Effect of Oxygen Vacancy on the Adsorption of O₂ on Anatase TiO₂(001): A DFT-Based Study

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Abstract

We performed density functional theory (DFT) based calculations to investigate the effects of O-vacancies on the adsorption of O₂ on anatase TiO₂(001). Our calculation results show that we can promote O₂ adsorption on an initially inert stoichiometric TiO₂(001) by introducing O-vacancy. The resulting excess electrons from the introduction of the O-vacancy redistribute around the neighboring Ti ions. An incoming O₂ can then adsorb at the O-vacancy site, either in the superoxide state (O₂⁻) or the peroxide state (O₂²⁻). In the O₂⁻ state, the O-O bond is oriented parallel to the surface, along [010]. In the O₂²⁻ state, the O-O bond is oriented perpendicular to the surface, along [001]. Healing of the surface occurs when one of the O atoms of the perpendicularly adsorbed O₂ fills the vacant site and the other atom diffuses, recovering the stoichiometric surface.

Keywords: oxygen, vacancy, orientation, TiO₂, anatase, surface, healing

1. Introduction

Titanium dioxide (TiO₂) has attracted a lot of attention because of its various promising industrial applications, e.g., photocatalytic water splitting and hydrogen production [1, 2], organic dye-sensitized solar cells [3], solar energy conversion [4], to name a few. In almost all these applications, O₂ adsorption on TiO₂ plays an important role. They act not only as the main oxidizing reagents but also as electron scavengers in photo-oxidation processes [5]. In addition, experiments report that doping nitrogen increases O-vacancy formation and enhances the oxygen reduction reactions (ORRs) on TiO₂ surfaces [6–9]. This makes TiO₂ even more attractive as an alternative material to replace the expensive platinum used, e.g., as electrocatalysts in fuel cells.

There are two polymorphs of TiO₂ used widely in the industry, viz., rutile and anatase. Rutile surfaces have been extensively studied in the last decade, both experimentally (using STM/STS: scanning tunneling microscopy/spectroscopy and FIM: field ion microscopy, among others) and theoretically (esp., DFT: density functional theory-based calculations) [10–12]. Anatase surfaces have also been studied (e.g., in terms of processes such as molecular adsorption, dissociation, and diffusion) and found to exhibit efficient catalytic reactivity [13, 14]. However, we still lack theoretical studies about ORRs on TiO₂ surfaces, esp., on the anatase phase.

Anatase surfaces are mostly exposed (101) facets together with a small amount of (001) facets (less than ca. 6%, according

to the Wulff construction [15]). However, the minority (001) surface exhibits high-reactivity [16, 17]. In particular, anatase TiO₂(001) was found to be active for oxygen adsorption, with a corresponding oxygen adsorption energy lower than anatase TiO₂(101) [18]. Both (high reactivity to oxygen adsorption and the small oxygen adsorption energy) play important roles in ORRs.

Depending on the experimental conditions [19–29], unreconstructed [22–24] and (1 × 4) reconstructed [25–27] anatase TiO₂(001), or both could be realized [20, 21]. Studies have shown that the unreconstructed (001)-(1 × 1) is rather unstable [20, 28, 29]. There is a large tensile stress present on the unreconstructed (001)-(1 × 1), which can be attributed to the symmetry breaking, resulting in the inequivalent Ti-O bond lengths on the surface. (1 × 4) reconstruction of anatase TiO₂(001), realized by replacing the rows of surface bridging oxygens with rows of TiO₃ species, relieves this large surface tensile stress [20, 28, 29].

Experimental studies [30–32], using Auger electron spectroscopy, low-energy-electron-diffraction, electron-energy-loss spectroscopy, confirmed the presence of Ti³⁺ ions in both rutile and anatase phases, upon removing O atoms from stoichiometric TiO₂. The presence of Ti³⁺ ions can also be associated with the appearance of a new state in the band gap, ca. 0.7 – 0.9 eV below the Fermi level (*E_F*) [33, 34]. Electron spin resonance (ESR) observations (done on TiO₂ P-25 powder, having a mixed phase of anatase and rutile, in the ratio of 4:1) suggest that the trapped electrons are excited to the conduction band (CB) upon illumination of light, with energy lower than the band gap, and are re-trapped as Ti³⁺ cations in the dark [35]. On the reduced (O-deficient) rutile TiO₂(110) surface, with Ti³⁺ ions present, studies have identified a non-vacancy-related O₂

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dissociation channel, resulting in O adatom pairs [36]. This is in addition to the O₂ dissociation channel that occurs at the vacancy site, which results in filled vacancies and isolated O adatoms [34]. However, the effect of vacancy sites on the interaction between O₂ and anatase surfaces, especially the (001) surface, still need further clarification.

Here we present results of our DFT-based study on the molecular adsorption of O₂ on (2 × 2) unreconstructed anatase (001) surface. We make a comparison between stoichiometric and reduced anatase TiO₂(001) surface and discuss the influence of O-vacancy on the O₂ adsorption in terms of the corresponding adsorption configuration, adsorption energy, and electronic properties.

2. Calculation details

To study the molecular adsorption of O₂ on anatase TiO₂(001), we performed spin-polarized, DFT-based total energy calculations [37]. The electron-ion interactions are described by projector-augmented wave (PAW) potentials [38]. For the exchange correlation energy, we adopt the Generalized Gradient Approximation (GGA), using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [39]. The Kohn-Sham equations are solved using plane waves with kinetic energies up to 520 eV. Surface Brillouin zone integration is performed using the special *k*-point sampling technique of Monkhorst-Pack [40], with (5 × 5 × 1) sampling meshes. No significant change in the numerical results is observed when we increase the kinetic energy cutoff and the number of sampling points. Dipole corrections are also taken into account in all the calculations.

We start from an optimized bulk anatase TiO₂ structure. The corresponding calculated bulk lattice parameters are $a = b = 3.79(4)$ Å and $c = 9.51(5)$ Å, in good agreement with previous theoretical studies [15, 41]. To model the anatase TiO₂(001) (2 × 2) surface, we used a four layer slab of TiO₂ units, consisting of 48 atoms: 16 Ti and 32 O, separated by 20 Å of vacuum space along [001], in a supercell geometry (cf., Fig. 1). The bottom two layers (of TiO₂ units) represent the bulk anatase TiO₂, and consist of 6-fold coordinated Ti ions (Ti_{6c}) and 3-fold coordinated O ions (O_{3c}). The top two layers (of TiO₂ units) represent the anatase TiO₂(001). The unsaturated 5-fold coordinated Ti ions (Ti_{5c}) are located on the same plane, the Ti-plane, which we use as the reference plane for the adsorption process. The planes containing the 2-fold coordinated O (O_{2c}) and the 3-fold coordinated O (O_{3c}) are located above and below the Ti-plane, respectively. Thus, the topmost layer consists of three atomic layers, viz., the O_{2c}-, the Ti_{5c}- (or Ti)-, and O_{3c}-planes, in order starting from the vacuum side. This amount of slab layers is sufficient to produce good convergence of the anatase TiO₂(001) surface energy [15, 16], ~1 J/m². We fixed the bottom two layers (of TiO₂ units) to the corresponding calculated bulk positions, to maintain the bulk characteristics, and allow the the top two layers to relax to the optimized surface geometry. We took into account the symmetry of the surface to obtain the ground-state structure. Note the small energy difference between the symmetry-preserving surface and

the symmetry-breaking surface, and the similarity in the corresponding surface electronic structures [22, 44].

3. Results and Discussions

3.1. Stoichiometric anatase TiO₂(001)

3.1.1. O₂ adsorption

On the optimized anatase TiO₂(001), the O_{2c} are displaced outwards (0.016 Å), while the O_{3c} and Ti_{5c} relax inwards (0.038 Å and 0.068 Å, respectively). As a result, the anatase TiO₂(001) is under tensile stress, as previously observed for bulk anatase and other anatase surfaces, and attributed to the repulsion between the O atoms [15, 41]. Each O_{2c} binds equally to two Ti_{5c}, forming a -Ti-O-Ti- chain, with a subtended angle of 149.9° (155.4° for the bulk). Because we took into account the structural symmetry of the system, no structural symmetry breaking was observed.

We set the concentration of O₂ adsorption to 0.25 monolayer (0.25 ML). O₂ can be adsorbed on four sites, in five stable adsorption configurations, as shown in Fig. 2. To evaluate the stability of the adsorption configuration, we calculate the corresponding adsorption energy E_{ads} , in terms of the difference in the corresponding energies for the surface after adsorbing O₂ ($E_{\text{O}_2/\text{surf}}$) and the isolated surface (E_{surf}) and O₂ ($E_{\text{O}_2}^{\text{gas}}$, in the triplet ground state [42, 43]), i.e.,

$$E_{\text{ads}} = E_{\text{O}_2/\text{surf}} - [E_{\text{surf}} + E_{\text{O}_2}^{\text{gas}}]. \quad (1)$$

In Table 1, we show the computed adsorption energy (E_{ads} , Eq. 1), bond length of adsorbed O₂ ($r_{\text{O-O}}$), and amount of charge transfer (ΔQ) from anatase TiO₂(001) to the adsorbed O₂ at each of the five stable adsorption configurations/sites. All five configurations show positive E_{ads} , indicating that O₂ cannot adsorb on the stoichiometric anatase TiO₂(001) surface, for all four sites and five configurations considered. The most stable configuration, with $E_{\text{ads}} = 0.37$ eV, corresponds to O₂ center-of-mass (CM) located atop O_{2c}, with the O-O bond oriented parallel to the surface along [010] (Fig. 2c). Adsorption at other sites, e.g., O₂ CM atop Ti_{5c} with the O-O bond oriented perpendicular to the surface along [001] (Fig. 2b), O₂ CM atop O_{2c} with the O-O bond oriented perpendicular to the surface along [001] (Fig. 2d), and O₂ CM atop O_{3c} with the O-O bond oriented parallel to the surface along [100] (Fig. 2e) have quite similar endothermic E_{ads} . The most endothermic corresponds to O₂ adsorption at the hollow site (Ho), with the O-O bond oriented parallel to the surface along [010] (Fig. 2f). At all the four sites, the O-O bond length of the adsorbed O₂ is longer than the corresponding gas phase bond length $r_{\text{O-O}}^{\text{gas}} = 1.21$ Å [45]. Bader charge analysis [46] of the adsorbed surface also shows that the adsorbed O₂ retain a triplet spin state, as O₂ does in the gas phase [42, 43].

O-O repulsion plays a significant role in deciding the structure of anatase surfaces [15]. This strong O-O repulsion on the surface is the reason why it is difficult for the O₂ to adsorb on the stoichiometric surface. It explains the endothermic adsorption on the stoichiometric surface. In order to make adsorption favorable on this surface, it is necessary to decrease

the O-O repulsion on the surface, and the easiest way to do that is to reduce the number of surface O atoms, i.e., by forming O-vacancies on the surface. In the next section, we discuss the reduced (O-deficient) anatase TiO₂(001).

3.2. Reduced anatase TiO₂(001)

3.2.1. O-vacancy

To study the role of O-vacancy on O₂ adsorption, we consider an anatase TiO₂(001) – (2 × 2), with the following four possible O-vacancy configurations/locations: O_{2c} and O_{3c} planes of the topmost layer (of TiO₂ units), and the O planes of the next layer (of TiO₂ units) (cf., Fig. 1). These are also alternatively labeled as 1st-, 2nd-, 3rd-, 4th-layers, respectively, in Fig. 3.

To evaluate the feasibility of realizing such O-vacancies, we calculate the corresponding formation energy ($E_{\text{O}}^{\text{vacancy}}$), in terms of the difference in the corresponding energies for a stoichiometric anatase TiO₂(001) – (2 × 2) ($E^{\text{stoichiometric}}$) with that of a reduced (O-deficient) surface (E^{reduced}) and a free O in the gas phase ($\frac{1}{2}E_{\text{O}_2}^{\text{gas}}$, cf., Eq. 1 [42, 43]), i.e.,

$$E_{\text{O}}^{\text{vacancy}} = E^{\text{reduced}} - [E^{\text{stoichiometric}} + \frac{1}{2}E_{\text{O}_2}^{\text{gas}}]. \quad (2)$$

The computed $E_{\text{O}}^{\text{vacancy}}$ are shown in Table 2. We see that the O_{2c} plane has the lowest O-vacancy formation energy, $E_{\text{O}}^{\text{vacancy}} = 4.00$ eV, in agreement with previous studies [47]. The deeper we go into the bulk, starting from the O_{2c}-plane, to the O_{3c} plane, and then the O planes (alternatively, the 1st-, 2nd-, 3rd-, 4th- layers, respectively, in Fig. 3), the larger the formation energy needed.

On the reduced anatase TiO₂(001), a missing O at O_{2c} (O_{2c}^{vacant}) breaks the symmetry, and generates two 4-fold coordinated Ti ions (Ti_{4c} in Fig. 4). Thus, there are two Ti_{4c} and two Ti_{5c} ions per unit cell of reduced anatase TiO₂(001). As shown in Table 3 (first column, $U = 0.0$ eV), the Ti_{4c} ions move 0.13 Å into the bulk. The nearest O_{2c} atom from the O_{2c}^{vacant} site (O_{2c}^{1st}) moves outward 0.56 Å from surface, decreasing the subtended angle of the chain –Ti_{4c}–O_{2c}^{1st}–Ti_{4c}– to 98.75° and shortening the Ti_{4c}–O_{2c}^{1st} bond length to 1.83 Å (from 1.96 Å in the stoichiometric anatase TiO₂(001)). Meanwhile, the other O_{2c}, viz., the 2nd nearest (O_{2c}) and the 3rd nearest O_{2c} (O_{2c}^{3rd}) move slightly (0.02 Å and 0.09 Å, respectively) into the bulk. The O_{3c} ions move slightly outwards (0.04 Å) from their initial positions. These displacements enhance the tensile stress of the surface. The presence of O_{2c}^{vacant} also breaks the equal proportionality/symmetry of the bonds between O_{3c} and its two nearest Ti ions (Fig. 4). The two O_{3c}–Ti bonds, which were 1.94 Å in a stoichiometric (001) surface, become Ti_{4c}–O_{3c} and Ti_{5c}–O_{3c}, with bond lengths 1.91 Å and 2.01 Å, respectively.

In bulk anatase, O-vacancy results in delocalized excess electrons [17, 48]. On the reduced anatase TiO₂(001) – (2 × 2), two excess electrons are created per O-vacancy (O_{2c}^{vacant}). As shown in Table 3 (first column, $U = 0.0$ eV), the Ti_{4c} gains almost all the excess electron (ca. 0.32 e) due to O_{2c}^{vacant}, leaving little to the other surface atoms, viz., O_{2c}^{1st}, O_{2c}^{2nd}, O_{2c}^{3rd}, O_{3c}, and Ti_{5c}. In the corresponding density of states (DOS) (Fig. 5b), we also

the excess electrons localized at the two neighboring Ti_{4c}, and appearing as defect states in the middle of the gap between the valence band maximum (VBM) and the conduction band minimum (CBM) (cf., Figs. 5(a),(b)). This localization induces antiferromagnetic coupling between the two Ti_{4c}, via the intermediate O_{2c}^{1st}, to conform with the Pauli Exclusion Principle. These defect states locate near the E_F , just below CBM. This result indicates that with standard GGA, we cannot clearly distinguish the experimentally observed the localized states in the band gap of the reduced anatase TiO₂(001) [34, 35, 49, 50].

In order to simulate the position of the defect states in the electronic structure of anatase TiO₂(001) [34, 35, 49, 50], we performed additional calculations, adding the on-site Coulomb interaction U [51] to the d electrons of the Ti atoms, using values $2.5 \text{ eV} \leq U \leq 5.0 \text{ eV}$, following previous studies for Ti $3d$ states in bulk anatase [47, 48].

As to be expected, we observe a corresponding change in the distributions of the excess electrons, which are mostly concentrated around the d states of the Ti_{4c} ions, and a modification of the Ti_{4c}–O_{2c}^{1st} interaction. Table 3 shows how the corresponding changes of the surface Ti and O atom in the surface layer and the charge transfer from O_{2c}^{vacant} varies with U . The optimized reduced anatase TiO₂(001), computed with GGA+ U shows an outward displacement of all surface atoms, elongating and releasing the tensile stress of the surface. Meanwhile, the Ti_{5c}–O_{2c}^{2nd} and Ti_{5c}–O_{2c}^{3rd} bonds are only slightly modified. This results in the enhancement of the O-O repulsion on the reduced anatase TiO₂(001).

Figs. 5(c)-(f) shows how the corresponding DOS changes with U . First thing we see is that most of the charge transfer still occur near Ti_{4c}, in the vicinity of O_{2c}^{vacant}. Next, we note that the inclusion of U weakens the exchange interaction of Ti_{4c}–O_{2c}^{1st}. It changes the nature of the interaction between the two Ti_{4c} atoms, from antiferromagnetic (cf., Fig. 5(b)) to ferromagnetic (cf., Fig. 5(c)-(f)).

We also see that the DOS of the surface O_{2c}, especially the O_{2c}^{1st}, become more localized. As we increase U , CB shifts further away from E_F , whereas valence band (VB) shifts towards E_F . The defect states appearing in the gap between VBM and CBM, near E_F , in turn, shifts towards VBM. With $U = 4.0$ eV (Fig. 5e), the defect states are located ca. 1.25 eV below CBM. With $U = 5.0$ eV (Fig. 5f), the defect states are located ca. 1.84 eV below CBM. Based on previous experimental [49, 50, 52–55] and theoretical [32] studies, we find that $U = 4.0$ eV could well-describe the localized states of the reduced anatase TiO₂(001).

3.2.2. O₂ (molecular) adsorption (at the O-vacancy site)

Since the excess electrons are localized at Ti_{4c}, we chose the neighboring O-vacancy site, i.e., O_{2c}^{vacant}, as the active site for O₂ adsorption. We have confirmed that unconstrained O₂ adsorption only occurs at O_{2c}^{vacant}, and O₂ cannot chemically absorb on the other sites on the reduced anatase TiO₂(001). This agrees with earlier studies [50]. We have also identified two relevant adsorption configurations, viz., O₂ located atop the O-vacancy site, with O-O bond oriented parallel to the surface along [010] ($D1$ configuration) and perpendicular to the surface along [001]

(D2 configuration), as illustrated in Figs. 6(a) and (b), respectively.

3.2.2.1 D1 configuration: O-O bond along [010] (cf., Fig. 6(a)). With O₂ located atop the O-vacancy site, and the O-O bond oriented parallel to the surfalong [010], $E_{\text{ads}} = -4.82$ eV. This indicates very stable O₂ adsorption in the D1 configuration on the reduced anatase TiO₂(001). The O₂ binds with the Ti_{4c}, at an O-Ti_{4c} distance of 1.87 Å, and gains $\Delta Q = 1.028e$ from the surface, to form a superoxide anion (O₂⁻). In this adsorbed O₂⁻ state, $r_{\text{O-O}}(\text{O}_2^-) = 1.37$ Å and the stretching frequency $\nu_{\text{O-O}}(\text{O}_2^-) = 1049.7$ cm⁻¹. We can compare this with the O₂ intermediates observed in ORRs on Pt electrodes by surface-enhanced infrared reflection adsorption spectroscopy with attenuated total reflection [57, 58], with $r_{\text{O-O}}(\text{O}_2^-) = 1.37$ Å and $\nu_{\text{O-O}}(\text{O}_2^-) = 1016$ cm⁻¹. This suggests that anatase could be a promising alternative catalyst in the ORRs. In comparison, on (101), the adsorbed O₂ can be observed in the peroxide state (O₂²⁻) with the same O₂ coverage, [55]. The results are in good agreement with studies of anatase particles using electron paramagnetic resonance (EPR) spectroscopy [59, 60]. We also found that the dissociation of adsorbed oxygen could not be realized on this surface, even with the presence of O-vacancy, which agrees with the experimental results from STM studies [50].

3.2.2.2 D2 configuration: O-O bond along [001] (cf., Fig. 6(b)). With O₂ located atop O_{2c}^{vacant}, and the O-O bond oriented perpendicular to the surface along [001], $E_{\text{ads}} = -4.00$ eV. This also indicates stable O₂ adsorption in the D2 configuration on the reduced anatase TiO₂(001). In this configuration, O₂ tends to come closer to the Ti_{4c}-plane, and the lower O atom fills up the O-vacancy site and bonds with two Ti_{4c} ions, at a O-Ti_{4c} distance of 2.02 Å, cf., Fig. 6(b). Compared to the D1 configuration, the D2 configuration exhibits a larger charge transfer $\Delta Q = 1.23e$ from the two Ti_{4c} ions, as shown in Table 4. In both the D1 and D2 configurations, there is negligible (one order of magnitude less) charge transfer between the incoming O₂ with the oxygen ions far from the O_{2c}^{vacant}, viz., O_{2c} and O_{3c}. Most of the charges transfer come from the Ti_{4c} ions to the adsorbed O₂. This indicates the critical role of the excess electrons on Ti_{4c}, which is due to the O-vacancy at O_{2c}, in making O₂ adsorption on this surface more favorable.

In this D2 configuration, the adsorbed O₂ forms a peroxide state (O₂²⁻), with $r_{\text{O-O}}(\text{O}_2^{2-}) = 1.47$ Å and $\nu_{\text{O-O}}(\text{O}_2^{2-}) = 908.0$ cm⁻¹. Again, we can compare this with the O₂ observed on Pt(111) [58, 61–63], with $r_{\text{O-O}}(\text{O}_2^{2-}) = 1.47$ Å and $\nu_{\text{O-O}}(\text{O}_2^{2-}) = 870$ cm⁻¹. Finally, we also found that the dissociation is unfavorable on this surface,

Note: The calculations results for $U = 0.0$ and 4.0 eV differ only in the corresponding E_{ads} (cf., Table 4). For both $U = 0.0$ and 4.0 eV, we get D1 as the more stable adsorption configuration, as compared to D2. As mentioned earlier, there is an enhancement of the O-O repulsion in the reduced surface, within the GGA+ U calculations. It interferes with the creation of bond between the incoming O₂ and the Ti_{4c} ions.

As a result, we expect a lower E_{ads} from GGA+ U calculations for anatase TiO₂(001), i.e., $E_{\text{ads}} = -4.08$ eV (cf., Table 4). In the D1 configuration, GGA+ U calculations indicate that the O₂ still has O₂⁻ character, with $r_{\text{O-O}}(\text{O}_2^-) = 1.39$ Å and $\nu_{\text{O-O}}(\text{O}_2^-) = 1033.1$ cm⁻¹. Similarly, in the D2 configuration, the O₂²⁻ character persists, with $r_{\text{O-O}}(\text{O}_2^{2-}) = 1.48$ Å and $\nu_{\text{O-O}}(\text{O}_2^{2-}) = 888.5$ cm⁻¹. The GGA+ U calculations give a better description of the energetic position of the defect states (in electronic structure) of the reduced anatase TiO₂(001). However, there seem to be no significant direct correlation between the location of the defect states with the corresponding E_{ads} , $r_{\text{O-O}}$, and ΔQ . Furthermore, we see that, on the reduced anatase TiO₂(001), the defect states disappear upon O₂ adsorption, for both GGA and GGA+ U results (cf., Figs. 5 and 7). This attenuation of the defect peak signal after oxygen adsorption has also been observed by resonant photoemission spectroscopy [49]. From Table 4, we see that almost all the excess electrons, which Ti_{4c} ions gained from the O_{2c}^{vacant}, transfer to incoming the O₂, and occupy the π^* antibonding states of the adsorbed O₂, with corresponding energy levels located just below E_F . DOS calculated with GGA+ U are more localized than those calculated with GGA. However, both GGA and GGA+ U calculations do not show any significant difference in electronic structure of the system after molecular adsorption. The adsorbed O₂ shares a strong bond with the nearest Ti ions on the reduced TiO₂(001). Due to the missing surface O_{2c}, the two neighboring Ti ions gain excess electrons. These excess electrons enable the Ti ions to attract the incoming O₂. As the result, O₂ can easily adsorb on this surface.

3.2.2.3 Healing on the reduced anatase TiO₂(001). The D2 configuration is not as stable as the D1 configuration. However, the D2 configuration cannot relax to the D1 configuration. Moreover, in the optimized D2 configuration, -Ti_{4c}-O_{ad1}-Ti_{4c}- subtend an angle of 155.5°, and -Ti_{4c}-O_{2c}^{1st}-Ti_{4c}- has a subtended angle of 146.8°, which is close to that of a stoichiometric anatase TiO₂(001) (i.e., 149.9°). According to our calculations, the stoichiometric anatase TiO₂(001), with an O adatom at the O_{2c} site is around 0.5 eV more stable than the reduced anatase TiO₂(001) with O₂ in D2 configuration. This implies that one O from the incoming O₂ can fill the O-vacancy of the reduced anatase TiO₂(001), *healing* the reduced surface, while the other O atom may become an O-adatom and diffuse to other sites, on the *healed* stoichiometric surface. The *healing* effect of the incoming O₂ corresponds to the disappearance of point defects observed in STM studies [50]. This behavior is also observed on rutile TiO₂(110) [64] and anatase TiO₂(101) [65]. Nevertheless, the potential energy surface (PES) for O-adatom diffusion on the stoichiometric anatase TiO₂(001) [66] shows that O-adatom can move to the position at the middle of the Ti_{5c}-O_{2c} bond without any barrier (Fig. 8). The configuration corresponding to the case when the O-adatom is at a local minima above the middle of the Ti_{5c}-O_{2c} bond can also be seen in oxygen evolution reaction (OER) [67]. It takes around 1.2 eV for the O-adatom to diffuse to the nearest Ti_{5c} site, and around 1.05 eV to diffuse to the nearest hollow site (Ho). Difficulty in the diffusion of the O-adatom on the stoichiometric

anatase $\text{TiO}_2(001)$ reduces the efficiency of the surface chemical reactions, and hence, slows down the rate of ORRs. In this situation, the $D2$ configuration would show a decreased rate in chemical reactions on the anatase $\text{TiO}_2(001)$.

4. Conclusions

We performed DFT-based calculations to investigate the effect of O-vacancy on the electronic structure and the adsorption of oxygen on anatase $\text{TiO}_2(001)-(2\times 2)$. Our calculation results show that the stoichiometric anatase $\text{TiO}_2(001)$ does not favor O_2 adsorption. Instead, we need a reduced anatase $\text{TiO}_2(001)$, i.e., the presence of O-vacancy, to promote O_2 adsorption. The absence of 2-fold coordinated O (O_{2c}) ion on the surface leads to excess electrons. These excess electrons redistribute locally around the two neighboring 4-fold coordinated Ti ions (Ti_{4c}) and an associated localized defect state appears in the corresponding electronic structure. The localized defect state can be described well with $\text{GGA}+U$. However, regardless of the value of U considered, we find no significant qualitative change in the results of the O_2 adsorption on this surface. On the reduced (O-deficient) anatase $\text{TiO}_2(001)$, the O-vacancy sites become active sites, making O_2 adsorption favorable and exothermic. Here, we considered two adsorption configurations, viz., O_2 adsorbs at the O-vacancy with the O-O bond oriented parallel to the surface along the $[010]$ ($D1$ configuration), and with the O-O bond oriented perpendicular to the surface along $[001]$ ($D2$ configuration). In the $D1$ configuration, the incoming O_2 adsorbs with a superoxide state (O_2^-). In the $D2$ configuration, the incoming O_2 adsorbs with a peroxide state (O_2^{2-}). Both results for the adsorbed states of O_2 in the corresponding $D1$ and $D2$ configurations agree with previous results observed for oxygen adsorption on Pt surfaces[60–62]. Healing of the reduced anatase $\text{TiO}_2(001)$ can take place with the $D2$ configuration, where one adsorbed O atom fills the O-vacancy and the other becomes an O-adatom on the healed surface. The O adatom can move easily to positions in the middle of the Ti–O bond along $[010]$, but it is difficult for the O-adatom to diffuse to other positions. It could reduce the efficiency of the surface chemical reactions and slow down the reaction rate. From this point-of-view, further studies are required to increase the diffusion process of O-adatom on the stoichiometric surface and make anatase $\text{TiO}_2(001)$ surface more chemically active.

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- [1] K. Rajeshwar, J. Appl. Electrochem. 37, 765 (2007).
- [2] M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. Mi, E. A. Santori, N. S. Lewis, Chem. Rev. 110, 6446 (2010).
- [3] B. O'Regan, M. Grätzel, Nature 353, 737(1991).
- [4] P. V. Kamat, Chem. Rev. 93, 207-300 (1993).
- [5] M. A. Henderson, Surf. Sci. Rep. 66, 185 (2011).
- [6] M. Batzill, E. H. Morales, U. Diebold, Phys. Rev. Lett. 96, 026103 (2006).
- [7] J.-H. Kim, A. Ishihara, S. Mitsushima, N. Kamiya, K.-I. Ota, Electrochim. Acta 52, 2492 (2007).
- [8] M. Chisaka, A. Ishihara, K. Suito, K. I. Ota, H. Muramoto, Electrochim. Acta 88, 697 (2013).
- [9] K. I. Ota, Y. Ohgi, K. D. Nam, K. Matsuzawa, S. Mitsushima, A. Ishihara, J. Power Sources 196, 5256 (2010).
- [10] A. Fujishima, K. Honda, Nature 238, 37 (1972).
- [11] A. Fujishima, X. Zhang, D.A. Tryk, Surf. Sci. Rep. 63, 515 (2008).
- [12] U. Diebold, App. Surf. Sci. 48, 63 (2003).
- [13] L. Kavan, M. Grätzel, S. E. Gilbert, C. Klemenz, H. J. Scheel, J. Am. Chem. Soc. 118, 118, 6716 (1996).
- [14] K. I. Hadjiivanov, D. G. Klissurski, Chem. Soc. Rev. 25, 61 (1996).
- [15] M. Lazzeri, A. Vittadini, A. Selloni, Phys. Rev. B63, 155409 (2001); Phys. Rev. B65, 119901(E) (2002).
- [16] Z. Zhao, Z. Li, Z. Zhou, J. Phys. Condens. Matter 22 (2010) 175008; A. Vittadini, A. Selloni, F.P. Rotzinger, M. Gratzel, Phys. Rev. Lett. 81, 2954 (1998).
- [17] H. Ariga, T. Taniike, H. Morikawa, M. Tada, Byoung koun Min, K. Watanabe, Y. Matsumoto, S. Ikeda, K. Saiki, Y. Iwasawa, J. Am. Chem. Soc. 131, 14670 (2009).
- [18] W. Zeng, T. Liu, Z. Wang, S. Tsukimoto, M. Saito, Y. Ikuhara, Mater. Trans. 51, 171 (2010).
- [19] R. Hengerer, B. Bolliger, M. Erbudak, M. Grätzel, Surf. Sci. 460, 162 (2000).
- [20] G. S. Herman, M. R. Sievers, Y. Gao, Phys. Rev. Lett. 84, 3354 (2000).
- [21] G.S. Herman, Y. Gao, T.T. Tran, J. Osterwalder, Surf. Sci. Rep. 447, 201 (2000).
- [22] M. Calatayud, C. Minot, Surf. Sci. 552, 169 (2004)
- [23] R. Herenger, L. Kavan, M. Grätzel, J. Electrochem. Soc. 147, 1467 (2000).
- [24] G. Shukri, H. Kasai, Surf. Sci. 619, 59 (2014).
- [25] Y. Liang, S. Gan, S. A. Chambers, E. I. Altman, Phys. Rev. B63, 235402 (2001).
- [26] A. G. Thomas, W. R. Flavell, A. K. Mallick, A. R. Kumarasinghe, D. Tsoutsou, N. Khan, C. Chatwin, S. Rayner, G. C. Smith, R. L. Tockbauer, S. Warren, T. K. Johal, S. Patel, D. Holland, A. Taleb, F. Wiame, Phys. Rev. B75, 035105 (2007).
- [27] G. Liu, H. G. Yang, X. Wang, L. Cheng, H. Lu, L. Wang, G. Q. (Max) Lu, H. M. Cheng, J. Phys. Chem. C 113, 21784 (2009).
- [28] M. Lazzeri, A. Selloni, Phys. Rev. Lett. 87, 266105 (2001).
- [29] U. Diebold, N. Ruzycki, G. S. Herman, A. Selloni, Catal. Today 85, 93 (2003).
- [30] V. E. Henrich, G. Dresselhaus, H. J. Geiger, Phys. Rev. Lett. 36, 1335 (1976).
- [31] G. Lu, A. Linsebigler, J. T. Yates, J. Phys. Chem. 98, 11733 (1994).
- [32] C. D. Valentin, G. Pacchioni, A. Selloni, J. Phys. Chem. C 113, 20543 (2009).
- [33] R. L. Kurtz, R. Stock-Bauer, T. E. Madey, Surf. Sci. 218, 178 (1989).
- [34] M. A. Henderson, W. S. Epling, C. H. F. Peden, C. L. Perkins, J. Phys. Chem. B 107, 534 (2003).
- [35] K. Komaguchi, H. Nakano, A. Araki, Y. Harima, Chem. Phys. Lett. 428, 338 (2006).
- [36] S. Wendt, P.T. Sprunger, E. Lira, G.K.H. Madsen, Z. Li, J.O. Hansen, J. Matthiesen, A. Blekinge-Rasmussen, E. Lægsgaard, B. Hammer, F. Besenbacher, Science 320, 1755 (2008).
- [37] G. Kresse, J. Furthmüller, Phys. Rev. B54, 11169 (1996).
- [38] G. Kresse, D. Joubert, Phys. Rev. B59, 1758 (1999).
- [39] J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
- [40] H. J. Monkhorst, J. D. Pack, Phys. Rev. B13, 5188 (1976).
- [41] A. Fahmi, C. Minot, B. Silvi, M. Causa, Phys. Rev. B47, 11717 (1993).
- [42] S. Yotsuhashi, Y. Yamada, W.A. Diño, H. Nakanishi, H. Kasai, Phys. Rev. B72, 033415 (2005).

- [43] S. Yotsuhashi, Y. Yamada, T. Kishi, W.A. Diño, H. Nakanishi, H. Kasai, Phys. Rev. B77, 115413 (2008).
- [44] Z. Hua, D. Songyuan, W. Kongji, Plasma Sci. Technol. 6, 2467(2004).
- [45] R. Weast, CRC Handbook of Chemistry and Physics (CRC, Boca Raton, 1985).
- [46] W. Tang, E. Sanville, G. Henkelman, J. Phys.: Condens. Mat. 21, 084204 (2009)
- [47] A. Roldan, M. Boronat, A. Corma, F. Illas, J. Phys. Chem. C 114, 6511 (2010).
- [48] E. Finazzi, C. D. Valentin, G. Pacchioni, A. Selloni, J. Chem. Phys. 129, 154113 (2008).
- [49] A. G. Thomas, W. R. Flavell, A. R. Kumarasinghe, A. K. Mallick, D. Tsoutsou, G. C. Smith, R. Stockbauer, S. Patel, M. Gratzel, R. Hengerer, Phys. Rev. B67, 035110 (2003).
- [50] Y. Wang, H. Sun, S. Tan, H. Feng, Z. Cheng, J. Zhao, A. Zhao, B. Wang, Y. Luo, J. Yang, J.G. Hou, Nat. Commun. 4, 2214 (2013).
- [51] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, A. P. Sutton, Phys. Rev. B57, 1505 (1998).
- [52] V. E. Henrich, R. L. Kurtz, Phys. Rev. B23, 6280 (1981).
- [53] Z. Zhang, S. P. Jeng, V. E. Henrich, Phys. Rev. B43, 12004 (1991).
- [54] R. Heise, R. Courths, S. Witzel, Solid State Commun. 84 (1992) 599-602.
- [55] U. Aschauer, J. Chena, A. Sellonia, Phys. Chem. Chem. Phys. 12, 12956 (2010)
- [56] *Note: All vibrational frequency calculations were done by using finite-difference method to determine the second derivative of energy with respect to atomic position.*
- [57] M. Shao, P. Liu, R. R. Adzic, J. Am. Chem. Soc. 128, 7408 (2006).
- [58] T. Q. Nguyen, M. C. S. Escaño, H. Nakanishi, H. Kasai, Surf. Sci. 288, 244 (2014).
- [59] T. Berger, M. Sterrer, O. Diwald, E. Knozinger, D. Panayotov, T. L. Thompson, J. T. Yates, J. Phys. Chem. B 109, 6061 (2005)
- [60] E. Carter, A. F. Carley, D. M. Murphy, J. Phys. Chem. C 111, 10630 (2007).
- [61] J. L. Gland, B. A. Sexton, G. B. Fisher, Surf. Sci. 95, 587 (1980).
- [62] H. Steininger, S. Lehwald, H. Ibach, Surf. Sci. 123, 1 (1982).
- [63] D. A. Outka, J. Stohr, W. Jark, P. Stevens, J. Solomon, R. J. Madix, Phys. Rev. B35, 4119 (1987)
- [64] R. Schaub, E. Wahlström, A. Rønnau, E. Lægsgaard, I. Stensgaard, F. Besenbacher, Science 17, 377 (2003).
- [65] Y. Lei, F. Niu, H. Mei, Q. Liu, C. Pan, W. Xiao, Comp. Mater. Sci. 63, 58-65 (2012).
- [66] *Note: O adatom was relaxed in z-direction with its x and y coordinates fixed at different positions to map the PES.*
- [67] Y. F. Li, Z. P. Liu, L. Liu, W. Gao, J. Am. Chem. Soc. 132, 13008-13015 (2010)
- [68] K. Momma, F. Izumi, J. Appl. Cryst. 44, 1272 (2011).

Table 1: Computed adsorption energy (E_{ads} , Eq. 1) of O_2 on the stoichiometric $\text{TiO}_2(001)$, bond length of the adsorbed O_2 ($r_{\text{O-O}}$), and amount of charge transfer (ΔQ) from anatase $\text{TiO}_2(001)$ to the O_2 adsorbed at each of the five stable adsorption configurations/sites, viz., Ti_{5c} , $\text{O}_{2c}[010]$, $\text{O}_{2c}[001]$, O_{3c} , and Ho (cf., Fig. 2.). A positive value of E_{ads} correspond to the endothermic adsorption of O_2

Site	Ti_{5c}	$\text{O}_{2c}[010]$	$\text{O}_{2c}[001]$	O_{3c}	Ho
E_{ads} [eV]	0.55	0.37	0.54	0.53	0.98
$r_{\text{O-O}}$ [Å]	1.23	1.24	1.23	1.23	1.23
ΔQ [e]	0.02	0.04	0.01	0.01	0.01

Table 2: Oxygen vacancy formation energy ($E_{\text{O}}^{\text{vacancy}}$, Eq. 2) in anatase $\text{TiO}_2(001) - (2 \times 2)$ (cf., Figs. 1 and 3).

	O_{2c} -plane	O_{3c} -plane	O-plane	
Vacancy site	1st layer	2nd layer	3rd layer	4th layer
$E_{\text{O}}^{\text{vacancy}}$ [eV]	4.00	4.77	4.76	4.96

Table 3: Displacement (Δz) along [001] from the stoichiometric surface, bond length (r) between the surface Ti atoms (i.e., Ti_{4c} and Ti_{5c}) and the surface O atoms (i.e., $\text{O}_{2c}^{\text{1st}}$, $\text{O}_{2c}^{\text{2nd}}$, $\text{O}_{2c}^{\text{3rd}}$ and O_{3c}), the subtended angle of the $-\text{Ti}_{4c}-\text{O}_{2c}^{\text{1st}}-\text{Ti}_{4c}-$ chain, and charge gain/loss ($\pm \Delta Q$) by the neighboring surface Ti and O atoms due to the formation of $\text{O}_{2c}^{\text{vacant}}$, for various on-site Coulomb parameters U (cf., Fig. 4). Negative values of Δz correspond to displacement of the surface ions toward the bulk.

U [eV]	0.0	2.5	3.0	4.0	5.0
$\Delta z_{\text{Ti}_{4c}}$ [Å]	-0.13	0.00	0.04	0.07	0.10
$\Delta z_{\text{Ti}_{5c}}$ [Å]	-0.04	0.05	0.07	0.09	0.12
$\Delta z_{\text{O}_{2c}^{\text{1st}}}$ [Å]	0.56	0.55	0.59	0.64	0.69
$\Delta z_{\text{O}_{2c}^{\text{2nd}}}$ [Å]	-0.02	0.12	0.14	0.18	0.22
$\Delta z_{\text{O}_{2c}^{\text{3rd}}}$ [Å]	-0.09	0.02	0.04	0.07	0.10
$\Delta z_{\text{O}_{3c}}$ [Å]	0.04	0.07	0.07	0.09	0.11
$r_{\text{Ti}_{4c}-\text{O}_{2c}^{\text{1st}}}$ [Å]	1.83	1.86	1.87	1.88	1.89
$r_{\text{Ti}_{4c}-\text{O}_{3c}}$ [Å]	1.91	1.93	1.95	1.95	1.96
$r_{\text{Ti}_{5c}-\text{O}_{2c}^{\text{2nd}}}$ [Å]	1.96	1.96	1.96	1.97	1.97
$r_{\text{Ti}_{5c}-\text{O}_{2c}^{\text{3rd}}}$ [Å]	1.97	1.98	1.98	1.98	1.98
$r_{\text{Ti}_{5c}-\text{O}_{3c}}$ [Å]	2.00	1.97	1.97	1.97	1.97
$-\text{O}_{2c}^{\text{1st}}-\text{Ti}_{4c}-\text{O}_{2c}^{\text{1st}}$ [°]	98.75	111.09	110.91	110.11	109.44
$\Delta Q_{\text{Ti}_{4c}}$ [e]	0.32	0.35	0.36	0.38	0.39
$\Delta Q_{\text{Ti}_{5c}}$ [e]	0.00	-0.02	-0.03	0.00	0.00
$\Delta Q_{\text{O}_{2c}^{\text{1st}}}$ [e]	0.02	0.06	0.06	0.05	0.04
$\Delta Q_{\text{O}_{2c}^{\text{2nd}}}$ [e]	0.00	0.03	0.03	0.01	0.00
$\Delta Q_{\text{O}_{2c}^{\text{3rd}}}$ [e]	0.01	0.03	0.03	0.02	0.01
$\Delta Q_{\text{O}_{3c}}$ [e]	0.06	0.07	0.08	0.05	0.04

Table 4: Computed adsorption energy (E_{ads} , Eq. 1) of O_2 on the reduced $\text{TiO}_2(001)$, bond length of the adsorbed O_2 ($r_{\text{O-O}}$), the stretching frequency ($\nu_{\text{O-O}}$), and charge gain/loss ($\pm\Delta Q$) by the neighboring Ti and O atoms on O-reduced surface due to the adsorption of O_2 , for various on-site Coulomb parameters U (cf., Fig. 6).

	D1 configuration		D2 configuration	
$U[\text{eV}]$	0.0	4.0	0.0	4.0
$E_{\text{ads}} [\text{eV}]$	-4.82	-4.08	-4.00	-3.36
$r_{\text{O-O}} [\text{\AA}]$	1.37	1.39	1.47	1.48
$\nu_{\text{O-O}} [\text{cm}^{-1}]$	1049.7	1033.1	908.0	888.5
$\Delta Q_{\text{Ti}_{4c}} [e]$	-0.3	-0.36	-0.32	-0.42
$\Delta Q_{\text{Ti}_{5c}} [e]$	-0.01	-0.02	-0.01	-0.02
$\Delta Q_{\text{O}_{3c}} [e]$	-0.05	-0.04	-0.06	-0.05
$\Delta Q_{\text{O}_{2c}^{\text{1st}}} [e]$	-0.05	-0.09	-0.04	-0.07
$\Delta Q_{\text{O}_{2c}^{\text{2nd}}} [e]$	-0.01	-0.02	~ 0.00	-0.02
$\Delta Q_{\text{O}_{2c}^{\text{3rd}}} [e]$	-0.01	-0.01	-0.01	-0.01
$\Delta Q_{\text{O}_2^{\text{adsorbed}}} [e]$	1.03	1.08	1.23	1.3

Figure 1: Side view (along $[100]$) of the slab model for anatase $\text{TiO}_2(001) - (2 \times 2)$. We used a four layer slab of TiO_2 units, consisting of 48 atoms: 16 Ti (large/blue spheres) and 32 O (small/red spheres), separated by $20 \text{ \AA}$ of vacuum space along $[001]$, in a supercell geometry. The bottom two layers (of TiO_2 units) represent the bulk anatase TiO_2 , and consist of 6-fold coordinated Ti ions (Ti_{6c}) and 3-fold coordinated O ions (O_{3c}). The top two layers (of TiO_2 units) represent the anatase $\text{TiO}_2(001)$. The unsaturated 5-fold coordinated Ti ions (Ti_{5c}) are located on the same plane, the Ti-plane, which we use as the reference plane for the adsorption process. The planes containing the 2-fold coordinated O (denoted as O_{2c}) and the 3-fold coordinated O (denoted as O_{3c}) are located above and below the Ti-plane, respectively. Thus, the topmost layer consists of three atomic layers, viz., the O_{2c} -, the Ti_{5c} - (or Ti-), and O_{3c} -planes, in order starting from the vacuum side. The top two layers (of TiO_2 units) are fully optimized, while the bottom two layers (of TiO_2 units) are fixed. Ti : large/blue spheres. O: small/red spheres.

Figure 2: (a) Top view of a stoichiometric anatase $\text{TiO}_2(001)$, with the corresponding symmetric sites, viz., atop Ti_{5c} : the 5-fold coordinated Ti; atop O_{2c} : the 2-fold coordinated O; atop O_{3c} : the 3-fold coordinated O located slightly below the surface; and Ho: the hollow site. Also shown are the stable configurations for an incoming O_2 : (b) atop Ti_{5c} , with the O-O bond along $[001]$; (c) atop O_{2c} , with the O-O bond along $[010]$; (d) atop O_{2c} , with the O-O bond along $[001]$; (e) atop O_{3c} , with the O-O bond along $[100]$; and (f) atop Ho, with the O-O bond along $[010]$. Ti: large/blue spheres. O: small/red spheres. O_2 : small/yellow paired spheres.

Figure 3: Four O-vacancy positions on anatase $\text{TiO}_2(001) - (2 \times 2)$, viz., in the O_{2c} and O_{3c} planes of the topmost layer (of TiO_2 units), and the O planes of the next layer (of TiO_2 units) (cf., Fig. 1). These are also alternatively labeled as 1st-, 2nd-, 3rd-, 4th-layers. Ti: large/blue spheres. O: small/red spheres.

Figure 4: The reduced anatase $\text{TiO}_2(001)$ after relaxation. On the surface, there are two Ti_{4c} near the O-vacancy ($\text{O}_{2c}^{\text{vacant}}$) site. $\text{O}_{2c}^{\text{1st}}$, $\text{O}_{2c}^{\text{2nd}}$, and $\text{O}_{2c}^{\text{3rd}}$ represent the nearest, 2nd nearest, and 3rd nearest O_{2c} from the $\text{O}_{2c}^{\text{vacant}}$ site. (Inset) Top view of the reduced reduced anatase $\text{TiO}_2(001)$. Ti: large/blue spheres. O: small/red spheres.

Figure 5: Calculated local density of states (DOS) of (a) the stoichiometric $\text{TiO}_2(001)$ with $U = 0.0$ eV, and the reduced $\text{TiO}_2(001)$ for several on-site Coulomb interaction values U : (b) 0.0 eV, (c) 2.4 eV, (d) 3.0 eV, (e) 4.0 eV, and (f) 5.0 eV. The solid black lines represent the DOS contribution from the top surface layer. The filled curves represent the DOS contribution from the Ti_{4c} . The dash red lines represent the DOS contribution from the nearest O_{2c} from the O-vacancy site, i.e., $\text{O}_{2c}^{\text{1st}}$. The dot blue lines represent the DOS contributions from the 2nd nearest, and 3rd nearest O_{2c} from the O-vacancy site, $\text{O}_{2c}^{\text{2nd}}$ and $\text{O}_{2c}^{\text{3rd}}$, respectively. The arrows indicate the corresponding valence band maximum (VBM) and conduction band minimum (CBM). Energies given in [eV] with respect to the Fermi level (E_F).

Figure 6: Optimized structure of the two relevant adsorption configurations at the O-vacancy site, viz., (a) D1 configuration: O₂ adsorbs with the O-O bond parallel to the surface along the [010] direction and (b) D2 configuration: O₂ adsorbs with the O-O bond perpendicular to the surface along the [001] direction. In the D2 configuration, the bottom O (O_{ad1}) of O₂ protrudes from the surface, and the top O (O_{ad2}) is near the Ti_{4c}-plane. Ti: large/blue spheres. O: small/red spheres. O₂: small/yellow paired spheres.

Figure 7: Calculated density of states (DOS) of the top layer of the reduced (O-deficient) anatase TiO₂(001) after oxygen adsorption along [001] direction with (a) standard GGA ($U = 0$ eV) calculations and (b) GGA+ U ($U = 4$ eV) calculations. The arrows indicate the corresponding valence band maximum (VBM) and conduction band minimum (CBM). Energies given in [eV] with respect to the Fermi level (E_F).

Figure 8: Potential energy surface for O-atom diffusion on the stoichiometric $\text{TiO}_2(001)$. The coordinates (x, y) of the O-atom are given as fractional units of the (2×2) surface. The top-view and the symmetric sites correspond to Figure 2. (Inset) The configuration corresponding to the case when the O-atom is at a local minima above $(x, y) = (0, 0.125)$ Ti: large/blue spheres. O: small/red spheres. O-atom: smaller/yellow sphere. Contour spacing: 0.15 eV. Surface lattice parameter $a = 3.79(4)$ Å.