Quantum chemical simulations of doped TiO_2 nanotubes for photocatalytic hydrogen generation

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Introduction

One of the ways how to generate H_2 is to use a photoactive catalyst. In the present study, we consider single-walled TiO_2-NTs with negative strain energy that can be folded from TiO_2 nanosheets (anatase, (001), 9 atomic layers) of tetragonal morphology. Dopants introduced into NT structure induce mid-gap states which adjusts band gap width and positions of bands increasing catalyst ability to split water – through allowing it to generate excited electrons and electron holes at a proper energetic level and therefore to employ visible light energy.

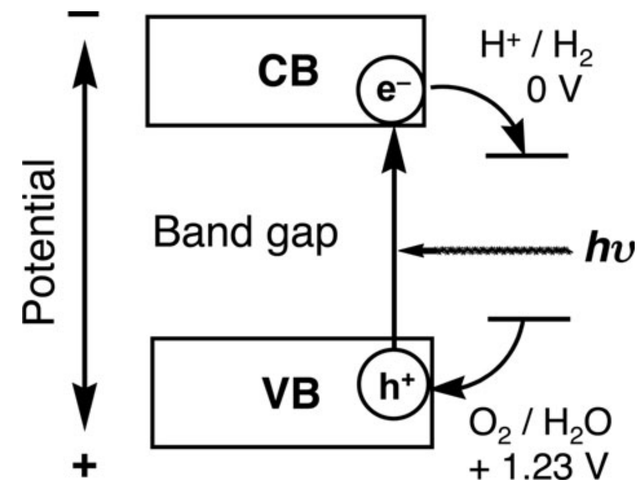

Fig. 1.Basic scheme of photocatalytic separation of water.

Computational details

To perform calculations, we used the Density Functional Theory/HartreeFock hybrid exchange-correlation method and the hybrid B3LYP exchange correlation functional consisting of the nonlocal HF exchange, DFT exchange, and generalized gradient approximation correlation functionals. HF contribution percentage occurred to play an important role it had to be optimized before further calculations. The calculations were carried out using the CRYSTAL computer code, with atom-centered Gaussian-type functions as basis set.

Results

We compared NTs with 8 different configurations - 4 morphologies and two different variations of chirality indexes for each morphology:

- Anatase (101), 3 layers (n,n) and (n,0)
- Anatase (101), 6 layers (n,0) and (0,n)
- Anatase (001), 6 layers (n,0) and (0,n)
- Anatase (001), 9 layers (n,0) and (0,n)

Anatase (001), 9 layers (0,n) appeared to be the most stable nanotube which means this configuration would prevail in synthesis mixture.

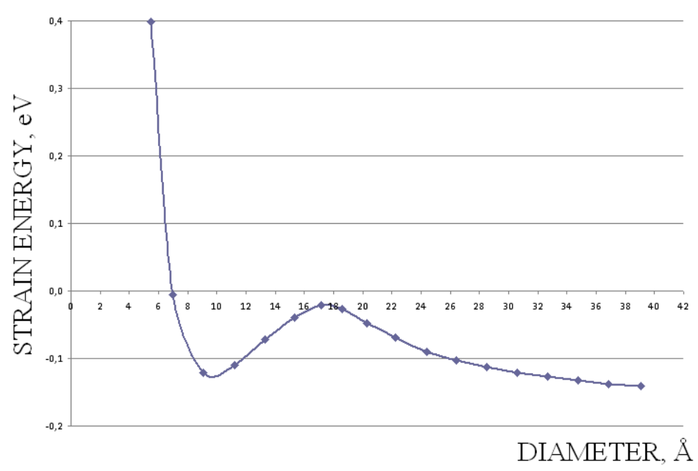

Fig.2. Strain energy for anatase (001) 9 layered nanotubes with different diameters

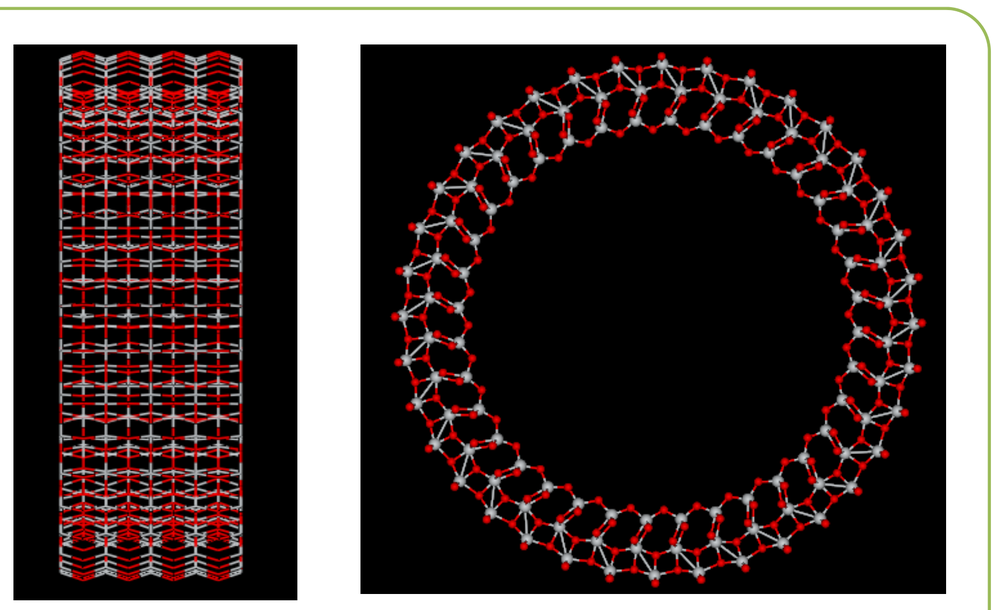

Fig. 3 Undoped TiO_2 nanotube (001), (0,36) 9 atomic layers, side view (left) and front view (right)

The latter NT were doped with Fe (Ti position), C, N and S (in all nonequivalent O positions). Nonequivalent O vacancies were simulated as well. N doped NT's are not presented on the graph as far as they occur to be conductors. Best results were acquired for S doped NT.

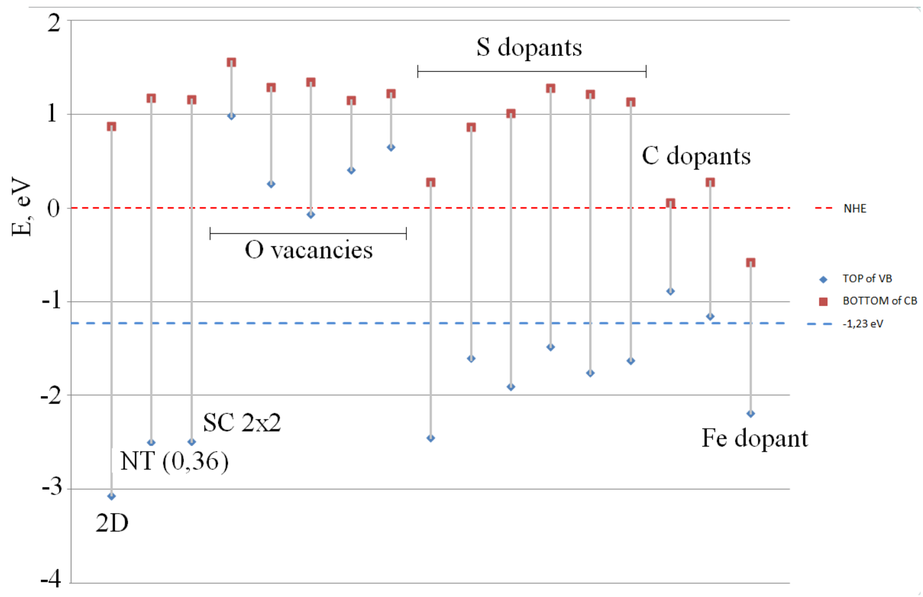

Fig. 4. Positions of band edges for TiO_2 nanosheet and doped NTs.

Table 1. Formation energies for S doped nanotubes were calculated in order to predict the most probable dopant position.

Dopant	E, eV
S1	2.61
S145	3.60
S217	4.34
S361	5.33
S433	5.65
S577	3.37

Summary

The most stable configuration of TiO_2 nanotubes is found – it is 9-layer anatase (001) structure with chirality indexes (0,n).

We predict that nanotubes with S dopants will demonstrate the highest photocatalytic activity. Energetically favorable S dopant position is in the outer NT surface.

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