Quantitative Structure of an Acetate Dye Molecule Analogue at the TiO$_2$−Acetic Acid Interface

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S *Supporting Information*

ABSTRACT: The positions of atoms in and around acetate molecules at the rutile TiO$_2$(110) interface with 0.1 M acetic acid have been determined with a precision of ± 0.05 Å. Acetate is used as a surrogate for the carboxylate groups typically employed to anchor monocarboxylate dye molecules to TiO$_2$ in dye-sensitized solar cells (DSSC). Structural analysis reveals small domains of ordered (2 × 1) acetate molecules, with substrate atoms closer to their bulk terminated positions compared to the clean UHV surface. Acetate is found in a bidentate bridge position, binding through both oxygen atoms to two 5-fold titanium atoms such that the molecular plane is along the [001] azimuth. Density functional theory calculations provide adsorption geometries in excellent agreement with experiment. The availability of these structural data will improve the accuracy of charge transport models for DSSC.
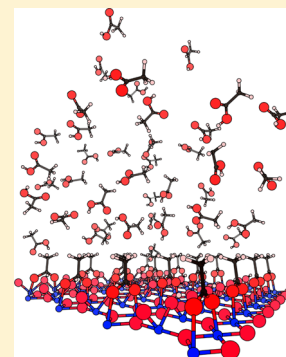
INTRODUCTION

The interaction of carboxylic acids with TiO$_2$ is important in a number of applications. For instance, dyes in dye-sensitized solar cells (DSSC) are typically anchored to TiO$_2$ via one or more carboxylate groups.[1,2] In this work, we use acetate as a surrogate for a dye molecule with a single functionality. However, structural studies have thus far focused on exposure of TiO$_2$ to carboxylic acids at/near ultra high vacuum (UHV) conditions with a large proportion focused on formic acid. Recently, we used UHV scanning tunneling microscopy (STM) to study the adsorption sites of carboxylates formed at aqueous interfaces, finding that the same sites are occupied as those identified in UHV adsorption.[3] Here we move even closer to measurements in a technologically relevant environment, examining in a quantitative fashion the *in situ* structure of the TiO$_2$(110) interface formed upon immersion in 0.1 M acetic acid using surface X-ray diffraction (SXRD). This concentration is chosen to match that used in an infrared spectroscopy study of the TiO$_2$ acetic acid interface, the results of which point to bidentate bonding of acetate.[3]

It is well established that exposing TiO$_2$(110) to CH$_3$COOH vapor at room temperature results in an ordered (2 × 1) overlayer at saturation coverage, i.e., 0.5 monolayers (ML).[4−6] The overlayer consists of acetate molecules ([CH$_3$COO]$^-$) formed via deprotonation, which bind to the surface through both oxygen atoms to two adjacent 5-fold surface titanium atoms, so that the molecular plane is aligned with the [001] azimuth. The cleaved H$^+$ is thought to adsorb on neighboring bridging oxygen atoms.[4−6] A ball and stick model of the adsorption geometry is shown in Figure 1. Density functional theory (DFT) calculations have confirmed that the bidentate adsorption mode is thermodynamically preferred over monodentate adsorption and that the p(2 × 1) pattern is more stable than the c(2 × 2) pattern with the same concentration.[7] Our SXRD results from the CH$_3$COOH$_{(aq)}$ interface with
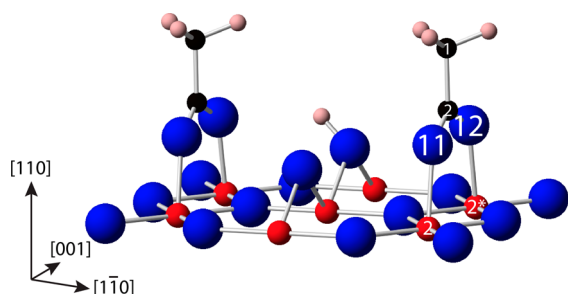
Figure 1. Ball and stick model of the TiO$_2$(110)(2 × 1)−[CH$_3$COO]$^-$ surface. In the current study, the adsorbed acetate was found to be in a bidentate bridge location with the cleaved H$^+$ thought to adsorb on neighboring bridging oxygen atoms. Large blue, small red, small black, and small pink spheres are oxygen, titanium, carbon, and hydrogen, respectively. The labeling identifies the atom positions in Tables 1, S1, S2, and S3.

TiO$_2$(110) show that carboxylate forms small overlayer domains of (2 × 1) symmetry.

■ EXPERIMENTAL DETAILS

SXRD measurements were carried out using the six-circle diffractometer end station on ID32 at the European Synchrotron Radiation Facility. The TiO$_2$(110) (Pi-Kem) sample was prepared in UHV using the Sample Characterization Laboratory at ID32 (base pressure ≈ 1 × 10^{-10} mbar).[8] This involved cycles of Ar$^+$ sputtering at room temperature and 1000 K annealing until a sharp (1 × 1) low energy electron diffraction pattern was obtained and row-resolution imaging in STM was achieved.[9,10] Auger electron spectroscopy was used to confirm a lack of contamination.

After preparation the sample was transferred under UHV to a small portable ion-pumped UHV chamber ("baby chamber") with a base pressure in the 10^{-9} mbar range. This chamber incorporates a dome shaped beryllium window to allow unrestricted transmission of the incident and reflected X-ray beams. Subsequently, this baby chamber was mounted on the ID32 six-circle diffractometer for SXRD measurements, with the sample surface in the horizontal plane. Measurements were performed with the sample at room temperature using a monochromatic focused beam with energy of 17.7 keV (λ = 0.7 Å), defined by slits to a size of (H × V: 200 μm × 20 μm). The angle of incidence of the X-ray beam with respect to the surface was kept constant at 0.3° for all measurements with 2 × 2 mm^2 slits in front of a point detector. The experimental data were measured using rocking scans in which scattered intensity is measured, while the sample is rotated about its normal. These intensities were then integrated, and geometrical correction factors[11] were applied to evaluate the structure factors, which, when represented versus perpendicular momentum transfer, are known as crystal truncation rods (CTRs). The TiO$_2$ (110) surface unit cell was described by lattice vectors (**a$_1$**, **a$_2$**, **a$_3$**) parallel to the [1$\bar{1}$0], [001], and [110] directions, respectively, where $a_1 = a_3 = a\sqrt{2}$ and $a_2 = c$ (a = 4.593 Å and c = 2.958 Å).

A large data set, comprising 1284 nonequivalent reflections, was recorded for the UHV-prepared surface. Immediately afterward, the baby chamber was vented with N$_2$ (99.998% purity) within a glovebag where the sample was transferred to a mylar thin film cell,[12] which was then mounted on the ID32 six-circle diffractometer. Next, a 0.1 M aqueous solution of acetic acid was injected into the mylar thin film cell, and a further 1479 nonequivalent reflections were measured. For these

SXRD measurements, the mylar thin film cell was in thin-layer-geometry, i.e., only a thin layer of CH$_3$COOH$_{(l)}$ (<1 μm) was in contact with the sample surface.[12] It should be noted that fractional order rods (FORs) were also investigated but no measurable intensity was found.

Determination of the surface structure involved the use of a least-squares fitting procedure implemented within a modified version of ROD[13] in which simulated CTRs are generated. By optimizing the geometry of the structure, a best-fit model between theory and experiment can be found as measured by optimized χ^2[14] and R-factor.[15] A χ^2 value close to 1 and an R-value close to 0.10 is considered an excellent fit between the experimentally observed and the theoretically calculated structure factors. We note that given their low X-ray scattering cross-section, H atoms were ignored in the fitting procedure.

Trial computer simulations for acetate adsorbed on TiO$_2$(110) (at the vacuum interface) were performed using the density functional theory (DFT) code VASP.[16] Geometries and total energies were obtained using the generalized gradient approximation (GGA) with the exchange-correlation functional of Perdew, Burke, and Ernzerhof (PBE).[17] A Hubbard-type correction to the Ti 3d orbitals was applied, with a value of U_{eff} = 3 eV.[18] No van der Waals corrections were applied as their contribution to the strong chemisorption of carboxylic acids at this surface can be expected to be small.[7] The TiO$_2$(110) surface was simulated using a periodic stack of quasi-two-dimensional slabs, where each slab is separated from the neighbor by a vacuum gap of 15 Å. We used slabs with four O−Ti−O trilayers, with the bottom two layers fixed to equilibrium bulk positions. A discussion about the adequacy of this model to simulate the adsorption of molecules at this surface can be seen in ref 19.

■ RESULTS AND DISCUSSION

SXRD analysis of UHV-prepared TiO$_2$(110)(1 × 1) considers a surface slab consisting of 2.5 unit cells (six TiO atomic layers) in the [110] direction that involved a total of 49 parameters: 34 atomic displacements, 12 Debye−Waller (DW) factors, a scale factor, a roughness parameter, and a surface fraction parameter. The best-fit model produced a χ^2 and R-value of 1.5 and 0.14, respectively. These values represent a high degree of agreement between experiment and simulated patterns. From the comparison of the atomic displacements from this study and that of a previous SXRD study[20] on TiO$_2$(110), listed in Table S1, it is clear that the two models are essentially in quantitative agreement with each other. This evidences the high reproducibility of the preparation procedure as described in the experimental section. All DW factors adopted reasonable values for both Ti and O atoms where the highest value corresponded to the topmost surface layer (B_{Ti} = 0.5 ± 0.1, B_O = 0.9 ± 0.1) progressively decreasing with depth to their bulk value (B_{Ti} = 0.3 ± 0.1, B_O = 0.2 ± 0.1). The β roughness parameter[21] adopted a value (β = 0.07) consistent with the very flat surface seen in STM images recorded prior to SXRD measurements. The surface fraction parameter confirmed that the entire surface adopted the geometry described by the best-fit model.

The optimized TiO$_2$(110)(2 × 1)−[CH$_3$COO]$^-$ structure obtained following analysis of the SXRD data produced a χ^2 of 1.05 and an R-value of 0.15. The total number of parameters used are the same as that for the UHV-prepared surface with an additional nine parameters associated with the acetate molecule; six parameters to determine orientation and site
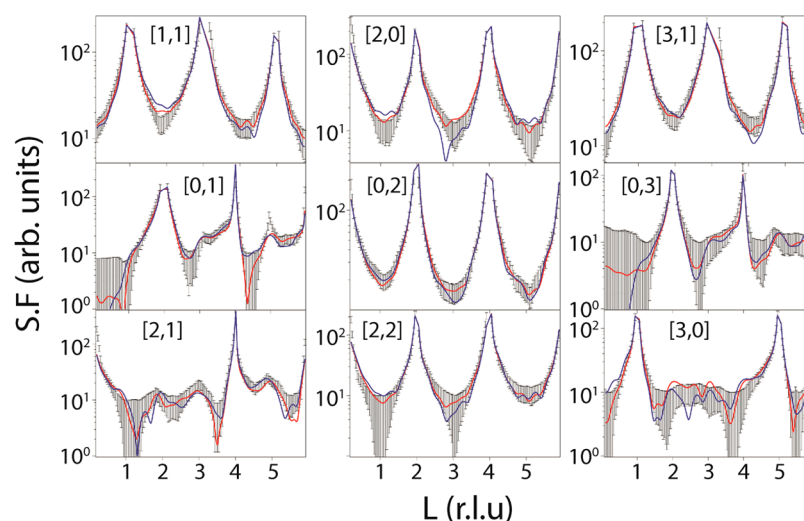
Figure 2. Experimentally observed (black error bars) and calculated CTRs for the $TiO_2(110)(2 \times 1)-[CH_3COO]^-$ surface model (red line) and after removing the acetate molecule (blue line). It is clear that the addition of the acetate molecule to the model improves the overall goodness-of-fit.

Table 1. Comparison of Molecular Acetic Acid (CH_3COOH) Bond Distances and Angles[26−28] with That of Acetate ($[CH_3COO]^-$) Resulting from SXRD and DFT-PBE in This Work[a]

atoms	bond distance (Å)/angle (deg)				
	SXRD $[CH_3COO]^-$	DFT-PBE $[CH_3COO]^-$	$[CH_3COOH]^{26}$	$[CH_3COOH]^{27}$	$[CH_3COOH]^{28}$
C(1)−C(2)	1.54 ± 0.03	1.51	1.49	1.52	1.52
C(2)−O(11)	1.31 ± 0.04	1.28	1.31	1.36	1.38
C(2)−O(12)	1.32 ± 0.04	1.28	1.23	1.21	1.23
Ti(2)−O(11)	2.13 ± 0.03	2.11			
Ti(2*)−O(12)	2.06 ± 0.03	2.08			
∠C(1)C(2)O(11)	117.7 ± 0.9	117.7		110.6	111.2
∠C(1)C(2)O(12)	116.9 ± 0.8	117.0		126.6	125.9

[a]Atom labels are given in Figures 1 and S1.

position, two DW factors (O and C atoms), and an occupancy parameter. Excellent agreement between the best-fit model and experiment is achieved, as can be seen from the comparison of the experimental and best fit simulated data in Figure 2. This displays experimental CTRs (black error bars), with their best-fit theoretical simulations for the surface after exposure to 0.1 M $CH_3COOH_{(aq)}$ (red line). It also shows the effect of removing the acetate molecule from the model and reoptimizing the structural and nonstructural parameters (i.e., DW factors) (blue line). This increases the χ^2 and R-factor to values of 1.56 and 0.19, respectively. It is clearly evident that the presence of the acetate molecule significantly improves the overall goodness-of-fit. The adsorbed acetate was found to be in a bidentate bridge location, i.e., binding through both oxygen atoms to two 5-fold titanium atoms such that its molecular plane is along the [001] azimuth (Figure 1), in excellent agreement with the literature for acetate and other simple carboxylates bound to this substrate at the vacuum interface.[22−24] The resulting bond distances are Ti(2)−O(11) = 2.13 ± 0.03 Å, Ti(2*)−O(12) = 2.06 ± 0.03 Å, which compare well with bond distances from the formate/$TiO_2(110)$ system.[23,24]

In contrast to refs 23, 24., here we allow the adsorbed carboxylate to be asymmetric in order to compare with DFT calculations. The results of the latter indicate an asymmetric carboxylate, which appears to arise from the orientational ordering of the hydroxyl groups. In the experiment, the hydroxyls will likely be disordered and this asymmetry will be

averaged, and indeed the nominal asymmetry is almost within the error bars (see Table 1). The expected orientational disorder of the hydroxyl groups was confirmed by DFT calculations in a 2×2 supercell, where the results indicate that all different orientational configurations are within 20 meV in energy.

The apparent volume of the molecule has also been investigated[25] by simulating a uniform expansion/compression of the molecule. The best fit is consistent with a small molecular expansion (2.9 ± 0.6%); however, this is considered to be insignificant because of the lack of sensitivity of the χ^2 and R-factor to this change in volume (Table S3 provides optimized positions of atoms in the acetate moiety).

Table 1 lists the internal bond distances and angles of acetate/acetic acid emerging from this study and previous literature values. There is excellent agreement with both previous experimental[26,27] and theoretical[28] work regarding the intramolecular bond distances. Discrepancies in bond angles are due to previous experimental work being on molecular acetic acid rather than acetate.

When comparing displacements of substrate atoms between the UHV-prepared $TiO_2(110)(1 \times 1)$ and the $TiO_2(110)(2 \times 1)-[CH_3COO]^-$ surfaces it is clear that adsorption of acetate reduces the clean surface relaxations (see Tables S1 and S2 for atomic displacements and atomic coordinates, respectively). This almost certainly arises from an increase in substrate surface atom coordination number and has been seen before for carboxylate/$TiO_2(110)$ at the vacuum interface[23] and other

metal oxide surfaces exposed to liquid water.[29] This is also reflected in the DW parameters, which return to close to their bulk value. Good agreement of atomic displacements can also be seen between SXRD and DFT-PBE calculations from this study (see Supporting Information for details). As regards the β roughness parameter, this now takes a value of 0.2, increasing from 0.07. This most likely arises from the small size of randomly distributed domains (a few nm) of both ordered acetate moieties and domains absent of molecules, as evidenced in STM images.[3] This would also explain the absence of fractional order rods.

In summary, the interface between 0.1 M acetic acid and TiO$_2$(110) comprises small domains of (2 × 1) ordered arrays of acetate moieties. The positions of the atoms within the molecule as well as the substrate determined by SXRD are in excellent agreement with PBE+U calculations. It is possible that steric hindrance will prevent the same ordering for mono-carboxylic dye molecules in DSSC for which we are using acetate as a surrogate. However, it seems likely that the same local bonding geometry will be adopted. On this basis, these data should allow more reliable calculations of charge transport at dye molecule−TiO$_2$(110) interfaces in DSSC.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b00186.

Density functional theory calculation results. A ball and stick model of the TiO$_2$(110)(2 × 1)−[CH$_3$COO]$^-$ surface. DFT-PBE calculated lateral view structure of TiO$_2$(110)(2 × 1)−[CH$_3$COO]$^-$. Atomic displacements for the as-prepared TiO$_2$ (110)(1 × 1) and TiO$_2$(110)(2 × 1)−[CH$_3$COO]$^-$ substrate atoms from SXRD and DFT-PBE. Atomic coordinates of the ideal bulk-terminated coordinate of each atom with the corresponding shift from this position after the fitting procedure. Experimental optimized positions of the atoms in the acetate molecule (PDF)

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Notes

The authors declare no competing financial interest.

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