Computer Modeling of Electronic Properties of Scroll-like V$_2$O$_5$-based Nanotubes

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Atomic models of quasi-one-dimensional (1D) vanadium oxide nanostructures - nanotubes of various morphology (cylinder or scroll-like) formed by rolling (010) single layers of V$_2$O$_5$ are constructed and their electronic properties are studied using the tight-binding band theory. Compared to the cylindrical \textit{zigzag} \((n,0)\) and \textit{armchair} \((n,n)\)-like nanotubes, which are uniformly semi-conducting with the bang gap of about 2.5-2.7 eV, the band gap of the scroll-like tubes trends significantly to vanish (up to about 0.1 eV) depending on the atomic configurations of the tubes and inter-wall distances.

Nanostructured transition metal oxides present a unique class of new materials with interesting electronic, chemical, and catalytic properties. Recent advances in synthesis provide appropriative methods for preparing vanadium oxide nanotubes (NT) (review \cite{1}). For instance, hollow V$_2$O$_5$ nanotubes have been produced using carbon NTs as templates \cite{2}. A wide family of vanadium oxide (VO$_x$) nanotubes has been discovered recently also as the main product of a sol-gel reaction that is followed by hydrothermal treatment \cite{3, 4}.

VO$_x$ NTs have attracted wide-spread attention due to their potential application in catalysis \cite{2}, as nanoscale materials for lithium batteries \cite{5, 6} etc. Current studies have been focused on the development of low-cost methods for fabricating VO$_x$ nanotubular materials \cite{7, 8}, and also on investigation of their properties. Recently, Ivanovskaya et al \cite{9} reported the first theoretical study of the electronic structure of cylindrical single-walled vanadium pentoxide-based NTs. It was established that both \textit{zigzag} - and \textit{armchair}-like tubes are semiconducting. Zig zag nanotubes were found to be more stable. V-O covalent bonds are the strongest interactions, whereas V-V bonds are much weaker.

However most of the VO$_x$ NTs synthesized by template-directed routes are multi-walled, the layer structure inside the tube walls is frequently disordered, and several types of defects appear. Moreover, as has been established by transmission electron microscopy (TEM) cross-sectional images, the bent VO$_x$ layers inside the tube walls are preferentially scrolls rather than concentric cylinders, and the wall structure of the tubes contains organic molecules (amine, diamine etc.) as structure-directing templates \cite{10, 11, 12}. Organic template molecules are embedded between VO$_x$ layers, and the inter-layer distances are proportional to the length of the molecules. In particular, a unique type of VO$_x$ tubes with alternating inter-layer distances is prepared by a template-assisted route \cite{12}.

In the current paper, we performed atomic simulation of the scroll-like morphology of nanotubes constructed from the V$_2$O$_5$ (010) single plane. Their electronic band properties were calculated and compared with cylindrical tubes in \textit{armchair}- and \textit{zigzag}-like forms.

\textbf{Atomic models.} We have considered the following structures as models. The orthorhombic crystal V$_2$O$_5$ (space group \textit{Pnnm}) is built up by stacking 2D-like layers along \((010)\) and is composed by distorted VO$_5$ pyramids. There are three structurally non-equivalent types of oxygen centers in V$_2$O$_5$: single coordinated vanadyl oxygen O(1), double coordinated O(2), and bridging oxygen O(3) triply coordinated to three vanadium atoms \cite{13}, see Fig. 1. The structure of the \((010)\) single-layer slab is formed by VO$_5$ units sharing edges and corners. We have analyzed the electronic properties of the following 1D nanostructures, which can be constructed from the mentioned above \((010)\) slab: (I) planar atomic strips; (II) cylindrical and (III) scroll-like NTs. The resulting NTs may be described as "fifty-wall" \((O^{in\text{-}V^{in\text{-}O^{in\text{-}V^{out\text{-}O^{out}}}}})\) tubular structures. Here the "outer" and "inner" single-atomic walls \((O^{out}, O^{in})\) are composed by vanadyl oxygen atoms, and the "central" wall \((O^c)\) is formed by O(2), O(3) atoms. For the cylindrical vanadium pentoxide tubes, three groups of structures can be constructed: non-chiral \textit{armchair} \((n,n)\), \textit{zigzag} \((n,0)\)-, and chiral \((n,m)\)-like nanotubes (for detail see \cite{3}). Our calculations were performed (using 365 atomic supercells) for \((26,0)\) and \((26,26)\) NTs with inner diameters \((D^{in})\) 2.96 and 8.71 nm, respectively, comparable to those observed experimentally (about 5-50 nm \cite{3}).

Models of V$_2$O$_5$ tubes with scroll-like morphology were constructed based on the aforementioned cylindrical \((26,0)\), \((26,26)\) NTs, which were "cut" along the tubular axis and rolled up in scrolls. The calculations were performed for infinite-long scrolls with two different inter-wall distances (minimal \(L_{min} = 0.45\) and maximal \(L_{max} = 1.50\) nm) chosen so that they are close to the inter-layer interval in the bulk V$_2$O$_5$ \((0.437\) nm \cite{14}) and experimental inter-wall distances of VO$_x$ tubes obtained with monoamine as a template \((1.5-1.7\) nm \cite{3}), respectively. The cross-sectional structure of the considered tube models is presented in Fig 1.

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The tight binding band structure method within the extended Huckel theory (EHT) approximation was employed to establish the densities of states (DOS), Fermi energies ($E_F$), and total band energies of the nanotubes ($E_{tot}$). The results obtained are given in Table 1 and in Figs. 2, 3.

**Cylindrical V$_2$O$_5$ nanotubes.** The calculated DOS of the cylindrical (26,0) and (26,26) V$_2$O$_5$ NTs (see Figs. 2, 3) are similar to all other (n,0) and (n,n)-like vanadium pentoxide tubes (6<n<13), respectively, obtained earlier. For example, for the armchair-like (26,26) tube the lowermost quasi-core band (not shown in Fig. 2) consists mainly of O2s states. The valence hybrid V3d-O2p band is fully occupied, and the DOS has three main peaks (A, B, and C, Fig. 2) corresponding to the distribution of electronic states of structurally non-equivalent atoms in the bulk V$_2$O$_5$, see. The most intensive peak B below $E_F$ is formed by 2p states of vanadyl ions O(1), whereas 2p states of other oxygen atoms O(2,3) contribute to the whole valence band with maxima near its edges (peaks A, C). According to our estimates, the band gap (BG) of the (26,26) tube is about 2.7 eV. The lower part of the conduction band (peak D) is made up predominantly of V3d states.

The differences in (26,26) and (26,0)-like NTs electronic spectra are connected with the DOS shape of the occupied V3d-O2p band and the lower energy part of the conduction band. From Fig. 3 it is seen that for the zigzag-like (26,0)NT the DOS shape is more close to that of the V$_2$O$_5$ (010) monolayer, in particular, it does not contain the lower unoccupied separate band (peak D, Fig. 2). On the whole, it may be concluded that all cylindrical tubes retain the semiconducting properties (Table 1), and their electronic spectrum roughly resembles that of the V$_2$O$_5$ planar strips considered as "precursors". The electronic properties of scroll-like tubes differ essentially.

**Scroll-like V$_2$O$_5$ nanotubes.** Fig. 2 displays the DOS of scroll-like nanotubes (SL-NT) constructed on the basis of the armchair-like (26,26) NT. The DOS of the SL-NT are seen to have the following features: (I) new states are formed in the BG region between the fully occupied valence V3d-O2p band and the unoccupied V3d-like conduction band; (II) the occupation of these states leads to an increase in $E_F$; (III) the lower unoccupied t$_{2g}$-like band (separate peak D, Fig. 2) is shifted upward the energy scale and merges with the lower edge of the conduction band; and (IV) the DOS shape of the valence band changes appreciably. The above effects are due both to the appearance of new non-bonding states in the spectrum of SL-NTs ("dangling" bonds of V, O atoms located near the inner and outer side of "sections lines" of the tubes) and partial restructuring of the energy bands of SL-NTs resulting from different radii of curvature of separate tube walls and inter-wall interactions. The latter factor most distinctly affects the DOS of the SL-NT having the minimum inter-wall distance ($L_{min}$ = 0.45 nm) and the minimum diameter of the "inner" scroll, Figs. 2, 3.

As was shown in the calculation, the BG of the scrolls are much smaller than those for cylindrical tubes of the corresponding atomic dimensions and may vary considerably up to about 0.1 eV (Table 1) depending on their structure. $E_{tot}$ values listed in Table 1 make it possible to perform semi-empirical estimations of relative stability of 1D nanostructures calculated using supercells of similar atomic dimensions (365 atoms per cell). So, for the family of nanostructures related to the (26,0) tube, the cylindrical tubular form is more stable. This can be qualitatively explained by the absence of "dangling" bonds of V, O atoms. On the contrary, infinite-long scrolls are more stable than the armchair-like (26,26) tube. It is worth noting that according to our estimations for the various infinite-long 1D nanostructures with the same size of cells are shown, that (26,26)-like scrolls are more stable, see Table 1. Therefore it may be stated that scroll-like V$_2$O$_5$ nanostructures are generally more stable than "ideal" cylindrical tubes, in accordance with recent experimental data. It is necessary to mention that we considered ideal "pure" V$_2$O$_5$-based nanostructures. Certainly, the correct description of energetic conditions of primary formation experimentally observed VO$_x$ scrolls should take into account the "stabilizing" role of organic molecules as templates.

In summary, atomic models of scroll-like V$_2$O$_5$ NTs have been constructed and their electronic properties have been investigated using the tight-binding band approach. We show that their electronic spectrum features (including the BG) depend on the scroll geometry and differ essentially from zigzag- and armchair-like cylindrical nanotubes. Semi-empirical estimations of $E_{tot}$ suggest that infinite-long scrolls should be more stable in comparison with ideal cylindrical nanostructures.

Future computer simulations of VO$_x$ NTs should be aimed at elaborating adequate theoretical models of actually produced VO$_x$ nanotubular composites containing various organic template molecules, and also at studying the effect of different tube wall defects on the electronic properties of these materials.

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TABLE I: Total energies ($E_{\text{tot}}$, per V$_2$O$_5$ unit, eV), Fermi energies ($E_F$, eV), and band gaps (BG, eV) of infinite-long strips, single-walled cylindrical (26,0), (26,26) vanadium pentoxide nanotubes and scrolls constructed from the corresponding NTs with two different inter-wall distances ($L_{\text{max}} = 1.50$ and $L_{\text{min}} = 0.45$ nm).

| System                        | $E_{\text{tot}}/V_2O_5$ | $E_F$  | BG      |
|-------------------------------|-------------------------|--------|---------|
| V$_2$O$_5$ monolayer          | 787.896                 | 14.30  | 2.70    |
| V$_2$O$_5$ (26,0) strip       | 787.812                 | 14.40  | 2.70    |
| V$_2$O$_5$ (26,0) scroll ($L_{\text{max}} = 1.50$ nm) | 787.420                 | 11.49  | 0.11    |
| V$_2$O$_5$ (26,0) scroll ($L_{\text{min}} = 0.45$ nm) | 787.402                 | 12.97  | 1.60    |
| V$_2$O$_5$ (26,0) tube        | 787.896                 | 14.30  | 2.70    |
| V$_2$O$_5$ (26,26) strip      | 787.244                 | 14.47  | 2.76    |
| V$_2$O$_5$ (26,26) scroll ($L_{\text{max}} = 1.50$ nm) | 788.428                 | 12.56  | 1.76    |
| V$_2$O$_5$ (26,26) scroll ($L_{\text{min}} = 0.45$ nm) | 787.450                 | 12.40  | 1.89    |
| V$_2$O$_5$ (26,26) tube       | 787.228                 | 14.37  | 2.71    |

FIG. 1: Cross-sectional images of the structures of 1 - the (010) single layer strip of orthorhombic V$_2$O$_5$ (exhibited is a fragment of the strip, where positions of non-equivalent oxygen atoms O(1)-O(3) are shown); 2 - the cylindrical armchair (26,26)-tube (exhibited is a fragment of the NT) and 3, 4 - scrolls constructed from the armchair (26,26)-like V$_2$O$_5$ tube with two different inter-wall distances (3 - $L_{\text{max}} = 1.50$ and 4 - $L_{\text{min}} = 0.45$ nm).
FIG. 2: Total DOS of the infinite-long 1 - cylindrical armchair (26,26)-tube and 2, 3 - scrolls constructed from the armchair (26,26)-like V₂O₅ tube with two different inter-wall distances (2 - L_max = 1.50 and 3 - L_min = 0.45 nm).
FIG. 3: Total DOS of the infinite-long 1 - cylindrical zigzag (26,0)-tube and 2 - the corresponding planar strip; 3, 4 - scrolls constructed from the zigzag (26,0)-like V_{2}O_{5} tube with two different inter-wall distances (3 - $L_{max} = 1.50$ and 4 - $L_{min} = 0.45$ nm).