

The Photon-Driven Hydrophilicity of Titania: A Model Study Using TiO₂(110) and Adsorbed Trimethyl Acetate

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The behavior of H₂O on clean and trimethyl acetate (TMA)-covered TiO₂(110)–(1 × 1), prepared with or without oxygen vacancies and associated Ti³⁺, reveals the hydrophilic nature of clean surfaces and the hydrophobic nature of TMA-covered surfaces. UV irradiation of a hydrophobic surface in the presence of 10^{−6} Torr of O₂ removes TMA and rapidly restores hydrophilicity. The presence of oxygen atom vacancies does not detectably alter the hydrophilicity of either clean or TMA-covered TiO₂(110).

I. Introduction

Recently the UV-induced wettability (hydrophilicity) of titania surfaces has been examined.^{1–9} With many potential applications, including self-cleaning and anti-fogging windows, this impressive body of work has conclusively shown that the bulk contact angle made by liquid water decreases dramatically when TiO₂ surfaces are irradiated in air with UV light and that the contact angle increases slowly after irradiation is terminated. While the empirical effects of UV irradiation on the contact angle are well-established, the detailed mechanistic paths remain an open question.

For example, recent observations of hydrophilicity increases on titania thin films have been interpreted in terms of UV-induced changes in the concentration and structure of surface OH groups.¹ With UV irradiation, the macroscopic contact angle decreased from 30 (±5)° to 7.5 (±2.5)°, a shoulder on the O(1s) core level XPS intensity distribution increased, and an H₂O thermal desorption peak assigned to bridging OH groups decreased. At a more detailed level, the interpretation presumes the presence, before irradiation, of a surface with bridging OH groups, i.e., where the proton removed, the O would be a lattice oxygen bound (bridged) to two Ti cations. These bridging OH groups are proposed to trap holes forming electron-deficient transition species that deprotonate available water to form two OH groups, each singly coordinated to different Ti cations. These singly coordinated OH groups are reportedly less acidic than the doubly coordinated species present before irradiation, and are proposed as the source of the lowered contact angle of water. In contrast, earlier reports suggested that photogenerated electrons trapped at Ti³⁺ surface sites were responsible for generating OH groups responsible for these changes in contact angle due to UV irradiation.^{2–4,7}

Building on a firm understanding of the behavior of water on single-crystal titania, TiO₂(110), surfaces prepared with or without oxygen vacancies,¹⁰ we have taken a model system approach that makes use of the tools of ultrahigh vacuum (UHV) surface science to probe this fascinating system. On the basis

of detailed H₂O TPD, we conclude that water microscopically wets clean TiO₂(110) surfaces whether or not oxygen vacancies (up to ~14%) are present. Since H₂O does not dissociate in the absence of oxygen vacancies, we conclude that dissociation of H₂O to form OH groups is not required for wetting. Since neither dissociation of H₂O nor oxygen vacancies control hydrophilicity, we examined the behavior of water on a surface covered with a chemisorbed organic species. From among the candidates of functionalized organic molecules that chemisorb on titania, e.g., alcohols, aldehydes, ketones, amines, and acids, we arbitrarily chose an acid, namely, trimethylacetic acid (TMAA, (CH₃)₃-CCOOH) that deprotonates to form trimethyl acetate (TMA) at 300 K. A monolayer of TMA should create a densely packed adlayer with little or no access of water to surface sites. While our results show that the TMA-covered surface is extremely hydrophobic, UV irradiation in the presence of 10^{−6} Torr of O₂ rapidly restores hydrophilicity by removal of TMA.

II. Experimental

The experimental equipment has been described previously.¹¹ Experiments were done in a standard UHV chamber (base pressure of 1 × 10^{−10} Torr) equipped for temperature-programmed desorption (TPD), Auger electron spectroscopy (AES), high-resolution electron energy loss spectroscopy (HREELS), rear-view low-energy electron diffraction (LEED), secondary ion mass spectrometry (SIMS), and oxygen plasma treatment.

The TiO₂(110) substrate was cleaned routinely by cycles of Ar⁺ sputtering and, to restore surface order, annealing to 850 K. Subsequently, the surface was dosed with O₂ at 220 K, a process that fills oxygen vacancies and leaves an oxidized surface exhibiting no evidence for surface oxygen anion vacancies.^{12–14} Annealing in UHV at 850 K for 10 min is accompanied by production of a small and reproducible concentration of oxygen vacancies evidenced by dissociating water and, in TPD, leading to a recombination water desorption peak with intensity that is 13 ± 1% of monolayer coverage of the undissociated (first layer) water (see below).

Water vapor was dosed at 100 ± 10 K through a pinhole tubular doser arranged to direct the incident vapor onto the sample rather than onto the surrounding support structure. By measuring the pressure (~1 Torr) behind the pinhole and the

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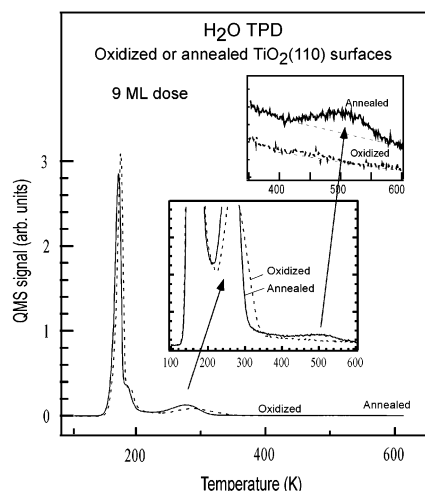


Figure 1. At a heating rate of 2 K s^{-1} , thermal desorption spectra (18 amu) following an 9 ML H_2O dose at 100 K on two forms of $\text{TiO}_2(110)$. Dashed and solid curves are, respectively, for fully oxidized and partially reduced $\text{TiO}_2(110)$ surfaces. The larger inset expands the ordinate scale to emphasize the 275 K peak. The smaller inset expands the ordinate even further to emphasize the presence and absence of a peak at 500 K.

dosing time, the relative doses are very reproducible ($\pm 3\%$) as determined by TPD peak areas. A dose of 20 Torr s saturates the first layer water TPD peak, and we define this area as a monolayer (1 ML).

Using a pinhole doser, TMA-saturated surfaces were prepared by exposing clean $\text{TiO}_2(110)$ held at $315 \pm 10 \text{ K}$ to TMAA for a time sufficient to saturate the subsequent TPD profiles. Deprotonation of TMAA forms bridged TMA species that are ordered along the Ti^{4+} cation rows as judged by a $(2 \times n)$ LEED pattern¹⁵ in our work that is consistent with strong AFM evidence from the literature.¹⁶ Since molecular TMAA desorbs at 200 K,¹⁷ dosing at 315 K precludes multilayer desorption.

Using UV photons from a 100 W high-pressure mercury arc, filtered through H_2O to remove infrared photons, the TMA-covered surface was irradiated at 300 K in the presence of 10^{-6} Torr of O_2 . A mirror and lens system focused this radiation and directed it onto the sample after passing through a fused silica window at the vacuum wall. At the sample, this source provides about $10^{17} \text{ photons cm}^{-2} \text{ s}^{-1}$ having energies exceeding the band gap. During illumination, the sample temperature rose between 10 and 20 K.

III. Results

3.1. Water Desorption Spectra for $\text{TiO}_2(110)$ with and without Oxygen Vacancies. In this section we compare water desorption spectra for two well-characterized types of $\text{TiO}_2(110)$ surfaces. In the first type, oxygen vacancies were minimized by exposing a clean $\text{TiO}_2(110)$ surface to oxygen at 220 K and subsequently avoiding heating above 400 K. In the second type, a reproducible concentration of oxygen vacancies was produced by heating a vacancy-free surface to 850 K for 300 s in UHV. LEED shows that both procedures give a highly ordered surface; a very sharp $p(1 \times 1)$ pattern is observed. In other work, the thermally produced oxygen vacancies have been imaged using STM.¹⁸

Obtained after dosing multilayer (9 ML) water, Figure 1 compares H_2O TPD spectra for these two surfaces. The major difference is the presence of a small peak near 500 K (inset) for the annealed surface that does not exist for the oxidized surface. As discussed in other work^{10,11} involving isotope

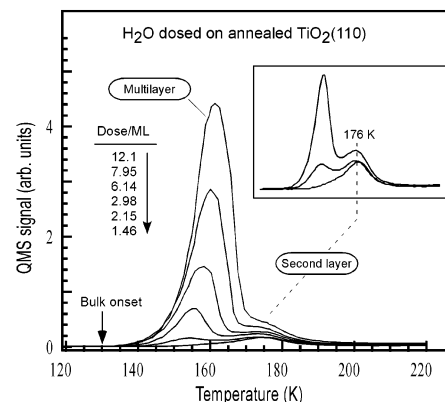


Figure 2. TPD of H_2O dosed on annealed $\text{TiO}_2(110)$ for coverages ranging from 1.46 to 12.1 ML. The first layer peak is off-scale toward higher temperature. The inset focuses on the three lowest coverages. The peak at 176 K is defined as the second layer peak. The arrow at 130 K marks the onset temperature for H_2O desorbing from TMA-covered surfaces.

labeling a $\text{TiO}_2(110)$ surface with ^{18}O , the 500 K peak is due to recombination of OH groups formed by H_2O dissociation on initially present oxygen vacancies (estimated to be 14% of the total number of exposed O^{2-} anions). This vacancy-mediated dissociation of H_2O has recently been imaged by STM.^{19,20} The H's of the resulting pair of OH groups migrate along the O anion rows at temperatures well below the water desorption temperature, so the resulting H_2O that desorbs is dominated by H_2^{18}O . There is negligible oxygen isotope exchange in the lower temperature H_2O desorption, i.e., it is dominated by H_2^{16}O . Since the oxidized $\text{TiO}_2(110)$ shows no desorption above 350 K, we conclude that the oxygen vacancy concentration is negligibly small (no more than 1% of the total number of surface O^{2-} anions).

Turning to the other local maxima in these TPD spectra, there are only small quantitative differences. In both spectra, there is a distinct and saturated peak (defined as 1 ML) at 275 K assigned to undissociated H_2O in direct contact with the exposed 5-coordinate Ti^{4+} cations.^{10,11,21} The peak areas are the same to within $\pm 5\%$. This result implies that adsorbed H_2O spreads in a monolayer over the $\text{TiO}_2(110)$ surface whether or not oxygen vacancies are present initially. The second noteworthy feature is, for both surfaces, a saturated shoulder near 175 K. The saturated shoulder peak area corresponds to 1 ML of desorbing H_2O and is assigned to adsorbed H_2O that is spread uniformly over the first layer, i.e., second layer water.^{10,11,21} As for first layer H_2O , second layer H_2O wets (spreads over) the first layer irrespective of whether the starting surface has or does not have oxygen vacancies. Finally, as expected, large doses lead to an unsaturable feature corresponding to multilayer desorption.

Turning to the evolution of these peaks with dose, Figures 2 and 3 show the 120 to 220 K portion of the H_2O TPD spectra measured after dosing various amounts (1.5 to 15 ML) of H_2O on $\text{TiO}_2(110)$ with and without vacancies, respectively. With the first layer intensity (not shown) saturated, this region emphasizes the coverage-dependent development of the second layer and multilayer features. For both surface types, the 1.5 ML spectra have a distinct peak at $176 \pm 1 \text{ K}$ that, for larger coverages, saturates but exhibits no shift of the peak temperature, i.e., describable in terms of first-order kinetics. For doses above 2 ML, a lower temperature peak emerges. Being unsaturable, it is assigned to desorption of multilayer H_2O . As typical for multilayers, the peak temperature increases with coverage. However, the kinetics are more complex than simple zero order

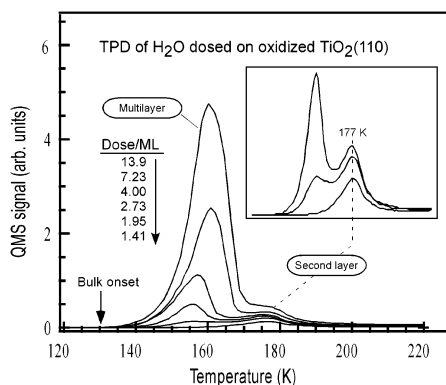


Figure 3. TPD of H_2O dosed on oxidized $\text{TiO}_2(110)$ for coverages ranging from 1.41 to 13.9 ML. The first layer peak is off-scale toward higher temperature. The inset focuses on the three lowest coverages. The peak at 177 K is defined as the second layer peak. The arrow at 130 K marks the onset temperature for H_2O desorbing from TMA-covered surfaces.

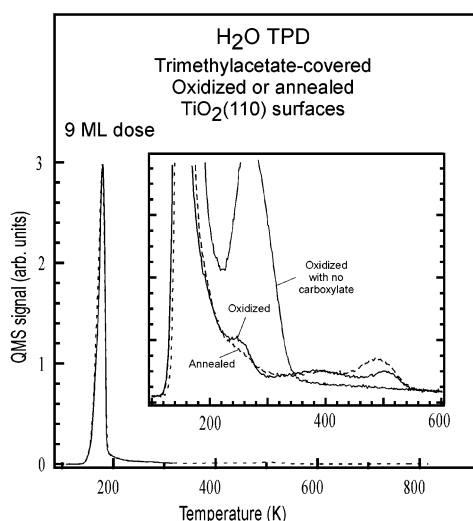


Figure 4. TPD of H_2O (9 ML) dosed on trimethyl acetate (TMA)-saturated $\text{TiO}_2(110)$ surfaces with (dashed) or without (solid) oxygen vacancies. For comparison, a third curve (no TMA), taken from Figure 1, is included.

since the leading edges do not align but shift to lower temperature as the multilayer coverage increases. The lowest onset is at 138 K, some 8 K higher than for TMA-covered surfaces (marked by the arrow and discussed below). As for the 9 ML case in Figure 1, second layer and multilayer H_2O desorption characteristics do not change when oxygen vacancies are present.

3.2. Water Desorption Spectra for $\text{TiO}_2(110)$ Covered with Trimethyl Acetate. We now turn to H_2O TPD from $\text{TiO}_2(110)$ surfaces prepared with or without oxygen vacancies and then saturated with TMA by 315 K doses of TMAA (Figure 4). For both, multilayer (9 ML) doses of H_2O at 100 K give rise to H_2O TPD spectra with overlapping multilayer onsets and, compared to the same dose on an oxidized surface with no carboxylate, with negligible first layer intensity and no second layer shoulder. As discussed elsewhere, the water desorbing between 350 and 600 K is attributed to the decomposition of TMAA since it is present when no H_2O is dosed.¹⁷

Figures 5 and 6 present H_2O TPD spectra for 0.5 to 17 ML doses of water on TMA-covered surfaces with and without initial oxygen vacancies, respectively. Irrespective of coverage or initial condition of the $\text{TiO}_2(110)$ surface, the water desorption onsets at 130 K, rises exponentially to a peak temperature that increases

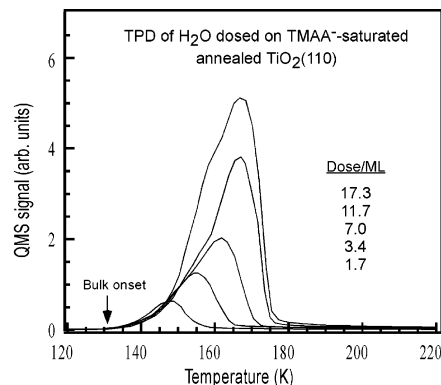


Figure 5. TPD of H_2O dosed on TMAA-covered $\text{TiO}_2(110)$ for coverages ranging from 1.7 to 17.3 ML (bottom to top). The surface was annealed at 850 K prior to TMAA adsorption. For this case, there is no first or second layer water peak.

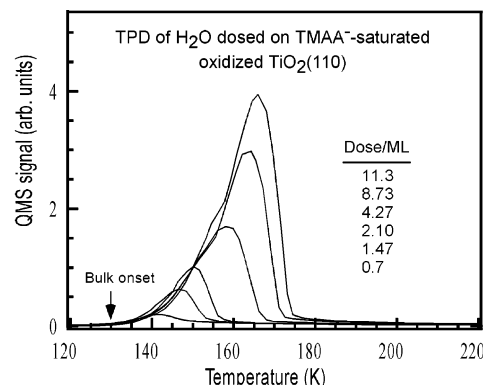


Figure 6. TPD of H_2O dosed on TMAA-covered $\text{TiO}_2(110)$ for coverages ranging from 0.7 to 11.3 ML (bottom to top). The surface was oxidized with O_2 at 300 K prior to TMAA adsorption. For this case, there is no first or second layer water peak.

with coverage, and then decays sharply with no evidence for the first layer peak or second layer shoulder that are typical for clean $\text{TiO}_2(110)$. The lowest intensity curve in Figure 6 is particularly noteworthy; while its area corresponds to only 0.7 ML of H_2O , the onset (130 K) and peak temperature are characteristic of thick multilayer water. The conclusion is clear; TMA-covered surfaces are very hydrophobic (nonwetting) and submonolayer amounts of water dosed on them desorbs with the properties of thick multilayers, i.e., bulk water.

There is one other informative difference in the TPD profiles for desorbing multilayers of H_2O from the $\text{TiO}_2(110)$ and TMA-covered $\text{TiO}_2(110)$ surfaces. When TMA is present, but not in its absence, there is a shoulder between 150 and 160 K on the leading edge of the multilayer desorption profile. This shoulder is attributed to a phase transition from amorphous to crystalline ice known to occur at this temperature and observed for water dosed at low temperatures on hydrophobic, i.e., nonwetting, metals such as gold.^{10,22} During the initial stages of dosing on such surfaces, adsorbed water molecules take no preferred orientation with respect to the substrate. This random, amorphous, and metastable character continues into multilayers. Thermal activation drives the transformation to crystallinity and is associated with a small increase in the activation energy for desorption. Thus, the desorption rate drops slightly. For multilayer H_2O dosed on clean $\text{TiO}_2(110)$, the absence of this shoulder and the 8 K higher desorption onset temperature is taken as evidence for the formation of crystalline ice either at 100 K or before the temperature reaches 130 K in TPD. This is consistent with multilayer water wetting clean $\text{TiO}_2(110)$, i.e.,

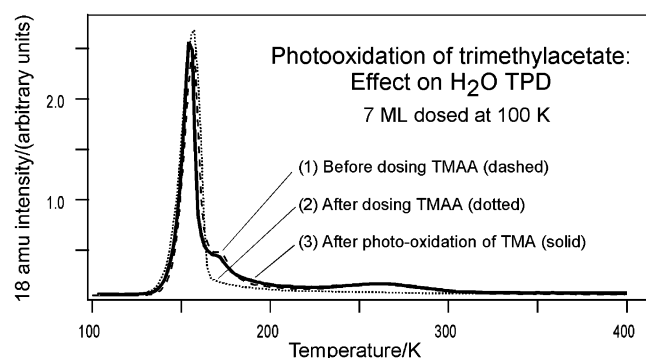


Figure 7. The effect on H₂O TPD of photolytic oxidation of TMA-covered TiO₂(110).

the titania substrate provides a thermodynamically favored and kinetically accessible template for the first layer of water and subsequent layers of water crystallize on this template.

3.3. Regeneration of Hydrophilicity by UV Irradiation.

To examine the effect of photochemistry of adsorbed TMA on the properties of adsorbed H₂O, a sequence of three H₂O TPD spectra were taken following 7.0 (± 0.5) ML doses of H₂O at 100 K (Figure 7). An annealed TiO₂(110) surface gave the expected first layer, second layer, and multilayer peaks (dashed line of Figure 7). After saturation with TMA, the TPD spectrum was devoid of first and second layer water peaks (dotted line of Figure 7). But after irradiation (300 s, 300 K, 5×10^{-6} Torr O₂, full UV portion of the Hg arc lamp), the H₂O TPD spectrum reverts to that characteristic of the clean initial TiO₂(110) surface (compare dashed and solid lines of Figure 7).

Discussed in depth elsewhere,¹⁷ TPD after 300 s photolysis indicates that the initial TMA coverage has dropped to about 7% of its original value and after 1.2×10^3 s irradiation, to about 0.1%. AES spectra taken before dosing with TMAA and after photooxidation for 3×10^2 s followed by TPD to 800 K show no C(KVV) signal. Thus, carbon surface coverages are less than 0.02 ML for both, and we conclude that the photo-oxidation produces no carbon-containing products that remain after TPD to 800 K.

IV. Discussion

Our data demonstrate unambiguously that, on clean TiO₂(110) with or without oxygen vacancies and the accompanying capacity to dissociate H₂O, a wetting film of solid, crystalline water forms either during dosing at 100 K or before any water desorbs during the early stages of TPD. Our data for these verifiably clean, flat TiO₂(110)-(1 \times 1) surfaces call into question the interpretation given to other work where nonwetting behavior of H₂O (large contact angles of $\sim 70^\circ$) was observed for what were thought to be suitably clean titania surfaces, both single-crystal solids and microcrystalline thin films.

We do find nonwetting behavior by covering the surface with carboxylate, i.e., trimethyl acetate, formed by dissociation of trimethylacetic acid. This is evidenced by the formation of amorphous solid water during dosing at 100 K and by the TPD of water that desorbs with the same kinetics as thick multilayers for all doses including submonolayers. In short, water does not wet this hydrocarbon-covered substrate.

The wetting characteristics are readily restored by UV irradiation in the presence of O₂ with the substrate temperature between 300 and 320 K. Under these conditions, the carboxylate species are removed by pathways presently under investigation.

When discussing our data, it is important to keep in mind that TPD measures kinetic properties of water removal and, only

indirectly, assesses properties of water adsorption. Contact angle measurements, on the other hand, probe equilibrium thermodynamic properties that involve interfacial tension at solid-liquid-gas interfaces and, thus, involve both adsorption and desorption. We associate observation of distinct first-layer, second-layer, and multilayer H₂O TPD peaks and the absence of evidence for amorphous solid water with wetting and, thus, low contact angles. Correlating these two is justifiable because there is no activation barrier for adsorption of water on TiO₂-(110), and good evidence, based on thorough mixing of isotopically labeled water layers, that adsorbed water molecules diffuse rapidly at 100 K and above.¹⁰

In comparing our results with other work focused on the hydrophobic or hydrophilic nature of titania surfaces, it is important to consider the vastly different measurement conditions. Our results involve a surface that has been rigorously characterized and maintained clean and highly ordered. As such, we have control of surface composition and impurity levels. Comparable control has not been available to work involving contact angle measurements.

It is clear from our data that none of the following are required for wetting TiO₂(110): (1) the presence of oxygen atom vacancies, (2) the dissociation of H₂O, and (3) the presence of Ti³⁺. Thus, proposals that relate wetting to photoinduced dissociation of water, initiated by trapped holes or electrons, need to be reevaluated.

While the presence or absence of vacancies is a moot point according to our results, a note regarding their production should be made. In unpublished work, we have been unable to form oxygen atom vacancies by UV irradiation of clean TiO₂(110)-(1 \times 1). This is consistent with very recent STM evidence that extensive UV irradiation does not produce oxygen atom vacancies on clean TiO₂(110)-(1 \times 1).²³ Vacancies are produced on TiO₂(110)-(1 \times 2), but with a cross-section of $\sim 10^{-23}$ cm² photon⁻¹, too low to account for the observed conversion of a titania surface from hydrophobic to hydrophilic.

While our work shows that a clean, carbon-free TiO₂(110) surface is sufficient to observe wetting, the question of necessity remains open. We conjecture that work carried out at ambient temperatures in laboratory atmospheres involves uncontrolled chemisorption and UV-driven removal of functionalized hydrophobic hydrocarbon species. When irradiated with intensities exceeding a critical minimum, the steady-state rate of adsorption and removal of these hydrocarbon species likely reduces the local surface concentration of hydrophobic moieties, allowing water to locally wet an otherwise hydrophobic surface. At some point, the surface becomes macroscopically hydrophilic. Once in this condition and placed in the dark, the surface returns to its hydrophobic condition at a rate depending on its chemical interactions with multiple species in the environment, particularly water, oxygen, and functionalized organics.

Conclusions

Thermal desorption spectra of H₂O dosed on clean TiO₂-(110)-(1 \times 1) surfaces reveal wetting behavior irrespective of the presence or absence of surface oxygen vacancies and the associated surface-exposed Ti³⁺ cations. When covered with trimethyl acetate (TMA), water TPD spectra exhibit nonwetting behavior for surfaces that have and do not have surface oxygen vacancies. Irradiation with UV light in the presence of 10^{-6} Torr of O₂ removes TMA and restores the wetting behavior of the surface.

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