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Chapter 1

The Reactivity of Anatase TiO$_2$ (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 TiO$_2$ surfaces through a study of anatase TiO$_2$ (211) surface—an idea model surface containing both four-coordinated Ti atom (Ti$_4$) and five-coordinated Ti atom (Ti$_5$). 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 Ti$_4$ site while it hardly dissociates on Ti$_5$ 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 TiO$_2$ surfaces including step edges and vacancies where the reactivity of surfaces enable to dissociate water attribute to the existence of Ti$_4$ atom or equivalent Ti$_4$ atom.

Keywords: TiO$_2$ 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
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 facets. 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 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 TiO$_2$ film deposited using RF magnetron sputtering [45]. N-doped TiO$_2$ 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 TiO$_2$ films was identified by X-ray diffraction (XRD). Figure 1 shows the XRD patterns of N-doped TiO$_2$ film. Diffraction peaks observed at 2θ = 25.28°, 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 TiO$_2$. It can be seen that N-doping can greatly influence the growth orientation of anatase TiO$_2$ 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 TiO$_2$ film, compared with those of the undoped TiO$_2$ film. Especially, the increase of exposed (211) facets can effectively improve the photocatalytic activity of TiO$_2$ 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 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 Å × 5.501Å × 27.677Å (γ = 101.44°) 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 O_{2γ}, O_{2σ}, and O_{3γ}, a fourfold-coordinated Ti_4, and a fivefold-coordinated Ti_5, respectively. The four fully-coordinated atoms are O_{31}, O_{32}, 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 (O_{2i}) atoms are displaced outward, while the under-coordinated Ti_4 and Ti_5 atoms are relaxed inward. Both angles ∠Ti_4-O_{22}-Ti_5 and ∠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_{3γ} which relaxes outward by approximately 0.35 Å, and O_{3σ} which relaxes inward by approximately 0.34 Å. 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 Å to 2.492–2.515 Å.

<table>
<thead>
<tr>
<th>Facet</th>
<th>N_a</th>
<th>E (J/m^2)</th>
<th>n(Ti_4) (10^{-5}Å^2)</th>
<th>n(Ti_5) (10^{-5}Å^2)</th>
<th>n(O_{2i}) (10^{-2}Å^{-2})</th>
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<tr>
<td>(101)</td>
<td>24</td>
<td>0.52</td>
<td>5.1</td>
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<td>18</td>
<td>1.08</td>
<td>6.9</td>
<td>6.9</td>
<td></td>
</tr>
<tr>
<td>(211)</td>
<td>54</td>
<td>0.97</td>
<td>2.4</td>
<td>2.4</td>
<td>7.2</td>
</tr>
<tr>
<td>(103)</td>
<td>48</td>
<td>0.99</td>
<td>3.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(110)</td>
<td>42</td>
<td>1.15</td>
<td></td>
<td>3.8</td>
<td></td>
</tr>
</tbody>
</table>

*Table 1.* Calculated surface energies (E in J/m^2) and surface densities Ti_4, Ti_5, and oxygen O_{2i} atoms [n(Ti_4), n(Ti_5), and n(O_{2i})]. N_a is the total number of atoms in the slab.
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, $E = (E_{\text{tot}} - nE_{\text{bulk}})/A$, where $E_{\text{tot}}$ is the total energy of the slab and $E_{\text{bulk}}$ is the energy of TiO$_2$ unit in the bulk, $n$ is the number of TiO$_2$ 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/m$^2$, which is nearly twice that of the most stable anatase (101) surface (0.52 J/m$^2$), in agreement with previous theoretical studies [14]. Similarly, the (211) surface has a high surface energy of 0.97 J/m$^2$, 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 Ti$_5$ (see Table 1). However, the surface energy of anatase (211) is large even
though the total density of under-coordinated Ti\textsubscript{4} and Ti\textsubscript{5} atoms is smaller than that on the (001) surface [even smaller than on (101)]. This result already suggests that Ti\textsubscript{4} atoms, with two unsaturated bonds, have a higher reactivity than Ti\textsubscript{5} atoms with one unsaturated bond. A similar behavior was found also for the anatase (110) and (103) 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 TiO$_2$ (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 (Ti$_4$ or Ti$_5$) 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 Ti$_5$ with bond length of 2.226 Å, and two surface oxygen atoms via

![Figure 4](image_url)

**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$_2$O on Ti$_4$ and one molecular H$_2$O 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.
Ti$_5$ form two bond angles $\angle_{\text{water}-\text{Ti}_5-\text{O}_{22}} = 99.85^\circ$ and $\angle_{\text{water}-\text{Ti}_5-\text{O}_{31}} = 77.18^\circ$, 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 Å 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$_{23}$ bond clearly deviates from its direction in the bulk, as shown by the two bond angles $\angle_{\text{OH}-\text{Ti}_4-\text{O}_{23}} = 130.86^\circ$ and $\angle_{\text{OH}-\text{Ti}_4-\text{O}_{22}} = 119.91^\circ$. 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$_4$ 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.
Now, let us consider more water adsorption case. For two adsorbed H$_2$O molecules (2/3 ML coverage), the first H$_2$O prefers to adsorb at a Ti$_4$ site in dissociative form according to the single water-adsorption results; next, another water molecule should adsorb on a Ti$_4$ or Ti$_5$ site. For the structure with one dissociated H$_2$O on a Ti$_4$ site and one molecular H$_2$O on a Ti$_5$ site [see Figure 4(c)], the O-Ti$_5$ bond is 2.230 Å, while the O-Ti$_4$ 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 Å) 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 H$_2$O on Ti$_4$ and Ti$_5$ 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 Ti$_5$ in the mixed structure. Moreover, for a structure with one dissociated H$_2$O and one associated H$_2$O on Ti sites and structure with two
dissociated H$_2$O 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$_2$O on a Ti$_4$ site and one molecular H$_2$O 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$_2$O on a Ti$_4$ site and one molecular H$_2$O on a Ti$_5$ site, the third molecule would adsorb molecularly on a Ti$_5$ 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 H-O$_{21}$ is 2.156 Å and H-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 Ti4 it is 1.934 Å. Two bond angles $\angle$O$_{21}$-Ti$_4$-O$_{33}$ and $\angle$O$_{water}$-Ti$_4$-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$_{22}$ atom to form an OH moiety and further interacts with an O$_{21}$ atom forming an HB of 1.835 Å. An additional HB of 1.652 Å also exists between these two adsorbed H$_2$O. 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$_2$O 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$_5$, and Ti$_7$ 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$_5$, and one molecular water on Ti$_7$.

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$_2$O 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$_2$O 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.
The adsorption states are shown as H\textsubscript{2}O = molecular and H\textsubscript{2}, OH = dissociative on a Ti\textsubscript{4} or Ti\textsubscript{5} site.

<table>
<thead>
<tr>
<th>( \theta ) (ML)</th>
<th>Structure</th>
<th>( \text{H}_2\text{O} )</th>
<th>( \text{H}_2\text{OH} )</th>
<th>( \Delta \text{H} ) (eV)</th>
</tr>
</thead>
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<tr>
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<td>Figure 4(a)</td>
<td>Ti\textsubscript{5}</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>Ti\textsubscript{4}</td>
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<td>Figure 4(b)</td>
<td>Ti\textsubscript{4}</td>
<td>Ti\textsubscript{5}</td>
<td>1.284</td>
</tr>
<tr>
<td>2/3</td>
<td>Figure 4(c)</td>
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<td>Ti\textsubscript{5}</td>
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</tr>
<tr>
<td></td>
<td></td>
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<td>Ti\textsubscript{5}</td>
<td>0.991</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>Ti\textsubscript{5}</td>
<td>0.960</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ti\textsubscript{4}</td>
<td>Ti\textsubscript{5}</td>
<td>0.916</td>
</tr>
<tr>
<td>3/3</td>
<td>Figure 4(d)</td>
<td>Ti\textsubscript{4}, Ti\textsubscript{5}</td>
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<td>0.946</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>0.909</td>
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<tr>
<td></td>
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<td></td>
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<td>0.883</td>
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</tbody>
</table>

Table 2. Adsorption energy (\( \Delta \text{H} \) in eV) per H\textsubscript{2}O 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 Ti\textsubscript{5} atom [13]. Therefore, whether Ti\textsubscript{5} atom can dissociate water is still a matter for controversy on TiO\textsubscript{2} 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\textsubscript{2}O = 2NaOH + H\textsubscript{2}\textsubscript{↑}. 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 TiO\textsubscript{2}.

In bulk TiO\textsubscript{2} each Ti atom has six nearest neighboring O atoms and Ti atom has four outmost electrons, i.e., each Ti\textsuperscript{4+} ion is surrounded by an octahedron of six O\textsuperscript{2−} 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$_2$O, 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 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/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
as in Figure 3(a) in Ref. [13]) is characterized by the breaking of the bond between the bridging 2c oxygen and the Ti atoms involved in the adsorption, i.e., the Ti atom actually becomes fourfold-coordinated after breaking its bond to a bridging O atom. Therefore, the dissociative water is absorbed on an equivalent Ti site. It is expected that such phenomenon of Ti atom breaking bond with neighboring oxygen becomes an effective Ti 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 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 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, the Ti atoms eventually become too effective Ti 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 $\gamma(\theta)$ in unit $10^{-2}$eV/Å$^2$ and rearrange in an order of containing Ti$_4$ and Ti$_5$ atoms as follows:

<table>
<thead>
<tr>
<th>Surface</th>
<th>$\gamma(\theta)$</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (Figure 7(a))</td>
<td>5.36</td>
<td>4.68</td>
</tr>
<tr>
<td>C (Figure 7(e))</td>
<td>5.49</td>
<td>4.81</td>
</tr>
<tr>
<td>CII (Figure 7(f))</td>
<td>6.22</td>
<td>5.22</td>
</tr>
<tr>
<td>E (Figure 7(h))</td>
<td>6.82</td>
<td>5.86</td>
</tr>
<tr>
<td>AII (Figure 7(b))</td>
<td>4.60</td>
<td>4.24</td>
</tr>
<tr>
<td>BI (Figure 7(c))</td>
<td>3.66</td>
<td>3.59</td>
</tr>
<tr>
<td>D (Figure 7(g))</td>
<td>4.52</td>
<td>4.11</td>
</tr>
</tbody>
</table>

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$_2$O 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]).](image-url)
(101) surface. Note BI has the smallest surface energy among all step structures. On the least
stable AI with the highest surface energy among steps containing Ti$_5$ atom, the water adsorp-
tion 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 Ti$_4$ atoms at the < 1-10 >
step edge, which lead to charge transfer to adsorbates more easily than fivefold coordinated
Ti$_5$ 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 Ti$_4$ atoms (ter-
minating the Ti rows of the upper terrace) and the Ti$_5$ atoms (see Figure 1(a), (b) in Ref. [42]).
They only considered the case of Ti bonds fully saturated. Their results show that the molecu-
lar and dissociative adsorptions of H$_2$O can both be observed on Ti$_4$ sites and the molecularly
absorbed water is more favorable on the Ti$_5$ sites. The lowest energy corresponds to the con-
figuration where water molecule on Ti$_5$ site and one dissociated and one molecular water on
Ti$_4$ 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$_5$ 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 dis-
sociation 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 Ti$_6$ atoms underneath the vacancy become Ti$_5$ atoms when O leaves the surface.
Thus, when O atom of water is to refill the O vacancy, the two Ti$_5$ 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 Ti₆ and Ti₅ atoms bridging this O atom tune into Ti₅ and Ti₄, respectively. Water oxygen bonds to Ti₄ and then dissociates through a dissociation pathway. Thus, the dissociation of water on O vacancy of anatase (101) is also attributed to that Ti₄ 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 Ti₄ 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 TiO₂ 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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