

FIRST PRINCIPLES SIMULATIONS ON DOPED TiO₂ AND SrTiO₃ NANOTUBULAR PHOTOCATALYSTS FOR WATER-SPLITTING HYDROGEN GENERATION

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First principles calculations have been performed to investigate ground state properties of monoperiodic TiO₂ and SrTiO₃ single-walled nanotubes containing extrinsic point defects. The hybrid exchange-correlation functionals B3LYP and B3PW within the framework of density functional theory have been applied to calculations for nanotubes with the following substitution impurities: C_O, N_O, S_O, and Fe_{Ti}. Variations in the formation energies obtained for equilibrium defective nanostructures allow us to predict the most stable compositions, irrespectively of the changes in growth conditions. Changes in the electronic structure show mid-gap states induced by defects.

1. Introduction

Metal oxide nanotubes (NTs) are important and widespread materials in modern nanotechnology. Moreover, imperfect nanotubes with a reproducible distribution of point defects attract enhanced interest due to potential generation of novel innovative nanomaterials and devices. Variety of experimental conditions accompanying their synthesis can certainly promote an appearance of point defects: native vacancies or antisites and substitution impurities. Point defects also play a role of chemically active sites for NT wall functionalization [1].

Titania (TiO₂) and strontium titanate (SrTiO₃ or STO) are well-known semiconductors comprehensively studied thanks to their widespread applications. During the last years nanotubes of different morphology obtained from these oxide compounds were systematically synthesized and carefully studied [2,3]. Very recent experimental studies performed on Nb-doped TiO₂ nanotubes fabricated by anodization of Ti-Nb alloys [4] demonstrate strongly enhanced photo-electrochemical water splitting efficiency without considerable photodegradation. Analogously, STO NTs after doping are potentially promising photoelectrodes for visible-light-driven photocatalytic applications [5].

In this paper, we have systematized a series of results obtained using *ab initio* simulations of perfect and defective TiO₂ and STO NTs [6-9] adapting them for current simulations. Using hybrid exchange-correlation functionals applied within the density functional theory (DFT), we have calculated the following extrinsic substitution impurities in both NTs: C_O, N_O, S_O, and Fe_{Ti},

since they essentially enhance photocatalytic activity of both types of metal oxide nanotubes [10].

2. Computational details

We have performed calculations for doped oxide NTs using formalism of the localized Gaussian-type functions (GTFs), which form the basis set (BS), and exploiting the periodic rototranslation symmetry for efficient ground-state calculations as implemented in *ab initio* code CRYSTAL developing the formalism of localized atomic orbitals (LCAO) for periodic systems [11]. For defective TiO₂ and STO NTs we have employed the hybrid B3LYP and B3PW exchange-correlation functionals, respectively. They consist of the non-local HF exchange, DFT exchange, and GGA correlation functionals as proposed by Becke [11]. Main advantage of the hybrid DFT calculations is that they make results of the band structure calculations more plausible. For Sr and Ti atoms in TiO₂ and STO NTs, the BSs have been chosen in the form of 311*sp-1d* and 411*sp-311d*, respectively, using ECP from Hay and Wadt [11], while all-electron BSs were adopted for other atoms in calculations of defective titania and strontium titanate nanotubes, *i.e.* O: 8*s-411sp-1d*; C: 6*s-411sp-11d*; N: 6*s-31p-1d*, S: 8*s-63111sp-11d*, and Fe: 8*s-6411sp-41d* [11]. Effective charges on the atoms as well as net bond populations have been calculated according to the Mulliken population analysis [11].

3. Results and discussion

Firstly, we have simulated nine-layer anatase-type TiO₂ (001) NT with (0,*n*) chirality indexes (Fig. 1), which possesses the negative strain energy, *i.e.* it is energetically more favorable to form a nanotube rather than to keep original plane sheet structure. Based on our strain energy calculations, we have chosen for further substitutional doping a 2×2 supercell of (0,36) 9-layer anatase (001) NT with the internal diameter of 3.47 nm, wall thickness of 0.67 nm, and having 648 atoms in the unit cell. Oxygen substitution impurities have replaced host atoms in six possible configurations, while three possible substitution positions have been available for Fe_{Ti} (Fig. 1). Thus, the overall concentration of defects in TiO₂ NT is 8%. In this paper, we discuss only the substitution impurities with the lowest energy of formation: C_{O1}/TiO₂ NT with $E_{form} = 1.16$ eV, N_{O2}/TiO₂ NT with $E_{form} = 3.56$ eV, S_{O1}/TiO₂ NT with $E_{form} = 2.61$ eV, and Fe_{Ti3}/TiO₂ NT with $E_{form} = 5.37$ eV. Effective Mulliken charges calculated for extrinsic substitution defects in TiO₂ NT have been found to be: -1.00 *e* (C_{O1}), -1.06 *e* (N_{O2}), -1.12 *e* (S_{O1}) and 2.17 *e* (Fe_{Ti3}). Mulliken charges calculated for host Ti and O atoms

along the wall of TiO_2 nanotubes are $2.25 e$ and $-1.19 e$, respectively. The band structures calculated for TiO_2 nanotubes containing substitution impurities reveals the tendency of formation of defect-induced levels inside the optical band gap.

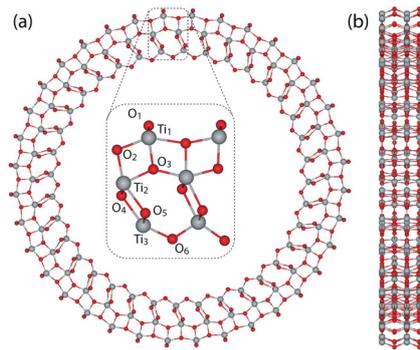


Figure 1. Monoperiodically repeated unit cell of (0,36) TiO_2 nanotube with the external diameter of 4.81 nm containing the substitution defects: (a) across section view, (b) side view. Ti atoms are shown as large gray balls, while oxygens as small light gray (red) balls. The inset shows the 2×2 extended "basic" unit cell of (0,36) TiO_2 nanotube repeated by 18 rototranslational symmetry operators. Numbered atoms of titanium and oxygen are substituted for impurity defect atoms (A_h , where h stands for "host").

Simultaneously, we have simulated STO NTs with (18,0) chirality indexes (Fig. 2) rolled up from a nanosheet cut parallel to (110) surface of bulk STO. This type of nanotubes, which possesses the negative strain energy, has been found to be the energetically most stable with respect to the STO bulk. Its 2×2 supercell consists of 180 atoms and allows for NT doping by impurities which do not interact between themselves. Oxygen substitution impurities have replaced host oxygen in three possible configurations, while only one possible substitution position has been considered for Fe_{Ti} (Fig. 2). Thus, the overall defect concentration in STO NT is 25%. We discuss only the substitution

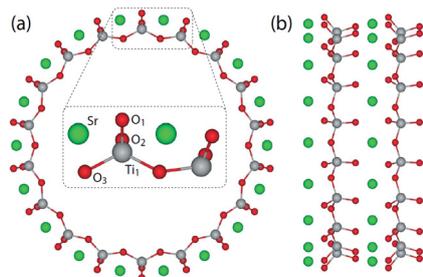


Figure 2. Monoperiodically repeated unit cell of (18,0) SrTiO_3 NT with the external diameter of 2.27 nm containing the substitution defects: (a) across section view, (b) side view. Ti atoms are shown as gray balls, oxygens as small light gray balls, and Sr atoms as large dark gray balls. The inset shows the 2×2 extended "basic" unit cell of (18,0) SrTiO_3 nanotube repeated by nine rototranslational symmetry operators. Numbered Ti and O atoms are substituted impurity defect atoms (A_h , where h stands for "host").

impurities with the lowest formation energy: $\text{C}_{\text{O}_3}/\text{SrTiO}_3$ NT with $E_{\text{form}} = 4.50 \text{ eV}$, $\text{N}_{\text{O}_3}/\text{SrTiO}_3$ NT with $E_{\text{form}} = 3.52 \text{ eV}$, $\text{S}_{\text{O}_1}/\text{SrTiO}_3$ NT with $E_{\text{form}} = 2.01 \text{ eV}$, and $\text{Fe}_{\text{Ti}_1}/\text{SrTiO}_3$ NT with $E_{\text{form}} = 5.97 \text{ eV}$. Effective Mulliken charges calculated for extrinsic substitution defects in STO NT have been found the following: $-1.21 e$ (C_{O_3}), $-1.13 e$ (N_{O_3}), $-1.44 e$ (S_{O_1}) and $2.15 e$ (Fe_{Ti_1}). Mulliken charges calculated for host Ti and O atoms along the wall of SrTiO_3 nanotubes are $2.19 e$ and $-1.27 e$, respectively. The projected density of states

calculated for the defective STO NTs shows that the top of their VB and the bottom of their CB consist of O $2p$ and Ti $3d$ orbitals, respectively, as in bulk STO. The band structures calculated for STO nanotubes containing substitution point defects reveal the tendency of the formation of defect-induced levels inside the band gap.

4. Conclusion

We presented the results of defect engineering when modeling of both TiO₂ and SrTiO₃ NTs using the first-principles calculations based on hybrid DFT. The variations in formation energies obtained for equilibrium defective nanostructures allow us to predict the most stable NT morphologies, irrespectively of the changes in growth conditions. Mid-gap levels positioned inside the band gap of defective NTs make them attractive for band gap engineering in, for example, photocatalytic applications.

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References

1. A. V. Krasheninnikov, K. Nordlund, *J. Appl. Phys.* **107**, 071301 (2010).
2. P. Roy, S. Berger, P. Schmuki, *Ang. Chem. Int. Ed.* **50**, 2904 (2011).
3. X. Zhu, Z. Liu, N. Ming, *J. Mater. Chem.* **20**, 4015 (2010).
4. C. Das, P. Roy, M. Yang, H. Jha, P. Schmuki, *Nanoscale* **3**, 3096 (2011).
5. J. Zhang, J. H. Bang, C. Tang, P. V. Kamat, *ACS Nano* **4**, 387 (2010).
6. R. A. Evarestov, A. V. Bandura, M. V. Losev, S. Piskunov, Yu. F. Zhukovskii, *Phys. E* **43**, 266 (2010).
7. R. A. Evarestov, A. V. Bandura, *IOP Conf. Series: Mater. Sci. Eng.* **23**, 012013 (2011).
8. S. Piskunov, E. Spohr, *J. Phys. Chem. Lett.* **2**, 2566 (2011).
9. O. Lisovski, S. Piskunov, Yu. F. Zhukovskii, J. Ozolins, *IOP Conf. Series: Mater. Sci. Eng.* **38**, 012057 (2012).
10. Y. C. Nah, I. Paramasivam, P. Schmuki, *ChemPhysChem* **11**, 2698 (2010).
11. R. Dovesi, V. R. Saunders, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, F. Pascale, B. Civalieri, K. Doll, N. M. Harrison, I. J. Bush, Ph. D'Arco, M. Llunell, *CRYSTAL09 User's Manual* (University of Torino, Torino, 2009), <http://www.crystal.unito.it/>.