

Localized Electronic States from Surface Hydroxyls and Polarons in TiO<sub>2</sub>(110)

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Hydroxyls on a TiO<sub>2</sub> surface and photoinduced e<sup>−</sup> polarons give rise to excess charges, the electronic structure of which is critical to the fundamental understanding of their role in the reactivity of surface absorbates and other photochemical processes. In this paper, we report on a **DFT+U characterization of the electronic structure of one excess electron in bare and singly hydroxylated rutile (110) surfaces**. The excess electron has the electronic structure of a small polaron with its spin density and associated lattice distortion localized around a single site. Calculations indicate that the most stable Ti trapping site in both bare and hydroxylated surfaces resides in the first subsurface layer under the Ti<sub>5c</sub> row. However, **trapping energy differences between several Ti sites are within 0.2 eV**, indicating that the Boltzmann population of these sites is significant at room temperature and that the excess electron will appear as fractionally occupying several sites. **On the basis of earlier calculations, the activation barrier for electron hopping from site to site is small (<0.1 eV)**. The stability ordering of the different Ti sites is very similar for the bare and hydroxylated surface, suggesting that the hydroxyl only weakly perturbs the surface electronic structure.

## 1. Introduction

Excess unpaired electrons play a critical role in the surface chemistry of TiO<sub>2</sub>, a popular photoactive material, but a firmly established description of these electrons has proven difficult to obtain. There has been much effort in the literature to gain a theoretical and experimental grasp on the degree of localization and the location (surface, subsurface, or bulk) of these electrons.<sup>1–13</sup> These electrons typically result from defects such as surface hydroxyls, or O vacancies, as well as photoexcited electron/hole pairs. These charges are described as polaronic Ti<sup>3+</sup> structures (TiO<sub>2</sub> consists formally of Ti<sup>4+</sup> and O<sup>2−</sup> ions) where the localized excess electrons occupy Ti 3d orbitals. Unfortunately, gradient corrected density functional theory (DFT), the method of choice for condensed phase simulations, fails in depicting localized electronic defects due to inherent deficiencies in the functionals, such as electron self-interaction or strong correlation-related effects; DFT assigns a delocalized character to these excess charges.<sup>1,3</sup> One approach to overcome these deficiencies is the use of hybrid exchange–correlation functionals that incorporate a fraction of Hartree–Fock exchange. In a seminal work, Di Valentin et al.<sup>1</sup> utilized the B3LYP hybrid functional to localize two unpaired electrons that result from a surface O vacancy. This method is computationally intensive and its application in the solid state remains very limited. A second viable approach is the DFT+U method<sup>11</sup> that adds an adjustable correcting potential, *U*, to enhance electron localization at negligible additional computational cost. Recent work<sup>8</sup> has shown that hybrid methods and DFT+U give similar types of localized states for reduced bulk TiO<sub>2</sub> when O vacancies or H atoms are present. Nonetheless, several authors have

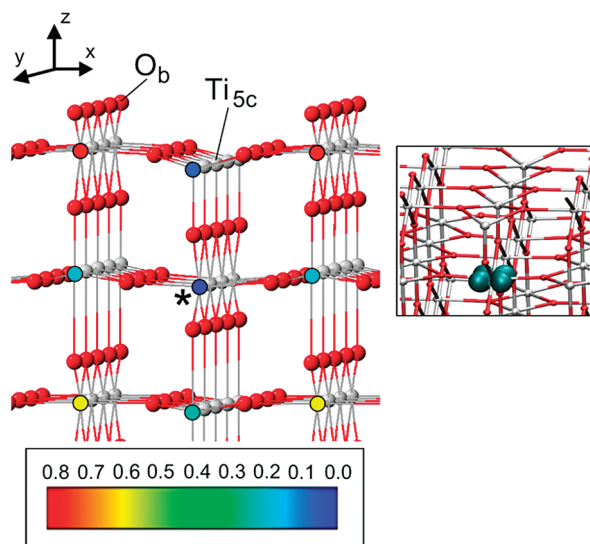
studied O vacancy formation using the DFT+U<sup>6,7</sup> approach, each obtaining different stable locations of the reduced Ti<sup>3+</sup> sites!

As an extension to previous work in understanding the nature of these excess electrons in TiO<sub>2</sub>, we report DFT+U calculations of structures associated with a single excess electron in a clean TiO<sub>2</sub> rutile (110) surface and a surface with one bridging hydroxyl group. Bridging hydroxyls are proposed as electron trapping sites.<sup>12</sup> We systematically examined states where the excess electron is localized at specific Ti sites, down to the second subsurface layer, in order to understand the relative polaron trapping characteristics. We find that for both charged surfaces and hydroxylated surfaces various sites exhibit similar trapping characteristics with subsurface sites below Ti<sub>5c</sub> rows being the energetically most favorable trapping sites. The issue of the trapped electron's proximity to a surface hydroxyl is of interest and our results show that a surface hydroxyl perturbs the electronic potential only slightly and that both clean and hydroxylated surfaces exhibit similar polaron stability.

## 2. Computational Details

All calculations were performed using the spin-polarized PBE exchange–correlation functional<sup>14</sup> as implemented in the CP2K density functional package.<sup>15–17</sup> Core electrons were treated by norm-conserving pseudopotentials,<sup>18,19</sup> while valence electrons were described as a double- $\zeta$  Gaussian basis set. We utilized a five-layer (4 × 2) periodic slab to describe the (110) surface. The (110) surface consists of rows of five-coordinated Ti atoms (Ti<sub>5c</sub>) and rows of two-coordinated O atoms (O<sub>b</sub>) bridged to Ti atoms (see Figure 1). The bare surface was given one net excess electron (compensated by a uniform positive background charge), while the hydroxylated surfaces were neutral and hence had no background charge. Electron localization was made possible by the DFT+U method<sup>20</sup> using *U* values of 3.3, 4.1,

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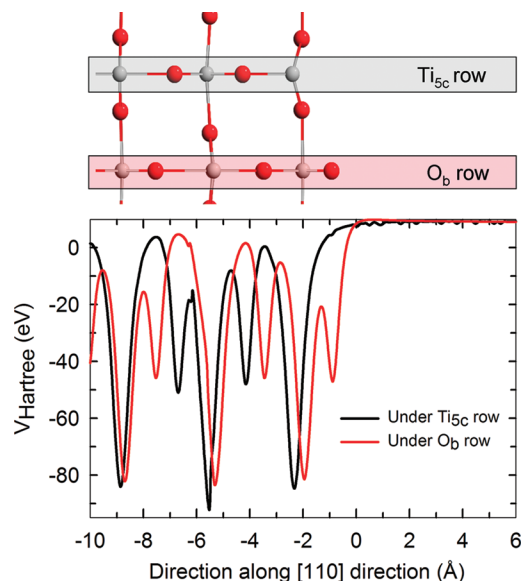
**Figure 1.** Relative energies (eV) for polaronic structures with an excess electron near a (110) surface for  $U = 4.1$  eV. Red spheres represent O atoms, and gray spheres represent Ti atoms. Colored circles indicate sites where excess electrons were localized to form  $\text{Ti}^{3+}$  centers, and the colors indicate their stability relative to the most stable Ti site (marked by an asterisk).  $\text{Ti}_{5c}$  and  $\text{O}_b$  atoms are also indicated. The inset shows the spin density at the most stable site with a filled  $d_{xy}$  orbital.

and 5.4 eV, consistent with previous studies.<sup>6,7</sup> Our results show that the main effect of different  $U$  values is to determine the location of gap states within the gap (see Figures S1–S4 in the Supporting Information), and reasonable gap states<sup>4,11,12</sup> (within 0.6–1.0 eV of the conduction band) occur for a value between 3.3 and 4.1 eV. The trends (e.g., relative energies between different sites) are not strongly affected by the choice of  $U$  value, and we therefore focus our results using a  $U$  value of 4.1 eV, a value that typically gives gap states near the middle of the gap. Further details of the methodology are found in the Supporting Information.

### 3. Results and Discussion

**3.1. Bare Surface.** We first discuss localized electrons in the bare surface slab. Figure 1 shows the Ti sites on the bare surface that we considered and their relative energies. A detailed account of all of the calculated  $\text{Ti}^{3+}$  sites is given in the Supporting Information. In accordance with simple ligand field arguments for octahedrally coordinated metal atoms,<sup>21</sup> the excess electron is most stable when it occupies a Ti 3d orbital from the  $t_{2g}$  set which minimizes Ti d–O p orbital overlap, leading to  $\pi^*$  interactions, as shown in Figure S5 of the Supporting Information. Upon relaxation of the geometry, the Ti–O bonds lengthen (approximately 0.08 Å) about the occupied site, leading to a polaronic state which has almost entirely Ti 3d character, as has been observed in previous work.<sup>1,9,10</sup> Further details of the specific d states are given in Table S1 of the Supporting Information. We have also observed other polaronic states in which the excess electron is trapped in an excited configuration with different d character. For example, occupying the Ti–O  $\sigma^*$   $d_{z^2}$  state of a surface  $\text{Ti}_{5c}$  site is 0.37 eV less stable than occupying the Ti–O  $\pi^*$   $d_{yz}$  state at the same site. It is stressed that particular attention is required to properly localize the electron at a desired site in the lowest energy d state.

We next consider the relative energetics of the various surface sites. The most stable site (relative energy defined as 0.0 eV)

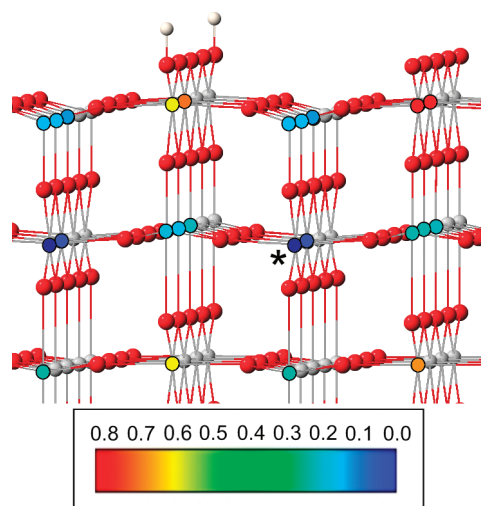


**Figure 2.** Hartree potential,  $V_H$ , slices taken parallel to the [110] surface normal direction. The plane underneath the  $\text{Ti}_{5c}$ -terminated rows is shown in black, while the plane under the  $\text{O}_b$ -terminated rows is shown in red. The positions of the atoms relative to the potential are shown above the plot.

occurs in the second Ti layer (first subsurface layer) under the  $\text{Ti}_{5c}$  row, marked by an asterisk in Figure 1. The next most stable site is at a surface  $\text{Ti}_{5c}$  atom (0.15 eV) with the third-layer site under the  $\text{Ti}_{5c}$  row and the second-layer site under the  $\text{O}_b$  row both at  $\sim 0.2$  eV. The Ti sites under the  $\text{O}_b$  row in the first and third layers are less stable by 0.76 and 0.58 eV, respectively. Our earlier characterization of electron transport in bulk  $\text{TiO}_2$  indicated that electron polarons thermally hop among low energy sites with activation energies on the order of  $\sim 0.1$  eV.<sup>10</sup> The current results suggest that an excess electron spends the majority of its time at the Ti site with the lowest energy and that facile motion to neighboring Ti sites takes place, leading to a temperature-dependent distribution of occupied sites.

This picture is consistent with recent resonant photoelectron diffraction measurements, suggesting that excess electrons associated with O vacancies reside in the subsurface with appearance of delocalization among several sites.<sup>9</sup> The results are especially relevant in the context of adsorbate–surface charge interactions. Our results suggest that excess electrons readily reside at  $\text{Ti}_{5c}$  sites, and subsurface  $\text{Ti}^{3+}$  sites are stable trapping sites, but subsurface electrons can diffuse to the surface for direct transfer to adsorbates.

To understand the underlying reasons for the observed energetics, we analyzed the geometrical distortions that result from the excess electron and the energy gain resulting from the relaxation around the  $\text{Ti}^{3+}$  sites. The distortion energies were found to lower the energy of the undistorted lattice between  $-0.59$  and  $-0.75$  eV for the six  $\text{Ti}^{3+}$  sites, but the lattice distortion does not change the relative stability order of the various sites (e.g., the Ti site under the  $\text{Ti}_{5c}$  row is still most stable, etc.). Rather, the difference in observed polaronic trapping energies is a fundamental electronic attribute of the system. In this regard, to first order, the relative energetics can be explained on the basis of the underlying Hartree potential,  $V_H$ , which reflects the electrostatic attraction felt by an excess electron within the  $\text{TiO}_2$  lattice. In Figure 2, we plot  $V_H$  in the plane of the  $\text{Ti}_{5c}$ - and  $\text{O}_b$ -terminated rows (see Supporting Information for further details). This quantity clearly shows that



**Figure 3.** Relative energies (eV) for  $\text{Ti}^{3+}$  formation in the presence of an  $\text{HO}_b$  in the (110) surface ( $U = 4.1$  eV). Colored spheres indicate sites where excess electrons were localized to form  $\text{Ti}^{3+}$  centers, and the most stable site is indicated by an asterisk. The  $\text{HO}_b$  appears twice due to the periodic boundary conditions.

the largest potential attraction basins reside about the Ti sites below the  $\text{Ti}_{5c}$  row compared to the Ti sites below the  $\text{O}_b$  row. Furthermore, the most preferred potential well occurs in the first subsurface layer beneath the  $\text{Ti}_{5c}$  site in agreement with the polaron energetics. Analysis of  $V_H$  for an unrelaxed surface cut from the bulk shows that there is an electrostatic drive for electrons to move from the bulk toward the surface layer. Relaxation of the surface however leads to an electrostatic destabilization of the first layer potential so that the first subsurface layer is preferred, as shown in Figure 2. In the end, the electron localization at a given site is strongly correlated with the underlying electrostatics of the bare surface slab.

**3.2. Hydroxylated Surface.** When a single surface hydroxyl forms, formally an unpaired electron on Ti is created (e.g.,  $\frac{1}{2}\text{H}_2 + \text{O}_b^{2-} + \text{Ti}^{4+} \rightarrow \text{HO}_b^- + \text{Ti}^{3+}$ ). We have accordingly modeled the formation of  $\text{Ti}^{3+}$  at various Ti sites in the presence of a surface hydroxyl. Following the same strategy as above, we show in Figure 3 the relative energies for the different Ti sites near a hydroxylated surface, with a full summary given in Table S2 of the Supporting Information. The presence of the surface hydroxyl leads to more inequivalent Ti sites compared to the clean surface, but the relative energy orderings among the different Ti sites are very similar for both surface types. The most stable site (0.0 eV) occurs in the second layer directly beneath the  $\text{Ti}_{5c}$  row, the very same site as in the clean surface. Localization of the electron in the surface  $\text{Ti}_{5c}$  row is  $\sim 0.1$  eV less stable, while localization at the Ti sites in the second layer below the  $\text{O}_b$  rows and at Ti sites in the third layer below  $\text{Ti}_{5c}$  rows are  $\sim 0.2$  eV less stable. Polaron formation at the Ti atoms coordinated to  $\text{O}_b$  atoms is 0.6–0.7 eV less stable, while third-layer Ti atoms below the  $\text{O}_b$  rows are 0.5–0.6 eV less stable. Further analysis (charge density differences and distance-dependent behavior), showing that the effect of the surface hydroxyl on the polaron stability is small, is given in the Supporting Information.

Previously, Di Valentin et al.<sup>1</sup> modeled a pair of surface hydroxyls (electrons) and found only one stable solution, so a direct comparison between their work and our work is not fully possible. Nonetheless, we have found some interesting new observations. Di Valentin et al. reported the electrons to localize at a Ti atom coordinated to the  $\text{HO}_b$  and a nearby  $\text{Ti}_{5c}$  site. We

found localization of a lone electron to be stable at  $\text{Ti}_{5c}$  sites but unstable at the Ti site bound to the  $\text{HO}_b$ . We also found the presence of  $\text{HO}_b$  has a negligible effect on the polaron trapping ability of a given site. Differences in electron structure techniques and wave function preconditioning, as well as the  $\text{HO}_b$  coverage ( $\frac{1}{8}$  in the current work versus  $\frac{1}{2}$  in the work by Di Valentin et al.) can give different results and may explain why similar results to our own have not been previously observed.<sup>22</sup> Our results nonetheless suggest that the electron associated with a surface hydroxyl is not necessarily restricted to the direct vicinity of the hydroxyl.

#### 4. Conclusions

We have systematically studied polaron electronic structures in the (110)-terminated rutile  $\text{TiO}_2$  surface at the DFT+U level of theory. The resulting picture is in accord with simple ligand field theory arguments and recent photoelectron diffraction measurements and can be correlated to the electrostatic potential of the lattice. Our results suggest that many of the underlying discrepancies in the literature regarding the ground state of reduced systems may, in part, be from difficulties in properly localizing the electron as a result of either initial wave function guess or geometric perturbation, or by using limited simulation cells. Future work will revolve around extending this systemic approach to understanding the interactions between pairs of polarons, as found with  $\text{O}_b$  vacancies, as well as the interaction between these polarons with more complex adsorbates such as  $\text{O}_2$  and organic species.

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**Supporting Information Available:** Further computational details, a full summary of the various energetics and the effect of  $U$  value choice, as well as further discussion of the trapping energies and a comparison of the clean/hydroxylated surfaces. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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