Trellises of Molecular Oxygen on Anatase TiO$_2$(101)

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Supporting Information

ABSTRACT: The adsorption of molecular oxygen has important implications for the catalytic activity of oxide surfaces, especially for oxidative TiO$_2$ catalysts. In the case of anatase TiO$_2$(101), several studies have noted the importance of surface defects which stabilize the adsorption of oxygen molecules because of charge transfer. Further oxygen adsorption via this mechanism is precluded once a stoichiometric TiO$_2$ surface is attained. Here, the adsorption of oxygen molecules was re-enabled through a simple modification of sample cleaning procedures, resulting in the formation of a well-ordered trellis arrangement of oxygen molecules. The trellis is strongly passivating and does not affect the band gap of the pristine anatase substrate. Furthermore, they induce the extension of anatase terraces up to 100 Å wide. The atomic and electronic structures of the trellis were investigated using scanning tunneling microscopy experimentation and density functional theory calculations.

INTRODUCTION

TiO$_2$ is ubiquitous in environmental, energy, and biomedical applications because of its excellent structural, optical, and chemical properties.$^{1-3}$ One of the most exciting aspects of TiO$_2$ surface engineering is the ability to control the oxygen moieties on TiO$_2$ because they significantly impact the chemical, optical, and electrical properties of the native oxide.$^{4-7}$ On the stoichiometric TiO$_2$ surface, the O:Ti ratio is 2; however, the actual ratio varies strongly with specific surface preparation methods.$^{8-11}$ Cleaning procedures that entail sputtering and annealing in ultrahigh vacuum (UHV) typically result in oxygen-deficient surfaces with oxygen vacancies of variable concentration and distribution. Previously, we have shown that these oxygen vacancies can be assembled to cover large regions by increasing the temperature of the oxygen annealing step from 670 to 920 K.$^{12}$ Moreover, the surface properties can be modified by an additional mechanism which involves oxygen vacancies diffusing into the subsurface owing to their low diffusion barriers, where they still remain as active centers for chemical reactivity.$^{13,14}$ Besides studying these oxygen vacancies, the step edges are equally interesting because they are comprised entirely of assembled oxygen vacancies which are catalytically active.$^{12}$

Additional to the oxygen vacancies, other atomic defects in TiO$_2$ such as Ti interstitials and dopants introduce new properties to the TiO$_2$ surface. The fundamental physical properties, electronic structure, and manipulation mechanisms of such defects, as well as their chemical activities, continue to be important subjects of research.$^{15-18}$ Especially, molecular oxygen interacts with nearby oxygen vacancies through changing its oxidation state.$^{14,19,20}$ It is activated at a 5-fold-coordinated surface Ti atom (Ti$_{5c}$) and adsorbs as either a singly charged superoxo (O$_2^-$) or doubly charged peroxo (O$_2^{2-}$), depending on the availability of excess electrons.$^{14}$ The adsorption of neutral oxygen, however, is unknown because of its relatively low reactivity toward the stoichiometric anatase surface.

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In this article, we report on an unprecedented well-ordered network composed of neutral oxygen molecules on the anatase TiO$_2$(101) surface. All references to anatase in the foregoing text refer to this particular surface facet. Through simple modifications of a common surface-cleaning procedure, oxygen molecules were made to adsorb on anatase terraces and ordered into rhombic-shaped superstructures. These oxygen networks often expanded over step edges, producing new, exceptionally large terraces compared to those of the pristine anatase surface. Moreover, the oxygen network is chemically inert and does not introduce any gap states into the band gap of anatase.

## EXPERIMENTAL SECTION

The experiments were carried out in a home-built 5K scanning tunneling microscope (STM) using constant-current mode with a typical bias voltage of 1 V and a set point current of 0.05–1 nA. The STM tips were electrochemically etched Pt–Ir tips (N9801A) bought from Agilent Technologies, USA. The dI/dV spectra were obtained using a lock-in amplifier modulating the bias voltage at a frequency of 2.5 kHz above the cutoff frequency of the feedback loop with an amplitude of 20 mV.

We employed a naturally grown anatase TiO$_2$(101) single crystal which was polished to a surface roughness of less than one lattice constant (SurfaceNet GmbH, Germany). The size of the crystal was 4 × 4 × 2 mm$^3$ with a metallic, opaque color.

We prepared the crystal in situ in a preparation chamber (base pressure in the low 10$^{-6}$ mbar range) with two cycles of annealing in vacuum (970 K, 30 min) followed by Ar$^+$-sputtering (1 keV, sputtering current 2.2 μA, 10 min) and a postannealing step at a slightly reduced temperature (920 K, 30 min). Afterward, we annealed the anatase sample at 670 K for 5 min followed by backfilling the chamber with oxygen (670 K, 30 min, 1 × 10$^{-6}$ mbar). In the last step we annealed the sample in a residual oxygen atmosphere (~3–6 × 10$^{-9}$ mbar). The temperature ramp rate for heating was 2 K/s while that for cooling was slower at ~0.5 K/s.

The oxygen network was prepared by reducing the temperature of the oxygen annealing from 670 to 620 K and increasing the duration of the postannealing from 30 to 60 min at 620 K. The composition and the chemical state of surface constituents were determined by X-ray photoelectron spectroscopy (XPS) measurements (Figures S1–S3).

We complement our experiments with density functional theory (DFT) calculations, performed using the Perdew–Burke–Ernzerhof exchange and correlation functional, as implemented in the Quantum ESPRESSO software package. Only valence electrons were explicitly described, including the Ti 3s and 3p semicore states. The core–valence interaction was taken into account through ultrasoft pseudopotentials. The wave functions and charge density were represented through plane-wave basis sets with energy cutoffs of 35 and 200 Ry, respectively. Spin polarization was included in our calculations. Surface Brillouin zone integrations were carried out using 2 × 2 Monkhorst–Pack meshes. The anatase surface was modeled with a slab containing four layers of TiO$_2$. All structures were optimized with repeated conjugate-gradient minimizations until the forces on every atom were less than 0.04 eV/Å. The STM images were calculated within the Tersoff-Hamann approximation at constant current, by considering all electronic states within 1 eV from the conduction band edge.

We investigated the thermodynamic stability of the oxygen monolayer, in relation to the stability of the stoichiometric anatase (101) surface, and of an oxygen-deficient anatase (101) surface, by computing surface formation energies. These specific calculations were carried out with Hubbard corrections to the Ti 3d states. While this allows us to correctly describe the surface state of the oxygen-deficient phase, it introduces a small penalty in the energetics of the O$_2$ monolayer on TiO$_2$ as we do not include Hubbard corrections to the O 2p states of O$_2$ molecules. The Hubbard correction was included via a simplified rotationally invariant formulation. We used a Hubbard parameter of 3.5 eV (Ti 3d). The formation energy, $\Delta E$, was calculated from the equation $\Delta E = 1/A (E_{\text{slab}} - n \mu_{\text{Ti}} - m \mu_{\text{O}})$, subject to the following equilibrium conditions: (1) $\mu_{\text{Ti}} + 2 \mu_{\text{O}} = E_{\text{TiO}_2,\text{bulk}}$ and (2) $\mu_{\text{O}} < -1/2 E_{\text{O}}$. In these expressions, $E_{\text{slab}}$ is the total energy of the slab of the oxygen-deficient surface, stoichiometric surface, or oxygen monolayer; $A$ is the area of the surface unit cell; $\mu_{\text{Ti}}$, and $\mu_{\text{O}}$ are the chemical potentials of Ti and O, respectively; $n$ and $m$ indicate the number of Ti and O atoms in the slab, respectively; $E_{\text{TiO}_2,\text{bulk}}$ and $E_{\text{O}}$ are the total energies per formula unit of bulk anatase and of an isolated O$_2$ molecule, respectively. The thermodynamic relation between the oxygen chemical potential and the O$_2$ partial pressure at a certain temperature is given by the following expression: $\mu_{\text{O}}(T,P) = \mu_{\text{O}}(T,P^0) + 1/kT \ln (P/P^0)$. In this equation, $T$ is the temperature, $P$ is the partial pressure of O$_2$, $k$ is the Boltzmann constant, and $\mu_{\text{O}}(T,P^0)$ is the oxygen chemical potential at standard conditions, that is, $P^0 = 1$ atm. The oxygen chemical potentials at standard conditions are taken from thermochemical tables.

## RESULTS AND DISCUSSION

Figure 1a is a STM image of a pristine anatase surface showing characteristic trapezoidal terraces with step edges oriented along the [010], [11̅−1], and [−111] directions. For the preparation of a pristine anatase surface, a combination of sputtering, annealing, and oxygen annealing is required as described above. By reduction of the temperature of oxygen annealing, a trellis-like structure is created on the anatase surface (Figure 1b–d, detailed procedure in the Experimental Section). The network forms a superstructure with a rhombic unit cell of 7.4 × 7.4 Å$^2$ and a small angle of $\alpha = 83.5^\circ$ as revealed by Fourier-transforming (FT) the STM image of Figure 1b, shown in Figure 1c. The long diagonal of the rhombus is oriented along the [010] crystallographic direction of the anatase surface. Moreover, after the trellis structures are formed, large terraces of up to several hundred nanometers wide were observed (Figure 1b). These terrace widths are significantly larger than the typical 30 nm terrace widths found on the pristine anatase sample (Figure 1a).

A high-resolution STM topography of several patches of trellis on the anatase surface is shown in Figure 2. The isolated protrusions circled in green in Figure 2b are frequently observed surrounding the trellis structure (~7 Å), whereas almost no additional isolated protrusions are observed on top of the trellis structure, indicating that the trellis structure is chemically less reactive. The larger features at the network edge (blue arrows, ~8 Å) are typically shifted 3.7 Å from the lattice positions of the network (black dotted circle), which indicates that they are not bound tightly into the network. The smaller features at the network edge (yellow arrows, ~5 Å) coincide with the lattice points of the trellis structure (yellow
dotted circle). Some of the trellis extends until it reaches other trellis structures. We often found grain boundaries between two different network patches (marked with blue dotted lines in Figure 2d) that are connected but misaligned (marked with red dotted lines in Figure 2d) by the distance of exactly two neighboring Ti–O moieties in the anatase (101) lattice. Moreover, a closer inspection of the trellis structures reveals that the border between the trellis structure and the step edges of anatase is not aligned along the crystallographic directions of pristine anatase surface (red arrows in Figure 2a,c). The modified step edges appear only when the trellis structures reach the anatase step edges, indicating that the extension of the trellis structure induces the modification of anatase surface. Figure 2e, (i) and (ii), shows differential conductance measurements performed on the network (the red circle in Figure 2a) which reveals a featureless large band gap identical to that of clean anatase (101) (measured at the black circle in Figure 2a).

The composition and the chemical state of trellis structure were studied by XPS experiment (Figures S1 and S2). The Ti 2p and O 1s peaks in the XPS spectra suggest that the network consists solely of oxygen molecules. We also exclude surface impurities as the main cause for the observed structures because there was any change in impurity-related peaks before and after trellis structure formation.

To gain further insight into the trellis structure on the anatase (101) surface, a set of first-principles calculations were carried out. We first explored several atomistic models for a single oxygen molecule on anatase (101). In Figure 3a, the atomistic model with the lowest total energy is presented. We found that this model is slightly more stable than the model for a single oxygen molecule proposed by Setvin et al.14,20 by as much as 45 meV. Therefore, the model of Figure 3a is more likely to be the ground-state structure. For clarity, our model and the model proposed by Setvin et al. are compared in Figure S4. In our model (Figure 3a, Figure S4a) one of the oxygen atoms of the molecule sits atop a surface Ti 5c atom and the principle axis of the molecule is almost normal to the surface, while in Setvin’s model the axis of the molecule is parallel to the surface (Figure S4b). We simulated the STM image of the single O2 molecule in the adsorption geometry of Figure 3a, and our result is presented in Figure 3b,c. As we can see, it is in excellent agreement with round-shaped protrusion in our experimental data (green circles in Figure 2b).

After having analyzed the adsorption structure of isolated oxygen molecule, we now turn our focus to the oxygen adsorbed on step edges. The pristine anatase surface has step edges oriented along the [010], [11−1], and [−111] directions.1 It is well-known that the [−111] and [11−1] step edges are highly reactive and possess many defects, even after several cleaning cycles (Figure S5).12,24 After the trellis structures are formed, the highly reactive step edges appear in stripelike contrast (white arrows in Figure 2b) and are adsorbates-free. Considering that the step edges along the [−111] and [11−1] direction of the pristine surface are covered with oxygen vacancies,25 we believe that excess oxygen species (which dissociatively adsorb during preparation25) fill the vacancies of the step edges. We calculated the oxygen-decorated [−111] step edge (Figure 3d). The additional oxygen atoms on the step edge lead to the stripelike contrast that exhibits round protrusions between the Ti–O dimer rows (Figure 3e and red circles in Figure S6), which shows a close agreement with STM experiment (Figure 3f). We believe that the passivation of the chemically active step edges with oxygen will lead to an overall reduction of the surface reactivity.

Figure 1. Topography of trellis structure grown on TiO2 anatase (101). (a) STM image of a pristine surface. (b) STM image reveals a large-scale trellis structure (local coverage up to 95% of a monolayer). (c) A Fourier transform of the STM image shows that the trellis forms a rhombic superstructure with a unit cell of 7.4 × 7.4 Å and a small angle of α = 83.5°. (d) STM image enlarged from the red square in (b). (Scale bars: (a,b) 10 nm, (c) 1 nm, and (d) 5 nm.)
Regarding the oxygen network, several structural candidates were considered, as shown in Figure S7. Among all the models considered, the most stable structure is presented in Figure 4a. The anatase (101) surface is composed of 2-fold coordinated oxygen (O$_{2c}$) and 5-fold coordinated titanium (Ti$_{5c}$), while the bulk consists of 3-fold coordinated oxygen (O$_{3c}$) and 6-fold coordinated titanium (Ti$_{6c}$). Each adsorbed molecular oxygen is coordinated to two surface Ti atoms with one oxygen atom having a Ti−O distance of 2.9 Å while the other one has a Ti−O distance of 4.2 Å (inset Figure 4a), which is relatively long for a chemical bond. As presented in the ball-and-stick model in Figure 4a, every third surface Ti$_{5c}$ atom has no oxygen molecule adsorbed on it, resulting in a total surface Ti to adsorbed atomic O ratio of 3 to 2 (Figure S7b). Figure 4b shows the calculated STM image of the ball-and-stick model overlaid with the anatase (101) lattice. The main contribution to the density of states (DOS) of the network comes from the oxygen molecule which is far away from the surface. The thick white lines denote the two-dimensional (2D) rhombic Bravais lattice that describes the periodicity of the oxygen network in the STM image with a unit cell of 7.7 Å$^2$ and a small angle of $\alpha = 84.9^\circ$. This agrees well with our experimentally obtained values for the network structure in Figure 1c. In the simulated STM image in Figure 4b, the network displays a reduced DOS at the individual sites of the rhombus and an enhanced DOS (brighter) between the intersections, whereas our STM image displays the homogeneously distributed DOS of the oxygen network without change in electronic contrast. However, experimental STM images with a functionalized tip in Figure S8b strongly resemble the calculated STM images.

Figure 2. Higher resolution STM images of the trellis structures. (a) Trellis grown from a surface terrace. (b) Isolated protrusions are observed near the networks (green circles). We propose that, during sample preparation, the adsorbed species are mobile on the surface and can be incorporated into the network. This mechanism is supported by the presence of partially incorporated protrusions (blue and yellow arrows) near the network. The highly reactive step edges appear as striplike structures (white arrows). (c) The directions of the step edges are not following those of the typical anatase (101) step edge configuration, indicative of the etching of the TiO$_2$ surface. (d) A grain boundary occurring in larger network patches. (e) Tunneling spectroscopy obtained (i) on the pristine surface (black dot in (a)) and (ii) on top of the network (red dot in (a)) reveal the same featureless large band gap with no gap states. (Scale bars: (a) = 5 nm, (b) = 1 nm, (c) = 2 nm, and (d) = 1 nm.)
We observed that the tip frequently became functionalized during scanning above the trellis structure, leading to higher scanning contrast that revealed further details in the electronic structure.

We calculated the electronic structure of the oxygen networks on anatase (101) in Figure 4d. The black curves in the differential conductance spectra resemble the projected DOS of the anatase substrate. It shows a large featureless band gap of 2 eV, which is in qualitative agreement with experiment, considering the band gap overestimation by tunneling spectroscopy\textsuperscript{12} and underestimation by DFT-based calculations.\textsuperscript{13} The projected DOS of the oxygen network are depicted in red. The electronic feature of the network around −0.5 V coincides with the onset of the valence band (VB) of the substrate, while the feature around +1.8 V coincides with the conduction band (CB) of the substrate. Hence, the calculated electronic structure of oxygen network on anatase explains the strong similarity between the differential conductance spectrum obtained on top of the substrate and on the network shown in Figure 2e. The calculated Löwdin charges of the single oxygen molecule (with a value of 5.94 e on average) and of the O\textsubscript{2} molecules\textsuperscript{4} forming the monolayer (5.93 e) are very similar to those calculated for an isolated O\textsubscript{2} molecule (5.95 e). Furthermore, in the single O\textsubscript{2} molecule and O\textsubscript{2} monolayer the calculated O−O bond length (1.21 Å) matches closely to the experimental bond length of molecular O\textsubscript{2} (1.2 Å). These results further support the notion that the monolayer consists of electrically neutral O\textsubscript{2} molecules.

We investigate the thermodynamic stability of the O\textsubscript{2} monolayer on anatase (101), in relation to the stability of the pristine anatase (101) surface (abbreviated hereafter as O-terminated surface), and of the O-deficient anatase (101) surface (referred to as a Ti-terminated surface). The experimental observation of the Ti-terminated surface was
We often observed step edges saturated with defects which may stabilize adsorbed oxygen molecules. Taken all together, the molecular oxygen favors being trapped either at a step edge or on a surface Ti_{1c} in the vicinity of subsurface extrinsic donor atoms along the [010] direction. We often observed step edges saturated with oxygen molecules even at very low oxygen coverage (~0.1 ML). During the sample preparation at elevated temperatures, the oxygen molecules can diffuse and subsequently get incorporated into the network (blue arrows in Figure 2b). In our XPS spectra (Figures S1, S2, and S3), the peak position of the lattice oxygen ($E_B = 530.5$ eV) was preserved; that is, the binding energy shift due to the adsorption of charged oxygen molecules was not observed, which confirms that the majority of the adsorbed oxygen species are neutral. Additionally, the XPS peak indicating adsorbed atomic oxygen, which should appear at lower binding energy, was not observed. We also observed that the oxygen network is stable at room temperature.

At the step edges, the reorientation after oxygen adsorption is indicative of the oxygen-induced restructuring of the pristine anatase surface. The oxygen-induced surface restructuring on rutile TiO$_2$(110) was already reported. At typical oxygen annealing temperatures (500–600 K), the rutile crystal exhibits a diverse variety of surface restructurings that include formation of hexagonal rosettes, strands, and (1 × 1) islands. These surface structures result from the oxidation of Ti interstitials that diffuse from the bulk to the surface. In contrast to the rutile, titanium interstitials and oxygen vacancies are not stable at the surface of anatase and, instead, are energetically favored to exist only in the subsurface region. Moreover, the reoriented step edges are existing only when the oxygen network reaches the step edge, which indicates that the oxygen network initiates the etching of the anatase surface at the step edges. However, the detailed mechanism of how the reconstruction proceeds between the oxygen network and the step edges will require further studies.

On the basis of the calculated adsorption energy of neutral oxygen molecules, the adsorption structure should not exist at 670 K. However, previous research shows that subsurface defects stabilize adsorbed oxygen molecules irrespective of the exact nature of the charge donors in the subsurface region. Moreover, elevated temperatures enable the diffusion of these subsurface defects and any consequent reorientation of adsorbed oxygen molecules, which can bring about additional stabilization. Additional to the effect of the subsurface defect, our calculations (Figure S9) show that the trellis structure is energetically favorable over the pristine anatase surface, even at higher temperature, as long as the oxygen pressure is high enough.
CONCLUSIONS

In summary, self-organization of oxygen molecules on the anatase (101) surface is studied using STM and DFT calculations. STM images reveal a well-organized rhombic superstructure with a unit cell size of 7.4 × 7.4 Å. The molecular oxygen networks are chemically inert and do not affect the band gap of the pristine anatase substrate, hence making it suitable to serve as a surface-protecting layer. When we compare sample preparation procedures of the O-terminated, Ti-covered, and oxygen-network-covered TiO2 anatase (101) surface, the difference is brought about by just modifying the oxygen annealing temperature and O2 pressure. This comparison emphasizes the vast variation in surface morphology and surface chemistry accessible on the anatase (101) surface through simple modifications of the sample preparation conditions.

ASSOCIATED CONTENT

Supporting Information

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*C.D. and M.A.P.-O. contributed equally to this work. C.D. conducted the research with the help of S.M. and analyzed the data with S.J.J.; M.A.P.-O. performed the theoretical simulations under the supervision of F.G.; S.J.J. and K.K. supervised the project. All authors discussed the results and made critical contributions to the article.

Notes

The authors declare no competing financial interest.

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