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Electronic structure of single-walled TiO_2 and VO_2 nanotubes

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The electronic properties and chemical bonding of new single-walled nanotubes based on TiO_2 (anatase) were studied using the tight-binding band theory and compared with hypothetical VO_2 nanotubes.

Inorganic nanotubes have been a focus of extensive research due to their scientific and technological importance.[1–3] Alongside the well-known tubular nanostructures based on layered materials (graphite, BN, BC_3, BC_2N and metal dichalcogenides MX_2),[1–3] some efforts were reported in preparation of nanotubes and nanowires of *d*-metal oxides (V_2O_5, Co_3O_4, MnO_2, WO_3 *etc.*).[4–8]

Among oxide nanostructures, much interest was aroused recently in titania nanotubular materials due to their chemical inertness, endurance, strong oxidising power, large surface area, high photocatalytic activity, non-toxicity and lower production cost. The application of TiO_2 nanotubes to photocatalysis, in solar cells[9,10] and as nanoscale materials for lithium-ion batteries[11] was discussed.

Considerable progress was achieved recently in fabrication of quasi-one-dimensional (1D) polycrystalline TiO_2 nanoscaled structures (tubes, wires and ribbons) and related nanosystems (trititanate nanotubes).[12] Several approaches have been developed to prepare titania nanotubes by using anodic alumina as a template or *via* sol–gel techniques.[13–19] For example, smaller tubes with diameters (*D*) about 8 nm were prepared.[13,14] TiO_2 nanotubes with *D* about 5 nm and wall thickness of ~1.3 nm have been synthesised by sonicating titania ultra-fine particles in an aqueous NaOH solution.[18] Models of possible growth mechanisms of titania tubes and wires were discussed.[16,17,19] It was noted[16,19] that anatase TiO_2 powder rather than rutile is preferred to form nanotubes. A schematic model of the titania 3D → → 2D → 1D transformation was proposed.[19] According to this model, the raw anatase phase first formed a lamellar product (3D → 2D) and then was bent and rolled to a nanotubular form (2D → 1D).

As compared with extensively investigated carbon, BN and MoS_2 nanotubes,[1–3,20,21] the morphology of titania nanotubes is much more complicated. Cross-sectional HRTEM images[16–19] confirm that the TiO_2 nanotubes are multi-walled and have a scroll-like morphology. The layered structure inside tube walls frequently contains various defects, and the ends of tubes are predominantly open. The exact atomic structure of the nanotube walls and their stacking mode remain unknown.

As a first step to understanding the electronic properties of titania nanotubes, we have performed an atomic simulation of their structure constructed from single {101} planes of semiconducting TiO_2 (anatase). We report the results of band structure calculations of TiO_2 nanotubes compared with those for hypothetical nanotubes based on metal-like VO_2 (rutile). Their electronic band structure and bond indices are analysed as a function of tube diameters (*D*) in armchair- and zigzag-like forms.

The anatase structure (space group $I4_1/amd$) is built up from TiO_6 octahedra with the lattice parameters $a = 0.3782$, $c = 0.9502$ nm and the internal parameter $u = d_a/c$ (0.208), where d_a is the apical Ti–O bond length (0.1979 nm).[22] A view of the

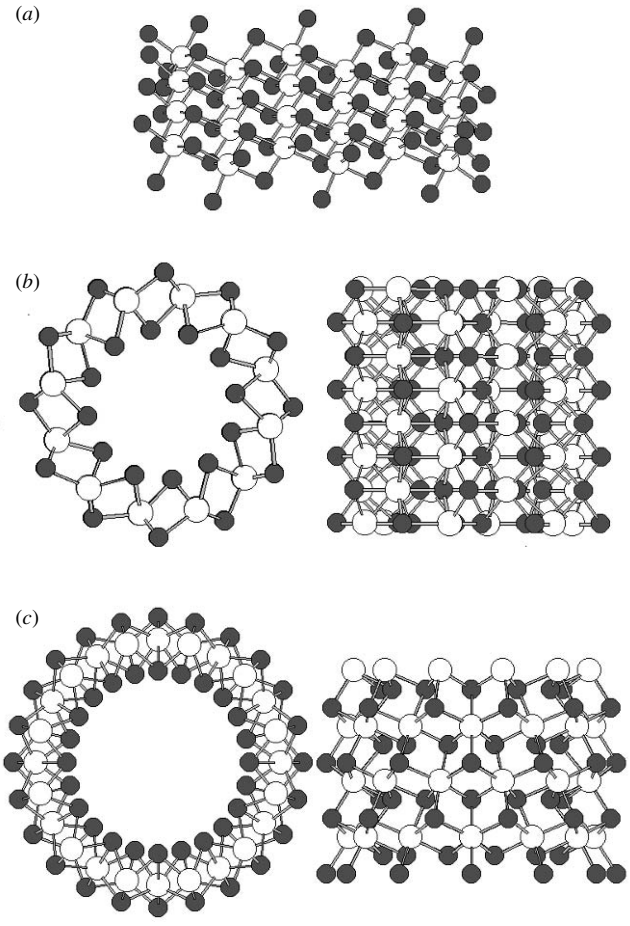

Figure 1 The structures of (*a*) the {101} layer of TiO_2 (anatase), (*b*) armchair (6,6)- and (*c*) zigzag (12,0) TiO_2 nanotubes. Side views and views along the tube axis are shown.

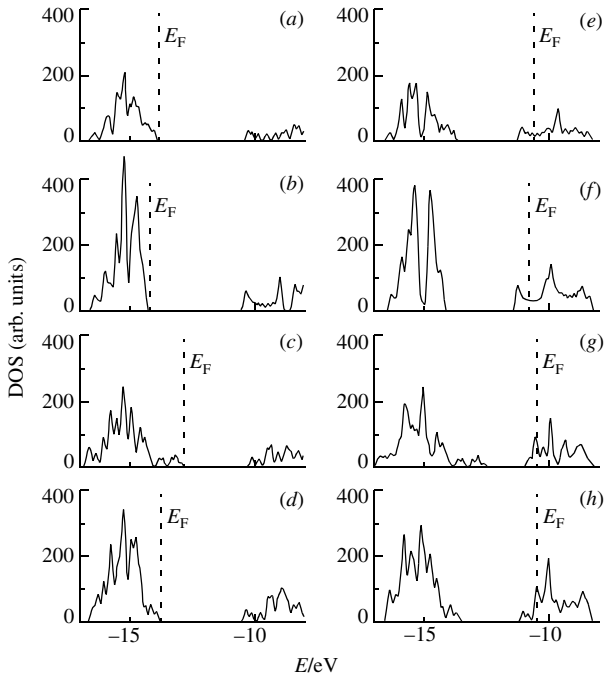

Figure 2 Total DOS of armchair (8,8)-, (15,15)- TiO_2 (*a*,*b*), VO_2 (*e*,*f*), and zigzag (11,0)-, (15,0)-like TiO_2 (*c*,*d*) and VO_2 (*g*,*h*) nanotubes.

Table 1 The number of atoms in unit cells, diameters (D/nm) and indices of intra-atomic bonds (COOPs, e) for TiO_2 and VO_2 nanotubes.

Tubes	Cell size	D(Ti)[a]	D(V)[a]	COOPs[b]					
				Ti–O^{in}	V–O^{in}	Ti–O^{out}	V–O^{out}	Ti–Ti	V–V
(8,0)	48	0.714	0.684	0	0.283	0.499	0	0.041	0.055
(9,0)	54	0.802	0.770	0	0.299	0.488	0	0.021	0.028
(10,0)	60	0.892	0.856	0	0.296	0.477	0	0.018	0.035
(11,0)	66	0.980	0.940	0	0.299	0.470	0	0.018	0.029
(12,0)	72	1.070	1.026	0	0.303	0.464	0	0.017	0.021
(13,0)	78	1.148	1.120	0	0.304	0.458	0	0.017	0.025
(14,0)	84	1.248	1.198	0	0.310	0.453	0	0.017	0.019
(15,0)	90	1.336	1.282	0	0.315	0.449	0	0.017	0.015
(4,4)	24	0.618	0.592	0.302	0.073	0.241	0.409	0.036	0.220
(5,5)	30	0.772	0.740	0.279	0.101	0.235	0.410	0.031	0.194
(6,6)	36	0.926	0.888	0.285	0.118	0.229	0.393	0.029	0.207
(7,7)	42	1.080	1.038	0.292	0.126	0.224	0.395	0.029	0.196
(8,8)	48	1.236	1.186	0.298	0.131	0.219	0.397	0.029	0.186
(9,9)	54	1.390	1.334	0.302	0.137	0.216	0.385	0.029	0.198
(10,10)	60	1.544	1.482	0.305	0.140	0.213	0.386	0.030	0.189
(11,11)	66	1.698	1.630	0.307	0.143	0.210	0.377	0.030	0.199
(12,12)	72	1.852	1.798	0.309	0.145	0.208	0.379	0.030	0.192
(13,13)	78	2.006	1.926	0.310	0.148	0.206	0.372	0.030	0.200
(14,14)	84	2.162	2.074	0.303	0.148	0.204	0.373	0.030	0.194
(15,15)	90	2.316	2.222	0.306	0.151	0.202	0.368	0.030	0.200

[a] D(Ti) and D(V) are the diameters of cylinders made up of metal atoms in TiO_2 and VO_2 nanotubes, respectively. [b] Ti(V)–O^{in} and Ti(V)–O^{out} are the couplings of Ti(V) with the atoms of inner and outer oxygen cylinders.

structure of a {101} TiO_2 layer is shown in Figure 1. Similar to the graphene sheets in carbon nanotubes,[1–3] these layers can be rolled in cylinders forming 'triple-wall' (O–Ti–O) tubes, and three groups of TiO_2 tubes can be constructed: armchair (n,n)-, zigzag (n,0)-like (Figure 1) and chiral (n,m) nanotubes. An analogous technique was used for constructing structural models of tubes based on VO_2 (rutile, space group $P4_2/mnm$, $a = b =$ $= 0.4555$, $c = 0.2851$ nm and $u = 0.305$[23]).

We performed calculations for (n,0)- and (n,n)-like TiO_2 and VO_2 nanotubes as a function of n in the ranges from (8,0) to (15,0) and from (4,4) to (15,15), which correspond to the tube diameters of ~0.6–2.3 nm (Table 1), where D(Ti) and D(V) are the diameters of cylinders made up of metal atoms for TiO_2 and VO_2 nanotubes, respectively. The largest diameters of our model titania tubes are half as small as the experimentally observed TiO_2 tubes of medium diameters.[15–19]

The tight-binding band structure method within the extended Hückel theory (EHT) approximation[24] was employed. The unit cell sizes are listed in Table 1. The total densities of states (DOS), crystal orbital overlap populations (COOP) and the total band energies of nanotubes (E_{tot}) were obtained.

The calculated DOS of some (n,n)- and (n,0)-like TiO_2 nanotubes are shown in Figure 2. They are similar for all the tubes and consistent with the DOS of crystalline anatase.[25] The valence band is composed by Ti 3d–O 2p states, the lower part of the conduction band is formed predominantly by Ti 3d states. The configuration type and the tube diameter affect most distinctly the band gap width (BG). For nanotubes with a maximum diameter, BG values are ~3.34 [armchair-like (15,15)-nanotube] and ~3.01 eV [zigzag-like (15,0)nanotube] compared with the calculated value[25] ~2.0 eV (direct transition at point Γ of the Brillouin zone) and the experimentally determined[26] (~3.4 eV) band gap of crystalline TiO_2. The BG size decreases as the nanotube diameters decreased [Figure 3(a)], the BG values for armchair-like nanotubes being still higher than those for zigzag-like nanotubes.

The electronic spectra of metal-like VO_2 nanotubes are also similar in general to the electronic band structure of crystalline vanadium dioxide.[21] The hybrid V 3d–O 2p-type nanotube bands are fully occupied, and the Fermi level (E_F) lies in region of the conduction V 3d-like band. For armchair nanotubes, the near-Fermi DOS is relatively small. On the contrary, for zigzag nanotubes E_F lying in the region of local DOS is maximal, (Figure 2). Note that an analogous near-Fermi DOS peak is responsible for the phase instability of crystalline VO_2.[27]

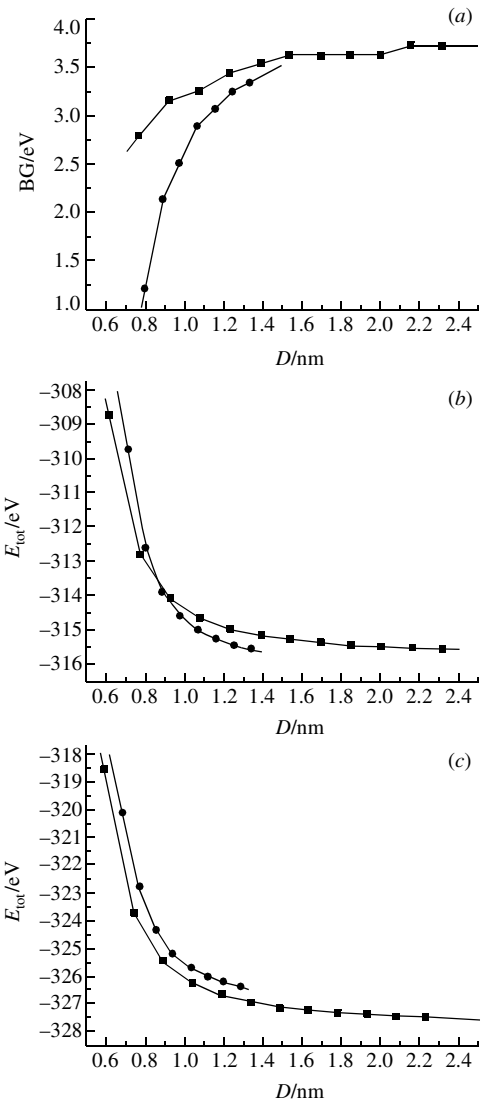

Figure 3 (*a*) Band gap size and (*b*), (*c*) total energies [per (Ti,V)O_2 unit] as functions of the diameter of Ti,V cylinders for (*b*) TiO_2 and (*c*) VO_2 tubes of armchair (n,n) (squares) and zigzag (n,0) (rings) configurations.

Figure 3(*b*) shows the calculated values of E_{tot} (per TiO_2 unit) as a function of titania nanotube diameters. The E_{tot} dependence follows ~$1/D^2$ behaviour indicating that the stability of TiO_2 tubes diminishes when D decreases. Analogous dependence of strain energy (the difference between the energies of the plane atomic layer and the corresponding nanotube characterises the chemical stability of tubular structures) is known for carbon and the majority of non-carbon tubes.[1–3,20,21]

Note that our results revealed that at small diameters ($D < 1$ nm) the most stable configurations are armchair-like configurations, whereas at large D, the zigzag-like configurations of titania nanotubes. For all VO_2 nanotubes, by contrast, armchair-like configurations are most stable [Figure 3(c)].

The covalent bonds coupling scheme in TiO_2 and VO_2 tubes can be clearly seen from the COOP values (Table 1). For all the tubes: (i) the main bonds are Ti(V)–O interactions; (ii) the occupation of Ti–Ti (V–V) bonds is by an order of magnitude smaller; and (iii) O–O interactions are absent (COOPs < 0). There is sharp anisotropy of bonds of metal and oxygen atoms belonging to inner (O^{in}) or outer (O^{out}) oxygen cylinders. The COOPs of V–V bonds are greater than those of Ti–Ti bonds.

In summary, single-walled TiO_2 and VO_2 were constructed and their electronic properties and chemical bonding parameters (COOPs) were studied using the tight-binding band theory. We found that zigzag- and armchair-like TiO_2 nanotubes are semiconducting, and the band gap trends to vanish for small nanotube diameters. The zigzag nanotubes are more likely to form at diameters $D > 1$ nm comparable with those observed experimentally.[15]

All VO_2 nanotubes are metal-like, and the most stable configurations for them are armchair-like. Ti(V)–O covalent bonds are the strongest interactions in the dioxide tubes, whereas Ti–Ti (V–V) bonds are much weaker.

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