Supporting information

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

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**Relationship between excitation maximum and polarization dependence of 2PPE**

The electric field of the laser light can be expressed as follows (see Figure 5a of main text):

\[ E \propto i \cos 33 \cos \Phi + j \sin \Phi + k \sin 33 \cos \Phi \]  \hspace{1cm} (S1)

Here \( i, j \) and \( k \) are unit vectors along X, Y and Z directions, respectively, while \( \Phi \) is the polarization angle, which is 0 and 90 degrees for \( p \)- and \( s \)-polarized light, respectively. The direction, [010], of the calculated transition dipole moment on \( A \)-TiO\(_2\)(101) lies in the surface (XY) plane and forms an angle of 30 degrees with the X axis, which can be written as:

\[ \mu_{A-TiO_2(101)} = i \cos 30 + j \sin 30 \]  \hspace{1cm} (S2)

The dot product between the electric field and the direction of the transition dipole on \( A \)-TiO\(_2\)(101) can then be written in the form:

\[ E \cdot \mu_{A-TiO_2(101)} \propto \cos 33 \cos 30 \cos \Phi + \sin 30 \sin \Phi = 0.88 \cos (\Phi - 34.5) \]  \hspace{1cm} (S3)

Expression (S3) has a maximum at \( \Phi = 34.5 \) degrees, which is in accord with the observed polarization dependence of the excited resonance in Figure 5c of main text.

For comparison, we performed a similar analysis for the \( R \)-TiO\(_2\)(110) surface, for which first-principles calculations predict transition dipole moment along [1\( \overline{1} \)0] and [110]. By taking the [1\( \overline{1} \)0] direction as X, we can write

\[ \mu_{R-TiO_2(110)} = i + k \]  \hspace{1cm} (S4)

The dot product between the electric field and the transition dipole moment leads then to the following expression:

\[ E \cdot \mu_{R-TiO_2(110)} \propto \cos 33 \cos \Phi + \sin 33 \cos \Phi = 1.38 \cos \Phi \]  \hspace{1cm} (S5)
Thus, when the incoming laser light is directed along [1\(^1\)0] (X) or [110] (Z), the maximal intensity appears at \(\Phi=0\) degree, which indicates that p polarized light can yield an excited resonance maximum for \(R\)-TiO\(_2\)(110).
Table S1: Computed band gap (evaluated as the difference CBM-VBM) and energies of the defect states relative to the CBM for pristine and reduced anatase (101) and rutile (110) surfaces, as given by different hybrid functionals. The fraction of Hartree Fock exchange is 25% for HSE06, 17.5% (anatase) or 15.8% (rutile) for \(1/\varepsilon\) PBE0, and 20% for B3LYP. To check whether the gap is direct or indirect we also calculated the full band structures of the pristine surfaces, see below and Figure S5.

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Functional</th>
<th>CBM-VBM (eV)</th>
<th>CBM-Egs (eV)</th>
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<tr>
<td>A-TiO(_2)(101) with one subsurface (O_v)</td>
<td>HSE06</td>
<td>4.10</td>
<td>1.44/1.49</td>
</tr>
<tr>
<td></td>
<td>HSE06</td>
<td>4.03</td>
<td>1.15/1.28</td>
</tr>
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<td></td>
<td>(1/\varepsilon) PBE0</td>
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<td>1.00/1.20</td>
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<tr>
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<td>B3LYP</td>
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<td>1.41/1.62</td>
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<td>Pristine A-TiO(_2)(101) (192 atoms)</td>
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<tr>
<td></td>
<td>(1/\varepsilon) PBE0</td>
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<tr>
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<td>1.54/1.71</td>
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<td>(1/\varepsilon) PBE0</td>
<td>3.52</td>
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Figure S1 Occupied gap state (blue contour) and unoccupied resonant state (green contour) on 1/6 ML hydroxylated anatase (101) surface (a), anatase (101) with subsurface $O_v$ (b) and rutile (110) with surface $O_v$. Red, grey and white spheres represent oxygen, titanium and hydrogen atoms, respectively. Enlarged figures of the circled zone are shown in the upper panel.
Figure S2 Projected DOS (upper panels) and oscillator strengths (lower panels) of Ti$^{3+}$ ions in: (a, c) hydroxylated (1/6ML) anatase (101), from HSE06 calculations; (b, d) reduced anatase (101) with one subsurface oxygen vacancy, from B3LYP calculations.
Figure S3 Projected DOS (upper panels) and oscillator strengths (lower panels) for Ti$^{3+}$ ions in: (a, c) hydroxylated (1/8 ML) rutile TiO$_2$ (110), from HSE06 calculations and (b, d) reduced rutile TiO$_2$(110) with one surface oxygen vacancy, from B3LYP calculations.
Figure S4 Gap state contribution to the imaginary part of the dielectric function of anatase TiO$_{2-x}$(101) (blue line) and rutile TiO$_{2-x}$(110) (red line). Each curve is averaged over the three different polarization directions ($\ell^\mu$) shown in Figure 2 and Figure 4, respectively, that is, $\epsilon_2 = \frac{1}{3} \sum_\mu \epsilon_2^\mu$. Calculations were performed using the HSE06 functional and slab models consisting of 64 TiO$_2$ units and one O$_v$ ($x = 1/64 = 0.0156$).

Band structures of pristine rutile (110) and anatase (101). To check whether the band gaps of anatase and rutile are direct or indirect, we performed additional calculations of the band structures (Figure S5) of the pristine rutile (110) and anatase (101) surfaces using the open source code Quantum Espresso$^{1,2}$. The core electrons were treated using ultrasoft pseudopotentials and the valence electron wavefunctions were expanded in plane waves using kinetic energy cutoffs of 25 Ry and 200 Ry for the wavefunctions and charge density, respectively. For simplicity, the Perdew-Burke-Ernzerhof (PBE)$^3$ functional was used, rather than hybrid functionals. Slab models consisting of 4 tri-layers with a 1×1 surface unit cell were considered for both rutile(110) and anatase(101). The k points sampled in our band structure calculations are shown in upper panel of the figure. It can be seen that rutile has a direct band gap at the $\Gamma$ point, while anatase has an indirect band gap. This should lead to longer electron-hole recombination times in anatase, which further contributes to the higher photoactivity of this polymorph.
Figure S5 Band structure along high symmetry directions of the surface Brillouin zone (upper panels) calculated using the PBE functional: (A) rutile (110), and (B) anatase (101). The red and green dots in the band structure denote CBM and VBM, respectively.

