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Metal oxide surfaces have been thought to be fairly rigid. On the example of rutile-TiO$_2$(011) we show that this is not necessarily the case. This surface restructures by interacting with molecules. Synergic effect of adsorbates causes a strictly directional re-organization of the substrate, which results in one-dimensional adsorbate cluster formation. The increase in the surface energy of the restructured surface is compensated for by the larger molecular adsorption energy. The reversible change of the surface structure suggests a dynamic surface that may change its properties in response to adsorbed molecules.

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The chemical properties of materials are controlled by the atomic scale structure of their surfaces. Surface activity of covalent materials comes from unsaturated, 'dangling' bonds at the structural discontinuity of the surface-gas interface and the coordination and separation of surface atoms relative to the adsorbed molecule [1,2]. The surface structure determined by vacuum surface science studies is often taken as the relevant structure for explaining their chemical functionalities [3]. This implies a rigid surface, with only small relaxations if molecules adsorb on it. In contrast to metals whose delocalized non-directional bonding allows large scale surface rearrangements in different gaseous environments [4], the picture of a rigid surface has been justified for metal oxides by the strong directional covalent bonding. The prototype transition metal oxide TiO_2 has been extensively studied due to its importance in photo- and heterogeneous catalysis [5]. However, most of these studies were focused on the (110) surface of the majority rutile polymorph [6]. Here we investigate the rutile-TiO_2(011) surface, which is the second most abundant surface orientation for an equilibrium rutile crystal and thus is critical for understanding, for example, the photocatalytic properties of TiO_2 powder catalysts. Unlike the (110) face, which often exhibits a bulk truncation, the (011) surface exhibits a 2×1 reconstruction at the vacuum interface [7]. This reconstruction lowers its surface free energy by reducing the number of dangling bonds and thus also reduces its chemical reactivity, which would make this surface fairly inert. However, the studies presented here demonstrate that the surface can restructure to increase interaction with molecular adsorbates. Therefore the picture of a rigid oxide surface does not hold and dynamic changes of the surface structure has to be considered to describe the chemical properties of TiO_2(011). Interestingly, the adsorbate induced surface instability is strongly anisotropic which results in the formation of directional adsorbate clusters and thus such adsorbate induced surface restructuring may also be an approach for structuring at the close to atomic scale.

Total energy density functional theory (DFT) calculations in conjunction with scanning tunnelling microscopy (STM) studies of adsorbate dosed TiO_2(011) surfaces have been used to explain the adsorbate interaction with this surface. The DFT studies have been carried out within the generalized gradient approximation (GGA) using the PWScf code included in the Quantum-Espresso package [8]. Detailed technical information is given in supplemental material [9].

To estimate the adsorption energies E_{ad}, the following expression was considered:

$$E_{ad} = -[\, E_{ads\,/\,TiO_2} - E_{TiO_2} - nE_{ads} \,]$$

in which $E_{ads\,/\,TiO_2}$ is the total energy of the interacting system containing adsorbates and TiO_2 support; E_{TiO_2} is the total energy of the $TiO_2(011)$-2×1 slab; E_{ads} is the total energy of a single adsorbed molecule in gas-phase; and n is the number of adsorbates in each surface cell.
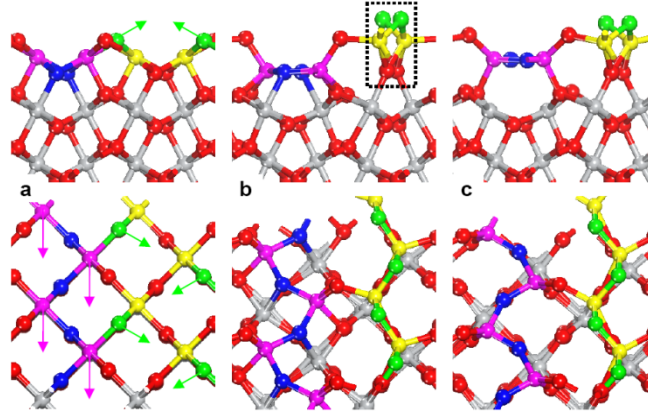

FIG. 1 (color online). Calculated structures (top row: side view, bottom row: top view against [001] direction) of a) bulk-truncated 1×1, b) most stable vacuum 2×1 and c) restructured 2×1 rutile TiO₂(011) surfaces. The bulk Ti atoms are in grey and O in red. The O in green and Ti in yellow form the sandwich-like Ti₂O₄ unit (square in black dotted line) and the O in blue and Ti in purple build the trough of the 2×1 surfaces. The arrows in a) indicate the movement of surface atoms to form the 2×1 reconstruction shown in b).

Fig. 1a and b schematically show the reconstruction of a bulk truncated surface to the low-energy 2×1 surface of $TiO_2(011)$. As one can see, the bulk-truncated $TiO_2(011)$ contains a high concentration (2 per primary surface cell, ~4.59×5.45 Å^2) of unsaturated 5-fold coordinated Ti (Ti_{5c}) with its broken, or 'dangling', bonds pointing into vacuum. Bond-rearrangement and movement of surface atoms along and perpendicular to the surface forms this 2×1 reconstructed surface. In this structure all Ti_{5c} sites, both in the trough and the middle of the sandwich-like Ti_2O_4 unit, are uniformly surrounded by O and thus are not extending any dangling bonds into vacuum. The surface energy for this 2×1 reconstructed surface was estimated to be 0.42 J·m^{-2}, nearly half of that of the bulk-truncated surface (0.89 J·m^{-2}) [7]. Because of the lack of dangling bonds, this reconstructed surface is fairly inert to the adsorption of molecules. Water, for example, only adsorbs at temperatures below 200 K in ultrahigh vacuum (UHV) and surface defects such as hydroxyl groups are necessary to stabilize this adsorption [10]. By contrast, it has

been shown by a recent DFT study, that the dangling bond-rich and high energy bulk truncated (011)-1×1 surface would be very active for water adsorption [11].

Carboxylic acids, such as formic acid or acetic acid, usually adsorb strongly on metal oxide surfaces and therefore are often used as anchoring groups of dye-molecules to TiO_2 in dye-sensitized solar cells. Previous temperature programmed desorption studies by us and others also show a strong adsorption of acetic acid on the $TiO_2(011)$ surface [12,13]. In the experimental studies, reactions of acetic acid with the surface are predominantly through dehydration reactions to ketene which desorbs from the surface above 500 K, indicating a binding energy of ~1.6 eV/molecule [14] and thus a dissociative adsorption of acetic acid as acetate at the surface. However, our STM study reveals a rather unusual adsorption structure of this acetate at room temperature. Unlike adsorption of acetic acid on $TiO_2(110)$ where a homogenous adsorption is observed that results in a uniform coverage of the surface [9, 15], acetic acid adsorbtion on the (011)-2×1 surface forms clusters even for very low coverage. This indicates that acetates are held together locally. Here, we show that this is not because of intermolecular forces, which are actually repulsive like on the (110) surface, but instead the cluster formation is a consequence of restructuring of the substrate underneath of the adsorbates. The cluster formation is then a consequence of the restructuring dynamics as is described below. As shown in Figs. 2a-c, these clusters often originate at surface defects such as step edges or antiphase domain-boundaries of the surface reconstruction, and each of these clusters are observed to have a width of the 2×1 substrate surface cell and have lengths up to tens of nanometers along the $[01\bar{1}]$ direction, apparently only limited by the terrace size. Molecularly resolved STM images shown in Figs. 2d and e further reveal that each cluster sits in the trough of the substrate and appears as three rows of protrusions in width. The row in the middle shows a brighter contrast compared to the two outer rows, which also exhibit a high number of 'missing' protrusions. Furthermore, the adsorption dynamics is very different on the (011) surface compared to, for example, the $TiO_2(110)$ surface. On the (110) surface carboxylic acids adsorb with a sticking probability close to unity [16], while a much lower sticking probability of acetic acid was determined on the (011) surface [9, 12] indicating either a low adsorption strength and/or a high barrier for adsorption on the defect free (011)-2×1 surface.
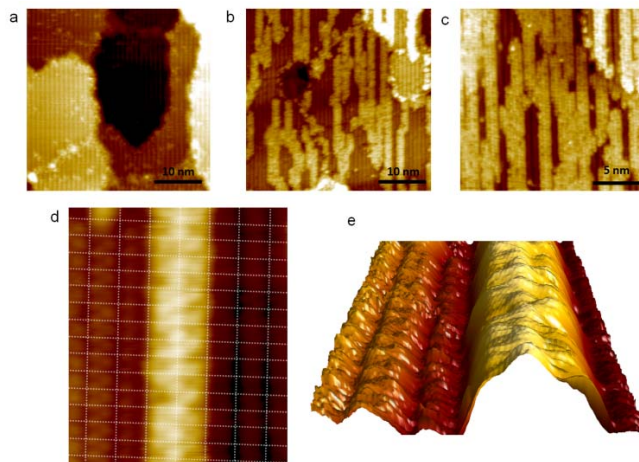
FIG. 2. STM of acetic acid adsorption on TiO$_2$(011) surface. a) For small acetic acid exposures, adsorption only occurs at surface defect sites. b) With increasing acetic acid exposure quasi-1D acetate clusters are formed that eventually cover most of the surface c). A detailed structure of the acetate clusters are shown in d). The dotted lines indicate the substrate 2×1 unit cell with the vertical lines aligned with the troughs. e) Quasi-3D view of an acetate cluster, highlighting the increased height of the center row protrusion.

To understand the adsorption behavior of acetic acid at TiO$_2$(011), we performed extensive DFT calculations. Surprisingly, we found that adsorption of a single acetic acid molecule on the vacuum prepared TiO$_2$(011)-2×1 surface is quite weak with an adsorption energy of only 0.45 eV/molecule and dissociative adsorption of acetate is not possible on this low energy surface. This is in agreement with the notion that the vacuum-reconstruction removes dangling bonds. It would also explain the experimental observation of the heterogeneous adsorption of acetate, which indicates low or no adsorption of acetic acid on defect free surfaces and initial adsorption only to occur at defects. However, it does not explain the formation of strongly bound extended acetate clusters for larger acetic acid exposures. It should be noted that intermolecular interactions, such as H-bonding and van der Waals effects, have been previously identified as means of increasing adsorption energies and as the reason for the formation of adsorbate clusters [10]. These are weak interactions, though, and cannot explain the thermal stability of the acetate clusters up to 500 K. Therefore the only reasonable explanation to explain the formation of extended acetate clusters is that the substrate does not maintain its vacuum termination underneath of the acetate but instead restructures to enable stronger bonding to the substrate.
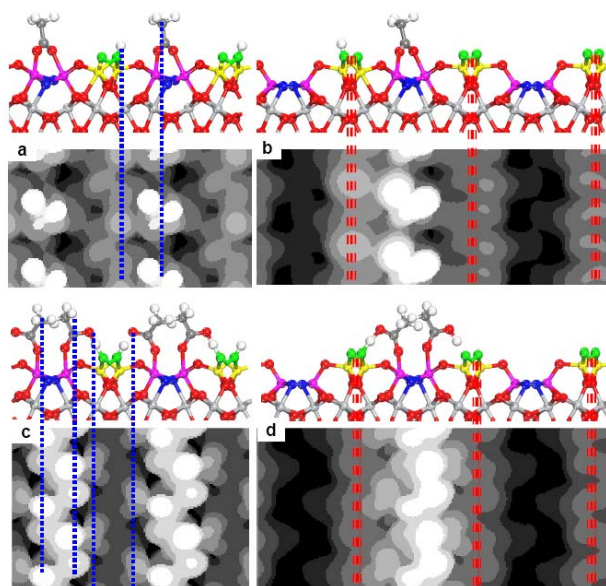
FIG. 3 (color online). Calculated structures (top row) and corresponding simulated STM images (bottom row) of acetic acid adsorbed at the a), c) fully restructured 2×1 (Fig. 1c) and b), d) partially restructured rutile TiO$_2$(011) in a), b) bidentate and c), d) monodentate configurations. The C atoms are in dark grey and H in white. The dotted lines show the alignment of surface species with protrusions in STM.

From the large number of surface structures examined in our DFT modelling, one low energy structure closely related to the most stable vacuum 2×1 surface can be identified. As shown in Fig. 1c, this new surface is constructed from the vacuum structure (Fig. 1b) by shifting the Ti$_{5c}$ cation row in the trough back to its position in the bulk truncated surface (Fig. 1a). This operation reduces the coordination of these Ti cations from 5-fold to 4-fold, and in the optimized structure, the O ions in the same trough raise up and change from 3-fold to 2-fold, turning the bulk Ti below into 5-fold. As a consequence of the decreased coordination of these surface atoms, the total energy of the surface slab increases by 1.4 eV/surface cell, i.e. to an estimated surface energy of 0.87 J·m^{-2}. At the same time, it inevitably makes the surface much more reactive, and more importantly, such a restructuring scheme is strongly directional and have no influence on the neighbouring sandwich-like Ti$_2$O$_4$ units or any other surface structures farther away. Since the lateral movement of trough Ti cations is key to the surface transformation, it can only originate at pre-existing surface defects that provide sufficient space for such translation of the Ti cations. Such a heterogeneous nucleation of acetate clusters is consistent with the STM observations.

Acetic acid adsorbed on this surface can have multiple configurations and they all give very strong adsorption. At low coverage, one acetic acid can dissociatively adsorb in either a bidentate (Fig. 3a) or monodentate (Fig. S2b) configuration with an estimated adsorption energy as high as 1.70 or 1.43 eV. At higher coverage, two acetic acid molecules can adsorb together in a surface cell in monodentate configuration (see Fig. 3c), giving the total adsorption energy of 2.15 eV. Although the average adsorption energy of ~1.1 eV is lower than that of the single monodentate molecule (1.43 eV) due to repulsive interaction of neighboring methyl groups, it is still significantly larger than that at the vacuum surface (0.45 eV), which suggests that such denser packing of ad-molecules is possible at the restructured surface regions. Therefore, the adsorption energy of acetate on this restructured surface easily compensates for its higher surface energy and the whole system of surface plus adsorbate has a lower energy than if it remained as a vacuum termination. We have also built the (011) face with mixed surface structures in a bigger surface cell: 2/3 of it keeps the vacuum structure and only one trough restructures. The adsorption of acetic acid at this surface gave nearly the same configurations (see Figs. 3b and d) and total adsorption energies (1.78 and 2.15 eV, respectively), verifying the experimental observation that the adsorption induced restructuring can readily occur along just one trough.

Thus the directional restructuring dynamics of the substrate (along the $[01\bar{1}]$ crystallographic direction) as indicated in Fig. 1, explains the unusual quasi-one dimensional adsorbate clusters on $TiO_2(011)$. Simulated STM images of these acetate clusters are in reasonable agreement with the measurements. The methyl groups at the center of the trough always give the brightest features, while the surface OH beside the bidentate acetate or the hydroxyl O of monodentate acetic acid give less bright features (see Figs. 4, S3 and S4 [9]). It should be considered that acetic acid may actually adsorb in mixed mono- and bidentate configurations and the H coming from the bidentate acetate may occur on either side of the restructured trough. This is then reproduced in the experimental data showing one center protrusion in every unit cell, but only partial occupation of the outer rows (Fig. 2d). We also have performed preliminary calculations to determine the barriers of the adsorption induced restructuring. For the surface cell containing two small formic acid molecules, we systematically fixed the two trough Ti_{5c} at a set of translation-vectors along the path from their positions in the vacuum 2×1 reconstructed surface to the restructured surface. We did observe formic acid adsorption in these set of calculations, and from the plotted potential energy diagram, we estimated the barrier to be as low as 0.6 eV

[9]. This barrier is consistent with observations of carboxylic acid adsorption to occur at mild temperatures and more complex adsorption configurations including more than one carboxylic acid molecule may lower this barrier even further. It should also be noted that since the surface restructuring occurs under the synergic effect of group of adsorbate molecules, it could be still affected by kinetic factors such as temperature and strong intermolecular interactions.

One dimensional adsorbate clusters have also been observed for *PTCDA* [17] and our calculations show that this adsorption behavior may be expected for a variety of other adsorbates. The calculation results for the adsorption energies for different molecules on the restructured surface are summarized in Table I and adsorption structure models can be found in [9]. Interestingly, water adsorption is predicted to be rather stable on the restructured surface. Molecular, partial dissociated and fully dissociated water adsorption are very close in the computed adsorption energy, i.e. 1.94, 1.85, and 1.83 eV, respectively, for the highest possible local water coverage of 1 monolayer (ML), and importantly, these adsorption energies are considerably larger than the restructuring energy (1.4 eV/surface cell).

TABLE I. Calculated adsorption energies of different molecules at restructured rutile TiO₂(011)-2×1. The coverage (in ML) was measured with respect to the number of trough Ti of the surface.

	Acetic Acid	Acetic Acid	Acetic Acid	Water	Methanol	Formic Acid	Catechol
Coverage	1/2	1/2	1	1	1	1	1/2
E_{ad} (eV)	1.70	1.43	2.15	1.94	1.58	2.45	1.57
Figure	3a	S2b [9]	3c	S2c [9]	S2f [9]	S2g [9]	S2h [9]

Previous experiments of water adsorption on a vacuum prepared surface showed water adsorption to be only possible below 200 K. This agrees with the weak adsorption of water on the vacuum interface structure of TiO₂(011)-2×1 (E_{ad}=0.19 eV/molecule) [10]. The lack of restructuring for water adsorption under UHV conditions is explained by the fact that a full adsorption layer of water, or at least over a significant length of a trough region is needed in order for making the restructured surface (or trough) energetically favorable. Furthermore, at low temperatures kinetic barriers will prevent the restructuring of the surface. Consequently, a higher water pressure at room temperature is needed to observe the predicted restructuring through water adsorption experimentally. To confirm this assertion, we exposed the vacuum prepared TiO₂(011)-2×1 surface to purified water by fully opening a valve that connects the vacuum

chamber to a water filled glass vial. In this process the water pressure in the chamber exceeded 10^{-3} Torr (the limit measurable by the vacuum gauge) [18]. After evacuation of the water vapor, we did successfully observe quasi one-dimensional clusters in STM measurements as shown in Fig. 4. The water clusters are less stable than acetic acid clusters, which is consistent with the calculated adsorption energies (Table I). This weaker adsorption of water is apparent from the less ordered appearance of the clusters and the change of the cluster by repeated scanning with the STM-tip (see Figs. 4c-e). This may also lead to a (partial) removal of the water which than reveals the underlying substrate. While the substrate is clearly altered the structure cannot be resolved in this area (Fig. 4f).
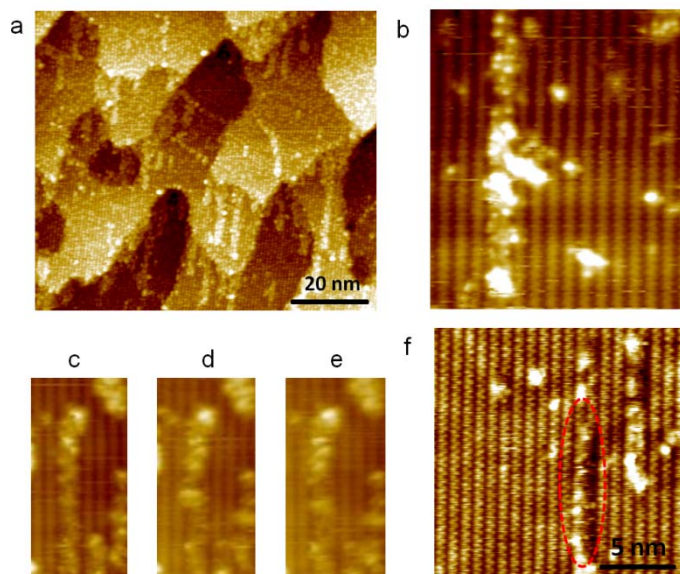

FIG. 4. Water adsorption on TiO$_2$(011) at room temperature. The STM images show the formation of one-dimensional clusters of unit-cell widths, a) and b). The tip effect in imaging clusters is clearly observable in the series of images shown in c) through e). The red dashed oval line in f) shows an area where the water cluster has been (partially) removed by the tip and the substrate is exposed.

In contrast to previously established structural relaxations [19] due to adsorbates or compositional changes [20] of metal oxide ceramics due to variation in the gas phase chemical potential, the current study shows that some metal oxides surfaces can also change their structural confirmation to enable adsorption and thus promote reactions that are not possible on the vacuum terminated surface. This discovery makes it now also conceivable that certain metal

oxide surfaces can have different structures for different adsorbates and therefore a single crystal orientation may exhibit unique chemical properties for different reactions and may even alter its physical properties which may affect light absorption and charge-transfer in photocatalysis. Furthermore, for extended surfaces it appears that the ability of the $TiO_2(011)$ surface to restructure along discrete quasi-one-dimensional atomic rows facilitates the restructuring process because (i) only a small energy cost is associated with the interface between restructured (adsorbate covered) and non-restructured (clean) domains, and (ii) it requires only few adsorbates to nucleate a restructured domain that then can 'unzip' the surface by further adsorption in one dimension. This directed re-structuring of the $TiO_2(011)$ substrate and consequent formation of extended quasi-one dimensional clusters may also be exploited for the formation of nanoscale nanostructures.

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