

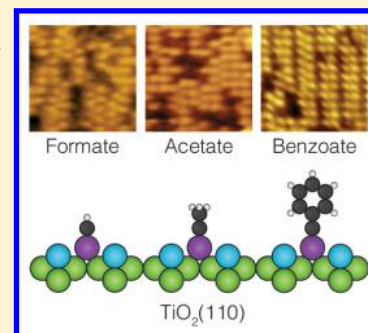
## Ordered Carboxylates on TiO<sub>2</sub>(110) Formed at Aqueous Interfaces

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**ABSTRACT:** As models for probing the interactions between TiO<sub>2</sub> surfaces and the dye molecules employed in dye-sensitized solar cells, carboxylic acids are an important class of molecules. In this work, we present a scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED) study of three small carboxylic acids (formic, acetic, and benzoic) that were reacted with the TiO<sub>2</sub>(110) surface via a dipping procedure. The three molecules display quite different adsorption behavior, illustrating the different interadsorbate interactions that can occur. After exposure to a 10 mM solution, formic acid forms a rather disordered formate overlayer with two distinct binding geometries. Acetic acid forms a well-ordered (2 × 1) acetate overlayer similar to that observed following deposition from vapor. Benzoic acid forms a (2 × 2) overlayer, which is stabilized by intermolecular interactions between the phenyl groups.

**SECTION:** Surfaces, Interfaces, Porous Materials, and Catalysis



The surface science of TiO<sub>2</sub> has been studied intensively for a number of years due to wide-ranging applications connected, for instance, to photocatalysis, gas sensing, heterogeneous catalysis, and electronic devices.<sup>1,2</sup> Although the interaction of small molecules with the surfaces of TiO<sub>2</sub> is of interest from a fundamental viewpoint, one particular application, that of dye-sensitized solar cells (DSSCs),<sup>3</sup> has prompted in-depth investigations of the behavior of carboxylic acids.<sup>4</sup> In a DSSC, the dyes (typically Ru complexes, conjugated organic molecules, or porphyrins) are anchored to the TiO<sub>2</sub> surface via carboxylate groups.<sup>5</sup> This anchoring plays a critical role in the operation of the cell as there must be efficient charge transfer between the dye and the semiconducting TiO<sub>2</sub> (photoexcitation of the dye results in injection of electrons into the conduction band of the oxide).<sup>6</sup> The large size of the dye molecules makes their study quite difficult. As such, rather than directly examining the anchoring of an entire dye molecule, it is common to use small carboxylic acids as models to probe the interactions between adsorbates and with the surface.<sup>7</sup> In typical surface science experiments, these acids are deposited from vapor onto the surface of a single crystal of TiO<sub>2</sub> under UHV conditions where their behavior is now well-characterized.<sup>8</sup> In this work, we present an alternative method for functionalizing the rutile TiO<sub>2</sub>(110) surface with carboxylates, namely, an aqueous deposition process (see the Experimental Methods section for details). A similar method has also been demonstrated previously for the deposition of zinc porphyrins onto TiO<sub>2</sub> from an ethanolic solution.<sup>9</sup> There are several advantages of this approach; it is relatively straightforward, provides conditions closer to those encountered in the real applications, and allows an opportunity for studying the effects of the solvent (water) on adsorption. A further advantage, as demonstrated in the work of Rangan et al.,<sup>9</sup> is the ability to deliver large molecules that are otherwise difficult to deposit via vapor. Although self-assembled

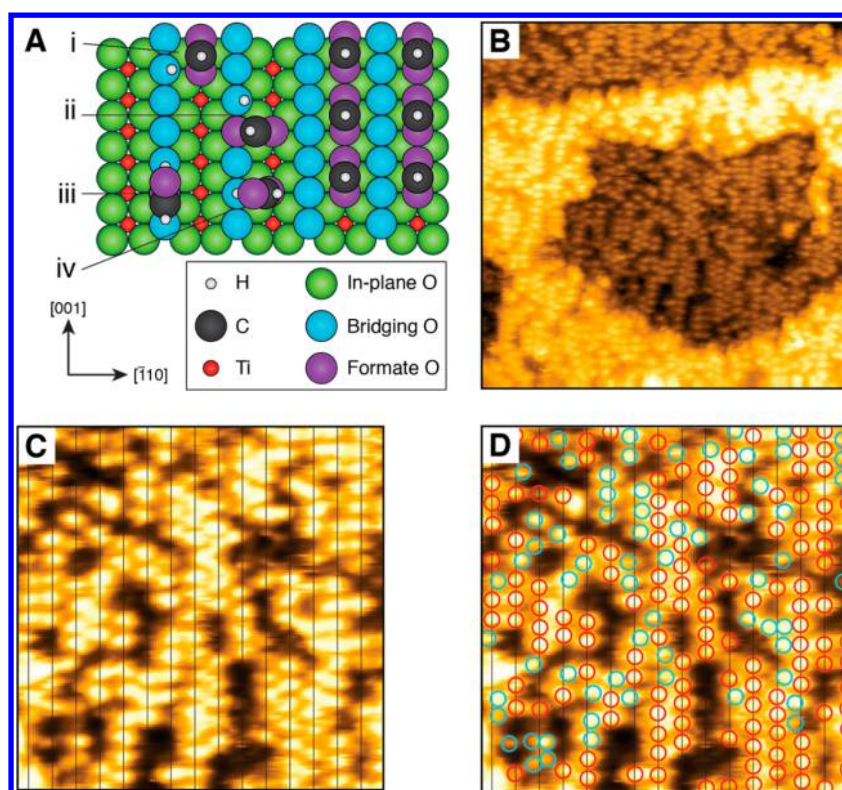
monolayer (SAM) formation via drop-casting on metal oxide surfaces has been previously reported,<sup>10</sup> there has not previously been any direct evidence for the formation of ordered overlayers as we observe here with our molecularly resolved, real space scanned probe measurements.

The simplest carboxylic acid, formic acid, on TiO<sub>2</sub> is considered a model for the adsorption of other simple monocarboxylic acids.<sup>1,8,11</sup> Room-temperature exposure of TiO<sub>2</sub>(110) to formic acid in the vapor phase is known to give rise to a (2 × 1) formate overlayer at a saturation coverage of 0.5 monolayers (ML), where 1 ML is the concentration of surface unit cells.<sup>12</sup> Multiple studies using several methods agree that formic acid adsorbs dissociatively on TiO<sub>2</sub>(110) by transfer of its acidic hydrogen to the surface, forming a bridging hydroxyl and chemisorbed formate moiety bonded primarily in a bidentate arrangement between two Ti<sub>5c</sub> atoms aligned along [001].<sup>12–19</sup> Four configurations of formate have been observed, as shown in Figure 1A, and these are dependent on sample history and evaporation conditions. Reflection–absorption IR spectroscopy (RAIRS) and near-edge X-ray absorption fine structure (NEXAFS) studies report the majority of formate to be in the bidentate geometry (type i in Figure 1A) with a minority (~1/3) of formate anions situated between a Ti<sub>5c</sub> site and an O<sub>vac</sub> (type ii in Figure 1A).<sup>14,20</sup> Type iii (Figure 1A) has the formate bound to a bridging O<sub>vac</sub> and H-bonded to an adjacent OH<sub>br</sub> along [001]. A scanning tunneling microscopy (STM) study found evidence of type i, ii, and iii formate on a surface annealed to 350 K following acid exposure.<sup>21</sup> A combined DFT and RAIRS investigation provided evidence of a formate geometry similar to type ii but with no involvement of an O<sub>vac</sub>.<sup>22</sup> Instead, the formate is adsorbed

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**Figure 1.** Formic acid (0.40 ML) on rutile TiO<sub>2</sub>(110) after deposition from a 10 mM aqueous formic acid solution. (A) Schematic model of the various proposed adsorption motifs for formate. (B) Large-area STM image of the formate overlayer ( $25 \times 25 \text{ nm}^2$ ,  $V_s = 1.2 \text{ V}$ ,  $I_t = 0.05 \text{ nA}$ ). (C) STM image of the formate overlayer with the Ti<sub>5c+</sub> rows along [001] marked with black lines ( $10 \times 10 \text{ nm}^2$ ,  $V_s = 1.2 \text{ V}$ ,  $I_t = 0.05 \text{ nA}$ ). (D) STM image with formate species bound on top of Ti<sub>5c+</sub> rows marked in red and formate bound between Ti<sub>5c+</sub> rows marked in blue ( $10 \times 10 \text{ nm}^2$ ,  $V_s = 1.2 \text{ V}$ ,  $I_t = 0.05 \text{ nA}$ ).

between a Ti<sub>5c+</sub> and bridging OH, labeled type iv in Figure 1A. Although type iv formate was predicted to be the least stable configuration, a signal assigned to it was observed for samples with differing O<sub>vac</sub> concentrations, the suggestion being that hydroxylation by background water blocked the formation of type ii and iii species.<sup>22</sup>

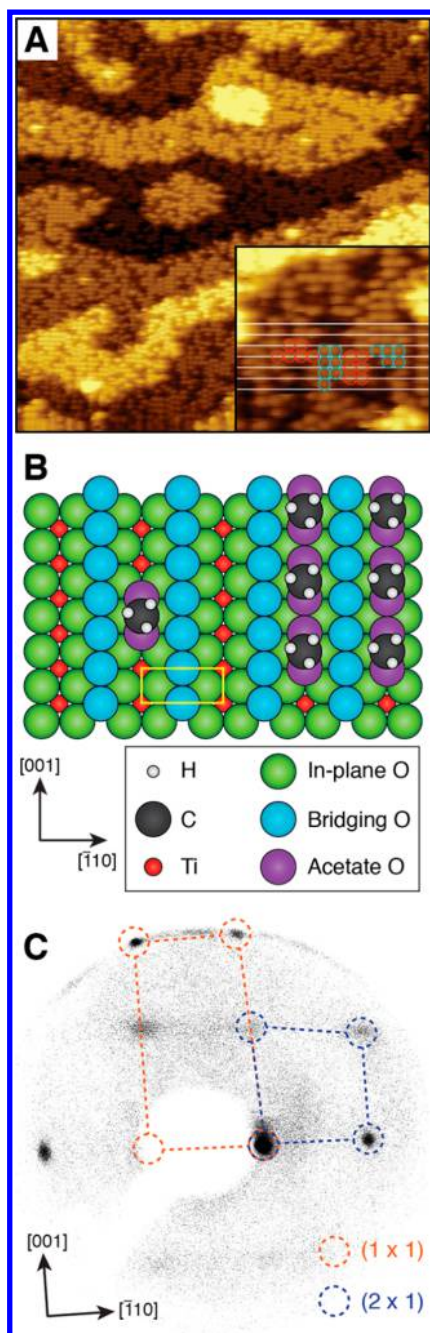
Following exposure to an aqueous solution of formic acid, a stable overlayer of  $0.40 \pm 0.02 \text{ ML}$  coverage is found. This overlayer is fairly disordered with nonuniform alignment of some features along [001] (Figure 1B). Furthermore, low-energy electron diffraction (LEED) measurements show no long-range ( $2 \times 1$ ) ordering, in contrast to observations from vapor deposition.<sup>12</sup> Analysis of the STM data in Figure 1B indicates the presence of a minority species of features positioned irregularly along  $[\bar{1}10]$ . Overlaying a grid with unit cell spacing that is aligned with the majority species (red circles) demonstrates that there is a minority species (blue circles) slightly offset from the grid lines (Figure 1C and D). This grid arrangement is consistent with the expected majority of type i formate (bound along the Ti rows) and a minority of either type ii or iv formate (Figure 1A). Quantification of the majority/minority species populations gives a ratio of 2.1:1, very similar to the ratio of type i to type ii formate reported in the RAIRS and NEXAFS studies.<sup>14,20</sup> We expect that all O<sub>vac</sub> present after sample preparation will be consumed by reaction with background water (partial pressure, mid- $10^{-10}$  mbar) present in the UHV chamber where the sample is held for at least 1 h prior to the acid deposition, so that none are available to form type ii or iii formate. It is therefore more feasible for the

minority species to consist of the type iv formate shown in Figure 1A.

Room-temperature exposure of TiO<sub>2</sub>(110) to acetic acid in the vapor phase is well-understood: a homogeneous, ordered ( $2 \times 1$ ) overlayer is observed at saturation coverage.<sup>23</sup> Adsorption is dissociative and results in acetate bonded in a bidentate configuration between adjacent Ti<sub>5c+</sub> sites, equivalent to the type i formate mentioned above.<sup>23–25</sup> Tao et al. report that at low coverages, adsorbed acetate moieties do not cluster and are instead arranged diffusely, indicative of a repulsive interaction between the molecules.<sup>23</sup> STM of TiO<sub>2</sub>(110) following exposure to a droplet of 10 mM acetic acid shows a relatively well-ordered overlayer of 0.38 ML coverage (Figure 2A) with spacing indicative of ( $2 \times 1$ ) periodicity relative to the substrate. A ball model illustrating the structure of the overlayer is shown in Figure 2B. The half-integer spots found in LEED along [001] (Figure 2C) confirm the longer-range order of the acetate overlayer compared with that for formate. The STM image inset in Figure 2A shows the domain structure that results from the ( $2 \times 1$ ) periodicity, with domains out of registry by one unit cell along [001] depicted in blue and red. The acetate moieties appear to align in phase with nearest neighbors in both [001] and  $[\bar{1}10]$  directions, with short chains formed both along and across rows.

The exposure of TiO<sub>2</sub>(110) to benzoic acid from the vapor phase displays similar adsorption behavior to other simple carboxylic acids, forming adsorbates bound in a bidentate fashion.<sup>26,27</sup> However, instead of forming a homogeneous ( $2 \times 1$ ) overlayer, benzoate dimers and trimers were observed, indicating additional interactions between the adsorbates.<sup>26,27</sup> A





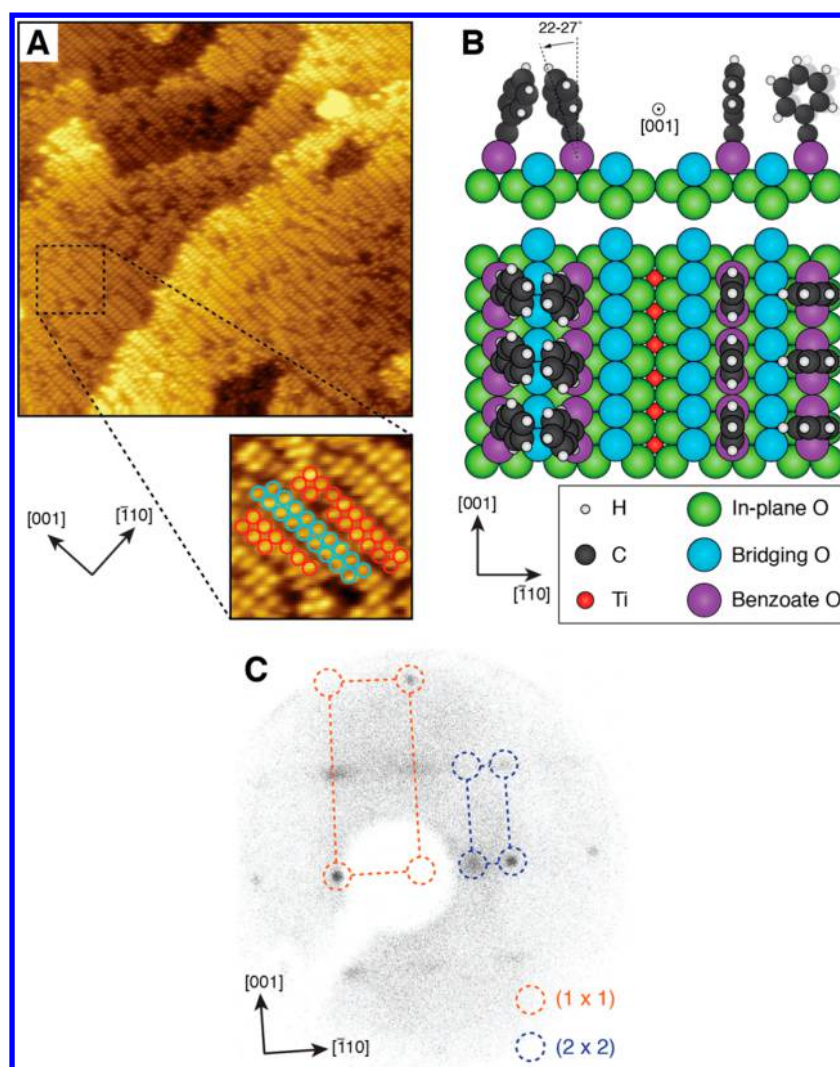
**Figure 2.** Acetic acid (0.38 ML) on rutile TiO<sub>2</sub>(110) after deposition from a 10 mM aqueous acetic acid solution. (A) STM image of the ordered overlayer (50 × 50 nm<sup>2</sup> (inset: 7 × 7 nm<sup>2</sup>),  $V_s = 1.2$  V,  $I_t = 0.2$  nA). (B) Schematic model of an acetate (2 × 1) overlayer. (C) LEED pattern (21 eV) showing the TiO<sub>2</sub>(110)(1 × 1) (orange) and the acetate-(2 × 1) (blue).

later study by Grinter et al. exposed the TiO<sub>2</sub>(110) surface to ~30 L of benzoic acid, which gave rise to a subsaturation coverage of 0.20 ML that exhibited no long-range ordering and only occasional short chains along  $[\bar{1}10]$ .<sup>28</sup> Annealing this surface to 370 K while exposing to a further ~60 L of acid resulted in a clear (2 × 1) overlayer of 0.45 ML coverage. Recent work by Zasada et al. combined STM and DFT calculations of terephthalic acid (TPA) on TiO<sub>2</sub>(110) to demonstrate the coexistence of multiple dimer conformations on TiO<sub>2</sub>(110).<sup>29,30</sup> They found four possible dimer configurations for TPA at saturation coverage due to repulsion

between the phenyl rings of the adsorbates and mutual tilting of the TPA molecules on adjacent Ti<sub>5c</sub> rows. Here, the second effect is dependent on the interactions between the extra apical carboxylate groups in TPA, although the phenyl repulsion is equivalent to what would be observed for benzoate. Zasada et al. also suggested that the (2 × 1) appearance reported in STM for benzoate<sup>28</sup> is in fact a tip effect whereby the observed contrast is attributed to sampling the base carboxylate part of the TPA/benzoate molecule.<sup>31</sup>

STM of the surface following liquid benzoic acid exposure as displayed in Figure 3A shows the overlayer to appear almost exclusively as rows of dimers similar to those reported by Guo et al. and Zasada et al. A subsaturation coverage of 0.43 ML is evident due to local misalignment of phase, which leaves small areas of the surface unoccupied. Interestingly, dimerization is found to occur either in a parallel (red dots) or alternating (blue dots) configuration, with the latter occupying a minority of the surface (see the expanded image in Figure 3A). The schematic models in Figure 3B present two possible arrangements that would account for the appearance of parallel benzoate dimers as observed in STM. The left-hand side of Figure 3B shows the phenyl groups with a slight tilt and twist, resulting in a paired arrangement as previously observed for TPA.<sup>31</sup> The right-hand side of Figure 3B depicts the arrangement proposed by Guo et al. where the phenyl ring is rotated by 90°, thereby permitting attractive interactions between neighboring molecules along  $[\bar{1}10]$ .<sup>26</sup> We speculate that OH groups, formed either by exposure to water during the dipping or due to the acid dissociative adsorption, may play a role in the formation of the staggered arrangement shown in blue in the inset STM in Figure 3A. Our LEED measurements of the benzoate-covered surface exhibit half-integer spots in both [001] and  $[\bar{1}10]$  (Figure 3C), confirming the observed (2 × 2) periodicity in STM. The LEED was recorded immediately following exposure of the sample to the electron beam to minimize any electron stimulated desorption of the benzoate. This desorption occurs rapidly at moderate electron energies (~50 eV) and is likely the reason that no (2 × 2) pattern was observed in the earlier work by Guo et al.<sup>26,27</sup> The half-integer spots along  $[\bar{1}10]$  are not as distinct as those along [001], indicative of poorer long-range order in this direction, as is also clearly evident in the STM in Figure 3A.

In summary, exposure of TiO<sub>2</sub>(110) to aqueous solutions (10 mM) of formic, acetic, and benzoic acids has been investigated using STM and LEED, with considerable differences between the overlayer structures formed. Formic acid forms a heterogeneous overlayer of 0.40 ML coverage whereby a majority of formate molecules are bonded in a bidentate fashion between Ti<sub>5c</sub> sites, as previously reported for exposure to formic acid in the vapor phase. Around a third of the formate overlayer is found to appear in an offset position, indicating binding to a single Ti<sub>5c</sub> site and H-bonding to a neighboring O<sub>br</sub> atom. Exposure to acetic acid solution leads to a (2 × 1) ordered overlayer in STM and LEED of 0.38 ML coverage, consistent with universal bidentate adsorption and only small regions of disorder near domain boundaries. Benzoic acid exposure results in an ordered overlayer of 0.43 ML coverage and (2 × 2) symmetry in STM and LEED. STM demonstrates the majority of the overlayer to be composed of parallel or alternating dimer chains. The observation of dimers is consistent with an early model proposed by Guo et al. whereby T-shaped dimers are formed by favorable interactions across O<sub>Br</sub> rows.<sup>26</sup>



**Figure 3.** Benzoic acid (0.43 ML) on rutile TiO<sub>2</sub>(110) after deposition from a 10 mM aqueous benzoic acid solution. (A) STM image of the ordered overlayer (40 × 40 nm<sup>2</sup> (inset: 7 × 7 nm<sup>2</sup>),  $V_s = 1.5$  V,  $I_t = 0.05$  nA). (B) Schematic model depicting benzoate arrangements for two potential (2 × 2) overlayers. (C) LEED pattern (43.5 eV) showing the TiO<sub>2</sub>(110)(1 × 1) (orange) and the benzoate-(2 × 2) (blue).

## EXPERIMENTAL METHODS

The experiments were performed in an ultrahigh vacuum (UHV) system comprising separate preparation and analysis chambers with a base pressure of  $1 \times 10^{-10}$  mbar. An Omicron AFM/STM was employed to record STM images with electrochemically etched W tips conditioned in vacuo. LEED and Auger electron spectroscopy (AES) were performed using Omicron SPECTALEED 4-grid optics. The TiO<sub>2</sub>(110) single crystals (Pi-Kem) were mounted on Ta sample plates and were prepared by repeated cycles of Ar sputtering and UHV annealing to 1000 K until they displayed a sharp (1 × 1) pattern in LEED and any contamination was below the detection limit of AES. Solutions of formic, acetic, and benzoic acid (Sigma-Aldrich) were prepared to a concentration of 10 mM with ultrapure water. The TiO<sub>2</sub>(110) surfaces were functionalized with the carboxylic acids via the following procedure: the sample was moved into the fast-entry-lock (FEL) of the UHV system where it was vented to oxygen-free N<sub>2</sub>. Under a positive pressure of N<sub>2</sub>, a droplet of the acid solution was then placed on top of the crystal for 2 min. After this exposure, the crystal and plate were immersed in ~10 mL of ultrapure water, dried with N<sub>2</sub>, and reinserted into the UHV

system following pump-down of the FEL. The final rinsing step was carried out to improve the stability during high-resolution STM measurements by removing any loosely bound adsorbates from the surface. A 10 mM acid concentration was observed to give a near-saturated coverage for all three acids in this work while avoiding multilayer formation. Experiments using a lower concentration (1 mM) and similar immersion time yielded surfaces less suitable for high-resolution imaging with STM. For comparison, the TiO<sub>2</sub>(110) surface was immersed in ultrapure water and subsequently analyzed in UHV. OH species were formed at the surface, as evidenced by photoelectron spectroscopy. These could be distinguished from the carboxylates by their height in STM and absence of a carbon KLL peak in AES.

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### Notes

The authors declare no competing financial interest.



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