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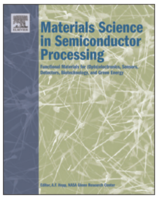

Ab initio calculations of doped TiO_2 anatase (101) nanotubes for photocatalytical water splitting applications

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ABSTRACT

TiO_2 (titania) is one of the promising materials for photocatalytic applications. In this paper we report on recently obtained theoretical results for N and S doped, as well as N+S co-doped 6-layer (101) anatase nanotube (NT). First principles calculations in our study have been performed using a modified B3LYP hybrid exchange-correlation functional within density functional theory (DFT). Here we discuss the energy of defect formation mechanism and electronic band structure for nanotubes under study. We also report on influence of dopant concentration on the NT's band structure and discuss the defect–defect interactions.

1. Introduction

TiO_2 (titania) is a promising photocatalyst for water splitting applications. However, bulk titania has low photocatalytic efficiency. It can be improved by making titania into nanotubes (NTs) with large surface area [1–3]. Further improvement of sunlight-driven TiO_2 NT catalytical activity is possible through the band gap engineering, *e.g.* by adding anion dopants. Theoretically, maximal solar energy conversion for a catalyst with a 3.2 eV wide band gap (*e.g.* TiO_2) is approximately 1%, but it can be as high as 15% for a catalyst with a 2.2 eV band gap [4]. Doped TiO_2 nanostructures have already shown improved efficiencies as inclusion of dopants leads to narrowing of the band gap from 3.2 eV (pristine material) to 2.0 eV. To shed more light on changes of the electronic structure made by the presence of dopants, we have performed *ab initio* calculations of TiO_2 NTs. In this study we model N and S doped, as well as N+S co-doped anatase NT with (101) morphology, which is reported to be the most stable NT [5]. From our recent calculations on less stable, but more chemically active TiO_2 NT rolled up from the (001) nanosheet we know that N+S co-doping may result in its visible-light-driven photoresponse enhancement [6]. Therefore from the modeling of the NT rolled-up from the titania nanosheet cut parallel to its (101) surface, we have revealed a number of dopant sites, and we have observed general trends in the composition of NT's electronic structure as a function of defect concentration in NT's wall.

2. Model and computational details

Modeling of S and N co-doped 6-layered (101) TiO_2 anatase nanotubes was performed using DFT method with the hybrid exchange-correlation functional (B3LYP having 14% of non-local Fock exchange) as implemented in the CRYSTAL computer code [7]. This computational approach is discussed by us in details elsewhere [6,8,9].

At a first stage of this study a number of undoped 6-layered anatase (101) NTs with chirality indices (n,0) and (0,n) have been modeled and their formation energies have been analyzed. Among them NT with chirality indexes (0,12) has been chosen for further doping. The choice is based on the compromise between a minimal formation energy and a number of atoms in the NT's unit cell. This nanotube consists of 432 atoms (Fig. 1). In the present study we consider NT's consisting of 1×3 and 2×3 periodically repeated "basic" unit cells (Fig. 1). The periodically repeated 1×3 unit cell consists of 36 atoms, while 2×3 one contains 72 atoms, giving dopant concentration of 2.78% (12 dopant per NT unit cell) and 1.39% (6 dopants per NT unit cell), respectively. Moreover we consider four possible dopant sites to substitute the non-equivalent oxygen atoms (Fig. 2). We denote the outermost oxygen

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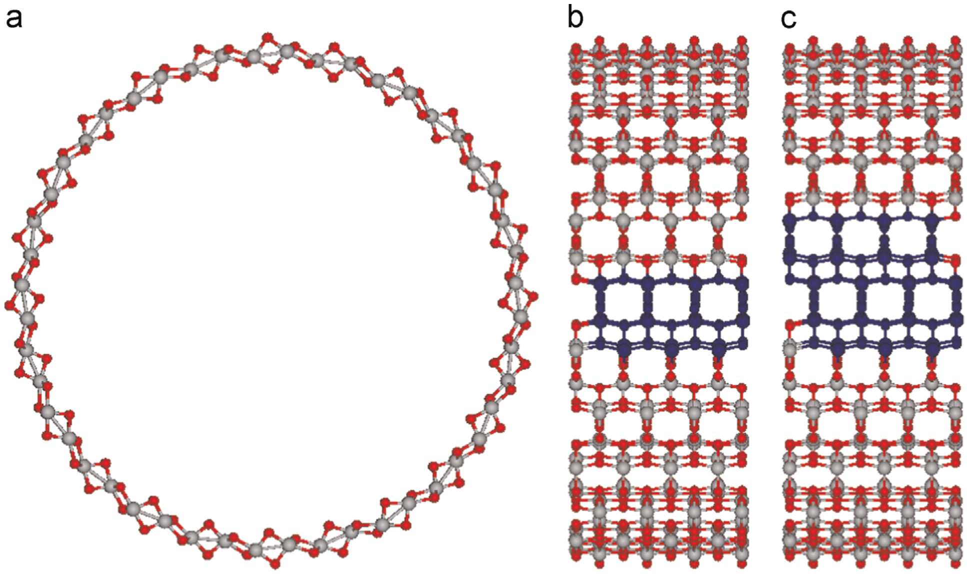

Fig. 1. 6-layered TiO_2 (101) nanotube with chirality indexes (0,12) – (a) front view, (b) side view of 1 × 3 periodically repeated unit cell and (c) 2 × 3 unit cell. Periodically repeated units are highlighted. Large balls represent titanium atoms, small balls represent oxygen atoms.

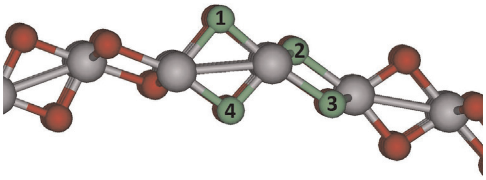

Fig. 2. Non-equivalent S or N dopant positions in the NT's wall.

position as the first dopant site, or Position 1, and the innermost the fourth, or the Position 4. The inner atoms follow the sequence as shown in Fig. 2.

The dopant formation energies in TiO_2 NT were estimated in a following way:

$$E^{form}_{A_h} = E^{tot}_{A_h/NT} + E^{tot}_h - E^{tot}_{A_h} - E^{tot}_{NT}, \qquad (1)$$

where $E^{tot}_{A_h/NT}$ is the calculated total energy of a nanotube containing dopant A_h, E^{tot}_h is the total energy of the host atom, which is removed from the nanotube, $E^{tot}_{A_h}$ is the total energy calculated for the dopant, and E^{tot}_{NT} stands for the total energy calculated for the perfect nanotube.

3. Results and discussion

3.1. S doped 6-layer (101) TiO_2 nanotubes

Since band structures does not experience essential alterations when doping at different concentrations are considered, we restrict ourselves to displaying only images related to 2.78% defect concentration. In Fig. 3 the band edge positions and defect-induced levels of S doped titania NTs are shown. Solid black lines denote the highest occupied induced levels, in this figure and in the figures below. For the two dopant sites lying closer to the outer surface, sites S_1 and S_2 (Fig. 2), there is a negative shift in energy for both the bottom of conduction band (CB) and the top of the valence band (VB). In fact, there is no difference between CB/VB positions of the pristine NT and the NTs containing S dopants at the positions S_3 and S_4. Doping at positions S_1 and S_4 promotes the highest photocatalytic enhancement, reducing the gap between the lowest unoccupied state and the highest occupied state, from 4.19 eV to 3.14 eV (3.12 eV) and 3.08 eV (3.07 eV) for 1.39% (2.78%) defect concentrations, respectively. It means that S atoms themselves do not provide sufficient rise of photocatalytic activity. S-induced occupied levels are lower at 1.39% concentration. Formation energies are equal for both types of dopants on outer and

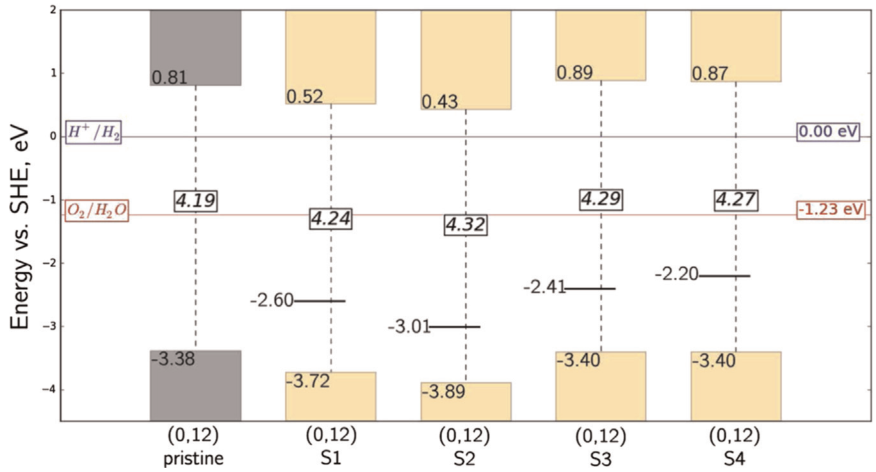

Fig. 3. Schematic representation of the band edges and mid-gap states of pristine and S doped TiO_2 NTs.

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