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Electronic properties and chemical bonding of single-walled MoO_3 nanotubes

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The atomic models of cylindrical zigzag- and armchair-like MoO_3 nanotubes are proposed and their electronic structure and chemical bonding indices are studied using the tight-binding band theory.

Carbon nanotubes discovered[1] in 1991 have attracted much attention because of their unique properties.[2,3] Besides carbon, the size effect on properties has been extensively studied on a nanometre scale for various inorganic species.[4–6] In particular, attention has been focused on the preparation and characterization of quasi-one-dimensional *d*-metal oxides such as TiO_2, V_2O_5, Co_3O_4, MnO_2, WO_3-based nanotubes and nanowires having potential applications as catalysts, electrodes, intercalation hosts for making new materials *etc*. The first theoretical models of the electronic properties of 3*d*-metal oxide nanotubes (TiO_2 and V_2O_5) were proposed.[7,8]

Various nanosized structures of MoO_3 (nanobelts, nanoplatelets, nanorods, fibers[9–12] and hollow nanotubes) were synthesised.[13,14] For example, multi-walled MoO_3 nanotubes were prepared[14] using carbon nanotubes as templates. Since the above tubular composites (MoO_3/C) have a complicated structure and composition and information on atomic distributions inside the tube walls is lacking, the electronic properties of MO_3 nanotubes have not been studied up to now.

As the first attempt to understand the electronic properties of MO_3 tubes, we performed an atomic simulation of their structure. Here we report the results of quantum-chemical studies of the band structure and chemical bonding as a function of tube diameters (*D*) and possible geometry types.

Crystalline MoO_3 has[15] orthorhombic symmetry (space group *Pbnm*). It is defined by the lattice constants $a = 0.392$, $b = 1.394$ and $c = 0.366$ nm and comprised of layers, which consist of the infinite chains of corner-sharing MoO_6 units. A view of the structure of a MoO_3 monolayer is shown in Figure 1. The models of molybdenum trioxide infinite-long tubes are constructed by mapping the above two-dimensional MoO_3 monolayer in exactly the same way as for graphene by folding the sheets into seamless cylinders.[2,3] Figure 1 illustrates this procedure and the atomic models of some tubes, which represent possible spiral arrangements of MoO_6 chains. Note that MoO_3 nanotubes, as compared with graphene-like tubes, are ‘perforated’ and contain wall pores inside the rings formed by MoO_6 units.

These ‘single-walled’ tubes consist of coaxial O–Mo–O cylinders; the tube geometry was determined by the basis vectors (a_1 and a_2) of the Mo atomic sheet introducing the so-called chiral vector $c_h = na_1 + ma_2$, whose modulus equals the perimeter of the molybdenum cylinder. In this way, three groups of MoO_3 nanotubes can be obtained depending on the rolling direction c_h. In terms of carbon-like nanotubes[2,3] they may be defined as non-chiral armchair (*n*,*n*)-, zigzag (*n*,0)-, and chiral (*n*,*m*)-like nanotubes.

We calculated the electronic structures of (*n*,0) and (*n*,*n*) MoO_3 nanotubes as a function of *n* in the ranges (3,0)–(23,0) and (3,3)–(23,23), which correspond to the intervals of the ‘central’ Mo cylinder diameters (D^{Mo}) 0.470–3.605 and 0.814–6.243 nm, respectively (Table 1). The tight-binding band structure approach within the extended Hückel theory (EHT) approximation[16] was employed. The densities of electronic states (DOS), crystal orbital overlap populations (COOP) and the total band energies of nanotubes (E_{tot}) were obtained.

The calculated DOSs of all (*n*,*n*) and (*n*,0)-like MoO_3 nanotubes are similar and consistent with the DOS of crystalline molybdenum trioxide.[17–19] The results indicate that the MoO_3 nanotube valence bands are composed of hybridised O 2*p*–Mo 4*d* states; however, the main contributions to the occupied bands come from the O 2*p* states. The lower near-Fermi part of the conduction band is formed predominantly by Mo 4*d* states. The tube geometry and diameter affect most distinctly the band gap width (BG), see Figure 2. For the nanotubes with a maximum diameter, the BG values are ~4.0 [(23,0)nanotube] and ~3.8 eV [(23,23)nanotube]. While in the EHT the BG is expected to be overestimated, our results are in reasonable agreement with the calculated and observed data for the insulating MoO_3 crystal.[17–19] The BG size decreases with decreasing nanotube diameter, whereas the BG values for zigzag-like nanotubes are still higher than those for the armchair-like nanotubes.

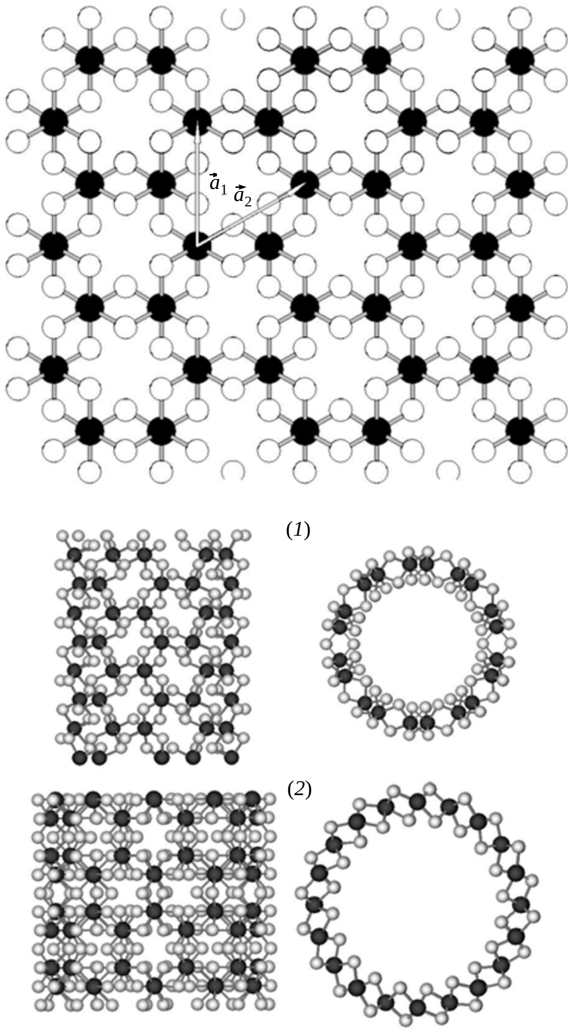

Figure 1 The structures of molybdenum trioxide monolayer ($\vec{a}_1$ and $\vec{a}_2$ are the basis vectors of the Mo sheet) and (*1*),(*2*) - armchair (5,5)- and zigzag (10,0) MoO_3 nanotubes. Side views and views along the tube axis are shown.

Figure 2 shows the calculated values of E_{tot} (per MoO_3 unit) as a function of nanotube diameter. The E_{tot} dependence indicates that the stability of MoO_3 tubes diminishes abruptly when *D* decreases starting from *D* of about 1 nm. Oppositely, with an

Table 1 The diameters (D/nm) and indices of intra-atomic bonds (COOPs/e) for MoO_3 nanotubes.

Tube	Diameters[a]			COOPs[b]			
	D(O^{in})	D(O^{out})	D(Mo)	Mo–O^{in} along	Mo–O^{in} across	Mo–O^{out} along	Mo–O^{out} across
(5,0)	0.471	0.961	0.783	0.200	0.309	0.452	0.370
(10,0)	1.298	1.768	1.567	0.296	0.348	0.417	0.371
(15,0)	2.094	2.562	2.351	0.322	0.356	0.402	0.370
(20,0)	2.884	3.350	3.134	0.333	0.359	0.393	0.370
(5,5)	1.093	1.562	1.357	0.291	0.349	0.472	0.367
(10,10)	2.194	2.659	2.443	0.327	0.370	0.439	0.365
(15,15)	3.829	4.294	4.072	0.340	0.374	0.428	0.364
(20,20)	5.189	5.654	5.429	0.346	0.376	0.422	0.363

[a] D(Mo) and D(O^{in,out}) are the diameters of cylinders made of molybdenum and oxygen atoms (Figure 1). [b] Mo–O^{in} and Mo–O^{out} are the couplings of molybdenum with oxygen atoms of the ‘inner’ and ‘outer’ cylinders.

increase in D, the E_{tot} is almost constant. This differs noticeably from analogous dependences (~1/D^2) of strain energy (the difference between the energies of the plane atomic layer and the corresponding nanotube characterises the chemical stability of tubular structures) known for carbon[2,3] and non-carbon tubes of layered phases (BN, MoS_2, *etc.*[4–6]). Obviously, the reason has to do with the differences in chemical interactions in MoO_3 and the above quasi-two-dimensional materials. In these materials, the atoms within the layers are bound by strong covalent interactions; bonding between the layers is very weak and is determined by van der Waals forces, and these materials show high propensity to form curve (cylindrical) nanostructures. On the contrary, for d-metal oxides (including MoO_3), the interatomic bonds are less anisotropic, and intra- and interlayer bonds are comparable. Therefore, d-metal oxide nanotubes can be prepared[6] with the participation of different templates, including carbon nanotubes.[14] This feature is likely to explain the preferably faceted morphology of MoO_3 tubes observed in experiments.[13]

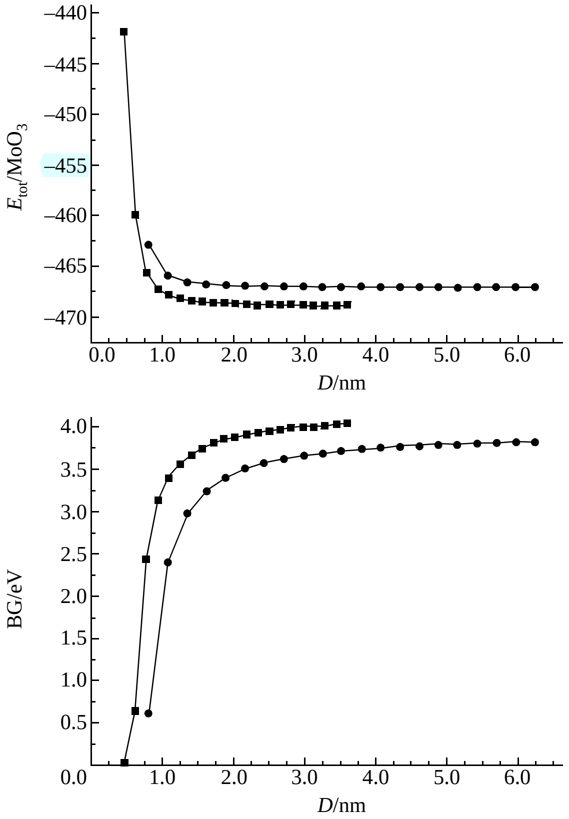

Figure 2 Band gaps and total energies (per MoO_3 unit) as functions of the diameter of molybdenum cylinders for MoO_3 tubes of (●) armchair and (■) zigzag-like configurations.

The covalent bonds coupling scheme in MoO_3 tubes can be seen from the COOP values (Table 1). For all the nanotubes, the main bonds are Mo–O, whereas the Mo–Mo and O–O covalent bonds are practically absent (COOPs ~ 0). There is a considerable anisotropy of the bonds of molybdenum and oxygen atoms (preferentially for the tubes having smaller D) belonging to inner (O^{in}) or outer (O^{out}) oxygen cylinders, which also depends on the orientation of paired Mo–O bonds along or across the tube axis.

Thus, the atomic models of cylindrical single-walled MoO_3 nanotubes 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 MoO_3 nanotubes are insulating, and the band gap trends to vanish for small nanotube diameters. The Mo–O covalent bonds were the strongest interactions in the trioxide tubes.

In conclusion, the above models of MoO_3 nanotubes with holey wall structures (large porosity) make it possible to dope these materials with various atoms, which is interesting from the point of view of intercalation processes. The role of MoO_3 nanotube layer numbers (in multi-layered tubes) and the electronic properties of actually produced[14] faceted MoO_3/carbon nanotubular composites invite further investigation.

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