

Applying formalism of a constrained 2D structure to modelling surfaces of TiO₂ nanotubes with different diameters

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Abstract

Research in the field of catalysts for solar water splitting grows constantly. In particular, nanotubular structures are intensively studied due to their attractive properties. In order to get deeper insight into photocatalytic water splitting, it is necessary to employ computationally costly methods, e.g. ab initio Molecular Dynamics. For large, stable nanotubes such approach is not affordable with the currently available computational resources. Due to this reason for simulations of such systems we proposed a computationally cheaper approach based on 2D-periodic models with structural motifs from full-size nanotubes. Earlier, two of the validated models exhibited decent performance in terms of water simulation on surfaces of (101) and (001) TiO₂ nanotubes of one specific size. In this study, we provide further validation of the models by testing them against a wide range of nanotubular diameters, and we investigate the lower and upper limits of the model's applicability.

Keywords: nanotubes, titania, surface, water adsorption, water splitting, simulation, DFT, MD

1 Introduction

Previously we have discovered prospective photocatalytic properties of (101) (0,n) and (001) (n,0) TiO₂ nanotubes (NTs), pristine and defective, via DFT simulations [1-5]. In order to get deeper insights into solar-driven splitting of water, one needs more advanced methods, e.g. ab initio Molecular Dynamics (MD). Since the size of the considered stable NTs is excessive for ab initio MD, we proposed three different 2D models with different constraints that would allow to simulate water adsorption on TiO₂ NT surfaces. These models were developed at the DFT level [6] and have already been used by us for water adsorption simulation at ab initio MD level [7]. Still, each model's performance was tested only for one specific NT. We understand that a broader validation is required, therefore we chose two best-performing models and investigated their applicability limits. Our hypothesis was that the models would fail for the smallest NTs, i.e. ones with the highest strain, and for the largest affordable NT models using a simple slab approach would be more cost-efficient, while the 2D models would in general be useful in the medium NT size interval. Identification of the interval's size was our goal.

2 Computational details

The 2D constrained models of TiO₂ NTs were developed at the hybrid DFT level of theory, employing the method of LCAO based on localized Gaussian-type functions in the form of atomic-nuclei-centered basis sets. The used computational program was CRYSTAL [8], and B3LYP was chosen as an exchange-correlation functional.

Motivation of this particular choice and further detailed are available in our previous papers [1-5].

3 Testing 2D models along different NT diameters

In our earlier work [6] we discovered that a 2D Fixed Volume Slab (FVS) model based on a TiO₂ slab with lattice constants modified according to a specific full-size NT, worked well for simulation of water adsorption on the inner surface of (101) NTs. The second, Constrained Fixed Volume Slab (CFVS) model, a mathematically stratified surface of a NT wall, exhibited decent performance for modelling of water adsorption on outer surface of (001) NTs. The third model – segments of a NT wall translated infinitely in a plane – did not show any promising results. The two promising models were tested for a broad range of NT diameters, starting from the smallest possible and up to chirality index $n = 50$. As validity criteria we used water adsorption energy, band edge positions, optimized geometry, and DOS similarity.

4 Conclusions

Both tested models were capable to provide decent agreement in terms of water adsorption energy along almost the whole range of NT diameters. In the small NT domain, the FVS model yielded somewhat better results in terms of DOS form, band edge positions, and geometry – the nature of CFVS model constraints seems to produce too high geometry distortion for the 2D models of the smaller NTs. In general, both the FVS and CFVS models proved to be useful in a NT range wide enough.

References

- [1] Lisovski O, Piskunov S, Zhukovskii Yu F, Bocharov D 2017 Quantum chemical simulations of titanium dioxide nanotubes used for photocatalytic water splitting *J. Surf. Investigation* **11**, 78–86
- [2] Lisovski O, Chesnokov A, Piskunov S, Bocharov D, Zhukovskii Yu F, Wessel M, Spohr E 2016 Ab initio calculations of doped TiO₂ anatase (101) nanotubes for photocatalytic water splitting applications *Mater. Sci. Semicond. Process* **42**, 138-41
- [3] Piskunov S, Lisovski O, Begens J, Bocharov D, Zhukovskii Yu F, Wessel M, Spohr E 2015 C-, N-, S-, and Fe-doped TiO₂ and SrTiO₃ nanotubes for visible-light-driven photocatalytic water splitting: Prediction from first principles *J. Phys. Chem. C* **119**, 18686–96
- [4] Chesnokov A, Lisovski O, Bocharov D, Piskunov S, Zhukovskii Yu F, Wessel M, Spohr E 2015 Ab initio simulations on N and S co-doped titania nanotubes for photocatalytic applications *Phys. Scr.* **90**, 094013 (p. 1-7)
- [5] Zhukovskii Yu F, Piskunov S, Begens J, Kazerovskis J, Lisovski O 2013 First-principles calculations of point defects in inorganic nanotubes *Phys. Status Solidi B* **250**, 793-800
- [6] Lisovski O, Kenmoe S, Piskunov S, Bocharov D, Zhukovskii Yu F, Spohr E 2018 Validation of a constrained 2D slab model for water adsorption simulation on 1D periodic TiO₂ nanotubes *Comput. Condens. Matt.* **15**, 69-78
- [7] Kenmoe S, Lisovski O, Piskunov S, Bocharov D, Zhukovskii Yu F, Spohr E 2018 Water adsorption on clean and defective anatase TiO₂ (001) nanotube surfaces: A surface science approach *J. Phys. Chem. B* **122**, 5432-40
- [8] Dovesi R 2009 *CRYSTAL'09 User's Manual* University of Torino, Torino