IOP Conf. Series: Materials Science and Engineering **23** (2011) 012014 doi:10.1088/1757-899X/23/1/012014

# First-principles calculations on double-walled inorganic nanotubes with hexagonal chiralities

**Yuri F Zhukovskii[*1], Robert A Evarestov[2], Andrei V Bandura[2], Maxim V Losev[2]**
[1]Institute of Solid State Physics, University of Latvia, 8 Kengaraga Str., LV-1063, Riga, Latvia.
[2]Department of Quantum Chemistry, St. Petersburg State University, 26 Universitetsky Ave., 198504, Petrodvorets, Russia.

E-mail: quantzh@latnet.lv

**Abstract.** The two sets of commensurate double-walled boron nitride and titania hexagonally-structured nanotubes (DW BN and $TiO_2$ NTs) possessing either armchair- or zigzag-type chiralities have been considered, *i.e.*, $(n_1,n_1)@(n_2,n_2)$ or $(n_1,0)@(n_2,0)$, respectively. For symmetry analysis of these nanotubes, the line symmetry groups for one-periodic (1D) nanostructures with rotohelical symmetry have been applied. To analyze the structural and electronic properties of hexagonal DW NTs, a series of large-scale *ab initio* DFT-LCAO calculations have been performed using the hybrid Hartree-Fock/Kohn-Sham exchange-correlation functional PBE0 (as implemented in *CRYSTAL-09* code). To establish the optimal inter-shell distances within DW NTs corresponding to the minima of calculated total energy, the chiral indices $n_1$ and $n_2$ of the constituent single-walled (SW) nanotubes have been successively varied.

## 1. Introduction

Various types of inorganic nanotubes with different morphology, *e.g.*, BN [1,2] and $TiO_2$ [3,4] NTs, synthesized during the last 10-15 years were carefully studied, both experimentally and theoretically, and applied as technologically prospective nanomaterials. As to structure of BN and $TiO_2$ nanotubes, the former possess mainly hexagonal morphology [2], while the latter were identified with prevailing rectangular morphology of either anatase or lepidocrocite structures [4]. Nevertheless, there were observed also the three-layered fragments of shells within the multi-walled (MW) $TiO_2$ NTs possessing a quasi-hexagonal morphology [3]. The simplest examples of MW nanotubular structures of both boron nitride and titania are coaxial double-walled (DW) nanotubes, which provide rational explanation for the dependence of their electronic and structural properties on the inter-shell interactions. These DW NTs consisting on constituent single-walled (SW) nanotubes, which are chosen for further theoretical simulations, have to keep rotohelical symmetry, in order to perform their efficient simulations. Unlike continuous sets of high-symmetric models for hexagonal SW BN and $TiO_2$ NTs with consequently growing diameter, as comprehensively considered in our recent paper [5], there exists rather limited number of DW configurations (formed from the single-walled nanotubes) which can be attributed to high-symmetry structures.

[*] To whom any correspondence should be addressed.

So far, large-scale *ab initio* calculations on inorganic DW NTs were performed mainly for BN, either for the only $(n_1,0)@(n_2,0)$ chirality [6,7] or for both $(n_1,0)@(n_2,0)$ and $(n_1,n_1)@(n_2,n_2)$ chiralities [8]. Both zigzag-type, *zz*-(8,0)@(16,0), and armchair-type, *ac*-(5,5)@(10,10), DW BN NTs were found to be the energetically most stable, although the inversely inter-walled stacking gives an energetic preference for the growth of *zz*-nanotubes [8]. Optimal inter-shell distances in them were found to be ~3.2 Å. It is important to describe theoretically the multi-walled structures for revealing the underlying physical phenomena, even though the inter-shell interaction might be weak [9].

In this paper, we describe perfect DW BN and $TiO_2$ nanotubes with the hexagonal morphology comparing their properties with those obtained by us in previous study for the corresponding single-walled nanotubes [5]. Section 2 presents the hexagonal models of DW NTs used in this study as well as the formalism of line group symmetry applied for their description. Section 3 briefly explains computational details, in order to perform *ab initio* calculations on nanotubes. In Section 4, we analyze and systematize the results calculated for hexagonal models of DW BN and $TiO_2$ nanotubes. Section 5 summarizes the main conclusions obtained in the current study.

## 2. Optimized models and symmetry of double-walled nanotubes

We have considered the two sets of commensurate DW NTs with either $(n_1,n_1)@(n_2,n_2)$ (armchair-type) or $(n_1,0)@(n_2,0)$ (zigzag-type) chiralities. To find the optimal inter-shell distances as well as stacking of atoms in nanotube rings corresponding to the binding energy maxima (Figs. 1,2), we have successfully varied chiral indices $n_1$ and $n_2$ as well as orientation of translation and chiral vectors in SW constituents.

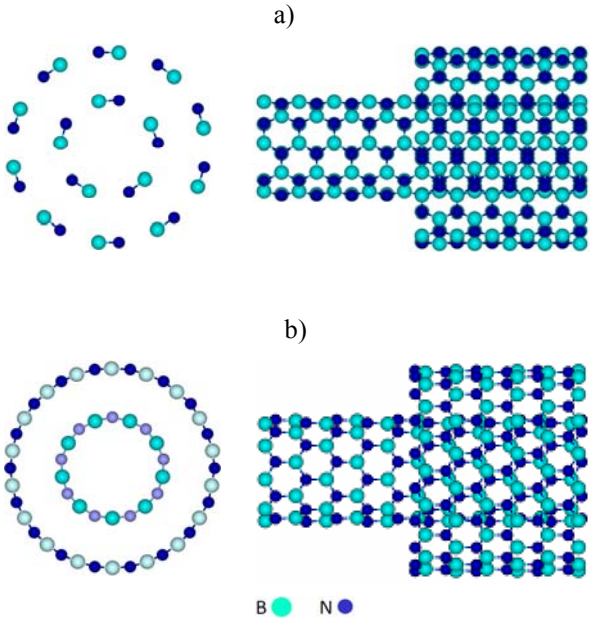


Figure 1 (Color online). Cross-sections and aside images of inversely-stacked DW BN NTs with optimized structures of (a) *ac*-(5,5)@(10,10) and (b) *zz*-(9,0)@(18,0) chiralities. For *zz*-DW NT (b), the atoms of the nearest ring behind the cross-section are shown as markedly more light circles. Aside images of the inner shells of nanotubes have been chosen as twice as longer than those of the outer shells.

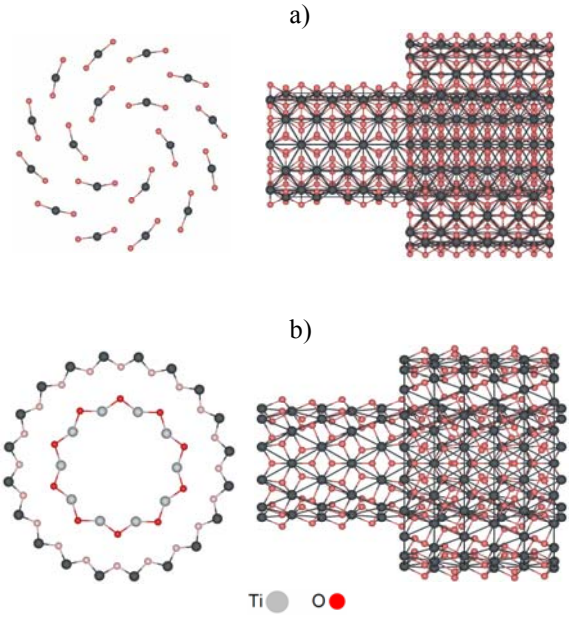


Figure 2 (Color online). Cross-sections and aside images of straightly-stacked DW $TiO_2$ NTs with optimized structures of (a) *ac*-(6,6)@(12,12) and (b) *zz*-(10,0)@(20,0) chiralities. The atoms of the nearest ring behind the cross-section for *zz*-DW NT (b) are shown as markedly more light circles. Aside images of the inner NT shells have been chosen as twice as longer than those of the outer shells.

The line symmetry group of concrete DW NT can be found as intersection $L_2 = Z_2P_2 = (L \cap L')$ of the symmetry groups $L$ and $L'$ of its single-walled constituents as earlier considered for DW CNTs [10]. The intersection $P_2 = (P \cap P')$ of the point groups is chosen independently of the generalized

translational factor $Z_2$. Let $(n_1,n_2)$ and $(n_1',n_2')$ define the chiral vectors of single-walled constituents of DW nanotube. Its axial point group $P_2 = C_N$ is the principal axis subgroup of DW NT line group $L_2$ with $N = G(n,n') = G(n_1,n_2,n_1',n_2')$. Only nanotubes composed exclusively of either armchair or zigzag SW constituents may have additional mirror and glide planes, as well as a rotoreflectional axis.

## 3. Computational details

The first principles DFT-LCAO method, as implemented in the *CRYSTAL-09* code [11] describes 1D nanotubes in their original space form. Calculations on DW NTs have been performed using the hybrid Hartree-Fock/Kohn-Sham (HF/KS) exchange-correlation Hamiltonian PBE0 by Perdew-Becke-Erzerhof [12] combining exact HF non-local exchange and KS exchange operator within the Generalized Gradient Approximation (GGA) as implemented in *CRYSTAL-09* code. All-valence basis set (BS) in the form of 6*s*–21*sp*–1*d*, 6*s*–31*p*–1*d* and 6*s*-311*sp*-1*d* Gaussian-type functions (GTFs) have been used for B, N and O atoms, respectively, while a small-core pseudopotential of Ti atom has been adopted for $TiO_2$ NTs calculations (3*s*, 3*p*, 3*d* and 4*s*-electrons were taken as valence electrons) [5].

The reciprocal space has been sampled according to a regular sublattice determined by the shrinking factor 12 (7 independent *k*-points in the irreducible part of the Brillouin zone). Calculations have been considered as converged when the total energy obtained in the self-consistency procedure differs by less than $10^{-7}$ a.u. in the two successive cycles. Calculations of DW NTs possessing large unit cells have been performed using the full exploitation of the helical rototranslational symmetry as implemented in the periodic *CRYSTAL-09* code [11]. All the atomic coordinates in the monoperiodic unit cell have been generated from 2D slabs for both constituent SW NTs separately. These coordinates have been allowed to relax when performing optimization procedure.

Stability of the DW NTs depends on the inter-shell distance, *i.e.*, a difference between the radii of constituent shells ($\Delta R_{\mathrm{NT}}$), as well as on the diameters of both inner and outer shells ( $D_{\mathrm{NT}}^{\mathrm{in}}$ and $D_{\mathrm{NT}}^{\mathrm{out}}$, respectively) [6-8]. The binding energy $E_{bind}$ between the constituent SW shells of double-walled nanotube has been chosen as a criterion of nanotube stability:

$$-E_{bind}(D_{\mathrm{NT}}^{\mathrm{in}}@D_{\mathrm{NT}}^{\mathrm{out}}) = E_{tot}(D_{\mathrm{NT}}^{\mathrm{in}}@D_{\mathrm{NT}}^{\mathrm{out}}) - E_{tot}(D_{\mathrm{NT}}^{\mathrm{in}}) - E_{tot}(D_{\mathrm{NT}}^{\mathrm{out}}), \quad (1)$$

where $E_{tot}$ are the calculated total energies of both DW NT and SW NTs with optimized structures.

## 4. Results and discussion

The binding energy curves $-E_{bind}(\Delta R_{\mathrm{NT}})$ for DW BN and $TiO_2$ NTs of both chiralities are shown in Figs. 3,4. The maxima of binding energies for these double-walled nanotubes correspond to both optimal (5,5)@(10,10) and (9,0)@(18,0) configurations as well as inter-shell distance 3.5-3.6 Å. The inversely-stacked B-N structure of *zz*-DW NTs (Fig. 1) is energetically slightly more favorable than that of the straightly-stacked B-B one, which confirms a presence of polarization effects in BN multi-walled nanotubes as predicted earlier [8]. Reliefs of the energy curves for DW BN NTs (Fig. 3) also give a small preference to the inversed double-walled *zz*-NTs *vs. ac*-NTs. These results favor to the experimentally observed dipolar-shell structured morphology of the MW BN NTs [6-8]. Obviously, the small values of $\Delta R_{\mathrm{NT}}$ and $D_{\mathrm{NT}}^{\mathrm{in}}$ result in instability of DW BN NTs (Fig. 3) while the large values of $\Delta R_{\mathrm{NT}}$ and $D_{\mathrm{NT}}^{\mathrm{out}}$ correspond to quasi-independent non-interacting pairs of constituent SW BN NTs.

Constructing the energy curves for $TiO_2$ nanotubes of both chiralities according to Eq. (1) we have found the minima of $-E_{bind}(\Delta R_{\mathrm{NT}})$ functions (Fig. 4) corresponding to (6,6)@(12,12) and (10,0)@(20,0) double-walled configurations of DW $TiO_2$ NTs with inter-walled distances 4.6-4.8 Å ($\Delta R_{\mathrm{NT}}$ is defined as a difference between the radii of middle Ti sub-shells) [5]. Meanwhile, when reducing $\Delta R_{\mathrm{NT}}$ in DW $TiO_2$ NTs below the optimal values (< 4.1-4.3 Å) we have observed structural overstrains, markedly larger as compared to DW BN NTs. This is especially true for *ac*-nanotubes of titania: (4,4)@(8,8), (5,5)@(10,10), and (6,6)@(11,11), where geometry optimization has resulted in destruction of double-walled morphology with formation of complicated non-hexagonal quasi-single-walled morphology.

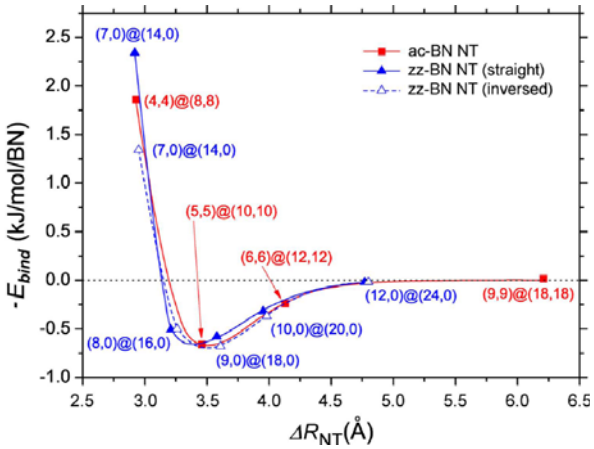


Figure 3 (Color online). Binding energies $E_{bind}$ *vs.* $\Delta R_{NT}$ for the three sets of DW BN NTs with *ac*- and *zz*-chiralities. Spline treatment of curves has been performed to make them smooth.

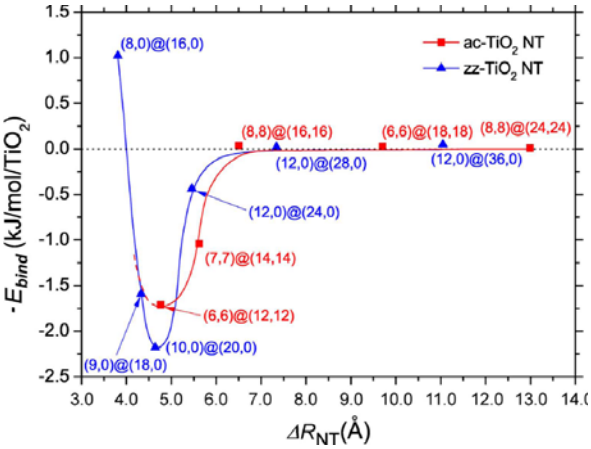


Figure 4 (Color online). Binding energies $E_{bind}$ *vs.* $\Delta R_{NT}$ for the two sets of DW $TiO_2$ NTs with *ac*- and *zz*-chiralities. Spline treatment of curves has been performed to make them smooth.

Comparison of Figs. 3 and 4 shows that the binding energies estimated *per* formula unit for optimal structures of hexagonal DW NTs are considerably larger for $TiO_2$ as compared to BN, while reliefs of minima on energy curves are sharper for the former. This is due to markedly larger ionic contribution to inter-shell interaction between the $TiO_2$ SW constituents. In both cases, DW NT structures with *zz*-chirality are energetically more favorable as compared to those with *ac*-chirality.

## 5. Conclusion

To estimate stability of DW NTs, we have chosen the binding energies between their constituent shells ($E_{bind}$) as a criterion. The energy curves $E_{bind}(\Delta R_{NT})$ for double-walled nanotubes of both chiralities permit to estimate their optimal configurations: (5,5)@(10,10) and (9,0)@(18,0) chiralities for DW BN NTs as well as (6,6)@(12,12) and (10,0)@(20,0) for DW $TiO_2$ NTs. The values of $\Delta R_{NT}$ and $D_{NT}^{in}$, smaller than those in optimal DW NT configurations, lead to their instability, while the large values of $\Delta R_{NT}$ and $D_{NT}^{out}$ correspond to quasi-independent non-interacting pairs of constituent SW NTs.

**Acknowledgements.** The authors thank S. Piskunov for a technical assistance. R.E., A.B. and M.L. are grateful to Russian Foundation for Basic Research for the financial support (grant 11-03-00466a).

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