Doped 1D Nanostructures of Transition-metal Oxides: First-principles Evaluation of Photocatalytic Suitability

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Abstract: The splitting of water molecules under the influence of solar light on semiconducting electrodes is a clean and renewable source for the production of hydrogen fuel. Its efficiency depends on the relative position of the band-gap edges or the induced defect levels with a proper band alignment relative to the redox H+/H2 and O2/H2O potentials. For example, TiO2 and ZnO bulk, as well as thick slabs (whose band gaps are ~3.2–3.4 eV), can be active only for photocatalytic applications under UV irradiation (possessing ~1% solar energy conversion efficiency). Nevertheless, by adjusting the band gap through formation of nanostructures and further doping, the efficiency can be increased up to ~15% (for 2.0–2.2 eV band gap). We analyse results of DFT (density functional theory) calculations on TiO2 nanotubes and ZnO nanowires, both pristine and doped (e.g., by Ag2zr, Co, FeTi, N2O and S2O substitutes). To reproduce the energies of one-electron states better, we have incorporated the Hartree-Fock (HF) exchange into the hybrid DFT + HF Hamiltonian. Both the atomic and electronic structure of nanomaterials, simulated by us, are analysed to evaluate their photocatalytic suitability, including positions of the redox potential levels inside the modified band gap, the width of which corresponds to visible-light energies. Analysis of the densities of states (DOS) for considered nanostructures clearly shows that photocatalytic properties can be significantly altered by dopants. The chosen hybrid methods of first-principles calculations significantly simplify selection of suitable nanomaterials possessing the required photocatalytic properties under solar light irradiation.

Keywords: anatase titania nanotubes · density functional calculations · doping · water splitting · wurtzite zinc oxide nanowires

1. Introduction

Proper choice of alternative energy sources for wide applications in modern technology and everyday life is one of the urgent research problems, because deposits of traditional fossil fuels (coal, gas, oil, etc.) run out at an extreme rate, while their restoration rate is obviously inferior. Dissociation of water molecules under the influence of solar light on semiconductor electrodes immersed in electrolyte is found to be a promising process for the production of hydrogen fuel, and is extraordinarily friendly towards the environment. In addition, hydrogen possesses a high energy density of ~237 kJ mol⁻¹.¹

Photocatalytic H2 production, often considered as artificial photosynthesis, is an attractive and challenging research field in the field of chemistry and renewable energy.¹⁻³ Moreover, the only combustion product of hydrogen is water, while traditional H2 production technologies (e.g., steam reforming) are accompanied by the release of CO2 and/or other undesirable side products.

A number of metal-oxide semiconductors were proposed and intensively studied as possible candidates for photoelectrochemical water splitting catalysts (e.g., SrTiO3, TiO2, ZnO, WO3, PbO2, Fe2O3, CuO and Cu2O).²⁻⁷ The major limitation for solar light conversion by photocatalysis relates to the band-gap position in corresponding photocatalytic materials. According to data on the solar irradiation spectrum (at the level of Earth’s surface), the theoretical maximum degree of solar energy conversion for a catalyst with a 3.2 eV wide band gap is approximately 1%. For efficient water splitting under visible light, the optimum band gap is estimated to be in the interval of 2.0–2.2 eV (with conversion of solar energy ~15%)⁸⁻⁹ which is small enough to absorb a significant amount of visible sunlight, but at the same time,

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Oleg Lisovski is a Ph.D. student at the University of Duisburg-Essen, Germany. He began his education as a chemical engineer, but soon switched this direction to theoretical chemistry. His bachelor thesis (developed and defended at Riga Technical University, Latvia), as well as his master’s thesis (developed and defended at Uppsala University, Sweden), were dedicated to DFT modelling of doped titania nanotubular photocatalysts. Presently, Oleg is working on his Ph.D. project, dedicated to ab initio MD simulations of water near defective metal-oxide nanostructures. Simultaneously, he is taking part in the ERA.Net RUS Plus Project WATERSPLIT (grant No 237). Lisovski’s main interest is renewable energy, in general, and modelling of catalysts for solar water splitting, in particular.

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it is larger than the energy required to split a water molecule (1.23 eV).\cite{10,11} Bulk materials that possess band gaps in the optimal energy range, e.g., FeO\(_2\) (2.2 eV) and CuO (1.7 eV), unfortunately, have relatively low efficiencies of incident photon-to-current conversion\cite{12} or experience photocorrosion.\cite{5,13}

On the other hand, ZnO, TiO\(_2\) and SrTiO\(_3\) oxides, which stand out due to superior chemical and optical stability as well as commercial availability, have broader band gaps (3.20 eV for cubic SrTiO\(_3\))\cite{2} 3.20 and 3.03 eV for anatase- and rutile-structured titania, respectively,\cite{4,14} vs. 3.44 eV for wurtzite-type ZnO\cite{15}). This consequently limits their activity to the near-ultraviolet region of the solar spectrum, so that only several percent of the sunlight can be harvested by such materials. Optimal widths of the band gaps must be also combined with a proper alignment of the band edges relative to both the reduction (H\(^+\)/H\(_2\)) and oxidation (O\(_2\)/H\(_2\)O) potentials estimated thermodynamically (–4.44 eV and ~5.67 eV, respectively),\cite{16} which should be positioned inside the band gap. Doping of these bulk oxides by certain substitutional atoms should result in the appearance of additional levels in the band gap, thus creating new optical absorption edges and reducing the energy threshold.\cite{17} Hence, visible-light photons become capable of overcoming the gap between newly formed edges.\cite{18} The efficiency of oxide doping can be noticeably enhanced through nanoscale transformation of their morphology.\cite{19}

In this review, we analyse applicability of large-scale first-principles calculations for the description of metal-oxide 1D nanostructures doped with cations and/or anions, thus evaluating their suitability to be used for photocatalytic water splitting. Here, we systematize our results obtained mainly for two classes of 1D nanostructures estimated as the effective photocatalysts during the last few years – anatase-structured titania nanotubes (NTs)\cite{17-20} and wurtzite-structured ZnO nanowires (NWs).\cite{21} At the same time, results of our recently performed \textit{ab initio} simulations of strontium titanate, including both nanotubes\cite{20} and nanowires\cite{22} with cubic morphology, clearly show that their efficiency for photocatalytic applications is markedly lower than in the case of TiO\(_2\) and ZnO nanostructures. This is why we do not analyse those results in the current review at all. Moreover, only the ground states of nanomaterials have been taken into account in our simulations performed so far, whereas a more detailed study of their excited states, for both pure and doped morphology, is necessary to make real progress in this field and to better interpret the huge amount of existing experimental data.\cite{23}

A tight collaboration between the coauthors from both University of Latvia and St. Petersburg State University (Russia) during the last few years has been focused on the theoretical description of inorganic 1D nanomaterials, including \textit{ab initio} simulations of their morphology and electronic structure, which has resulted in a number of joint publications.\cite{21,22,24-31} From 2016, this collaboration is supported by the ERA.Net RUS Plus Project No. 237 WATERSPLIT.

2. Progress in Contemporary Research of Doped TiO\(_2\) Applicability for Photocatalysis

2.1 Experimental Studies

TiO\(_2\) is a well-known and inexpensive semiconductor with a number of prospective properties and numerous technological applications, which are comprehensively studied in materials science.\cite{32} Although the total number of bulk titania polymorphs discovered so far under different conditions, e.g., nonequilibrium ones, is seven (each of them is constructed using octahedrally coordinated Ti atoms),\cite{33} only rutile- and anatase-structured TiO\(_2\) play a substantial role in practical applications, due to the higher energetic stability than other phases. At the same time, for theoretical simulations, stable titania nanotubes are considered to be mainly anatase-structured.\cite{34}

Numerous experiments focused on titania doping by different metal ions (e.g., Cr, Fe, Mn, Mo, Ni, V, etc.) were performed earlier.\cite{35} In 1982, Borgarello \textit{et al.} discovered that Cr\(^{3+}\)-doped titania could generate hydrogen and oxygen in the process of water splitting under sunlight irradiation (corresponding wavelength interval is 400–550 nm, which corresponds to values of 3.15–2.29 eV on the energy scale).\cite{36} Cao \textit{et al.} reported that Sn\(^{4+}\)-doped titania nanoplanes, synthesized by chemical vapour deposition (CVD) exhibit noticeably higher photocatalytic efficiency than ordinary TiO\(_2\) crystal.\cite{37} Experimental studies performed on Nb-doped titania nanotubes fabricated by anodization of Ti–Nb alloys clearly exhibit enhanced photoelectrochemical splitting of H\(_2\)O molecules, accompanied by negligible photodegradation.\cite{38} Klosek and Raftery demonstrated that visible-light absorption in V\(^{4+}\)-doped TiO\(_2\) is a result of the electron transfer from the V(3\(d\)) electron-induced energy level to the conduction band.\cite{39} Their research became a key to more effective ways of ethanol photooxidation under visible light (another route to hydrogen generation). Fe\(^{3+}\)-doped titania also exhibits enhanced photocatalytic activity. Moreover, electrons from Fe\(^{3+}\)(3\(d\)) state induce additional levels in the TiO\(_2\) CB.\cite{38} Doping of titania photocatalysts by Cr, Mg, and Fe cations can improve their efficiency; for example, magnesium can reduce the energy barrier for interphase transfer of electrons.\cite{40} On the other hand, the newly induced electronic states can behave as recombination centres, e.g., by shifting the impurity levels to lower than the reduction SHE (standard hydrogen electrode) level.

Usually TiO\(_2\) doped by nonmetal anions exhibits a squeeze of the band gap directly, by shifting the top of the VB upwards, and not an appearance of induced levels, like in metal-doped titania. Nevertheless, Chen
et al. used X-ray photoelectron spectroscopy to show the appearance of extra mid-gap states in the electronic structure of C-, N-, or S-doped TiO$_2$ between the VB and the CB induced by dopants.$^{[40]}$ This additional density of the electronic states explains the redshift mentioned above. Braun et al. discovered an additional $\epsilon_g$ resonance state in the O(1s) NEXAFS (near-edge X-ray absorption fine structure) pre-edge of titania caused by N dopants.$^{[41]}$ This observation was used to explain enhanced photocatalytic activity of N-doped TiO$_2$ under visible light. At the same time, S dopants substituting host O or Ti atoms can improve the photocatalytic activity of nanorods too.$^{[42,43]}$ S-doped TiO$_2$ also exhibits higher photocatalytic activity than the N-doped system.$^{[44]}$ C-doped TiO$_2$ compounds, also synthesized, exhibit a quite narrow forbidden gap and an enhanced photocatalytic activity than pure titania with mixed rutile and anatase domains, while doped nanotubes possess better photocatalytic activity.$^{[45]}$ Levels induced in their band gap were shown to broaden the activity of doped NTs from the visible to the infrared region. A complex study of the chemical modification of titanium isopropoxide with different nonmetal reagents was performed by Pillai et al.$^{[46,47]}$ It was discovered that introduction of N and S dopants (applying urea and sulfur acid, respectively), improved both chemical stability and photocatalytic activity of titania.

Rather limited information on the codoping of TiO$_2$ photocatalysts is available for nonmetallic dopants so far. Yan et al.$^{[48]}$ reported on N- and S-codoping of TiO$_2$ nanotube-array films by treatment with thiourea and calcination under vacuum and high temperature. Codoped NTs exhibit broadened absorption spectra, as well as enhanced photocatalytic activity in the methylene blue degradation process. Alternatively, Lv et al.$^{[49]}$ studied N + S codoped TiO$_2$/fly ash bead composite material and its photocatalytic activity in the visible-light range. The material’s ability to degrade methyl orange was compared with both undoped and P25 samples (commercially available nanopowder mixture of TiO$_2$, anatase and rutile phases); the former showed much higher efficiency. Li et al. suggest that Sn-doped nanotubes (Sn/O$_{vac}$ NTs) with oxygen vacancy possess better photocatalytic performance than pure TiO$_2$ samples or samples without an Sn dopant or O vacancy.$^{[50]}$ At the same time, Sn/O$_{vac}$ NTs achieve the highest photodegradation rate among similar samples. Besides doped photocatalysts, the appearance of vacancies as point defects can result in the growth of electrical conductivity and changes in band-gap structures.$^{[51]}$

A series of EPR and XPS studies have been performed on nitrogen,$^{[52]}$ and fluorine-doped,$^{[53]}$ as well as N + F$^{[54]}$ and N + B$^{[55]}$ codoped titania powders synthesized via the sol-gel method in aqueous solutions of inorganic compounds (N-, F-, and B-containing), with subsequent calcination in air. In doped TiO$_2$ powders prepared using methods of wet chemistry, it is necessary to take into account the possible formation of both surface and bulk dopants.$^{[56]}$ N, F, and B substitutes for O behave similarly to paramagnetic (or diamagnetic) centres, which can be effectively studied within spectral analysis of the electronic paramagnetic resonance.$^{[57]}$

### 2.2 Theoretical Simulations

In spite of numerous efforts undertaken so far, comprehensive understanding of fundamental changes in the electronic structure of the doped semiconductors is still not sufficient for the rational design of their atomic composition. It is necessary to formulate a theoretical procedure to predict prudently the electronic structure and the charge redistribution in photocatalysts. A number of simulations performed so far deal mainly with doped and co-doped photocatalytic bulk materials$^{[52,55,57-64]}$ and their low-index surfaces$^{[65-67]}$ as well as 0D and 1D nanostructures.$^{[68,69]}$ There are two critical issues that are important for photocatalysis, but not yet well treated in conventional density functional theory, as well as other first-principles packages: 1) the lack of resources, essential for simulations of the strong polarization on the charged electrode surfaces in aqueous electrolyte; and 2) the inaccuracy of existing DFT functionals for a proper alignment of the $H^+/H_2$ and $H_2O/O_2$ potentials with the edges of the band gap or the induced dopant levels.$^{[70]}$ These great challenges still exist for the simulation of photocatalytic reaction kinetics driven by excess holes/electrons accumulated in catalysts.

Using the DFT method with the Perdew–Burke–Ernzerhof functional in the framework of the generalized gradient approximation (GGA) method, Khan et al. have shown that simultaneous anatase-phase bulk codoping with Mo and N atoms leads to TiO$_2$ band-gap reduction from 2.12 eV to 1.50 eV, as well as enhancing visible-light photocatalytic activity due to the effective utilization of electron–hole pairs in the oxidation/reduction process.$^{[58]}$ For the same anatase, spin-polarised DFT calculations predict that 2N + W codoped TiO$_2$ bulk can be considered as a quite efficient visible-light photocatalyst.$^{[59]}$ Hou et al. modelled transition-metal ions implanted into TiO$_2$ bulk, using the full-potential linearized augmented plane-wave (FP LAPW) method, and found that the 3$d$ states of V, Cr, and Fe ions play a key role for the redshift of the ultraviolet-visible absorption spectrum.$^{[60]}$ DFT + U studies of Nb–N–S tri-doped anatase within the GGA approach and PBE exchange-correlation functional have shown that the mixture of new N(2p) and S(3p) states on the top of the valence band, as well as the Nb(4$d$) states in the bottom of conduction band, reduce the band gap from 3.2 to 2.0–2.5 eV.$^{[61]}$ Nishikawa et al. demonstrated within the DV-Xa calculations that V, Cr, Mn, Fe, Co, Ni, or Rh dopants can shift the absorption of TiO$_2$ anatase and rutile phases into the visible-light region.$^{[62]}$ After that, they also considered the correlation between the dopants’ radii and changes in their electronic structure.
concluding that Ni$^{3+}$ and V$^{5+}$ dopants produce the best contribution to water splitting. Asahi et al. studied the band structure of the C-, N-, F-, P-, and S-doped anatase structure of titania bulk using the same FP LAPW method. The substitution of O by N, leading to mixing of the N(2p) and O(2p) states, produces the best conditions for photocatalytic applications, since such structural modification results in an upward shift of the top of the VB, thus reducing the width of the band gap. Finally, Harb used screened Coulomb hybrid DFT calculations within the projected augmented wave (PAW) approach to calculate the positions of bands for Se-modified anatase bulk.

Using the PAW method for DFT calculations, Nolan found that small iron-oxide clusters can be stable at the TiO$_2$ surface, and their presence squeezes the band gap towards the frequency range of visible light arising from the presence of iron-oxide states lying above the valence band of titania. PW DFT calculations, in combination with ultraviolet photoelectron spectroscopy, have been used to study the origin of the band-gap states of a rutile-structured TiO$_2$(110) slab induced by surface –OH groups. C-, N- and S-doped (TiO)$_2$ nanoclusters were studied by Shevlin and Woodley using both standard and time-dependent DFT calculations. The phase structure, surface morphology, optical properties, and photocatalytic activities of TiO$_2$ nanoparticles monodoped and codoped by Mn and/or N were studied using DFT-GGA calculations, as well as X-ray powder diffractometry, Raman spectra, scanning electron microscopy, X-ray photoelectron spectroscopy, and UV-Visible diffuse reflectance. The Mn + N codoped specimen manifested a higher photocatalytic activity.

Various doped materials exhibit a large mismatch between the length scales over which the photon absorption occurs (up to micrometres). On the contrary, at relatively short distances, within the limit of a few tens of nanometres, at which electrons can be extracted, electron–hole recombination was observed. A reliable approach for solving this problem was found to be the synthesis of nanostructured electrodes with orthogonalised directions of photon and electron propagation, which was achieved by markedly increased surface-to-volume ratios. Nanotubes synthesized from the wide-gap materials exhibit not only large surface areas, but also high mechanical stability and integrity, leading to both charge transport and electron–hole separation. TiO$_2$ (6,6) NTs built as regularly distributed bundles consisting of rutile (110) monolayers were calculated recently using the DFT method. The reported electronic properties of such a structure are predicted to be close to those of TiO$_2$ bulk. Possibilities of band-gap modification in C-doped TiO$_2$ NTs were estimated within the DFT-PAW approach. Interaction between C(2p) and O(2p) states provides no contribution to band-gap modification.

For the majority of DFT calculations on doped TiO$_2$ structures mentioned above, the standard LDA or pure GGA (mainly PBE) exchange-correlation functionals were applied. These approaches resulted in severe underestimation of the band gaps (except for those applied in Refs. [58,64,65], where both GGA and Hubbard DFT+U functionals were used). Obviously, results obtained in such calculations cannot be properly compared with experimentally estimated distributions of photoinduced levels in the band gap of doped titania. However, for simulations of N- and F-doped, as well as codoped, TiO$_2$ particles (experimentally studied too, as mentioned in Section 2.1), B3LYP hybrid functionals were used (together with standard PBE), for adequate comparison with EPR and XPS spectra of titania powder doped with paramagnetic atoms.

Finally, very little has been reported so far on the computer simulations of realistic defective titania NTs: the lack of periodicity makes their theoretical study computationally very time-consuming and expensive. Another obstacle is the fact that a consistent first-principles computational methodology has been missing, until recently, which could exploit periodic roto-translational symmetry for efficient ground-state calculations, as well as provide detailed simulations of the excited-state and charge-transfer processes.

3. Progress in Contemporary Researches of Doped ZnO Applicability for Photocatalysis

3.1 Experimental Studies

Zinc oxide is one of the most attractive materials, since it is chemically stable, nontoxic, cheap, and it has both a high charge mobility and long lifetime of excited electrons. Stable ZnO structures are mainly formed for the wurzite phase, whereas sphalerite (zinc-blende) and cubic (rock-salt) phases are usually considered metastable for zinc oxide. Wurtzite-structured ZnO is found to be advantageous over titania in terms of charge mobility; on the other hand, it is more vulnerable to photocorrosion, especially under UV irradiation (nevertheless, photocorrosion can be inhibited, e.g., by coupling with various carbon structures).

A number of experiments focused on applications of zinc oxide for photocatalytic H$_2$ generation have been performed so far, mainly using their doping by carbon. To improve the performance of ZnO–C photocatalysts, it was found necessary to utilize the structural advantage of the carbon nanomaterials for controlling the morphology of the ZnO nanocrystals, rather than to introduce carbon nanomaterials merely as the precursor for the ZnO–carbon composite. Surface functional groups on the carbon nanomaterials were able to act as favourable nucleation sites for ZnO nanoparticles, thus tailoring their microstructure and size. A method allowing suppression of photocorrosion for ZnO nanoparticles by surface hybridization with graphite-like carbon layers was devel-
oped by L. Zhang et al.\[80\] The photocatalytic suitability of these nanoparticles was also enhanced, which can be attributed to the improved adsorption ability and crystallinity, thus providing their high activity for significantly longer time intervals than pure ZnO nanoparticles. In accordance with the first systematic study of C-doped ZnO nanostructures as catalysts for water splitting performed by Lin et al.\[81\] they were found to be advantageous over many other approaches for increasing solar-light utilization. Another advantage of porous carbon-doped ZnO nanoarchitectures was exemplified by their stability in photooxidation processes, showing significantly increased efficiency after long-term experiments, as compared with pure ZnO nanostructures. A synthesis route of C-doped ZnO through urea-assisted thermal decomposition of zinc acetate, and further formation of nanorods and nanoparticles, evaluated via degradation of methylene blue under sunlight irradiation, was recently reported by X. Zhang et al.\[82,83\] Carbon incorporation reduced the band gap of synthesized ZnO nanostructures and improved the charge separation efficiency, thereby enhancing sunlight photocatalytic activity. Alshammar et al.\[84\] studied C-doped 2D ZnO nanoflakes with large surface areas, which could be successfully synthesized via a pyrolysis process using a polymer-directed agent. Carbon doping resulted in enhanced UV and visible-light absorption, which did not affect the electron-transition characteristics of ZnO. The direct band gap of C-doped nanoflakes was found to be 2.98 eV, though its light adsorption tailed beyond the visible-light region, because of coexisting O vacancies ($V_0$) and C dopants, which can lead to significant charge recombination. An alternative conclusion was drawn on the efficiency of C-doped photocatalysts was drawn by Flores et al.\[85\] who studied ZnO samples of different morphologies. When using C-containing reagents for the synthesis of non-carbon-doped structures in their experiments, carbon could play the role of a contaminant, deteriorating the photocatalytic efficiency in specific cases.

Alternatively, Ag-doped ZnO nanostructures were also investigated as potential photocatalysts.\[85-87\] M. Hsu and C. Chang studied photocatalysts fabricated of Ag-doped ZnO nanorods grown on stainless-steel wire meshes.\[85\] It was shown that silver dopants enhance absorption of solar light. Moreover, the hydrophilic properties of nanorods, combined with an increased surface area and an improved separation of excited electrons and holes, enhance their overall photocatalytic activity. Thomas et al. synthesized Ag-doped ZnO NWs using a low-temperature electrochemical process,\[86\] and found that Ag dopants are likely to occupy regular Zn sites. Khosravi-Gandomani et al. studied Ag-doped ZnO nanoparticles synthesized by a sol-gel method.\[87\] Both pristine and Ag-doped ZnO are crystallized in a wurtzite phase. XPS clearly shows dopant incorporation into the crystalline structure, while in UV-Vis absorption spectra, the band gaps of the considered nanostructures decrease simultaneously with the increase of dopant concentration. Pristine and Ag-doped ZnO nanoparticles were used as source materials to grow pristine and Ag-doped ZnO nanowires on n-type Si substrates, while the Ag-doped ZnO NWs per se exhibit p-type properties.

Gallino et al. synthesized N-doped ZnO powders starting from commercial ZnO nano-sized particles (with $<100$ nm size).\[88\] Nitrogen impurities incorporated into polycrystalline ZnO upon annealing in an NH$_3$ atmosphere demonstrate effective p-type doping. EPR experiments were performed when using 580 Bruker spectrometer (with microwave frequency 9.76 GHz) equipped with a liquid helium cryostat. All experiments were done at 5 K, with a repetition rate of 1 kHz. The magnetic field was measured with a Bruker NMR Gaussmeter. Wang et al. studied solution-based ZnO nanorod arrays modified by controlled N doping using an advanced ion-implantation method.\[89\] They subsequently utilized NW arrays as photoanodes for photoelectrochemical water splitting under visible-light irradiation. The gradually distributed N dopants shift the optical absorption edges to the visible-light region, which results in the efficient driving of photo-induced electrons and transfer of holes.

### 3.2 Theoretical Simulations

Unlike experimental studies on ZnO photocatalysts, their theoretical simulations are rather scarce.\[78,80,86,88,90,91\] DFT calculations on C-containing ZnO supercells\[83\] revealed that the origin of the visible-light response of carbon-doped ZnO is related to the additional mid-gap energy levels arising due to doping, and corresponding creation of $V_0$ vacancies in the presence of carbon,\[83\] which are energetically well correlated with XPS data. In pure zinc oxide, O(2p) and Zn(4s) states mainly form the top of the VB and the bottom of the CB, respectively. Unlike pristine ZnO, the VB of C-doped ZnO is dominated by the C(2p) state, as well as hybridised O(2s) and O(2p) states induced by $V_0$, while the CB mainly contains Zn(4s), partially accompanied by Zn(3d) states.

Pan et al.\[78\] explored the band structure, optical absorption, and thermodynamic stability of both monodoped (C or N anions and Cr, Sc, V, or Ti cations), as well as co-doped ZnO bulk, employing hybrid DFT calculations. The obtained results show that compensated (Ti + C) and non-compensated (Sc + C) and (Cr + C) codoped ZnO are rather strong candidates for photoelectrochemical (PEC) hydrogen production from water, because of their narrowed band gap to the visible-light region, potentially suppressed recombination of the electron–hole pairs, suitable band edge positions, and good thermodynamic stability for PEC water splitting.

Li et al. performed DFT calculations to study the influence of Ag dopants on structural, electronic, and optical properties of ZnO NWs,\[90\] focusing on the thinnest nanowires only. An expected finding was that Ag dopants sub-

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**References:**

stitute Zn sites (but not regular oxygen or interstitial sites), regardless of defect concentration, and prefer sites on the NW edges. Simulations of optical properties show enhanced absorption in the visible-light region, which supports the hypothesis that ZnO NWs possess high potential as photocatalysts. Moreover, DFT calculations on Ag-doped ZnO NWs confirm earlier experimental conclusions on Ag atoms in ZnO nanowires, which produce an impurity band, along with an absorption redshift.

The hybrid B3LYP functional was first adapted by Pacchioni et al. to compute the optical and thermodynamic transition levels between different charge states of defect impurities (H and Zn impurities, oxygen vacancies, and N dopants) in bulk ZnO. Nitrogen species were found to be rather deep acceptors, as confirmed by a combined EPR and DFT/B3LYP study. The substitutional lattice site is more stable and better fits the experimental evidence. However, N$_2$ substitutes do not provide a viable route for p-type doping of ZnO.

### 4. Theoretical Background

#### 4.1 Computational Details

A series of large-scale *ab initio* calculations have been performed by us for the two classes of monoperiodic nanostructures found to be suitable for photocatalytic applications. Firstly, we have studied anatase-structured TiO$_2$ (001) and (101) NTs, with a fixed number of atomic layers and chiral indexes: $(n,0)$ vs. $(0,n)$, respectively, monodoped by either C, N, or Fe atoms, as well as codoped by N and S atoms, simultaneously. Alternative nanomaterials potentially suitable for photocatalysis have been considered to be [0001]-oriented and hollow-centred wurtzite-structured ZnO NWs monodoped by C, N, or Ag atoms.

To perform *ab initio* calculations on both types of 1D structures, we have applied the DFT-LCAO method within the formalism of localised atomic orbitals, as implemented in the CRYSAL14 code. For calculations on pristine and doped TiO$_2$ NTs, we have used the B3LYP hybrid exchange-correlation functional. For better reproduction of TiO$_2$ atomic and electronic structure obtained in experiments and simulations, the standard B3LYP Hamiltonian has been modified by us in such a way that the contribution of nonlocal HF exchange has been reduced from the original 20% to 14%, (B3LYP-mod). For ZnO NWs, we have applied hybrid functional PBE0, without any change of the original 25% contribution to the hybrid Hamiltonian from the HF exchange.

To construct the basis sets (BSs) for each chemical element of considered nanostructures, we have used the formalism of the localised Gaussian-type functions (GTFs) implemented in CRYSAL code. For TiO$_2$ NTs (e.g., dopants), BSs have been chosen as either the all-valence, in the forms of 8s–411sp–1d for O, 6s–311sp–1ld for C, 6s–31lp–1d for N, 8s–63111sp–1ld for S, and 8s–6411sp–41d for Fe, or constructed using the effective core potential (ECPs) implemented by Hay and Wadt for the Ti atom, in the forms of 411sp–31ld. For doped ZnO NWs, we have chosen the all-valence BSs for oxygen, and doped N, S, and Ag atoms.

### Table 1. Lattice parameters of TiO$_2$ and ZnO crystals calculated by us and measured experimentally

<table>
<thead>
<tr>
<th>Method</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$u$</th>
<th>Space group</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.80</td>
<td>9.65</td>
<td>0.21</td>
<td>14, /amd</td>
</tr>
<tr>
<td>B3LYP-mod</td>
<td>3.79</td>
<td>9.52</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>PBE0 experiment</td>
<td>3.26</td>
<td>5.20</td>
<td>0.38</td>
<td>P6$_3$mc</td>
</tr>
<tr>
<td>experiment</td>
<td>3.25</td>
<td>5.21</td>
<td>0.38</td>
<td></td>
</tr>
</tbody>
</table>

[a] Experimental values are taken from Ref. [31].
Defective (e.g., doped) nanostructures can be characterized by the presence of induced levels inside the band gaps. The energy balance for water splitting under the influence of solar light photons is found to be more complicated in this case. The differences between the highest occupied and lowest unoccupied impurity levels inside the band gap (HOIL and LUUL, respectively) are reduced, as compared with pristine nanostructures. At the same time, the proper disposition of these levels must be preserved relative to the edges of the band gaps, as well as both redox potentials (corresponding to $\mathbf{H^+/H_2}$ and $\mathbf{O_2/H_2O}$ electrode processes) being separated by $\approx 1.23$ eV\(^{[13]}\). Thus, the conditions of nanomaterial suitability for photocatalytic applications can be expressed by the inequalities:

\[
\varepsilon_{\text{VB}} < \varepsilon_{\text{HOIL}} < \varepsilon_{\text{O_2/H_2O}} < \varepsilon_{\text{H^+/H_2}} < \varepsilon_{\text{LUUL}} < \varepsilon_{\text{CB}}
\]  

(1)

Distribution of energy levels inside the band-gap and redox potentials described by this inequality can be illustrated by Figures 3, 5–7 in Sections 5.1, 5.2, and 6, respectively. Due to the dissipation of a small amount of energy during the photocatalysis, two additional requirements must be fulfilled as well:

\[
\varepsilon_{\text{O_2/H_2O}} - \varepsilon_{\text{HOIL}} > \varepsilon
\]  

(2a)

\[
\varepsilon_{\text{LUUL}} - \varepsilon_{\text{H^+/H_2}} > \varepsilon.
\]  

(2b)

To estimate the possibility of forming a single substitutional dopant in a nanotube or nanowire, we have calculated the corresponding impurity defect formation energy:

\[
E_{\text{form}}^\text{tot} = E_{\text{A}_\text{dop}/\text{NT}}^\text{tot} + E_{\text{host} \to \text{imp}}^\text{tot} - E_{\text{A}_\text{dop}}^\text{tot} - E_{\text{NT}_\text{NW}}^\text{tot},
\]  

(3)

where: $E_{\text{A}_\text{dop}/\text{NT}}^\text{tot}$ is the calculated total energy of a nanotube or nanowire containing the substitutional $A_{\text{dop}}$ dopant atom; $E_{\text{host} \to \text{imp}}^\text{tot}$ is the total energy of the host atom, which is removed from the nanotube or nanowire; $E_{\text{A}_\text{dop}}^\text{tot}$ is the total energy calculated for the impurity (dopant) atom; while $E_{\text{NT}_\text{NW}}^\text{tot}$ stands for the total energy calculated for the perfect nanotube or nanowire.

### 4.3 Atomic Models of Doped TiO\(_2\) Nanotubes

According to our preliminary calculations, a 9-layered NT with (36,0) chirality possesses a negative strain energy, corresponding to an energy minimum, as compared with analogous nanotubes with other (n,0) chirality.\(^{[17,101]}\) Such a nanotube contains 324 atoms per NT unit cell (or 648 per supercell, as given in Table 3); it is described by a di-

<table>
<thead>
<tr>
<th>TiO(_2) NTs</th>
<th>$n_{\text{nt}}$</th>
<th>$l_{\text{nt}}$ (nm)</th>
<th>$d_{\text{nt,inner}}$ (nm)</th>
<th>$d_{\text{nt,outer}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(001) (36,0)</td>
<td>648</td>
<td>0.35</td>
<td>3.48</td>
<td>4.82</td>
</tr>
<tr>
<td>(101) (−12,12)</td>
<td>432</td>
<td>0.53</td>
<td>3.75</td>
<td>4.23</td>
</tr>
</tbody>
</table>

Table 3. Number of atoms per NT supercell ($n_{\text{nt}}$), optimized SC length ($l_{\text{nt}}$), as well as inner and outer diameters of NT ($d_{\text{nt,inner}}$ and $d_{\text{nt,outer}}$, respectively) as calculated for titania (001) and (101) nanotubes (Figures 1a, 1b and Figures 1c, 1d, respectively).

\[\text{Isr. J. Chem. 2017, 57, 461–476} \quad \text{© 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim} \quad \text{www.ijc.wiley-vch.de} \quad 468\]
4.4 Atomistic Models of Doped ZnO Nanowires

The regular hexagonal prismatic shape of wurtzite-type ZnO nanowires, synthesized in numerous experiments, e.g., Refs. [84,86], can only be formed if the NW axis is oriented along the [0001] crystallographic direction, being hollow-centred.\textsuperscript{[31]} Arbitrary nanowires can be stabilized when they are terminated by lateral facets, which possess the smallest surface energy among any wurtzite faces. This requirement is fulfilled for the family of six identical \{1100\}, \{1100\}, \{1010\}, \{0110\}, \{0110\} and \{0110\} facets of zinc oxide, since they possess the smallest surface energy among wurtzite faces.\textsuperscript{[102]} The last edition of CRISTAL14 code, used for our calculations on ZnO nanowires, contains the new option NANOROD, allowing users to generate differently structured NWs when setting the properly chosen Miller indices of their lateral facets, and thus, simultaneously defining their crystallographic orientations.\textsuperscript{[92]}

To estimate the suitability of doped [0001]-oriented ZnO NWs of different sizes for photocatalytic applications, we have preliminarily considered pristine NWs of three different diameters (Table 4), which can be cut from a host wurtzite-type crystal. We have performed a number of ab initio calculations on each of them, accompanied by total geometry optimization. The initial values of $d_{\text{NW}}$ have been varied from 2.1 to 3.2 nm, which correspond to a consequent extension of the hexagonal NW cross-section containing from four \((4 \times 4)\) to six \((6 \times 6)\) coordination cylinders around the NW axis. (Since the calculated band gaps of the thinnest nanowires with \(2 \times 2\) and \(3 \times 3\) extensions considerably exceed the values of $\Delta E_{\text{gap}}$ for wurtzite-structured ZnO bulk, i.e., \(3.7-4.0\) eV vs. \(3.3-3.4\) eV\textsuperscript{[15]} we have excluded estimates of their photocatalytic suitability from further consideration).

Figure 2 shows that the structural optimization of nanowires results in the noticeable relaxation of the outer atomic layers, while the inner atoms practically remain in the regular cross-section sites, whereas the UC length along the NW axis \(l_{\text{NW}}\) is noticeably reduced with growing nanowire diameter (Table 4).

We have studied whether dopants favour the inner or outer NW regular sites for substitution (Figure 2), since one expects the photocatalytic process to be mostly influenced by outer defects.\textsuperscript{[21]} Further modelling is focused on
those of titania (101) (their surface energies are 0.90 J m\(^{-2}\) vs. 0.44 J m\(^{-2}\), respectively).\([102]\) the former possess markedly higher chemical reactivity,\([104]\) and mechanical plasticity (as follows from the aforementioned effect of negative strain energy).\([101]\) Nevertheless, this is true for chemically clean and structurally perfect surfaces only, because for F-terminated surfaces, the relative stability of crystalline facets of anatase-structured titania is reversed: the (001) surface is energetically more preferable than the (101) one.\([105]\) On the basis of theoretical predictions, uniform anatase TiO\(_2\) single crystals with a high percentage (47\%) of F-doped \{001\} facets were synthesized (using a hydrofluoric acid medium as a morphology-controlling agent). These data allow us to analyse the calculated properties of TiO\(_2\)(001) NTs first.

5.1 \{(001)\}-oriented TiO\(_2\) Nanotubes

The choice of (36,0) chirality for pristine anatase-type 9-layered TiO\(_2\)(001) NTs (Figures 1a, 1b) is described in Section 4.3; it corresponds to the minimum of the \(E_{\text{form}}(d_{\text{FW}})\) curve.\([92]\) Comparison of dopant formation energies defined by Eq. (3) allows one to estimate the preference of their formation in nanostructures: impurity atoms have substituted each possible irreducible host O or Ti atom in the nanotubes with the roto-translationally and periodically repeated UCs shown in Figure 1a. Therefore, one of the six \(O\) sites and one of the three \(Ti\) sites have been consequently substituted by C\(_{\text{O}}\), N\(_{\text{O}}\), S\(_{\text{O}}\) and Fe\(_{\text{Ti}}\). According to our calculations, both C and S dopants would prefer to be positioned at the site of the outermost oxygen, and nitrogen in proximity of the second oxygen surface is energetically more preferable than the (101) one.\([105]\) On the basis of theoretical predictions, uniform anatase TiO\(_2\) single crystals with a high percentage (47\%) of F-doped \{001\} facets were synthesized (using a hydrofluoric acid medium as a morphology-controlling agent). These data allow us to analyse the calculated properties of TiO\(_2\)(001) NTs first.

5. Predictions on Photocatalytic Efficiency of Doped Titania Nanotubes

Although anatase-structured titania (001) nanolayers and nanotubes were found to be energetically less stable than

\[\text{Figure 2. (a) Cross-sectional and (b) lateral images of the doped wurtzite-based hexagonal-shaped ZnO NW extended by 6 × 6 \text{atomic shells around the hollow-centred [0001]-oriented axis, containing 216 formula units (or 432 = 12 × 6}^2 \text{atoms) per NW unit cell. The diameter and period of a nanowire are shown by the double arrows \(d_{\text{NW}}\) (a) and \(h_{\text{FW}}\) (b), respectively. An example of defect distribution at 3\% concentration in a wurtzite-based hexagonal-shaped ZnO NW unit cell is given. Zn and O atoms are shown as small red and middle blue-grey balls, respectively. Outer (yellow) or inner (green) site alternatives are highlighted. The magnitudes of the UC lengths (\(l_{\text{UC}}\), the diameters of the nanowires (\(d_{\text{NW}}\), as well as the number of atoms per unit cell (\(n_{\text{UC}}\) are systematized in Table 4.} \]

\[\text{Table 5. Defect formation energies (}\mathbf{E_{\text{form}}}\text{, eV) in doped anatase-type TiO}_2\text{(001) NTs and bulk estimated using Eq (3).} [\text{a}] \]

<table>
<thead>
<tr>
<th>inset site (Figure 1a)</th>
<th>(C_{\text{O}})</th>
<th>(N_{\text{O}})</th>
<th>(S_{\text{O}})</th>
<th>(Fe_{\text{Ti}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(4%) concentration of dopants</td>
<td>(8%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1.16([8])</td>
<td>3.79</td>
<td>2.61([8])</td>
<td>5.58</td>
</tr>
<tr>
<td>2</td>
<td>3.23</td>
<td>3.56([8])</td>
<td>3.6</td>
<td>5.42</td>
</tr>
<tr>
<td>3</td>
<td>2.99</td>
<td>3.95</td>
<td>4.34</td>
<td>5.37([8])</td>
</tr>
<tr>
<td>4</td>
<td>3.13</td>
<td>3.88</td>
<td>5.33</td>
<td>–</td>
</tr>
<tr>
<td>5</td>
<td>3.31</td>
<td>4.08</td>
<td>5.65</td>
<td>–</td>
</tr>
<tr>
<td>6</td>
<td>3.78</td>
<td>4.11</td>
<td>3.37</td>
<td>–</td>
</tr>
<tr>
<td>bulk([8])</td>
<td>4.12</td>
<td>3.22</td>
<td>5.36</td>
<td>4.44</td>
</tr>
</tbody>
</table>

[\text{[a] Host atoms A}\(_i\) substituted by impurities (h) are labelled in Figure 1. [b] The lowest formation energies for dopants are shown in bold. [c] For the bulk, concentration is one dopant per \(2 \times 2 \times 2\) supercell.} \]
quired for the formation of the N\textsubscript{0} dopant vs. 5.37 eV for Fe\textsubscript{V}. The formation energy of the N + S pair has been obtained to be 5.64 eV, which fulfills the inequality:

$$2E_{\text{form}}(S_0) < E_{\text{form}}(S_O + N_O) < 2E_{\text{form}}(N_O),$$

thus confirming the approximate additivity of estimated dopant formation energies. When calculating the band structure of the doped nanotubes, only the nanotubes with the lowest defect formation energies have been taken into account, irrespectively of their chemical nature and number of impurity atoms.

The energy balance between the band-gap edges of semiconductors (e.g., mid-gap levels induced by defects) and the redox levels, as described by Eq. (1), is considered as a criterion for the efficiency of photocatalytic water splitting.\[2\,13,90\] The total and projected DOSs computed for both the monodoped (C\textsubscript{C}, N\textsubscript{O}, S\textsubscript{O}, and Fe\textsubscript{V}) and codoped (N\textsubscript{O} + S\textsubscript{O}) titania (001) nanotubes have been recently described by us in detail.\[19\] An alternative description of the electronic structure for doped TiO\textsubscript{2} NTs has been suggested by us in the same paper, where the schematic representation of the band-gap edges of pristine and doped nanotubes ($E_{\text{CB}}$ and $E_{\text{VB}}$), as well as the mid-gap states of doped TiO\textsubscript{2} nanotubes ($E_{\text{OHOL}}$ and $E_{\text{LULH}}$), has been given in the form of either solid or dashed horizontal segments (for occupied or empty levels, respectively), while both the conduction and valence bands have been imaged as filled rectangular columns, as shown in Figure 3.\[18\,20\] The blue and red horizontal dashed lines correspond, in this representation, to the oxidation ($E_{\text{O}_2/H_2}$) and reduction ($E_{H_2/O}$) potentials, respectively. As the zero of the energy scale, the potential of the standard hydrogen electrode (SHE) has been chosen.\[2\,10\]

As can be observed in Figure 3, for pristine titania nanotubes, the bottom of the conduction band is ~1.0 eV above the H$^+/\text{H}_2$ potential, whereas the top of its valence band is ~1.2 eV below the O$_2$/H$_2$O potential. A carbon substitutional impurity in a TiO\textsubscript{2} NT induces an unoccupied defect level ~0.2 eV above the oxidation potential. This leads to an unsuitable valence-band position for the oxygen evolution reaction and can cause electron–hole recombination after photoexcitation. The N-doped TiO\textsubscript{2} NT possesses an occupied impurity state practically at the level of the O$_2$/H$_2$O potential (i.e., inequality Eq. (2b) is not fulfilled), while the bottom of the CB relative to the pristine NT is almost unchanged. For the sulfur-doped titania nanotube, we predict that the bottom of the conduction band is located almost at the level of the reduction potential (but in this case Eq. (2a) is fulfilled), while the top of the valence band corresponds to that of the pristine nanotube being practically unchanged; therefore, it is a good candidate for photocatalytic applications. The iron-doped titania NT exhibits defect-induced mid-gap states about 0.5 eV lower than the $E_{\text{H}_2/O}$ level, which certainly results in the recombination of photoexcited electrons and holes. At the same time, considering the possible configurations of the doped titania (001) nanotube, we predict that a much more efficient nanophotocatalyst for visible-light-driven H$_2$O splitting could be N + S codoped TiO\textsubscript{2} NTs.

### 5.2 (101)-oriented TiO\textsubscript{2} Nanotubes

The choice of (−12,12) chirality for pristine anatase-type 6-layered (101) titania NT (Figures 1c, 1d) is also explained in Section 4.3.\[20\] We consider four possible dopant sites for this 6-layered nanotube, to substitute the nonequivalent oxygen atoms, as shown in inset of Figure 4a. The outer S\textsubscript{O} dopants are found to be the energetically favourable (Table 6). As it has been found, in all cases the sulfur dopant shows a trend of being displaced from its initial position. The direction of this displacement is orthogonal to the tangent line passing through the initial dopant position, and it is protruding out of the nanotube wall. Obviously, it is easier to follow such displacement from the initial S1 and S4 positions (Figure 4a), which explains why formation energies of dopants are lower in these cases. Values of $E_{\text{form}}$ for S dopants almost do not depend on their concentration, unlike N dopants, for which this dependence is noticeable, excluding the external N1 site. For the two sulfur dopant sites lying closer to the external S1 and S2 surface sites (Figure 4a), there is a negative shift in energy for both the $E_{\text{CB}}$ and $E_{\text{VB}}$ values. In fact, there is no difference between the CB/VB positions of the pristine nanotube and the NTs containing S dopants at the O3 and O4 sites.
Doping at S1 and S4 promotes the highest photocatalytic enhancement, reducing the gap between the \( E_{\text{LUMO}} \) and \( E_{\text{HOMO}} \) states, from 4.19 eV to 3.14 eV (3.12 eV) vs. 3.08 eV (3.07 eV) for 1.4% (2.8%) defect concentrations, respectively. It means that sulfur atoms alone do not provide sufficient rise in the photocatalytic activity. S-induced occupied levels have been found to be lower at 1.4% concentration. Unlike S-doped nanotubes, N dopants do not induce any visible shift in the position of the VB top, and the CB bottom levels are almost the same as in the case of the pristine structure. N dopants, however, induce empty states inside the band gap.

The suitability of N\(_{0.3}+S_0\) codoped TiO\(_2\) (101) nanotubes is noticeably higher than S and N monodoped ones. Indeed, in the latter, there are only four nonequivalent dopant positions (Figure 4a). However, after one dopant is introduced, a larger number of options for different combinations of codopant positions appear. Due to limited computational resources, we have decided to put the S dopant in its most preferable position, S1. Therefore, in every modelled codoped structure the S atom is fixed in position 1, while N dopants can be inserted into different surrounding positions. Possible dimer-type sites for S+N codopants are assigned by additional indexes for identification; note that not all the possibilities were implemented by us due to limited resources.

The energy diagram of the six studied N\(_{0.3}+S_0\) codoped TiO\(_2\) NTs, each with a defect concentration of 2.8%, is shown in Figure 5. Obviously, the (N3-S1)\(_B\) and (N3-S1)\(_N\) configurations are identical, and one of them (the latter) is excluded from further consideration. The general observation is that the photocatalytic efficiency of the simulated structures may be expected. In four cases out of six, the lowest empty state \( E_{\text{LUMO}} \) is induced slightly below the \( E_{\text{O}2=\text{H}_2\text{O}} \) level (oxygen potential), and the highest occupied state \( E_{\text{HOMO}} \) is located between the empty state and the VB top. In two cases, the distance between the empty and occupied induced state is not that of (N1-S1)\(_B\) or (N4-S1)\(_B\), which means that it might be relatively easy for electrons to transfer to the empty state, and consequently, to overcome the energy interval between both redox potentials (Figure 5). The general observation is that, in most cases, S and N atoms have a trend to be found closer to each other. Based on our calculations, we predict that S or N monodopants introduced into the 6-layered TiO\(_2\) (−12,12) NT cannot result in a marked rise in the photocatalytic response. On the other hand, the S+N codoping of this nanotube can result in the enhancement of photocatalytic efficiency, at least qualitatively. Moreover, we conclude that changes in the electronic structure of TiO\(_2\) NTs, induced by codoping, depend on defect distribution, both for (001) and (101) chiralities.

<table>
<thead>
<tr>
<th>inset site</th>
<th>Concentration of defects</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Figure 4a)</td>
<td>1.4% S(_0) N(_0) 2.8% S(_0) N(_0)</td>
</tr>
<tr>
<td>1</td>
<td>2.47(^{[a]}) 3.39(^{[a]}) 2.47(^{[a]}) 3.39(^{[a]})</td>
</tr>
<tr>
<td>2</td>
<td>2.89 3.49 2.90 4.10</td>
</tr>
<tr>
<td>3</td>
<td>3.43 3.51 3.47 4.15</td>
</tr>
<tr>
<td>4</td>
<td>2.62 3.51 2.62 3.39</td>
</tr>
</tbody>
</table>

\(^{[a]}\) The lowest formation energies for dopants are shown in bold.

Figure 4. (a) Nonequivalent positions of N or S dopants in a segment of 6-layered (−12,12) TiO\(_2\) (101) NT; (b) considered sites (1.4% defect concentration) for N dopants if the S atom is located in position S1. Figure 4b “FR” stands for “front”; “B” for “between”; “N” for “near”; and “UND” for “under”.

Table 6. Defect formation energies \( E_{\text{form}} \) (eV) in doped anatase-type TiO\(_2\) (101) NTs and bulk estimated using Eq. (3).

Figure 5. Schematic of the band edges and mid-gap states of pristine and N+S codoped 6-layered (−12,12) TiO\(_2\) (101) nanotubes (for 2.8% defect concentration). The nomenclature of the codopants is described in Figure 4b. The description of the graphical details and numbers is the same as that given in the caption of Figure 3.
6. Predictions on Photocatalytic Efficiency of Doped Zinc Oxide Nanowires

To estimate the photocatalytic suitability of doped ZnO nanowires, we have calculated both their formation energies and energy diagrams, depending on NW diameter \( d_{\text{NW}} \) and defect concentration (Figure 2). In accordance with above analysed results of experimental and theoretical studies on doped zinc oxide nanowires (Section 3), we have considered mainly C, O, and Ag dopants (model parameters of doped ZnO NWs are considered in Section 4.4).

To estimate the ability of forming a substitutional dopant in ZnO NW, we have calculated the corresponding energies (Table 7) using Eq. (3). Obviously, they are larger for inner NW defects (Figure 2), since their coordination number is larger than that for outer ones. The smallest formation energy of doped ZnO NWs has been found for outer C dopant (3.3–3.4 eV per atom, irrespectively of defect concentration and \( d_{\text{NW}} \)), analogously to C defect in TiO \(_2\) NTs. Values of \( E^{\text{form}} \) for the outer Ag and N dopants are similar for the \( \sim 6\% \) concentration, while for the smaller \( \sim 3\% \) defect density, the former are markedly smaller. According to our simulations of doped titania NTs, the larger the difference between the dopant and host ionic radii, the larger the relaxation around the defect.

The energy diagrams, analogous to those presented for TiO \(_2\) nanotubes in Figures 3 and 5, are shown for different nanowire diameters and defect concentrations in Figures 6 and 7, respectively. Since comparison of the electronic structure of ZnO NWs for 3% and 6% defect concentrations clearly shows a higher photocatalytic efficiency of nanostructures with higher concentration of dopants per NW unit cell, we constructed the energy diagram depending on the values of the NW diameter, just for the fixed 6% concentration (Figure 6).

It allows us to predict that C-doped ZnO NWs show the most promising suitability for water splitting under the influence of visible light in the yellow-green range around 2.0–2.2 eV, which can occur when the NW diameter grows up to 3.0–3.5 nm while the concentration is \( \sim 6\% \). In this case, 15% efficiency of solar-light energy conversion can be achieved. This result is even more promising than that observed by us for C + O co-doped TiO \(_2\) (001) NTs. Still, the energy gaps for the two thickest NWs are larger, and roughly equal to 2.4 eV. The benefit of the lower carbon concentration is the lower position of the conduction bands, while the lower filled rectangles stand for the valence bands. Other details of the diagram are the same as described in the caption of Figure 3.

![Figure 6. Energy diagram for pristine and structurally modified ZnO nanowires with \( \sim 6\% \) defect content, depending on \( d_{\text{NW}} \). The red and blue horizontal dotted lines correspond to the redox \( E_{\text{O/H,O}} \) and \( E_{\text{H}_2/\text{H}_2\text{O}} \) potentials, respectively. The zero of the energy scale corresponds to the standard hydrogen electrode (SHE) level. Solid and dashed horizontal lines describe the \( E_{\text{HOL}} \) and \( E_{\text{LVL}} \) levels, respectively. The upper filled rectangles correspond to the conduction bands, while the lower filled rectangles stand for the valence bands. Other details of the diagram are the same as described in the caption of Figure 3.](Image 302x648 to 554x771)

<table>
<thead>
<tr>
<th>NW Size</th>
<th>Defect Concentration</th>
<th>C Defect (eV)</th>
<th>Ag Defect (eV)</th>
<th>N Defect (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 × 4</td>
<td>3.37</td>
<td>4.11</td>
<td>5.39</td>
<td></td>
</tr>
<tr>
<td>5 × 5</td>
<td>3.34</td>
<td>4.40</td>
<td>5.33</td>
<td></td>
</tr>
<tr>
<td>6 × 6</td>
<td>3.30</td>
<td>4.37</td>
<td>5.29</td>
<td></td>
</tr>
<tr>
<td>4 × 4</td>
<td>3.33</td>
<td>5.74</td>
<td>5.33</td>
<td></td>
</tr>
<tr>
<td>5 × 5</td>
<td>3.36</td>
<td>4.29</td>
<td>4.17</td>
<td></td>
</tr>
<tr>
<td>6 × 6</td>
<td>3.37</td>
<td>4.11</td>
<td>4.15</td>
<td></td>
</tr>
</tbody>
</table>

[a] In the case of \( \sim 3\% \) concentration of inner defects, the calculations have been found to be unstable.

Table 7. \( E^{\text{form}} \) energies (in eV) as calculated using the hybrid PBED functional. The defect concentration in ZnO NWs is fixed at \( \sim 3\% \) or \( \sim 6\% \). The “inn” stands for the inner defect configuration, while “out” for that of outer defects (Figure 2).
the position of the $\varepsilon_\text{HOMO}$ level is rather unfavourable at \(-6\%\) defect concentration, it moves downwards with growing $d_{NW}$ and also with decreasing Ag content. Unfortunately, the lowest unoccupied $\varepsilon_\text{LUMO}$ levels, adjacent to both the $\varepsilon_\text{HOMO}$ and $\varepsilon_\text{O$_2$/H$_2$O}$ levels (Figure 6), might promote charge recombination.

For thinner ZnO NWs with \(-6\%\) N content, $\varepsilon_\text{HOMO}$ is located above the $\varepsilon_\text{O$_2$/H$_2$O}$ level (Figure 6), which is a major drawback. For thicker NWs, $\varepsilon_\text{HOMO}$ is located below that level, while the $\Delta E_\text{gap}$ is too large to ensure efficient photocatalysis. A more promising result has been obtained for N doping at \(-3\%\) concentration (Figure 7). Here, the width of $\Delta E_\text{gap}$ exceeds 2.2 eV for thicker NWs. Although the $\varepsilon_\text{HOMO}$ level is slightly above the oxidation level, it shifts downwards with growing NW diameter, which allows us to make an optimistic prediction, since results for larger N-doped ZnO nanowires are rather relevant to real structures.

### 7. Perspectives

We have constructed atomistic models of pristine and doped anatase-structured TiO$_2$ nanotubes of two different morphologies, as well as [0001]-oriented ZnO nanowires with varied $d_{NT}$ and $d_{NW}$ diameters and defect concentration, in order to perform hybrid DFT-HF calculations and to analyse their suitability for photocatalytic applications. We have considered anionic C$_\text{P}$, N$_\text{P}$, S$_\text{P}$, and N$_\text{O}$ + S$_\text{O}$ mono- and codopants, as well as cationic Ag$_{Zn}$ and Fe$_{Ti}$ monodopants for simulations of TiO$_2$ nanotubes and ZnO nanowires. When performing large-scale ab initio simulations, we have established the highest photocatalytic efficiency for N$_0$ + S$_0$ codoped anatase-type TiO$_2$ NTs, as well as C$_\text{O}$ monodoped wurtzite-type [0001]-oriented ZnO NWs, corresponding to an optimal 15% solar energy conversion efficiency.

Comparing the results obtained by us recently with those published elsewhere, we can conclude that the hybrid DFT+HF method used by us for large-scale LCAO calculations on doped nanostructures of metal oxides, aiming at their suitability for photocatalytic applications, can be properly used for further calculations on new nanomaterials. We have established that electronic-state levels of 1D and 2D nanomaterials can be properly compared with redox potential levels when using DFT-LCAO CRYSTAL code, since the absolute zero vacuum level is reproduced correctly in these calculations.

Since structural reproducibility of experimentally synthesized ZnO nanowires is noticeably higher than that obtained so far for TiO$_2$ nanotubes, we believe that the suitability of ZnO NW-based photocatalysts is more reliable for practical applications. We are planning to extend the number of simulated nanostructures, both pristine and doped, for a theoretical estimate of their photocatalytic applicability, as well as to compare the calculated properties with those obtained for the corresponding newly synthesized nanomaterials.

Since our simulations in the framework of the ERA.Net RUS PLUS Project 237 WATERSPLIT are not limited by ground-state calculations, we are planning: 1) to combine them with the time-dependent first-principles calculations (TD DFT) as considered, e.g., in Ref. 23, to achieve a proper description of nanophotocatalysts in excited states (e.g., to determine the absorption spectra of doped nanostructures and to predict the conditions necessary to promote the generation of electrons and holes by photoexcitation); as well as 2) to perform nonadiabatic molecular dynamics simulations, combined with TD-DFT calculations, to investigate the charge-transfer processes at the surface of doped nanostructures immersed in an aqueous solution.

### Acknowledgements

This study has been supported by the EC ERA.Net RUS Plus project No 237 WATERSPLIT. R. E. appreciates the assistance of St. Petersburg State University Computer Center in high-performance calculations. The authors are indebted to A. V. Bandura, A. Chesnokov, E. A. Kotomin, A. Kuzmin, B. Polyakov, and E. Spohr for stimulating discussions. The technical assistance of A. Chesnokov is highly appreciated as well.

### References


Received: July 26, 2016
Published online: December 12, 2016