

X-ray photoelectron spectroscopy of fluorescein adsorbed on model solar-cell surfaces

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Abstract

We report on the X-ray photoelectron spectroscopy of fluorescein molecules adsorbed under UHV conditions on single crystal rutile $\text{TiO}_2(110)$ and $\text{Au/TiO}_2(110)$ surfaces. The molecule is thought to bond covalently to these model solar-cell surfaces primarily through the deprotonated carboxylic group, with an additional interaction arising between the triple ring structure of the molecule and the surface.

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1. Introduction

The emergence of dye-sensitised solar-cells [1,2] as strong contenders for cost-effective photovoltaic devices has led to a great interest in the interactions of dyes and related molecules [3] with model solar cell surfaces. The adsorption of bi-isonicotinic acid on rutile [4–7] and anatase [8,9] TiO_2 has, for example, led to a greater understanding of the processes which occur in the Grätzel solar-cell [1,2] on the molecular level. In this paper we investigate a model system for a solid state solar cell recently demonstrated which is based on the dye mercury dibromofluorescein (merbromin) adsorbed on Au-

covered rutile TiO_2 [10]. As the full name of merbromin suggests, it is essentially a fluorescein molecule (Fig. 1) with two additional Br and one HgOH side groups, and as such both molecules are expected to adsorb on TiO_2 and Au surfaces in a very similar way. Here we compare the X-ray photoelectron spectroscopy (XPS) of fluorescein molecules in a thick film with monolayers adsorbed on both rutile TiO_2 and Au-covered TiO_2 . Aromatic carboxylic acids have a tendency to chemisorb to TiO_2 surfaces through the deprotonated carboxylic group in a 2M bi-dentate fashion (each oxygen atom bonded to one Ti atom) [11,12]. Adsorption of aromatic carboxylic acids on Au surfaces has also been shown to be via the deprotonated carboxylic group [13]. We would therefore expect fluorescein to bond to the surface in a similar fashion although there are significant steric considerations as illustrated in Fig. 1.

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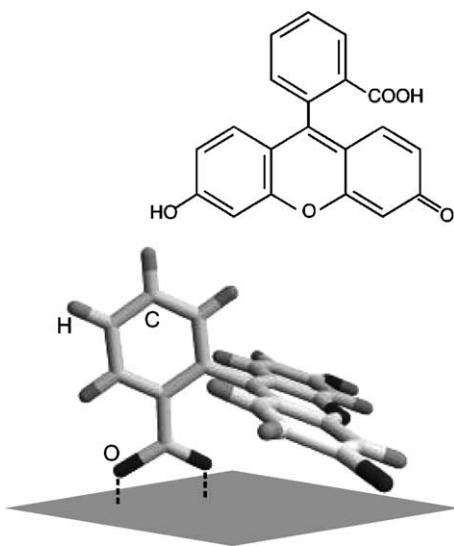


Fig. 1. Schematic representation of fluorescein (top) and possible adsorption geometry (bottom).

2. Experimental details

Experiments were performed using a Kratos Analytical Axis Ultra X-ray photoelectron spectrometer with monochromatised AlK_{α} (1486.6 eV) radiation and a hemispherical energy analyser. The spectrometer was also equipped with a magnetic immersion lens and a charge neutralisation system, which gave a high flux of low energy electrons to provide a uniform neutralising charge density. An overall resolution of around 400 meV was achieved and the base pressure in the preparation chamber was 3×10^{-10} Torr.

The substrate used for this investigation was a rutile $\text{TiO}_2(110)$ single crystal (Pi-Kem, Shropshire, UK). The surface was cleaned by sputtering with 1 keV Argon ions. The crystal was made conducting by the creation of bulk defects through annealing at ~ 800 °C (during this process a new crystal changes colour from clear to deep blue). The number of defects at the surface was then minimised by annealing (~ 800 °C for 10 min) with subsequent cooling in 10^{-6} Torr of oxygen (99.999%). This process can be followed by monitoring the shape of the Ti 2p spectrum until a single oxidation state is observed.

Fluorescein was evaporated at a temperature of 240 °C using a home-built evaporator placed at a distance of ~ 20 cm from the TiO_2 surface. We define a thick film as the point at which the substrate Ti 2p, or Au 4f signal was completely quenched. Fluorescein monolayers were produced by annealing the thick films to 240 °C which results in desorption of the physisorbed multilayers to leave a single chemisorbed monolayer.

Gold was evaporated from a Knudsen cell located at a distance of ~ 20 cm from the sample, at a temperature of 1160 °C. This resulted in a deposition rate of around 0.15 nm min^{-1} . The thickness of the gold film used in this study was estimated from the attenuation of the substrate O 1s signal to be $3.4 \pm 0.3 \text{ nm}$.

The binding energy scale of the monolayer spectra were calibrated to the O 1s signal of the substrate which has previously been measured at 530.05 eV [12] using the O 1s ionisation potential for a monolayer of an aromatic carboxylic acid monolayer on $\text{TiO}_2(110)$ [14] and an estimate of the substrate conduction band edge [15]. Since the spectra obtained for the multilayer films contain no substrate signal the multilayer spectra were aligned to the ring carbon C 1s signal of the monolayer adsorbed on clean $\text{TiO}_2(110)$. The calibration procedure is adequate in this case since the following discussion is concerned only with relative binding energy differences. However we stress that in this case, the binding energies for the multilayer spectra do not correspond to absolute values.

3. Results

3.1. Fluorescein multilayers

We first present the photoelectron spectra of fluorescein, essentially isolated from the surface, in its molecular form in a thick condensed film. We then proceed in Sections 3.2 and 3.3 to discuss the changes that occur when the molecule is chemisorbed on the surfaces of TiO_2 and Au. Multilayer adsorption is presented here only for rutile $\text{TiO}_2(110)$ but we note that results obtained using the Au surface are identical.

The C 1s spectrum of fluorescein multilayers adsorbed on a rutile $\text{TiO}_2(110)$ single crystal surface is shown in Fig. 2. The spectrum has been curve fitted with four Voigt line shapes (combination of Gaussian & Lorentzian) as indicated. The dominant peak at 284.5 eV is attributed to the 15 ring carbon atoms of the molecule (Fig. 1). The peak at 286.2 eV arises from the four carbon atoms each bonded to a single oxygen atom. There is no significant chemical shift between those ring carbon atoms bonded to oxygen via a *formally* single or double bond due to the delocalised nature of the π -electron system. This assignment is supported by the ratio of this component to the main peak ($\sim 4:15$) and the energy separation from the ring signal (1.7 eV) [16]. The peak at 288.8 eV is attributed to the carboxylic carbon atom. Similarly, this assignment is supported by the component area ratios ($\sim 1:4:15$) and an energy separation of 4.3 eV from the main ring carbon peak, consistent with previous studies of aromatic carboxylic acids [12]. The broad feature at 291.3 eV is thought to be due to a shake-up process and is observed in all of the molecular C 1s and O 1s spectra measured during this investiga-

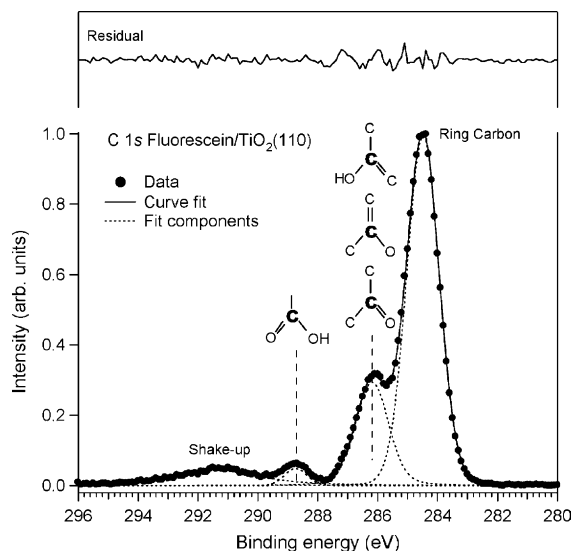


Fig. 2. C 1s photoemission spectrum of a fluorescein thick film adsorbed on rutile $\text{TiO}_2(110)$ at room temperature (normal emission). Emitter atoms are indicated in bold in the peak assignments.

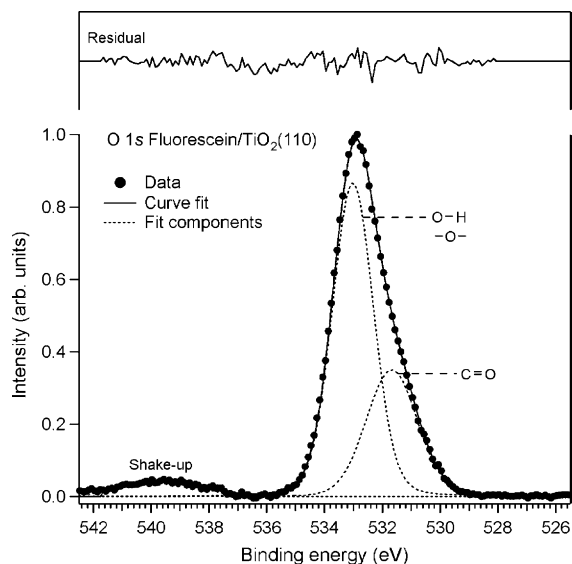


Fig. 3. O 1s photoemission spectrum of a fluorescein thick film adsorbed on rutile $\text{TiO}_2(110)$ at room temperature (normal emission).

tion at an energy of around 6.5 eV above the main peak.

The corresponding O 1s spectrum for the thick film is shown in Fig. 3. It is possible to resolve two components and a broad shake-up feature for the molecule in this spectrum. The peak at 531.6 eV is attributed to the C=O groups of which there are two in the fluorescein molecule (Fig. 1) present in the carboxylic acid group and the ring carbonyl. We attribute the peak at 533.0 eV to oxygen atoms of predominantly O—H character of which there are again two in the molecule (in the carboxylic acid group and the ring hydroxyl). The ratio of the fitted components ($\sim 3:2$) suggests that the oxygen located in the central ether ring (Fig. 1) also contributes to the peak at 533.0 eV. The assignments of the C=O and O—H groups are consistent with previous studies of carboxylic acids [14].

3.2. *Fluorescein/TiO₂(110)*

Fig. 4 shows the C 1s spectrum of a fluorescein monolayer adsorbed on rutile $\text{TiO}_2(110)$. This spectrum is very similar to that of the fluorescein multilayer (Fig. 2) and as such the assignment of the peaks is generally the same. The most

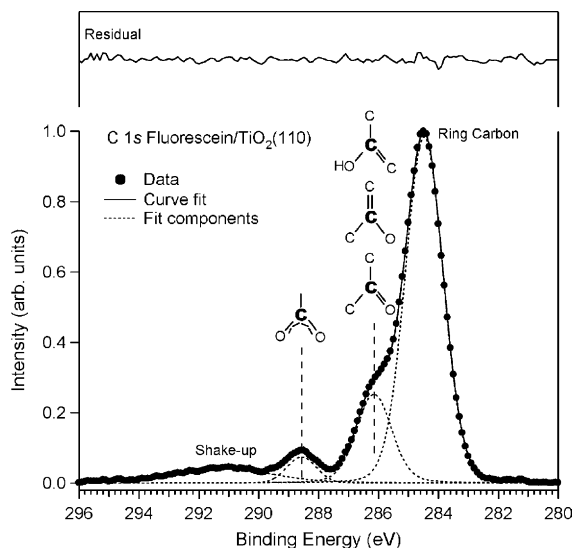


Fig. 4. C 1s photoemission spectrum of a fluorescein monolayer adsorbed on rutile $\text{TiO}_2(110)$ (normal emission). Emitter atoms are indicated in bold in the peak assignments.

noticeable difference is the slight broadening of the peaks compared to the thick film due to the interaction with the surface. We also note a slight change in the peak separation of the carboxylic group and the ring carbon signal of -0.2 eV (Table 1). Similar shifts have been observed previously for pyridine carboxylic acids on $\text{TiO}_2(110)$ and are attributed to a combination of both the covalent bonds formed with the surface and the intermolecular interactions of the adsorbed molecules [12]. It is proposed that the screening of the core-hole in the carboxylic group is largely defined by the

highly polarisable TiO_2 substrate to which it is chemically bonded, while the rest of the molecule relies heavily on the screening provided by intermolecular interactions with its neighbours. In the case of fluorescein adsorbed on $\text{TiO}_2(110)$, one could argue (based on the C 1s data) that the carboxylic group is covalently bound to the surface which provides efficient screening of the core-hole thus pulling the peak down in binding energy, while the ring structure of the molecule is less efficiently screened by both the surface and its nearest neighbours. It is worth noting though that a shift of -0.3 eV has been observed for picolinic acid adsorbed upright on $\text{TiO}_2(110)$ where intermolecular interactions are very weak and interaction of the ring with the surface is geometrically hindered. The much smaller shift observed for fluorescein in this case might suggest an interaction of the 3-ring structure with the surface as the molecule is free to rotate around the central single bond (Fig. 1).

Direct evidence of the chemical bonds formed with the surface can be obtained from the O 1s spectra as the 2M bi-dentate bonding geometry predicted for many carboxylic acids involves deprotonation of the COOH group to COO^- . The result is that the two inequivalent oxygen atoms of the free acid become equivalent in the O 1s spectrum upon adsorption. The O 1s data for a fluorescein monolayer on rutile $\text{TiO}_2(110)$ is shown in Fig. 5. Although the spectrum is clearly dominated by the substrate oxide signal, curve fitting reveals that the molecule peaks do not resemble those of the isolated molecule (thick film). The ratio of the two molecule peaks has clearly changed and their energy separation has increased (Table 2). The highest binding energy (BE) peak (M2, 533.1 eV) can be attributed to the ring hydroxyl (O–H) and the oxygen atom in the ether ring (–O–) as discussed for the multilayer in Section 3.1. The lower binding energy peak (M1, 531.0) can instead be attributed to those oxygen atoms with more $\text{C}=\text{O}$ character. The component area ratio in this case would be reversed compared to the multilayer spectrum (Fig. 3). This is indicative of the deprotonation of the carboxylic group [14] to form two equivalent oxygen atoms (Fig. 5) and suggests that fluorescein does indeed bond to TiO_2 via the car-

Table 1
Parameters for the C 1s spectra (all values in eV)

	Fluorescein film, substrate		
	Thick film, TiO_2	Mono-layer, TiO_2	Mono-layer, Au/TiO_2
(1) BE ring C peak	284.5	284.5	284.0
(2) BE carbonyl, etc. C peak	286.2	286.2	285.7
(3) BE carboxylic C peak	288.8	288.6	288.2
(4) BE shake-up feature	291.3	291.2	290.5
Separation of (2) from (1)	1.7	1.7	1.7
Separation of (3) from (1)	4.3	4.1	4.2
Separation of (4) from (1)	6.8	6.7	6.5

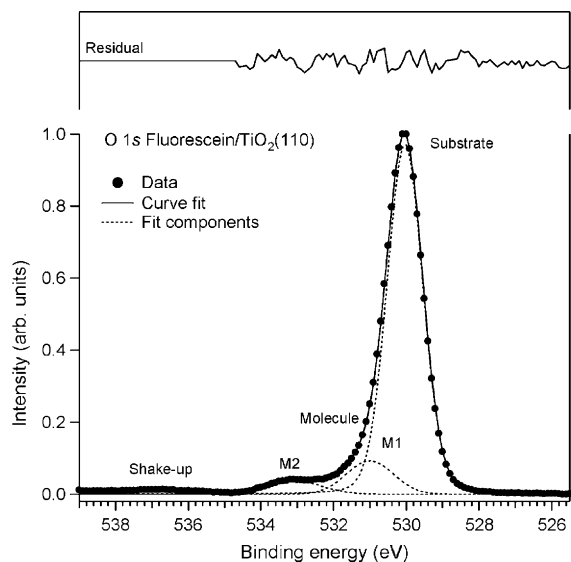


Fig. 5. O 1s photoemission spectrum of a fluorescein monolayer adsorbed on rutile $\text{TiO}_2(110)$ (normal emission).

Table 2
Parameters for the O 1s spectra (all values in eV)

	Fluorescein film, substrate		
	Thick film, TiO_2	Mono-layer, TiO_2	Mono-layer, Au/TiO_2
BE substrate peak	–	530.05	530.05
BE C=O peak	531.7	–	–
BE O–H peak	533.0	–	–
BE shake-up	539.7	537.0	–
BE molecule peak M1	–	531.0	531.3
BE molecule peak M2	–	533.0	532.5

boxylic group. Based on the multilayer O 1s spectrum, we would expect the O 1s signal arising from the remaining carbonyl group to be found around 1.3 eV lower in binding energy than the O–H and –O– signal. However, this scenario is not consistent with the shape of the spectrum. The optimum fit is obtained with only two molecule related peaks with an increased separation of 2.1 eV. This suggests that the remaining carbonyl has shifted in energy in line with the deprotonated carboxylic acid. This can be rationalised by looking at the geometry of the fluorescein molecule as shown in Fig. 1. There are significant constraints

on where the planar ring structure can lie if the molecule is bonded via the carboxylic group. This places the ring carbonyl in close proximity to the surface and it is feasible in this case for the C=O group to bond covalently to the surface. The differences in screening discussed above in the context of the C 1s spectrum can also be applied here to the O 1s data to explain the increased M1–M2 separation in the chemisorbed monolayer compared with the multilayer. The M1 peak now contains those oxygen atoms which are directly bonded to $\text{TiO}_2(110)$ and as such are efficiently screened by the substrate, while the M2 peak represents oxygen atoms in the planar triple ring structure of the molecule.

3.3. Fluorescein/Au/TiO₂(110)

In addition to the adsorption of fluorescein on TiO_2 we have also investigated the adsorption of the molecule on a thin Au film (~3.4 nm) supported on rutile $\text{TiO}_2(110)$. This model solar-cell surface is based on a recent photovoltaic device (as described in Section 1) [10]. The C 1s spectrum of the fluorescein monolayer adsorbed on this surface is shown in Fig. 6. The components have been

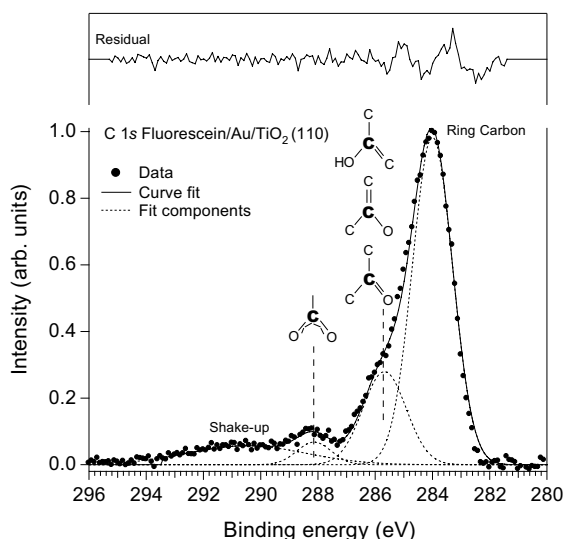


Fig. 6. C 1s photoemission spectrum of a fluorescein monolayer adsorbed on $\text{Au/TiO}_2(110)$ (normal emission). Emitter atoms are indicated in bold in the peak assignments.

fitted using the same procedure as described above and the peak assignments are therefore similar to those for the monolayer adsorbed on $\text{TiO}_2(110)$. Again we observe a broadening of the spectrum due to the interaction with the surface and a negligible change in the energy separation (-0.1 eV) between the ring carbon and the carboxylic peak. A shift of -0.6 eV has been reported for the adsorption of anthraquinone-2-carboxylic acid (AQ-2-COOH) on Au which is similarly bonded to the surface via the carboxylic group [13]. The key difference here is that the AQ-2-COOH molecules were found to be bonded upright on the surface (30° off normal) with therefore minimal interaction of the rest of the molecule with the surface. The negligible shift observed here for fluorescein supports a bonding geometry in which the triple ring structure strongly interacts with the surface (in line with the discussion of the surface-induced screening of the ring structure above). That the non-covalently bound part of the molecule will attempt to align parallel with the surface is not surprising. Aromatic molecules, both small [17–19] and large [20], tend to interact with Au (and metals in general) with the molecular plane parallel to the surface. This maximises π -electron donation into the unoccupied states in the Au and back donation from the occupied states to the π^* molecular orbitals.

The corresponding O 1s spectrum for the fluorescein monolayer is shown in Fig. 7. The data have been fitted as described earlier and three components can be identified. The low binding energy component at 530.05 eV is due to the substrate oxide peak. This is confirmed by comparing O 1s spectra measured at different emission angles where the only observable change in the fit parameters is the diminishing intensity of the substrate component with increasing emission angle and therefore surface sensitivity. The M1 component at 531.31 eV is assigned, as in the case for $\text{TiO}_2(110)$, to the carbonyl group and the deprotonated carboxylic acid. The M2 component at 532.55 eV is attributed to the hydroxyl ($-\text{OH}$) and cyclic ether ($-\text{O}-$) groups. Here the energy separation between M1 and M2 at 1.24 eV is significantly less than on $\text{TiO}_2(110)$ at 2.42 eV. The M1–M2 separation on Au is therefore much

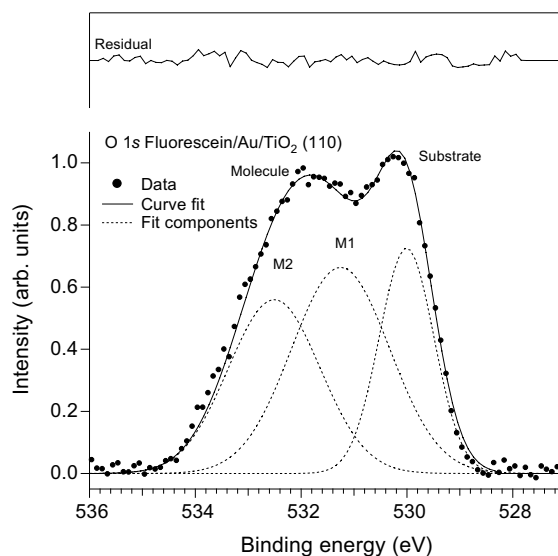


Fig. 7. O1s photoemission spectrum of a fluorescein monolayer adsorbed on $\text{Au/TiO}_2(110)$ (normal emission).

closer to that of the isolated molecule. Applying the same discussion of the screening properties of the surface as for TiO_2 above, we can understand the decreased separation in terms of more efficient screening of the triple ring structure by the metal surface compared to the semiconducting oxide.

4. Summary

We have investigated the XPS of fluorescein multilayers and monolayers adsorbed on rutile $\text{TiO}_2(110)$ and $\text{Au/TiO}_2(110)$ surfaces. Monolayers are shown to chemisorb on both surfaces through the deprotonated carboxylic group. Due to the geometry of the molecule the triple ring structure of fluorescein is forced to lie in close proximity to the surface. The nature of this interaction appears to differ between TiO_2 and Au, where the former might possibly lead to the formation of a covalent bond between the ring carbonyl and the surface, while the latter is characterised predominantly by a strong interaction between the π -orbitals and the Au valence states.

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