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Inhibitive Influence of Oxygen Vacancies for Photoactivity on $\text{TiO}_2(110)$

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Scanning tunneling microscopy results reveal a pronounced site-selectivity in the hole-mediated photooxidation of trimethyl acetate (TMA) on $\text{TiO}_2(110)$, wherein the reaction readily occurs at regular Ti sites but is completely inhibited at oxygen vacancy (V_O) defects. Utilizing electron energy loss spectroscopy and density functional theory, we show that the lack of reactivity of TMA groups adsorbed at V_O 's cannot be attributed to either a less active adsorption conformation or electron transfer from the V_O defect. Instead, we propose that the excess unpaired electrons associated with the V_O promptly recombine with photoexcited holes approaching the surface, effectively 'screening' TMA species at V_O site. We also show that this screening effect is predominately localized at the V_O , only mildly affecting TMA's at adjacent Ti sites.

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Photo-driven processes involving TiO₂-based materials play a central role in catalysis, solar energy generation, and environmental remediation. The majority of fundamental research has employed the rutile TiO₂(110)-(1×1) surface, which has, in fact, become the model transition-metal oxide surface [1, 2]. This surface consists of alternating rows of 5-fold coordinated Ti (Ti_{5c}) and 2-fold coordinated bridging O (O_b) atoms. Conventional sample preparation by ion sputtering and annealing in ultrahigh vacuum (UHV) leads to its partial reduction, as manifested by a creation of bridging oxygen vacancies (V_O's) [3]. Although one may assume that V_O's are only present under UHV conditions and thus irrelevant in real applications, actually, they are created in a number of catalytic reactions that involve lattice oxygen [4]. Additionally, the electronic signature and reactivity of the V_O defects on TiO₂(110) closely resemble those of photochemically trapped electrons on high surface area TiO₂ catalysts [5]. The origin of the enhanced reactivity of V_O site is commonly related to a nominal presence of unpaired excess electrons [1, 3, 6, 7]. While the exact location and degree of localization of these excess electrons are still under debate, recent studies indicate that they are distributed across multiple Ti sites adjacent to the V_O defect, with subsurface sites showing preference [8-14]. In photoinduced processes, surface point-defects (such as V_O's) might be expected to act as charge trapping and/or recombination centers [5, 15]. However, the direct impact of surface defects on photoreactivity of TiO₂(110) is not well explored.

Beyond the indirect role of V_O as adsorption site, a *direct* role of V_O and its electrons in TiO₂(110) photochemistry has been considered, perhaps, only for O₂ desorption [16]. In particular, it was suggested that the electrons percolating through a network of V_O sites affect the kinetics of O₂ photodesorption from the V_O sites. However, recent scanning tunneling microscopy (STM) studies revealed that O₂ desorption occurs from Ti_{5c} rather than V_O sites [17].

Evidently, additional investigations into any correlations between the surface point-defects and $\text{TiO}_2(110)$ photoreactivity, utilizing different probe molecules, are needed. One of the attractive probe molecules for such studies is trimethyl acetic acid (TMAA, $(\text{CH}_3)_3\text{CCOOH}$). Similar to other carboxylic acids, TMAA adsorbs dissociatively at ≥ 150 K by O-H bond cleavage, whereas the resulting trimethyl acetate (TMA, $(\text{CH}_3)_3\text{CCOO}$) group bridge-bonds across two Ti_{5c} sites (termed TMA/ Ti_{5c}) and the acid proton forms an adjacent OH_b group [18-21]. The adsorbed TMA species exhibits relatively straightforward hole-mediated photo-decomposition on $\text{TiO}_2(110)$, generating CO_2 and a tert-butyl radical $((\text{CH}_3)_3\text{C}\cdot)$, which undergoes rapid thermal reactions yielding only gaseous products [20, 22]. Furthermore, our recent STM studies uncovered a second, V_O -mediated adsorption channel, where one O atom of TMA fills a V_O and the other O bonds to a neighboring Ti_{5c} site (termed TMA/ V_O) [23]. Hence, an intriguing question arises about the relative photoreactivities of these two site-specific adsorption channels of TMA.

In this Letter, we report the first observation of a suppressing effect of V_O defects on $\text{TiO}_2(110)$ photoreactivity, as evidenced by direct STM imaging of site-specific depletion of TMA upon ultra-violet (UV) light irradiation. Based on STM, electron energy loss spectrometry (EELS) and density functional theory (DFT) studies, we invoke a distinct role of the excess unpaired electrons of V_O , which fully prevent the reaction of photoexcited holes with TMA adsorbed at the V_O site. We show that this effect is spatially short-ranged, affecting (mildly) only TMA's at Ti sites nearest to the V_O defect.

Figure 1 shows STM images of the same area of $\text{TiO}_2(110)$ surface before and after TMAA exposure (coverage ~ 0.015 ML), and following UV irradiation [24]. The empty-state STM image of clean reduced $\text{TiO}_2(110)$ in Fig. 1(a) displays a typical pattern of periodic bright and

dark rows of Ti_{5c} and O_b atoms, respectively [3]. The V_O defects are seen as faint bright spots on dark rows. Several brighter features, also centered on O_b rows are OH_b groups, have resulted from a minor amount of background water dissociation at V_O sites. As discussed above, TMAA molecules adsorb dissociatively through deprotonation and occupy two distinct adsorption sites (Ti_{5c} and V_O) [18-20]. After the low-coverage TMAA exposure, individual TMA groups appear in Fig. 1(b) as isolated large bright spots. However, TMA's residing at different sites can be identified by their relative positions, as illustrated in the inset in Fig. 1(b). Specifically, slightly larger, round spots centered on Ti_{5c} rows are TMA/ Ti_{5c} 's. In contrast, often "fuzzy" looking features centered on O_b rows are TMA/ V_O 's [25]. Each TMA/ V_O species indeed appears at a former V_O site, as can be seen from comparison of panels (a) and (b) in Fig. 1. For both adsorption channels, the OH_b 's are virtually invisible to STM observation while residing alongside adsorbed TMA's [18]. After UV irradiation, Fig. 1(c) demonstrates that all of the TMA/ Ti_{5c} 's disappeared, due to the photoinduced TMA decomposition process that produces volatile products [20, 22], as discussed earlier. Since OH_b groups are not photoreactive [5, 26], they become visible at the adjacent sites in Fig. 1(c) after TMA/Ti's are removed. Remarkably, every TMA/ V_O species appears intact after UV irradiation, as can be seen in Fig. 1(c). Note that even after prolonged UV irradiation, we did not observed disappearance of TMA/ V_O 's (from analysis of ~ 700 events, with a statistical error $< 0.7\%$). This apparently indicates that the photooxidation of TMA species adsorbed at V_O sites is completely hindered.

STM images in Figure 2 demonstrate the effect of UV irradiation at a higher, near-saturation TMA coverage, where TMA/ V_O 's are not isolated but rather surrounded by adjacent TMA/ Ti_{5c} species. For a coverage of ~ 0.43 ML, a dense TMA monolayer consisting of ordered (2×1) -domains can be seen in Fig. 2(b). Individual TMA groups are seen as ordered round spots

centered at Ti_{5c} rows. Though the $\text{TMA}/\text{V}_\text{O}$'s are not clearly seen in the close-packed TMA overlayer, a translational shift in the across-row alignment and/or a missing $\text{TMA}/\text{Ti}_{5c}$ is often observed in a close proximity, which can be seen by superimposing the original V_O positions into Fig. 2(b). It is likely that steric hindrance between neighboring $\text{TMA}/\text{Ti}_{5c}$ and $\text{TMA}/\text{V}_\text{O}$ species is responsible for both missing $\text{TMA}/\text{Ti}_{5c}$'s and/or unfilled V_O 's. After UV irradiation, the majority of remaining species were identified as $\text{TMA}/\text{V}_\text{O}$ (and OH_b) species [27, 28]. (Once again, TMA's centered at O_b rows in Fig. 2(c) can be traced back to the original V_O 's in Fig. 2(a)). On the other hand, the majority of $\text{TMA}/\text{Ti}_{5c}$'s are depleted as only a few species can be seen in Fig. 2(c) (a longer irradiation would completely remove these (not shown)). An analysis of the TMA distribution during UV irradiation reveals that $\text{TMA}/\text{Ti}_{5c}$'s adjacent to the V_O sites have a slightly lower depletion rate (by $\sim 30\%$) than those located farther from V_O 's [29]. This can also be seen in Fig. 2(c), where the remaining $\text{TMA}/\text{Ti}_{5c}$'s usually reside in the vicinity of either a $\text{TMA}/\text{V}_\text{O}$ or an unfilled V_O .

The above STM results unambiguously show that TMA photochemistry on $\text{TiO}_2(110)$ is strongly site-specific, with a significant difference existing between the reactivity of TMA species bound at V_O and Ti_{5c} sites. In an attempt to comprehend this, we considered the distinct properties of these active sites and potential differences between TMA adsorption at V_O and Ti_{5c} sites. We explored with DFT calculations [24] the bonding conformations (both molecular and dissociative) of TMAA/TMA at V_O 's and compared those with corresponding conformations at Ti_{5c} sites examined in our earlier work [23]. Binding of TMAA at V_O sites is an exothermic process, as Figure 3 shows. Molecular adsorption energies in V_O are all near -0.7 eV, while dissociation of TMAA at the V_O site (with one O atom in the vacancy and on O atom bound to Ti_{5c}) and formation of an OH_b group has an adsorption energy of -1.36 eV. We also modeled a

geometry with two O atoms of TMAA in the V_O (not shown), but this was unstable by ~ 1.5 eV. Thus, dissociation is the preferred binding mode of TMAA at a V_O site. In comparison, the dissociative adsorption of TMAA at two Ti_{5c} 's has a slightly smaller adsorption energy of -1.28 eV [23]. Evidently, TMA species residing at V_O and Ti_{5c} sites both have bidentate configurations and rather similar adsorption energies, and hence similar stabilities/reactivities [30]. In addition, the calculations of projected density of states show that TMA species in these two configurations have similar electronic states (see Fig. S3 in the Supplemental Material), and should therefore interact with a photoexcited hole in a similar manner.

We utilized EELS to probe the surface electronic properties of the reduced $TiO_2(110)$ and the effect of TMAA adsorption to explore, in particular, whether (non-photochemical) charge-transfer between the V_O and TMA might occur and inhibit photoreactivity. In the electronic mode of EELS (i.e., at beam energies ≥ 10 eV), specularly scattered electrons preferentially excite surface transitions in a manner similar to optical excitation. Figure 4 shows EELS spectra for the clean reduced, TMAA-saturated, and oxidized surfaces (latter was prepared by O_2 exposure at 300 K). The reduced surface shows the prominent, relatively wide feature at ~ 0.85 eV attributable to localized excitation of the polaronic state associated with the excess unpaired electrons of V_O [31]. As seen with other electronic spectroscopies [3], oxidation of the surface results in near complete removal of this signature of the defect state. On the other hand, the saturation of the reduced surface with TMAA resulted in a partial decrease of loss intensity at 0.85 eV in the EELS spectrum. However, the remaining intensity of the V_O -related loss feature was significantly greater than for the spectrum of the oxidized surface, which suggests that TMA is not oxidizing the V_O . A similar effect was previously observed after water adsorption on the reduced $TiO_2(110)$ [32]. It is more likely that loss of intensity in the V_O -related feature was

because the TMA overlayer partially shielded scattered electrons from electronically exciting the V_O electronic state. Whether this was because TMA species resided at V_O 's and/or formed the ordered (2×1) overlayer is unclear. Nevertheless, the EELS data does not provide evidence for any substantial charge transfer from the V_O to TMA; i.e., extra charge still remains at the V_O sites. Furthermore, this correlates with the Mulliken electronegativity of TMAA calculated by DFT to be only ~ 0.13 eV, which indicates that it is unlikely to take up any substantial amount of electrons from the reduced surface. Consequently, it is possible that after TMAA adsorption, the distribution of unpaired electrons around the V_O defect remains largely unaffected.

The lack of photoreactivity of TMA species at a V_O site cannot be attributed either to a considerably different adsorption conformation or charge transfer from the V_O defect. Instead, we suggest that the excess unpaired electrons associated with V_O 's recombine with incoming photoexcited holes and thus *prevent* holes from reacting with TMA/ V_O 's, as schematically illustrated in Figure 5. Essentially, TMA's residing at V_O sites are effectively 'screened' by the latter's unpaired delocalized electrons, which are dynamically distributed across adjacent subsurface Ti sites, as discussed earlier. In contrast to TMA/ V_O 's, the TMA/ Ti_{5c} species can readily react with holes. Note that though photoexcited electrons do not directly react with TMA species, they likely contribute to the replenishing of depleted negative charge at V_O sites. Otherwise, these electrons are expected to be trapped at the surface, most likely as Ti^{3+} -OH_b groups [20]. Interestingly, the 'screening' effect of V_O excess electrons appears to be rather spatially confined, as TMA photooxidation was observed even at the nearest Ti_{5c} sites, albeit with a smaller rate than more distant TMA/ Ti_{5c} 's, as discussed above. Evidently, the screening influence is most effective when the species (TMA/ V_O) is fully 'encircled' by the dynamically distributed excess electrons. As a side comment, note that while unpaired electrons hinder the

hole-induced reactions at V_O sites, it appears they (predictably) do not have a similar inhibiting effect on the *electron*-mediated processes, e.g., the photodissociation of O_2 at V_O sites [17, 33].

The observed direct impact of O vacancies on TMA photoreactivity over $TiO_2(110)$ is expected to have similar implications for other hole-mediated (e.g., photooxidation) reactions in which adsorption at or near electronic point-defects is possible. The localized influence of these defects on hole-mediated chemistry offers opportunities for additional study of site-selective photocatalysis on TiO_2 . The reported results also demonstrate that structure–reactivity relationships, a customary subject in heterogeneous catalysis, are clearly relevant to photocatalysis.

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- [28] The lack of TMA photoreactivity at V_O sites has been also confirmed at more than ten intermediate TMA coverages (between 0.015 and 0.43 ML).
- [29] The site-specific photoreaction rates are estimated on a basis of the normalized concentrations of TMA species measured after UV-irradiation at several time intervals (see Table S2 in the Supplemental Material).
- [30] Furthermore, TMA species at V_O and Ti_{5c} sites have similar thermal reactivities, and the calculated reaction energies for decomposition of TMA (to gas-phase CO_2 and tert-butyl radical) are 3.2 and 3.0 eV, respectively.
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Figure 1. STM images of the same $(18 \times 17) \text{ nm}^2$ area of $\text{TiO}_2(110)$ surface (a) before and (b) after TMAA exposure of ~ 0.015 ML, and (c) after UV irradiation for 5 min (all at 250 K). Inset in panel (b) displays the magnified area marked by a rectangle, with positions of TMA's and Ti_{5c} rows are marked.

Figure 2. STM images of the same (8×8) nm^2 area (a) before and (b) after near-saturation TMAA exposure (~ 0.43 ML), and (c) after UV irradiation for 30 min. The black dashed squares and circles represent positions of original V_o 's and photodepleted TMA/Ti_{5c} 's, respectively.

Figure 3. Calculated adsorption states of TMAA at V_O site of $\text{TiO}_2(110)$. For molecularly-adsorbed states, in (a) the TMAA binds via O filling the V_O , while in (b) the TMAA binds via HO filling the V_O , and in (c) the TMAA binds to two Ti atoms (one inside and other outside of V_O). In (d) the TMAA is dissociated and OH_b group is formed nearby. Red spheres represent O atoms, light grey spheres Ti atoms, white spheres H atoms, and large grey spheres C atoms.

Figure 4. EELS spectra from clean reduced (red), TMA-saturated (blue), and oxidized (dashed black) TiO₂(110) surfaces. The elastic peak count rates were all within 10% of each other for the three experiments shown.

Figure 5. Schematic representation of the tentative mechanism responsible for inhibiting hole-mediated photoreactivity of TMA at V_O sites of $\text{TiO}_2(110)$. The V_O defect (black) has two unpaired excess electrons dynamically distributed across multiple adjacent subsurface Ti sites, and the distribution changes minimally after TMA adsorption. During UV irradiation, the excess electrons recombine with incoming holes and effectively ‘screen’ TMA/ V_O species (red). The TMA/ Ti_{5c} species (green) promptly react with holes and become depleted, while electrons are trapped at the surface (schematically shown inside dashed circles).