

Communication

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## Photochemical Charge Transfer and Trapping at the Interface between an Organic Adlayer and an Oxide Semiconductor

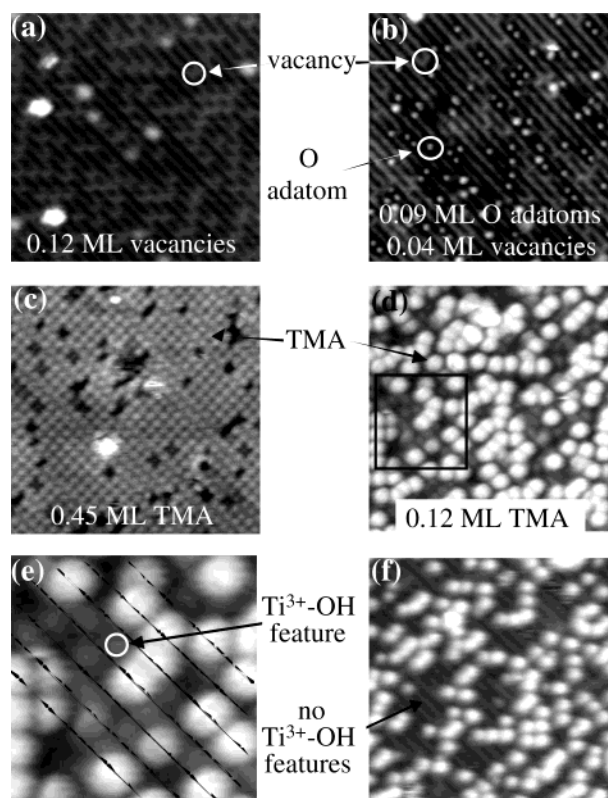
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Photocatalysis on oxides has attracted considerable attention due to ambitions of water splitting, pollutant destruction, and bacterial disinfection.<sup>1,2</sup> These processes are catalyzed using photon-excited electron–hole pairs that perform surface-mediated redox chemistry. Little is known at the site-specific level about interfacial charge transfer and trapping because most heterogeneous photocatalyst surfaces possess a complex and poorly defined distribution of sites and the media in which typical studies are performed (aqueous or high-pressure conditions) are inhospitable to many molecular-level probes. Studies on single-crystal oxide surfaces under ultrahigh vacuum (UHV) provide new insights into molecular-level processes on oxides, with the rutile TiO<sub>2</sub>(110) surface emerging as a prototypical oxide for study of photocatalytic phenomena.<sup>3</sup> In this study, we identify surface sites associated with charge transfer and trapping during photodecomposition of an organic adsorbate using scanning tunneling microscopy (STM), electron energy loss spectroscopy (EELS), and photodesorption. Trimethyl acetic acid (pivalic acid or TMAA) was selected because it decomposes on TiO<sub>2</sub>(110) at room temperature (RT) to form a densely packed trimethyl acetate (TMA) adlayer in which each TMA group bridges two Ti<sup>4+</sup> sites and the acid proton is transfer to a bridging O<sup>2-</sup> site.<sup>4</sup> The carboxylate moiety, which binds the molecule strongly to the surface, is also the main anchoring point for most organic sensitizers.<sup>5</sup>

Figure 1 shows STM images obtained at 280 K for various stages of UV irradiation of a TMA-covered TiO<sub>2</sub>(110) surface. Image a, obtained from the vacuum-annealed surface, shows an oxygen vacancy (example circled) population of 0.12 ML (1 ML = 5.2 × 10<sup>14</sup> sites/cm<sup>2</sup>). (The large bright spots are unidentified impurities.) The bright and dark rows correspond to surface Ti<sup>4+</sup> and bridging O<sup>2-</sup> sites, respectively.<sup>6</sup> Image b shows that a 100-L O<sub>2</sub> exposure at 280 K oxidized about two-thirds of the vacancy sites and deposited an equivalent number of oxygen adatoms (example circled) at Ti<sup>4+</sup> sites.<sup>7</sup> TMAA exposure resulted in a dense TMA adlayer (image c), where the O adatoms blocked some TMA adsorption sites (empty spaces). UV irradiation for 1 h (image d) decomposed 0.33 ML TMA and resulted in a change in the TMA spot size possibly associated with the change in TMA coverage or with a tip-related change. Also, faint spots appeared among the remaining TMA spots. Expansion of the square region in image d shows that the faint spots (example circled) were present at about 50% of the level of the depleted TMA and were located on the rows of bridging O<sup>2-</sup> sites and not on the rows of TMA groups (dashed lines in image e). We ascribe the faint spots on the dark rows to bridging OH groups bound to underlying Ti<sup>3+</sup> cations on the basis of similarities with features observed after water dissocia-



**Figure 1.** STM images of TMA-covered TiO<sub>2</sub>(110) at 280 K. (a) Clean TiO<sub>2</sub>(110) annealed in UHV; (b) a exposed to 100 L of O<sub>2</sub>; (c) saturation of b with TMA; (d) irradiation of c in UHV for 1 h with a 300-W Xe arc lamp; (e) square region indicated in d; and (f) d exposed to 100 L of O<sub>2</sub>. Image sizes (with exception of e) are 16 × 16 nm<sup>2</sup>.

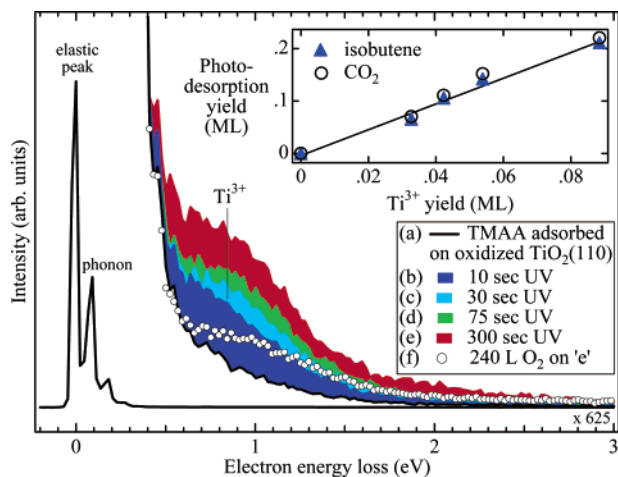
tion at oxygen vacancies<sup>8</sup> or after exposure of the oxidized surface to atomic H.<sup>9</sup> After an additional 30 min UV exposure, the surface of d was exposed to 100 L of O<sub>2</sub> in the dark, and the faint spots associated with Ti<sup>3+</sup>–OH groups disappeared revealing the underlying clean TiO<sub>2</sub>(110) surface (image f).

Photodecomposition of TMA resulted from hole transfer to the carboxylate followed by R–COO bond cleavage similar to the Hunsdiecker decarboxylation<sup>10</sup> and “photo-Kolbe”<sup>11</sup> reactions. CO<sub>2</sub> and *tert*-butyl radical desorption, the latter detected as isobutene after wall reactions in the UHV chamber, were detected in amounts approximately equivalent to the amount of depleted TMA. The accompanying electron-trapping pathway was monitored using EELS. This technique, analogous to optical absorption, excites surface oscillators (vibrational or electronic) using a monochromatic electron beam. Figure 2a, taken from an oxidized surface saturated at room temperature with TMAA, shows that the electronic region is devoid of signal between the phonon tail (<0.5 eV) and the onset of band-to-band excitation of TiO<sub>2</sub> (>3.2 eV, not shown). UV

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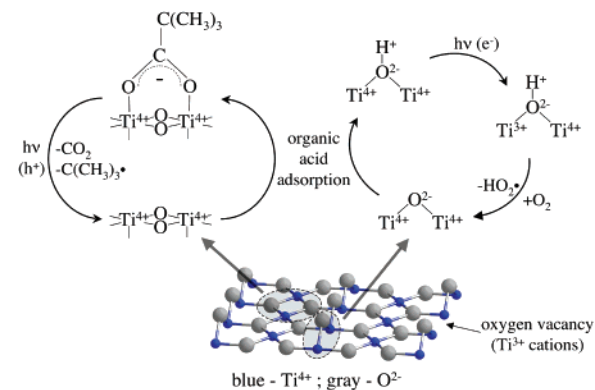


**Figure 2.** EELS spectra from TMAA-covered TiO<sub>2</sub>(110), oxidized prior to TMAA adsorption. (a) TMAA-covered surface prior to UV; (b–e) after irradiation with a 100 W Hg arc lamp; (f) exposure of e to 240 L of O<sub>2</sub>. Inset: correlation between the isobutene and CO<sub>2</sub> photodesorption yields and the Ti<sup>3+</sup> signal generated during photolysis.

irradiation of the TMAA-covered surface in the absence of O<sub>2</sub> resulted in a feature at about 0.8 eV (spectrum b) that grew with additional UV irradiation (spectra c–e). This feature is indicative of Ti<sup>3+</sup>,<sup>3</sup> in this case resulting from photogenerated electrons trapped at the surface of TiO<sub>2</sub>(110) as Ti<sup>3+</sup>–OH groups. Irradiation of the clean, oxidized TiO<sub>2</sub>(110) surface with UV did not result in any new features ascribable to Ti<sup>3+</sup>, in agreement with recent STM results by Mezheny et al.<sup>12</sup> As in the case of the STM data in Figure 1f, the Ti<sup>3+</sup> signal arising from photodecomposition of TMAA was largely removed by postexposure to O<sub>2</sub> (spectrum f).

Using the Ti<sup>3+</sup> EELS signal intensity from the vacuum-annealed surface<sup>3</sup> as a standard, we correlated the amount of Ti<sup>3+</sup> generated during UV photodecomposition of TMAA with the isobutene (from *tert*-butyl radical conversion) and CO<sub>2</sub> photodesorption yields. The latter were calibrated using the thermal desorption signals from saturated monolayers on the TiO<sub>2</sub>(110) surface at 100 K. The inset of Figure 2 shows that the accumulation of Ti<sup>3+</sup> increased linearly with the amount of photodesorption product. The ratio between photodesorbed isobutene/CO<sub>2</sub> and Ti<sup>3+</sup> was about 2:1.

The scheme in Figure 3 illustrates the two redox channels associated with UV photodecomposition of TMAA on TiO<sub>2</sub>(110). TMAA adsorbs via decomposition of the acid's O–H bond, generating a bridging TMA and a bridging OH group. Hole transfer to TMA results in decarboxylation. On the basis of STM and ELS results, it was determined that electrons trap at surface cations. The role of O<sub>2</sub> in this process involves titrating the accumulated trapped electrons to reoxidize the surface, presumably via H• abstraction from the bridging OH sites bound at Ti<sup>3+</sup> sites.<sup>13</sup> The product is likely a short-lived HO<sub>2</sub>• species that reacts at room temperature to form gaseous water and adsorbed O adatoms. These data reveal that charge transfer and trapping channels can be tracked on a model TiO<sub>2</sub> photocatalyst using molecular-level probes. Substantial pho-



**Figure 3.** Reaction scheme illustrating the separate redox processes associated with photodecomposition of TMAA on TiO<sub>2</sub>(110), along with the sites associated with charge transfer and charge trapping.

to decomposition of an organic adlayer can occur in the absence of gas-phase O<sub>2</sub> because of the ability of the surface to trap electrons while permitting hole-related processes to proceed.

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