Analysis of Titanium Dioxide Nanotubes, Rutile (110) and Anatase (101)

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Introduction

The experimental and theoretical studies of nanotubes have increased over the past decade[1-3]. Nanostructured compounds containing Ti oxides are fairly investigated due to their electronic properties and the application possibilities in areas such as medicine[4,5], molecular biology[6], solar[7,8], photocatalytic processes[9,10]. It is also the subject of study in the application as gas sensor[11-13]. Theoretical investigations are carried out on different materials (nanotube surfaces) formed of various compounds (TiO_2, ZnO, SnO_2, C, GaAs,). From quantum mechanical calculations, it is possible to access the energy parameters (the interaction and surface energy, gap) and compare these results with experimental data. Among the structures that have interest due to their potential applicability in the experimental and theoretical studies, titanium dioxide nanotubes[14-18] is widely used.

In the present work, using a programming language, we selected the atoms of specific crystal planes of both the anatase and rutile faces to yield several nanotubes of different diameters and lengths, depending on the number of TiO_2 units. This methodology seeks nanotubes formed by basic units having the same geometry of the source structure. Models with geometries of the armchair and zig-zag[19-22] were generated.

Computational Details

The simulations was conducted with small tubes of rutile and anatase titanium dioxide structures. The entire process is carried out through algorithms created in bash shell language in the Linux system, to obtain the structures of surfaces and nanotubes of TiO_2, of rutile and anatase using their experimental lattice parameters[23]. From the crystal lattice parameters of rutile and anatase, a basic unit was formed for the nanotubes. In the case of anatase crystal, we selected the (101) plane, and for the rutile crystal the (110) plane was investigated. The choice for these planes is due to these planes were well known in the literature for their properties and potential applications[24-29]. Figures 1 and 2 show a representation of the structures and sequence of the formation of anatase and rutile nanotubes, respectively:

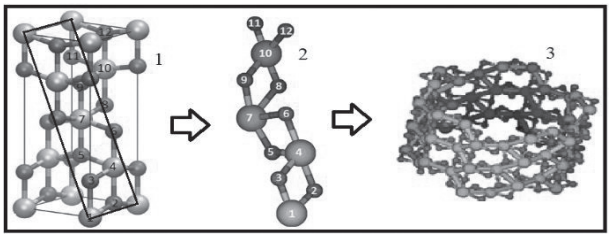

Figure 1. Representation of the following structures for (101) anatase nanotubes. 1 – Unit Cell (Anatase); 2 – Monomer for anatase; 3 - Nanotube TiO2 (Anatase).

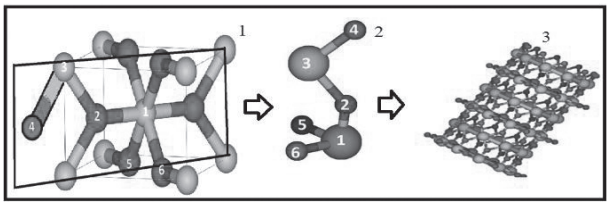

Figure 2 - Representation of the following structures for (110) rutile nanotubes. 1–Unit Cell (Rutile); 2–Monomer for rutile; 3- TiO_2 nanotube (Rutile).

The models were subjected to the energy calculation with semi-empirical method based on PM7 and abinitio HF and DFT, with 6-31G and 6-311G basis functions. MOPAC2012 software was used for the semi-empirical method, while the RHF and DFT the Gaussian 03 was used. The models were generated from the experimental cell parameters crystals of rutile and anatase, in the cartesian coordinate system. The optimization was performed in all structures with semi-empirical PM7. The RHF and DFT calculations were performed using the optimized coordinates from semi-empirical method.

The energy values variation was obtained from the chemical equation (1.1):

$$(nxm)[(TiO_2)Y] \rightleftharpoons \{[(TiO_2)Y]_n\}_m$$

$$\Delta E = E\{[(TiO_2)Y]_n\}_m - [(mxn) \times Y] \times E(TiO_2)$$

Y is the index the TiO2 units and is related to the structure, rutile (Y=2) and anatase (Y=4). 47 models were obtained of anatase nanotubes with 1, 2 and 3 layers, while for rutile 31 models were obtained. Only the results for the variation energy of anatase are shown in Figure 3. The results of rutile presents the same behavior. A decrease of energy variation follows the stability of increasing nanotube length.

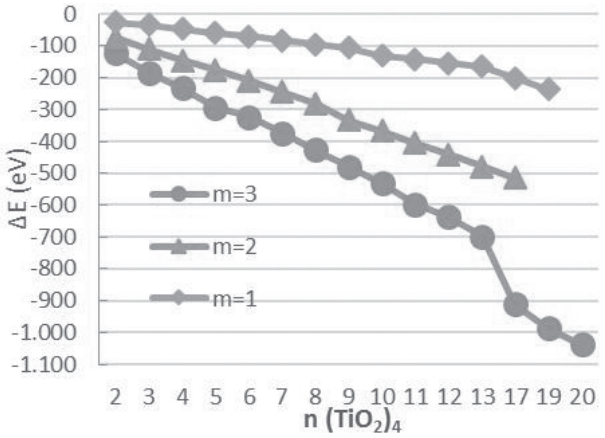

Figure 2. a – PM7 ΔE in relation to the number of units (n [(TiO2)4]) of anatase.

DFT and RHF (Table 3) result were performed and show the same trend for the variation energy. The results of anatase nanotubes demonstrate that increasing the length and diameter not contribute significantly in changing the gap values, without changing the conductivity properties thereof. Anatase nanotubes kept the gap values in the range between 6.00 eV and 8.00 eV, behaving as an insulator material.

Table 3 - Comparison between the calculations of the semi-empirical method and ab initio calculations.

	ΔE (eV)				
	DFT/B3LYP		HF		PM7
	6-31G	6-311G	6-31G	6-311G	
{[(TiO2)4]2}1	-34.8674	-34.6987	-35.0023	-35.1008	-26.5585
{[(TiO2)4]3}2	-125.6752	-125.7489	-123.9780	-124.0187	-109.9690
{[(TiO2)4]6}3	-372.6210	-372.9514	-370.9832	-371.1296	-323.1400

The DOS results demonstrate that nanotubes valence band of anatase concentrated in the range between -15.00 -10.00 eV to eV, while the conduction band had values in the range from -2.50 eV to 5.00 eV. In the case of rutile nanotubes, the results show that the valence band are concentrated in the range of -16.00 eV to -6.00 eV, and the conduction band showed values ranging from -3.00 eV to 5 00 eV.

Table 4 - Comparison between the calculations of the semi-empirical method and ab initio calculations of gap (eV).

Gap (eV)					
Structure	DFT/B3LYP		HF		
	6-31G	6-311G	6-31G	6-311G	PM7
{[(TiO2)4]2}1	2.47	2.46	9.43	9.70	8.46
{[(TiO2)4]3}2	2.03	2.05	8.95	-	7.69
{[(TiO2)4]6}3	2.29	2.29	9.28	9.48	7.00

The results showed in Table 4 a large difference between the results of the HF and DFT method. The HF method overestimated values of the gap compared with the semi-empirical method, since the values of the DFT method gave values below compared with the semi-empirical and HF. In comparing the 6-31G and 6-311G bases, considerable variation between their values was not found. Compared to experimental and theoretical results in the literature, the values found by the DFT method with values between 2.00 eV to 2.50 eV, are the closest.

Conclusions

The energy variation analysis with the length of 3 levels of anatase and rutile nanotubes have shown that stability is achieved with increasing the diameter. RHF and DFT results showed the same trend.

The rutile nanotubes had a gap values of about 2.00 to 4.00 eV, while anatase nanotubes had values in the range of 6.00 eV to 8.00 eV, for the calculation PM7; The results of the gap calculations with the DFT method for anatase nanotubes (2.00 eV to 2.50 eV) underestimated values found with the semi-empirical method.

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