



Coverage-dependent two-photon photoexcitation at the H₂O/TiO₂ interface



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ARTICLE INFO

Available online 2 March 2016

Keywords:

TiO₂
Hydroxyls
Photoexcitation
Water
2PPE

ABSTRACT

Excited electrons and holes are crucial for redox reactions on metal oxide surfaces. However, precise details of this charge transfer process are not known. We report two-photon photoemission ($h\nu = 3.23$ eV) measurements of rutile TiO₂(110) as a function of exposure to water below room temperature. The two-photon resonance associated with bridging hydroxyls is enhanced following water exposure, reaching a maximum at a nominal coverage of one monolayer. Higher coverages attenuate the observed resonance. Ultraviolet photoemission spectroscopy ($h\nu = 21.22$ eV) of the initial, band gap states shows little change up to one monolayer water coverage. It is likely that the enhancement arises from dissociation within the adsorbed water monolayer, although other mechanisms cannot be excluded.

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1. Introduction

The photoactivity of titanium dioxide (TiO₂) has received significant attention since it was first demonstrated in the 1970s [1]. Irradiation by ultraviolet light excites electrons across the band gap, leaving behind a hole. These excited-state electrons and holes are thought to initiate redox reactions at the surface [2]. Hence, information concerning both filled and empty states is crucial for the fundamental understanding of photocatalysis on TiO₂.

As excited states are typically difficult to measure, the details behind the photocatalytic process are not fully understood [3]. However, two-photon photoemission (2PPE) is capable of measuring the energies of both occupied and excited states simultaneously [4–8]. In this technique, the absorption of a pump photon results in the excitation of an electron to a state above the Fermi level (E_F), but below the vacuum level, from which it is subsequently probed by a second photon. By delaying the probe pulse relative to the pump, the lifetime of the unoccupied state may also be investigated. 2PPE is inherently surface sensitive, as only electrons from the first few atomic layers may escape the surface without being scattered inelastically [9]. This is vital when studying states that are important in redox reactions at the surface.

Here, we use 2PPE and ultra-violet photoemission spectroscopy (UPS) to examine the filled and empty states of rutile TiO₂(110) at

various water coverages. The TiO₂(110) surface contains bridging oxygen (O_b) rows which run in the [001] direction [10]. Standard UHV sample preparation cycles of argon ion sputtering and thermal annealing can remove these O_b , creating O_b vacancies (O_b -vac). The resulting O_b -vac coverage is typically 0.05–0.10 monolayers (ML), where 1 ML is defined as the number of surface unit cells. A space-filling model of the TiO₂(110) surface is shown in Fig. 1a, which is based upon long-range crystallography, scanning probe and photoemission measurements [11–14]. Such a reduced surface will be referred to as r -TiO₂(110).

Though the adsorption of water on r -TiO₂(110) has been characterised extensively in a range of experimental and theoretical studies, its behaviour remains a source of controversy [5,6,14–30]. Above 170 K water adsorbs dissociatively at O_b -vac, forming two bridging hydroxyls (OH_b) per O_b -vac [10]. Such a hydroxylated surface, which is still reduced [11], will be referred to as h -TiO₂(110). OH_b are stable up to about 520 K, above which temperature they recombine and desorb as H₂O. Hence, the desorption of OH_b regenerates O_b -vac at the surface [10,16]. Additionally, it has been shown that r -TiO₂(110) presents oxygen vacancies at step edges that are also active sites for water dissociation at room temperature [31].

Below room temperature, but above ~170 K, monolayer coverage can be achieved with water exposures between 1.4 and 1.8 L (1 L = 1.33×10^{-6} mbar.s) [6,15]. Though many studies suggest that monolayer water adsorbs molecularly (for example [14–17,20,25]), there is also evidence for a mixed monolayer of hydroxyls and molecular water [28, 32–35]. Photoemission measurements have evidenced water dissociation on the defect-free TiO₂(110) surface, where one bridging and terminal hydroxyl (OH_t) pair is created per water molecule. On r -TiO₂(110), one dissociation event at an O_b -vac substitutes one in a

Abbreviations: 2PPE, Two-photon photoemission; O_b -vac, Bridging oxygen vacancy; OH_b , Bridging hydroxyl; OH_t , Terminal hydroxyl; r -TiO₂, Reduced titanium dioxide; h -TiO₂, Hydroxylated titanium dioxide; BGS, Band gap states; HB, Hydrogen bonds.

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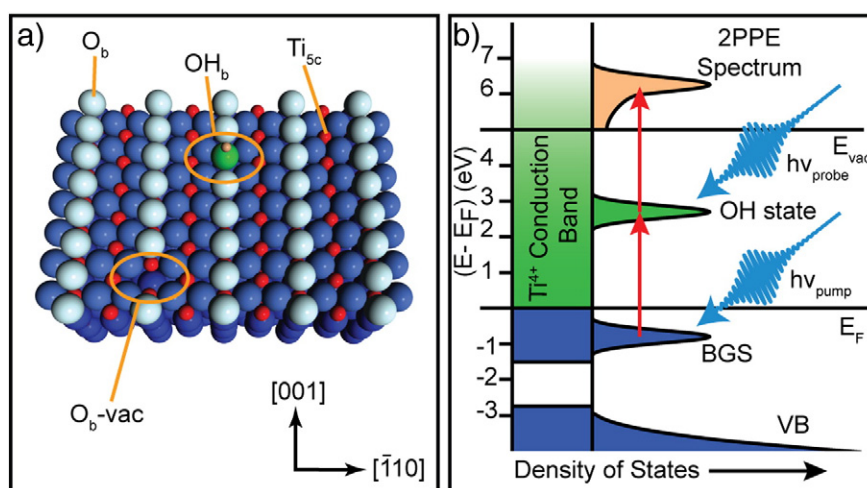


Fig. 1. Model of the $\text{TiO}_2(110)$ surface and the 2PPE excitation process. a) Space-filling diagram of the $\text{TiO}_2(110)$ surface, showing the common defects: $\text{O}_b\text{-vac}$ and OH_b . b) Schematic of the resonant 2PPE excitation process from the BGS to an unoccupied state (OH state), induced by the adsorption of OH_b on $r\text{-TiO}_2(110)$.

defect-free region of the surface, such that the total hydroxyl coverage of the mixed monolayer remains the same. The competitive nature of these two dissociation channels leads to a maximum hydroxyl coverage of 0.4 ML, for initial $\text{O}_b\text{-vac}$ densities of ≤ 0.2 ML [34]. In the text below, ‘1 ML water’ denotes an overlayer that may be partially dissociated.

There is clear evidence that $\text{O}_b\text{-vac}$ and OH_b are important in chemical reactions on $\text{TiO}_2(110)$, however it is not yet known in detail what role they play in photocatalysis [3,36]. Both $\text{O}_b\text{-vac}$ and OH_b create Ti 3d band gap states (BGS) ~ 1 eV below E_F [11,17,18,37–43], and these states may be important for photocatalysis [44]. The presence of $\text{O}_b\text{-vac}$ is believed to have a detrimental effect on the rate of some photocatalytic processes [45] and a positive effect on others [46,47]. Moreover, photocatalytic TiO_2 surfaces are known to be extensively hydroxylated [48].

2PPE spectra of $\text{TiO}_2(110)$ display a resonance visible in the photon energy range of 3.1–4 eV [49–52]. Based upon 2PPE measurements and density functional theory (DFT) calculations, this resonance has been attributed by others to bulk $d\text{-}d$ transitions between the BGS and the t_{2g} or e_g levels in the conduction band. Hence it was associated with the presence of $\text{O}_b\text{-vac}$ [50,51].

Our measurements have subsequently demonstrated that the 2PPE resonance is absent on the $r\text{-TiO}_2(110)$ surface, and is in fact related to the density of OH_b [49]. In this earlier work, we showed that OH_b induce a new state (OH state) centered ~ 2.7 eV above E_F , as well as being associated with the BGS [49]. In passing, we note that data from the $r\text{-TiO}_2(110)$ surface is not presented in Ref. [50] and the absence of OH_b is not proven in Ref. [51]. Though Ref. [49] shows a small 2PPE feature without OH_b , this does not imply resonant photoexcitation via an unoccupied state since it is also seen in s-polarised 2PPE and single photon photoemission ($h\nu = 5.9$ eV) spectra [51]. Instead, we believe that this small feature arises from two-photon coherent excitation from the BGS via a virtual state [7].

DFT calculations, showing OH-induced states of p -character in the conduction band region, are consistent with our interpretation [18,19]. A schematic of the 2PPE process for $h\text{-TiO}_2(110)$, determined in Ref. [49], is shown in Fig. 1b.

2. Experimental details

A $r\text{-TiO}_2(110)$ sample was prepared by cycles of Ar^+ sputtering and thermal annealing. The surface order and lack of contamination were confirmed by low-energy electron diffraction and Auger electron spectroscopy, respectively. After annealing, as the surface cools in the residual vacuum it hydroxylates with a coverage of 0.1–0.2 ML [10]. The sample was then cooled further to 100 K and exposed to 1.8 ± 0.2 L

H_2O . The 2PPE ($h\nu = 3.23$ eV, 383 nm) and UPS (He-I, $h\nu = 21.22$ eV, 58 nm) spectra were both recorded using a pass energy of 10 eV. These measurements employed an instrument (base pressure $\sim 4 \times 10^{-10}$ mbar) and laser system described elsewhere [49].

All 2PPE measurements were made with p-polarised light, with the scattering plane perpendicular to the surface [001] azimuth. The incident angle of the laser was $68 \pm 1^\circ$ from the surface normal. A bias voltage of -6 V was applied to the sample during 2PPE measurements. Photoemission from the Ta sample plate was used to determine the position of E_F . The combined energy resolution of the electron energy analyser and the optical bandwidth of the laser pulse is estimated as 170 ± 30 meV.

The 2PPE and UPS spectra were measured as the sample warmed to 290 K at a rate of ~ 1 K/min. Following this, the sample was heated to 330 K. The sample temperature was measured using a K-type thermocouple mounted on the sample holder, ~ 5 mm from the sample. Temperatures below room temperature were subsequently calibrated with reference to the known adsorption behaviour of water on $r\text{-TiO}_2(110)$ [15] (see below).

3. Results

The UPS spectra are shown in Fig. 2a. It is known from temperature-programmed desorption (TPD) measurements that a monolayer coverage of water is stable between ~ 190 and 230 K [15]. In this regime there will be little variation in the UPS spectra as the surface condition is constant. This allows calibration of the sample temperature. Fig. 3 shows that the UPS spectra are nearly identical over a range of 40 K, which occurred between ~ 160 and 200 K according to the thermocouple. Further insight can be gained from the saturation of the sample workfunction change and the onset of BGS signal attenuation in UPS, which occur at and above monolayer coverage, respectively [5,20,21]. The sample workfunction change saturated at ~ 200 K in 2PPE measurements, and BGS signal attenuation occurred below 160 K in UPS. These diagnostics are discussed in detail later in this article.

The coincidence of these three diagnostic tools supports our assignment of monolayer coverage between 160 and 200 K. Since this range is ~ 30 K lower than that in TPD results [15], where the surface temperature is much better defined, we use these to calibrate our sample temperature. Hence, the temperature associated with the UPS and 2PPE spectra measured below room temperature have been shifted by 30 K to higher temperatures to correct for this systematic offset. The corrected temperatures are those shown throughout this paper.

The UPS spectra were fitted in the region 3.5 eV below to 1 eV above E_F , as shown in Fig. 4. The BGS appear 0.90 ± 0.05 eV below E_F in the UPS

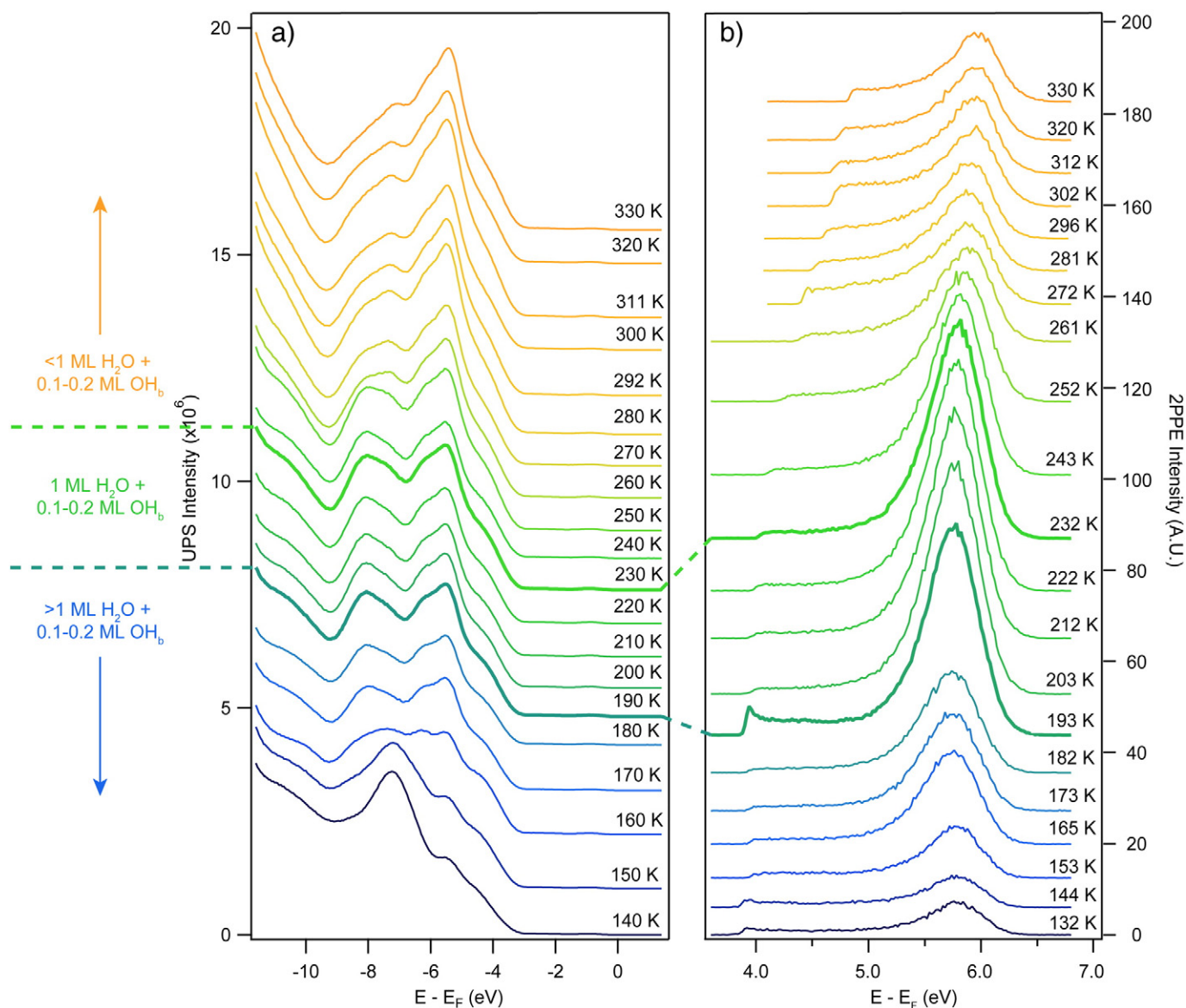


Fig. 2. UPS (21.22 eV) and 2PPE (3.23 eV) spectra acquired between 132 K and 330 K, after exposure to 1.8 ± 0.2 L H₂O at 130 K. a) UPS spectra showing the valence band region. The spectra are nearly identical between 190 K and 230 K (shown in bold), indicating monolayer water coverage. b) 2PPE spectra showing maximum intensity between 193 K and 232 K.

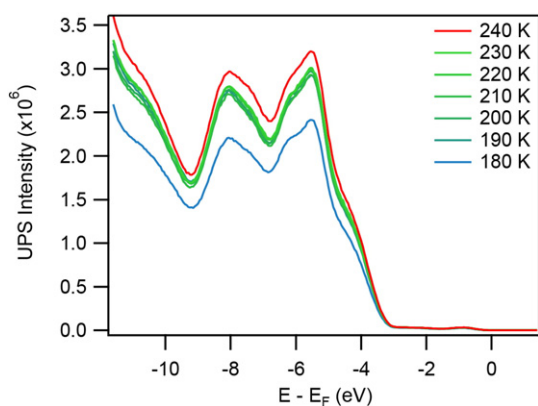


Fig. 3. Selected UPS (21.22 eV) spectra from Fig. 2a, measured between 240 K and 180 K. The spectra are identical in the range 190–230 K (green), suggesting that the sample's surface maintains a constant coverage of water. This is attributed to 1 ML water [15].

spectra. Fig. 5 shows that the UPS BGS peak area is smallest at 140 K (dark-blue), but increases until 190 K (light-blue) after which it is approximately constant. In order to improve the agreement of the fitting procedure, a second peak was added 2.1 eV below E_F in addition to the BGS at -0.9 eV, labelled Satellite. To our knowledge this feature has not previously been reported.

Investigation into the origin of the Satellite feature showed that it was observed only when relatively low He pressure was used in the emission lamp, suggesting that it arises from photoemission via additional He emission lines. Furthermore, this feature does not appear in monochromatic synchrotron measurements [17,38]. We propose that this feature arises from photoemission from both the valence band and O 2s core level caused by He I β and He II α , respectively. The Satellite feature showed no significant change in area with water coverage.

The 2PPE spectra shown in Fig. 2b contain a feature at ~ 5.9 eV above E_F at all temperatures. Based upon previous work [49], this is attributed to photoexcitation from the BGS to an OH state in the conduction band region, and then above the vacuum level. The feature is smallest at low

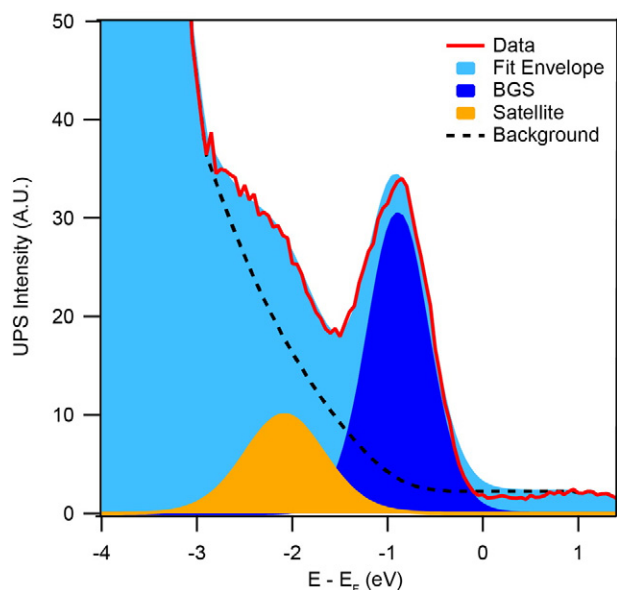


Fig. 4. Example of the fitting procedure for UPS spectra, showing the spectrum measured at 240 K. Two Voigt peaks, representing the BGS (dark-blue) and the Satellite feature (orange), are superimposed upon a Tougaard background (dashed line). The Satellite feature appears only when low He pressure is used, and is thought to arise from photoemission from both the valence band and O 2s core level caused by He I β and He II α , respectively.

temperatures, increasing in intensity until 193 K. It then remains roughly constant until 232 K, above which it again reduces in intensity.

It is known that both coherent two-photon and incoherent, stepwise excitation can contribute to 2PPE spectra [7]. In a previous publication we decomposed 2PPE spectra into the sum of two Voigt lineshapes (Lorentzian plus a Gaussian contribution representing instrumental broadening), which were assigned to independent coherent and incoherent excitation processes [49]. The 2PPE spectra are more correctly described as the sum of one purely coherent contribution, resulting from two-photon ionisation of the initial state, and a second that arises from both coherent and incoherent excitation processes [7]. This means that non-resonant virtual excitation contributes to the intensity of the intermediate state peak when ionisation occurs within the electronic dephasing time of the material.

Here, we describe our 2PPE spectra as the sum of two contributions arising from photoemission from the initial BGS and intermediate OH state. In our fitting procedure, contributions from the BGS and the OH state are represented by individual Voigt lineshapes, as shown in

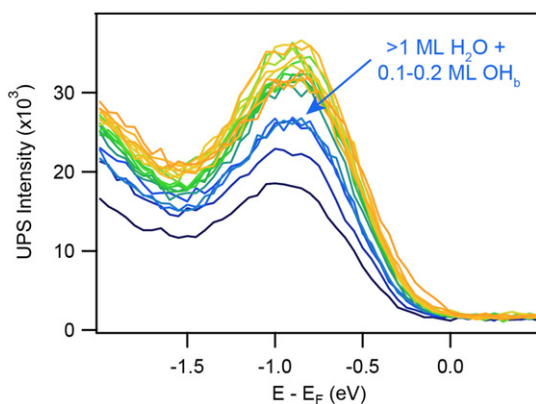


Fig. 5. UPS measurements from Fig. 2a, magnified to show the BGS. At ≤ 1 ML water coverage the BGS are essentially constant (330 K–190 K, orange to green). Above 1 ML the signal is attenuated by physisorbed water (180 K–140 K, light- to dark-blue).

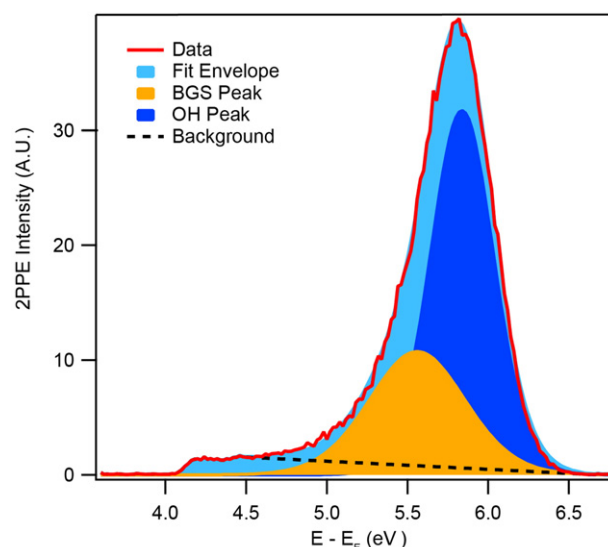


Fig. 6. Example of the fitting procedure for 2PPE spectra, showing the spectrum measured at 243 K. Two Voigt peaks, representing coherent excitation from the BGS (orange) and coherent and incoherent excitation via the OH state (dark-blue), are superimposed upon a linear background (dashed line).

Fig. 6. The position of the 2PPE BGS peak is given by $E - E_F = E_{BGS} + 2h\nu$, with the BGS energy (E_{BGS}) being taken from the UPS spectra. The position of the 2PPE OH peak was not fixed.

A shift of 0.10 ± 0.05 eV further below E_F has been observed previously for all occupied states of h -TiO₂(110) after the adsorption of water in both UPS and X-ray photoemission spectroscopy [49]. In addition to this, water adsorption leads to a further shift of the OH state to lower energy by 0.1 eV [49]. Similarly, in this work the 2PPE OH peak was seen to shift ~ 0.15 eV away from E_F as the sample warmed from 222 K to 296 K. This is attributed to the reduction in band-bending at the surface, caused by the desorption of water.

Chemisorption of molecular water was accompanied by a concomitant change in the sample workfunction, as expected from previous work [5]. This was measured from the low energy threshold of the 2PPE spectra. TPD measurements characterising the adsorption behaviour of water on r -TiO₂(110) serve as a useful comparison to workfunction measurements in the monolayer coverage regime. The workfunction measurements were fit using a sigmoid curve as shown in Fig. 7, representing the integrated area of the monolayer adsorption peak in TPD measurements [15]. Other TPD features were not considered, as only the first, chemisorbed layer of water is expected to influence the workfunction [5,20]. The width of the sigmoid curve is approximately 50 K, in good agreement with the full width at half maximum of the TPD monolayer peak centered at 270 K [15]. The center of the fitted sigmoidal curve was 264 ± 2 K.

Our results show a maximum workfunction change of -0.92 ± 0.04 eV between the hydroxylated and water-covered surfaces. This value is similar to the ~ 1 eV reported from X-ray photoemission [20] and 2PPE [5] measurements but greater than the ~ 0.6 eV change seen in metastable impact electron spectroscopy [25]. The photoemission results are directly comparable, as it has been observed that the effect of water adsorption on the workfunction has little dependence on the sample preparation [5].

Fig. 7 displays the results obtained from fitting our UPS and 2PPE spectra. The BGS peak area obtained by fitting our UPS spectra (red) is normalised to its intensity at 280 K. The 2PPE BGS (green) and OH (blue) peak areas are normalised to the area of the 2PPE OH peak at 203 K. The change in the sample workfunction (black) is measured relative to h -TiO₂(110) at 330 K.

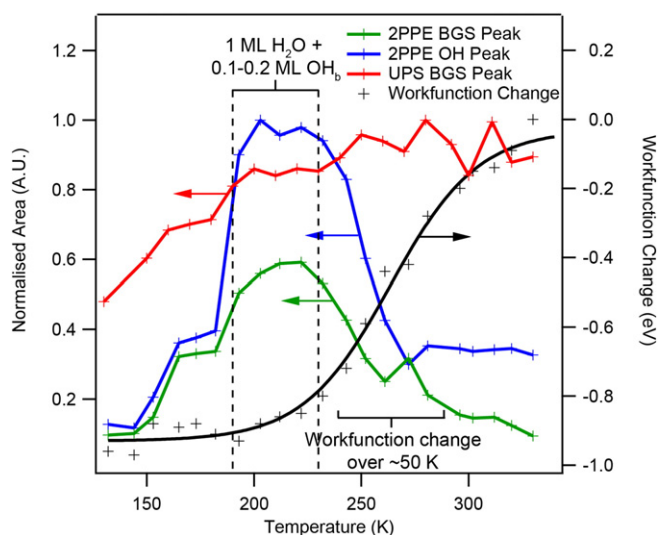


Fig. 7. Results from fitting the 2PPE and UPS spectra. The excited state resonance reaches a maximum at 1 ML H₂O + 0.1–0.2 ML OH_b, indicated by two dashed lines. Since the BGS intensity is constant above 190 K, we assign changes in the 2PPE spectra to the excited state. The workfunction change, measured relative to the hydroxylated surface at 330 K, saturates at -0.92 ± 0.08 eV. This limit is known to correspond to 1 ML H₂O coverage, supporting our previous assertions.

4. Discussion

As seen in Fig. 7, the BGS peak area in the UPS spectra decreases below 190 K. Whilst the adsorption of OH_b on *r*-TiO₂(110) has been shown not to affect the BGS intensity [17,18], molecular water is known to significantly attenuate the photoemission signal from the surface at coverages greater than 1 ML [21]. Hence the reduction in the UPS BGS peak area below 190 K is attributed to the presence of a physisorbed, second layer of H₂O. Above 190 K there is ≤ 1 ML H₂O and the change in the UPS BGS peak area is negligible. Since the BGS signal is only attenuated at water coverages above 1 ML, the lower temperature limit of monolayer coverage in this experiment can be identified.

The upper temperature limit of monolayer coverage can be found from the change in the sample workfunction. The workfunction provides insight into the electronegativity of TiO₂, hence determining when redox chemistry may occur. Tuning the workfunction of TiO₂ may allow the surface chemistry to be controlled [53]. Chemisorbed water decreases the workfunction of TiO₂, whereas physisorbed water does not [5,20]. From the change in the sample workfunction we are able to identify the upper temperature limit of monolayer water coverage as ~ 230 K. The lower limit was ~ 190 K, given by the attenuation of the BGS signal caused by physisorbed water above 1 ML coverage. These bounds coincide with the temperature range over which the UPS spectra are identical (see Fig. 3). Hence it is clear that the sample is covered with 1 ML of water between 190 and 230 K.

Both the 2PPE BGS and OH peaks show maxima between 193 K and 232 K. This temperature range corresponds to 1 ML H₂O, in addition to 0.1–0.2 ML OH_b. As the temperature further increases, the coverage decreases below 1 ML [15], and the 2PPE peak areas decrease. An increase in the 2PPE OH peak at monolayer coverage can be explained by changes in the unoccupied density of states. However, considering that the BGS peak area in UPS is constant above 190 K, it is less obvious why similar changes are seen for purely coherent, virtual excitation from the BGS in 2PPE. To explain this we draw an analogy with resonance-enhanced four-wave mixing, $\omega_{\text{FWM}} = 2\omega_1 \pm \omega_2$, in which the presence of a nearby resonance at the two-photon level ($2\omega_1$) enhances the intensity of light generated at the sum and difference frequencies (ω_{FWM}) [54].

As monolayer water coverage is reached, the OH state shifts 0.1 eV to lower energy relative to the BGS [49], bringing the fixed photon energy

closer to resonance. This increases the intensity of 2PPE BGS peak through resonant enhancement. This is supported by previous 2PPE measurements as a function of photon energy [49], which showed similar ratios of intensity for the 2PPE BGS and OH peaks for the water-covered and hydroxylated surface, for the same detuning from their respective resonant photon energies.

There are three possible origins of the 2PPE signal enhancement following monolayer water adsorption on *h*-TiO₂(110). Firstly, DFT calculations by Onda et al. of the water-covered *h*-TiO₂(110) surface have pointed to the creation of a hydrogen bonding network of diffuse orbitals, referred to by the authors as a ‘wet electron’ state [5,6]. Though Onda et al. calculated the energy of the unoccupied state to be ~ 2 eV higher than that observed experimentally by us on *h*-TiO₂(110) [49], their calculations of the water-covered surface are in good agreement with our results. The delocalised nature of the ‘wet electron’ orbitals may explain the reduced energy and slightly longer lifetime observed for the unoccupied state on the water-covered surface relative to *h*-TiO₂(110) [6,49]. It could also be the origin of the enhanced resonance intensity.

Above 1 ML H₂O coverage the 2PPE intensity is also greatly reduced. The ‘wet electron’ state interpretation attributes this to the disruption of the network of hydrogen bonds (HB), caused by physisorbed water [6]. The existence of HB between the first and second layers of water on *h*-TiO₂(110) has been debated over the last decade. High resolution electron energy loss spectroscopy (HR-EELS) measurements do not show a redshift in the OH stretching region when the water coverage is increased above 1 ML [15]. This was believed to indicate the absence of HB between the first and second layers of water. However, DFT calculations revealing the presence of HB between water layers were able to recreate the behaviour observed in HR-EELS [23]. This work showed that the second layer of water changes the structure of the monolayer, in agreement with the ‘wet electron’ state picture. Additionally, features in infrared reflection–absorption spectroscopy and ab initio molecular dynamics calculations were assigned to HB between water layers [24].

Though photoemission measurements [5,20] demonstrate that only the first layer of water alters the sample workfunction, supporting the lack of interaction between water layers, Huguenschmidt et al. [20] explained this by proposing that physisorbed water lies parallel to the surface in order to increase hydrogen bonding with the chemisorbed monolayer, without altering the workfunction.

In addition to possible changes in HB configuration, physisorbed water may also decrease the 2PPE signal via attenuation, similar to the reduction of the UPS BGS peak in Fig. 5. Since the UPS BGS peak area decreases below 190 K, it is not possible to attribute changes in the 2PPE spectra solely to changes in the OH state.

The second possible origin of the 2PPE signal enhancement is related to the suggestion that the resonance is more prominent on water-covered surfaces as the reduced workfunction allows greater separation between the secondary electrons and the excited resonance signal [51]. To test this assertion, the photon energy was increased from 3.02 eV to 3.22 eV; indeed, the resonance was more pronounced. This increase was also partly attributed to the photon energy dependence of the 2PPE resonance [51]. Our work shows that the 2PPE signal increases when the photon energy is closer to the central resonant energy of ~ 3.5 eV [49]. The reduced workfunction likely plays a role in the enhanced 2PPE resonance observed for the water-covered surface, however it is not easily separated from the photon energy dependence. Given that the resonance feature is well separated from the workfunction cutoff in all spectra in Fig. 2b, it seems unlikely that this is the sole origin of the 2PPE enhancement at monolayer water coverage.

Finally, an alternative interpretation of the enhancement of the 2PPE resonance at monolayer coverage arises from the possibility of a mixed monolayer of dissociated and molecular water. In this case, the enhancement of the 2PPE resonance would arise from the creation of additional hydroxyls and therefore would have little to do with molecular water. In support of this mechanism, the OH_b–OH_t pairs thought to

be formed by water dissociation on *h*-TiO₂(110) desorb above 230 K, which coincides with the onset of the reduction of our 2PPE signal (Fig. 7) [34]. The dissociation of neutral water molecules on *h*-TiO₂(110) is not expected to further reduce the surface, and indeed the UPS BGS peak remains constant between 190 K and 330 K.

5. Conclusion

UPS and 2PPE measurements have been used to characterise the filled and excited states of *h*-TiO₂(110) at various water coverages. The 2PPE resonance, correlated with the density of OH_b, is enhanced by water exposure below room temperature. The enhancement of this resonance was greatest at a nominal coverage of 1 ML H₂O. The 2PPE signal depends on both the initial and excited state density of states, and UPS measurements confirm that the BGS are not altered by a nominal coverage of one monolayer water. This suggests that the unoccupied state is altered, either through the creation of a ‘wet electron’ state or more simply due to an increased density of hydroxyl groups. The reduction of the workfunction following the adsorption of monolayer water may also play a role in the enhancement of the 2PPE signal. Conversely, the second, physisorbed layer of water was found to diminish the 2PPE signal. These observations provide insight into the nature of charge transfer at the H₂O/*h*-TiO₂(110) interface.

Acknowledgements

This work was supported by the European Research Council Advanced Grant ENERGYSURF (GT), EPSRC (UK) (EP/D068673/1), EU COST Action CM1104, the Royal Society (UK), and the Alexander von Humboldt Stiftung (Germany).

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