Oxygen Adsorption on Anatase TiO₂ (101) and (001) Surfaces from First Principles

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The structural, adsorptive, and electronic properties of oxygen adsorption on anatase TiO₂ are investigated by first-principles calculations with special focus on two experimentally confirmed surfaces. We find that compared with (101) surface, the (001) surface exhibits lower oxygen adsorption energy, reduced band gap, and larger charge transfer, thereby holding the potential for the improvement of sensitivity to reductive gases. Moreover, the (001) surface is found to be more active in oxygen adsorption. These findings render a careful synthesis of anatase TiO₂ crystals so as to form, to the largest extent, the (001) surface primarily important for further improving gas-sensing properties of TiO₂-based sensors. [doi:10.2320/matertrans.M2009317]

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1. Introduction

Titania (TiO₂) has attracted a wide range of attentions recently, largely because its unique properties, for example, electrical and optical properties, are important for many promising applications including photo electrode, gas sensor, and so on.^{1–3)} In general, it has three types of phases: anatase, rutile, and brookite.⁴⁾ Of all the phases, only the anatase and rutile are relevant for a variety of technological applications,⁴⁾ between which the anatase TiO₂ is of stronger current interest especially in surface chemistry field due to its higher catalytic activity.⁵⁾

As well known, the crystal facets in most currently available anatase TiO₂ are dominated by thermodynamically stable (101) surface (for example, over 94%) rather than chemically more reactive (001).^{6,7)} The philosophy behind the substantially low composition of (001) surface is that as a result of surface energy minimization, the surface with higher reactivity is generally easier to transform to other types of facets during crystal growth. For this reason, much effort has been focused on the TiO₂ (101) surface in the past decades.^{8–10)} Recently, a large percent of (001) facets (as large as 47%) have been successfully synthesized in anatase TiO₂ crystals,¹¹⁾ which stimulates extensive investigations focusing on this facets, since the presence of large amount of (001) facets may affect significantly surface properties of anatase TiO₂ and therefore many of its practical applications.

One important application that might be affected dramatically is the functional role of TiO₂ as a gas-sensing material because sensing properties have long been known to be dominantly controlled by surface. Specifically, once reductive gas reaches TiO₂ surface, its molecules interact directly with pre-adsorbed oxygen rather than surface atoms of TiO₂,

which gives rise to oxidation reaction on surface and thus resistance change, i.e., sensitivity. In this sense, gas-sensing properties of TiO₂ are generally governed by the chemisorbed surface oxygen,¹²⁾ thereby making a fundamental understanding of the pre-adsorbed oxygen and how it interacts with TiO₂ on surface timely and relevant. Surprisingly, considering its central importance for many functional applications such as gas sensors, there have been few experimental or theoretical studies of the interaction between chemisorbed oxygen and TiO₂ surface especially from electronic point of view.

In this work, we investigate atomic and electronic structures of an adsorption system between oxygen molecule and TiO₂ surface from first-principles calculations. In particular, we focus on two distinct but realistic facets of anatase TiO₂, (101) and (001) surfaces. The main objective of this study is to understand the sensing origin of anatase TiO₂ and provide insight into how the two remarkably different surfaces affect sensing properties of single TiO₂ crystal.

2. Calculation Models and Methods

It is known that bulk anatase TiO₂ belongs to the tetragonal $D_{4h}^{19} - I4_1/amd$ space group with $a = 3.782 \text{ \AA}$ and $c = 9.502 \text{ \AA}$.¹³⁾ As for surface models, a vacuum region of $15 \text{ \AA}$ is embedded along surface normal to avoid the unwanted interaction between the slab and its period images. The established (101) and (001) surface models are schematically shown in Figs. 1(a) and 1(b), respectively, where six atomic layers are assumed for TiO₂. Along the surface, the slabs utilize 1×1 cells, which are composed of a finite number of layers of infinite extent. On the surfaces, the O atoms can fill either two-fold (O_{2C}) or three-fold (O_{3C}) coordinated positions, while the Ti atoms five-fold (Ti_{5C}) or six-fold (Ti_{6C}) coordinated positions, as indicated in Fig. 1. To investigate the effect of O adsorption, we have constructed

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Fig. 1 Schematic models of anatase TiO_2 surfaces: (a) (101) and (b) (001). The different occupation sites for both the surface Ti and O are marked.

Fig. 2 Illustration of adsorption of an oxygen molecule on anatase TiO_2 surfaces: (a) A1, (b) A2, (c) B1, and (d) B2 models.

a total of four possible models, inducing two surface terminations and two possible adsorption cases.¹⁴⁾ In the four models, the two atoms in the O molecule are located on top of (a) one $\text{Ti}_{5\text{C}}$ atom of (101) surface (A1), (b) two $\text{Ti}_{5\text{C}}$ atoms of (101) surface (A2), (c) one $\text{Ti}_{5\text{C}}$ atom of (001) surface (B1), and (d) two $\text{Ti}_{5\text{C}}$ atoms of (001) surface (B2), as illustrated in Fig. 2. These four adsorption possibilities can be classified into two modes: dissociative (A1 and B1) and simultaneous adsorption mode (A2 and B2). It is worth noting that the oxygen atom mentioned in this paper represents one of the two atoms in the adsorbed oxygen molecule.

Calculations of total energy and electronic structure were carried out using the CASTEP program within the framework of density-functional theory (DFT).¹⁵⁾ The ultrasoft pseudopotential¹⁶⁾ was used for electron-ion interactions and the Perdew-Burke-Ernzerhof form of generalized gradient approximation was employed to describe exchange-correlation functional. A cutoff energy of 340 eV and a regular Monkhorst-Pack grid of $6 \times 6 \times 1$ k points were adopted to ensure energy convergence to within 1–2 meV/atom. The optimum lattice constant of bulk TiO_2 calculated using the above parameters is 100.2% of the experimental value.⁴⁾

3. Results and Discussion

3.1 Relaxation of (101) and (001) surfaces

As a starting point, we present in Fig. 3 views of relaxed anatase TiO_2 (101) and (001) surfaces. A careful comparison of optimized surface structures (Fig. 3) with their bulk counterparts (Fig. 1) reveals that atoms in the outmost layer of both surfaces are displaced noticeably. From Fig. 3(a), one can see that the $\text{O}_{2\text{C}}$ and $\text{O}_{3\text{C}}$ atoms on the (101) surface are shifted outwards along surface normal, while the $\text{Ti}_{5\text{C}}$ and $\text{Ti}_{6\text{C}}$ atoms are displaced inwards. By comparing the positions of surface atoms with those of their bulk ones quantitatively, we observe further that the outward displacement of $\text{O}_{3\text{C}}$ atoms (0.20 Å) is much larger than that of $\text{O}_{2\text{C}}$ atoms (0.05 Å), reflecting more significant optimization of $\text{O}_{3\text{C}}$ on TiO_2 (101) surface. The inward movement of surface Ti atoms is, however, very similar by showing a value of 0.24 Å for the $\text{Ti}_{5\text{C}}$ and 0.21 Å for the $\text{Ti}_{6\text{C}}$. As in the case of (101) surface, the $\text{Ti}_{5\text{C}}$ and $\text{O}_{2\text{C}}$ atoms on (001) surface are also relaxed inwards and outwards, respectively (0.28 Å for the $\text{Ti}_{5\text{C}}$ and 0.19 Å for the $\text{O}_{2\text{C}}$). The major difference is that the $\text{O}_{3\text{C}}$ atom in the (001) case is displaced inwards (0.12 Å) rather than outwards along surface normal. Moreover, the

Fig. 3 Optimized atomic configurations of anatase TiO₂ surfaces: (a) (101) and (b) (001). The arrows indicate the direction of reconstruction along surface normal for the surface atoms.

calculation results agree well with available theoretical reports.^{14,17)}

3.2 Adsorption of oxygen on TiO₂ surfaces

3.2.1 Adsorption energy

To examine which adsorption model is the most energetically stable, we calculated the *adsorption energy* (ΔE_{ads}), a key quantity in predicting adhesive property of an adsorption system. The ΔE_{ads} , which is defined as reversible energy required to separate an adsorption system into a clean surface and an adsorbed molecule, can be expressed by subtracting the sum of total energy of optimized oxygen molecule (E_{O}) and clean surface (E_{Surf}) from total energy of adsorption system (E_{ads}),^{18,19)}

$$\Delta E_{\text{ads}} = E_{\text{ads}} - E_{\text{Surf}} - E_{\text{O}}. \quad (1)$$

In general, a negative ΔE_{ads} indicates that the molecule adsorption is exothermic and thus the adsorption system is energetically stable. For the purpose of comparison, all energies are calculated using the supercell of identical size, independent of whether it contains oxygen molecule, TiO₂ surface, or O-TiO₂ adsorption system. It should be noted that an exact quantitative determination of ΔE_{ads} may not be likely in present calculations due to the possible deviations of experimental conditions from ideal theoretical models.²⁰⁾ However, qualitative comparison between calculated ΔE_{ads} for different atomic geometries of the same adsorption system should be reliable.

Table 1 lists the adsorption energies of the four adsorption models, where one can see that all ΔE_{ads} have negative values, suggesting that the adsorption process can take place naturally. Of the four models, the one with two oxygen atoms sitting simultaneously atop the Ti_{5C} of (001) surface (B₂ model) turns out to have the lowest exothermic ΔE_{ads} (−2.24 eV), indicating that the B₂ configuration is the most stable. This can be understood by considering the strong interaction between the oxygen and the Ti_{5C} cations on the (001) surface. In addition, we also note in this table that the two oxygen atoms prefer to adsorbing on TiO₂ surface simultaneously and that the (001) surface is more favorable for oxygen adsorption. This demonstrates that the (001) surface is more inclined to adsorb oxygen than the (101) under identical circumstances.

3.2.2 Electronic structures

To gain insight into the electronic structure of TiO₂ surface and how it evolves as oxygen is adsorbed, we first present in Fig. 4 band structures for the four adsorption models. In the left panels of Fig. 4, we show, for comparison,

Table 1 Relaxed values of adsorption energies, ΔE_{ads} (in eV), as defined in eq. (1), for the four models, A1, A2, B1, and B2. Refer to Fig. 2 for their corresponding atomic structures.

Surface	(101)		(001)	
Model	A1	A2	B1	B2
ΔE_{ads}	−0.58	−0.9	−1.03	−2.24

band structures of the pristine surfaces as well. A simple looking at this figure shows that the overall shapes of band structures alter remarkably via adsorption and that the band structure in the dissociative adsorption case also differs from that in the oxygen adsorption case. Evidently, these differences show the significant variation of surface electronic states by adsorption. One feature in common is that there appear no gap states in all cases, which indicates semiconducting nature. Interestingly, band gap for pristine surface is always the smallest, followed by the dissociative and simultaneous adsorption case, independent of whether surface is terminated with (101) or (001). This obvious broadening of band gap after adsorption reveals that electrons may be harder to transfer from valence band (VB) to conduction band (CB), thereby suggesting more semiconducting nature of the adsorbed surfaces. In comparing the band-gap values of (101) cases with those of (001) cases, we notice further that the (001) cases are of less semiconducting character, as their band gaps are always smaller. This infers that electrons in the (001) case are less difficult to be excited from VB to CB, which enables more possible conductivity when they are produced externally.

Figure 5 shows density of states (DOS) for both the TiO₂ (101) and (001) surfaces before and after adsorption. A looking at this figure confirms the sharp change of electronic states by adsorption and the absence of gap states in all cases, as what was seen in the band-structure plots (Fig. 4). A key feature is that the VB for the adsorbed cases, which consists mainly of oxygen states, shifts towards low-energy region after adsorption. This could be important for the conductivity degradation of adsorbed surfaces because the shift may lower the probability of electron transfer from VB to CB states or CB traps if intrinsic electrons are excited thermally or electrically. Positively, the worsening of conductivity may facilitate a sharp change of electrical signal after the introduction of reductive gas, thereby contributing to the high sensitivity of TiO₂-based sensors.

Table 2 lists Mulliken population for a typical oxygen atom before and after adsorption. From this table, one can see that oxygen in all four cases gains electrons from surface

Fig. 4 Band structures of (101) and (001) surfaces before and after adsorption: (a) pristine (101) surface (A_0 model), (b) A_1 , (c) A_2 , (d) pristine (001) surface (B_0 model), (e) B_1 , and (f) B_2 . The numbers show band-gap values in each case.

Fig. 5 Density of states (DOS) for TiO_2 (a) (101) and (b) (001) surfaces before and after oxygen adsorption.

Table 2 Mulliken population for a representative oxygen atom before and after adsorption. Refer to Fig. 2 for the atomic configurations of A_1 , A_2 , B_1 , and B_2 .

Before		After		
O	A_1	A_2	B_1	B_2
6.458	6.845	6.956	6.985	7.254

TiO_2 atoms. The numbers of obtained electrons in the two (101) cases are 0.387 e (A_1) and 0.489 e (A_2), respectively, while those in the two (001) cases 0.527 e (B_1) and 0.796 e (B_2). This clearly shows that the electron transfer on the (001) surface is larger than that on the (101), which can be explained by the more oxygen atoms adsorbed on the (001) surface. Further, the large charge transfer may cause depletion of charge surrounding TiO_2 surface, thereby impeding possible current flow across the surface.

To shed light on electron transfer and gas-sensing characteristic qualitatively, we illustrate in Fig. 6 the adsorption process. As the operating temperature (i.e., TiO_2 surface temperature) increases, the atmospheric oxygen

Fig. 6 Schematic illustration of the electron transfer process between the adsorbed oxygen and the TiO_2 surface.

molecule is ready to be adsorbed on surface and decomposed into two atomic oxygen atoms. In light of aforementioned energy calculations, the two atoms can be adsorbed simultaneously on TiO_2 surface and exchange electrons with the surface, which eventually evolve into several forms of oxygen ions. The entire adsorption and reaction process can be expressed as follows.²¹⁾

The adsorbed O atoms, which are of strong electron negativity, may act as traps for CB electrons of TiO₂ and therefore increase electric resistance across the surface. When reductive gas is introduced, these adsorbed oxygen atoms react first with the gas on the oxide surface, as schematically shown in Fig. 6. Further incorporation of gas may deoxidize the lattice oxygen of TiO₂ and therefore result in the formation of oxygen vacancies surrounding the surface. These lattice defects can also serve as electron traps, which affect the electric properties of TiO₂ surface significantly, although further studies on such effect are required. The electrons produced by the surface reactions may enhance the conductivity through the oxide, thereby resulting in an increase of output voltage, as generally observed at the working stage of a sensor.

Based on the Mulliken population analysis, the adsorbed oxygen on the (001) surface is found to be able to obtain more electrons from the TiO₂ surface, inferring that higher response signal (i.e., higher sensitivity) can be likely. In addition, the larger band gap observed in the adsorbed (001) case may contribute further to the enhancement of response signal. These calculation results suggest that the increase of concentration of TiO₂ (001) facets would be a potential technique for better sensitivity improvement of TiO₂-based gas sensors.

4. Conclusions

We have performed a first-principles study of oxygen adsorption on anatase TiO₂ aimed at determining stable configuration, estimating adsorption energetics, and providing insight into electronic structures of adsorbed surfaces. We have found that the model with double oxygen atoms sitting simultaneously atop the Ti_{5C} of (001) surface shows the lowest exothermic ΔE_{ads} , suggestive of fundamental effect of surface on strong adsorption. Between the two experimentally observed surfaces, (101) and (001), the latter is found to be able to absorb more oxygen and have larger charge transfer with adsorbed oxygen, which deteriorates surface conductivity of TiO₂ but ultimately results in sensitivity enhancement. This indicates that a careful preparation of novel anatase TiO₂ crystals with a large amount of (001) facets may be important for further improvement of sensing properties of TiO₂-based gas sensors.

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