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Electronic structure and photoabsorption of Ti$^{3+}$ ions in reduced anatase and rutile TiO$_2$

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We have used two-photon photoemission (2PPE) spectroscopy and first-principles density functional theory calculations to investigate the electronic structure and photoabsorption of the reduced anatase TiO$_2$(101) and rutile TiO$_2$ (110) surfaces. 2PPE measurements on anatase (101) show an excited resonance induced by reduced Ti$^{3+}$ species centered around 2.5 eV above the Fermi level ($E_F$). While this state is similar to that observed on the rutile (110) surface, the intensity of the 2PPE peak is much weaker. Calculation of the oscillator strengths of the transitions from the occupied gap states to the empty states in the conduction band show peaks between 2.0-3.0 eV above the conduction band minimum (CBM) on both surfaces confirming the presence of empty Ti$^{3+}$ resonances at these energies. Although the crystal field environment of Ti ions is octahedral in both rutile and anatase, Ti$^{3+}$ ions exhibit distinct $d$ orbital splittings, due to different distortions of the TiO$_6$ units. This affects the directions of the transition dipoles from the gap states to the conduction band, explaining the polarization dependence of the 2PPE signal in the two materials. Our results also show that the Ti$^{3+}$ induced states in the band gap are shallower in anatase than in rutile. Most importantly, $d$-$d$ transitions from the occupied gap states to the empty Ti$^{3+}$ excited states in anatase can occur at energies well below 3 eV, consistent with the observed visible-light photocatalytic activity of Ti$^{3+}$ self-doped anatase.

Introduction

TiO$_2$ is an attractive photocatalyst for many applications$^{1-9}$, but its performance is limited by the large band gap, requiring the use of ultraviolet light for photoexcitation$^{10}$. As efforts at increasing TiO$_2$’s visible light activity by narrowing its band gap through doping have proven difficult$^{11-14}$, recently attention has been directed to the potentially beneficial role of reduced Ti$^{3+}$ ions. However, while there is evidence that the photocactivity of TiO$_2$ in the visible could be substantially enhanced by high concentrations of Ti$^{3+}$ ions$^{15-21}$, understanding of the mechanism of this enhancement is still limited.

Ti$^{3+}$ ions in TiO$_2$ are usually associated with oxygen vacancies (O$_v$s), whose excess electrons tend to localize in the 3d orbitals of nearby Ti atoms forming states with energies in the band gap. Many properties of the gap states have been studied extensively, including their energetics, localization and transport behaviour, but less is known about their photoexcitation, which is crucial for understanding their role in TiO$_2$’s photoactivity. Experimental studies have generally been performed by two-photon photoemission spectroscopy (2PPE), an optimal technique for the study of excited states. Using 2PPE, Onda et al. first identified a resonant state at about 2.3 eV above the conduction band minimum (CBM), which they originally ascribed to a wet electron state induced by water adsorption.$^{22,23}$ Thornton et al. observed a similar feature at 2.7 eV$^{24}$, and suggested that this peak originates from $d$-$p$ transitions from the gap state to states induced by surface hydroxyls. Argondizzo et al. also observed a resonant transition from Ti 3$d$ defect states, and attributed it to transitions between Ti 3$d$ bands of $t_2g$ and $e_g$ symmetry.$^{25}$ A more precise assignment was proposed by Wang et al., who showed that both the gap state and the resonant state above the CBM originate from the Ti$^{3+}$ ions, and $3d$$\rightarrow$$3d$ transitions from the gap states to the empty resonant states affect the photoabsorption significantly.$^{26}$

While providing useful information, a limitation of all the above studies is that they were performed on a single well-defined surface, the rutile TiO$_2$ (110) surface, a typical model system for surface science studies of TiO$_2$. On the other hand, only a preliminary report is available for anatase (101)$^{27}$, the majority surface of the TiO$_2$ form that is generally used in photocatalysis and other energy conversion applications. A distinctive feature of anatase (101) with respect to rutile (110) is its lack of surface O$_v$s, since...
these defects prefer to reside in subsurface and deeper layers than at the very surface of anatase.\textsuperscript{27,28} Also at variance with rutile, there is evidence of both deep (strongly localized) and shallow (more extended) Ti\textsuperscript{3+}-like gap states in anatase.\textsuperscript{29,34} Therefore, understanding the excited state properties of reduced anatase is of considerable scientific interest, as well as important for applications.

The aim of this work is to provide a detailed characterization of the excited state properties of the reduced (101) surface of anatase (A-TiO\textsubscript{2}), the technologically most relevant form of TiO\textsubscript{2}. Using 2PPE measurements in combination with density functional theory (DFT) calculations, we show that Ti\textsuperscript{3+} species in A-TiO\textsubscript{2} have both similar and distinct features in comparison to rutile (R-TiO\textsubscript{2}). Most importantly, transitions from the gap states to the corresponding Ti\textsuperscript{3+}-resonant states can induce visible light absorption and thus enable photocactivity in this spectral region.

\section*{Method}

\subsection*{Experimental details}

2PPE experiments were carried out in an ultrahigh vacuum (UHV) apparatus with a base pressure better than \(5\times10^{-11}\) mbar.\textsuperscript{35} The A-TiO\textsubscript{2}(101) sample (Princeton Scientific Corp.) was prepared by cycles of Ar\textsuperscript{+} sputtering and UHV annealing at 850 K until the impurity concentration was below the detection limit of X-ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED) showed a clear sharp (1×1) pattern. The second harmonic (SH, 2.95 eV – 3.59 eV) of a Ti: Sapphire oscillator (MaiTai eHP DeepSee, Spectra-Physics) was delivered in pulses of 90-fs duration and 1.5-kJ at 80-kMHz repetition rate for the two-photon excitation. The laser incident plane was at about 30 degrees relative to the \([010]\) direction of the anatase (101) surface. One-phonon photoemission measurements were performed using a helium lamp (UVS 10/35, SPECS) and the Fermi level was measured exclusively from the band gap states. Calculations for the A-TiO\textsubscript{2} (110) surface were performed using periodically repeated slabs of four TiO\textsubscript{2} tri-layers with a (4×2) (11.84 Å×12.99 Å) surface cell. We modeled hydroxylated A-TiO\textsubscript{2} (110) by adding one or more hydrogen atoms to the bridging oxygen sites; reduced surfaces were modeled by removing a subsurface oxygen atom. All atoms in the slab were relaxed until the maximum residual force was less than 0.02 eV/Å. Calculations for the R-TiO\textsubscript{2} (110) surface were performed using periodically repeated slabs of four TiO\textsubscript{2} tri-layers with a (4×2) (11.84 Å×12.99 Å) surface cell. We modeled hydroxylated R-TiO\textsubscript{2} (110) by adding one or more hydrogen atoms to the surface bridging oxygen sites, and reduced R-TiO\textsubscript{2} (110) by removing a surface bridging oxygen atom to create a surface oxygen vacancy.

The oscillator strength in the \(\vec{e}_ \mu\) direction, \(f^\mu_{cv}\), was calculated from the expression: \textsuperscript{49}

\[ f^\mu_{cv} = \frac{2m_e(E_c - E_v)}{\hbar^2} |\langle v|\vec{\epsilon}\mu|c\rangle|^2 \]  

(1)

Using the relationship between position and momentum operators \((p_\mu)_\text{vc} = -im_e(E_c - E_v)/(p_\mu)_\text{vc}\), (equation (1) can be transformed to:

\[ f^\mu_{cv} = \frac{2}{m_e(E_c - E_v)} |\langle v|p_\mu|c\rangle|^2 \]  

(2)

where \(\langle v|p_\mu|c\rangle\) denotes a Kohn-Sham orbital corresponding to a state in the valence band (VB) or an occupied gap state and \(\langle c|p_\mu|v\rangle\) denotes a Kohn-Sham orbital corresponding to an unoccupied MO above \(E_c\). \(E_v\) and \(E_c\), denote the eigenvalues corresponding to \(|c\rangle\) and \(|v\rangle\), respectively. \(p_\mu\) is the momentum along the \(\vec{e}_ \mu\) direction. The oscillator strength was also utilized to evaluate the imaginary part of the dielectric function as \(\varepsilon'_2(\omega)\): \textsuperscript{50,51}

\[ \varepsilon'_2(\omega) = \frac{2\hbar^2}{m_e c^2} \sum_{\sigma_\mu} f^\mu_{cv} \delta(\omega_{cv} - \omega) \]  

where \(\omega\) denotes valence and conduction band states. In our calculations, the sum over the valence band states was restricted to the gap state.

\section*{Results and discussion}

\subsection*{Experimental results}

Previous 2PPE studies on R-TiO\textsubscript{2}(110) by our group were performed on an hydroxylated surface,\textsuperscript{9} which is more relevant to real photocatalysis compared to the clean surface. Unlike R-TiO\textsubscript{2}(110), however, A-TiO\textsubscript{2}(101) does not exhibit surface oxygen vacancies,\textsuperscript{52} making it difficult to create hydroxyls through dissociation of water at such sites. We intended to introduce surface hydroxyls using various methods including methanol photo dissociation,\textsuperscript{53,54} photolysis of trimethyl acetic acids\textsuperscript{55} and atomic hydrogen dosing\textsuperscript{56}, as used on R-TiO\textsubscript{2}(110). Unfortunately, besides producing surface hydroxyls, these methods inevitably introduce other species such as water (from hydration of methanol, trimethyl acetic acids and heating of the
cracking zone) onto the surface. Even worse, we could not control the amount of water, which is known to significantly affect the intensity of 2PPE spectra on R-TiO$_2$(110). In fact, 2PPE spectra on A-TiO$_2$(101) are also water coverage sensitive. In order to remove water and other reaction species, one needs to heat the substrate to temperatures above 300 K, which results in the diffusion of H atoms into the bulk of A-TiO$_2$(101), as suggested by our UPS measurements and also by calculations. We found that it is essentially impossible to assess the amount of surface hydroxyls during the 2PPE measurements using current experimental techniques. As a result, all the photoemission spectra in this work were acquired from the clean reduced A-TiO$_2$(101) surface.

Figure 1a shows the polarization dependent 2PPE spectra on a clean A-TiO$_2$(101) at a photon energy of 2.95 eV. These spectra are quite similar to those for R-TiO$_2$(110) with the incident plane along the [110] direction (see representative spectra in Figure 1b). An additional feature $F$ is detected in $p$-polarized 2PPE ($p$-2PPE) when compared to s-polarized 2PPE ($s$-2PPE); the difference between $p$-2PPE and the normalized $s$-2PPE at the secondary electron edge, is a 0.48 eV wide peak centred at 5.50 eV; linear fitting of the photon energy dependence (Figure 1c) of the final state level yields a slope close to one, suggesting the additional feature $F$ comes from an intermediate state; since no adsorbates are present on the A-TiO$_2$(101) surface, we can conclude there is an intrinsic excited state located at 2.55 eV above the Fermi level on this surface. No angular distribution of the excited resonance was detected, suggesting it is a rather localized state. Time-resolved measurements showed the two-pulse correlation from the excited state to be identical to the autocorrelation of the 2PPE pulses, implying that the lifetime of the excited state is much shorter than the pulse width (90 fs).

An important difference between the 2PPE signals from the clean A-TiO$_2$(101) and R-TiO$_2$(110) surfaces is the intensity. Although the photon energy chosen for the 2PPE acquisition on both TiO$_2$ surfaces are within ±0.06 eV, the 2PPE intensity on R-TiO$_2$(110) (Figure 1b) is about 8 times larger than that on A-TiO$_2$(101) (Figure 1a). To find out the reason of the significant 2PPE intensity difference on these two surfaces, we studied the band gap states, which are the initial states in the 2PPE measurements, by ultraviolet photoelectron spectroscopy (UPS) using the He I line. Figure 1d compares the valence electronic structure of A-TiO$_2$(101) and R-TiO$_2$(110) measured by UPS with identical experimental setups. The UPS spectra can be divided into three regions: the secondary electron signal, centered at a binding energy of 13.4 eV, the O 2p signal of the TiO$_2$ surface, between 10 and 3 eV, and the band gap states signal, below 3 eV. The valence band maximum (VBM) of A-TiO$_2$(101) is at lower energy (higher binding energy) compared to the VBM of R-TiO$_2$(110), which is consistent with the band gap difference between anatase and rutile. The band gap states also show significant differences (see inset graph of Figure 1d): in contrast to the high DOS with a binding energy of 1 eV on R-TiO$_2$(110), A-TiO$_2$(101) has an extremely weak signal in the band gap, in agreement with previous reports indicating that there are essentially no oxygen vacancies on this surface. Further analysis of the band gap states by subtracting the Tougaard background of the UPS spectra in Figure 1d yields the detailed structure in the band gap (Figure 1c). The band gap structure of R-TiO$_2$(110) shows a broad peak with a maximum around 1.0 eV, which is characteristic of the polaronic defect-induced states on this surface. Different from R-TiO$_2$(110), the band gap structure of A-TiO$_2$(101) consists of two separate features, a peak at about 2.60 eV and a smaller feature at about 0.45 eV. The energy level together with the intensity of the signal around 2.60 eV correlates with the excitation of the O 2p states by the satellite lines of He I. From the energy difference point of view, the signal around 0.45 eV is not interfered by the satellite lines. Therefore, it is likely to represent the band gap state of A-TiO$_2$(101).

To confirm this result, we tuned the 2PPE photon energy so as to find the resonance of the transitions between the gap states and the excited states on the A-TiO$_2$(101) surface (Figure 1f). By combining the energy of the resonance with the measured energy level of the excited states, we can then infer the energies of the initial states.

On R-TiO$_2$(110), the resonant photon energy in 2PPE is at 3.55 eV, a value reproduced in the present study (red circles in Figure 1f). On A-TiO$_2$(101), although the energy of the excited states is
similar to that on R-TiO$_2$(110), the resonant photon energy in 2PPE is 0.52 eV lower, suggesting that the center of the initial states is 0.48 eV below the Fermi level, in agreement with the level position obtained by UPS. The weak signal at 0.45 eV in the UPS spectra may be thus ascribed to the gap states of A-TiO$_2$(101). Such shallow gap states in anatase have been reported previously.$^{31, 62}$ The peak intensity of the band gap states on R-TiO$_2$(110) is about 65 times that on A-TiO$_2$(101), largely explaining the difference in the 2PPE intensities of the two materials.

Theoretical results

We further investigate the electronic structure of reduced A-TiO$_2$(101) with subsurface oxygen vacancies by means of hybrid density functional calculations, and compare the results to analogous calculations for R-TiO$_2$(110) with surface O$_2$s. Figure 2 shows the projected DOS of Ti$^{3+}$ (a), and Ti$^{4+}$ (b, c) ions in pristine and reduced A-TiO$_2$(101) slabs, computed using HSE06 (a, b), which is widely used for oxide materials, and the 1/$\epsilon_{so}$ PBE0 functional (c). In pristine A-TiO$_2$(101), the octahedral field splits the $d$ states of Ti$^{3+}$ ions into $t_2g$ and $e_g$ orbitals (Figure 2a)$.^{33}$ In reduced A-TiO$_2$(101), the nominal $t_2g$ configuration of Ti$^{3+}$ ions undergoes a Jahn-Teller splitting.$^{60, 64}$ The occupied $d$ orbital, with predominant $d_{x^2-y^2}$ character, is stabilized and splits from the other $d$ orbitals of the Ti$^{2+}$ manifold to form a state in the band gap around 1 eV below the CBM. At the same time, the remaining unoccupied $t_2g$ orbitals upshift in energy, and give rise to resonant states in the range 2.0-3.0 eV above the CBM (highlighted by the pink shading in Figure 2b, c).

It is interesting to compare the crystal field splittings of Ti 3$d$ orbitals in anatase and rutile, see Figure 3a. While the overall orbital splittings of $d$ orbitals in $t_2g$ or $e_g$ are similar in the two polymorphs, the finer splitting of the $t_2g$ or $e_g$ manifolds are distinct for the two phases. In particular, the excess electron donated by a $n$-type defect occupies a $d_{x^2-y^2}$ orbital in rutile$^{29}$, while the same kind of excess electron occupies a $d_{z^2}$ or $d_{xy}$ orbital in anatase. The octahedral TiO$_6$ units for anatase and rutile are shown in Figure 3b, c. The octahedral field of rutile is almost perfect. The two apical Ti-O bonds along the main axis are about 1.98 Å, while the four equatorial Ti-O bonds form a square with a slightly smaller bond length of 1.949 Å. An excess electron forming a Ti$^{3+}$ ion in rutile occupies a $d_{xy}$ orbital; this affects the four nearby equatorial Ti-O bonds, which become all slightly elongated.$^{29, 65}$ The octahedral field of anatase is significantly more distorted in comparison to rutile. The mirror plane symmetry perpendicular to the apical bonds (~1.973 Å) is lost, and the four equatorial Ti-O bonds (~1.93 Å) are not in a plane. For a Ti$^{3+}$ ion with an excess electron in $d_{xy}$, or $d_{z^2}$, only the two equatorial bonds in the plane of the occupied orbital become longer, about 1.962 Å on average, making the distortion of the TiO$_6$ units even more pronounced.

We can further compare the characteristics of Ti$^{3+}$ ions in anatase and rutile by considering the projected DOS and oscillator strengths for the pristine and reduced R-TiO$_2$(110) surfaces. Results obtained using different hybrid functionals are shown in Figure 4 and Figure S5 (SI). Similar to anatase, the oscillator strengths of the
VBM→CB transitions on R-TiO$_2$(110) (Figure 4a, d) are very small in comparison to the transitions from the defect-induced gap states to the CB. The positions of the oscillator strength peaks for the reduced rutile surface correspond to the region of $d_{xy}$ and $d_{yz}$ states in the projected DOS of Ti$^{3+}$ ions, implying that transitions mainly occur from $d_{xy}$ to $d_{yz}$ or $d_{xz}$. At variance with anatase, the overall distribution of oscillator strengths on reduced R-TiO$_2$(110) shows a significant dependence on the functional used; for example, HSE06 and 1/$\epsilon_\infty$ PBE0 yields a series of peaks of similar intensity between 1 and 2.5 eV (Figure 4e, f), while B3LYP results show a prominent sharp feature at $\sim$ 2.5 eV (Figure S3d), which appears to be in better agreement with the resonant feature observed in 2PPE. These differences can be related to the different localization of the corresponding defect states, which are predicted to be significantly more localized using B3LYP (see Figure S3 in SI) than HSE06 or 1/$\epsilon_\infty$ PBE0.

From the oscillator strengths, the imaginary parts of the dielectric function $\varepsilon_2(\omega)$ of reduced anatase and rutile were also determined. As shown in Figure S4, the computed absorption edge is at about 1.0 eV for reduced anatase, while it is at somewhat higher energy, $\sim$ 1.5 eV for reduced rutile. This result, combined with the longer electron-hole recombination time at anatase (101) in comparison to rutile (110)\(^\text{30}\) (see also the computed surface band structure in Figure S5) supports the conclusion that reduced anatase is a better photocatalyst than rutile.

The spatial distributions of gap and excited states on R-TiO$_2$(110) are shown in Figure S1c (SI). Independent of the hybrid functional used, the excess electrons are always localized in the subsurface of R-TiO$_2$(110), in agreement with previous studies.\(^{71, 72}\) Comparison of the defect state energy levels in anatase and rutile (Table S1) shows that levels computed with the same theoretical approach are always deeper in rutile than in anatase, in agreement with the experimental finding in Figure 1e.

**Polarization dependence of 2PPE signal**

Another interesting consequence of the different crystal field splittings in anatase and rutile is the different direction of the transition dipole in the two polymorphs. As shown in Figure 2 and 4, the transition dipoles on R-TiO$_2$(110) are mainly along [110] and [110], i.e. perpendicular to the surface and along a surface symmetry direction, while the intensities are strongest mainly along [010] on A-TiO$_2$(101). To verify these predictions, the polarization dependence of the 2PPE excited resonance signal on A-TiO$_2$ was measured (Figure 5). In our experimental configuration, the incident plane is the horizontal (XZ) plane along the X axis, which forms a 30-degrees angle with the [010] direction, as revealed by LEED (Figure 5b). Based on the electric field of the laser light and the direction, [010], of the calculated transition dipole momentum, the maximum excitation on A-TiO$_2$(101) is expected at $\Phi$ = 34.5 degrees (see details in SI). As shown in Figure 5c, the secondary electrons signal, proportional to the substrate absorption,\(^{73}\) displays a maximum and a minimum at 0 (p-polarization) and 90 degrees (s-polarization), respectively. To exclude the effect of light absorption on the polarization dependent excited resonance, the 2PPE spectra were normalized at the work function edge before the excited
resonance was integrated. The resulting spectra show that though both \( p \) and \( s \) polarized light can induce the excitation, the \( p \)-polarization is more efficient than \( s \)-polarization on \( A\)-TiO\(_2\)(101).

The polarization dependence of the 2PPE excited resonance signal for the \( A\)-TiO\(_2\)(110) surface has been reported previously.\(^{\text{19}}\) The predicted transition dipole moments for this surface are along [1\( \overline{1} \)0] and [1\( \overline{1} \)0]. When the laser light is incident along the [1\( \overline{1} \)0] (X)

transitions between \( d_{xy} \) and \( d_{xz} \) orbitals in anatase, and from \( d_{yz} \) to \( d_{xz} \) orbitals in rutile, explaining the polarization dependence of 2PPE intensities on the rutile and anatase surfaces. Our results also show that the Ti\(^{3+}\) induced occupied states in the band gap are shallower in anatase than in rutile, and \( d\rightarrow d \) transitions from the occupied band gap state to the empty Ti\(^{3+}\) excited states occur at lower energy in anatase than in rutile (Figure 6). Most importantly, our study provides clear evidence that \( d\rightarrow d \) transitions in anatase can reduce the threshold of photoabsorption to values well below 3 eV, which can explain the observed photocatalytic activity of Ti\(^{3+}\) self-doped anatase under visible light.

![Figure 6 Schematic diagram of the electronic structure of Ti\(^{3+}\) ions in anatase and rutile TiO\(_2\).](image)

Figure 5 (a) 2PPE experimental configuration showing the incident plane (KZ) and the polarization of the laser light. The incidence angle is 33 degrees. The electric field of \( p \)-polarized light is along the X axis and the surface normal, while that of \( s \)-polarized light is along the Y axis. (b) [1\( \overline{1} \)0] LEED pattern of the \( A\)-TiO\(_2\)(101) surface. The light blue arrows and words label the directions in the reciprocal space, whereas those in red represent the direction in the real space. The [0\( \overline{1} \)0] direction deviates from the X axis by about 30 degrees. (c) Dependence of the 2PPE signal on the laser light polarization. Both secondary electron signal (red dots) and the excited resonance (blue dots) are integrated from -5 degrees to +5 degrees. The secondary electron signal is integrated directly at the work function edge. While the excited resonance signal is integrated from the 2PPE spectra which are normalized at the work function edge to correct the absorbance variation induced by polarization tuning. The zero point on the bottom axis stands for the \( p \)-polarization. The maxima of excited resonance deviates from the \( p \)-polarization by about 30 degrees due to the specific configuration of the laser plane and the orientation of \( A\)-TiO\(_2\)(101) surface as specified in (b).

or [1\( \overline{1} \)0] (Z) direction, the maximal intensity is expected at \( \Phi = 0 \) (see SI). This means that \( p \) polarized light can yield an excited resonance maximum, which agrees well with experiment.

### Conclusions

Our comparative study of the electronic properties and photoabsorption of the reduced anatase (101) and rutile (110) surfaces has highlighted several similarities as well as significant differences in the characteristics of Ti\(^{3+}\) ions in the two materials. Our 2PPE measurements on anatase (101) show a Ti\(^{3+}\) induced excited state resonance at about 2.5 eV above \( E_g \) that is similar in energy and shape to the one observed on the reduced rutile (110) surface. First principles calculations confirm the presence of Ti\(^{3+}\)-derived resonant states in a range of about 2.0-3.0 eV above the CBM on both surfaces, and further show that transitions from the gap state to the CB have pronounced peaks of the oscillator strengths in correspondence of the resonant states. Because of the different crystal field splittings in rutile and anatase, the peaks correspond to

### Conflicts of interest

The authors declare no conflicts of interests.

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