Symmetry and Stability of the Rutile-Based TiO₂ Nanowires: Models and Comparative LCAO-Plane Wave DFT Calculations

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ABSTRACT: The rod symmetry groups for monoperiodic (1D) nanostructures have been applied for construction of models for bulk-like titania nanowires (NWs) cut from a rutile-based 3D crystal along the direction of a chosen crystallographic symmetry axis (in this study we consider only Ti atom-centered axes). The most stable [001]-oriented TiO₂ NWs with rhombic cross sections are found to display the energetically preferable {110} facets only, while the nanowires with quasi-square sections across the [110] axis are formed by the alternating {110} and {001} facets. For simulations on rutile-based nanowires possessing four different diameters for each NW type, we have performed comparative large-scale ab initio Density Functional Theory (DFT) calculations with total geometry optimization within the Generalized Gradient Approximation (GGA), using the two different formalisms: (i) linear combination of localized atomic functions (LCAO) and (ii) plane waves (PW). Both approaches have been used for calculations of: (a) the key properties of defectless rutile titania bulk (structure parameters a, c, and u, Ti–O bond lengths, and effective atomic charges q₉ and q₄ plus a band gap Δₑ₉) and (b) the structural and electronic properties depending on orientation, shape, and diameter of TiO₂ [001]- and [110]-oriented NWs (changes of diameters d_{NW} and unit cell lengths l_{NW} of nanowires during geometry optimization, correlated with difference of total energies per formula unit in a nanowire and bulk, as well as effective charges and band gaps). Values of d_{NW} slightly increase, whereas l_{NW} are found to be reduced after optimization, except for the thinnest [110]-NW (d_{NW} ~ 3 Å) for which the unit cell contains only three formula units, making it similar to a nanofilament. The larger the NW diameter, the closer its structural and electronic parameters are to those of rutile TiO₂ bulk. We have obtained the semiquantitative correlation between the results of DFT-LCAO and DFT-PW calculations.

1. INTRODUCTION

Metal oxide nanowires possess a well-defined one-dimensional (1D) monoperiodic crystalline structure, which makes them advanced materials for basic and applied research.¹ Titania nanowires (TiO₂ NWs) attract enhanced attention in modern nanotechnology due to a variety of promising applications such as humidity sensors, photovoltaic and photocatalytic cells, optical devices, field-effect transistors, etc.² TiO₂ NWs based on the rutile phase were mainly synthesized using thermal evaporation³ via vapor–liquid–solid and vapor–solid growth mechanisms, applying Ni or Au as a catalyst, and by chemical vapor deposition.⁴ Such titania nanowires were found to be single crystalline with diameters of 10–100 nm possessing the [110]⁵ and [001]⁶ orientations of growth. On the other hand, TiO₂ NWs were recently synthesized with diameters on the Ångström scale.⁷ In this case, nanowires show effects not present in the bulk, thus opening their new applications. A number of theoretical studies on atomic-scale TiO₂ nanowires have been published so far. Simulations on the formation energy for titania nanowires showed stability of structures assembled from Ti₃O₄ building blocks (with tetrahedral coordination of the Ti atoms instead of the usual octahedral one).⁸ Large-scale calculations on the thinnest filaments consisting of periodically repeated TiO and TiO₂ molecules along chosen 1D axes as well as on bulk-like TiO₂ [110]-oriented NWs were performed too.¹⁰ First-principles simulations indicated an increase in band gap values due to quantum confinement effects of hydrogenated rutile-based TiO₂ NWs with the [001] orientation.¹¹ In particular, [001]-oriented nanowires were cut along a central axis passing through Ti atoms (resulting in mirror plane symmetry but without screw axis in nanowires). Large-scale ab initio calculations on thermodynamically preferable TiO₂ NWs in the rutile phase clearly display only the energetically preferable {110} facets in the case of their [001] orientation as well as the alternating {110} and {001} facets in the case of [110] NW orientation, in accordance with the Wulff construction formalism.¹² The influence of O and Ti vacancies on energetic,
structural, and electronic properties of rutile-based titania [110] nanowires and their reactivity toward water molecules were evaluated as well. Two main reasons cause simulation of both [001] and [110] orientations of rutile-based TiO₂ NWs to be a necessity: (i) the thermodynamic contribution to nanowire stability is independent of NW morphology for diameters more than 10 nm as mainly synthesized experimentally (while ab initio calculations can be performed only for nanowires with diameters <5 nm) and (ii) the interface between a catalytic substrate and a nucleation titania seed should display rather low energy to surpass the nucleation barrier. This is why the [110]-oriented rutile-based TiO₂ NWs have been synthesized more frequently so far.

The structure and electronic properties of TiO₂ anatase-based nanowires were calculated as well, with different orientations and surface terminations varied as a function of diameter. In a recent study, the stability and electronic structure of both anatase-based and rutile-based [001] nanowires were compared for a series of first-principles calculations. With diameters of up to 2.1 nm in anatase-based and 3.7 nm in rutile-based nanowires, those {100}-walled anatase and {110}-walled rutile NWs were found to be the most stable, which retain the nonsymmetric character of the bulk space group. As for construction of 1D atomic models for titania nanowires, both the Ti atom- and hollow-centered symmetry axes (i.e., translation 2-fold rotation axis and 4-fold screw axis, respectively) were considered in recent studies.

The localized atomic function (LCAO) method, which is implemented in the CRYSTAL-09 code, allows one to describe single 1D nanowires, whereas the plane wave (PW) method, being implemented in a number of codes, not only the VASP, is more widespread for large-scale calculations on low-dimensional periodic systems. Indeed, to restore the 3D periodicity in the PW nanowire calculations, the 1D nanostructure supercell is artificially introduced; i.e., the NWs are placed into a square array with large enough intertube distances. At such separations, the NW-NW interaction is usually found to be rather small. However, the convergence of results obtained using DFT-PW calculations depends on the artificial interwire interactions, thus the additional computational efforts should be provided to ensure their negligibility. Such an artifact is certainly absent in the LCAO nanowire calculations. From this point of view, comparison of results obtained in DFT-LCAO and DFT-PW calculations can be very important for their verification.

In this paper, we apply the rod group symmetry for comparative Density Functional Theory (DFT) calculations on the rutile-based [001] and [110]-oriented TiO₂ nanowires with Ti atom-centered symmetry axes introduced within the formalism of localized atomic orbitals (LCAO) and plane waves (PW). In Section 2, we describe application of the rod group symmetry for construction of 1D models for energetically stable rutile-based TiO₂ NWs. Section 3 describes computational details as applied for comparative ab initio calculations using the Generalized Gradient Approximation (GGA) in the form of the Perdew–Becke–Ernzerhof (PBE) exchange–correlation functional. In Section 4, we compare parameters of the bulk rutile calculated using DFT-LCAO and DFT-PW methods with those obtained previously. Then we analyze results of the corresponding calculations of four models for each of [001] (rhombic shape) and [110] (quasi-square shape) rutile-based TiO₂ NWs comparing them again with analogous results calculated earlier. Section 5 summarizes the main conclusions obtained in the current study.

2. SYMMETRY OF RUTILE NANOWIRES

The symmetry of the rutile TiO₂ bulk structure can be described by a 3D tetragonal lattice and space group P4/nnm with the two titania formula units per the primitive cell (Figure 1). Nanowires are constructed as 1D systems cut from the 3D crystal along the direction of one of the bulk crystal symmetry axes. The translational periodicity is maintained along this direction. In the case of a rutile-based [001] titania nanowire, NW-1 (Figure 2), a direction of the translation axis is orthogonal to a pair of [110] and [110] vectors, while both titania formula units of the primitive cell lie in the two cross-sectional planes. For a rutile-based [110] nanowire, NW-2 (Figure 3), the translation axis is orthogonal to [001] and [110] vectors, while four TiO₂ units of the primitive cell lie in the six cross-sectional planes. In both nanowire types, the translation symmetry is maintained along the fixed symmetry direction of the bulk crystal, so that the symmetry of nanowires can be described by the monoperiodic (1D) symmetry group.

The monoperiodic groups are known as the commensurate line groups being the symmetry groups of 3D objects (i.e., stereoregular polymers, nanotubes). A total number of line groups is infinite as the translation axis is the rotation or screw axis of any integer order.

The symmetry of nanowires is described by one of the 75 rod groups (RG) which are known in crystallography as subperiodic subgroups of space groups (SG) and form the finite subset of the infinite number of line groups as the order of rotation or screw axes can be only the same as in a bulk crystal (1, 2, 3, 4, 6). Analogously to the space (three-periodic) and layer (two-periodic) groups, the rod groups are factorized RG = TF as an extension of the one-dimensional translation group T (invariant subgroup of RG) by the factor group F = RG/T. The subperiodic rod group RG can contain the following elements: translations α in one direction which by the convention is denoted as the z-axis; the 2-, 3-, 4- or 6-fold rotation or screw axis pointed in this direction; the rotation U around 2-fold axes perpendicular to it; reflection planes containing the translation vector (vertical planes σ₅) and reflection planes perpendicular to it (horizontal planes σₓ). Every RG is in correspondence with some three-periodic space group SG: it is a subgroup of SG and has the same isogonal point symmetry group (crystal class). To obtain RG, it is sufficient to keep translations only in one direction of a related SG. The related RG and SG groups have the same international notations.

Figure 1. Unit cell of rutile-based TiO₂ bulk.
One can find the information about rod groups on the Bilbao Crystallographic Server. These groups are specified by their number or by the international symbols. The first symbol $P$ (primitive) is the same for all rod groups as the translations are made along the principal symmetry axis, formally forming a primitive one-periodic lattice. Then, information about symmetry elements is given. The screw axis of order $q$ has a subscript $p$ ($p = 0, 1, 2, ..., q - 1$). The corresponding symmetry operations are rotations through $2\pi p/q$ around the $z$-axis. The reflection planes are denoted by $m$ (mirror planes) and $c$ (vertical glide planes containing the translation axis). The factor groups $F$ of rod groups (called in crystallography crystal classes) are isomorphic to axial point groups $C_q$, $D_{qh}$, $S_{2q}$, $C_{qv}$, $D_{2q}$, and $D_{qh}$. For $q = 1, 2, 3, 4, 6$, there are 31 different axial point groups, defining the crystal class of the related space and rod groups. The point groups $D_{1v}$, $D_{1h}$, and $D_{1k}$ are isomorphic to point groups $C_{1v}$, $C_{3v}$, and $C_{2v}$, respectively, while the point groups $C_{1k}$ and $C_{1v}$ are isomorphic to point group $C_{1}$.

This isomorphism is used in a crystallographic description of rod groups distributed over 27 crystal classes.

Being a subset of line groups, the rod groups can be distributed over 13 families as is accepted for the line groups. Each family is characterized by the isogonal point group (one of the seven axial point groups) and by the fractional translation along the translation axis or in the symmetry $\sigma_v$ plane.

At first, we consider the symmetry of a [001] rutile-based nanowire. Let the translation 2-fold rotation axis go through a Ti atom. From Figure 2, one can see that the reflection in the horizontal ($h$) plane (orthogonal to the translation axis) and rotations around the two second-order axes in this plane are the symmetry operations for rutile-based NW-1 nanowires. Therefore, the rod symmetry group of this NW is $P_{mmm}$.

The symmetry of a rutile-based [110] NW-2 coincides with the symmetry of analogous type of [001] NW-1 if the

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**Figure 2.** Cross-sectional (a) and lateral (b) images of nonoptimized large rutile-based titania [001]-oriented NW-1 possessing the Ti atom-centered $D_{2h}$ symmetry axis and containing 81 formula units per NW unit cell (UC), with aside (110) and (110) facets shown in b. Red rhombs in a show borders for prism models of middle, small, and smallest TiO$_2$ NWs (49, 25, and 9 formula units per UC, respectively). The diameter of a nanowire is shown by the twice-terminated arrow ($d_{[001]}$), while its period (length of UC) is shown in b as $l_{[001]}$.

**Figure 3.** Cross-sectional (a) and lateral (b) images of the nonoptimized large rutile-based titania [110]-oriented NW-2 possessing the Ti atom-centered $D_{2h}$ symmetry axis and containing 105 formula units per NW UC, with aside (001) and (110) facets (the former is shown in b). Red quasi-square rectangles in a show borders for prism models of middle, small, and smallest TiO$_2$ NWs (55, 21, and 3 formula units per UC, respectively). Diameter of a nanowire is shown by the twice-terminated arrow ($d_{[110]}$), while its period (length of UC) is shown in b as $l_{[110]}$.
translation axis with rotation by \( \pi \) goes through Ti atoms. Indeed, from Figure 3, one can see that the reflection in the vertical (\( v \)) plane (containing the translation axis) and rotation around the 2-fold translation axis in this plane are the symmetry operations for rutile-based \([110]\) NW-2. The symmetry operations include also rotations around the 2-fold axis in the horizontal (\( h \)) plane (orthogonal to the translation axis). Therefore, the rod symmetry group of the system is again \( Pmmm \) (number 20, belongs to family 11); i.e., the point symmetry of this nanowire is again \( D_{2h} \).

Analysis of the symmetry of nanowires is important as it allows the calculation of systems consisting of many (up to several hundred) atoms necessary for the NW modeling. Such a modeling requires the choice of nanowire facets defining the thickness of the nanowire and its stability. It is known that the most stable NW model corresponds to such a facet choice which describes the most energetically favorable surfaces of the bulk crystal. In the case of rutile-based structure, these surfaces are \([110]\).

### 3. COMPUTATIONAL DETAILS

Large-scale DFT-GGA-PBE LCAO calculations on rutile-based TiO\(_2\) nanowires with total geometry optimization have been performed using the CRYSTAL-09 computer code.\(^{15,17}\) A similar computational formalism was successfully applied by us earlier for the proper simulation on single- and double-wall titanatubes with anatase and fluorite morphology.\(^{23,24}\) An all-valence basis set (BS) in the form of 6s-311sp-1d Gaussian-type functions (GTFs) has been used for O atoms;\(^{25}\) for Ti atoms, the small-core effective-core pseudopotential (ECP)\(^{15}\) has been employed for internal shells, and the BS includes 16 valence (3s, 3p, 3d, 4s electrons) and virtual shells, i.e., GTF configuration is SC_ECP-5s-6sp-5d.\(^{26}\) Optimization of BSs for both O and Ti atoms was performed earlier,\(^{23}\) using the program package OPTBAS interfaced with the CRYSTAL code. To provide a balanced summation in direct and reciprocal lattices, the reciprocal space integration for titania nanowires has been performed by sampling the 1D Brillouin zone with the \( \Gamma \)-meshes. In the case of the rutile-based TiO\(_2\) bulk, the self-consistent procedure has been performed on the \( 6 \times 6 \times 6 \) Monkhorst–Pack\(^{27}\) \( k \)-meshes. To estimate effective atomic charges within the LCAO method, the Mulliken population analysis has been used.\(^{15}\)

For large-scale DFT-PW calculations on rutile-based titanatubes with total geometry optimization, we have employed the scalar relativistic pseudopotentials combined with the Projector Augmented Wave (PAW) method,\(^{29}\) as implemented in the VASP computer code.\(^{16,30}\) In current calculations, the same PBE-GGA nonlocal exchange-correlation functional\(^{17}\) has been used as in analogous DFT-LCAO calculations. The Monkhorst–Pack scheme for generation of \( k \)-point mesh in a reciprocal lattice\(^{27}\) has been set to \( 1 \times 1 \times 6 \), while the cutoff energy\(^{16}\) has been optimized to be 420 eV. The vacuum gap has been chosen by such a way that a distance between the nanowires of 7 Å was achieved, which has been found to be enough to ensure a negligible interaction between the neighboring NWs. This issue has been checked by varying the vacuum thickness and monitoring variations in total energy. In previous VASP calculations of rutile-based titania nanowires with Ti atom-centered symmetry axes,\(^{7}\) the total-energy ultrasoft pseudopotentials (USPP) method\(^{31}\) with PW basis set was applied, while exchange and correlation potentials were included using the generalized gradient approximation of Perdew and Wang (PW91).\(^{32}\) To estimate effective charge distribution on atoms within plane wave methods, the Bader analysis has been used.\(^{16}\) Results calculated in the current and a previous study using both DFT-PW approaches have been compared between themselves (in Tables 2 and 3) and with the data obtained in the corresponding DFT-LCAO calculations. From numerous possible shapes of symmetric prism models used for simulation of rutile-based titania nanowires,\(^{1,2,10,11,14}\) we have chosen the two energetically favorable configurations: square rhomb-type (Figure 2) and quasi-square rectangle-type (Figure 3) possessing Ti atom-centered symmetry axes. As found recently,\(^{2}\) just for these shapes of TiO\(_2\) NWs, the total nanowire energy per formula unit achieves minimum values. Only a limited number of studies performed so far considered not just bare titania nanowires but NWs with vacancies and their chemical reactivity,\(^{7}\) hydrogen-passivated NWs.\(^{11}\)

Such a restriction can be explained by reduced symmetry of defective NWs, down to the \( P1 \) rod group (\( C_1 \) point group), and thus by substantial growth of computational time. For the smallest defectless nanowires with \([001] \) and \([110] \) orientations (containing 9 and 3 formula units, respectively, as shown in Figures 2 and 3), we have analyzed the dependence of key optimized parameters (total energy per unit cell and NW period) on rod group set before the corresponding calculations (Table 1). It has been clearly demonstrated that qualitatively both parameters are similar, irrespective of the chosen symmetry. On the other hand, when comparing, for example, CPU time necessary for the parallel CRYSTAL calculations on the smallest \([001]\)-oriented titania nanowire performed using 24 processes of INTEL XEON 2 GHz computer cluster, we could observe a tremendous difference: 61 960 s for non-symmetric NW (\( C_1 \) group) vs 4887 s for maximum (8) symmetry operations (\( D_{2h} \) group). Analogous conclusions can be drawn also from DFT-PW parallel calculations performed using the VASP code.\(^{16}\)

Substantial expenditures of CPU time necessary for calculations on titania nanowires described by point group \( C_1 \)
are accompanied by noticeable limitation on NW size. The CRYSTAL code restricts a number of basis functions by 10 000,15 whereas the TiO$_2$ formula unit is described by 84 optimized functions (48 per Ti and 18 per O atoms). Thus, the maximum number of atoms per NW unit cell, which can be calculated using the DFT-LCAO method in the case of only one symmetry operation (C$_1$ group), is so restricted that we can calculate only the smallest and small [001]- and [110]-oriented TiO$_2$ nanowires (Figures 2 and 3). It means that calculations on defective titania nanowires cannot be performed for their corresponding data obtained earlier.

### Table 2. Structural and Electronic Properties of Optimized Rutile-Based TiO$_2$ Bulk (Figure 1)

<table>
<thead>
<tr>
<th>calculation method and reference source</th>
<th>lattice parameters</th>
<th>parameters of bonds and atoms</th>
<th>band gap $\Delta E_g$ eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT-LCAO-PBE</td>
<td>$a, \AA$</td>
<td>$\varepsilon, \AA$</td>
<td>$\mu$</td>
</tr>
<tr>
<td>DFT-PAW-PBE</td>
<td>4.647</td>
<td>2.980</td>
<td>0.306</td>
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<tr>
<td>DFT-USPP-PW91</td>
<td>4.619</td>
<td>2.964</td>
<td>0.305</td>
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<tr>
<td>results of other calculations</td>
<td>4.54–4.65$^{35}$</td>
<td>2.93–3.00$^{35}$</td>
<td>0.303–0.307$^{35}$</td>
</tr>
<tr>
<td>experimental data</td>
<td>4.593$^{33}$</td>
<td>2.958$^{33}$</td>
<td>0.305$^{33}$</td>
</tr>
</tbody>
</table>

**Table 3. Structural and Electronic Properties of Optimized Rutile-Based TiO$_2$ [001]-Oriented Nanowires (Figures 2 and 4)**

<table>
<thead>
<tr>
<th>nanowire size (number $N_{UC}$ of TiO$_2$ formula units per UC)</th>
<th>initial diameter of NW</th>
<th>optimized diameter (its change)</th>
<th>initial length of NW UC</th>
<th>optimized NW period (its change)</th>
<th>central atoms</th>
<th>corner atoms</th>
<th>total energy difference per formula unit</th>
<th>band gap [(its deviation from that of bulk, Table 1)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>9 (smallest)</td>
<td>11.122</td>
<td>11.493 (+3.33)</td>
<td>2.980</td>
<td>2.911 (−2.37)</td>
<td>-1.05</td>
<td>+2.11</td>
<td>-1.16</td>
<td>+2.17</td>
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<tr>
<td>25 (small)</td>
<td>20.240</td>
<td>21.720 (+2.32)</td>
<td>2.944</td>
<td>2.11 (−1.22)</td>
<td>-1.11</td>
<td>+2.19</td>
<td>-0.99</td>
<td>+2.16</td>
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<tr>
<td>49 (middle)</td>
<td>29.400</td>
<td>30.241 (+1.84)</td>
<td>2.956</td>
<td>2.08 (−0.81)</td>
<td>-1.08</td>
<td>+2.18</td>
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<td>+2.16</td>
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<tr>
<td>81 (large)</td>
<td>38.670</td>
<td>39.507 (+1.55)</td>
<td>2.963</td>
<td>2.10 (−0.57)</td>
<td>-1.10</td>
<td>+2.19</td>
<td>-0.99</td>
<td>+2.16</td>
</tr>
<tr>
<td>DFT-LCAO-PBE calculations$^{15}$</td>
<td>9 (smallest)</td>
<td>11.191</td>
<td>11.474 (+2.53)</td>
<td>2.964</td>
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<td>+2.21</td>
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<td>49 (middle)</td>
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<td>30.393 (+1.46)</td>
<td>2.967</td>
<td>2.08 (−0.10)</td>
<td>-1.08</td>
<td>+2.17</td>
<td>-1.03</td>
<td>+2.22</td>
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<tr>
<td>81 (large)</td>
<td>38.803</td>
<td>39.720 (+1.21)</td>
<td>2.972</td>
<td>2.08 (−0.27)</td>
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<td>+2.21</td>
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<td>+2.21</td>
</tr>
<tr>
<td>DFT-USPP-PW91 calculations$^{16}$</td>
<td>9 (smallest)</td>
<td>11.218</td>
<td>11.484 (+2.37)</td>
<td>2.981</td>
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<td>-1.06</td>
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<tr>
<td>25 (small)</td>
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<td>21.775 (+1.53)</td>
<td>2.963</td>
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<td>-1.10</td>
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<td>+2.23</td>
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<tr>
<td>49 (middle)</td>
<td>29.650</td>
<td>30.489 (+1.24)</td>
<td>2.969</td>
<td>2.09 (−0.40)</td>
<td>-1.09</td>
<td>+2.25</td>
<td>-1.03</td>
<td>+2.22</td>
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<tr>
<td>81 (large)</td>
<td>38.898</td>
<td>39.725 (+1.02)</td>
<td>2.973</td>
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<td>-1.16</td>
<td>+2.34</td>
<td>-1.03</td>
<td>+2.13</td>
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</tbody>
</table>

$^{a}$Difference of $E_{tot}/N_{UC}$ for the nanowire and bulk; i.e., zero at the energy scale corresponds to the total energy of rutile bulk, which is also defined as a relative formation energy.$^{14}$

4. RESULTS AND DISCUSSION

4.1. Rutile Titania Bulk. The structural and electronic properties of the rutile TiO$_2$ bulk calculated using DFT-LCAO-PBE$^{15,17}$ DFT-PAW-PBE$^{16,17,29}$ and DFT-USPP-PW91$^{15,31,32}$ methods as well as measured experimentally are presented in Table 2. Comparison of parameters for titania bulk calculated using different methods clearly shows qualitative correlation between themselves and their correspondence to the experimental values, although a certain dispersion of results (obtained using different methods) can be observed. It is also true for Ti–O bond lengths inside the first (I) and second (II) coordination shells consisting of four and two O atoms, respectively, around each Ti atom (Figure 1). Calculated values of the effective charges $q_{Ti}$ and $q_{O}$ look also quite reasonable, which are found to be qualitatively comparable with the corresponding data obtained earlier.

As for the large difference between the experimental and calculated values of band gaps ($\Delta E_g$), it is well-known that standard DFT calculations essentially underestimate $\Delta E_g$ for semiconductors and insulators. Our experience$^{25,24,35}$ demonstrates that only the hybrid exchange-correlation functionals, e.g., PBE0,$^{36}$ are able to reproduce the band gaps of nanostructures with relatively high accuracy. Nevertheless, DFT-PW-GGA methods have been found to be quite applicable for qualitative description of a number of properties for rutile-based TiO$_2$ NWs.$^{1,2,10,11,13,14}$

4.2. [001]-Oriented Titania Nanowires. Results of large-scale ab initio calculations on rutile-based rhomb-shaped titania [001]-oriented nanowires possessing four different diameters (Figure 2) with a full geometry optimization are systematized in Table 3, while Figure 4 shows the distorted structure of these NWs with the frozen initial symmetry $Pmmn$. Structural relaxation leads to an increase of optimized $d_{NW}$ and decrease of $l_{NW}$. The larger $d_{NW}$ is, the closer its equilibrium value to initial
nonoptimized $d_{NW}$ whereas $l_{NW}$ also approaches to the initial value of NW UC length. Figure 4 also demonstrates a decrease of NW distortion with increasing $d_{NW}$. At the edges and corners of [001]-oriented NWs, Ti–O bonds have been found to be

**Table 4. Structural and Electronic Properties of Optimized Rutile-Based TiO$_2$ [110]-Oriented Nanowires (Figures 3 and 5)**

<table>
<thead>
<tr>
<th>nanowire size (number $N_{UC}$ of TiO$_2$ formula units per UC)</th>
<th>initial diameter of NW</th>
<th>optimized NW diameter (its change)</th>
<th>initial length of NW UC</th>
<th>optimized NW period (its change)</th>
<th>effective atomic charges</th>
<th>total energy difference per formula unit</th>
<th>band gap (its deviation from that of bulk, Table 1)</th>
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<tr>
<td></td>
<td>$d_{NW}$, Å</td>
<td>$d_{NDT}$, Å ($\delta_{NDT}$, %)</td>
<td>$l_{NW}$, Å</td>
<td>$l_{NDT}$, Å ($\delta_{NDT}$, %)</td>
<td>$q_{Ti}$, $\epsilon$</td>
<td>$q_{Ti}$, $\epsilon$</td>
<td>$q_{O}$, $\epsilon$</td>
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<tr>
<td>3 (smallest)</td>
<td>2.958</td>
<td>2.882 ($-2.64$)</td>
<td>6.572</td>
<td>6.251 ($-5.14$)</td>
<td>$-1.05$</td>
<td>$+2.11$</td>
<td>$-1.16$</td>
</tr>
<tr>
<td>21 (small)</td>
<td>10.996</td>
<td>11.237 ($+2.19$)</td>
<td>6.377 ($-3.06$)</td>
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<tr>
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<td>20.094 ($+2.09$)</td>
<td>6.424 ($-2.30$)</td>
<td>$-1.11$</td>
<td>$+2.19$</td>
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<td>$+2.04$</td>
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<tr>
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<td>28.966 ($+1.88$)</td>
<td>6.452 ($-1.86$)</td>
<td>$-1.09$</td>
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<td>$-1.05$</td>
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<tr>
<td>3 (smallest)</td>
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<td>6.333 ($-3.14$)</td>
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<tr>
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<tr>
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<tr>
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<tr>
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<td>$+2.32$</td>
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</table>

*Difference of $E_{tot}/N_{UC}$ for the nanowire and bulk; i.e., zero at the energy scale corresponds to the total energy of rutile bulk, which is also defined as a relative formation energy.*

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**Figure 4.** Cross-sectional views of optimized rutile-based TiO$_2$ [001] NWs of smallest (a), small (b), middle (c), and large (d) diameters calculated using the DFT-LCAO method (parameters of relaxation are present in Table 3). Section planes for the present images are chosen the same as in Figures 2.
more covalent than those in the proximity of a nanowire axis or in the bulk (Table 3), thus explaining the appearance of structural distortion after geometry relaxation, e.g., shortening of corner and edge Ti–O bonds. These conclusions are confirmed by a consequent decrease of the difference between total energies per formula unit $E_{\text{tot}}/N_{\text{UC}}$ in TiO$_2$ nanowire and bulk. The latter confirms profiles of the corresponding energy curves approaching to zero. As for the change of band gaps with increasing $d_{\text{NW}}$, these values approach to $\Delta \varepsilon_g$ for bulk beginning with smaller gaps for the ultrathin NW. However, in several previous studies, the decrease of the calculated band gap with increasing $d_{\text{NW}}$ was observed. This issue occurs when TiO$_2$ NWs are terminated by hydrogen.

Comparison of results calculated for TiO$_2$ [001] NWs using DFT-LCAO and DFT-PW methods clearly shows their qualitative proximity (Table 3). Due to this, we show cross sections of optimized nanowires obtained in DFT-LCAO calculations only since no visible differences with those obtained using the DFT-PW method are observed. On the whole, this issue verifies the main conclusions made in the previous paper on energetic preference of rhomb-shaped titania nanowires that displayed only aside {110} facets.2

4.3. [110]-Oriented Titania Nanowires. Analogously to TiO$_2$ [001] NWs, we have performed also large-scale calculations on titania [110]-oriented NWs (Table 4 and Figure 5). It is important to find similarities and differences between properties of these types of structurally different TiO$_2$ NWs. The main qualitative conclusions for NW properties depending on $d_{\text{NW}}$ are found to be close.

Indeed, a distorted structure of [110]-oriented NWs possesses the same frozen initial symmetry $Pmmm$, although analysis of total energies per formula unit clearly demonstrates a preference of TiO$_2$ [001] NWs (cf. Tables 3 and 4). Structural relaxation leads to an increase of optimized $d_{\text{NW}}$ and decrease of $h_{\text{NW}}$ except for the ultrathin [110]-oriented NW which possesses only three formula units per UC (Figure 5a). This type of a nanowire can be rather attributed to a nanofilament whose properties noticeably differ from bulk-like nanowires which are mainly simulated by us in this study. Corner and edge Ti–O bonds are more covalent (Table 4) and slightly shorter than those in the proximity of symmetry axes of [110]-oriented NWs. The same is true for a change of band gaps with increasing $d_{\text{NW}}$ since these values approach to $\Delta \varepsilon_g$ for bulk beginning with the nanowire containing 21 formula units per unit cell. Detailed analysis of band structures for different diameters of both [001]- and [110]-oriented titania nanowires was done in a previous paper.2

When comparing results calculated for titania [110]-oriented nanowires using DFT-LCAO and DFT-PW methods, we can again observe their qualitative proximity (Table 3). This is why we show cross sections of optimized nanowires obtained in DFT-LCAO calculations only since no noticeable differences with those obtained using the DFT-PW method are observed. Obviously, energetic preference of rhomb-shaped titania [001] nanowires as compared to those obtained for [110] NWs can be explained by the fact that only each second lateral facet in the latter nanowire is energetically favorable {110}.2

5. CONCLUSIONS

1. In this study, the rod group formalism has been applied, to construct models for bulk-like titania nanowires (NWs) cut from the rutile-based 3D crystal along the direction of a chosen crystallographic symmetry axis. In this study, we have considered only Ti atom-centered axes. Meanwhile, the rutile-based NWs with a hollow-centered screw axis were earlier found to be more stable than those without it.14 Such a conclusion requires an additional study as the calculations of the relative formation energy for both types of NWs was performed for the diameter dependence of the total energy. However, the properties of rutile-based nanowires are both size and shape dependent.11 Therefore, the comparison of the nanowire relative stability requires
the calculation of the surface energy per formula unit as was done recently.\(^1\)

2. Our comparative ab initio calculations using DFT-LCAO and DFT-PW methods clearly demonstrate that more energetically preferable titania nanowires in the rutile phase (without hydrogen passivation and the presence of vacancies) display the [110] facets in the case of their [001] orientation and the [110] and [001] facets in the case of their [110] orientation. We have also shown morphology to affect stability of TiO\(_2\) NWs at very small diameters (<3 Å), while at larger diameters its role is attenuated.

3. Both methods have been used for calculations on key properties of defectless rutile titania bulk (i.e., lattice parameters \(a, c\) and \(u\)) correlated with difference of total energies per formula unit in nanowires and bulk, plus the corresponding band gap \(\Delta E_g\) as well as on structural and electronic properties depending on orientation, shape and diameter of TiO\(_2\) [001] and [110] NWs (i.e., changes of diameters \(d_{NW}\) and unit cell lengths \(l_{NW}\) of nanowires during geometry optimization as well as effective atomic charges correlated with formation energies per formula unit \(E_{\text{el}}\) and band gaps \(\Delta E_g\)). Since a few hybrid functionals are incorporated into the CRYSTAL-09 code,\(^{15}\) we do intend to perform the large-scale PBE0 calculations on titania nanowires, to obtain more realistic values of band gaps for both titania bulk and nanowires.

4. Values of \(d_{NW}\) slightly increase, whereas \(l_{NW}\) are found to be reduced after NW geometry optimization, except for the thinnest [110] NW (\(d_{NW} \sim 3\) Å) which UC contains three formula units making this nanostructure closer to the nanofilament. The larger the NW diameter is, the closer its geometry parameters as well as the band gap to those of rutile-based TiO\(_2\) bulk.

5. In the case of reduced symmetry applied for models of defective and adsorbate-covered titania nanowires,\(^1,11\) the number of formula units per NW unit cell is restricted by \(N_{UC}\) incorporated inside NWs of small and smallest diameters only, while computational time is substantially larger than for symmetric nanowires. Thus, we cannot consider for these cases models of middle and large [001] and [110] nanowires.

6. We have established a good quantitative correlation between results of DFT-LCAO and DFT-PW calculations on both titania bulk and nanowires.

## REFERENCES

(16) Kresse, G.; Furthmüller, J. VASP the Guide; University of Vienna: Austria, 2009.