The 2 × 1 reconstruction of the rutile TiO$_2$(011) surface: A combined density functional theory, X-ray diffraction, and scanning tunneling microscopy study

Xue-Qing Gong [a,*], Navid Khorshidi [b], Andreas Stierle [b], Vedran Vonk [b], Claus Ellinger [b], Helmut Dosch [b], Hongzhi Cheng [c], Annabella Selloni [c], Yunbin He [d], Olga Dulub [d], Ulrike Diebold [d]

[a] Labs for Advanced Materials, Research Institute of Industrial Catalysis, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, PR China
[b] Max-Planck-Institut für Metallforschung, Heisenbergstr., 3, D-70569 Stuttgart, Germany
[c] Department of Chemistry, Princeton University, Princeton, NJ 08544, USA
[d] Department of Physics, Tulane University, New Orleans, LA 70118, USA

ARTICLE INFO

ABSTRACT

An extensive search for possible structural models of the (2 × 1)-reconstructed rutile TiO$_2$(011) surface was carried out by means of density functional theory (DFT) calculations. A number of models were identified that have much lower surface energies than the previously-proposed 'titanyl' and 'microfaceting' models. These new structures were tested with surface X-ray diffraction (SXRD) and voltage-dependent STM measurements. The model that is (by far) energetically most stable shows also the best agreement with SXRD data. Calculated STM images agree with the experimental ones for appropriate tunneling conditions. In contrast to previously-proposed models, this structure is not of missing-row type; because of its similarity to the fully optimized brookite TiO$_2$(001) surface, we call it the 'brookite (001)-like' model. The new surface structure exhibits two different types of undercoordinated oxygen and titanium atoms, and is, in its stoichiometric form, predicted to be rather inert towards the adsorption of probe molecules.
© 2008 Elsevier B.V. All rights reserved.

1. Introduction

TiO$_2$ is a versatile material used for a wide variety of applications, most prominently for the harvesting of solar light for conversion into electrical energy and for photocatalysis [1,2]. Since these and many other applications involve the TiO$_2$ surface in a distinct way, the atomic and electronic structures of TiO$_2$ surfaces as well as their associated chemical and photochemical properties have been among the most intensely investigated subjects in surface science over the last decade [3]. While the lowest-energy surface, rutile TiO$_2$(110) is very well understood [4], and its structural determination has recently been refined [5,6], other phases and surface orientations of TiO$_2$ have been far less explored [7,8].

TiO$_2$ crystallites exhibit several surface facets, and pronounced differences in the photocatalytic activity have been reported for differently-oriented rutile TiO$_2$ surfaces [9–12]. In one report, the photo-induced oxidative and reductive half-reactions were observed to take place predominantly on the (011) and (110) surfaces of well-faceted TiO$_2$ microcrystals, respectively [11]. The need to understand such phenomena and the dearth of information on rutile (011) as compared to other TiO$_2$ surfaces has recently stimulated several surface science studies on single crystal TiO$_2$ (011) [13–18].

The bulk-terminated TiO$_2$ rutile (011)-1 × 1 surface shows an undulated surface topography with exposed two-fold O (O$_{2c}$) at the apices, five-fold Ti (Ti$_{5c}$) with dangling bonds at each sides, and bulk-like three-fold O (O$_{3c}$) at valleys (Fig. 1a). This (1 × 1) surface has never been observed experimentally, however. Instead, the surface forms a rather stable reconstruction with a (2 × 1) periodicity [13]. Based on atomically-resolved scanning tunneling microscopy (STM) images, which show a pronounced zig-zag structure, and first-principles density functional theory (DFT) calculations, the so-called 'titanyl' model was proposed as a likely surface termination (Fig. 1b) [13]. The distinctive feature of this structure with respect to other TiO$_2$ surfaces is that it is terminated by singly-coordinated O (O$_{1c}$) atoms each forming a Ti=O double bond with the underlying Ti atom (Ti$_{5c}$, Fig. 1b). From STM and photoemission experiments, it was established that (i) bombardment of TiO$_2$(011)-2 × 1 with electrons desorbs surface oxygen atoms and results in missing bright spots [16], (ii) water adsorbs in a mixed molecular/dissociated form at low temperatures, and the molecular water desorbs around 200 K [14,15], (iii) hydroxyls (formed via dissociation of water from the residual gas on O vacancies) are apparent as bright spots on bright zig-zag rows [15,17],

* Corresponding author. Tel.: +86 21 64253703; fax: +86 21 64252923.
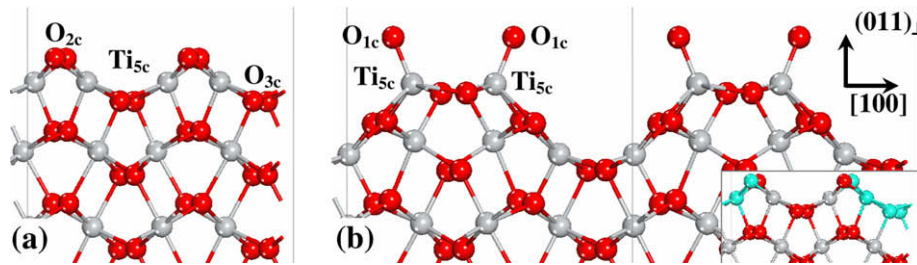*E-mail address:* xgong@ecust.edu.cn (X.-Q. Gong).

Fig. 1. Models for the TiO$_2$(011) surfaces (optimized structures in two neighboring surface cells, side view). Oxygen and Ti atoms are represented as red and gray spheres, respectively. (a) The unreconstructed TiO$_2$(011)-(1 × 1) surface. (b) The previously-proposed 'titanyl' model for the (2 × 1) reconstruction. This structure is obtained from the unreconstructed surface by removing the atoms shaded in light blue (b, inset) and relaxing the surface. (011)⊥ refers to the normal of the (011) surface. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

and (iv) adsorbates such as formic acid adsorb in between the bright rows [13].

While the titanyl model could explain these results in a satisfactory way, it was pointed out by us earlier that it is rather similar in surface energy to the (1 × 1) terminated surface [17], putting into question the driving force behind this particular reconstruction. Also, its validity has recently been challenged by Kubo et al. [18], who instead proposed a 'microfaceting' missing-row-type structure (Fig. 2a). Meanwhile, additional calculations by our group have revealed several structures with a (2 × 1) periodicity and significantly lower surface energies than the titanyl model (see Fig. 2b–d). In the present work, we test these structures with surface X-ray diffraction (SXRD), and voltage-dependent STM measurements. We in fact find that a new structure with a very low surface energy, and quite different from both the titanyl and the microfaceting models, agrees very well with the SXRD measurements (Fig. 2d), and with STM images under appropriate tunneling conditions. It is thus suggested that this new structure, which we term 'brookite (001)-like' model for its clear similarity with the fully relaxed brookite TiO$_2$(001) in structures, is a much better description of the geometry of TiO$_2$(011)-2 × 1, and should be useful for obtaining molecular-scale insights into surface chemical processes which occur at this interesting TiO$_2$ surface.

2. Theoretical and experimental details

2.1. DFT calculations

DFT calculations for the geometric and electronic structures of TiO$_2$ surfaces have been carried out within the generalized gradient approximation (GGA) using the PWscf code included in the Quantum-Espresso package [19]. Electron–ion interactions were described by ultrasoft pseudopotentials [20], with electrons from Ti 3s, 3p, 3d, 4s and O 2s, 2p shells explicitly included in the calculations. Plane-wave basis set cut-offs for the smooth part of the wavefunctions and the augmented density were 25 and 200 Ry, respectively. Calculated lattice parameters of bulk rutile TiO$_2$ are $a = b = 4.586$ Å and $c = 2.949$ Å, in good agreement with the experiment. The unreconstructed and various 2 × 1 reconstructed rutile TiO$_2$(011) surfaces were modeled in (2 × 1) surface cells, the Brillouin zone was sampled with a $1 \times 2 \times 1$ k-point mesh. The surface energies γ were estimated from total energy calculations on slabs of different thicknesses using the expression [21]

$$E_{slab} = nE_{TiO_2} + 2A\gamma, \qquad (1)$$

where E_{slab} is the total energy of the slab, E_{TiO_2} is the energy of a bulk TiO$_2$ unit, n is the number of TiO$_2$ units in the slab and A is the exposed area of one side of the slab (we used symmetric slabs so the two sides are equivalent). We considered slabs with at least 6 layers of the oxide, systematically increased the number of layers,

which in turn changed n in Eq. (1), and obtained γ from a linear fit of the computed values of E_{slab} vs. n (at least 3 points were considered). The energy of a bulk TiO$_2$ unit (E_{TiO_2}) can be also determined from this fit; the difference between the value of E_{TiO_2} obtained from this procedure and that directly obtained from a bulk TiO$_2$ calculation is generally within 0.005 eV. All the atoms in slabs were allowed to relax in structural optimizations until the residual forces were below 0.05 eV/Å.

Simulated STM images were calculated within the Tersoff–Hamann approach (TH) [22], under empty-state (positive sample biasing) conditions with a 1 eV energy window and a fixed distance of ∼2 Å above the highest O$_{2c}$. Lighter shadings in simulated images correspond to regions with denser unoccupied states. STM images were calculated up to distances of 3 Å and always showed the same general features.

2.2. SXRD experiments

The surface X-ray diffraction (SXRD) measurements have been performed at the MPI-MF beamline at the Angstrom Quelle Karlsruhe (ANKA, KIT) in z-axis diffraction geometry [23] with a photon energy of 10 keV. The experiments were carried out at room temperature in a dedicated portable UHV X-ray diffraction chamber which is equipped with a sputter gun and a sample heater. The commercially available TiO$_2$ samples showed a miscut of less than 0.1° from the (011) direction. Standard sputter/annealing cycles (1 keV Ar+ ion energy, 920 K) [15,17] were used for surface preparation.

Structure factors have been collected for a total number of 38 so-called surface Braggs rods, consisting of 20 surface rods which are sensitive to the (2 × 1) reconstruction and 18 crystal truncation rods (CTR) which interrogate its epitaxial relation to the underlying bulk TiO$_2$. After applying standard corrections [24] and averaging pg symmetry-equivalent rods, a dataset containing 573 structure factors with an average error bar of 16% was obtained. During the experiment, reference scans on the $(0, \bar{1}, 0.1)$ surface reflection were performed to ensure that surface structure is stable during the data acquisition time. Structure factors were calculated using the program package 'Rod' [25]. A monoclinic surface coordinate system was used with $a_S = 2a$, $b_S = c_S = \sqrt{a^2 + c^2}$ $\alpha = 65.585°$, $\beta = \gamma = 90°$, with $a = b = 4.593$ Å, $c = 2.958$ Å as the tetragonal bulk TiO$_2$ lattice constants. Note that in this coordinate system, the surface axis a_S points along the tetragonal a direction, c_S along the tetragonal real space [011] direction and b_S perpendicular to a_S as well as to the reciprocal c_S^* direction (which is perpendicular to the (011) crystal planes). The χ^2 value was calculated as the following:

$$\chi^2 = \frac{1}{(N - P)} \sum_N \frac{|F_{ex,N} - F_{cal,N}|}{\Delta F_{ex,N}} \qquad (2)$$