A direct view at polarons in TiO$_2$ rutile and anatase

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A combination of Scanning Tunneling Microscopy/Spectroscopy and Density Functional Theory (DFT+U) is used to characterize the nature of excess electrons in TiO$_2$ rutile and anatase, two prototypical materials with identical chemical composition but slight differences in their crystal lattices. In rutile, the excess electrons can localize at any lattice Ti atom, forming a small polaron, which can easily hop to neighboring sites. In contrast, in anatase, electrons prefer a delocalized (band-like) state and small polarons only form in the direct proximity of oxygen vacancies. The present study conclusively explains the differences between the two polymorphs and indicates that even small structural variations in the crystal lattice can lead to very different behavior.

The behavior of charge carriers in oxides is of key importance in virtually all applications of these materials. When excess electrons are added to the conduction band of an oxide, they may either remain delocalized or, assisted by the electron-phonon interaction, form localized (small) polarons [1,2]. The degree of electron localization affects a materials' physical and chemical properties, yet it remains controversial how to model it appropriately from first principles [3,4]. Here we investigate TiO$_2$, a prototypical metal oxide. TiO$_2$ is used in photocatalysis [5-8], photoelectrochemical (Grätzel) solar cells, memristors [9], and transparent optical conductors [10]. Industrially two forms of TiO$_2$ are employed, rutile and anatase. The metastable anatase form is generally present in nanomaterials and shows better performance in energy-related applications and in optoelectronics. Even after several decades of research, a consensus on the origin of the difference between the two materials is still absent, and our aim is to resolve this issue theoretically as well as experimentally.

Stoichiometric rutile and anatase are both insulators with a 3 eV band gap. TiO$_2$ can be turned into an n-type semiconductor by adding excess electrons by various means - doping, UV irradiation, or chemical reduction. Electrons in the conduction band of TiO$_2$ compete between delocalized (band-like) and localized configurations. The extent to which this happens has remained highly controversial, yet strongly affects the material’s transport properties and catalytic activity. The electrons can localize at Ti 3$d$ orbitals, forming Ti$^{3+}$ ions. This induces relaxations of the surrounding lattice atoms by typically 0.1 Å. The quasiparticle consisting of an electron coupled to the lattice relaxations in its immediate surrounding is called a small (or Holstein) polaron [1].

The energy balance for polaron formation is sketched in Fig. 1(a). The formation energy, $E_{\text{POL}}$, is defined as the total energy difference between the polaronic (i.e. localized) and delocalized solution, and results from the competition between the energy required to distort the lattice ($E_{\text{ST}}$), and the electronic energy gained by localizing the electron at a Ti site in such a distorted lattice, $E_{\text{EL}}$. Small polarons show a complex behavior. On the one hand, the trapped electrons appear typically $\approx 1$ eV below $E_F$ when investigated by photoemission spectroscopy [5] or quantum tunneling. Here the lattice atoms are "frozen" within the timescale of the experimental probe, thus the electronic energy $E_{\text{EL}} = E_{\text{POL}} + E_{\text{ST}}$ [see Fig. 1(a)] is measured. In electrical conductivity...
measurements, however, activation energies are typically of the order of tens of meV. This is indicative of either a low energy barrier for hopping between neighboring trapping sites, or a small excitation energy from the localized to the delocalized state [11].

Figure 1(b) illustrates why theoretical modeling of the polaron behavior in TiO$_2$ and other oxides remains a challenging and controversial issue. While one can often calculate the energy for structural distortions, $E_{ST}$, reliably with DFT methods, standard DFT always yields delocalized solutions. Electrons can be localized by applying a Hubbard $U$; the value of $U$, and thus $E_{EL}$, will then determine whether or not a small polaron will be stable [12,19]. The situation is equally critical with hybrid functionals, where the value of $E_{EL}$ depends on the amount of exact exchange incorporated in the DFT functional [4,11,17,18].

From Fig. 1(b) we infer that $E_{POL}$ is 0.4 eV larger in rutile than anatase, and that a larger $U$ is required to form a small polaron in anatase ($U > 5$ eV) than in rutile ($U > 3.5$ eV). Both materials have a similar $E_{ST}$ (0.41 eV), while the difference in $E_{POL}$ originates from the electronic energy $E_{EL}$. The formation of a polaron involves the depletion of the conduction band minimum (CBM), which has a different character in the two TiO$_2$ polymorphs. Figure 1(c,d) shows that the conduction band in anatase is 1 eV wider than in rutile, and the CBM lies lower in energy as a result of the formation of a strong bonding linear combination between neighboring Ti $d_{xy}$ orbitals. Thus, a larger $U$ is required to alter this energetically favorable configuration and to form a polaron in anatase, and the associated energy gain $E_{EL}$ is lower as compared to rutile.

The most commonly used values of $U$ for TiO$_2$ range between 2.5 and 4.5 eV, but values as large as 10 eV have been also employed [12]. The first major achievement of the present work is that we calculate the $U$ parameter entirely from first principles. The most accurate method to achieve this is the constrained Random Phase Approximation (cRPA) [19]. In this approach, the full microscopic screening tensor excluding the $d$ states is determined, and the $U$ parameter is calculated by projecting the screened Coulomb interaction onto the $d$ Wannier orbitals [22]. This yields a value of $U^{cRPA} = 3.9$ eV for TiO$_2$. The cRPA is highly accurate and predictive and has been used with great success for the description of correlated materials [20,21]. All results in the present work have been consistently determined using $U^{cRPA}$, the VASP code with PAW potentials [23,24] and the generalized gradient approximation of Perdew-Burke-Ernzerhof (PBE) [25]. From Fig. 1, it is clear that $U^{cRPA} = 3.9$ eV suffices to stabilize the polaron in rutile, albeit just, whereas polaron formation in anatase is clearly unfavorable at bulk lattice sites.

We now show that this prediction is fully consistent with our own as well as previous experimental observations. Since polarons are a local effect, the most direct probe is Scanning Tunneling Microscopy/Spectroscopy (STM/STS). Filled-states STM images reflect the spatial distribution of electrons within the bandgap, and STS should reveal the characteristic signature of either small polarons, i.e., $E_{EL} \sim 1$ eV [5] or delocalized, weakly bound electrons $\sim 40$ meV [26] below $E_F$, respectively. We experimentally show that, indeed, small polarons form in rutile at lattice sites with bulk coordination with high mobility at $T = 78$ K, whereas in anatase the small polaron is only stable in direct proximity to an oxygen vacancy and never moves to Ti sites with bulk-like coordination.
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band-gap-state is found 0.7 ± 0.1 eV below \( E_F \); again,
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STM/STS measurements for rutile (110) and
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measured at open loop with a lock-in amplifier. As in
previous work on rutile (110) [27, 28], we take advantage
of surface O vacancies (V\(_O\)) that readily form under
standard preparation conditions [20] to provide excess
charge (donors). At anatase (101), V\(_O\)s migrate to the
bulk at temperatures as low as 200 K, but surface V\(_O\)s
can be created non-thermally [29]. Here subsurface V\(_O\)s
were pulled to the surface using the field of the STM tip
as shown in ref. [30].

For rutile [Fig. 2(c)] the filled local density of states
(LDOS) directly at the V\(_O\) is small; most of the current
comes from the rows of 5-coordinated surface Ti
atoms, as the polarons are not localized at the V\(_O\). This is even
more apparent when scanning at very close tip-sample
distances (see lower part of the image in Fig. 2(c), and
the Supplement for details). In contrast, the electrons
stay at the vacancy at anatase [Fig. 2(d)], as suggested
by the vanishing LDOS at the rest of the surface.

Point tunneling spectra were measured at different
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FIG. 3. Calculated polaronic configurations around surface
V\(_O\). In rutile, small polarons can assume many, energeti-
cally almost equivalent positions. a) Configurations with two
subsurface polarons \( P_{surf} \) (top) and one \( P_{sub} \) plus one sur-
faced polaron \( P_{surf} \) (bottom). b) The only stable configuration
in anatase, with both polarons localized at the surface near
the V\(_O\). c) Polaron dynamics in rutile (orange) and anatase
(blue) and corresponding statistical analysis for rutile. The
small polarons stay mostly in the subsurface (S-1) below the
vacancy and at surface (S) Ti
sites. (d)-(g) Calculated STM
images for empty (d, e) and filled (f, g) states in rutile (left,
the three most frequent polaronic configurations according to
the MD analysis) and anatase (right, the polaron is always at
the surface V\(_O\)).
the prowess of STM to identify and probe truly-localized small polarons.

When electrons are introduced via a dopant that modifies the lattice structure only slightly, polaron formation remains favorable in rutile, whereas delocalized electronic solutions are preferred in anatase. This is reflected in the 4 orders of magnitude larger conductivity of Nb-doped anatase compared to Nb-doped rutile: anatase exhibits metal-like conductivity, whereas rutile remains a semiconductor [10, 34]. Our DFT+U calculations suggest that the higher conductivity in Nb doped anatase is due to the absence of localized small polarons, whereas in rutile – with the same U – small polarons are formed. The STM results are again entirely consistent with this prediction. In an anatase sample doped with ∼1% Nb [30], fairly extended bright regions in the STM images with a measurable density of states below EF (Fig. 4) are visible. Spatially resolved STS [Fig. 4(c)] images reveal a peak at (∼40 ± 10) meV and the absence of any gap state at 1 eV. The bright regions shown in Figs. 4(a,b) are stable in time and do not migrate within a temperature range from 6 to 78 K, suggesting that the electron is stabilized at the positively-charged subsurface donors, most likely Nb. Fig. 4(d) shows a simple model. The ionized donor creates a quantum well, where the electron occupies a single energy level. The electron wave function is delocalized across several unit cells around the donor, and is modulated by the periodic potential of the crystal lattice; a calculated STM image of a slab with a Nb impurity [inset Fig. 4(b)] agrees well with the experiment (see Supplement). In recent ARPES measurements [20] the peak at (40 ± 10) meV below EF was attributed to a "large polaron". The distinction between a shallow delocalized donor level and a large polaron is subtle. However, the DFT+U calculations support the notion of a large polaron, since the STM image is only reproduced when lattice relaxations (polaronic effects) are taken into account. Furthermore, in STM images the density distribution has an anisotropic shape, with spatial extensions of ∆r[010] = 12−25 Å and ∆r[101] = 4−8 Å. This agrees well with Fröhlich’s model for large polarons [11], from which we obtain ∆r[010] = 19.0 Å, and ∆r[101] = 3.5 Å related to the anisotropy of the screening and effective masses (see Supplement).

Our study illustrates the basic principles of electron localization in the model oxide TiO2. The different stacking of octahedrally-coordinated Ti in the two polymorphs, and the resulting subtle variances in the electronic structure around the CBM, provide for a higher energy gain upon electron localization in rutile than in anatase. With a U of 3.9 eV that is derived from first-principles the competition between electron localization and delocalization is well-described theoretically. Filled-states STM clearly shows the various cases: small polarons that are located directly at a structural defect in anatase, yet readily hop in rutile, and delocalized electrons in a shallow donor state in Nb-doped anatase. STS also shows distinct signatures, with an apparent deep (~eV) polaronic state for rutile, yet a much shallower state (40 meV) at anatase. The latter shows spectroscopic similarities with recent ARPES results [20] and its lateral extension is well-described by Fröhlich’s theory for large polarons.

Polarons are central to the often exotic behavior of oxides [35] as well as their technological applications. In the specific case of TiO2, anatase is used as an electrode in photovoltaic solar cells. Band-like charge transport and the lack of small polaron formation is the key requirement for increasing the cell efficiency. On the other hand, the formation of small polarons at bulk lattice sites in rutile is an asset in catalysis, where the trapping of electrons allows for the build up of a charge reservoir that facilitates the electron–induced adsorption and subsequent charge transfer to catalyzed species [6]. In mixtures of the two TiO2 phases, anatase provides a good electron conductor that transports charge carriers to the interface with rutile, where they are trapped [37].

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