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The Reactivity of Anatase TiO₂ (211) Surface and the Bond-Charge Counting Model

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Abstract

In this chapter, we intend to present a generic understanding of surface reactivity and water dissociation on TiO₂ surfaces through a study of anatase TiO₂ (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, TiO₂ crystallizes in three different structures: rutile, anatase, and brookite, all formed by TiO₆ 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 TiO₂, anatase TiO₂ is the most widely studied phase and is extensively used in many industrial applications such as photovoltaic

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/m^2 , while the (001) surface is the highest reactivity surface with a high surface energy of 0.98 J/m^2 . 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 remarks in Section 4.

2. The reactivity of anatase TiO₂ (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 $2\theta = 25.28^\circ, 36.95^\circ, 37.88^\circ, 38.55^\circ, 48.05^\circ, 54.09^\circ, 54.88^\circ, 62.67^\circ,$ 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.

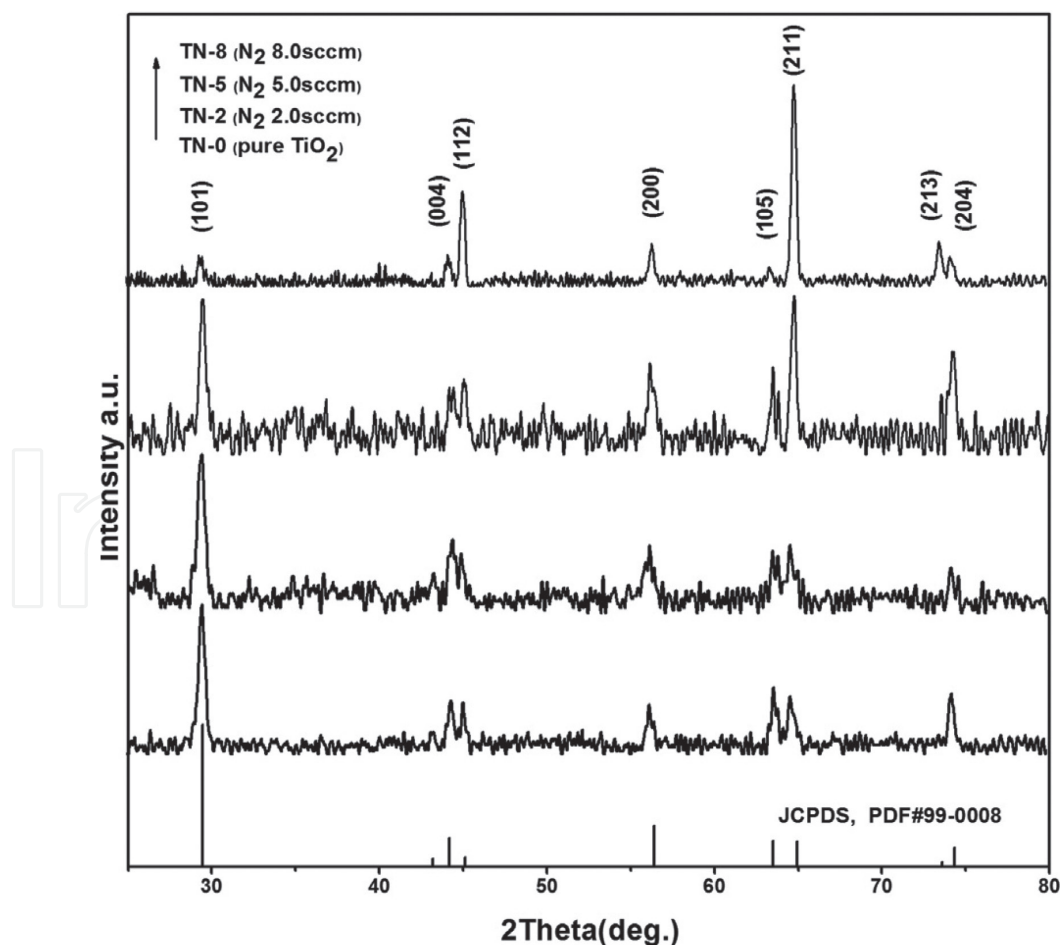


Figure 1. The X-ray diffraction (XRD) on N-doped TiO₂ film.

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 TiO_2 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 $7.706 \text{ \AA} \times 5.501 \text{ \AA} \times 27.677 \text{ \AA}$ ($\gamma = 101.44^\circ$) comprising a total of 54 atoms separated by a vacuum region of 12 \AA . The Monkhorst-Pack scheme [53] was adopted for the Brillouin zone integration with a $6 \times 6 \times 1$ 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/ \AA 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 $\text{O}_{21'}$, $\text{O}_{22'}$, and $\text{O}_{23'}$, a fourfold-coordinated Ti_4 and a fivefold-coordinated Ti_5 , respectively. The four fully-coordinated atoms are $\text{O}_{31'}$, $\text{O}_{32'}$, $\text{O}_{33'}$, and Ti_6 [see **Figure 2(a)**]. Different from (001) and (101) surfaces [12], fourfold-coordinated Ti_4 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 ($\text{O}_{2i'}$) atoms are displaced outward, while the under-coordinated Ti_4 and Ti_5 atoms are relaxed inward. Both angles $\angle \text{Ti}_4\text{-O}_{22'}\text{-Ti}_5$ and $\angle \text{Ti}_5\text{-O}_{31'}\text{-Ti}_6$ become smaller, 100.3° and 147.7° , respectively. The largest relaxations are those of the fully-coordinated oxygen $\text{O}_{31'}$, which relaxes outward by approximately 0.35 \AA , and $\text{O}_{32'}$, which relaxes inward by approximately 0.34 \AA . Meanwhile, the surface atoms form four-membered-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 \AA to 2.492–2.515 \AA .

Facet	N_{at}	E (J/m ²)	$n(\text{Ti}_5)$ (10^{-2}\AA^{-2})	$n(\text{Ti}_4)$ (10^{-2}\AA^{-2})	$n(\text{O}_2)$ (10^{-2}\AA^{-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 [$n(\text{Ti}_5)$, $n(\text{Ti}_4)$, and $n(\text{O}_2)$]. N_{at} is the total number of atoms in the slab.

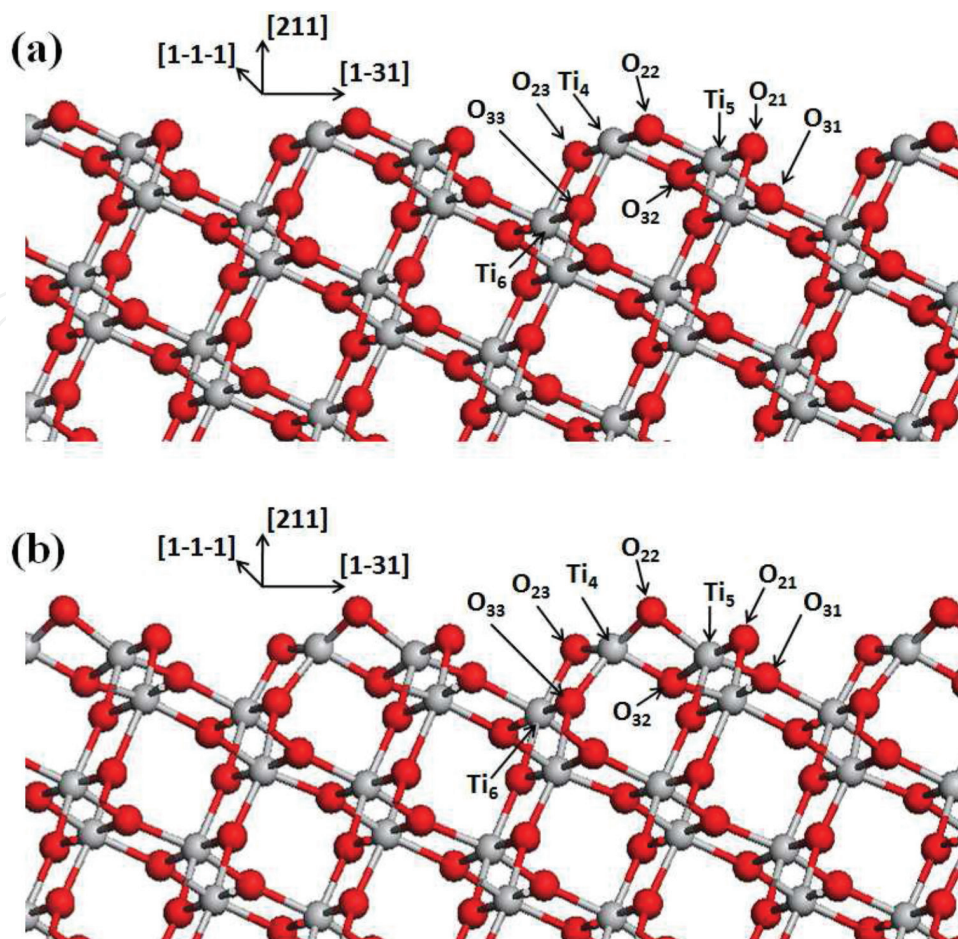


Figure 2. Structures of the unrelaxed (a) and relaxed (b) anatase (211) surfaces. The O and Ti atoms are in red and grey spheres, respectively, indicated with different coordination numbers.

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 TiO₂. 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 under-coordinated 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

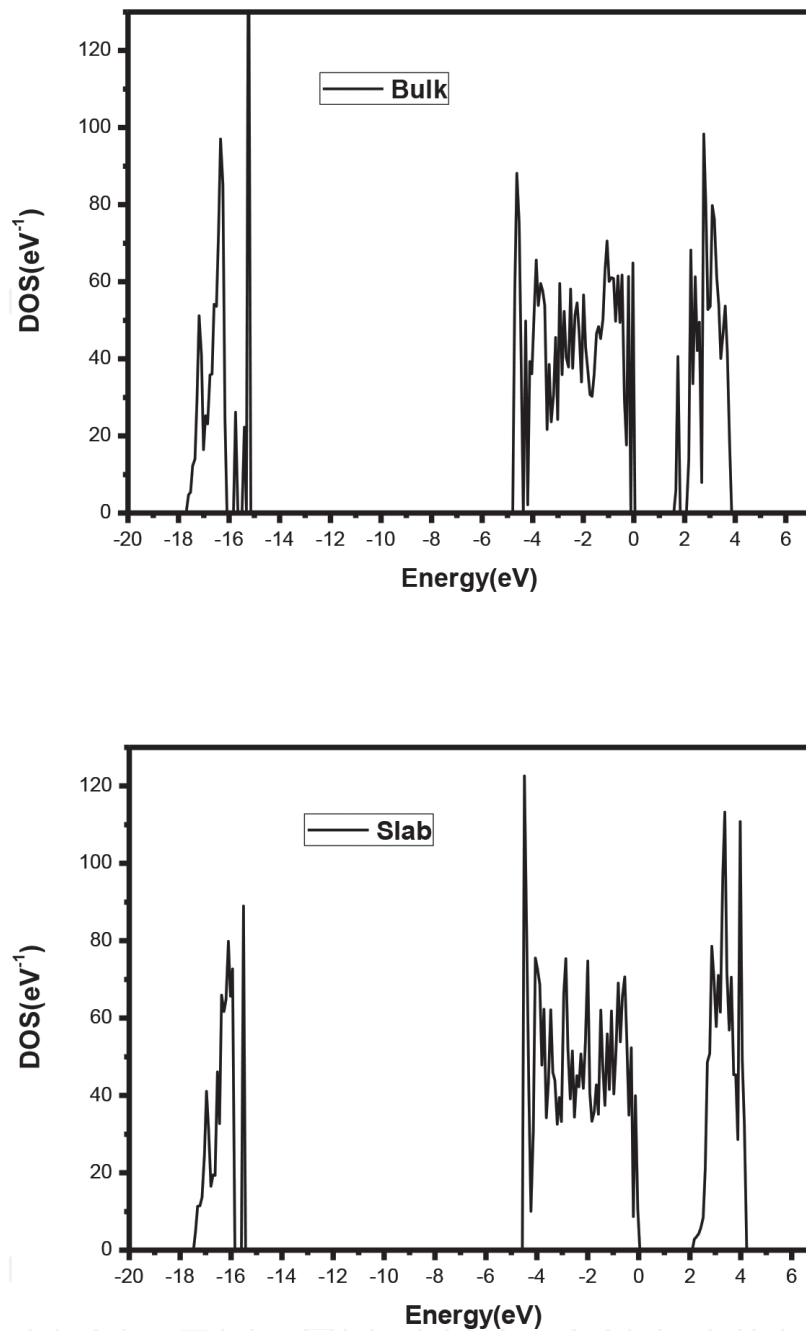


Figure 3. Electronic density of states for the bulk TiO_2 and bare anatase (211) surface after relaxation. The Fermi level is set at 0 eV.

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 Ti₅ 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

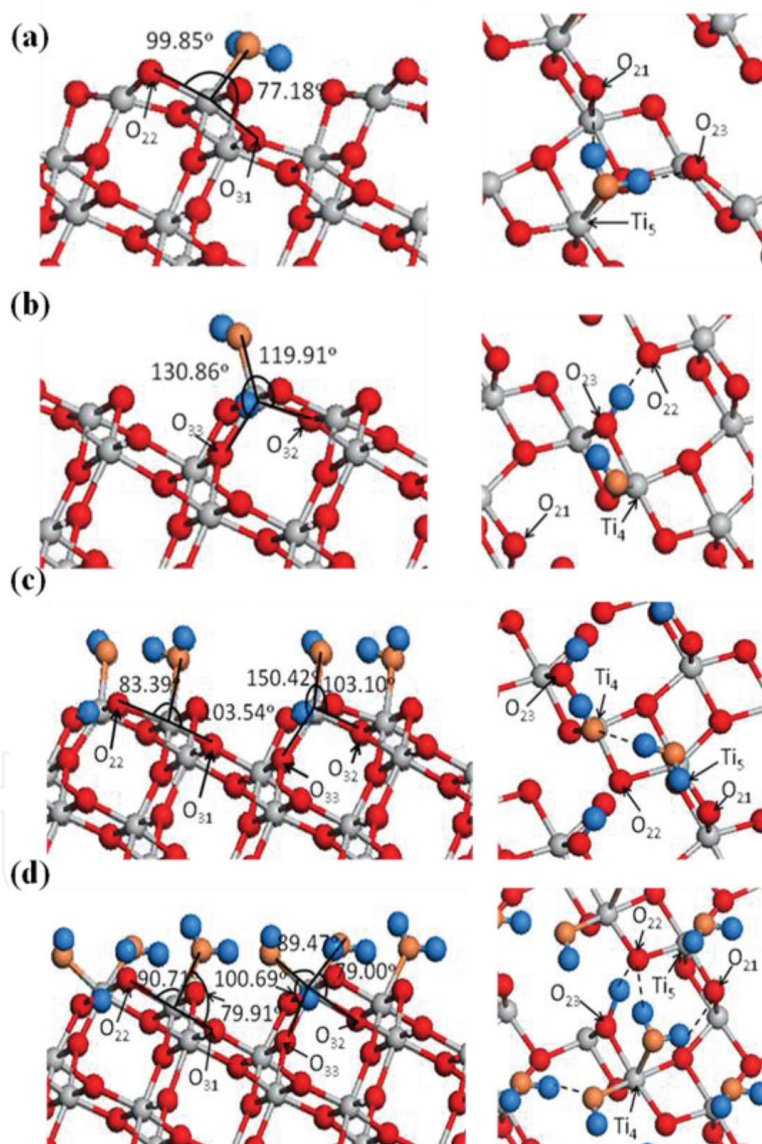


Figure 4. Side (left) and top (right) views of the structures for water adsorption on the anatase TiO₂ (211) surface. (a) Molecular water on a Ti₅ site. (b) Dissociative water on a Ti₄ site. (c) Mixed state with one dissociative H₂O on Ti₄ and one molecular H₂O on Ti₅ sites at 2/3 ML. (d) Mixed state on Ti₄ and Ti₅ 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.

Ti_5 form two bond angles $\angle O_{\text{water}}-Ti_5-O_{22} = 99.85^\circ$ and $\angle O_{\text{water}}-Ti_5-O_{31} = 77.18^\circ$, close to the bulk angles of 101.90° and 78.10° , respectively. Upon water adsorption, the Ti_5 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 Ti_5 site is 0.784 eV. For dissociative water adsorption on Ti_5 site, the water molecule is dissociated into hydroxyl (OH) and H fragments. The OH group bonds to Ti_5 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 Ti_5 site is 0.77 eV, which is slightly smaller than that of molecular adsorption. Thus, molecular adsorption is preferred on Ti_5 site.

On the other hand, for molecular water on a Ti_4 site, the oxygen atom of water binds to Ti_4 with a bond length of 2.207 Å, and Ti_4 is located at the position of one of the bulk Ti-O bonds indicating that there is one Ti bond left. The Ti_4 adsorption site becomes fivefold-coordinated and the adsorption energy for molecular water on Ti_4 site is estimated to be 0.99 eV. Finally, for dissociative water on Ti_4 site [see **Figure 4(b)**], the O atom of the OH group is strongly bonded to the Ti_4 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 Ti_4 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 Ti_4-O_{OH} bond clearly deviates from its direction in the bulk, as shown by the two bond angles $\angle O_{\text{OH}}-Ti_4-O_{33} = 130.86^\circ$ and $\angle O_{\text{OH}}-Ti_4-O_{32} = 119.91^\circ$. 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 O_{23} atom of length 2.534 Å. The dissociated H from water interacts with a surface oxygen O_{23} 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 Ti_4 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.

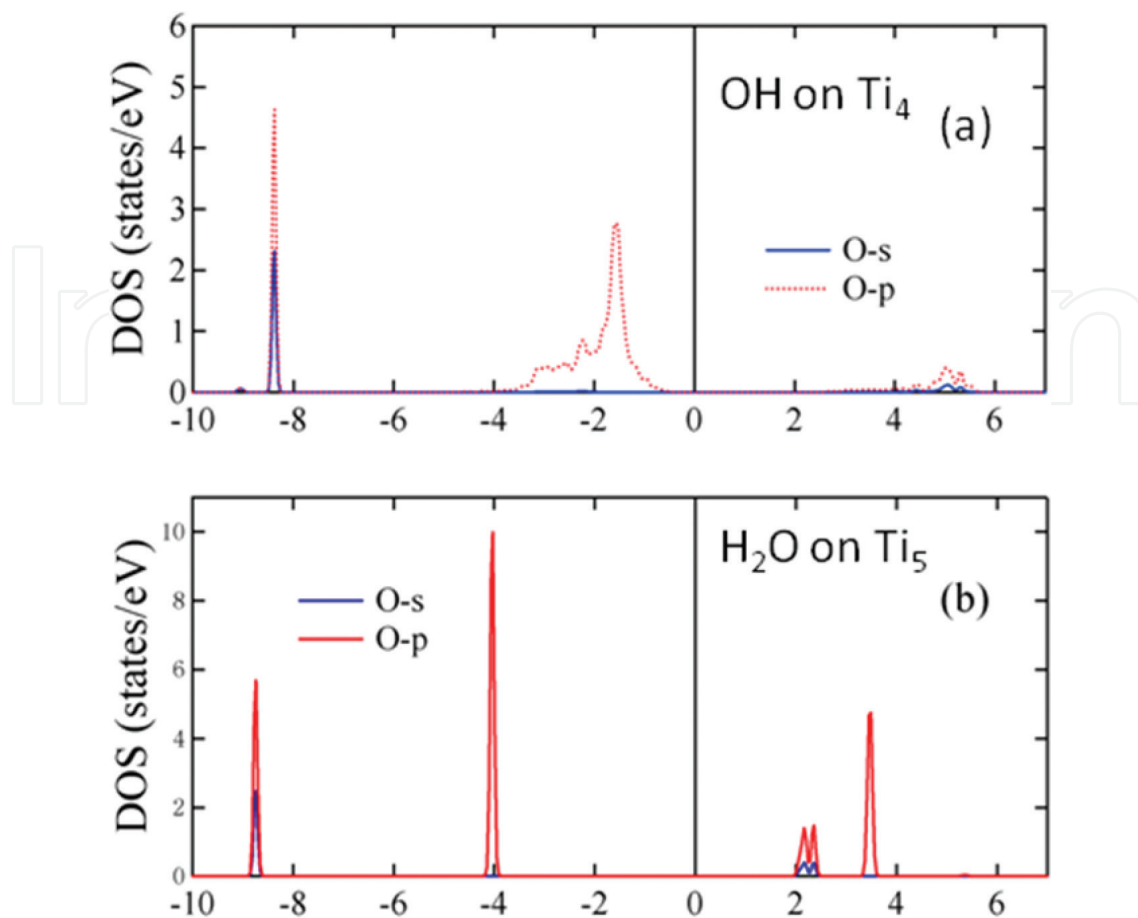


Figure 5. Projected electronic density of states on anatase (211) surface (a) for O-2s,p in the OH group on Ti₄ site; (b) for O-2s, p in water on Ti₅ site; The Fermi level is set at 0 eV.

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 H₂O on a Ti₄ site and one molecular H₂O on a Ti₅ 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 O₂₃ atom forming a new OH moiety and further forms a strong HB (1.590 Å) with an O₂₂ 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 Ti₄ and Ti₅ 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 H_2O on a Ti_4 site and one molecular H_2O on a Ti_5 site, the third molecule would adsorb molecularly on a Ti_4 site [see **Figure 4(d)**]. It is an O atom that binds to Ti_4 with a bond length of 2.259 Å, while the two H atoms form HBs with nearby O atoms, where $\text{H}-\text{O}_{21}$ is 2.156 Å and $\text{H}-\text{O}_{22}$ is 1.907 Å. The bond length for molecular water on a Ti_5 atom is 2.221 Å, while for dissociated water on Ti_4 it is 1.934 Å. Two bond angles $\angle\text{O}_{\text{OH}}-\text{Ti}_4-\text{O}_{33}$ and $\angle\text{O}_{\text{water}}-\text{Ti}_4-\text{O}_{32}$ 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 O_{23} atom to form an OH moiety and further interacts with an O_{22} atom forming an HB of 1.835 Å. An additional HB of 1.652 Å also exists between these two adsorbed H_2O . All surface atoms become saturated. The adsorption energy has a larger value of 0.946 eV/mol for this mixed configuration on Ti_4 sites. For comparison, we also consider configuration with two dissociated water molecules on Ti_4 sites and one molecular H_2O on Ti_5 . 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 Ti_4 . Thus, molecular adsorption is favored on Ti_4 for the second water molecule. Meanwhile, for structure with one intact water on Ti_4 and two dissociated water molecules on Ti_4 and Ti_5 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 Ti_4 , 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 H_2O 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 TiO_2 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

θ (ML)	Structure	H ₂ O	H, OH	ΔH (eV)
1/3	Figure 4(a)	Ti ₅		0.784
			Ti ₅	0.770
		Ti ₄		0.994
2/3	Figure 4(b)		Ti ₄	1.284
	Figure 4(c)	Ti ₅	Ti ₄	1.045
			Ti ₄ , Ti ₅	0.991
		Ti ₄	Ti ₄	0.960
			Ti ₄ , Ti ₄	0.916
3/3	Figure 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

The adsorption states are shown as H₂O = molecular and H, OH = dissociative on a Ti₄ or Ti₅ site.

Table 2. Adsorption energy (ΔH in eV) per H₂O molecule on anatase (211) at various water coverages $\theta = 1/3, 2/3,$ 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 Ti₅ atom [13]. Therefore, whether Ti₅ 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., $2\text{Na} + 2\text{H}_2\text{O} = 2\text{NaOH} + \text{H}_2\uparrow$. 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 than 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 TiO₂, 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 TiO_6 octahedra structure. Therefore, we could make a simple bond-charge counting for this system. When a Ti_4 atom interacts with the oxygen atom of H_2O , 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 Ti_4 is more active than H atom. Then, one H atom can be released from the water molecule on a Ti_4 site. In fact, one H atom dissociates spontaneously from the water molecule as this adsorbs on a Ti_4 atom. On the other hand, Ti_5 can only provide about 2/3 electron charge to the water O atom, less than the charge contribution from an H atom. Therefore, Ti_5 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 Ti_5 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/m^2 , 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 Ti_5 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/m^2 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

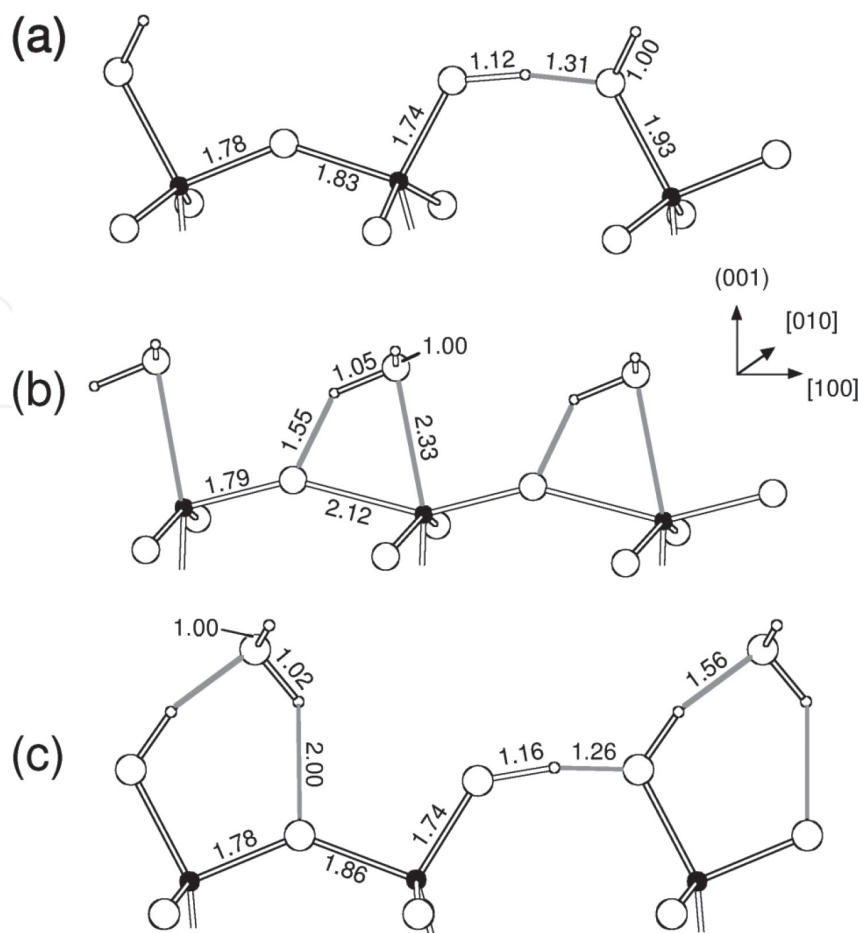


Figure 6. (Figure 3 in Ref. [13]) Atomic structure (side view) for adsorbed water molecule(s) on anatase (001). (a) Dissociated state. (b) Molecular state. (c) Mixed state. Gray lines in (b) and (c) indicate hydrogen bonds. Bond lengths are in Å.

as in **Figure 3(a)** in Ref. [13]) is characterized by the breaking of the bond between the bridging 2c oxygen and the Ti₅ atoms involved in the adsorption, i.e., the Ti₅ atom actually becomes fourfold-coordinated after breaking its bond to a bridging O atom. Therefore, the dissociative water is absorbed on an equivalent Ti₄ site. It is expected that such phenomenon of Ti₅ atom breaking bond with neighboring oxygen becomes an effective Ti₄ atom which would be held for the anatase (103)_f surface with the high surface energy of 0.9 J/m².

However, for the other surfaces only containing Ti₅ 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 Ti₅ 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 Ti₅, the Ti₅ atoms eventually become too effective Ti₄ 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 Ti_4 (in **Figure 7(a), (d), (e), (f), and (h)**) and without Ti_4 atoms (in **Figure 7(b), (c), and (g)**). Then, we recapitulate their surface energy calculation results γ (θ) in unit $10^{-2}eV/\text{\AA}^2$ and rearrange in an order of containing Ti_4 and Ti_5 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 TiO_2 (101). For BI step, the adsorption energies are smaller than that on the

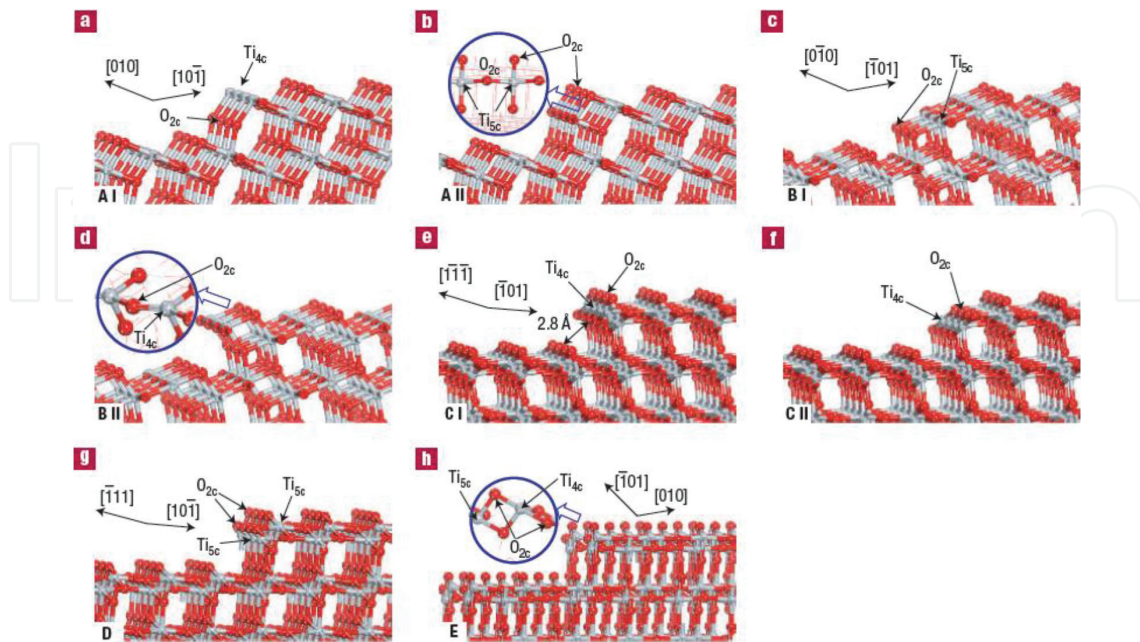


Figure 7. Structure models of step edges A–E on anatase (101) (**Figure 2** in Ref. [40]).

(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 Ti₅ 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 Ti₅ atom becomes Ti₄ by breaking a bond with neighboring oxygen.

Hong et al. [41] investigated water adsorption behavior step edges on rutile TiO₂ (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 TiO₂ (110) surface with step defects by DFT calculations. The step structures were created by removing the TiO₂ 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 adsorbed 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 Ti₄ atoms and/or equivalent Ti₄ 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 Ti_3 atom

Recently, the three-coordinated Ti atom (Ti_3) are found on the (111) anatase TiO_2 surfaces. Xu et al [34] reported that they prepared anatase TiO_2 single crystals exposed (111) facet. Their DFT calculations showed that the (111) facet has a much higher surface energy of 1.61 J/m^2 , 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 Ti_3 and Ti_5 atoms with the ratio 1:3 on the (111) surface. According to our model, the Ti_3 atom could contribute two electrons participating interaction. Thus, it is expected that two water molecules could be dissociated on a single Ti_3 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 Ti_5 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/m^2 . In addition, the four-coordinated Ti_4 atoms with two unsaturated bonds have a stronger chemical reactivity in comparison to the Ti_5 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 Ti_5 sites and the other to dissociated water on Ti_4 sites. These results indicate that the Ti_4 atoms will play a critical role in water decomposition. According to TiO_2 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 Ti_4 atom or equivalent Ti_4 can dissociate water. The controversy about whether Ti_5 can dissociate water is resolved that Ti_5 atom will eventually become Ti_4 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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