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First principles modeling of 3*d*-metal doped three-layer fluorite-structured TiO_2 (4,4) nanotube to be used for photocatalytic hydrogen production

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ABSTRACT

We have estimated theoretically the photocatalytic suitability of thinnest single-wall fluorite-structured titania (4,4) nanotube (NT) possessing three layers each (O-Ti-O) and doped by Sc, V, Cr, Mn, Fe, Co, Ni, Cu and Zn atoms substituted for host Ti atoms. For this goal, we have performed large-scale *ab initio* calculations on TiO_2 NTs with three-layer morphology doped by 3*d* transition metals, using (*i*) the method of linear combination of atom-centered Gaussian-type orbitals (LCAO) based on the hybrid density functional theory (DFT) incorporating the Hartree-Fock (HF) exchange contribution (DFT+HF) and (*ii*) the method of linearized augmented cylindrical waves (LACW) with the muffin-tin approximation based on the local density functional approach (LDA). We have compared the ground state electronic structure, particularly the one-electron densities of states (DOSs) from the LCAO and LACW calculations for periodic arrangements of the 3*d*-metal dopant atoms. The results show clear evidence for a potential photocatalytic application for water splitting in the case of the Sc-doped titania nanotubes only. These NTs show both a reduced band gap of 2.0 eV relative to the pristine NT and an absence of defect-induced levels between the redox potentials of hydrogen and oxygen, so that electron-hole recombination becomes unlikely. Other 3*d* dopants with higher atomic number, although their band gap also covers the favorable green to orange region of the solar spectrum, are unsuitable because their defect-induced levels are positioned between the redox potential of oxygen and hydrogen, which can be expected to lead to rapid electron-hole recombination.

1. Introduction

The discovery of H_2O photolysis on a TiO_2 electrode [1] was an important event in the development of electrochemical splitting of water or aqueous solutions under the influence of solar irradiation, which releases molecular hydrogen. Because of the chemical activity of TiO_2 (titania), its high stability, nontoxicity and low cost, this photocatalytic material has attracted much attention during the last two decades. However, its application in the field of renewable energy and ecological environmental protection is limited by the large value of optical gap $\Delta\varepsilon_{gap}$ of stable TiO_2 crystalline phases (3.2 eV for anatase- and 3.0 eV for rutile-structured titania [2]). Due to the wide band gap, this compound utilizes only a few percent of solar light in the UV range for photocatalysis, while almost half of the solar energy is emitted in the visible light range [3]. Thus, to make progress in the utilization of TiO_2 photocatalysts one must find ways to extend effectively the spectral TiO_2 response to the visible light region.

Electronic band modification is a promising way to extend the absorption edge of the TiO_2 [4–7] and possible by doping titania crystals with several 2*p* and 3*p* non-metal elements (C, N, F, and S) or by doping with transition 3*d*-, 4*d*-, and 5*d*-metal elements. The doping can either insert an impurity band into the original band gap, or it can modify the conduction or valence band somewhat, thereby improving the conditions for photocatalytic activity of the crystal. *Ab initio* calculations on the electronic structure of the

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titania crystals show that, particularly, Sc, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn 3*d*-metal dopants produce mid-gap states [8–15].

At the same time, a more effective way to improve the photocatalytic activity of titania was found to be the reduction of its dimensionality from 3D crystalline bulk to TiO_2 2D nanothin sheets or to 1D nanotubes. These materials possess, in addition, large surface areas and unique shapes with few interfacial grain boundaries, which promote charge transport and electron-hole pair separation [16]. Nano-tubular TiO_2 can be prepared by the hydrothermal method, *via* a sol–gel process, or when the carbon nanotubes (CNTs) being used as templates for titania growth, and a few others [17–23]. It has been found recently that NT surface structure, shape and diameter could be controlled for arrays of anodized TiO_2 nanotubes when applying an electric field [24].

Transformation of bulk to the nanotubes *via* formation of nanosheets can be expected to lead to an unfavorable growth of the band gap due to confinement effects, which, however, can fortunately be compensated or even used advantageously by implementation of transition metal dopants in NT using the ion-exchange technique with band gap states.

There are seven structural types of titania crystals, the majority of which are metastable [25]. Similar to the formation of minimum-thick CNTs from a graphene sheet, fluorite-type TiO_2 NTs can be constructed by rolling-up stoichiometric three-layer O-Ti-O nanosheets initially formed from more stable rutile (110) or anatase (101) slabs. The geometry optimization of three-layer anatase-structured O-Ti-O (101) slab spontaneously transforms it to a centered hexagonal (111) fluorite-structured nanosheet, which can be rolled up to form single-wall (SW) NTs with either armchair- or zigzag-type chirality [26,27].

The main purpose of the current study is to calculate the electronic structure of morphologically simple hexagonal TiO_2 nanotubes (which are metastable due to their extremely thin thickness), doped by 3*d* metal atoms. As it was shown in Ref. [28], when using DFT+*U* method, transition metal doping of titania anatase-structured crystals results in a reduction of the band gap. The number of experimental studies of TiO_2 nanostructures doped by 3*d* metal atoms is quite small. The efficiency of Sc-doped anatase nanoparticles was found to be 6.7% larger than the efficiency of dye-sensitized solar cells with pure anatase [29]. On the other hand, the conditions of synthesis are extremely important for photocatalytic properties of experimentally synthesized nanomaterials. In Refs. [30,31], Sc-doped and V-doped TiO_2 show lower photocatalytic activity as compared to non-doped anatase, which can be associated with a presence of metal oxide islands covering the reactive sites of Sc-doped TiO_2, and thus increased electron-hole pair recombination [31]. The photocatalytic activity of Rhodamine B caused by oxidation of TiO_2 NTs doped by Ag, Al, Mn, Ni and Zn was studied in Ref. [32] indicating preferable photocatalytic suitability of Zn-doped nanotubes.

With the goal in mind to obtain unbiased information and to estimate the importance of theoretical simulations, we have applied two different *ab initio* techniques, namely, the method of the linear combination of atomic orbitals (LCAO) with Gaussian-type orbitals [33,34] and the method of linearized augmented cylindrical waves (LACW) [35,36]. Previously, we studied the structural stability and the electronic band structure for pristine single- and multi-layer fluorite as well as anatase-type TiO_2 nanotubes with first-principle quantum chemistry [16,26,27,37,38]. The photocatalytic suitability of C, Fe, N, and S doped (*e.g.*, N+S co-doped) anatase-structured TiO_2 NTs with either the [001] or the [101] orientation of the chiral vectors was evaluated by us theoretically too [16,39–42]. In the present study, all calculations have been performed to estimate the suitability for the particular case of 3*d*-metal doped fluorite-structured (4,4) TiO_2 SW NTs with 24 atoms *per* translational unit cell (Fig. 1).

The paper is organized as follows. Models of pristine and doped fluorite-type (4,4) titania nanotubes as well as methods used to calculate their structural, electronic and photocatalytic properties are given in Section 2. Section 3 contains the analysis of TiO_2 SW NT features obtained from the Gaussian-basis LCAO method, a comparison of the LCAO- and LACW-simulated total and projected densities of states, and a comparative analysis of the photocatalytic capabilities of NTs under study. Obtained results are summarized in Section 4.

2. Theoretical background

2.1. Atomistic model of single-walled fluorite-structured (4,4) titania nanotube

Three-layer titania nanosheets with the hexagonal fluorite-type (111) structure can be rolled up to form 3-layer titania SW NTs with either (*i*) armchair-type (*n*,*n*) chirality or (*ii*) zigzag-type (*n*,0) chirality [26,27]. For our simulations, we have chosen the former with $n = 4$ (Fig. 1).

2.2. LCAO calculations

When constructing a 1D periodic model of SW nanotubes using CRYSTAL code [34], the formalism of periodic rototranslation symmetry has been exploited successfully. This approach has been applied earlier by us for simulations of perfect SW TiO_2 NTs belonging to either the anatase or fluorite type [26,27].

In the hybrid density functional theory approach, which incorporates an admixture of the Hartree-Fock exchange contribution (DFT+HF) together with the generalized gradient approximation (GGA), a modified B3LYP exchange-correlation functional [43] has been adopted by us for the LCAO calculations on both pristine and doped titania nanotubes. The reason for this approach is that it leads to a better reproduction of their atomic and electronic structure obtained earlier in experiments and theoretical simulations [39–42]. For the DFT-LCAO calculations, we have used the formalism of the localized Gaussian-type functions (GTFs), which form the basis set (BS) of atomic orbitals for each chemical element as implemented in the CRYSTAL code [34]. The following configurations of localized GTF functions have been adopted for

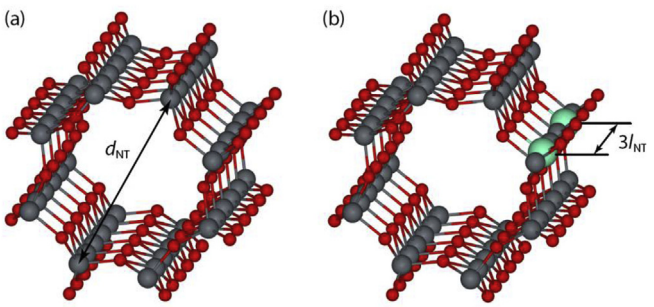

Fig. 1. Axonometric images of non-optimized pristine (a) and doped (b) armchair-type (4,4) fluorite-structured TiO_2 NT fragments containing three unit cells ($3l_{NT}$ corresponds to the tripled length of the unit cell). Small red, middle gray and large turquoise balls describe O, Ti, and 3*d*-metal dopant atom substituted for Ti atom, respectively. The nanotube diameter (d_{NT}), defined to be equal to the distance between two opposite Ti atoms inside one cross-layer of pristine NT (a) is 0.84 nm. The distance between the nearest dopant atoms along the NT axis is the tripled length of the nanotube unit cell (l_{NT}) containing 24 atoms *per* UC (8Ti+16O) (b). Thus, dopant concentration in considered fluorite-structured titania nanotubes equals to 4.17%. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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