

## Supporting Information:

# State Selective Dynamics of TiO<sub>2</sub> Charge Carrier Trapping and Recombination

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## S1. Experimental setup and sample preparation

Measurements were performed using the Artemis condensed matter end station at the Central Laser Facility, Rutherford Appleton Laboratory<sup>1</sup>. The end station consists of a SPECS Phoibos 100 hemispherical energy analyser as well as a SPECS low energy electron diffraction (LEED) and Auger electron spectroscopy (AES) instrument. The base pressure of the end station was  $9 \times 10^{-11}$  mbar. A reduced rutile TiO<sub>2</sub>(110) crystal, blue in color, was cleaned by a few Ar<sup>+</sup> sputtering (1 kV, 1  $\mu$ A/cm<sup>2</sup>, 15 min) and annealing (1100 K, 5 min) cycles. This resulted in an ordered surface showing a sharp (1 $\times$ 1) rutile TiO<sub>2</sub>(110) LEED pattern, and AES confirmed its cleanliness. The surface was allowed to hydroxylate through reaction of the oxygen vacancies with water in the residual vacuum. The expected coverage of hydroxyls being approximately 10% of a monolayer (1 ML=5.22 $\times$ 10<sup>14</sup> unit cells/cm<sup>2</sup>)<sup>2,3</sup>. This surface, which is denoted h-TiO<sub>2</sub>(110), was chosen for study because of its long term stability<sup>4</sup>.

An s-polarised experimental geometry was employed for time resolved photoemission spectroscopy measurements (see Figure 1) to avoid laser-assisted photoelectric effects<sup>5</sup>. Both pump and probe pulses are driven by a Ti:Sapphire chirped pulse amplification system (RedDragon, KMLabs, 1 kHz repetition rate). The pump pulses of 0.95 eV (1300 nm, 50 fs pulse width, IR) and 3.5 eV (350 nm, 50 fs pulse width, UV) were generated from a high-energy optical parametric amplifier (HE-TOPAS, Light Conversion Ltd). The p-polarized extreme UV (XUV) probe pulse (10<sup>8</sup> photons/sec, 30 fs pulse width) was generated using a higher harmonic generation apparatus<sup>1</sup>, with photon energies of 20.9 eV and 30.4 eV used for the IR and UV pumped experiments, respectively. The pump and the probe laser beams were coincident at 45° from the surface normal. As the pump-probe signal is very small, delay scans were typically repeated more than 2000 times, with an accumulation time of up to 12

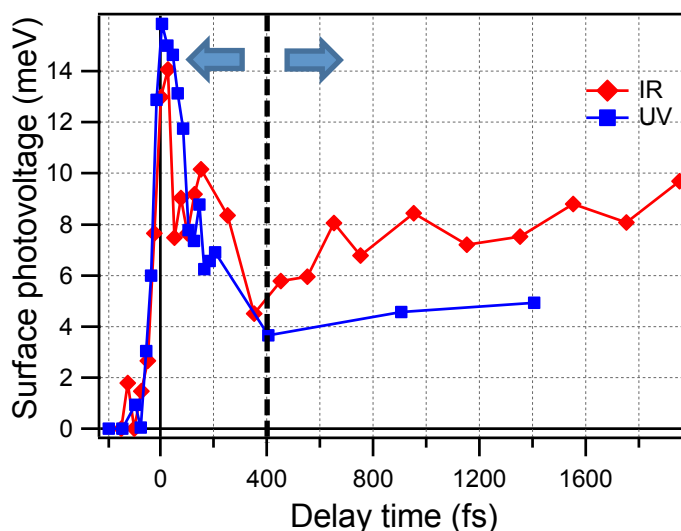
hours, to achieve an acceptable signal to noise ratio. No photodegradation was observed in the measurements. Photoemission spectra were recorded at normal emission ( $\pm 13^\circ$  collection angle), collecting a 5 eV binding energy window from about 4 eV below  $E_F$  to 1 eV above. This encompasses the top of the valence band, the BGS and the bottom of the conduction band. The position of  $E_F$  was identified from the Ta sample holder.

## S2. Correction of the surface photovoltage (SPV) effect

In order to correct the difference spectra in Figures. 2,3 of the manuscript we monitored the SPV at  $3.0 \pm 0.5$  eV binding energy (the edge of the valence band) for the IR measurements. For UV measurements we monitored the SPV at  $2.6 \pm 0.2$  eV. This excludes the top of the valence band, which will be depleted when the UV pump is employed.

As will be discussed in the next section, the spectra experience both an SPV shift and a time dependent change in the secondary electron emission (SEE) background. By analogy to the Shirley background applied in XPS analysis, the inelastic scattering is regarded as a slowly varying function in the range of a few electron volts of energy loss. Hence, we can assume that the SEE contributes a constant spectral intensity in the selected ranges to correct for SPV. Spectra were shifted so that the difference spectra are flat in the range  $2.6 \pm 0.2$  eV and the integrated spectral intensity in this range is equal to that in range of 2.0-2.4 eV, where the gradient of spectra is essentially zero, so the SPV effect is negligible.

The time dependence of the SPV is shown in Figure S1. For both IR and UV excitations there is rapid change within the first 400 fs after which the shift is essentially constant within the data point scatter.



**Figure S1.** Time dependence of the h-TiO<sub>2</sub>(110) SPV observed following IR and UV pumping derived from spectra in Figures. 2,3 in the main manuscript. The method used to determine these results is described in the text. Blue arrows indicate the two characteristic time domains.

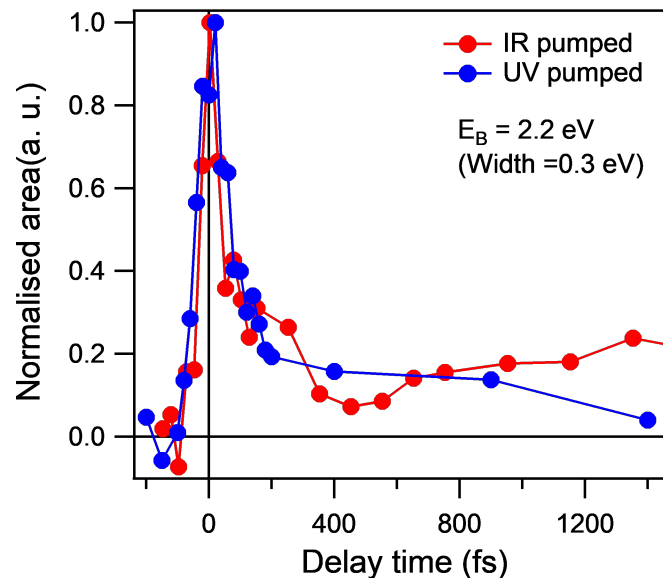
The onset of the SPV will arise from the rapid redistribution of electrons associated with the elevated electron temperature, with a corresponding fast decay arising from (re-) trapping of

these carriers into polaronic states. Hence, it has a similar, but inverted profile to the hot electron peak in the photoemission difference spectra (Figures. 2,3 main manuscript). Hot electrons experience the band bending voltage and redistribute accordingly, which in turn reduces the band bending. In another picture, this process may be regarded as the sudden increase of the dielectric constant because of the increase of conductivity occasioned by excitation of electrons into the conduction band. Evidence for such an ultrafast reaction of dielectric screening can be found in a recent attosecond-pump-probe study<sup>6</sup>. Since the magnitude of band bending is inversely proportional to the dielectric constant<sup>7</sup>, the band bending is reduced following excitation by the pump pulse. Subsequent transfer of energy to phonons results in a recovery towards the ground state value of the band bending. In the polaron picture applicable here, this corresponds to the (re-)trapping of electrons following photon-assisted polaron excitation.

The lack of change in the SPV in the IR pumped spectra between 400 fs and 2 ps is consistent with the temperature of electrons and lattice being in equilibrium at an elevated temperature. As for the UV pumped results, a further recovery of band bending at longer timescales is expected from electron-hole recombination processes. A component will have a lifetime on a ns timescale [6], which will provide the background above 400 fs seen in Figure S1. This likely obscures any effect arising from the ps lifetime processes seen in the photoemission data.

### S3. The secondary electron emission background

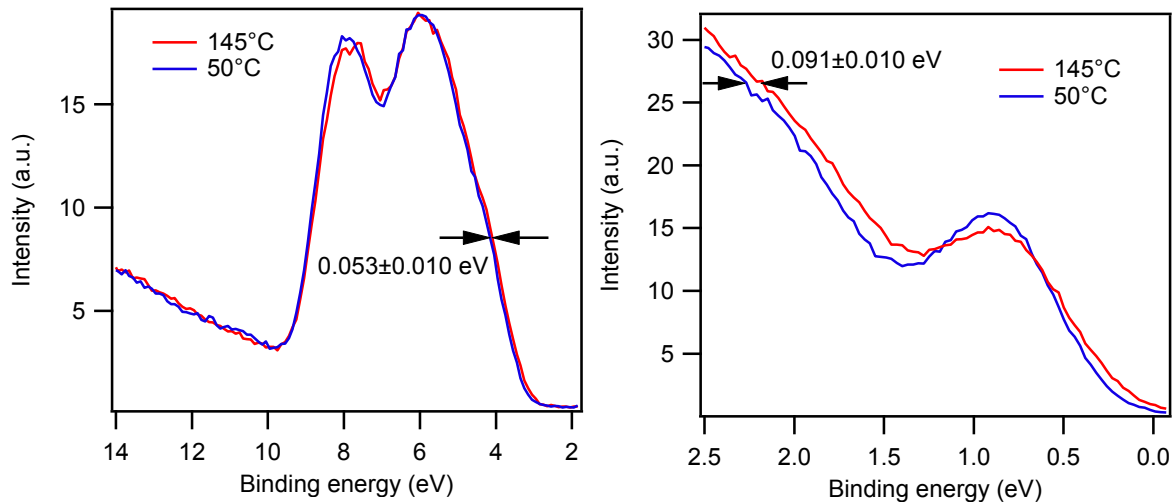
In the pump-probe measurements the spectra contain a significant contribution from the secondary electron emission (SEE) background. This is known from previous UPS work by Zhang and Henrich et al<sup>8</sup>, which shows a significantly enhanced SEE background when the photon energy is lower than 30 eV. In the current work, the region between the band gap state and the top of valence band, from 2.2 to 3 eV binding energy, is within the band gap of TiO<sub>2</sub>. Nevertheless, a non-vanishing spectral intensity is always observed that can be attributed to the SEE. Furthermore, the intensity within this range has a temperature dependence with both IR and UV pumps, as shown in Figure S2.



**Figure S2.** Time dependence of the h-TiO<sub>2</sub>(110) SEE intensity at 2.2 eV binding energy, with an energy window of 0.3 eV. The data were obtained from the SPV-corrected spectra in Figures. 2,3 of the manuscript.

A rapid change is observed within the first 100 fs around 2.2 eV. The dynamics of the spectral intensity from the SEE may be understood as the variation of inelastic scattering with temperature following the pump pulses. Previous work, including theory and experiment, reported a lack of temperature dependence of SEE<sup>9,10</sup>. On the one hand, the inelastic scattering of electrons is enhanced at high temperatures, which increases SEE. On the other hand, the escape depth of electrons is reduced, which decreases SEE. The overall effect is that the SEE show little temperature independence.

In our work, however, the SEE background around 2.2 eV arises from inelastic scattering of the band gap states, which are localized at the surface. Hence, the escape depth is not influenced by temperature and an increase in SEE with temperature is expected.



**Figure S3.** UPS measurements of the valence band (left,  $h\nu = 40.8$  eV) and the band gap states (right,  $h\nu = 21.2$  eV) on TiO<sub>2</sub>(110) at temperatures of 145 and 50 °C.

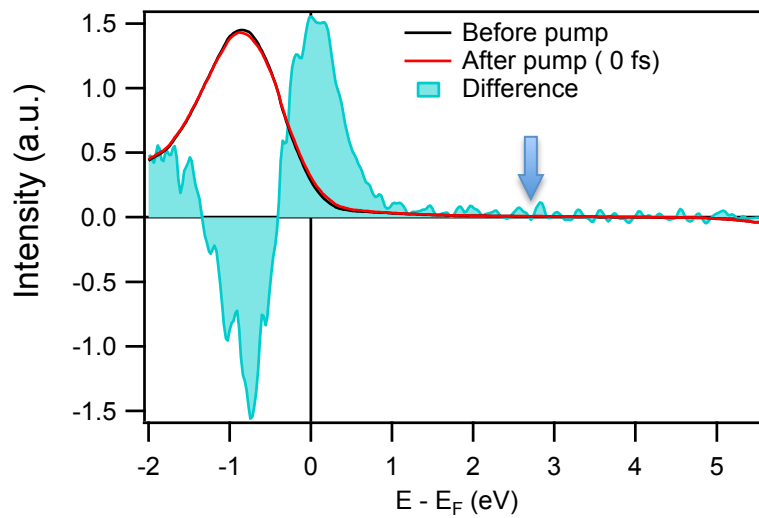
This is supported by UPS results at temperatures of 145 °C and 50 °C, as shown in Figure S3. The upper edge of the valence band shifts to lower binding energy by  $0.053 \pm 0.010$  eV at 145 °C as compared to that at 50 °C, which can be attributed to a decrease in downward band bending. Under the same conditions, the spectra around the BGS seem to shift by  $0.091 \pm 0.010$  eV as measured at He I. The apparent larger shift can be attributed to the increase of the SEE background.

#### S4. Dynamics of hot electrons in higher conduction band

The extended energy range dynamics of hot electrons excited from the BGS by the 3.5 eV UV light is shown in Figure S4. One spectrum was recorded before the pump, at a delay time of -200 fs (black), the second at 0 fs (red). The population of electrons around  $E_F$  and depletion of the BGS at 0 fs can clearly be observed in the difference spectrum. However, in

the energy range above 1 eV the spectral intensity of hot electrons is extremely low. These states are populated by electrons excited from the BGS. To achieve a good signal to noise ratio, the measurement involved only two time delay values and repeated for 4 hours. In the difference spectrum it is clear that the spectral intensity is very small in the range below the 2.7 eV, which is the highest energy of the electrons excited from the BGS by 3.5 eV UV light.

The low spectral intensity of the hot electrons is attributed to the fast decay of electrons due to scattering by phonons. The time scale is expected to be around a few fs according to recent calculations<sup>11</sup>. This is beyond the temporal resolution of our measurements, where the cross-correlation of the UV and XUV pulses are about 60 fs.



**Figure S4.** UV-pump XUV probe measurement on rutile  $\text{h-TiO}_2(110)$  showing an extended energy range above the Fermi level. The experimental conditions are the same as those in Figure 3 of the manuscript. The two spectra are recorded before the pump pulse ( $< -50$  fs, black) and at a delay time of 0 fs (red). The difference of the two spectra is multiplied by a factor of 20, and shown as the light blue filled spectrum. The blue arrow marks the energy position of 2.7 eV, which is the highest energy of BGS electrons pumped by a 3.5 eV UV light.

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