outward, while the under-coordinated Ti₄ and Ti₅ atoms are relaxed inward. Both angles $\angle Ti_4 - O_{22} - Ti_5$ and $\angle Ti_5 - O_{31} - Ti_6$ become smaller, 100.3° and 147.7°, respectively. The largest relaxations are those of the fully-coordinated oxygen O_{31} , which relaxes outward by approximately 0.35 Å, and O_{32} , which relaxes inward by approximately 0.34 Å. Meanwhile, the surface atoms form fourmembered-ring (O-Ti-O-Ti) structures on the surface. These O-Ti-O-Ti rings are slightly deformed and the distances between oxygen atoms in these rings increased from the bulk value of 2.458 Å to 2.492–2.515 Å.

Facet	N _{at}	E (J/m ²)	n(Ti ₅) (10 ⁻² Å ⁻²)	n(Ti ₄) (10 ⁻² Å ⁻²)	n(O ₂) (10 ⁻² Å ⁻²)
(101)	24	0.52	5.1		5.1
(001)	18	1.08	6.9		6.9
(211)	54	0.97	2.4	2.4	7.2
(103) _s ¹⁴	48	0.99		3.5	
$(110)^{14}$	42	1.15		3.8	

Table 1. Calculated surface energies (E in J/m²) and surface densities $Ti_{5'} Ti_{4'}$ and oxygen O_2 atoms [n(Ti_5), n(Ti_4), and n(O_2)]. N_{at} is the total number of atoms in the slab.

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Figure 2. Structures of the unrelaxed (a) and relaxed (b) anatase (211) surfaces. The O and Ti atoms are in red and grey spheres, respectively, indicated with different coordination numbers.

To investigate the surface stability, we calculated the electronic density of states (DOS) for bare anatase (211) surface after relaxation. The result is shown in **Figure 3** in comparison with the bulk TiO_2 . There is a big gap, as large as in bulk, in the DOS of relaxed bare anatase (211) surface, which indicates the chemical stability of the (211) surface.

2.2. Surface energetics

The surface energies for (101), (001), and (211) are estimated using the expression, $E = (E_{tot} - nE_{bulk})/A$, where E_{tot} is the total energy of the slab and E_{bulk} is the energy of TiO₂ unit in the bulk, *n* is the number of TiO₂ units in the slab, *A* is the total surface area of the slab, including both sides of the slab. The calculated surface energies are listed in **Table 1**. The surface energy of the (001) surface is estimated to be 1.08 J/m², which is nearly twice that of the most stable anatase (101) surface (0.52 J/m²), in agreement with previous theoretical studies [14]. Similarly, the (211) surface has a high surface energy of 0.97 J/m², close to that of the (001) surface.

The value of the surface energy is known to be strongly correlated to the presence of undercoordinated Ti atoms on the surface [14]. The (001) surface energy is large because of the high surface density of Ti₅ (see **Table 1**). However, the surface energy of anatase (211) is large even



Figure 3. Electronic density of states for the bulk TiO_2 and bare anatase (211) surface after relaxation. The Fermi level is set at 0 eV.

though the total density of under-coordinated Ti_4 and Ti_5 atoms is smaller than that on the (001) surface [even smaller than on (101)]. This result already suggests that Ti_4 atoms, with two unsaturated bonds, have a higher reactivity than Ti_5 atoms with one unsaturated bond. A similar behavior was found also for the anatase (110) and (103)_s surfaces [14].

From the above calculation results in subsections 2.1 and 2.2, we can see that the (211) surface has a large electronic band gap and high surface energy. It shows those two surface properties, stability and reactivity, seem contradictory, could uniformly hold on the (211) surface.

2.3. Water adsorption

We next present a detailed picture for the adsorption of water on the TiO₂ (211) surface by considering one, two and three adsorbed water molecules corresponding to various coverages $\theta = 1/3$, 2/3 and 1 ML per surface unit cell, respectively.

For a single water molecule (1/3 ML), there are four possible adsorption modes, corresponding to different adsorption positions (Ti₄ or Ti₅) and different (molecular or dissociative) adsorption conformations. *For molecular water adsorption on Ti*₅ site [see **Figure 4(a)**], the oxygen of water bonds to Ti₅ with bond length of 2.226 Å, and two surface oxygen atoms via



Figure 4. Side (left) and top (right) views of the structures for water adsorption on the anatase TiO_2 (211) surface. (a) Molecular water on a Ti_5 site. (b) Dissociative water on a Ti_4 site. (c) Mixed state with one dissociative H_2O on Ti_4 and one molecular H_2O on Ti_5 sites at 2/3 ML. (d) Mixed state on Ti_4 and Ti_5 sites at 1 ML coverage. The O atom of water is plotted in orange, the H atom is in blue, and the H-bond is indicated by a dashed line.

Ti₅ form two bond angles $\angle O_{water}$ -Ti₅- $O_{22} = 99.85^{\circ}$ and $\angle O_{water}$ -Ti₅- $O_{31} = 77.18^{\circ}$, close to the bulk angles of 101.90° and 78.10°, respectively. Upon water adsorption, the Ti₅ site becomes sixfold-coordinated: the Ti atom has six Ti-O bonds with their orientations similar to those in the bulk. At the same time, the two hydrogen atoms of water form H-bonds (HBs) with two neighboring surface under-coordinated oxygen atoms, O_{21} and O_{23} , with bond lengths 2.339 and 1.873 Å, respectively. As a result, the computed molecular adsorption energy on the Ti₅ site is 0.784 eV. For dissociative water adsorption on Ti₅ site, the water molecule is dissociated into hydroxyl (OH) and H fragments. The OH group bonds to Ti₅ with a length of 1.857 Å and then further bonds to O_{23} with a weak HB. The H fragment forms a new OH moiety with a nearby O_{21} . As a result, the adsorption energy for a dissociated water on Ti₅ site is 0.77 eV, which is slightly smaller than that of molecular adsorption. Thus, molecular adsorption is preferred on Ti₅ site.

On the other hand, for molecular water on a Ti₄ site, the oxygen atom of water binds to Ti₄ with a bond length of 2.207 A, and Ti₄ is located at the position of one of the bulk Ti-O bonds indicating that there is one Ti bond left. The Ti₄ adsorption site becomes fivefold-coordinated and the adsorption energy for molecular water on Ti₄ site is estimated to be 0.99 eV. Finally, for dissociative water on Ti₄ site [see Figure 4(b)], the O atom of the OH group is strongly bonded to the Ti_{A} atom with a short bond length of 1.847 Å (as compared to the Ti-O bond length of 2.207 Å in the molecular adsorption case) so that the Ti₄ adsorption site becomes fivefold-coordinated. It is worthwhile to point out that the adsorption position of the O atom of the OH group does not correspond to the position of a bulk Ti-O bond, but is in the middle of the two missing bulk Ti-O bonds, and the orientation of Ti₄-O_{OH} bond clearly deviates from its direction in the bulk, as shown by the two bond angles $\angle O_{OH}$ -Ti₄- O_{33} = 130.86° and $\angle O_{OH}$ -Ti₄- O_{32} = 119.91°. This adsorption geometry with short bond length and a middle position indicates that the dissociated water interacts with two unsaturated Ti_4 bonds indeed. Furthermore, the hydrogen atom of OH forms a weak HB with a neighboring O₂₃ atom of length 2.534 Å. The dissociated H from water interacts with a surface oxygen O₂₃ forming a new OH moiety with a bond length of 1.013 Å and further forms an HB of 1.598 Å with O_{22} . As a result, the adsorption energy for dissociated water on Ti₄ site is estimated to be 1.28 eV, which is significantly larger than the value of 0.99 eV obtained for molecular adsorption.

To obtain further insight, we show the projected densities of states of the surface with a dissociative water on a Ti_4 site and molecular water on Ti_5 site in **Figure 5**. We can see that the O-2p orbitals in the OH group are extended to a wide range between -3.2 and -0.9 eV, indicating that the O atom of OH is strongly interacting with the substrate. On the other hand, for the case with a molecular water adsorption on a Ti_5 site, all peaks from the water molecule are sharp and are simply superimposed on those of the bare surface, indicating that they interact weakly with the surface.

Combined together the above four calculation results: the adsorption energy, bond length, bond angle, and DOS, we can conclude that dissociative adsorption can *easily* happen at the Ti_4 site while *hardly* happens on Ti_5 . In fact, these different behaviors can be understood in terms of a simple model based on the bond-charge distribution, which is the key issue in this paper and will be discussed in the next section.

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Figure 5. Projected electronic density of states on anatase (211) surface (a) for O-2*s*, *p* in the OH group on Ti₄ site; (b) for O-2*s*, *p* in water on Ti₅ site; The Fermi level is set at 0 eV.

Now, let us consider more water adsorption case. For two adsorbed H₂O molecules (2/3 ML coverage), the first H₂O prefers to adsorb at a Ti₄ site in dissociative form according to the single water-adsorption results; next, another water molecule should adsorb on a Ti₄ or Ti₅ site. For the structure with one dissociated H_2O on a Ti_4 site and one molecular H_2O on a Ti_5 site [see Figure 4(c)], the O-Ti₅ bond is 2.230 Å, while the O-Ti₄ bond length is much shorter, 1.992 Å. The dissociated H combines with an O_{23} atom forming a new OH moiety and further forms a strong HB (1.590 A) with an O_{22} atom. An additional HB between two water molecules forms with a bond length of 1.775 Å, which makes two water molecules closer and changes the values of the bond angles. In this mixed structure (c), the adsorption energy is 1.045 eV/mol, which is a little larger than the averaged value of 1.034 eV [(1.284 + 0.784)/2] for the single water adsorption on Ti_4 and Ti_5 sites due to the contribution of the new HB. On the contrary, for the structure with two dissociated H₂O on Ti₄ and Ti₅ sites, the adsorption energy is estimated to be 0.991 eV/mol, which is about 0.036 eV smaller than the averaged value of 1.027 eV [(1.284 + 0.770)/2] for the single water adsorption and also 0.054 eV lower than that of the mixed configuration. These results confirm that molecular adsorption is preferred on Ti₅ in the mixed structure. Moreover, for a structure with one dissociated H₂O and one associated H₂O on Ti₄ sites and structure with two dissociated H_2O on Ti_4 sites, the adsorption energy is estimated to be 0.960 and 0.916 eV/mol, respectively. Those are clearly lower than 1.045 eV/mol for the mixed structure. Therefore, with increasing coverage, water molecules prefer to be adsorbed in a mixed form with one dissociated H_2O on a Ti_4 site and one molecular H_2O on a Ti_5 site.

Finally, we discuss the monolayer coverage where three water molecules are adsorbed per surface unit cell. Following the 2/3 ML result with one dissociated H₂O on a Ti₄ site and one molecular H₂O on a Ti₅ site, the third molecule would adsorb molecularly on a Ti₄ site [see Figure 4(d)]. It is an O atom that binds to Ti, with a bond length of 2.259 Å, while the two H atoms form HBs with nearby O atoms, where H-O₂₁ is 2.156 Å and H-O₂₂ is 1.907 Å. The bond length for molecular water on a Ti₅ atom is 2.221 Å, while for dissociated water on Ti4 it is 1.934 Å. Two bond angles $\angle O_{OH}$ -Ti₄- O_{33} and $\angle O_{water}$ -Ti₄- O_{32} are 100.69° and 79.00°, respectively. Thus, all Ti atoms are sixfold-coordinated with orientations similar to those of a bulk Ti atom. The dissociated H is captured by an O₂₃ atom to form an OH moiety and further interacts with an O₂₂ atom forming an HB of 1.835 Å. An additional HB of 1.652 Å also exists between these two adsorbed H₂O. All surface atoms become saturated. The adsorption energy has a larger value of 0.946 eV/mol for this mixed configuration on Ti₄ sites. For comparison, we also consider configuration with two dissociated water molecules on Ti₄ sites and one molecular H₂O on Ti₅. Though all surface atoms are also saturated, its adsorption energy is 0.909 eV/mol, which is lower than that of the mixed configuration with one dissociative and one molecular adsorption on Ti₄. Thus, molecular adsorption is favored on Ti_4 for the second water molecule. Meanwhile, for structure with one intact water on Ti₄ and two dissociated water molecules on Ti₄ and Ti₅ sites, the computed adsorption energy is 0.902 eV/mol; for structure with three dissociated water molecules on $Ti_{4'}$ Ti_4 , and Ti_5 sites, the adsorption energy is 0.833 eV/mol (see **Table 2**). These results suggest that a mixed water configuration is formed at monolayer coverage, with one dissociated water on Ti₄, one molecular water on Ti_4 , and one molecular water on Ti_5 .

Our results show that Ti_4 is an only active site which can dissociate water. Once Ti_4 is saturated with a water, there will be no more water can be dissociated. It corresponds well with the experimental observations that the dissociation does occur only at low coverages and the probability of H₂O dissociation is decreased with increasing surface coverage. That is the purpose that we describe adsorption in detail from low water coverage to full coverage in this section.

3. The bond-charge counting model for TiO₂ surfaces

3.1. The mechanism and a simple phenomenological model

According to the above results, the adsorption energies of water on a Ti_4 site are always larger than those on a Ti_5 site (see **Table 2**). Moreover, a water molecule can be easily dissociated on a Ti_4 site while it hardly dissociates on Ti_5 . We use a word "hardly" here because there is still controversy for the adsorption of H_2O on Ti_5 site. In our case, the adsorption energy for a molecular adsorption on Ti_5 site is only slightly higher than the dissociated one, which is not adequately to convince that water cannot be dissociated on Ti_5 . Actually, there are a lot of arguments on this issue in literature. Lindan et al. [12] suggested that dissociative adsorption happened on the rutile

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ure 4(a)	Ti ₅ Ti ₄	Ti ₅	0.784 0.770 0.994
1re 4(b)	Ti ₄	Ti ₅	0.770 0.994 1.284
11re 4(b)	Ti ₄	Ti	0.994
1re 4(b)		Ti	1 28/
···· 4(-)		4	1.201
tre 4(c)	Ti ₅	Ti ₄	1.045
		Ti ₄ ,Ti ₅	0.991
GC	Ti ₄	Ti ₄	0.960
		Ti ₄ , Ti ₄	0.916
1re 4(d)	Ti _{4,,} Ti ₅	Ti_4	0.946
-	Ti ₅	Ti_{4} , Ti_{4}	0.909
	Ti ₄	$Ti_{4}Ti_{5}$	0.902
		Ti_{4} , Ti_{4} , Ti_{5}	0.883
1	re 4(d)	Ti_{4} re 4(d) $Ti_{4,,,}Ti_{5}$ Ti_{5} Ti_{4} Ti where and H. OH = disserved the transmission of trans	$\mathbf{Ti}_{4}, \mathbf{Ti}_{5}$ $\mathbf{Ti}_{4}, \mathbf{Ti}_{4}, \mathbf{Ti}_{4}$ $\mathbf{Ti}_{4}, \mathbf{Ti}_{4}$ $\mathbf{Ti}_{4}, \mathbf{Ti}_{4}$ $\mathbf{Ti}_{5}, \qquad \mathbf{Ti}_{4}, \mathbf{Ti}_{4}$ $\mathbf{Ti}_{5}, \qquad \mathbf{Ti}_{4}, \mathbf{Ti}_{4}, \mathbf{Ti}_{5}$ $\mathbf{Ti}_{4}, \mathbf{Ti}_{4}, \mathbf{Ti}_{5}$ $\mathbf{Ti}_{4}, \mathbf{Ti}_{4}, \mathbf{Ti}_{5}$ $\mathbf{Ti}_{4}, \mathbf{Ti}_{4}, \mathbf{Ti}_{5}$ $\mathbf{Ti}_{4}, \mathbf{Ti}_{5}, \qquad \mathbf{Ti}_{5}, \mathbf{Ti}$

Table 2. Adsorption energy (Δ H in eV) per H₂O molecule on anatase (211) at various water coverages θ = 1/3, 2/3, and 1 ML.

(110) surface, while Schaub's result [43] is in contrast to that. However, there is an important case that water is indeed dissociated on anatase (001) surface with only Ti_5 atom [13]. Therefore, whether Ti_5 atom can dissociate water is still a matter for controversy on TiO₂ surfaces.

Many research works are only concentrated on the total energy calculations in literature. DFT total energy calculations are a definitely powerful tool. But here there is a shortcoming that total energy calculations just tell the total energy of the system, not the local interaction energy. For example, in dissociative adsorption, the total energy includes the adsorption site of the dissociated H as well as H-bond energy at high coverage case. Thus, it is difficult to extract the onsite interaction energy and it is hard to obtain a clear conclusion just from the total energy. All those controversies come from the information of total energy and less considerations for the reaction mechanism. Therefore, it is necessary to think it over from the origin of physics and chemistry beyond total energy calculation.

The water dissociation on surface is a chemical adsorption, which can be regarded as a chemical reaction analogue to a chemical displacement reaction, e.g., $2Na + 2H_2O = 2NaOH + H_2\uparrow$. In this displacement reaction, the necessary condition is that more active metal atom can substitute the less active metal atom or hydrogen. Also, from a physical point of view, the O atom in water must gain more electrons that H atom provided so that such a dissociation process happens by losing an H atom. From these considerations, we propose a simple bond-charge counting model based on the charge distribution on Ti bond in TiO₂.

In bulk $TiO_{2'}$ each Ti atom has six nearest neighboring O atoms and Ti atom has four outmost electrons, i.e., each Ti⁴⁺ ion is surrounded by an octahedron of six O²⁻ ions. Thus, on an average,

each Ti atom can offer 4/6 electron charge at each Ti-O bond. It holds for both rutile and anatase since they have the same TiO₆ octahedra structure. Therefore, we could make a simple bond-charge counting for this system. When a Ti₄ atom interacts with the oxygen atom of H₂O, two unsaturated Ti bonds participate in the interaction and offer about 4/3 electron charge to this O atom by forming a strong bond [see **Figure 4(b)**]. Thus, it satisfies the reaction requirement and Ti₄ is more active than H atom. Then, one H atom can be released from the water molecule on a Ti₄ site. In fact, one H atom dissociates spontaneously from the water molecule as this adsorbs on a Ti₄ atom. On the other hand, Ti₅ can only provide about 2/3 electron charge to the water O atom, less than the charge contribution from an H atom. Therefore, Ti₅ is less active than H atom and hardly causes dissociation of an H atom. Although there is very little difference in energy (0.014 eV) between molecular and dissociated structures, we can clearly judge that water favors molecular adsorption and is unfavorable on Ti₅ site.

The essence of the model is qualitatively taking account of average charge on each Ti bond in TiO_2 material. The model is phenomenological and does not intend to provide the precise value of charge transferred during interaction due to the complex of 3d orbitals of Ti atom in TiO_6 octahedra. Nevertheless, the bond-charge counting model clarifies the intrinsic charge difference between Ti_4 and Ti_5 atoms on surfaces where Ti_4 can provide more than one electron and Ti_5 much less one electron. The necessary condition for water splitting is that the surface Ti atoms must provide more than one electron to O atom of water. The charge contributed from a single Ti bond is not sufficient for water dissociation. Therefore, two unsaturated Ti bonds satisfy the condition corresponding to the four-coordinated Ti_4 atom that has chemical reactivity, while Ti_5 atom not.

3.2. Typical examples

In order to verify this model, we have made an intensive investigation for TiO_2 surface as much as we could find in literature including steps and vacancies. We found that all reactive surfaces splitting water are associated with Ti_4 atom or equivalent Ti_4 atom without any exception. We are not able to exhaust all surfaces here, rather list typical and important surfaces in different geometric categories as follows.

3.2.1. Surfaces with Ti_4 atom

We start the survey from the TiO_2 surfaces with Ti_4 atoms. At anatase surfaces, the (110) and (103)s contain Ti_4 atoms. Therefore, their surface energies are 1.15 and 0.99 J/m², respectively [14]. Those rather high values indicate that the surfaces have a very high reactivity contributed from Ti_4 atoms.

3.2.2. Surface with only Ti_5 atom

The surfaces with only Ti5 atom are more interesting. Whether the surfaces can dissociate water is controversy. We will see it strongly depends on its surface energy. As anatase (001) surface, the surface energy has a rather high value of 0.98 J/m² indicating a high reactivity. Thus, it is clearly pointed out in Ref. [13] that the structure of the dissociated state (in **Figure 6(a)** same

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Figure 6. (**Figure 3** in Ref. [13]) Atomic structure (side view) for adsorbed water molecule(s) on anatase (001). (a) Dissociated state. (b) Molecular state. (c) Mixed state. Gray lines in (b) and (c) indicate hydrogen bonds. Bond lengths are in Å.

as in **Figure 3(a)** in Ref. [13]) is characterized by the breaking of the bond between the bridging 2c oxygen and the Ti_5 atoms involved in the adsorption, i.e., the Ti_5 atom actually becomes fourfold-coordinated after breaking its bond to a bridging O atom. Therefore, the dissociative water is absorbed on an equivalent Ti_4 site. It is expected that such phenomenon of Ti_5 atom breaking bond with neighboring oxygen becomes an effective Ti_4 atom which would be held for the anatase (103), surface with the high surface energy of 0.9 J/m².

However, for the other surfaces only containing Ti_5 atoms, their surface energies are very small. The values are 0.49 and 0.58, and 0.35 J/m² for anatase (101) and (100), and rutile (110), respectively. Note that the rutile (110) surface has smallest surface energy. Thus, the anatase (101) [13] and rutile (110) [11] are thermodynamically most stable structures. We can rule out the possibility of water dissociation on those surfaces [10].

Combined with the surface energy, we may estimate which surface with only Ti_5 atom can dissociate water by breaking a Ti bond. According to calculations, the surface energy should approach to ~1 J/m². For the high reactive surfaces with only $Ti_{5'}$ the Ti_5 atoms eventually become too effective Ti_4 atoms during the interaction.

3.2.3. Surfaces with steps

Step edges are the most common intrinsic defects on the surface. In this subsection, we give two examples of steps on two most stable surfaces, anatase (101) and rutile (110) surface.

Gong et al. [40] have made an intensive investigation on anatase (101) surface. The structure models of step edges they studied are shown in **Figure 7**. We can divide those surface step structures into two categories with Ti₄ (in **Figure 7(a)**, (**d**), (**e**), (**f**), and (**h**)) and without Ti₄ atoms (in **Figure 7(b**), (**c**), and (**g**)). Then, we recapitulate their surface energy calculation results γ (θ) in unit 10⁻²eV/Å² and rearrange in an order of containing Ti₄ and Ti₅ atoms as follows:

AI(Figure 7(a))	5.36	4.68	4.34	Ti ₄
CI(Figure 7(e))	5.49	4.81	4.46	Ti_4
CII(Figure 7(f))	6.22	5.22	4.78	Ti_4
E(Figure 7(h))	6.82	5.86	5.34	Ti_4
AII(Figure 7(b))	4.60	4.24	4.06	Ti ₅
BI(Figure 7(c))		3.66	3.59	Ti ₅
D(Figure 7(g))	4.52	4.11	3.94	Ti ₅

We omit the labels of vicinal surfaces here for simplicity. The surface energies with Ti_4 are larger than that with Ti_5 in each column. Gong et al. further studied water adsorption on D, BI, and AII with Ti_5 atom (see Supplementary Information in Ref. [40]). On D-type step edge, both molecular and dissociative H_2O adsorption can occur, but energy difference is much smaller than on flat TiO₂ (101). For BI step, the adsorption energies are smaller than that on the



Figure 7. Structure models of step edges A-E on anatase (101) (Figure 2 in Ref. [40]).

(101) surface. Note BI has the smallest surface energy among all step structures. On the least stable AII with the highest surface energy among steps containing Ti_5 atom, the water adsorption is found to be similar to the anatase (001) surface where water is dissociatively adsorbed with adsorption energy 1.28 eV. Again, here surface Ti_5 atom becomes Ti_4 by breaking a bond with neighboring oxygen.

Hong et al. [41] investigated water adsorption behavior step edges on rutile TiO_2 (110) surface using DFT calculations. They found that the < 1-10 > edge exhibits significantly enhanced water adsorption, especially dissociative adsorption, as compared to the pristine (110) surface and < 001 > step edge due to the existence of fourfold coordinated Ti₄ atoms at the < 1-10 > step edge, which lead to charge transfer to adsorbates more easily than fivefold coordinated Ti₅ atoms on the (110) surface and < 001 > step edge.

Later, Zheng et al. [42] studied the associative and dissociative adsorption of water molecules on rutile TiO_2 (110) surface with step defects by DFT calculations. The step structures were created by removing the TiO_2 unit along the <1-11 > direction and exposing the Ti₄ atoms (terminating the Ti rows of the upper terrace) and the Ti₅ atoms (see **Figure 1(a)**, (**b**) in Ref. [42]). They only considered the case of Ti bonds fully saturated. Their results show that the molecular and dissociative adsorptions of H₂O can both be observed on Ti₄ sites and the molecularly absorbed water is more favorable on the Ti₅ sites. The lowest energy corresponds to the configuration where water molecule on Ti₅ site and one dissociated and one molecular water on Ti₄ site, same as our result for anatase (211) surface [47].

Thus, dissociative adsorption is also attributed to the existence of Ti_4 atoms and/or equivalent Ti_4 atoms exposing at step edges on anatase (101) and rutile (110) surfaces.

3.2.4. Surfaces with O vacancy

Oxygen vacancy is also one of the most common defects on the surface. Again, in this subsection, we give two examples of O vacancy on two most stable surfaces, rutile (110) and anatase (101).

Schaub et al. [43] investigated the O vacancy on rutile (110) through both experiments and DFT calculation and determined the O vacancies as active sites responsible for the dissociation of water molecules. Their DFT calculation results show that the dissociation of water is only at oxygen vacancies with an adsorption energy of 0.94, while on the perfect (100) surface, water molecule binds to the surface by 0.56 eV and the dissociation of water is even endothermic by 0.23 eV. The dissociative adsorption is unfavorable on the perfect (100) surface. They explained that the large reactivity of the vacancies is associated with the high-energy defect and water dissociation is simply to refill the coordination shell of Ti underneath the vacancy. However, there will be something more than that. Note that the *two* Ti₆ atoms underneath the vacancy become Ti₅ atoms when O leaves the surface. Thus, when O atom of water is to refill the O vacancy, the *two* Ti₅ atoms interact with O of water simultaneously. Then, in this case, we should count two Ti bonds participating in interaction. Therefore, the dissociation of water is due to the combined contribution of two unsaturated Ti atoms.

On the anatase (101) surface, dissociation of water close to the oxygen vacancy is energetically favored compared to molecular adsorption. Tilocca and Selloni [44] have done a detailed calculation of energy barrier between the molecular and dissociated states. When a surface O atom is removed, the Ti_6 and Ti_5 atoms bridging this O atom tune into Ti_5 and Ti_4 , respectively. Water oxygen bonds to Ti_4 and then dissociates through a dissociation pathway. Thus, the dissociation of water on O vacancy of anatase (101) is also attributed to that Ti_4 atom.

3.2.5. Surfaces with Ti₃ atom

Recently, the three-coordinated Ti atom (Ti₃) are found on the (111) anatase TiO₂ surfaces. Xu et al [34] reported that they prepared anatase TiO₂ single crystals exposed (111) facet. Their DFT calculations showed that the (111) facet has a much higher surface energy of 1.61 J/m², which is attributed to the large percentage of under-coordinated atoms. They also found that this material has much higher photocatalytic activity than other surfaces. Here, there are Ti₃ and Ti₅ atoms with the ratio 1:3 on the (111) surface. According to our model, the Ti₃ atom could contribute two electrons participating interaction. Thus, it is expected that two water molecules could be dissociated on a single Ti₃ site. It could explain the (111) surface has much higher photocatalytic activity than other surfaces.

4. Conclusions

In conclusion, we use the anatase (211) surface as an idea model surface, containing one Ti_{4} and one Ti₅ under-coordinated atoms in unit cell, to investigate their distinct properties. Our ab initio calculations show that the (211) surface is indeed a high reactivity surface with a high surface energy of 0.97 J/m². In addition, the four-coordinated Ti₄ atoms with two unsaturated bonds have a stronger chemical reactivity in comparison to the Ti₅ atoms with one unsaturated bond. Studies of water adsorption suggest two distinct states of adsorbed water on the (211) surface, one related to molecular water on Ti₅ sites and the other to dissociated water on Ti₄ sites. These results indicate that the Ti₄ atoms will play a critical role in water decomposition. According to TiO₂ structure, we propose a simple bond-charge counting model where each unsaturated Ti bond contributes 2/3 charge in average. As a necessary requirement of chemical reaction, the dissociation of water only occurs when Ti atoms provide more electrons to oxygen in water than H atom. Then, we reach to a conclusion that only Ti₄ atom or equivalent Ti₄ can dissociate water. The controversy about whether Ti₅ can dissociate water is resolved that Ti₅ atom will eventually become Ti₄ by breaking bond to neighboring O atom at surface with high surface energy while the dissociation will not happen for surface with low surface energy. Besides traditional DFT total energy calculation, this model is considered in a fundamental way. We can also declare that the bond charge offered by surface Ti atoms is the mechanism for water dissociation on TiO_2 surface. Furthermore, the model is generic and applicable to both rutile and anatase surfaces including defects, e.g., step edges and vacancies.

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Author details

Jing Xu¹, Li-Fang Xu²*, Jian-Tao Wang^{2,3} and Annabella Selloni⁴

*Address all correspondence to: lfxu@iphy.ac.cn

1 Beijing Key Laboratory of Optoelectronic Functional Materials and Micro-nano Devices, Department of Physics, Renmin University of China, Beijing, China

2 Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing, China

3 School of Physics, University of Chinese Academy of Sciences, Beijing, China

4 Department of Chemistry, Princeton University, Princeton, New Jersey, USA

References

- [1] Fujishima A, Honda K. Electrochemical photolysis of water at a semiconductor electrode. Nature (London). 1972;238: 37-38. DOI: 10.1038/238037a0
- [2] Regan BO, Grätzel M. A low-cast, high-efficiency solar-cell based on dye-sensitized colloidal TiO, films. Nature. 1991;**353**: 737-740. DOI: 10.1038/353737a0
- [3] Linsebigler AL, Lu G, Yates JT. Photocatalysis on TiO₂ surface principles, mechanisms, and selected results. Chemical Reviews. 1995;**95**: 735-758. DOI: 10.1021/cr00035a013
- [4] Grätzel M. Photoelectrochemical cells. Nature. 2001;414: 338-344. DOI: 10.1038/35104607
- [5] Fujishima A, Zhang X, Tryk DA. TiO₂ photocatalysis and related surface phenomena Review, Surface Science Reports. 2008;63: 515-582. DOI: 10.1016/j.surfrep.2008.10.001
- [6] Li Y, Somorjai GA. Nanoscale advances in catalysis and energy applications, Nano Letters. 2010;**10**: 2289-2295. DOI: 10.1021/nl101807g
- [7] Liu G, Yang HG, Pan J, Yang YQ, Lu GQ, Cheng HM. Titanium dioxide crystals with tailored facets, Chemical Reviews. 2014;**114**: 9559-9612. DOI: 10.1021/cr400621z

- [8] Fang WQ, Gong XQ, Yang HG. On the unusual properties of anatase TiO₂ exposed by highly reactive facets, The Journal of Physical Chemistry Letters. 2011;2: 25-734. DOI: 10.1021/jz200117r
- [9] Hagfeldt A, Boschloo G, Sun L, Kloo L, Pettersson H. Dye-sensitized solar cells, Chemical Reviews. 2010;**110**: 6595-6663. DOI: 10.1021/cr900356p
- [10] Henderson MA. Structural sensitivity in the dissociation of water on TiO₂ single-crystal surfaces, Langmuir. 1996;12: 5093-5098. DOI: 10.1021/la960360t
- [11] Charlton G, Howes PB, Nicklin CL, Steadman P, Taylor JSG, Muryn CA, Harte SP, Mercer J, McGrath R, Norman D. Relaxation of TiO2(110)-(1x1) using surface X-ray diffraction, Physical Review Letters. 1997;78: 495-498. DOI: 10.1103/PhysRevLett.78.495
- [12] Lindan, PJD, Harrison NM, Gillan MJ. Mixed dissociative and molecular adsorption of water on the rutile (110) surface, Physical Review Letters. 1998;80: 762-765. DOI: 10. 1103/PhysRevLett.80.762
- [13] Vittadini A, Selloni A, Rotzinger FP, Grätzel M. Structure and energetics of water adsorbed at TiO₂ Anatase (101) and (001) surfaces, Physical Review Letters. 1998;81: 954-2957. DOI: 10.1103/PhysRevLett.81.2954
- [14] Lazzeri M, Vittadini A, Selloni A. Structure and energetics of stoichiometric TiO₂ anatase surfaces, Physical Review B. 2001;63: 155409. DOI: 10.1103/PhysRevB.63.155409
- [15] Diebold U. The surface science of titanium dioxide. Surface Science Reports. 2003;48: 53-229. DOI: 10.1016/S0167-5729(02)00100-0
- [16] Gong XQ, Selloni A. Reactivity of anatase TiO₂ nanoparticles: The role of the minority (001) surface, The Journal of Physical Chemistry B. 2005;**109**: 19560-19562. DOI: 10.1021/ jp055311g
- [17] Gong XQ, 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, The Journal of Physical Chemistry B. 2006;**110**: 2804-2811. DOI: 10.1021/jp056572t
- [18] Yang HG, Sun CH, Qiao SZ, Zou J, Liu G, Smith SC, Cheng HM, Lu GQ. Anatase TiO₂ single crystals with a large percentage of reactive facets, Nature (London). 2008;453: 638-641. DOI: 10.1038/nature06964
- [19] Selloni A. Crystal growth—Anatase shows its reactive side, Nature Materials. 2008;7: 613-615. DOI: 10.1038/nmat2241
- [20] Angelis FD, Valentin CD, Fantacci S, Vittadini A, Selloni A. Theoretical studies on anatase and less common TiO₂ phases: Bulk, surfaces, and nanomaterials, Chemical Reviews. 2014;**114**: 9708-9753. DOI: 10.1021/cr500055q
- [21] Li JM, Cao K, Li Q, Xu DS. Tetragonal faceted-nanorods of anatase TiO₂ with a large percentage of active {100} facets and their hierarchical structure. CrystEngComm. 2012;14: 83-85. DOI: 10.1039/c1ce06229h

- [22] Wu L, Yang BX, Yang XH, Chen ZG, Li Z, Zhao HJ, Gong XQ, Yang HG. On the synergistic effect of hydrohalic acids in the shape-controlled synthesis of anatase TiO₂ single crystals, CrystEngComm 2013;15: 3252-3255. DOI: 10.1039/c2ce26744f
- [23] Lai ZC, Peng F, Wang Y, Wang HJ, Yu H, Liu P, Zhao HI. Low temperature solvothermal synthesis of anatase TiO₂ single crystals with wholly {100} and {001} faceted surfaces, Journal of Materials Chemistry. 2012;22: 23906-23912. DOI: 10.1039/c2jm34880b
- [24] Li JM, Xu DS. Tetragonal faceted-nanorods of anatase TiO₂ single crystals with a large percentage of active {100} facets, Chemical Communications (Cambridge). 2010;46: 2301-2303. DOI: 10.1039/b923755k
- [25] Ding XK, Ruan HC, Zheng C, Yang J, Wei MD. Synthesis of TiO₂ nanoparticles with tunable dominant exposed facets (010), (001) and (106), CrystEngComm. 2013;15: 3040-3044 DOI: 10.1039/c3ce27097a
- [26] Wu BH, Guo CY, Zheng NF, Xie ZX, Stucky GD. Nonaqueous production of nanostructured anatase with high-energy facets {001} or {010} facets, Journal of the American Chemical Society. 2008;130: 17563-17567. DOI: 10.1021/ja8069715
- [27] Wu D, Gao Z, Xu F, Chang J, Gao S, Jiang K. Anatase TiO₂ nanocrystals enclosed by welldefined crystal facets and their application in dye-sensitized solar cell, CrystEngComm. 2013;15: 516-523. DOI: 10.1039/c2ce26454d
- [28] Gordon TR, Cargnello M, Paik T, Mangolini F, Weber RT, Fornasiero P, Murray CB. Nonaqueous synthesis of TiO₂ nanocrystals using TiF₄ to engineer morphology, oxygen vacancy concentration, and photocatalytic activity. Journal of the American Chemical Society. 2012;**134**: 6751-6761. DOI: 10.1021/ja300823a
- [29] Wu N, Wang J, Tafen DN, Wang H, Zheng J-G, Lewis JP, Liu X, Leonard SS, Manivannan A. Shape enhanced photocatalytic activity of single-crystalline anatase TiO₂ (101) nanobelts, Journal of the American Chemical Society. 2010;132: 6679-6685. DOI: 10.1021/ja909456f
- [30] Chen C, Hu R, Mai K, Ren Z, Wang H, Qian G, Wang Z. Shape evolution of highly crystalline anatase TiO₂ nanobipyramids {001} and {101} facets, Crystal Growth & Design. 2011;11: 5221-5226. DOI: 10.1021/cg200457g
- [31] Pan JH, Han G, Zhou R, Zhao XS. Hierarchical N-doped TiO₂ hollow microspheres consisting of nanothorns with exposed anatase {101} facets, Chemical Communications (Cambridge). 2011;47: 6942-6944. DOI: 10.1039/c1cc11796c
- [32] Horvat B, Rečnik A, Dražić G. The growth of anatase bipyramidal crystals during hydrothermal synthesis, Journal of Crystal Growth. 2012;347: 19-24. DOI: 10.1016/j. jcrysgro.2012.03.027
- [33] Liu M, Piao L, Zhao L, Ju S, Yan Z, He T, Zhou C, Wang W. J. Anatase TiO₂ single crystals with exposed {001} and {110} facets: Facile synthesis and enhanced photocatalysis, Chemical Communications (Cambridge). 2010;46: 1664-1666. DOI: 10.1039/b924172h

- [34] Xu H, Reunchan P, Ouyang SX, Tong H, Umezawa N, Kako T, Ye JH. Anatase TiO₂ single crystals exposed with high-reactive {111} facets toward efficient H₂ evolution, Chemistry of Materials. 2013;25: 405-411. DOI: 10.1021/cm303502b
- [35] Yang WG, Xu YY, Tang Y, Wang C, Hu YJ, Huang L, Liu J, Luo J, Guo HB, Chen YG, Shi WM, Wang YL. Three-dimensional self-branching anatase TiO₂ nanorods: Morphology control, growth mechanism and dye-sensitized solar cell application, Journal of Materials Chemistry A. 2014;2: 16030-16038. DOI: 10.1039/c4ta02761b.
- [36] Jiang HB, Cuan Q, Wen CZ, Xing J, Wu D, Gong X-Q, Li C, Yang HG. Anatase TiO₂ crystals with exposed high-index facets (105), Angewandte Chemie International Edition. Ed. 2011;50: 3764-3768. DOI: 10.1002/anie.201007771.
- [37] Wu L, Jiang HB, Tian F, Chen Z, Sun C, Yang HG. Ti_{0.89}Si_{0.11}O₂ single crystals bound by high-index {201} facets showing enhanced visible-light photocatalytic hydrogen evolution, Chemical Communications (Cambridge). 2013;49: 2016-2018. DOI: 10.1039/ c3cc38105f
- [38] Yang MH, Chen PC, Tsai MC, Chen TT, Chang IC, Chiu HT, Lee CY. Alkali metal ion assisted synthesis of faceted anatase TiO₂ {101} and {301} exposed were synthesized, CrystEngComm. 2013;15: 2966-2971. DOI: 10.1039/c3ce26965e
- [39] Wu HB, Chen JS, Lou XW, Hng HH. Asymmetric anatase TiO₂ nanocrystals with exposed high-index facets and their excellent lithium storage properties. Nanoscale. 2011;3: 4082-4084. DOI: 10.1039/c1nr10854a
- [40] Gong XQ, Selloni A, Batzill M, Diebold U. Steps on anatase TiO₂(101), Nature Materials.2006;5: 665-670. DOI: 10.1038/nmat1695
- [41] Hong F, Ni YH, Xu WJ, Yan YF. Origin of enhanced water adsorption at <1-10> step edge on rutile TiO₂ (110) surface, The Journal of Chemical Physics. 2012;137: 114707. DOI: 10.1063/1.4753951
- [42] Zheng T, Wu C, Chen MJ, Zhang Y, Chummings PT. A DFT study of water adsorption on rutile TiO₂ (110) surface: The effects of surface steps, The Journal of Chemical Physics. 2016;145: 044702. DOI: 10.1063/1.4958969
- [43] Schaub R, Thostrup P, Lopez N, Lægsgaard E, Stensgaard I, Nørskov JK, Besenbacher F. Oxygen vacancies as active sites for water dissociation on rutile TiO₂ (110), Physical Review Letters. 2001;87: 266104. DOI: 10.1103/PhysRevLett. 87. 266104
- [44] Tilocca A, Selloni A. Reaction pathway and free energy barrier for defect-induced water dissociation on the (101) surface of TiO₂-anatase, The Journal of Chemical Physics. 2003;119: 7445. DOI: 10.1063/1.1607306
- [45] Wang C, Hu QQ, Huang JQ, Wu L, Deng ZH, Liu ZG, Liu Y, Cao YG. Efficient hydrogen production by photocatalytic water splitting using N-doped TiO₂ film. Applied Surface Science. 2013;283: 188-192. DOI: 10.1016/j.apsusc.2013.06.080

- [46] Wang C, Hu QQ, Huang JQ, Deng ZH, Shi HL, Wu L, Liu ZG, Cao YG. Effective water splitting using N-doped TiO₂ films: Role of preferred orientation on hydrogen production, International Journal of Hydrogen Energy. 2014;**39**: 1967-1971. DOI: 10.1016/j. ijhydene.2013.11.097
- [47] Xu J, Xu LF, Li ZZ, Wang JT, Lin ZS, Liu K, Cao YG, Selloni A. *Ab Initio* study of water adsorption and reactivity on the (211) surface of anatase TiO₂, Physical Review Applied. 2016;5: 064001. DOI: 10.1103/PhysRevApplied.5.064001
- [48] Kresse G, Hafner J. *Ab initio* molecular dynamics for liquid metals, Physical Review B. 1993;**47**: 558-561. DOI: 10.1103/PhysRevB.47.558
- [49] Kresse G, Furthmüller J. Efficiency of *ab-initio* total energy calculations for metals and semiconductors using a plane-wave basis set, Computational Materials Science. 1996;6: 15-50. DOI: 10.1016/0927-0256(96)00008-0
- [50] Kresse G, Furthmüller J. Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set, Physical Review B. 1996;54: 11169-11186. DOI: 10.1103/ PhysRevB.54.11169
- [51] Blöchl PE. Projector augmented-wave method. Physical Review B. 1994;50: 17953-17979. DOI: 10.1103/PhysRevB.50.17953
- [52] Wang Y, Perdew JP. Correlation hole of the spin polarized electron gas, with exact smallwave-vector and high-density scaling, Physical Review B. 1991;44: 13298-13307. DOI: 10.1103/PhysRevB.44.13298
- [53] Monkhorst HJ, Pack JD. Special points for Brillouin zone integrations, Physical Review B. 1976;13: 5188-5192. DOI: 10.1103/PhysRevB.13.5188





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