Symmetry and Models of Double-Wall BN and TiO₂ Nanotubes with Hexagonal Morphology

R. A. Evarestov,^{*,†} Yu. F. Zhukovskii,[‡] A. V. Bandura,[†] S. Piskunov,^{‡,§,||} and M. V. Losev[†]

⁺Department of Quantum Chemistry, St. Petersburg State University, 26 Universitetsky Avenue, Petrodvorets 198504, Russia

^{*}Institute of Solid State Physics, University of Latvia, 8 Kengaraga Street, Riga LV-1063, Latvia

[§]Faculty of Computing, University of Latvia, 19 Raina Boulevard, Riga LV-1586, Latvia

 $^{\parallel}$ Faculty of Physics and Mathematics, University of Latvia, 8 Zellu Street, Riga LV-1002, Latvia

ABSTRACT: The line symmetry groups for one-periodic (1D) nanostructures with rotohelical symmetry have been applied for symmetry analysis of double-wall boron nitride and titania nanotubes (DW BN and TiO₂ NTs) formed by rolling up the stoichiometric two-periodic (2D) slabs of hexagonal structure with the same or opposite orientation of translation and chiral vectors. We have considered the two sets of commensurate DW BN and TiO₂ NTs with either armchair- or zigzag-type chiralities, i.e., $(n_1,n_1)@(n_2,n_2)$ or $(n_1,0)@(n_2,0)$, respectively. To establish the equilibrium interwall distances corresponding to the minima of energy, we have varied chiral indices n_1 and n_2 of the constituent single-wall (SW) nanotubes. To analyze the structural and electronic properties of hexagonal DW NTs, we have performed ab



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initio LCAO calculations using the hybrid Hartree–Fock/Kohn–Sham exchange-correlation functional PBE0 as implemented in CRYSTAL-09 code. The inversely stacked structure of zigzag-type DW BN NT, characterized by arrangement of positively and negatively charged rings in each atomic cross section (consisting of either B or N atoms, respectively), has been found to be energetically more preferable as compared to the straightly stacked structure containing nanotube rings consisting of the same type of atoms in cross sections, i.e., B(N) and B(N). In armchair-type DW BN NTs, each atomic ring contains the whole number of B-N bonds, which reduces the electrostatic interaction between both walls. On the other hand, main contribution to interwall bonding in DW TiO₂ NTs is provided by interaction between the nearest oxygen and titanium ions of neighboring shells. The interaction between the walls results in a decrease of band gaps for double-wall NTs as compared to those for SW NTs, which is substantially larger for TiO₂.

1. INTRODUCTION

As widespread semiconductors with a numerous technological applications, both boron nitride¹ and titania² are thoroughly studied in materials science. Correspondingly, BN³⁻⁶ and TiO₂⁷⁻¹⁰ nanotubes (NTs) synthesized using different methods are also carefully studied as technologically very prospective nanomaterials. As to structure of these NTs, the former possess mainly hexagonal morphology,⁶ while the latter were identified with prevailing rectangular morphology of either anatase or lepidocrocite structures.¹⁰ Nevertheless, the three-layered fragments of shells inside the multiwall TiO₂ NTs (possessing a quasi-hexagonal morphology) were observed too.⁹

The two types of tubular nanostructures for boron nitride and titania were mainly observed so far: cylindrical-like multiwall (MW) BN NTs⁵ and TiO₂ NTs⁹ as well as scroll-like BN nanoscrolls (NSs)¹¹ and TiO₂ NSs.¹² Additionally, the bundles containing a number of either single-wall (SW) or double-wall (DW) BN NTs were synthesized too.¹³ The simplest examples of MW nanotubular structures of both boron nitride and titania are

coaxial DW NTs which provide rational explanation for the dependence of their electronic and structural properties on the interwall interactions. These DW NTs consisting on constituent SW NTs, which are chosen for further theoretical simulations, have to keep rotohelical symmetry, in order to perform their efficient simulation. Unlike continuous sets of high-symmetric models for SW BN and TiO₂ NTs with growing diameter, as considered in our previous paper,¹⁴ rather a limited number of DW configurations (formed from the single-wall nanotubes) can be attributed to high-symmetry structures.

The efficient plasma-arc method of BN NT synthesis was elaborated earlier which provides almost exclusively double-wall nanotubes in high yield.¹⁵ These NTs had a narrow diameter distribution, centered at about 2.7 nm (outer diameter), with a standard deviation of 0.4 nm. The distance between the outer

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Figure 1. (color online). Cross sections and aside images of hexagonal DW BN NTs (left and right parts of models a – d, respectively) corresponding to optimized diameters for *ac*- and *zz*-chiralities. For *zz*-DW BN NTs (models c and d), the atoms of the nearest ring behind the cross section are shown as half-shaded balls. Arrows above each aside image show directions of the cross sections. For convenience of visualization, aside images of the inner shells of nanotubes have been chosen as twice as long as those of the outer shells.

and the inner walls was found to be 0.36 ± 0.03 nm. Moreover, while a SW BN NT should naturally undergo out-of-plane buckling, producing a dipolar shell,¹⁶ the DW NT may help to stabilize the growth of BN nanotubes (i.e., NTs with an even number of walls are generally favored). With most of methods for synthesis of MW BN NTs, the majority of nanotubes were found to have the atomic arrangement corresponding to zigzag-type chirality of walls.¹⁷ (The rare exception from this rule was obtained in a molecular dynamics simulation that showed a preference for armchair over zigzag structure for growth of MW BN NTs.¹⁸) The newly formed DW BN NTs in turn self-assemble into bundles or ropes.¹⁵

The already-synthesized \overline{MW} TiO₂ NTs possessed diameters as thin as several nanometers with interwall distances <0.8 nm.¹⁹ (The multiwall titania nanotube structure described in ref 9 was characterized by 8.7 Å interwall spacing.) The reproducible formation of double-wall TiO₂ NTs with well-observed wall separation was obtained in a recent study.²⁰ However, description of the equilibrium atomic-level morphology of MW titania nanotubes is rather scarce as compared to that for BN NTs.

Large-scale first-principles simulations on DW NTs were performed up to now for BN only, either for only $(n_1,0)@(n_2,0)$ chirality^{21,22} or for both $(n_1,0)@(n_2,0)$ and $(n_1,n_1)@(n_2,n_2)$ chiralities.²³ In these studies, the band gaps of DW NTs were found to be smaller than those of the corresponding SW NTs. Owing to the large curvature of the BN nanotubes which induces the hybridization between σ and π states of both nanotubes, the top of valence and the bottom of conduction bands were found to be localized on the outer and inner nanotubes, respectively.²¹ Both zigzag, *zz*-(8,0)@(16,0), and armchair, *ac*-(5,5)@(10,10), DW NTs were found to be the most stable energetically among double-wall BN nanotubes with different chiralities, although the interwall stacking gives an energetic preference for the growth of zigzag nanotubes.²³ Meanwhile, theoretically described second-order nonlinear optical coefficients of DW BN NTs were found to be significantly reduced by the interwall interaction, as compared to SW BN NTs.²⁴ Thus, it is very important to consider the multiwall structures for revealing the underlying physical phenomena, even though the interwall interaction might be weak.²⁵

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 study¹⁴ for the corresponding single-wall nanotubes. In section 2, we consider the line group symmetry for the double-wall hexagonal nanotubes. Section 3 describes computational details as applied for their ab initio calculations. In sections 4 and 5, we analyze and systematize the results calculated for hexagonal models of DW BN and TiO_2 nanotubes. Section 6 summarizes the main conclusions obtained in the current study.

2. SYMMETRY OF HEXAGONAL BN AND TIO₂ DW NTS

The symmetry and structure of single-wall nanotubes can be simply described using the so-called layer folding which means the construction of the cylindrical surfaces of nanotubes by rolling up the two-periodic (2D) crystalline layers (sheets and slabs).

In the case of BN, the folding procedure is applied to the graphene-like (0001) nanosheet cut from the most stable phase of bulk crystal described by hexagonal space group 194 ($P6_3/mmc$). The sheet symmetry is described by layer group 78 (P6m2),¹⁴ all the atoms of sheet rolled up as a nanotube are distributed over the NT cylindrical surface.

In the case of TiO₂, the folding procedure is applied to the three-layer (111) fluorite-type slab described by layer group 72 ($P\overline{3}m1$).¹⁴ In both cases the layer group belongs to hexagonal plane lattice with the primitive translation vector **a** and **b**. The nanotube is defined by translation vector **L** = l_1 **a** + l_2 **b** and chiral vector **R** = n_1 **a** + n_2 **b**, (l_1 , l_2 , n_1 and n_2 are integers). The nanotube of the chirality (n_1 , n_2) is obtained by folding the layer in a way that the chiral vector **R** becomes the circumference of the nanotube.

For hexagonal lattice, the orthogonality relation $(\mathbf{RL}) = 0$ can be written in the form

$$\frac{l_1}{l_2} = -\frac{2n_2 + n_1}{2n_1 + n_2} \tag{1}$$

The symmetry of armchair (n,n) and zigzag (n,0) SW BN and TiO₂ NTs with hexagonal morphology is described by line groups $(2n)_n/m$ (family 4, point symmetry C_{2nh}) and $(2n)_nmc$ (family 8, point symmetry $C_{2n\nu}$), respectively.¹⁴

In general case, the symmetry of SW NTs is described by a line group L = ZP being a product of axial point group P and infinite cyclic group Z of generalized translations. The latter consists of rotations C_q^r for $2\pi r/q$ around the q-order screw axis, translations (N/q)a (a denotes the translational period) or reflections in glide plane $(\sigma_v|a/2)$. Here $N = G(n_1,n_2)$ is the greatest common divisor and (n_1,n_2) defines the chiral vector of SW NT.

The line symmetry group of a double-wall nanotube can be found as intersection $L_2 = Z_2P_2 = (L \cap L')$ of the symmetry groups L and L' of its single-wall constituents as earlier considered for DW CNTs.^{26,27} The intersection $P_2 = (P \cap P')$ of the point groups is chosen independently of the generalized translational factor Z_2 .²⁶

Let (n_1,n_2) and (n_1',n_2') define the chiral vectors of single-wall constituents of the double-wall nanotube. Its axial point group $P_2 = C_N$ is the principal axis subgroup of the 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. The translational factor Z_2 is completely absent for incommensurate DW NTs, i.e., when the ratio a/a' is not rational.²⁶ As an example, we can mention DW NT formed from the hexagonal SW NTs with different types of chirality, both armchair and zigzag, i.e., $(n_1,n_1)@(n_2,0)$, where the ratio $a/a' = \sqrt{3}$.

The coaxial hexagonal DW NTs with $(n_1,n_1)@(n_2,n_2)$ and $(n_1,0)@(n_2,0)$ chiralities are commensurate: their translation period is the same as for constituents: $\mathbf{L} = -\mathbf{a} + \mathbf{b}$ (*ac* chirality), $\mathbf{L} = -\mathbf{a} + 2\mathbf{b}$ (*zz* chirality), as described by eq 1. In this case, the translational factor Z_2 contains rotations around the screw axis, common to both SW components. Two possibilities for periodic DW NTs were considered:²⁶ (i) both n_1/N and n_2/N are odd, L_2 contains the screw axis $(2N)_{Nj}$ (ii) one or both n_1/N and n_2/N are even, L_2 contains the rotation axis of order *N*. As an example of the first case we can consider hexagonal DW NT (6,6)@(10,10):

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Table 1. Symmetry of DW BN and TiO₂ NTs with Hexagonal Morphology

(a) Multiple Double-Wall Nanotubes $(n_1,n_1) @M(n_1,n_1)$ and									
$(n_1, 0)(aM(n_1, 0))$									
DW NT	multiple	line	point						
chiralities	divisor M	group	group	substance					
(4,4)@(8,8)	2	4/m	C_{4h}	BN					
(4,4)@(12,12)	3	$8_4/m$	C_{8h}	TiO ₂					
(5,5)@(10,10)	2	10	C_{5h}	BN					
(6,6)@(12,12)	2	6/ <i>m</i>	C_{6h}	BN, TiO ₂					
(6,6)@(18,18)	3	$12_6/m$	C_{12h}	TiO ₂					
(7,7)@(14,14)	2	14	C_{7h}	TiO_2					
(8,8)@(16,16)	2	8/ <i>m</i>	C_{8h}	TiO_2					
(8,8)@(24,24)	3	$16_8/m$	C_{16h}	TiO ₂					
(9,9)@(18,18)	2	18	C_{9h}	BN					
(6,0)@(12,0)	2	6 <i>mm</i>	$C_{6\nu}$	BN					
(7,0)@(14,0)	2	7m	$C_{7\nu}$	BN					
(8,0)@(16,0)	2	8 <i>mm</i>	$C_{8\nu}$	BN, TiO ₂					
(8,0)@(24,0)	3	16_8mc	$C_{16\nu}$	TiO ₂					
(9,0)@(18,0)	2	9 <i>m</i>	$C_{9\nu}$	BN, TiO ₂					
(10,0)@(20,0)	2	10 <i>mm</i>	$C_{10\nu}$	BN, TiO ₂					
(12,0)@(24,0)	2	12 <i>mm</i>	$C_{12\nu}$	BN, TiO ₂					
(12,0)@(36,0)	3	24 ₁₂ mc	$C_{24\nu}$	TiO ₂					

(b) Nonmultiple Double-Wall Nanotubes $(n_1,n_1)@(n_2,n_2)$ and									
$(n_{1},0)@(n_{2},0)$									
DW NT	common	line	point						
chiralities	divisor N	group	group	substance					
(4,4)@(9,9)	1	т	C_s	BN					
(6,6)@(10,10)	2	$4_2/m$	C_{4h}	BN					
(12,0)@(28,0)	4	8 ₄ mc	$C_{8\nu}$	TiO_2					

N = 2, $n_1/N = 3$, $n_2/N = 5$, the screw axis 4₂. For DW NT (12,0)@(18,0), we have N = 3, $n_1/N = 4$, $n_2/N = 6$, the rotation axis of the order 6.

In a particular case of the commensurate armchair (n_1,n_1) @ $M(n_1,n_1)$ and zigzag $(n_1,0)$ @ $M(n_1,0)$ DW nanotubes with hexagonal morphology (i.e., $n_2 = Mn_1$), the symmetry group can be found from the results obtained in ref 26 for full symmetry of multiwall nanotubes. For armchair and zigzag DW NTs with odd M, the line symmetry groups are the same as for their SW constituents, $(2n_n)/m$ (family 4, point symmetry C_{2nh}) and $(2n)_nmc$ (family 8, point symmetry $C_{2n\nu}$), respectively. For even M, the rotations about screw axis of order 2n are changed by rotations around the pure rotation axis of order n so that DW NT line symmetry groups become n/m (family 3, point symmetry C_{nh}) and nm (family 6, point symmetry $C_{n\nu}$), for armchair and zigzag chiralities, respectively.

For each SW NT, the coordinate system can be chosen with fixing the origin in initial nanosheet (slab), which the folding procedure has to be applied to. The normal to slab plane passing through the origin can be defined as the *x* axis in the SW NT coordinate system. Because of the coaxiality, mainly the two parameters completely determine the relative positions of SW constituents in DW NT: the angle φ and length Δz by which the outer tube is rotated around *z* and translated along *z*, respectively (in regards to the initial configuration with coinciding *x* and *x'* axes of both

					per BN formula unit					
DW NT chirality indices	initial $\Delta R_{\rm NT}$ (Å)	optimized $\Delta R_{\rm NT}$ (Å)	initial $D_{\mathrm{NT}}^{\mathrm{in}}$ (Å)	optimized $D_{\mathrm{NT}}^{\mathrm{in}}$ (Å)	$E_{\rm relax}$ (eV)	E _{bind} (kJ/mol)	band gap $\Delta \varepsilon_{\mathrm{gap}}{}^{a}$ (eV)			
		straight (<i>n</i>	$(n_1, n_1) @ (n_2, n_2)$ nan	otubes, Figure 1a						
(4,4)@(8,8)	2.77	2.93	5.49	5.40	-0.030	-1.86	5.84 ⁱ			
(4,4)@(9,9)	3.46	3.46	5.49	5.48	-0.02	0.66	5.95 ⁱ			
(5,5)@(10,10)	3.46	3.47	6.88	6.88	-0.019	0.67	6.29 ⁱ			
(6,6)@(12,12)	4.15	4.13	8.26	8.28	-0.0002	0.24	6.47 ⁱ			
(9,9)@(18,18)	6.13	6.21	12.41	12.41	-0.0001	0.001	6.71 ⁱ			
straight $(n_1,0) @(n_2,0)$ nanotubes with B(N)-B(N) pairs of rings in cross sections, Figure 1c										
(7,0)@(14,0)	2.79	2.92	5.59	5.50	-0.065	-2.34	4.65 ^d			
(8,0)@(16,0)	3.18	3.21	6.38	6.37	-0.039	0.51	5.28 ^d			
(9,0)@(18,0)	3.58	3.58	7.18	7.18	-0.018	0.58	5.43 ^d			
(10,0)@(20,0)	3.98	3.96	7.97	7.99	-0.0001	0.33	5.72 ^d			
(12,0)@(24,0)	4.78	4.77	9.56	9.56	-0.0001	0.001	6.13 ^d			
	inversed (n	$(n_1,0)@(n_2,0)$ nanotubes	with $N(B)-B(N)$	pairs of rings in cross	sections, Fig	ure 1d				
(6,0)@(12,0)	2.39	2.69	4.79	4.65	-0.224	-7.38	4.81 ^d			
(7,0)@(14,0)	2.79	2.95	5.59	5.51	-0.054	-1.34	5.11 ^d			
(8,0)@(16,0)	3.18	3.26	6.38	6.36	-0.030	0.50	5.31 ^d			
(9,0)@(18,0)	3.58	3.61	7.18	7.19	-0.028	0.68	5.51 ^d			
(10,0)@(20,0)	3.98	3.99	7.97	7.99	-0.017	0.37	5.74 ^d			
(12,0)@(24,0)	4.78	4.80	9.56	9.57	-0.014	0.001	6.13 ^d			
Indirect and direct gaps	are superscripted	l as ⁱ and ^d , respective	elv.							

Table 2. The Structural and Electronic Properties of Optimized DW BN NTs (Figure 1)

shells).^{26,27} Thus, the initial position of both SW constituents in DW NTs is characterized by $\varphi = 0$ and $\Delta z = 0$. In this case the maximum possible number of symmetry elements for both SW NTs coincide, and symmetry of initial DW NT structure is described by one of the line groups considered above. After atomic relaxation (Figure 1) the values of φ and Δz can differ from zero. Presumably, the roto-translational part of the DW NT symmetry group (independent of the relative SW NT positions) is not changed after relaxation. However, other common symmetry elements of SW NTs (second-order U axes normal to the translation vector, reflection, and glide planes) can be lost. Thus, the total symmetry of DW NT is reduced.

The two different commensurate DW NTs can be constructed from a given pair of SW NTs rolled up from the hexagonal sheets of BN or TiO₂. There is no second-order symmetry axis perpendicular to considered BN or TiO₂ layers. This means that rotation by 180° around the U axis, normal to the nanotube translation vector, is not a symmetry operation and rotated SW NT cannot be superimposed with the original one by any rototranslational operation. When rotating one of the constituents (for example the outer shell) around the U axis, one obtains the "inversed" DW NT structure, which is different from the "straight" structure initially constructed by the folding procedure. If the *U* axis belongs to one of existing (common) mirror planes σ_h or σ_v , the total symmetry of DW NT is unaffected. To satisfy this condition in the case of BN NTs, the U axis should pass through the BN hexagon center (particularly, this axis can coincide with *x*). As shown in Figure 1, if one SW NT constituent rotates by 180° around the *U* axis ("inversed" DW NT structure) its B and N atoms permute as compared to the "straight" DW NT structure. For TiO₂ DW NT, the U axis should pass through the Ti atom and can coincide with the *x* axis.

In Table 1, we describe the symmetry of those double-wall nanotubes which are considered in this paper. The upper part of this table (a) gives the symmetry of multiple DW BN and TiO₂ NTs with armchair (n,n)@M(n,n) and zigzag (n,0)@M(n,0) chiralities, while DW NTs in a lower part of the table (b) contain nonmultiple SW constituents with armchair $(n_1,n_1)@(n_2,n_2)$ and zigzag $(n_1,0)@(n_2,0)$ chiralities.

The calculations on double-wall nanotubes have been performed using the CRYSTAL-09 computer code²⁸ containing HELIX option which takes into account only the rototranslational symmetry (the order of rototranslational axis has to be not larger than 48). As seen from Table 1, the initial structures of DW NTs have two times more symmetry operations than the order of rotohelical axis since reflections in horizontal or vertical planes (σ_h or σ_ν , respectively) are added to rotohelical operations.

3. COMPUTATIONAL DETAILS

The first principles DFT-LCAO method, as implemented in the CRYSTAL-09 code,²⁸ allows us to describe 1D nanotubes in their original space form, unlike the Plane-Wave methods, which are quite widespread nowadays for ab initio calculations on low-dimensional periodic systems, including DW BN NTs.^{21–23} Indeed, to restore the 3D periodicity in the PW nanotube calculations, the x-y supercell of nanotubes is artificially introduced: the NTs are placed into a square array with the intertube distance equal to 2–3 nm. At such separations the NT–NT interaction is found to be rather small; however, the convergence of results obtained in such calculations depends on the artificial inter-NT interactions demanding additional computational efforts to ensure their negligibility.

	Table 3. Ionic Charges	(q) and Bond Populat	tions (p)	for DW BN NTs	Shown in	Figure 3
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	outer shell		inı	ner shell	intershell bond populations			
nanotube configuration vs charge plot in Figure 3	$q_{\mathrm{B}}^{a}\left(\mathrm{e}\right)$	$p_{\mathrm{B-N}}^{b}(\mathrm{e})$	$q_{\mathrm{B}}{}^{a}\left(\mathrm{e}\right)$	$p_{\mathrm{B-N}}^{b}(\mathrm{e})$	$p_{\mathrm{B-N}}^{c}(\mathrm{e})$	$p_{\mathrm{B-B}}^{c}(\mathrm{e})$	$p_{\mathrm{N-N}}^{c}(\mathrm{e})$	
ac-(5,5)@(10,10)-(a)	1.012	0.640	1.010	0.694	0.008^{d}	0.004	-0.004	
ac-(9,9)@(18,18)-(b)	0.999	0.616	1.010	0.648	0	0	0	
<i>zz-s-</i> (9,0)@(18,0)–(c)	1.014	0.622	1.010	0.656	0.004 ^e	0.002	-0.002	
zz-s-(12,0)@(24,0)-(d)	1.003	0.618	1.013	0.648	0	0	0	
<i>zz-i-</i> (9,0)@(18,0)–(e)	1.021	0.620	1.013	0.656	0.004 ^e	0.002	-0.002	
<i>zz-i-</i> (12,0)@(24,0)–(f)	1.003	0.618	1.013	0.648	0	0	0	

^{*a*} Averaged effective charge q_N is almost the same as q_B , with opposite sign. ^{*b*} Averaged bond population is estimated between the nearest in-wall B and N atoms (Figure 1). ^{*c*} Averaged bond population is estimated between the nearest intershell atoms (Figure 1). ^{*d*} Integrated intershell bond population for *ac*-(5,5)@(10,10) BN NT achieves 0.080 e per ring (Figure 1). ^{*e*} Integrated intershell bond population for *zz*-(9,0)@(18,0) BN NT achieves 0.072 e per ring (Figure 1).

Our calculations on DW NTs have been performed using the hybrid Hartree–Fock/Kohn–Sham (HF/KS) exchange-correlation Hamiltonian PBE0 by Perdew–Becke–Erzerhof^{29,30} combining exact HF nonlocal exchange and KS exchange operator within the Generalized Gradient Approximation (GGA) as implemented in CRYSTAL-09 code.

An all-valence basis set (BS) in the form of 6s-21sp-1d and 6s-31p-1d Gaussian-type functions (GTFs) have been used for B and N atoms,¹⁴ respectively. Calculated equilibrium lattice constants for the bulk of hexagonal BN have been found to be qualitatively close to their experimental values (a_0 of 2.51 Å vs 2.50 Å obtained in experiment and c_0 of 7.0 vs 6.7 Å),³¹ thus, indicating reliability of BN calculations.

A small-core pseudopotential of Ti atom has been adopted in 5s-6p-5d GTF BS for titania nanotube calculations (3s, 3p, 3d, and 4s electrons were taken as valence electrons),³² while an allelectron 6s-311sp-1d GTF BS for O-atom has been taken from ref 33. The atomic and electronic properties of TiO₂ bulk with anatase-type morphology have been reproduced in a good agreement with the experiment (measured values are given in brackets): the lattice parameters $a_0 = 3.784$ Å (3.782 Å) and $c_0 = 9.508$ Å (9.502 Å), the dimensionless parameter for relative position of oxygen atom u = 0.2074 (0.2080), although values of $\Delta \varepsilon_{gap}$ are being slightly overestimated: 4.0 eV vs 3.2 eV.³⁴

The reciprocal space has been sampled according to a regular sublattice determined by the shrinking factor 12 (seven independent *k* points in the irreducible part of the Brillouin zone). Calculations have been considered as converged only 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 double-wall nanotubes having large unit cells (containing up to 288 atoms in the case of (12,0)@(36,0) TiO₂ NTs) have been performed using the full exploitation of the helical rototranslational symmetry as first implemented in the periodic CRYSTAL-09 code.²⁸ With the TESTGEOM-NANOTUBE option, as foreseen in this code, 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, which criterion is a convergence of structure parameters within the given precision.

Results of our calculations on hexagonal BN(0001) monolayer and TiO₂(111) three-layer slabs as well as SW BN and TiO₂ NTs are described in detail elsewhere.¹⁴ Those nanostructures were calculated using the CRYSTAL-06 code.³⁵ Since the rotohelical formalism was not yet implemented in previous



Figure 2. Binding energies E_{bind} vs ΔR_{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.

release of this computational package (for nanotube calculations, the polymer rod groups were applied), we have performed recalculations on the corresponding SW NTs using the CRYSTAL-09 code.²⁸ No noticeable quantitative differences between the corresponding results have been found (e.g., the total energies of (12,0) BN nanotube calculated using both CRYSTAL codes differ only by 0.0000074 eV per BN formula unit). Advantage of CRYSTAL-09 is a markedly smaller CPU time spent for calculations on nanotubular structures which contain rotation axes not coinciding with those of second, third, fourth, and sixth orders (Table 1).

4. STRUCTURAL AND ELECTRONIC PROPERTIES OF HEXAGONAL DW BN NTS

For double-wall boron nitride nanotubes, we have considered the two mutual orientations of chiral and translation vectors of constituent shells (Figure 1): coinciding and opposite (i.e., straight and inversed configurations, respectively, as described in section 2). For *ac*-chirality of DW NTs, the cross sections of inner and outer shells contain pairs of B and N atoms (B–N bonds) in the corresponding rings with straight and inversed orientations of the chiral vector (panels a and b of Figure 1, respectively), which make each of them electrostatically neutral. The difference of energies for equilibrium configurations of



Figure 3. Difference electron density plots $\Delta\rho(\mathbf{r})$ (the total electron densities in the perfect DW BN NT minus the sum of these densities in the two constituent SW BN NTs) calculated for the cross sections of nanotubes depicted in Figure 1: (a) (5,5)@(10,10), (b) (9,9)@(18,18), (c) straight (9,0)@(18,0), (d) straight (12,0)@(24,0), (e) inversed (9,0)@(18,0), (f) inversed (12,0)@(24,0). Solid (red), dashed (blue), and dot-dashed (black) isolines describe positive, negative, and zero values of the difference density, respectively. Isodensity curves are drawn from -0.001 to +0.001 e Å⁻³ with increments of 0.00004 e Å⁻³.

ac-DW BN NTs with the same chirality indices and straight vs inversed orientations of chiral vectors has been found negligible $(\sim 10^{-4} \text{ eV per formula unit})$. Thus, we present in this section only results calculated for straightly stacked configuration (Figure 1a). For zz chirality, both straightly stacked configuration, i.e., the outer B(N) ring across the inner B(N) ring (Figure 1c), and inversely stacked configuration, i.e., the N(B)across the B(N) (Figure 1d) have been considered because the corresponding energy difference between them is noticeable (Table 2). Obviously, from the electrostatic point of view, the inversely stacked configuration of zz-DW NTs should be energetically more favorable (i.e., the positively charged B ring of one shell is the nearest neighbor to the negatively charged N ring of other shell, although in-wall B-N interactions are certainly stronger than those between the walls). A similar conclusion was earlier drawn in ref 23.

Stability of the DW NTs depends mainly on the interwall distance, i.e., a difference between the radii of constituent shells

 $(\Delta R_{\rm NT})$, and the diameter of inner shell $(D_{\rm NT}^{\rm in})$.^{17,21–23} The binding energy $E_{\rm bind}$ between the constituent shells of the double-wall nanotube has been chosen as a criterion of nanotube stability

$$-E_{\text{bind}}(D_{\text{NT}}^{\text{in}}@D_{\text{NT}}^{\text{out}}) = E_{\text{tot}}(D_{\text{NT}}^{\text{in}}@D_{\text{NT}}^{\text{out}}) - E_{\text{tot}}(D_{\text{NT}}^{\text{in}}) - E_{\text{tot}}(D_{\text{NT}}^{\text{out}})$$
(2)

where $E_{\rm tot}$ are the calculated total energies of DW NT and its constituent SW NTs with optimized structure. As in our previous paper¹⁴ we have also estimated relaxation energies $E_{\rm relax}$ (the difference between total energies of DW NT before and after geometry optimization) which are usually large for small values of $\Delta R_{\rm NT}$ and $D_{\rm NT}^{\rm in}$. The main results of calculations on DW BN NTs are given in Tables 2 and 3 and Figures 2 and 3.

The binding energy curves $-E_{\text{bind}}(\Delta R_{\text{NT}})$ for DW BN nanotubes of both chiralities are shown in Figure 2. The maxima of binding energies for these double-wall nanotubes correspond to



Figure 4. Cross sections and aside images of hexagonal DW TiO_2 NTs (i.e., left and right parts of models a and b, respectively) corresponding to optimized diameters for armchair and zigzag chiralities. For *zz*-DW TiO_2 NTs (model b), the atoms of the nearest ring behind the cross section are shown as half-shaded balls. For description of graphical details of models, see clarification in caption of Figure 1.

both optimal (5,5)@(10,10) and (9,0)@(18,0) configurations as well as interwall distance 3.5-3.6 Å (cf. (5,5)@(10,10), (8,0) (a)(16,0), and 3.2 Å as described in ref 23). The inversed B-N configuration of zz-DW NTs is slightly more favorable energetically than that of the straight B-B one (Table 2) which confirms a presence of polarization effects in boron nitride multiwall nanotubes as predicted earlier.^{17,23} Reliefs of the binding energy curves (Figure 2) also give a small preference to the inversed doublewall zz-NTs vs ac-NTs. These results also favor to the experimentally observed dipolar-shell structured morphology of the MW BN NTs.¹⁶ Obviously, the small values of $\Delta R_{\rm NT}$ and $D_{\rm NT}^{\rm in}$ accompanied by the large values of E_{relax} result in instability of DW NTs (Figure 2) while the large values of $\Delta R_{\rm NT}$ and $D_{\rm NT}^{\rm out}$ (and neglecting relaxation energies) correspond to quasi-independent noninteracting pairs of SW NTs. On the other hand, E_{bind} is sensitive to ΔR_{NT} while influence of $D_{\rm NT}^{\rm in}$ on $E_{\rm bind}$ is rather negligible (Table 2).

Figure 3 shows the difference electronic charge redistributions drawn for both optimal and increased values of $\Delta R_{\rm NT}$ and $D_{\rm NT}^{\rm m}$ for double-wall *ac*- and *zz*-BW NTs (Figure 1). For optimal structures of DW NTs, considerable redistributions of the electronic density can be observed with clearly visible polarization effects, especially around the inner shells. The latter are largest for the inversely stacked configuration of zz-BN NTs, while $\Delta \rho(\mathbf{r})$ function for *ac*-BN NTs is characterized by more pronounced localization effects. For double-wall nanotubes with large interwall distances (Figure 3b,d,f), the interaction between the outer and inner shells is very weak, which reduces stability of DW BN NTs, according to the reliefs of potential curves (Figure 2). The Mulliken population parameters (Table 3) calculated for both chiralities of the optimal and quasi-independent DW BN NT structures qualitatively confirm results extracted from the drawn electron density redistributions (Figure 3).

As follows from our previous simulations on SW BN NTs,¹⁴ the band gap $\Delta \varepsilon_{gap}$ reduces with increasing nanotube diameter asymptotically approaching to the energy limit of BN(0001) monolayer (7.09 eV). For double-wall BN nanotubes, the band gap is the most dependent on the diameter of inner shell $D_{\rm NT}^{\rm in}$ being almost insensitive on $\Delta R_{\rm NT}$ (Table 2). For both nanosheet and nanotube morphologies, the N(2p) states prevail near the top of valence band while the B(2p) states are mainly



Figure 5. Binding energies E_{bind} vs ΔR_{NT} for the two sets of DW TiO₂ NTs with *ac*- and *zz*-chiralities. Spline treatment of curves has been performed to make them smooth.

distributed near the bottom of conduction band. When comparing values of $\Delta \varepsilon_{\rm gap}$ for DW NTs presented in Table 2 with band gaps for SW NTs (Table 3 of our previous paper),¹⁴ one can conclude that $\Delta \varepsilon_{\rm gap} < 6$ eV for chiralities (4,4), (6,0)-(10,0) of inner shells which correspond to $D_{\rm NT}^{\rm in} < 7.5$ Å. With a further increase of $D_{\rm NT}^{\rm in}$ and $\Delta R_{\rm NT}$ the band gap gradually approaches to the energy limit of BN(0001) monolayer (7.09 eV).¹⁴ On the other hand, if we compare values of $\Delta \varepsilon_{\rm gap}$ for SW and DW BN NTs for the same outer diameter $D_{\rm NT}^{\rm out}$, the band gaps of the latter are noticeably smaller, by 0.5–1.5 eV (depending on diameter of inner shell). Thus, the band gaps for multiwall BN nanotubes can be easier adjusted by morphology composition of inner walls.

5. STRUCTURAL AND ELECTRONIC PROPERTIES OF HEXAGONAL DW TIO₂ NTS

To our knowledge, no ab initio simulations on double-wall titania nanotubes have been performed so far. We have considered only straightly stacked configurations for both *ac*- and *zz*- chiralities of DW TiO_2 NTs with a hexagonal morphology



Figure 6. Difference electron density plots $\Delta \rho(\mathbf{r})$ of DW TiO₂ NTs calculated for the cross sections of nanotubes depicted in Figure 4: (a) (6,6)@(12,12), (b) (8,8)@(24,24), (c) (10,0)@(20,0), (d) (12,0)@(36,0). For technical and graphical details, see caption of Figure 3.

4)
4

					per TiC	₂ formula unit					
DW NT chirality indices	initial $\Delta R_{\rm NT}$, Á	optimized $\Delta R_{\rm NT}$, Á	initial $D_{ m NT}^{ m in}$, Á	optimized $D_{\rm NT}^{\rm in}$, Á	$E_{ m relax}$ eV	E _{bind} , kJ/mol	band gap $\Delta \varepsilon_{\text{gap}}^{a}$ eV				
$(n_1,n_1) \mathscr{Q}(n_2,n_2)$ nanotubes, Figure 4a											
(6,6)@(12,12)	4.84	4.76	10.06	10.13	-0.07	1.71	3.00 ⁱ				
(7,7)@(14,14)	5.66	5.62	11.66	11.69	-0.05	1.08	3.19 ⁱ				
(4,4)@(12,12)	6.31	6.30	7.12	7.12	-0.23	0.09	3.90 ⁱ				
(8,8)@(16,16)	6.48	6.48	13.26	13.27	-0.02	0.07	3.40 ⁱ				
(6,6)@(18,18)	9.73	9.70	10.06	10.09	-0.05	0.001	3.04 ⁱ				
(8,8)@(24,24)	13.00	12.99	13.26	13.27	-0.02	0.0001	3.49 ⁱ				
		$(n_1,0)$	@(n ₂ ,0) nanotub	es, Figure 4b							
(8,0)@(16,0)	3.61	3.81	8.16	8.25	-0.81	-1.02	2.94 ⁱ				
(9,0)@(18,0)	4.10	4.33	9.02	8.94	-0.32	1.59	3.08 ⁱ				
(10,0)@(20,0)	4.59	4.62	9.90	9.92	-0.07	2.17	3.21 ^d				
(12,0)@(24,0)	5.59	5.48	11.41	11.73	-0.04	0.45	3.31 ^d				
(12,0)@(28,0)	7.36	7.10	11.41	11.69	-0.04	0.04	3.35 ^d				
(12,0)@(36,0)	9.33	9.34	11.41	11.69	-0.03	0.001	3.38 ^d				
^{<i>a</i>} Indirect and direct gaps	are superscripted	as ⁱ and ^d , respective	ely.								

(panels a and b of Figure 4, respectively). Unlike DW BN NTs, no permutation of Ti and O atoms occurs in the case of inversed configurations. In *ac*-DW TiO₂ NTs, such an inversion means angular reorientation of O–Ti–O shells (Figure 4a) which does not cause noticeable rearrangement of the intershell bonding. A similar conclusion can be drawn also for *zz*-DW TiO₂ NT although the interwall polarization causes such a Δz shift

(section 2) when the cross section of nanotube contains Ti and O atoms which belong to different shells (Figure 4b). Analogously to DW BN NTs (Table 2 and Figures 2 and 3), we have performed similar calculations for DW TiO_2 NTs, their results are presented in Tables 4 and 5 and Figures 5 and 6.

Constructing the binding energy curves for titania nanotubes of both chiralities in accordance with eq 2, we have localized the

Table 5. Tollic Charges (q) and bolic Populations (p) for DW 1102 NTS shown in Figure	Table 5.	Ionic Charges ((q) and Bond	Populations (p)	for DW	TiO ₂ NTs	Shown in	Figure
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	outer shell					inr	1er shell		
nanotube configuration vs charge plot in Figure 6	$q_{\text{O-out}}^{a}(e)$	$q_{\mathrm{Ti}}\left(\mathrm{e}\right)$	$q_{\text{O-in}}{}^{b}(e)$	$p_{\mathrm{Ti}-\mathrm{O}}^{c}\left(\mathrm{e}\right)$	$q_{\text{O-out}}^{a}(e)$	$q_{\mathrm{Ti}}\left(\mathrm{e}\right)$	$q_{\text{O-in}}{}^{b}(e)$	$p_{\mathrm{Ti}-\mathrm{O}}^{c}(\mathrm{e})$	
<i>ac</i> -(6,6)@(12,12)–(a)	-1.250	2.445	-1.200	0.051	-1.162	2.426	-1.257	0.056	
<i>ac</i> -(8,8)@(24,24)–(b)	-1.241	2.457	-1.216	0.054	-1.178	2.434	-1.256	0.060	
<i>zz-</i> (10,0)@(20,0)-(c)	-1.250	2.445	-1.198	0.048	-1.160	2.425	-1.258	0.047	
<i>zz-</i> (12,0)@(36,0)-(d)	-1.236	2.444	-1.205	0.062	-1.173	2.431	-1.258	0.052	
^{<i>a</i>} Effective charge q_{O-out} of external shell layer (Figure 4). ^{<i>b</i>} Effective charge q_{O-in} of internal shell layer (Figure 4). ^{<i>c</i>} Averaged in-wall Ti–O bond population.									

minima of $-E_{\text{bind}}(\Delta R_{\text{NT}})$ functions (Figure 5) which correspond to (6,6)@(12,12) and (10,0)@(20,0) double-wall configurations of DW TiO₂ NTs with interwall distances 4.6–4.8 Å (ΔR_{NT} is defined as a difference between the radii of middle Ti subshells).¹⁴ Meanwhile, when reducing ΔR_{NT} in DW TiO₂ 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), (6,6)@(10,10), (5,5)@(10,10), and (6,6)@(11,11), where geometry optimization has resulted in destruction of double-wall morphology with formation of complicated nonhexagonal quasi-single-wall morphology.

It is seen from Figures 2 and 5 that the binding energies estimated per formula unit for optimal configurations of hexagonal DW NTs are considerably larger for titania as compared to boron nitride, while reliefs of minima on $-E_{\text{bind}}(\Delta R_{\text{NT}})$ curves are more sharp for the former. Obviously, this is caused by substantially larger ionic contribution to interwall interaction between the titania SW constituents (Table 5). In both cases, the double-wall nanotube configurations with zz-chirality are energetically more favorable as compared to those with ac-chirality. Analogously to DW BN NTs, the small values of $\Delta R_{\rm NT}$ and $D_{\rm NT}^{\rm in}$ (Table 4) accompanied by the large values of $E_{\rm relax}$ result in instability of DW TiO₂ NTs while the large values of $\Delta R_{\rm NT}$ correspond to almost neglecting interaction within pairs of constituent SW NTs. Analogously to DW BN NTs, Ebind for titania nanotubes is sensitive to $\Delta R_{\rm NT}$ while influence of $D_{\rm NT}^{\rm in}$ on E_{bind} is rather negligible (Table 4).

Comparison of Figures 3 and 6 showing the difference electronic charge redistributions drawn for both optimal and increased values of $\Delta R_{\rm NT}$ within *ac*- and *zz*-DW NTs (both BN and TiO₂) clearly demonstrates higher electron density localization within the latter (especially for armchair-type nanotubes), while comparison of results presented in Tables 3 and 5 show a noticeably higher bond ionicity in DW TiO₂ NTs. Bond populations between the shells in DW TiO₂ NTs have been found to be close to zero. For large $\Delta R_{\rm NT}$ in double-wall titania nanotubes (Figure 6b,d), the intershell interaction again becomes weak, i.e., stability of these DW TiO₂ NTs is low enough, analogously to DW BN NTs (Figure 3b,d,f).

Unlike boron nitride nanotubes, the difference between the values of $\Delta \varepsilon_{\rm gap}$ for double-wall and single-wall TiO₂ NTs is considerably larger. Additional difference between them is that for small values of $\Delta R_{\rm NT}$, the band gaps of *zz*-DW TiO₂ NTs are indirect while for *zz*-DW BN NTs, these band gaps are direct for all configurations. This can be explained by substantially smaller stability of DW TiO₂ NTs with reduced values of $\Delta R_{\rm NT}$ Moreover, when increasing both $D_{\rm NT}^{\rm in}$ and $\Delta R_{\rm NT}$ the band gaps of double-wall titania nanotubes are still too far from the band gap

limit of TiO₂(111) trilayer (4.89 eV).¹⁴ However, dependence of band gaps on both $\Delta R_{\rm NT}$ and $D_{\rm NT}^{\rm in}$ is similar for both DW BN and TiO₂ NTs, i.e., $\Delta \varepsilon_{\rm gap}$ is the most dependent on the diameter of inner shell. The Mulliken population analysis shows that O(2p) states prevail near the top of valence band while Ti(3d) states are mainly distributed near the bottom of conduction band.

We have also compared the total energies for optimal DW TiO₂ NTs with hexagonal fluorite-type morphology and SW TiO₂ NTs with anatase-type centered rectangular morphology³⁶ containing the same number of atoms per nanotube unit cell. For similar chiralities, we observe energetic preference of the latter: (i) energy gain for (-9,9) SW NT vs (6,6)@(12,12) DW NT with number of atoms equal to 108 has been found to be 0.09 eV per TiO₂ formula unit; (ii) analogous energy gain for 180-atomic unit cells of SW and DW nanotubes with chiralities (15,15) and (10,0)@(20,0) achieves 0.17 eV per TiO₂ formula unit. Thus, the growth of anatase-type NTs is preferable.

6. CONCLUSIONS

- 1 The line group formalism is applied for description of double-wall nanotubes of BN and TiO₂. The hexagonal DW NTs (n,n)@(m,m) and (n,0)@(m,0) are commensurate; the translation period of such nanotubes is the same as for single-wall constituents of either armchair or zigzag chiralities. The exploitation of the rotohelical symmetry of DW NTs permits drastic reduction of the computational time.
- 2 Large-scale first-principles LCAO calculations using the hybrid PBE0 Hamiltonian have been performed for the analysis of the atomic and electronic structure of double-wall BN and TiO_2 nanotubes simulated using different models for different morphology. To the best of our knowledge, calculations on DW TiO_2 NTs have been performed by us for the first time.
- 3 To estimate stability of DW BN and TiO₂ NTs, we have chosen the binding energies between their constituent shells (E_{bind}) as a criterion. These binding energies depend mainly on the interwall distance (ΔR_{NT}) and the diameter of the inner shell ($D_{\text{NT}}^{\text{in}}$). The potential energy curves $E_{\text{bind}}(\Delta R_{\text{NT}})$ for double-wall nanotubes of both chiralities permit estimation of 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 TiO₂ NTs. The values of ΔR_{NT} and $D_{\text{NT}}^{\text{in}}$, which are smaller than those in optimal DW NT configurations, lead to their instability, while the large values of ΔR_{NT} and $D_{\text{NT}}^{\text{out}}$ correspond to quasi-independent noninteracting pairs of constituent SW NTs.

- ⁴ The inversely stacked structure of double-wall *zz*-BN NT has been found to be energetically more preferable than its straight configuration, due to additional electrostatic attraction of the closest positively and negatively charged nanotube rings and repulsion of analogous rings consisting of the same type of atoms. Obviously, results obtained for inversed configuration favor to the dipolar-shell structural morphology of MW BN NTs observed experimentally elsewhere.¹⁶
- 5 Due to a noticeably larger ionic contribution to interwall interaction between three-layer O-Ti-O shells within DW TiO_2 NTs, their polarization effects are certainly larger than those in DW BN NTs which results in the higher electron density localization as compared to DW BN NTs.
- 6 Considerable interaction between the walls in optimal DW NT configurations results in a decrease of band gaps in double-wall nanotubes as compared to those for SW NTs (this decrease is more pronounced for DW TiO₂ NTs).

AUTHOR INFORMATION

Corresponding Author

*E-mail: re1973@re1973.spb.edu.

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