Energetic stability and photocatalytic activity of SrTiO$_3$ nanowires: *ab initio* simulations†

Andrei V. Bandura,$^a$ Robert A. Evarestov$^a$ and Yuri F. Zhukovskii*$^{,b}$

First principles periodic calculations based on the density functional theory within the localized atomic orbital approach (DFT-LCAO) using the hybrid exchange–correlation potential PBE0 have been performed in order to simulate the structural and electronic properties of both stoichiometric and non-stoichiometric [001]-oriented four-faceted SrTiO$_3$ (STO) nanowires (NW) of cubic structure. Their diameters have been varied from 0.3 up to 2.4 nm with a corresponding consequent change of NW cross-section from $2 \times 2$ to $5 \times 5$ extension of the lattice constant in bulk. Energetic stability of STO NW (both stoichiometric and non-stoichiometric) has been found to increase with the decrease of their formation energies together with the increase of NW diameter. The electronic structure calculations have shown that the width of the band gap changes in STO NWs of different structural types as compared to that in bulk being consequently reduced with the growth of NW diameter although the character of such a decrease depends on the morphology of the nanowire. Analysis of these changes shows that stoichiometric and non-stoichiometric TiO$_2$-terminated strontium titanate nanowires can be quite promising candidates for further applications in photocatalytic processes under solar irradiation whereas SrO-terminated NWs are rather not suitable for this purpose.

1. Introduction

Recent advances in the science and technology of perovskites (ABO$_3$) and other ternary metal oxides (A$_2$B$_2$O$_7$) have resulted in the marked decrease of their sizes down to nanoscale dimensions which manifest an essential deviation from the properties of their 3D bulk and 2D film counterparts. The two most widespread technological applications determine permanently growing interest to A$_2$B$_2$O$_7$ nanomaterials. Firstly, as a result of ferroelectric transition, the equilibrium crystalline structure of these materials is expected to be non-cubic, mainly tetragonal (e.g., BaTiO$_3$, PbTiO$_3$) and trigonal (e.g., LiNbO$_3$). On the other hand, ternary oxides are suitable for the photocatalytic water splitting into H$_2$ and O$_2$ gas components under solar irradiation. Materials with perovskite cubic (CaTiO$_3$, SrTiO$_3$) and non-cubic, e.g., orthorhombic (NaNbO$_3$, KNbO$_3$) as well as hexoctahedral (Bi$_2$Ti$_2$O$_7$), equilibrium structures are found to be fitted for such applications. As compared to other 0D and 1D nanoscale structures, ternary oxide nanowires (NWs) possess a higher efficiency in ferroelectric and photocatalytic applications. A unique feature of nanowires is that they are two-dimensional quantum confinement, while still leaving one unconfined direction for the transport of carriers, due to the uniformity along the chosen crystallographic axis, strong dependence of NW properties on intrinsic size effects and configuration of lateral facets.

A number of electrochemical and thermochemical methods were used for synthesis of single-crystalline A$_2$B$_2$O$_7$ (e.g., SrTiO$_3$) nanowires: (i) sol–gel or aqueous routes for fabrication of ordered NW arrays inside nanoporous silicon or alumina used as templates, (ii) solution-phase decomposition of bimetallic precursor in presence of coordinating ligands, (iii) molten-salt technique, (iv) hydrothermal or solvothermal methods. Diameters of these NWs were found to be in range of 5–200 nm, while their lengths achieved several tens µm.

Numerous experimental studies were accompanied by several *ab initio* calculations (using mainly the density functional theory) on the structural and electronic properties of nanowires exhibited both the ferroelectricity (BaTiO$_3$ (ref. 13 and 14) and PbTiO$_3$ (ref. 15–17)) as well as the photocatalytic activity towards water splitting (Bi$_2$Ti$_2$O$_7$, SrTiO$_3$ (ref. 19) and CaTiO$_3$ (ref. 20)). Initial shapes of ternary metal oxide NWs mentioned above corresponded to square cross-sections chosen as: (i) non-stoichiometric, symmetrically terminated by either AO or BO$_2$ facets (PbTiO$_3$, SrTiO$_3$, CaTiO$_3$ (ref. 20)), (ii) stoichiometric, terminated by either two pairs of adjoining AO and BO$_2$ facets (BaTiO$_3$, Bi$_2$Ti$_2$O$_7$ (ref. 18)) or alternated AO and BO$_2$ facets (Bi$_2$Ti$_2$O$_7$ (ref. 18)), (iii) both non-stoichiometric and stoichiometric (BaTiO$_3$ (ref. 14)).

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Photocatalytic H₂ production under solar light irradiation of aqueous electrolytes in a presence of semiconducting electrodes (e.g., nanowires) might be a clean and renewable source for hydrogen fuel. Splitting of water molecules in this catalytic process generally involves four stages: (i) generation of electrons and holes by photoexcitation; (ii) charge separation and migration of the photo-generated carriers to the surface; (iii) recombination of the photogenerated electron–hole pairs during migration; (iv) subsequent reduction/oxygenation of the adsorbed reactants directly by electrons/holes or by reactive oxygen species. Efficiency of the water splitting reactions depends on both the semiconductor band gap width and the relative position of band gap edges (hole and electron energies) with respect to the redox (reduction or oxidation) levels, which are defined as measure of the affinity of the semiconducting substance for electrons (electronegativity) compared with the redox potentials, e.g., the Fermi level if $E_F > E_{CB\_bottom}$ (Fig. 8) of the p-type photocathode should be higher than the reduction potential H⁺/H₂, while the top of the valence band (VB maximum) of the n-type photoanode, should be lower than the oxidation potential O₂/H₂O: 

$$\Delta E = E_{CB\_bottom} - E_{VB\_top}$$

The width of band gap ($\Delta E$) can be regulated mainly by differently substituted dopants as well as vacancies, which made them to be fitted for visible-light range photocatalysis (within the energy range 1.23–2.50 eV (ref. 24)). Thereafter, positions of the edges of band gaps ($E_{CB\_bottom}$ and $E_{VB\_top}$) which must correspond to correlation of energy levels, can be effectively changed by structural reconstruction. Both experimental and theoretical studies suggest that the electron transfer between semiconductor surface and aqueous redox species can occur at their interface only when the two orbitals, one belonging to the semiconductor and a second one belonging to the aqueous species, are of similar energy.

Strontium titanate was well-known along ago as an effective catalyst for splitting H₂O molecules into H₂ and O₂ components in stoichiometric amounts in photoelectrode system consisting of two electrodes SrTiO₃ (anode) and Pt (cathode) in aqueous electrolytes with or without applied external potential. Among the different semiconductors used as photocatalysts, SrTiO₃ is a promising material due to its thermal stability and high resistance against photocorrosion. To increase specific areas of photoelectrodes and to modify their properties, they were mainly composed from SrTiO₃ powders or nanoparticles fixed at substrates. Pristine powder is directly active photocatalyst for water splitting under ultraviolet (UV) irradiation only whereas to achieve its visible-light sensitivity to solar irradiation, either chemical or structural modification of strontium titanate (or both together) must be done. For example, SrTiO₃ doped by various metal species (Cr–Ta, Mn and noble metal dopants, Pt, Rh and Cr–La) were found to be a highly active photocathode for sacrificial H₂ evolution under solar irradiation. On the contrary, for effective O₂-evolving photocatalysis in the visible-light range, BiVO₄ and WO₃ photoanodes in the presence or absence of electron mediators were suggested. In such a case, the two-step overall water splitting can be realized in the presence of suitable redox couple although for the latter, the two differently modified SrTiO₃ photoelectrodes were applied too (redox shuttle). Not only SrTiO₃ powders and nanoparticles, but also arrays of Ag-doped SrTiO₃ nanotubes studied experimentally were found to be photocatalytically active too.

Strontium titanate nanowires have been synthesized a number of times during the last decade. However, to the best of our knowledge, only two references on the experimental studies of their photocatalytic properties can be given: (i) mixed mesh film assembled from Ru-doped SrTiO₃ NWs and BiVO₄ NWs or mesh bilayer composed of the same types of nanowires (either Ru-doped SrTiO₃ or BiVO₄ NWs) separated between themselves, (ii) bundles of TiO₂ NWs covered by cubic SrTiO₃ nanoclusters each. Diameters of these types of synthesized nanowires were found within the range from several tens up to 100–150 nm. The only theoretical study of SrTiO₃ NWs found so far in literature has been performed recently using plane-wave DFT calculations on non-stoichiometric SrO- or TiO₂-terminated four-faceted nanowires described by $D_{4h}$ point group and oriented along [001] crystallographic axis. Surface atoms of these nanowires result in appearance of the electronic states inside the band gaps of SrTiO₃ NWs. In TiO₂-terminated NWs, mid-band states induced by the combination of O and Sr atoms positioned on the facets shift the top of the VB toward the conduction band, thus reducing the band gap as compared to SrTiO₃ bulk. These states have not been found interfering with the CB bottom, which plays an essential role for determining the driving force of H₂ evolution. In contrary, the electronic states induced by the combination O and Sr atoms (positioned on the facets) shift the CB bottom toward the valence band which excludes application of this type of SrTiO₃ NWs for photocatalysis.

To verify results reported in ref. 19 and to extend the notions on photocatalytic applications of strontium titanate nanowires in dependence on their structural and electronic properties, we have consequently performed in this study the large-scale periodic calculations based on the atomic orbital basis and hybrid exchange–correlation potential. We have simulated the structural and electronic properties of both stoichiometric and non-stoichiometric [001]-oriented four-faceted SrTiO₃ nanowires cut from cubic bulk structure. Their diameters have been varied from 0.3 up to 2.4 nm with a correspondance to a consequent change of NW cross-section from $1 \times 1$ to $5 \times 5$ extension of the lattice constant of bulk.

The paper is organized as follows. Atomistic models of both stoichiometric and non-stoichiometric SrTiO₃ NWs as well as details of methods to calculate their electronic and thermodynamic properties are discussed in Section 2. Main results obtained for optimized nanowires of different terminations and thicknesses are analyzed in Section 3. Discussion on possible photocatalytic applications of SrTiO₃ nanowires depending on their structure is given in Section 4 while the main conclusions are summarized in Section 5.
2. Theoretical background

2.1. Atomistic models of [001]-oriented SrTiO$_3$ nanowires

The symmetry of simple cubic (sc) structure for Ti-centered unit cell (UC) of SrTiO$_3$ bulk (Fig. 1) is described by the space group $Pm3m$ (point group $Oh$). Square-shaped Ti-centered non-stoichiometric nanowire with the smallest thickness ($1 \times 1$) cut from SrTiO$_3$ bulk can be considered as four-faceted [001]-oriented infinite prism, which unit cell with length $a_0$ is terminated by lateral SrO-containing square facets of nanocube imaged in Fig. 1, since its lateral facets {100}, {100}, {010}, and {010} possess the smallest surface energy among any other cubic STO facets. Analogously, non-stoichiometric ($1 \times 1$) [001]-oriented STO NW can be constructed from Sr-centered bulk UC. In this study, we consider $3 \times 3$, $4 \times 4$, $5 \times 5$ SrO- or TiO$_2$-terminated and simultaneously Sr- or Ti-centered non-stoichiometric SrTiO$_3$ NWs (Fig. 2a--f), then optimize their geometry and calculate their properties. All these [001]-oriented nanowires can be described by $D_{2d}$ point group, while for NWs axes, which contain O atoms only, the local symmetry is reduced to $D_{2d}$ point group.

In stoichiometric STO NW (Fig. 3), the two pairs of SrO-terminated and TiO$_2$-terminated adjoined facets form nanowire described by two mirror planes oriented along nanowire axis and cross-section diagonals so that $C_{2v}$ point group represents the NW symmetry. Models of stoichiometric SrTiO$_3$...
nanowires of different thicknesses (Fig. 4) have been constructed and calculated in this study as well. Geometry optimization has resulted in structural relaxation in proximity of NW corners.

2.2. Computational details

*Ab initio* calculations on [001]-oriented SrTiO₃ nanowires of different diameters described above, both non-stoichiometric and stoichiometric, have been performed within the periodic hybrid DFT-LCAO method, which utilizes localized Gaussian-type functions (GTFs) in the form of basis set (BS) for expansion of crystalline orbitals as linear combinations of atomic orbitals, implemented in CRYSTAL14 computer code using exchange–correlation functional PBE0 with 16% contribution of Hartree–Fock (HF) exchange. The all-electron basis set 6s-311sp-1d has been chosen for O atoms, while both the small-core relativistic effective core potentials (ECPs) and the corresponding BSs have been applied for Sr 111s-111p-1d and Ti 11111s-111111p-111111d which include sub-valence, valence and virtual orbitals. For optimization of O, Sr and Ti basis sets performed recently for STO bulk using original program OPTBAS, the Powell’s conjugate directions minimization method has been applied. To exclude BS linear dependence in LCAO crystal calculations, the diffuse s-, sp-, p- and d-orbitals with exponents less than 0.1 have been removed from the corresponding basis sets. As a result, the optimized lattice constant of cubic STO bulk (Fig. 1) has been found to be different from the experimental value by less than 1%.

The Brillouin zone for 3D cubic SrTiO₃ crystal has been sampled using Monkhorst–Pack 12 × 12 × 12 k-point mesh. For 1D STO NWs, this k-mesh has been reduced to 12 × 1 × 1 correspondingly. Tolerance of the energy convergence on the self-consistent field (SCF) cycles has been set to 10⁻⁶ a.u. (an extra-large pruned DFT integration grid has been adopted). Both spin-restricted and spin-polarized calculations on SrTiO₃ nanowires have been performed in the current study, the latter are especially important for non-stoichiometric nanowires. To evaluate the Coulomb and exchange series appearing in the SCF equations for periodic systems, five tolerances have been controlled: 10⁻³, 10⁻⁴, 10⁻⁵, 10⁻⁶ and 10⁻¹⁸ (related to estimates of overlap or penetration for integrals of Gaussian functions on different centers, which define cutoff limits for series summation). The full structural optimization has been performed for all aforementioned configurations of STO NWs (Fig. 2 and 4). Prismatic nanowires of chosen orientation and Miller indices of their lateral facets have been generated using keyword NANOROD implemented recently in CRYSTAL14 code.

2.3. Formation energy of stoichiometric and non-stoichiometric SrTiO₃ nanowires

The formation energy for stoichiometric and non-stoichiometric SrTiO₃ nanowires can be calculated within the unified approach using the chemical potential formalism. Let firstly consider the composition of the nanowires. The stoichiometric SrTiO₃ nanowires (Fig. 4) comprise the entire number of the bulk unit cells. For n × n NWs the number of STO formula units (FU) is n². In symmetric non-stoichiometric SrTiO₃ NWs of size n × n (Fig. 2), the overall NW composition can be represented as (TiO₂)ₙ(Ti₂O₃)(SrO)ₘ where k, l, and m are the integer numbers uniquely determined by the value of n and the type of the termination:

\[
\begin{align*}
    k &= n^2 + 2n - 1 \\
    l &= 1 \\
    m &= n^2
\end{align*}
\]

for TiO₂-terminated NW;

\[
\begin{align*}
    k &= n^2 - 2 \\
    l &= 1 \\
    m &= (n + 1)^2
\end{align*}
\]

for SrO-terminated NW.

The concrete values of k, l, and m for non-stoichiometric STO NWs are considered in Table 1.

The formation energy ΔGₜᵢᵢ of any object is defined in thermodynamics as the excess (free) energy in order to form an object from the substances i taken from the reservoir with chemical potential μᵢ:

\[
\Delta G_{\text{form}} = G - \sum_i N_i \mu_i.
\]

This definition obviously depends on the set of substances i chosen. Frequently, the separated atoms in the gas phase, or atoms in the elementary substance (solid/gas) are represented as the reference set. However, both those choices are not well applied to NW systems, mainly because of the relatively low accuracy of the energies calculated for isolated atoms and
metallic phases using the LCAO basis set chosen. Also, in this case the difference between two terms in the right side of eqn (2) can reach several tens of eV, which may lead to additional accuracy loss. Moreover, the coexistence of perovskite phases with Sr or Ti atoms in the gas phase or with Sr metallic phase can hardly be realized. Due to these reasons, we have selected subunits TiO$_2$, Ti$_2$O$_3$ and SrO as the reference constituents for calculation of the formation energies of SrTiO$_3$ NWs. This approach is similar to that used by Padilla and Vanderbilt in their study of SrTiO$_3$ surfaces. Consequently, to calculate the NW formation energy we use the following equation:

$$
DG_{\text{form}}(\text{NW}) = G(\text{NW}) - k \mu_{\text{TiO}_2} - l \mu_{\text{Ti}_2\text{O}_3} - m \mu_{\text{SrO}}.
$$

(3)

The stable oxide phases are considered as the reference states of subunits:

$$
\mu_X = G_X^0 + \Delta \mu_X,
$$

(4)

where $G_X^0$ is the molar (free) energy of the corresponding bulks ($X = \text{TiO}_2$, Ti$_2$O$_3$, SrO). In the oxygen atmosphere, the TiO$_2$ and Ti$_2$O$_3$ species are not independent, and we should take into account the equilibrium between them: $2\text{TiO}_2 \rightleftharpoons \text{Ti}_2\text{O}_3 + \frac{1}{2} \text{O}_2$. Thus, instead of TiO$_2$, Ti$_2$O$_3$ and SrO components we can consider the substances TiO$_2$, O$_2$ and SrO, and substitute $\Delta \mu_{\text{Ti}_2\text{O}_3}$ by $\Delta \mu_{\text{TiO}_2}$ as follows:

$$
\Delta \mu_{\text{Ti}_2\text{O}_3} = 2 \Delta \mu_{\text{TiO}_2} + 2 G_{\text{Ti}_2\text{O}_3}^0 - G_{\text{TiO}_2}^0 - \frac{1}{2} \mu_{\text{O}_2}.
$$

(5)

The chemical potential of the gaseous O$_2$ ($\mu_{\text{O}_2}$) can be introduced in the following form:

$$
\mu_{\text{O}_2}(T, P) = E_{\text{O}_2} + \Delta \mu_{\text{O}_2}(T, P);
$$

$$
\Delta \mu_{\text{O}_2}(T, P) = \Delta \mu_{\text{O}_2}(T, P_0) + kT \ln \frac{P}{P_0}
$$

(6)

where $E_{\text{O}_2}$ is the total (electronic) energy of the isolated oxygen molecule at $T = 0$ K, $P_0$ is the standard atmospheric pressure (1 bar), and $\Delta \mu_{\text{O}_2}(T, P_0)$ contains all temperature dependent free energy contributions at $P = P_0$ tabulated in standard thermochanical data tables.$^{45}$

Assuming the equilibrium of the nanowire with its own bulk,

$$
\mu_{\text{TiO}_2} + \mu_{\text{SrO}} = \mu_{\text{SrTiO}_3} = G_{\text{SrTiO}_3}^0;
$$

$$
\Delta \mu_{\text{TiO}_2} + \Delta \mu_{\text{SrO}} = G_{\text{SrTiO}_3}^0 - G_{\text{TiO}_2}^0 - G_{\text{SrO}}^0 = \Delta G_{\text{SrTiO}_3},
$$

(7)

and taking into account eqn (4)–(7), we can rewrite the eqn (3) as follows:

$$
\Delta G_{\text{form}}(\text{NW}) = G(\text{NW}) - (k + 2l - m)G_{\text{TiO}_2}^0 - mG_{\text{SrO}}^0 + \frac{1}{2} E_{\text{O}_2} -
$$

$$
- (k + 2l - m) \Delta \mu_{\text{TiO}_2} + \frac{1}{2} \Delta \mu_{\text{O}_2}(T, P).
$$

(8)

Under an equilibrium condition, the chemical potential can admit a limited value. For the thermodynamically stable STO NW, the variations of chemical potentials are restricted by possible NW disintegration due to formation of competing phases such as TiO$_2$, Ti$_2$O$_3$, and SrO. The extreme reduction conditions correspond to equilibrium between NW and Ti$_2$O$_3$ phase ($\Delta \mu_{\text{Ti}_2\text{O}_3} = 0$). Using eqn (8), we can obtain the NW formation energies for TiO$_2$–Ti$_2$O$_3$-rich point ($\Delta \mu_{\text{Ti}_2\text{O}_3} = 0$):

$$
\Delta G_{\text{form}}(\text{NW}) = G(\text{NW}) - (k - m)G_{\text{TiO}_2}^0 - lG_{\text{Ti}_2\text{O}_3}^0 - mG_{\text{SrO}}^0;
$$

(9)

and for SrO–Ti$_2$O$_3$-rich point ($\Delta \mu_{\text{Ti}_2\text{O}_3} = 0$):

$$
\Delta G_{\text{form}}(\text{NW}) = G(\text{NW}) - kG_{\text{SrO}}^0 - lG_{\text{Ti}_2\text{O}_3}^0 - (m - k)G_{\text{SrO}}^0.
$$

(10)

Basic DFT-LCAO calculations cannot give Gibbs free energy including entropy of vibration without additional methodology like frozen phonon method which is out of scope of the present study. It may be assumed that the entropy and volume contributions to the energy differences in eqn (8)–(10) are not large enough. Based on this assumption, the total energy per formula unit, $E_X$, of solid phase X obtained in DFT LCAO simulations is allowed to be substituted for molar Gibbs free energy of the corresponding phase, i.e., in first approximation $G_X^0 = E_X$. To estimate formation energies, the total energies of bulk TiO$_2$, Ti$_2$O$_3$, SrO and isolated O$_2$ molecule have been obtained within the same computational approach as specified in Subsection 2.2. Spin-polarized calculations have been performed for Ti$_2$O$_3$ bulk and isolated O$_2$ molecule.

In Table 1, we present the reduced formation energies $\Delta E_{\text{form}} = 2\Delta G_{\text{form}}/(k + l + m)$ calculated for non-stoichiometric NWs at TiO$_2$–Ti$_2$O$_3$-rich and SrO–Ti$_2$O$_3$-rich conditions. The scale factor $(k + l + m)/2$, which is the same for TiO$_2$- and SrO-terminated NWs, provides the proper comparison between both types of non-stoichiometric terminations and with stoichiometric NWs (see discussion below). Table 1 also shows that the content of Ti$_2$O$_3$ subunits is small and constant $(l = 1)$ in all the nanowires considered. Maximal stability at reduction condition is found for the SrO-terminated NWs in SrO-rich region.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Reduced formation energy of non-stoichiometric SrTiO$_3$ NWs at reduction conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanowire</td>
<td>$k$</td>
</tr>
<tr>
<td>TiO$_2$-terminated</td>
<td></td>
</tr>
<tr>
<td>$3 \times 3$</td>
<td>14</td>
</tr>
<tr>
<td>$4 \times 4$</td>
<td>23</td>
</tr>
<tr>
<td>$5 \times 5$</td>
<td>34</td>
</tr>
<tr>
<td>SrO-terminated</td>
<td></td>
</tr>
<tr>
<td>$3 \times 3$</td>
<td>7</td>
</tr>
<tr>
<td>$4 \times 4$</td>
<td>14</td>
</tr>
<tr>
<td>$5 \times 5$</td>
<td>23</td>
</tr>
</tbody>
</table>

$^a$ The average between TiO$_2$- and SrO-rich values is given for comparison with stoichiometric NW results (Table 2).
In the stoichiometric case \((k = m = n^2, l = 0)\), eqn (8)-(10) turn into the trivial form which does not depend on chemical potentials mentioned above, and the reduced formation energies can be calculated as usually:

\[
\Delta E_{\text{form}}^{\text{(NW)}} = E(\text{NW})n^2 - E_{\text{SrTiO}_3}. \tag{11}
\]

Formation energies of stoichiometric SrTiO\(_3\) NWs calculated using eqn (11) are given in Table 2. Comparison of these values with averaged values for non-stoichiometric SrTiO\(_3\) NWs, given in the last column of Table 1, shows that both cases exhibit similar stability at reduction conditions. More information can be achieved from the analysis of formation energy dependence on the chemical potentials. In Fig. 5, we show the dependence of reduced formation energy \(\Delta G_{\text{form}}\) for \(4 \times 4\) NWs on TiO\(_2\) chemical potential \(\Delta \mu_{\text{TiO}_2}\) at \(T = 298.15\) K and \(P_{\text{O}_2} = P_0\) calculated using eqn (8) and standard thermodynamic data\(^{47}\) for the oxygen gas phase. The TiO\(_2\) chemical potential is allowed to vary over the range: \(0 \geq \Delta \mu_{\text{TiO}_2} \geq \Delta G_{\text{SrTiO}_3}\). As expected, the TiO\(_2\)-terminated SrTiO\(_3\) nanowires are more stable at TiO\(_2\)-rich conditions whereas the SrO-terminated NW more stable at SrO-rich conditions. For comparison, we depict the horizontal lines corresponding to \(4 \times 4\) and \(5 \times 5\) stoichiometric SrTiO\(_3\) nanowires. This clearly shows that at low values of \(n\) the stoichiometric nanowires are more favorable than non-stoichiometric nanowires in the middle range of \(\Delta \mu_{\text{TiO}_2}\). However, the SrO-terminated nanowires are found to be preferable in SrO-rich region (as follows from the left area of Fig. 5).

As mentioned above, present calculations on SrTiO\(_3\) nanowires cannot provide the strict description of dependence of their formation energy on pressure and temperature, unlike their evident dependence on NW diameter. However, the analysis of oxygen gas phase contribution demonstrates that those terms have a relatively low influence on the calculated formation energies, due to the low fraction of Ti\(_2\)O\(_3\) subunits \((l = 1)\) in overall nanowire composition. Indeed, contribution of the temperature-dependent term estimated at 1000 K is equal to 5 kJ mol\(^{-1}\). The sign of these contributions is the same for TiO\(_2\)- and SrO-terminated NWs. Growth of the oxygen pressure reduces the stability of non-stoichiometric nanowires and does not affect the stability of stoichiometric nanowires.

### 3. Main electronic properties of SrTiO\(_3\) nanowires

#### 3.1. Non-stoichiometric STO NWs

While Table 1 describes the dependence of formation energies for various non-stoichiometric SrTiO\(_3\) nanowires on their terminations and thicknesses, then Table 3 gives for them the optimized values of NW diameters \(d_{\text{NW}}\) and UC lengths \(l_{\text{NW, UC}}\) as well as “band gap” widths \(\Delta \varepsilon_{\text{gap}}\) defined as \(\varepsilon_F - \varepsilon_{\text{VB, top}}\), i.e., differences of the Fermi levels crossing the conduction bands (Fig. 6) and the tops of the corresponding valence bands. Obviously, \(\Delta \varepsilon_{\text{gap}}\) here is not a regular band gap because it corresponds to a distance between the occupied states. We discuss only results of spin-polarized calculations on the non-stoichiometric STO NWs with SrO and TiO\(_2\) terminations as more realistic for systems with non-zero total spin moment.

Analogously to rutile-phase TiO\(_2\) NWs of different orientations and terminations calculated by us previously using the same DFT-LCAO PBE0 Hamiltonian,\(^{26}\) dependences of \(\Delta d_{\text{NW}}\) and \(\Delta l_{\text{NW, UC}}\) on TiO\(_2\)-terminated SrTiO\(_3\) NW thicknesses are found to be qualitatively similar, i.e., the larger is the NW diameter the smaller an increase of \(d_{\text{NW}}\) and decrease of \(l_{\text{NW, UC}}\) as compared to those in non-optimized NW structures. In contrary, \(d_{\text{NW}}\) of SrO-terminated SrTiO\(_3\) nanowires decreases with the growth of thickness, although such a reduction is slowed down with larger values of diameter while \(l_{\text{NW, UC}}\) is reduced down to UC length for non-optimized NW structure. It means that the structural parameters of STO NW approach to those in correspondingly sectioned SrTiO\(_3\) crystal with increase

<table>
<thead>
<tr>
<th>Nanowire</th>
<th>Number of formula units per unit cell</th>
<th>(\Delta E_{\text{form}}), kJ mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>1 × 1</td>
<td>1</td>
<td>508</td>
</tr>
<tr>
<td>2 × 2</td>
<td>4</td>
<td>263</td>
</tr>
<tr>
<td>3 × 3</td>
<td>9</td>
<td>178</td>
</tr>
<tr>
<td>4 × 4</td>
<td>16</td>
<td>134</td>
</tr>
<tr>
<td>5 × 5</td>
<td>25</td>
<td>108</td>
</tr>
</tbody>
</table>

![Fig. 5](image-url) Reduced formation energy of non-stoichiometric TiO\(_2\)- and SrO-terminated 4 × 4 (Fig. 2) as well as stoichiometric 4 × 4 and 5 × 5 (Fig. 4) SrTiO\(_3\) nanowires vs. TiO\(_2\) chemical potential \(\Delta \mu_{\text{TiO}_2}\) is considered at \(T = 298.15\) K and \(P_{\text{O}_2} = P_0\).
of $d_{\text{NW}}$. In particular, a length of NW unit cell approaches to bulk unit cell parameter $a_0$ (Fig. 1). Obviously these results correlate with decrease of formation energies $\Delta E_{\text{form}}$, depending on increase of $d_{\text{NW}}$ (Table 1) confirming a growth of NW stability with enlarging thickness.

The NW band widths decrease for both SrO- and TiO$_2$-terminated SrTiO$_3$ nanowires with growing values of $d_{\text{NW}}$ for $3 \times 3$, $4 \times 4$ and $5 \times 5$ thicknesses (Fig. 2) although values of $\Delta E_{\text{gap}}$ of the former are essentially larger than those in bulk (Table 3). Meanwhile, as compared to the band structures of non-stoichiometric $4 \times 4$ STO nanowires calculated earlier by plane wave DFT method, the values obtained in the current study (Fig. 6a and b) looks noticeably different. One of the most important differences is observed for $\Delta E_{\text{gap}}$ values which are essentially underestimated when using standard plane wave DFT methods, unlike hybrid DFT + HF LCAO method PBE0 used by us as described in Subsection 2.2. Moreover, essential differences can be observed in band distributions for both SrO- and TiO$_2$-terminated nanowires when using both first principle approaches. The band structure of Sr-terminated STO NW obtained in ref. 19 contains a deep explicit energy level inside the gap chipped off the CB bottom. Such a level has not been observed in our calculations at all (Fig. 6a and SI1a in ESI†). The shallow explicit band below the bottom of CB of TiO$_2$-terminated STO NW (Fig. 6b and SI1b in ESI†) has been found in our study to be completely populated. Most important result of our calculations is that the Fermi levels $E_F$ cross the CB bottoms for both terminations of STO NWs, i.e., a few virtual bands are partly populated and NWs become conducting. Therefore, aforementioned factors explain why the real values of interband gaps $\Delta E_{\text{gap}}$ obtained in the current study essentially exceed the band gaps discussed in ref. 19.

For different types of atoms positioned at either edges or centers of SrTiO$_3$ nanowires, their PDOSs are present for both SrO- and TiO$_2$-terminated STO NWs (Fig. 6a and b, respectively). In both cases, the bottoms of the conduction bands are crossed by the Fermi levels, thus increasing $\Delta E_{\text{gap}}$ values. In the former case, the top of the VB is predominantly composed of O(2p) spin-paired states at both NW center and facets while the bottom of the CB is mainly composed of Ti(3d) spin-unpaired states of outmost titanium atoms particularly accompanied by surface O(2p) states too (Fig. 6a). On the contrary, the top of the valence band in non-stoichiometric NWs with TiO$_2$ terminations is composed of O(2p) spin-paired states of oxygen atoms located on TiO$_2$-terminated facets (edges), while the bottom of the conduction band contains mainly Ti(3d) spin-unpaired states of titanium atoms at the NW center (Fig. 6b). These results clearly exhibit predominance of Ti(3d)-O(2p) bonds possessing ionic-covalent nature as compared to evidently ionic

### Table 3 Geometry and band structure of non-stoichiometric STO NW vs. termination and thickness

<table>
<thead>
<tr>
<th>Nanowire</th>
<th>$d_{\text{NW}}^{a} (\Delta d_{\text{NW}})$, nm</th>
<th>$l_{\text{NW, UC}}^{a} (\Delta l_{\text{NW, UC}})$, nm</th>
<th>$\Delta E_{\text{gap}}^{b}$, eV</th>
<th>$E_F$, eV</th>
<th>$E_{\text{VB, top}}$, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrO-terminated</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$3 \times 3$</td>
<td>$1.57 [-0.09]$</td>
<td>$0.387 [-0.004]$</td>
<td>$3.92$</td>
<td>$1.32$</td>
<td>$-2.60$</td>
</tr>
<tr>
<td>$4 \times 4$</td>
<td>$2.12 [-0.10]$</td>
<td>$0.388 [-0.003]$</td>
<td>$3.60$</td>
<td>$0.94$</td>
<td>$-2.65$</td>
</tr>
<tr>
<td>$5 \times 5$</td>
<td>$2.67 [-0.10]$</td>
<td>$0.389 [-0.003]$</td>
<td>$3.34$</td>
<td>$0.69$</td>
<td>$-2.65$</td>
</tr>
<tr>
<td>TiO$_2$-terminated</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$3 \times 3$</td>
<td>$1.74 [0.08]$</td>
<td>$0.374 [-0.017]$</td>
<td>$3.18$</td>
<td>$-3.09$</td>
<td>$-6.27$</td>
</tr>
<tr>
<td>$4 \times 4$</td>
<td>$2.28 [0.07]$</td>
<td>$0.379 [-0.012]$</td>
<td>$2.74$</td>
<td>$-3.30$</td>
<td>$-6.03$</td>
</tr>
<tr>
<td>$5 \times 5$</td>
<td>$2.83 [0.06]$</td>
<td>$0.382 [-0.009]$</td>
<td>$2.50$</td>
<td>$-3.42$</td>
<td>$-5.91$</td>
</tr>
</tbody>
</table>

$^{a} \Delta d_{\text{NW}}$ and $\Delta l_{\text{NW, UC}}$ are changes of diameters and UC lengths as compared to non-optimized NWs. $^{b}$ Values of $\Delta E_{\text{gap}}$ and $E_{\text{VB, top}}$ calculated for STO bulk: $3.08$ and $-4.00$ eV, respectively.
Sr(5s)-O(2p) bonds although the latter binding type affects the electronic structure of both types of non-stoichiometric NWs, which well correlates with the conclusion drawn in ref. 19. As to the populated explicit levels of TiO2-terminated NWs located at the vicinity of the bottom of the conduction band for the SrO-terminated nanowire, they mainly consist of edge states (Fig. 6a), while for SrTiO3 NWs, the explicit level of TiO2-terminated NW is composed mainly of edge states (Fig. 6e). The latter results can witness on local spin-unpaired Ti(3d) and partly O(2p) states generated by NW and SrO atomic planes. The upper value is for O ion in SrO atomic plane, and the lower value is for O ion in TiO2 atomic plane.

Results discussed when analyzing PDOS states are well-correlated with the values of the effective charges $q_{O\text{r}}$, $q_{Sr}$ and $q_{Ti}$ calculated in both NW centers and at their edges (Table 4). Except for edges of SrO-terminated NWs, in other nanowire configurations, strontium ion is very close to pure ionic Sr$^2+$ state, which practically excludes any Sr involvement in covalent bonding. Effective charges of titanium and especially oxygen ions are much more sensitive to their arrangement in nanowires, for example, while Sr-ionicity reduces when the oxygen positions change from the edges of SrO-terminated nanowires to the edges of TiO2-terminated STO NWs. For the fixed arrangement of oxygen or titanium ions, their effective charges have been found to be almost insensitive on value of $d_{NW}$.

Table 4 Mulliken charges of atoms (e) in centers and at edges of non-stoichiometric STO NWs

<table>
<thead>
<tr>
<th>Nanowire</th>
<th>$q_{Sr}$</th>
<th>$q_{Ti}$</th>
<th>$q_{O\text{r}}$</th>
<th>$q_{Sr}$</th>
<th>$q_{Ti}$</th>
<th>$q_{O\text{r}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrO edge</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO2 edge</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

SrO-terminated

<table>
<thead>
<tr>
<th>$3 \times 3$</th>
<th>1.95</th>
<th>2.28</th>
<th>$-1.46$</th>
<th>$1.85$</th>
<th>2.22</th>
<th>$-1.54$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$4 \times 4$</td>
<td>1.95</td>
<td>2.28</td>
<td>$-1.43$</td>
<td>$1.85$</td>
<td>2.22</td>
<td>$-1.54$</td>
</tr>
<tr>
<td>$5 \times 5$</td>
<td>1.95</td>
<td>2.28</td>
<td>$-1.42$</td>
<td>$1.85$</td>
<td>2.23</td>
<td>$-1.53$</td>
</tr>
</tbody>
</table>

TiO2-terminated

<table>
<thead>
<tr>
<th>$3 \times 3$</th>
<th>1.95</th>
<th>2.19</th>
<th>$-1.46$</th>
<th>$1.94$</th>
<th>2.09</th>
<th>$-1.24$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$4 \times 4$</td>
<td>1.95</td>
<td>2.22</td>
<td>$-1.45$</td>
<td>$1.94$</td>
<td>2.09</td>
<td>$-1.23$</td>
</tr>
<tr>
<td>$5 \times 5$</td>
<td>1.95</td>
<td>2.24</td>
<td>$-1.44$</td>
<td>$1.94$</td>
<td>2.09</td>
<td>$-1.23$</td>
</tr>
</tbody>
</table>

$^a$ The upper value is for O ion in TiO2 atomic plane, and the lower value is for O ion in SrO atomic plane.

3.2. Stoichiometric STO NWs

Unlike non-stoichiometric nanowires, Fig. 5 clearly demonstrates independence of the formation energies for stoichiometric SrTiO3 NWs on TiO2 chemical potential, keeping dependence on their thickness only. Moreover, $1 \times 1$ stoichiometric SrTiO3 NW is found to be energetically too unstable as compared to more thick nanowires (Table 2), and we do not consider this ultrathin NW configuration anymore. Table 5 describes the optimized values of $d_{NW}$, $l_{NW, UC}$, $\Delta \varepsilon_{gap}$, $\varepsilon_{CB, bottom}$ and $\varepsilon_{VB, top}$ for stoichiometric nanowires, analogously to Table 3 in previous Subsection. Since the total spin moment of stoichiometric SrTiO3 NWs is zero, the spin-restricted DFT-LCAO calculations of their properties have been performed. Similarly to SrO-terminated STO NWs (Table 3), both $d_{NW}$ and $l_{NW, UC}$ decrease with growing SrTiO3 NW thicknesses as compared to those in non-optimized NW structures. It means that the structural parameters of nanowire approach to those in corresponding sectioned SrTiO3 crystal with increase of $d_{NW}$. In particular, a length of NW unit cell approaches to bulk unit cell parameter $a_0$ (Fig. 1). Obviously, these results correlate with decrease of the formation energies $\Delta E_{form}$ while $d_{NW}$ increases (Table 1) confirming a growth of NW stability with enlarging thickness.

As to the band gaps of SrTiO3 nanowires, their widths are consequently reduced (Table 5) with growing NW thicknesses ($2 \times 2$, $3 \times 3$, $4 \times 4$ and $5 \times 5$ as shown in Fig. 4). Moreover, unlike partial conductivity of non-stoichiometric SrTiO3 nanowires observed in our calculations (Fig. 6), their stoichiometric counterparts remain semiconducting irrespectively on the value

Table 5 Geometry and band structure of stoichiometric STO NW depending on its thickness

<table>
<thead>
<tr>
<th>Nanowire</th>
<th>$d_{NW}^{a}$ (Å)</th>
<th>$l_{NW, UC}^{a}$ (Å)</th>
<th>$\Delta \varepsilon_{gap}^{b}$, eV</th>
<th>$\varepsilon_{CB, bottom}^{c}$, eV</th>
<th>$\varepsilon_{VB, top}^{c}$, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2 \times 2$</td>
<td>0.82 (−0.01)</td>
<td>0.379 (−0.012)</td>
<td>3.04</td>
<td>−1.60</td>
<td>−4.64</td>
</tr>
<tr>
<td>$3 \times 3$</td>
<td>1.37 (−0.01)</td>
<td>0.381 (−0.010)</td>
<td>2.41</td>
<td>−1.82</td>
<td>−4.23</td>
</tr>
<tr>
<td>$4 \times 4$</td>
<td>1.92 (−0.02)</td>
<td>0.384 (−0.007)</td>
<td>2.15</td>
<td>−1.92</td>
<td>−4.07</td>
</tr>
<tr>
<td>$5 \times 5$</td>
<td>2.47 (−0.02)</td>
<td>0.386 (−0.006)</td>
<td>2.01</td>
<td>−1.99</td>
<td>−4.00</td>
</tr>
</tbody>
</table>

$^{a}$ $\Delta d_{NW}$ and $\Delta l_{NW, UC}$ are changes of diameters and UC lengths as compared to non-optimized NWs. $^{b}$ Values of $\Delta \varepsilon_{gap}$, $\varepsilon_{CB, bottom}$ and $\varepsilon_{VB, top}$ calculated for STO bulk: 3.08, −0.92 and −4.00 eV, respectively.
of $d_{\text{NW}}$, i.e., the width of band gap can be defined as usually: $\Delta E_{\text{gap}} = E_{\text{CB bottom}} - E_{\text{VB top}}$ (Fig. 7). Analogously to both types of non-stoichiometric nanowires, the band gap remains non-direct since the CB bottom is achieved at $I$ point of the BZ, whereas the VB top corresponds to $Z$ point (Fig. SI2 in ESI†). Values of $\Delta E_{\text{gap}}$ are noticeably smaller than those for TiO$_2$-terminated SrTiO$_3$ nanowires and markedly smaller as compared to SrO-terminated STO NWs when comparing those for close values of $d_{\text{NW}}$ (cf. Table 3 and 5).

Analysis of Fig. 7 indicates that in stoichiometric STO NWs, the top of valence band is predominantly composed of O(2p) states from the edge oxygen atoms on TiO$_2$-terminated facets while the bottom of the conduction band is composed of Ti(3d) states from the outmost Ti atoms in SrO-terminated facets (Fig. 3). Contribution from central NW atoms as well as Sr atoms is practically neglecting for both edges of band gap which essentially differs from the case of non-stoichiometric STO NWs, where influence of central atoms is essentially large which can be explained by different morphology of both types of nanowires (cf. Fig. 2 and 4).

Distribution of the effective charges in STO NWs is presented in Table 6, they can be compared with both PDOS plot (Fig. 7) and analogous values for non-stoichiometric nanowires (Table 4). Again, except for edges of SrO-terminated NW facets, strontium ion in other nanowire configurations can be attributed to pure ionic Sr$^{2+}$ state, which practically excludes any Sr involvement in covalent bonding. Analogously to non-stoichiometric NWs, O ionicity reduces from positions at edges of SrO-terminated NW facets down to that in proximity of edges at TiO$_2$-terminated facets while the effective charge of central oxygen ions can be considered as averaged between those for edge atoms (cf. Tables 4 and 6). Similar conclusion can be drawn on insensitivity of the effective charges on oxygen or titanium ions on value of $d_{\text{NW}}$ for their fixed arrangement in both non-stoichiometric and stoichiometric nanowires.

### Table 6  Mulliken effective charges of atoms (e) in stoichiometric SrTiO$_3$ nanowires

<table>
<thead>
<tr>
<th>Nanowire</th>
<th>NW center</th>
<th>SrO edge</th>
<th>TiO$_2$ edge</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_{\text{Sr}}$</td>
<td>$q_{\text{Ti}}$</td>
<td>$q_{\text{O}}^a$</td>
</tr>
<tr>
<td>2 × 2</td>
<td>—</td>
<td>—</td>
<td>$-1.40, -1.37$</td>
</tr>
<tr>
<td>3 × 3</td>
<td>1.95</td>
<td>2.25</td>
<td>$-1.40, -1.36$</td>
</tr>
<tr>
<td>4 × 4</td>
<td>1.95</td>
<td>2.26</td>
<td>$-1.41, -1.40$</td>
</tr>
<tr>
<td>5 × 5</td>
<td>1.95</td>
<td>2.28</td>
<td>$-1.41, -1.40$</td>
</tr>
</tbody>
</table>

$^a$ The left value is for oxygen in TiO$_2$ atomic plane, and the right value is for oxygen in SrO atomic plane.

4. Suitability of regular SrTiO$_3$ nanowires for photocatalytic applications

On the basis of the standard thermodynamic conditions for H$_2$O molecule splitting, we discuss and evaluate the influence of cubic STO NW morphology on the photocatalytic activity of [001]-oriented non-stoichiometric and stoichiometric nanowires possessing different faceting and thickness (Fig. 2–4). We perform comparison of the band edge positions and Fermi levels with those for perfect SrTiO$_3$ bulk as well as with levels of reduction H$^+$/H$_2$ and oxidation O$_2$/H$_2$O potentials. Fig. 8 presents the energy diagram drawn using results discussed in Section 3, which allows one to estimate eligibility of all the types of nanowires in proximity of the inter-band gap edges and redox potentials for H$_2$O molecule dissociation. Striped areas of columns consist of the virtual (non-populated) energy levels in the band structure unlike filled areas, the levels in which are populated.
of strontium titanate nanowires considered here for photocatalytic applications.

The first energetic criterion of material suitability as photoelectrode is a proper ratio between its band gap edges as well as the potentials of reduction (H\textsuperscript{+}/H\textsubscript{2}) and oxidation (O\textsubscript{2}/H\textsubscript{2}O) for water splitting reaction under solar irradiation is: $E_{CB\_bottom} \geq E_{H\_reduction} > E_{O2\_oxidation} > E_{VB\_top}$. On the other hand, the band gap width of potential photoelectrode must correlate with the energy range of visible light spectrum between the infrared and ultraviolet regions of electromagnetic irradiation which is fitting for H\textsubscript{2}O molecule dissociation, i.e., $1.23 \, eV < \Delta_{gap} < 2.50 \, eV$. Although structural reconstruction of the corresponding material can provide necessary correlation of $E_{VB\_top}$, $\Delta_{gap}$ and $E_{CB\_bottom}$ the proper choice of potential candidates according to both criteria has to be done first.

Obviously, for [001]-oriented $3 \times 3$, $4 \times 4$ and $5 \times 5$ stoichiometric SrTiO\textsubscript{3} nanowires, the second criterion is fulfilled (Fig. 8), the same is certainly true for more thick nanowires, $6 \times 6$, $7 \times 7$, etc. However, the alignment criterion of band gap edges with redox potentials is rather far from realization for stoichiometric SrTiO\textsubscript{3} nanowires, at least the strategy of the corresponding structural reconstruction is not clear. Much closer for both aforementioned criteria are non-stoichiometric TiO\textsubscript{2}-terminated STO NWs (Fig. 8), especially $5 \times 5$ and more thick nanowires ($2.50 \, eV$ corresponds to energy of "violet" photon). However, our calculations have shown that non-stoichiometric SrTiO\textsubscript{3} nanowires rather possess local conductivity: SrO-terminated NWs possess it in areas of facets, whereas TiO\textsubscript{2}-terminated NWs in the center. Thus, the latter can be considered as possible candidates for nanophotocathodes since the surface areas of these nanowires can be described as semiconductors whereas transition of the electron from the VB towards the CB can initiate dissociation of H\textsubscript{2}O molecule under influence of visible light. Meanwhile, this result confirms conclusion drawn in ref. 19 on suitability of TiO\textsubscript{2}-terminated STO NWs for photocatalytic applications. As to SrO-terminated SrTiO\textsubscript{3} nanowires, Fig. 8 clearly demonstrates that they cannot be applied as photocathodes since both energy criteria are not fulfilled in this case.

5. Summary

We have performed comprehensive first-principles simulations of a few thin [001]-oriented SrTiO\textsubscript{3} NWs, both non-stoichiometric (either SrO- or TiO\textsubscript{2}-terminated) and stoichiometric, diameters of which have been varied from 0.3 up to 2.4 nm. The current study can be considered as the first step in development of NW models for photocatalytic applications, the next steps will include implementation of vacancies and dopants in nanowires as has been done for SrTiO\textsubscript{3} nanotubes. To estimate stability of these nanostructures, we have calculated their formation energies $E_{form}$ according to approximate thermodynamic formalism. Dependence of reduced Gibbs energies $\Delta G_{form}$ of non-stoichiometric STO NWs on chemical potential of TiO\textsubscript{2} formula unit $\Delta \mu_{TiO_2}$ has been shown, while stoichiometric NWs are insensitive to $\Delta \mu_{TiO_2}$. Irrespective on nanowire termination, growth of NW thickness reduces its formation energy.

Hybrid DFT-LCAO calculations have shown that the values of $\Delta_{gap}$ for SrTiO\textsubscript{3} NWs of different structural types are consistently reduced with the growth of NW diameter although character of such a decrease depends on morphology of nanowire. Stoichiometric STO NWs are found to be semiconducting irrespectively on their thickness, while non-stoichiometric nanowires expose local conductivity caused by crossing of the CB bottoms by Fermi levels. In the case of SrO-termination, it is prevailed upon NW facets, while in TiO\textsubscript{2}-terminated NWs, local conductivity is more expressed around the nanowire axis. This is confirmed by analysis of projected densities of states containing mainly O(2p) contributions at the top of the VB and Ti(3d) contribution at the bottom of the CB or around the Fermi level.

Comparison of the band edge positions and Fermi levels relatively the levels of reduction H\textsuperscript{+}/H\textsubscript{2} and oxidation O\textsubscript{2}/H\textsubscript{2}O potentials as well as analysis of the band gap widths allows us to suggest the probable STO NW configurations for application in photocatalytic splitting of water molecules under solar irradiation in the visible range. Both stoichiometric and non-stoichiometric TiO\textsubscript{2}-terminated strontium titanate nanowires can be used as photocathodes, after additional structural and chemical modification of the former or directly in the latter case. On the other hand, SrO-terminated STO nanowires are rather not suitable for this purpose.

Acknowledgements

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References
