Defects at the (1 1 0) surface of rutile TiO$_2$ from *ab initio* calculations

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ARTICLE INFO

ABSTRACT

Defect segregation of oxygen vacancies, protons, titanium vacancies, and the mutual complex between the two latter (*i.e.* Ruetschi type defects) at the (1 1 0) surface of rutile TiO$_2$ has been studied through *ab initio* Density Functional Theory calculations (DFT). Oxygen vacancies and protons form mainly on the 2-fold coordinated oxygen sites, while titanium vacancy related defects are expected to be most prominent at the 5-fold titanium sites. All included defects are shown to be more stable at the surface than in the bulk oxide, and the relative tendency to segregate is most pronounced for oxygen vacancies. Based on the obtained defect segregation energies and previously calculated bulk defect chemistry at lower temperatures, our estimated surface defect formation energies indicate that the surface of TiO$_2$ can be expected to be dominated by titanium vacancies, protons and their mutual complexes at lower temperatures under wet, oxidizing conditions. Finally, possible routes of dissociative water adsorption on the surface, involving the aforementioned defects are discussed.

1. Introduction

Rutile TiO$_2$ is a binary oxide semiconductor with a band gap of ~3 eV which has attracted much attention due to its numerous applications based on its optical and photocatalytic properties [1]. However, several aspects of the properties and mechanisms of operation remain unknown, some possibly related to neglectance of obvious sides of its defect chemistry. Traditionally, it has been assumed that the defect chemistry of bulk rutile TiO$_2$ mainly is dominated by oxygen vacancies, titanium interstitials and electronic defects, as this is the signature of most of its high temperature and/or high-vacuum equilibrium properties. However, we recently showed that hydrogen in the form of protonic defects, $OH_O^\cdot$, plays a major role in the defect chemistry of rutile TiO$_2$ [2]. Incorporation of protons in acceptor doped TiO$_2$ from water vapor can be written:

$$H_2O(g) + O_O^x + v_O^{\cdot\cdot} = 2OH_O^\cdot \qquad (1)$$

i.e. by replacement of oxygen vacancies as the majority positive charge compensating defect, for which a hydration enthalpy of −1.35 eV (for Eq. (1)) was deduced from conductivity measurements [2]. In our recent study of bulk defects in rutile TiO$_2$ using hybrid DFT calculations and thermodynamic

modeling, we showed that cation vacancies and protons will dominate the defect structure of undoped TiO_2 at moderate temperatures and wet oxidizing conditions, according to [3];

$$2H_2O(g) + 2O_O^x = v_{Ti}^{4/} + 4OH_O^\bullet \qquad (2)$$

At lower temperatures, these oppositely charged defects tend to associate, thereby forming Ruetschi type defects, $i.e.$ $(v_{Ti}nOH_O)^{(4-n)/}$, with a simplified electroneutrality given by, $e.g.$ $3[(v_{Ti}OH_O)^{3/}] = [OH_O^\bullet]$. Although such defects are well known in $e.g.$ bulk MnO_2 [4,5] and have also been described in anatase TiO_2 [6], their impact on the surface defect chemistry of oxides has been neglected so far. However, in the case of sol-gel prepared anatase TiO_2, it has been indicated that the Ti site occupancy decreases with decreasing particle size [6], thus possibly indicating an enrichment of cation vacancies at the surface. Regarding surface studies of TiO_2, the (1 1 0) surface of rutile TiO_2 has become the model system due to its high stability, and has been extensively studied in recent years. The majority of computational studies of surface defects on the (1 1 0) surface have focused on elucidating the electronic nature of surface oxygen vacancies and hydrogen defects [7–10], and adsorption sites and reaction paths of water molecules [11–14], but, as stated above, with an unquestioned assumption that oxygen vacancies are dominating defects.

In this work, we focus on determining the relative stability of oxygen vacancies, protons, Ti vacancies and Ruetschi type defects in bulk and at the (1 1 0) surface of rutile TiO_2, and thus the segregation properties of the defects from bulk to the surface through ab $initio$ calculations. Throughout this manuscript, all defects and defect reactions are expressed by the standardized Kröger–Vink notation, in which defects are given by the general term, A_s^q, where A denotes the defect ($e.g.$ vacancies and hydroxide defects/protons), s the site on which the defect is formed ($e.g.$ bulk oxygen and titanium site, O and Ti, 2-fold and 5-fold surface oxygen and titanium site, O2f and Ti5f), and q the effective charge of the defect. The defects included are;

- effectively positive oxygen vacancies, $v_O^{\bullet\bullet}$
- effectively positive protonic defects, $OH_O^\bullet$
- effectively negative Ti vacancies, $v_{Ti}^{4/}$
- Ruetschi type with $n = 1–4$ associated $OH_O^\bullet$ entities, $(v_{Ti}nOH_O)^{(4-n)/}$
- effectively negative surface hydroxide add-ions, $OH_{add}^{/}$
- effectively negative surface oxide add-ions, $O_{add}^{//}$

2. Computational details

All surface calculations in this work are performed within the Density Functional Theory (DFT) formalism as implemented in the VASP code [15,16]. Exchange and correlation effects are described with the Generalized Gradient Approximation functional due to Perdew, Burke and Ernzerhof (GGA-PBE) [17] and the projector augmented-wave (PAW) method for the electron-ion interactions [18], with a constant cut-off energy of 500 eV for the plane-waves.

The (1 1 0) slab model is constructed from the relaxed bulk unit cell of rutile TiO_2 by combining seven elemental surface unit cells, thus yielding a slab thickness of ~ 23 Å. The odd number of unit cells further assures the presence of a central mirror plane. All surface calculations are performed by relaxing all ionic positions with residual forces and energy convergence criteria of 0.02 eV/Å and 10^{-6} eV, respectively, for self-consistency, while fixing the volume of the slab model.

The pristine slab is optimized prior to all defect calculations. The surface energy is obtained through;

$$\Delta E_{surface} = \frac{E_{surface}^{tot} - nE_{bulk}^{tot}}{2A_{surface}} \qquad (3)$$

where $E_{surface}^{tot}$ and E_{bulk}^{tot} are the total energies of the slab model and the bulk unit cell, respectively, and n is the number of bulk unit cells comprising the slab model. The calculated surface energy is 0.456 mJ m^{-2} for the 7 layer slab chosen for all defect calculations, which is in reasonable agreement with previous PBE studies [8,19,20]. The reader should note that the surface energy is not fully converged with respect to slab thickness as the value for a 15 layer slab (50 Å) amounts to 0.389 mJ m^{-2}. Further, the band gap along the gamma point amounts to 1.63 eV, $i.e.$ slightly lower than the bulk PBE value of 1.77 eV. In all calculations of surface defects, a 2×4 supercell expansion (336 atoms in total) is used to limit spurious effects of defect–defect interactions, with a $2 \times 2 \times 1$. Monkhorst-Pack k-mesh [21]. A vacuum layer thickness of 20 Å was further found sufficient for all calculations.

When evaluating effectively charged defects in bulk systems, it is customary to adjust the total number of electrons so as to simulate the desired charge state of a defect ($e.g.$ removing an O atom is accompanied by removal of two electrons to simulate a $v_O^{\bullet\bullet}$), thereby creating an overall charged system. To avoid divergence of the coulomb energy, the additional charge is compensated by introduction of a uniform jellium background charge. Following this procedure for a slab model would consequently result in occupied states in the vacuum layer due to the jellium background charge, which has been avoided in this work. As such, all defect calculations in this work are performed by maintaining overall neutral slab supercells upon defect formation. This procedure thus results in either an excess of electrons in case of donor defects ($e.g.$ $v_O^{\bullet\bullet} + 2e^{/}$) or deficit of electrons in case of acceptor defects ($e.g.$ $v_{Ti}^{4/} + 4h^\bullet$). Whether or not the defects are fully ionized depends on their charge transition levels, or whether they behave as shallow or deep donors/acceptors. It has been argued that surface oxygen vacancies in rutile TiO_2 give rise to in-gap defect states in the form of Ti^{3+} ions (which necessitates the application of post-DFT techniques) [22]. However, for oxygen vacancies in bulk TiO_2, it has recently been shown (by hybrid HF-DFT calculations) that this is not a property of the defect itself, but relates to the strongly correlated nature of the Ti 3d orbitals, and thermodynamically speaking, the oxygen vacancy is in fact a shallow donor [23]. Hence, it is sensible to assume that also the surface versions of the donor defects do behave as shallow donors. Further, as in our calculations, the excess electrons will be delocalized in the conduction band, and the vacancy itself will be fully ionized. Similarly, both $v_{Ti}^{4/}$ and $OH_O^\bullet$ are also shown to display shallow transition levels in bulk rutile TiO_2 [3]. Further, all included defects behave as shallow donors/acceptors within the GGA framework, and