

## Surface Science Perspectives

## The many faces of rutile titania

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Titania has been extensively studied for over three decades since it was discovered in 1972 that it acts as a photocatalyst for the water-splitting reaction [1]. This led to a proliferation of surface science studies focused on single crystal rutile  $\text{TiO}_2(110)$ , as it is the most thermodynamically stable face [2]. This enormous body of work gives  $\text{TiO}_2(110)$  its status as *the* model substrate [3] with which to explore the surface science of metal oxides. The superb real space insights made possible by scanning probe microscopy have enabled this surface to be understood to an extraordinary level on the atomic-scale [3–9]. The article by Dulub et al. [10] in this issue of *Surface Science* employs the scanning tunneling microscope (STM) to image point defects on the  $\text{TiO}_2(011)$  surface. As with  $\text{TiO}_2(110)$  [3–7], the (011) face contains a rich array of defects. However, whereas the (110) surface is dominated by individual O-vacancies, to the extent that theoretical calculations suggest that O-vacancies repel each other [11], the results for the (011) surface indicate that the majority of O-vacancies lie in pairs with a smaller number arranged in triangles or linear arrays.

Theoretical calculations show that an ideal rutile  $\text{TiO}_2$  crystal is predominantly terminated by (110), (100), and (011) faces [2]. Thus, in order to advance the understanding of titania in real applications, it is imperative to expand our knowledge of both the (100) and (011) planes. An illustration of how the literature is skewed towards the (110) face is given with a search for single crystal rutile  $\text{TiO}_2$  studies in 2005 which gives 38 hits for the (110) surface, 6 for the (100) face, two for the (001) face, and only one for the (011) face.

Although lagging behind in detail and volume to the (110) studies, the (100) face is relatively well-understood [12–16]. Individual steps in the  $1 \times 1$  to  $1 \times 3$ -microfacet transition mechanism were imaged with STM and non-contact atomic force microscopy (NC-AFM) [16] with one of the intermediate phases proposed receiving some support from theoretical calculations [15]. On the  $\text{TiO}_2(110)$  surface, a series of high temperature STM and low energy electron microscopy movies give evidence for mass-flow during the transition from  $1 \times 1$  to  $1 \times 2$  surfaces [8,9,17,18]. The STM movies suggest that interstitial Ti species react at the surface of  $\text{TiO}_2(110)$  so that the crystal grows outwards in cycles of  $1 \times 1$  and  $1 \times 2$  terminations. Similar high temperature experiments could yield valuable insights into the  $\text{TiO}_2(100)$   $1 \times 1$  to  $1 \times 3$  phase transition.

The (111), (210), and (001) faces of rutile  $\text{TiO}_2$  are not exposed to any sizeable extent on rutile  $\text{TiO}_2$  crystals. However, these surfaces may still be important because they represent phases which could be engineered to be exposed in order to enhance or suppress some reaction. For instance, whereas formate anions bridge between two Ti sites on the (110) surface, because of the greater distances between Ti sites on the (111) surface, the formate appears to be coordinated in a mixture of monodentate and bidentate chelating configurations [19,20]. For the  $\text{TiO}_2(210)$  surface which lies formally between the (110) and (100) planes, atomic-scale rows were observed in STM and, with support from atomistic modelling, attributed to a sawtooth nanofacet model [21]. This model is similar to that initially proposed for the (100)- $1 \times 3$  reconstruction [12], whereby nanoscale (110) planes are exposed. As for the (001) surface, various terminations have been observed, two of which were attributed to (011) facets and (114) facets [22–25]. However, a more recent article suggests that the various terminations all result from combinations of (111) and (001) microfacets [26].

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Two things separate the (011) surface from the myriad other  $\text{TiO}_2$  surfaces described above. Firstly, previous work suggests that the (011) face of rutile  $\text{TiO}_2$  may have an enhanced activity towards water dissociation [27,28]. As such surfaces make up a large part of an ideal rutile crystal, this face of  $\text{TiO}_2$  may have a special importance for water dissociation. Secondly, as a result of pioneering work by Beck et al., a singular termination has been unravelled on  $\text{TiO}_2(011)2 \times 1$  [29]. A combination of theoretical modelling, STM, and simulations of STM suggest a surface terminated by titanyl groups ( $\text{Ti}=\text{O}$ ) which have not hitherto been observed on titania surfaces. Might this be responsible for the proposed enhanced reactivity of the  $\text{TiO}_2(011)$  surface? Water adsorption studies certainly suggest this is a possibility [30,31]. Water was shown to dissociate, forming hydroxyl groups on 30% of the titanyl groups on  $\text{TiO}_2(011)$  even without considering the effect of defects such as O-vacancies.

This contrasts sharply with the situation on the  $\text{TiO}_2(110)$  surface where recent studies have provided compelling evidence that O-vacancies play the pivotal role in the dissociation of water [4–6]. STM images recorded before and after water exposure in these experiments showed the O-vacancies being filled as the water molecules dissociate in them.

Returning to the article by Dulub et al. [10], the different arrays of O-vacancies are likely to have different reactivities to gases and vapours offering exciting possibilities for tuning the reactivity of the surface by controlling the relative densities of each type of defect. Indeed, the extended defects appear to be highly reactive, as evidenced by the adventitious adsorption of some impurity between consecutive images. As for the tuneability of the surface defects, the authors have already shown that the density of O-vacancies can be increased by increasing the degree of bulk reduction, in a similar way to that shown on the (110) face [4]. Conversely, preliminary experiments suggest that the density of O-vacancies can be dramatically reduced by re-annealing the vacuum-annealed surface in a pressure of oxygen. It would be interesting to test if these O-vacancies can be healed simply by exposure to  $\text{O}_2$  at room temperature, as has been observed on  $\text{TiO}_2(110)$  [4,5].

Another interesting feature of the surface is that it consists of added rows separated by relatively deep troughs. This means the surface may act as a template for one-dimensional growth of both molecules and metal nanoparticles. Preliminary results suggest that molecules and metal nanoparticles adsorb in the troughs. Whilst diffusion across these troughs is difficult, diffusion along the troughs is facile. Mild tunnelling conditions were required in order to prevent the tip from pushing adsorbates along these troughs. Larger currents or smaller bias enabled the adsorbates to be pushed along the troughs. Thus the (011) surface is a promising support on which to build nanostructures with the STM tip as well as being an exciting new model oxide surface.

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