

## New Reconstructions of the (110) Surface of Rutile TiO<sub>2</sub> Predicted by an Evolutionary Method

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Reconstructions of the (110) surface of rutile TiO<sub>2</sub> (the dominant surface of this important mineral and catalyst) are investigated using the evolutionary approach, resolving previous controversies. Depending on thermodynamic conditions, four different stable reconstructions are observed for this surface. We confirm the recently proposed “Ti<sub>2</sub>O<sub>3</sub>-(1 × 2)” and “Ti<sub>2</sub>O-(1 × 2)” reconstructions and predict two new reconstructions “Ti<sub>3</sub>O<sub>2</sub>-(1 × 2)” and “Ti<sub>3</sub>O<sub>3</sub>-(2 × 1),” which match experimental results. Furthermore, we find that surface electronic states are sensitive to reconstructions and, therefore, depend on thermodynamic conditions.

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TiO<sub>2</sub> nanocrystals and low-dimensional materials are widely applied in the remediation of pollutants and photoelectron chemical conversion of solar energy [1,2]. In these applications, surface structures are the key to understanding reactivity and reaction mechanisms [3,4]. After sputtering or annealing samples in high vacuum at different temperatures, the rutile TiO<sub>2</sub>(110) surface reconstructs to (1 × 1) [5,6], single-linked (1 × 2) [7–9], cross-linked (1 × 2) [10,11], and pseudohexagonal rosette structures [12]. However, the exact atomic configurations are under debate, and this uncertainty hampers the understanding of related photocatalytic reactions.

Two models are being considered for the single-linked (1 × 2) reconstruction. The “Ti<sub>2</sub>O<sub>3</sub>-(1 × 2)” model adding Ti<sub>2</sub>O<sub>3</sub> stripes along the [001] direction was originally proposed by Onishi *et al.* [7,9]. However, later, the “Ti<sub>2</sub>O-(1 × 2)” model adding Ti<sub>2</sub>O stripes along the [001] direction was proposed by Park *et al.* [5,6]. The Ti<sub>2</sub>O<sub>3</sub>-(1 × 2) model was confirmed by low-energy electron diffraction investigations [8,13], while the Ti<sub>2</sub>O-(1 × 2) model was supported by a transmission electron microscopy investigation [14]. Consequently, atomic structures of the single-linked (1 × 2) reconstruction are under debate.

The formation of the cross-linked (1 × 2) reconstruction requires higher temperature than that of the single-linked (1 × 2) reconstruction [10], corresponding to an environment with a lower O chemical potential. From the thermodynamic viewpoint, the cross-linked (1 × 2) reconstruction should be more O deficient. However, the proposed “Ti<sub>3</sub>O<sub>6</sub>-(1 × 2)” model [10] losing an O-Ti-O unit is stoichiometric, which appears counterintuitive. In a previous study, the rosette reconstruction was regarded as an incomplete TiO<sub>2</sub> layer [12], but the atomic structure was

not fully resolved. Therefore, atomic structures of the single-linked (1 × 2), cross-linked (1 × 2), and rosette reconstructions are questionable.

To resolve these controversies, we performed a systematic study, searching for stable surface structures using the USPEX code [15–18], which has been successfully applied for predicting stable structures of bulk crystals [16], nanoclusters [17], surfaces [18], and polymers [19]. As a global optimization method, the USPEX code uses three ways (heredity, mutation, and transmutation) to produce next-generation surface structures, and the whole prediction requires hundreds or thousands of individual structure relaxations [18]. Each candidate surface structure is divided into vacuum, surface region, and substrate, and only the surface region is optimized [18]. In this way, surface structures can be explored efficiently, allowing for both structural and compositional variation.

In our calculations, at most, four multiplications of the unit cell (namely, 1 × 1, 1 × 2, 2 × 1, 1 × 3, 3 × 1, 2 × 2, 1 × 4, and 4 × 1) were considered, and maximally, two Ti and four O atoms were allowed for per surface unit cell. Each of the supercells contained a vacuum layer of 13 Å and a substrate slab of 4–5 TiO<sub>2</sub> layers with the top region of 3.5 Å being relaxed. We explored 1791 structures, or 40 generations, in the whole structure search. These structures were ranked according to the well-designed fitness function of Ref. [18]; the found structures contained added stripes (e.g., TiO, TiO<sub>2</sub>, Ti<sub>2</sub>O, Ti<sub>3</sub>O<sub>2</sub>, Ti<sub>2</sub>O<sub>3</sub>, or Ti<sub>3</sub>O<sub>3</sub>) and defects (such as O vacancy or Ti interstitial). Low-energy structures were selected for detailed analysis. The additional low-energy structures are given in the Supplemental Material [20], which may be observed experimentally. Slabs and the vacuum layer were increased to 6–7 TiO<sub>2</sub> layers and 15 Å,



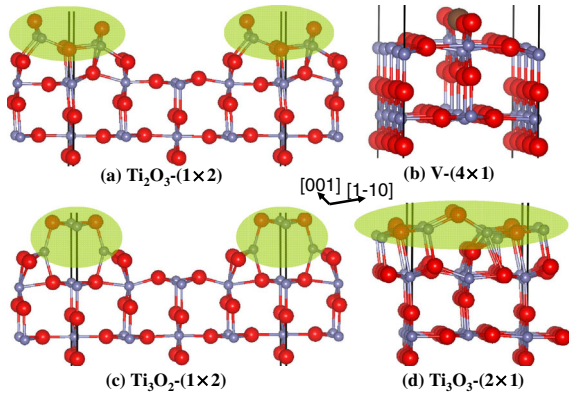


FIG. 2 (color online). Side views of stable structures of rutile  $\text{TiO}_2(110)$ : (a)  $\text{Ti}_2\text{O}_3-(1 \times 2)$ , previously proposed in Refs. [7,9], (b)  $\text{V}-(4 \times 1)$ , (d)  $\text{Ti}_3\text{O}_3-(2 \times 1)$ , as well as (c) metastable  $\text{Ti}_3\text{O}_2-(1 \times 2)$ . Ti and O atoms are represented by small gray and big red balls, respectively. An O vacancy in  $\text{V}-(4 \times 1)$  is represented by the dark gray ball. Structural features are highlighted by yellow shades.

[31,32].  $\text{V}-(4 \times 1)$  is a reduced rutile  $\text{TiO}_2(110)$  surface ( $\Delta n = -0.25$ ), containing a bridge oxygen vacancy [Fig. 1(b)]. Such defects were observed experimentally [23]. The predicted  $\text{Ti}_2\text{O}_3-(1 \times 2)$  reconstruction ( $\Delta n = -0.5$ ) adding  $\text{Ti}_2\text{O}_3$  stripes along the [001] direction is identical to the earlier proposed model [7–9,13]. As to the predicted  $\text{Ti}_3\text{O}_3-(2 \times 1)$  reconstruction [Fig. 2(d)] ( $\Delta n = -1$ ), its predicted dimensions are 6.5 and 6 Å along the [1–10] and [001] directions, respectively, which are the same as those of the rosette reconstruction [12], and we propose  $\text{Ti}_3\text{O}_3-(2 \times 1)$  to be the atomic configuration of the rosette reconstruction. Surface stoichiometries of our predicted reconstructions ( $\Delta n: 0 \rightarrow -1$ ) systematically change as a function of O chemical potential ( $\Delta\mu_{\text{O}}: 0 \rightarrow -4.96$  eV) from the unreconstructed rutile  $\text{TiO}_2(110)$  to  $\text{V}-(4 \times 1)$  to  $\text{Ti}_2\text{O}_3-(1 \times 2)$  to  $\text{Ti}_3\text{O}_3-(2 \times 1)$ . Clearly, surface reconstructions depend on thermodynamic conditions.

At each given stoichiometry, the stable structure tends to minimize the number of dangling bonds, as revealed through the analysis of structural geometry. Taking  $\text{Ti}_3\text{O}_3-(2 \times 1)$  as an example, more surface O atoms are three-coordinate than in the unreconstructed rutile  $\text{TiO}_2(110)$  surface: O atoms in the bulk are also three-coordinate. Several metastable structures [e.g.,  $\text{Ti}_3\text{O}_2-(1 \times 2)$  [Fig. 2(c)],  $\text{Ti}_2\text{O}-(1 \times 2)$  [Supplemental Material [20], Fig. 1(a)], “ $\text{TiO}-(1 \times 1)$ ” [Supplemental Material [20], Fig. 1(c)], and “ $\text{Ti}_3\text{O}_3-(1 \times 3)$ ” [Supplemental Material [20], Fig. 1(e)]] also have more surface O atoms in a threefold coordination, supporting our conclusion. As a wide-gap semiconductor,  $\text{TiO}_2$  has mixed ionic-covalent bonding, and, thus, the driving force behind reconstructions is complex for different low-index surfaces. For example, Kubo *et al.* reported that the reduction of dangling bonds leads to a reconstruction for rutile  $\text{TiO}_2(011)$  [33], while Lazzeri and Selloni concluded that the reconstruction of

anatase  $\text{TiO}_2(001)$  is stress driven [34]. The rutile  $\text{TiO}_2(110)$  has the lowest density of dangling bonds [33]. Therefore, stoichiometry deviations are necessary to cause reconstructions of rutile  $\text{TiO}_2(110)$ .

$\text{Ti}_2\text{O}-(1 \times 2)$  reconstruction adding  $\text{Ti}_2\text{O}$  stripes along the [001] direction is the same as the proposed model [5,6,14]. The predicted  $\text{Ti}_3\text{O}_2-(1 \times 2)$  [Fig. 2(c)] and  $\text{TiO}_2-(1 \times 2)$  [Supplemental Material [20], Fig. 1(b)] contain added  $\text{Ti}_3\text{O}_2$  and  $\text{TiO}_2$  stripes along the [001] direction, respectively. The predicted structures of  $\text{TiO}-(1 \times 1)$ ,  $\text{TiO}_2-(1 \times 1)$  [Supplemental Material [20], Fig. 1(d)] and  $\text{Ti}_3\text{O}_3-(1 \times 3)$ , correspond to the observed  $(1 \times 1)$  and  $(1 \times 3)$  reconstructions in experiments, respectively [5,35].

Scanning tunneling microscopy (STM) images were simulated by calculating electronic density of states over an energy window above the Fermi level, as done in previous studies [35,36]. For O-deficient structures, Ti atoms at surface are imaged because the Fermi levels locate at conduction band minima [35,36]. Accordingly, the obtained structural information is attributed to the arrangement of Ti atoms. Therefore, we consider the heights ( $H_{[110]}$ ) of the topmost Ti atoms relative to the underlying Ti-O layer and distances ( $D_{[1-10]}$ ) between surface Ti rows along the [1–10] direction for  $\text{Ti}_2\text{O}_3-(1 \times 2)$ ,  $\text{Ti}_3\text{O}_2-(1 \times 2)$ , and  $\text{Ti}_3\text{O}_3-(2 \times 1)$  reconstructions.

The simulated STM image of  $\text{Ti}_2\text{O}_3-(1 \times 2)$  [Fig. 3(a)] shows a single-linked pattern along the [1–10] direction, in agreement with the reported STM image of the single-linked  $(1 \times 2)$  reconstruction [Fig. 3(b)] [35]. Simultaneously, its  $H_{[110]}$  (2.87 Å) and  $D_{[110]}$  (3.70 Å) agree well with the corresponding experimental values (Table I) [7,10]. Both  $\text{Ti}_2\text{O}_3-(1 \times 2)$  and  $\text{Ti}_2\text{O}-(1 \times 2)$  were argued to correspond to the atomic structure of the single-linked  $(1 \times 2)$  reconstruction [5,6,8,13,14]. Certainly, the simulated STM image of  $\text{Ti}_2\text{O}-(1 \times 2)$  reconstruction also shows a single-linked pattern, but unlike  $\text{Ti}_2\text{O}_3-(1 \times 2)$ , it is metastable.

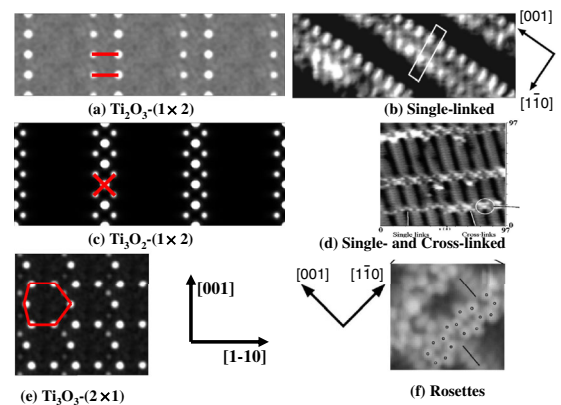


FIG. 3 (color online). Simulated STM images of (a)  $\text{Ti}_2\text{O}_3-(1 \times 2)$ , (c)  $\text{Ti}_3\text{O}_2-(1 \times 2)$ , and (e)  $\text{Ti}_3\text{O}_3-(2 \times 1)$ , where STM features are highlighted, as well as reported STM images of (b) single-linked  $(1 \times 2)$  [35], (d) single- and cross-linked  $(1 \times 2)$  [10], and (f) rosette reconstructions [12].

TABLE I. Heights ( $H_{[110]}$ ) of the topmost Ti atoms relative to the underlying Ti-O layer and distances ( $D_{[1-10]}$ ) between surface Ti atom rows along the  $[1-10]$  direction. “(exp)” denotes the corresponding experimental value.

Structure	$H_{[110]}$ (Å)	$H_{[110]}$ (exp)	$D_{[1-10]}$ (Å)	$D_{[1-10]}$ (exp)
Ti <sub>2</sub> O <sub>3</sub> -(1 × 2)	2.87	2.6–2.8 [10]	3.70	3.5–3.6 [7]
Ti <sub>3</sub> O <sub>2</sub> -(1 × 2)	4.19	4.0 [10]	...	...
Ti <sub>3</sub> O <sub>3</sub> -(2 × 1)	2.97	...	...	...

For the simulated STM image of Ti<sub>3</sub>O<sub>2</sub>-(1 × 2) [Fig. 3(c)], big bright round spots are surrounded by four small bright round spots together forming a cross-linked pattern, in agreement with the reported STM image of the cross-linked (1 × 2) reconstruction [Fig. 3(d)] [10]. Furthermore, its  $H_{[110]}$  (4.19 Å) is close to the experimental value (4.0 Å) [10]. Experimentally, the temperature of formation of the cross-linked (1 × 2) reconstruction is higher than that of formation of the single-linked (1 × 2) reconstruction [10]. The cross-linked (1 × 2) reconstruction is more O deficient than the single-linked (1 × 2) reconstruction, favoring Ti<sub>3</sub>O<sub>2</sub>-(1 × 2) reconstruction over the earlier proposed Ti<sub>3</sub>O<sub>6</sub>-(1 × 2).

For completeness, the earlier proposed “Ti<sub>3</sub>O<sub>5</sub>-(1 × 2)” [35] and Ti<sub>3</sub>O<sub>6</sub>-(1 × 2) [10] models (Supplemental Material [20], 2) were analyzed, and these turned out to be unstable or metastable according to our calculations. The Ti<sub>3</sub>O<sub>5</sub>-(1 × 2) reconstruction has indeed been questioned [37]. The Ti<sub>3</sub>O<sub>6</sub>-(1 × 2) model [10,11] is similar to Ti<sub>3</sub>O<sub>5</sub>-(1 × 2): both of them lose one of the O-Ti-O units, and new dangling bonds make them unfavorable.

In the simulated STM image of Ti<sub>3</sub>O<sub>3</sub>-(2 × 1) [Fig. 3(e)], bright round spots form a distorted hexagonal pattern, which is the same as the reported STM image of the rosette reconstruction [Fig. 3(f)] [12]. As mentioned, the dimensions of Ti<sub>3</sub>O<sub>3</sub>-(2 × 1) are the same as those of the rosette reconstruction, and its  $H_{[110]}$  (2.97 Å) is close to the reported value (about a monatomic step height, 3.24 Å) [12]. Consequently, Ti<sub>3</sub>O<sub>3</sub>-(2 × 1) is the rosette reconstruction.

Clearly, the predicted reconstructions agree with experimental results in STM patterns and structure parameters. Ideally, these reconstructions can be further confirmed by surface x-ray diffraction and transmission electron diffraction methods, which could provide atomic coordinates, such as on rutile TiO<sub>2</sub>(011) [38] and TiO<sub>2</sub>(100) [39]. To facilitate experimental studies, atomic fractional coordinates of the upper layers of the predicted reconstructions are given in the Supplemental Material [20].

Since  $\Delta\mu_o$  is a function of temperature and pressure, stable surface structures of rutile TiO<sub>2</sub>(110) change with temperature and pressure, as shown in Fig. 4. Experimentally, the unreconstructed rutile TiO<sub>2</sub>(110) surface formed under conditions  $\log(p/p^0) = -13$  and  $1000 \leq T \leq 1100$  K [31], which just falls into the white region of Fig. 4. Bridge-O vacancies were observed

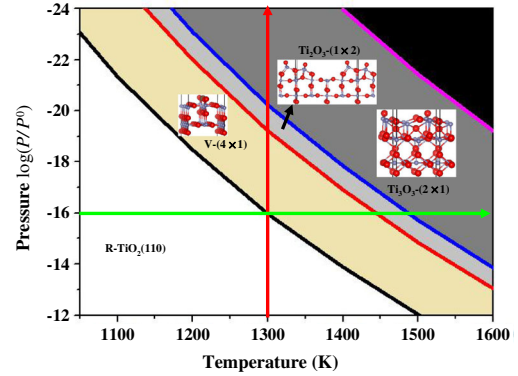


FIG. 4 (color online). Oxygen pressure-temperature phase diagram of the rutile TiO<sub>2</sub>(110) surface. Metal Ti deposition is favorable in the black region.

experimentally [23]. Here, they are demonstrated to have a stability field, since the V-(4 × 1) structure has a bridge-O vacancy.

Ti<sub>2</sub>O<sub>3</sub>-(1 × 2) is stable in a narrow temperature region (light blue region in Fig. 4). It should transform into Ti<sub>3</sub>O<sub>3</sub>-(2 × 1) upon increasing temperature or decreasing oxygen partial pressure. Experimentally, the single-linked (1 × 2) reconstruction [namely, Ti<sub>2</sub>O<sub>3</sub>-(1 × 2) or Ti<sub>2</sub>O-(1 × 2)] transformed into the cross-linked (1 × 2) reconstruction [i.e., metastable Ti<sub>3</sub>O<sub>2</sub>-(1 × 2)] upon increasing temperature [10]. We interpret this transition as driven by kinetics.

The densities of states (DOS) and band structures of stable reconstructions are illustrated in Fig. 5. Compared with the unreconstructed rutile TiO<sub>2</sub>(110) surface, gap states appear for Ti<sub>2</sub>O<sub>3</sub>-(1 × 2), Ti<sub>3</sub>O<sub>2</sub>-(1 × 2), and Ti<sub>3</sub>O<sub>3</sub>-(2 × 1) reconstructions, corresponding to electrons localized at surface Ti atoms. In other words, rutile TiO<sub>2</sub>(110) reconstructions have surface Ti<sup>3+</sup> ions, i.e., reduced Ti ions.

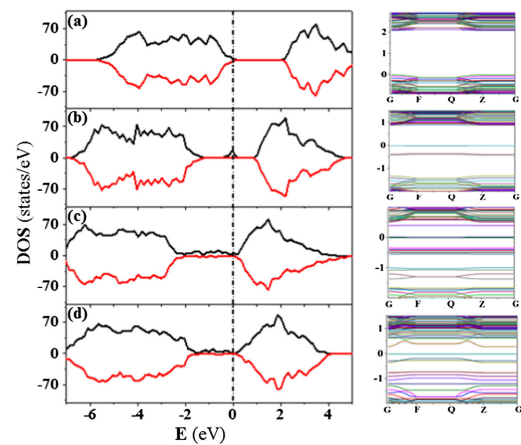


FIG. 5 (color online). DOS and band structures for (a) unreconstructed rutile TiO<sub>2</sub>(110), (b) Ti<sub>2</sub>O<sub>3</sub>-(1 × 2), (c) Ti<sub>3</sub>O<sub>2</sub>-(1 × 2), and (d) Ti<sub>3</sub>O<sub>3</sub>-(2 × 1), respectively. The vertical line at 0 eV is the Fermi level. The spin-up and -down states are represented by black and red lines, respectively.

The calculated band gap of bulk rutile  $\text{TiO}_2$  is 2.3 eV, to be compared with the experimental value of 3.0 eV [40]. The band gap of unreconstructed rutile  $\text{TiO}_2(110)$  is similar to that of bulk rutile  $\text{TiO}_2$ , being lower by just 0.2 eV. As shown in Fig. 5(b), deep donor energy levels are created for the  $\text{Ti}_2\text{O}_3-(1 \times 2)$  reconstruction; these which are occupied states. For the heavier reduced reconstructions, more gap states are created, leading to further reduction of the band gap. The computed (corrected for GGA +  $U$  underestimation) band gaps of the  $\text{Ti}_3\text{O}_2-(1 \times 2)$  and  $\text{Ti}_3\text{O}_3-(2 \times 1)$  are 1.50 (2.20) and 1.00 (1.70) eV, respectively. In contact with the environment, these gap states would be changed because of the interactions with exterior molecules (e.g.,  $\text{H}_2\text{O}$  molecules), due to orbital mixing and charge transfer. Therefore, environmental factors must be considered when investigating the effects of surface reconstructions on photocatalytic reactivity.

In conclusion, we present a complete and renewed understanding of stable reconstructions of rutile  $\text{TiO}_2(110)$  surface.  $\text{Ti}_2\text{O}_3-(1 \times 2)$  [8,13] and  $\text{Ti}_2\text{O}-(1 \times 2)$  [5,14] are found to be stable and metastable structures of the single-linked  $(1 \times 2)$  reconstruction, respectively. Our predicted  $\text{Ti}_3\text{O}_2-(1 \times 2)$  and  $\text{Ti}_3\text{O}_3-(2 \times 1)$  models correspond to the reported cross-linked  $(1 \times 2)$  [10] and rosette [12] reconstructions, respectively. Our work resolves previous controversies on this subject and will play an important role in the related surface engineering and explanation of experimental results.

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