Charge Localization Dynamics Induced by Oxygen Vacancies on the TiO$_2$(110) Surface

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The dynamics of an $F$ center created by an oxygen vacancy on the TiO$_2$(110) rutile surface has been investigated using $ab$ initio molecular dynamics. These simulations uncover a truly complex, time-dependent behavior of fluctuating electron localization topologies in the vicinity of the oxygen vacancy. Although the two excess electrons are found to populate preferentially the second subsurface layer, they occasionally visit surface sites and also the third subsurface layer. This dynamical behavior of the excess charge explains hitherto conflicting interpretations of both theoretical findings and experimental data.

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Titanium dioxide (TiO$_2$) is one of the most thoroughly investigated metal oxides, due to its broad range of uses in several key technologies including heterogeneous catalysis, pigment materials, photocatalysis, and energy production, to name but a few [1–3]. It is well known that bulk and surface defects govern the properties of titania, and are thus of fundamental importance in virtually all its applications [4–6]. The most common point defects on the TiO$_2$(110) rutile surface are oxygen vacancies (O$_{\nu}$) in the twofold coordinated O rows and Ti interstitials [7,8]. In particular, removal of an O atom gives rise to two excess electrons and the appearance of new electronic states in the band gap at about 0.7–0.9 eV below the conduction band edge creating a $F$ center [9–11]. Although the two excess electrons can in principle be localized on any Ti atom, they are believed to preferentially occupy specific Ti-3$d$ orbitals, thus formally creating Ti$^{3+}$ sites [10,12]. In stark contrast, recent experiments [13] suggest a qualitatively different viewpoint: charge localization is found to be more disperse, with the excess electrons being shared by several surface and subsurface Ti ions. Furthermore, STM and STS experiments have revealed charge delocalization involving more than ten Ti sites [14].

Unfortunately, different computational methods yield conflicting results [11]. Local or semilocal density functionals (LDA/GGA) predict a rather delocalized defect level for O vacancies on TiO$_2$(110) with an energy right at the bottom of the conduction band [11]. However, it is well known that such functionals bias against localization on strongly correlated $d$ states, and hence alternative methodologies are welcome. Recent studies of defective TiO$_2$ surfaces [15–21] have focused on “pragmatic and practical” correction schemes using hybrid functionals or a Hubbard correction. Although both schemes yield the expected gap states, they each predict vastly different localization topologies of the excess charge.

Using B3LYP on a c(4 × 2) slab with an O vacancy, the defect charge is found to be localized on $\delta$ orbitals of two surface Ti atoms [15]. In particular, one unpaired electron is found on the undercoordinated Ti(11) site, while the other moves to an adjacent fivefold coordinated Ti$_{sc}$ atom, such as Ti(7); see Fig. 1 for our site labeling scheme. By contrast, LDA/GGA + $U$ studies [16–21] on the reduced TiO$_2$(110) surface have reported charge localization on different surface and/or subsurface sites. For instance, a combination of surface and subsurface localization immediately beneath the defect on Ti(11) and Ti(27) (see Fig. 1) has been found [16]. However, the results are reported to be strongly dependent on the supercell size. Using a (2 × 1) cell, the electrons are found at Ti(7) and Ti(23), while using a (4 × 1) cell complete subsurface localization is observed [21] at Ti(23) and Ti(39). On the other hand, a (4 × 2) cell yields localization of the electrons on Ti(11) and Ti(12) when using $U \geq 4.2$ eV, whereas smaller values of $U$ lead instead to delocalization [19]. Interestingly, some recent GGA + $U$ studies [22,23] which focussed on

FIG. 1 (color online). (a) Ball and stick model of the defective TiO$_2$(110) surface. Red (dark gray) and blue (light gray) spheres are O and Ti atoms, respectively. Panels (b), (c), and (d) depict the spin density (at 0.005 $e$/Å$^3$) of three configurations from Table 1 with different charge localization topologies.