

**Ab initio** simulations on N and S co-doped titania nanotubes for photocatalytic applications

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Abstract

In this paper we present the results of quantum chemical modeling for energetically stable anatase (001) TiO\(_2\) nanotubes, undoped, doped, and codoped with N\(_2\)O and S\(_2\)O atoms. We calculate the electronic structure of one-dimensional (1D) nanotubes and zero-dimensional (0D) atomic fragments cut out from these nanotubes, employing hybrid density functional theory with a partial incorporation of an exact, nonlocal Hartree-Fock exchange within the formalism of the linear combination of atomic orbitals, as implemented in both CRYSTAL and NWChem total energy codes. Structural optimization of 1D nanotubes has been performed using CRYSTAL09 code, while the cut-out 0D fragments have been modelled using the NWChem code. The electronic properties of the studied systems prove that the band structure of the pristine TiO\(_2\) nanotube can be substantially modified by introducing substitutional impurity defects. The N-doped nanotube creates a midgap state that largely has a nitrogen \(p_2\) character. The S-doped nanotube has a defect state that almost coincides with the top of the valence bond for the pristine material. For nanotubes codoped with both S and N, we observe a downward shift of the gap state of nitrogen relative to the purely N-doped state by about 0.3 eV. This results in a system with a filled gap state about 0.3 eV below the O\(_2\)/H\(_2\)O oxidation level, making it a very promising candidate for photocatalytic hydrogen generation under visible light, because due to the presence of sulfur, the bottom of the conduction band is only about 2.2 eV above the occupied midgap state, and also, clearly above the standard hydrogen electrode level.

Keywords: titanium dioxide, ab initio, photocatalysis, nanotubes, cluster model

1. Introduction

It is possible to convert the energy of the Sun into chemical energy via the water-splitting reaction, which is amply demonstrated by the existence of photosynthesis in green plants and algae [1]. Some metal oxides are capable of driving the water-splitting reaction when irradiated with sunlight, and titanium dioxide (TiO\(_2\) or titania) is among these materials [2]. It is a relatively cheap, easily obtainable, chemically stable and well-studied material [3–5]. It also can form nanostructures such as nanotubes (NTs), thereby creating large surface areas that can improve their catalytic activity. Despite all these beneficial properties and the fact that TiO\(_2\)-based photocatalysts are commercially available, a significant problem still exists with this material: its band gap is too large for efficient conversion of sunlight. The 3.2 eV-wide band gap in pure titania is active only under ultraviolet light, and the maximal theoretical efficiency of sunlight energy conversion is thus only about 1%. By adjusting the material’s band gap through the introduction of impurities (dopants), its theoretical efficiency can be increased; for a 2.2-eV band gap, the efficiency rises to about 15% [6–9]. Nevertheless, many open questions concerning TiO\(_2\) still remain and require a deeper understanding, including the optimal doping scheme,
or changes in electronic structure for the nanostructured material, which may or may not lead to a reduction of the band gap (and thus a further increase in efficiency).

Recently, we have studied the electronic properties of TiO$_2$ NTs; their atomic structure and the influence of various dopants onto their electronic band structure have been predicted [10, 11]. In [10], the energetically most stable titania NT has been found to be one folded from a nine-layered anatase (001) nanosheet with chirality indices (0, n). Furthermore, changes in the band gap caused by the introduction of a sulphur impurity have been estimated. Doping nanotubular TiO$_2$ with sulphur results in both a narrowing of the band gap and in a shift of the gap edges, bringing them closer to the limits required for efficient water splitting [10]. In [11] some of us estimated the charge redistribution and formation energies for C$_{O}$, N$_{O}$, S$_{O}$, and Fe$_{Ti}$ substitutional defects. So far, our findings concerning the optimal geometry of NTs have been in good agreement with results obtained in the literature [12]. These results can, in principle, be used to suggest more efficient TiO$_2$-based photocatalysts when analyzing band shifts and the energy levels of defect states. This was done recently for the changes in a titania NT’s electronic band structure upon introducing C$_{O}$, N$_{O}$, S$_{O}$, and Fe$_{Ti}$ substitutional dopants [13]. The calculations for single dopants have led us to conclude that nanotubes codoped with S and N atoms might create a photocatalyst that will function even better under visible light. One of the goals of this manuscript is to investigate this hypothesis in more detail.

Another goal of this manuscript is the investigation of the suitability of zero-dimensional (0D) cluster models for describing the electronic structure of one-dimensional (1D) NTs. Within the framework of standard density functional theory (DFT), the correct description of excited states is very difficult. A more realistic approach is likely to bring significant changes of the calculated band structure of the photocatalyst, which will be a central issue in forthcoming calculations, where we intend to use time-dependent DFT (TD-DFT) as implemented in the NWChem code [14]. To reduce the computational efforts for such calculations, we plan to replace the NT by a cluster model, which will be described in more detail in the next section. In the present work we compare results obtained by means of two different approaches: 1D NTs modeled using the CRYSTAL computer code [15, 16] and 0D cluster fragments of the NT simulated with the NWChem code. In this way we can verify the CRYSTAL results in an independent manner and also estimate the applicability of 0D cluster models.

2. Theoretical background

For computational analysis of 1D NTs, we have used quantum mechanical DFT using the linear combination of atomic (crystalline) orbitals, LCAO(CO) method, as implemented in the CRYSTAL program developed at the University of Torino [15, 16]. The NWChem computer code [14] is used for ab initio calculations of 0D clusters. To perform both the 1D NT and 0D cluster calculations in the same theoretical framework, we use a modified B3LYP hybrid exchange-correlation functional that has been adopted within DFT to perform the calculations on the doped titania NTs in all cases [11, 13]. This approach, inter alia, reduces the admixture of a nonlocal Hartree–Fock exchange to 14%, to obtain quantitative agreement with the experimentally observed band gap width for bulk anatase TiO$_2$ (experimental 3.18 eV, calculated 3.16 eV) and the absolute positions of the band edges.

To be consistent with earlier studies, we have used the energetically stable TiO$_2$ NTs (as obtained by calculations of the strain energy) as the basis for the construction of doped NTs. The NTs studied here have been folded from a nine-layered anatase slab cut parallel to the (001) surface (figure 1). Such nine-layered (001) NTs with (0, n) chirality indices possess a negative strain energy (i.e., it is energetically more favorable to form NTs than to retain the original two-dimensional sheet structure [10]). It is worth mentioning that our prediction is in a good agreement with earlier theoretical studies performed by Ferrari et al [12]. For the substitutional doping we have chosen the 2 × 2 supercell of the nine-layered anatase (001) nanosheet rolled up to a (0, 36) NT with an internal diameter of 3.47 nm and a wall thickness of 0.67 nm, which has 648 atoms in the unit cell (figure 1) and 36 atoms in the irreducible cell. Substitutional C, N, and S impurities have been studied on the most favorable atom position for replacement of an oxygen atom, which is found to be in the NT’s outer wall.

For both approaches, the following configurations of Gaussian-type basis sets (BS) have been adopted: (i) For the Ti atom, the BSs have been chosen in the form of 411sp–311d using the effective core potentials implemented by Hay and Wadt [17]; (ii) full-electron BSs have been adopted for all
other atoms in calculations of doped titania NTs (i.e. O: 8s–411sp–1d; N: 6s–31p–1d, and S: 8s–63111sp–1ld [15, 16]).

To provide a balanced summation over the direct and reciprocal space cells of defective NTs in the 1D model, the reciprocal space integration has been performed by sampling the Brillouin zone (BZ) of extended 2 × 2 supercells with the 6 × 1 × 1 Pack-Monkhorst k-mesh [18], which results in four evenly distributed k-points over the segment of the irreducible BZ. For both the 1D and the 0D systems the calculations are considered to be converged when the total energy obtained in the self-consistent field procedure differs by less than 10⁻⁷ a.u. in two successive self-consistent field cycles. For N-doped nanostructures, spin-polarized calculations have been performed.

The rationale behind investigating the 0D cluster models of the 1D periodic NTs is to perform TD-DFT calculations to obtain improved excited-state properties for the NTs. Such calculations are unfortunately not currently possible using the periodic CRYSTAL code. It is, however, implemented in NWChem [14]. Since NWChem, on the other hand, does not allow periodic 1D calculations that fully account for symmetry, we created 0D clusters cut from the NT so as to preserve geometry and stoichiometry. This is done to substantially reduce the number of atoms, so that the calculations become feasible (figure 2). It is, however, possible to perform the calculations on the models in both codes on the same level of theory with the same parameter values. Thus, the computational results for the 1D NTs serve as benchmarks for the 0D cluster models. We have studied different size clusters by cutting n × n × d segments from the full NT (figure 1), where n is the number of Ti atoms per layer and d is the thickness (number of layers) of the NT. Since d is constant, we refer to a particular model simply as n×n. n was chosen to be 2, 3, and 4. Atom positions of the clusters have not been further relaxed, but rather are kept fixed to avoid relaxation and reconstruction of the curved NT fragments.

To avoid significant changes of the density of states through states from atoms whose bonds were broken, we saturated all dangling bonds by H, F, or Cl atoms or OH groups, similar to the procedure suggested in [19] (see below).

3. Results and discussion

3.1. Optimization of computational scheme for the 0D cluster model

We have studied undoped (pristine) 0D clusters (i.e., segments cut out of the precalculated NT) for various cluster sizes, n, and terminations of the bonds broken by cutting the cluster. Saturating the broken bonds with hydrogen is a commonly used procedure based upon chemical intuition [19]. Nevertheless, we also explored several other saturation modes to check whether we can model the partial charge on the outermost titanium atoms reasonably well. This is a concern, since a hydrogen atom is considerably less electronegative than the oxygen atom that is removed from the Ti coordination shell during the cutting procedure. To compensate for the lack of oxygen, we also tried to saturate broken Ti–O bonds with hydroxyl groups (–OH) and with halogens (–F; –Cl). Calculations showed that halogens or hydroxyl groups introduce too many electronic levels of their own, which pollute the gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital (HOMO/LUMO) and which also shift the band edges by 1~2 eV. Hydrogen atoms also affect the electronic levels near the HOMO/LUMO gap, but their impact on the position of edges is considerably smaller than that of halogen atoms or hydroxyl groups.

Another important influence variable is the position of the terminating atoms. Changes of as little as 0.1 Å in the Ti–H bond length (which corresponds effectively to the difference between relaxed and unrelaxed structures) can shift the position of the band edges by as much as 0.5 eV. We found that the best results—the calculated HOMO/LUMO edges of the 0D model that were closest to those obtained for the periodic model—are obtained using hydrogen-terminated clusters. For these clusters, only the hydrogen atom coordinates have been relaxed relative to the TiO₂ scaffold, which has been kept rigid during the optimization to avoid destroying the overall nanotubular atom arrangement. Therefore, all the calculations we report below are for saturation of the broken bonds with hydrogen atoms, which are relaxed relative to the TiO₂ scaffold. To avoid gap pollution from the hydrogen states, we have decided to omit from consideration all states below which are dominated by hydrogen orbitals. This has been achieved by removing all states where one of the hydrogen orbitals contributed by more than 2.25% to the electron density.

3.2. 1D periodic model

Figure 3 shows the projected density of states as calculated by means of the CRYSTAL total energy code for pristine, N-doped, the S-doped, and N and S codoped titania NTs. The top of the valence band (VB) in the case of the perfect TiO₂
NT is formed by O 2p orbitals, while the bottom of the conductance band (CB) consists of Ti 3d states. Substitutional point defects in titania NTs clearly show the tendency to form defect-induced levels inside the optical band gap. In the case of the NO/TiO₂ NT impurity, the induced level is found to be close to the top of the VB (0.8 eV above it), while the defect-induced level calculated for the S₂-doped TiO₂ NT almost coincides with the top of the VB. Simultaneously, the bottom of the CB is shifted down toward the hydrogen standard electrode in the S-doped NT. For the N + S codoped titania NT, the nitrogen-dominated gap state shifts downward in energy by about 0.3 eV, bringing the occupied gap level 0.3 eV below the oxygen O₂/H₂O redox level. However, due to the presence of the S codopant, the bottom of the CB also shifts downward, yielding an energy gap of about 2.2 eV that reduces the photon energy required for water splitting.

Figure 3. Projected density of states for (a) a pristine TiO₂ NT, (b) an N-doped NT, (c) an S-doped NT, and (d) an N and S codoped TiO₂ nanotube, as calculated by means of the 1D periodic CRYSTAL program.
3.3. Verification of cluster model

As mentioned before, the 0D cluster models have been investigated with the goal of using NWChem’s implementation of the TD-DFT method to perform non-adiabatic simulations of the relaxation of the NT and its environment following absorption of a photon. Here we wish to discuss only the results obtained for the three cluster models of different sizes with all dangling bonds terminated by hydrogen atoms. Specifically, we have investigated 2 × 2, 3 × 3, and 4 × 4 clusters, where the numbers denote the number of elementary cells along and perpendicular to the NT axis, respectively.

We have denoted the respective highest occupied and lowest unoccupied levels that do not contain significant contributions from dopant atom orbitals as the top of the VB and the bottom of the CB, respectively. The results for the band edge positions using this definition are shown in figure 4 and indicate a converging trend. While for the 2 × 2 undoped clusters the discrepancies relative to the 1D undoped NT model are sizable, the differences become significantly smaller for the 3 × 3 clusters and even more so for the 4 × 4 clusters. Quite expectedly, the top of the VB is generally reproduced more accurately by the 0D models than the bottom of the CB. It is interesting to note that the relative position of the defect-induced midgap states with respect to the band edges are similar, in spite of the large differences in defect concentration between the 1D and 0D systems.

For example, the left side of figure 5 shows the level diagram of the N-doped 4 × 4 0D cluster. It clearly shows the single level at −5.1 eV, which is dominantly composed of N 2p, levels (along the NT axis). The right side of the figure shows the density of states for the N-doped 1D NT model. While the band edges of 0D and 1D models converge when the 0D cluster size increases (figure 4), the defect-level position does not converge. At −5.1 eV, it is significantly higher for the 4 × 4 0D cluster than the value of −5.8 eV for the 1D NT.

This may be a consequence of the effectively larger defect concentration in the 1D NT, which is 1 dopant per 24 oxygens in the periodically repeated unit cell (∼4%), versus 1 dopant per 96 oxygens (∼1%) for the 4 × 4 0D cluster.
For sulfur-doped NTs (figure 4), the defect levels vary with cluster size, and they also differ between the clusters and the NT. While the overall differences are smaller than in the N-doped case, the proximity of the defect level to the top of the VB does produce a discernible defect state in the gap for the 2 × 2 and 3 × 3 clusters, whereas for both the 4 × 4 cluster and the NT, the defect state is in fact located below the top of the VB.

Note that in this paper we do not consider the formation mechanism of N + S codoped TiO₂ NTs. The predictions on the thermodynamic stability of doped and codoped titania NTs are also beyond the scope of the current study. These aspects are discussed in detail elsewhere [20]. However, for the periodic model, we checked the influence of distance between the N and S atoms on the electronic structure of codoped NTs and found it to be negligible.

4. Summary

We have performed periodic (1D) calculations of the electronic structures of undoped and doped TiO₂ NTs. To compare the performance of 0D clusters cut from the periodic NT as models for the entire NT, we have also studied fragments containing 2 × 2, 3 × 3, and 4 × 4 elementary cells, which have been saturated with hydrogen atoms. In addition to pristine (undoped) NTs, we have studied the effect of N doping, S doping, and N + S codoping on the VB and CB positions, as well as the defect levels.

The N-doped systems exhibit a (filled) gap state that is located about 0.8 eV (1D) and 1.6 eV (4 × 4 cluster) above the top of the VB, corresponding to excitation energies from the gap state to the bottom of the CBs of 2.5 eV and 1.7 eV, respectively. The calculations for the N-doped 4 × 4 cluster, however, place the defect-induced mid gap state ~0.6 eV above the O₂/H₂O level, which would thus make this system unsuitable for photocatalytic water splitting.

The N + S codoped system, for which only 1D calculations have been performed, also exhibits a gap state that is somewhat lowered relative to the top of the VB due to defect-defect interactions. For this system, the top of the VB and the bottom of the CB shift downward relative to the N-doped system. Relative to the bottom of the CB of the S-doped system, the CB shifts upward again toward the CB position of the pristine or the N-doped system, which are similar in energy. The overall effect of codoping gives rise to an excitation energy from the gap level of approximately 2.3 eV, which is slightly smaller than that of the (1D) N-doped NT. This allows us to predict that N + S codoped titania NTs can be suggested as a promising candidates for visible-light-driven photocatalytic applications, which is in good agreement with recent experimental observations [20].

Pure S doping produces a downward shift of the bottom of the CB for the periodic 1D systems, but has little effect on the gap in the larger clusters. The defect states are, depending on system, slightly above or slightly below the top of the VB.

We can draw several conclusions from this study, in which we have treated 1D NTs and their 0D fragments on the same level of theoretical description. First, the investigated coding with N and S is less beneficial than can be expected on the basis of single-dopant calculations, which showed a pronounced occupied gap level in the N-doped case and a substantial lowering of the CB in the S-doped case. Rather than reducing the gap between these levels, codoping does shift all energies upward, which may be due to the relatively strong defect interactions in the codoped NT, where 8.3% of the oxygen atoms have been replaced by the two defects.

Second, we observe that the results for periodic 1D and cluster 0D models are by and large consistent as far as the band edges are concerned. However, the positions of the gap states are different between the NTs and the fragment clusters, and furthermore change substantially with cluster size, notably for the N-doped cluster. While part of this behavior may be associated in the nitrogen case with the spin polarization of the system, it is more likely that the chosen relatively primitive embedding scheme with hydrogen saturation is inadequate. More elaborate schemes are possible, such as embedding into a polarizable polar background [21], but are beyond the scope of this manuscript.

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