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Stability and electronic properties of single-walled γ-AlO(OH) nanotubes

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Atomistic models for cylindrical hydroxyalumina AlO(OH) nanotubes are proposed and their stability and electronic properties are discussed using the density functional tight-binding theory (DFTB) method.

In addition to carbon nanotubes, many similar tubular nanostructures based on layered inorganic compounds such as BN, metal chalcogenides and halides are known.[1,2] Progress in the synthesis of nanotubular compounds commemorates in the synthesis of oxide nanotubes.[3] These nanostructures are of considerable interest due to the perspectives of their application in technology because of unique combination of the functionality caused by sizes and topology, the industrially important properties of oxides and comparatively low production costs.[4] The basic regularities of stability and electronic properties were revealed in the oxide nanotubes with different structures: SiO_2,[5] V_2O_5,[6] VO_2,[7] TiO_2,[8] MoO_3,[9] MgO[10] and Al_2O_3.[11]

Recently, the nanotubes of the layered form of hydroxyalumina AlO(OH) (boehmite) were also produced.[12,13] The importance of their synthesis lays in a possibility to transform nanotubular AlO(OH) into other oxide nanotubes (nonlayered Al_2O_3 allotropes) without the use of templates and surfactants. This method allows one to avoid the introduction of undesirable impurities into Al_2O_3 in contrast to all other methods of nanotubular Al_2O_3 synthesis. AlO(OH) can be used as a catalyst, a catalyst support and an adsorbent.[14] The increase of the specific surface area and the surface curvature by the nanostructuring of AlO(OH) will considerably change the physico-chemical properties.

Here, we present the atomistic models of the AlO(OH) nanotubes and report the results of quantum-chemical investigations of the stability and electronic properties of hydroxide nanotubes.

Hydroxyalumina AlOOH exists in two stable crystalline modifications (α and γ). The three-dimensional structure of the α-modification (diaspore) is composed by double chains of AlO_6 octahedra. At heating α-AlO(OH) will be transformed directly to α-Al_2O_3. The synthesised AlO(OH) nanotubes have the atomic structure of the layered γ-AlO(OH) modification, which is close to lepidocrocite,[15] and have been transformed by heating to γ-Al_2O_3.[12]

The atomistic models of the γ-AlO(OH) nanotubes can be constructed by rolling a monolayer into cylinders. Analogously to the TiO_2 lepidocrocite nanotubes,[8] the tubes of γ-AlO(OH)

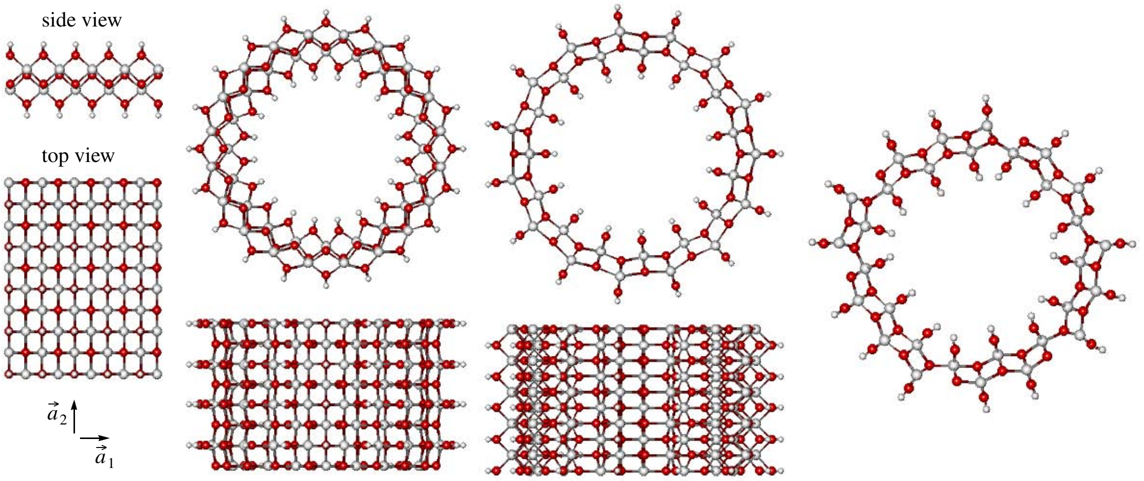

Figure 1 A sheet (**1**) of the layered γ-AlO(OH) phase and based on it (20, 0) and (0, 15) nanotubes (**2**, **3a**). Cylindrical shape of (0, 15) nanotube and other (0, *n*) nanotubes in general is not stable during geometry optimization and transforms into a bundle of stripes (**3b**).

can be described in terms of primitive 2D rectangular lattice vectors $\vec{a}_1$ and $\vec{a}_2$. Therefore, both chiral indexes *n* and *m* may become zero – (0, *n*), (*n*, 0), where $\vec{a}_1$ and $\vec{a}_2$ are parallel to the tube axis, respectively. The structure of a γ-AlO(OH) monolayer and nanotubes based on it are shown in Figure 1. Like an AlO(OH) monolayer, the walls of these nanotubes can be considered composed of six atomic layers: two H and two O layers of hydroxyl groups and two layers of Al-O skeleton. These nanotubes have the walls thickest among others considered oxide nanotubes.

Our calculations were performed for the (0, *n*) and (*n*, 0) AlO(OH) single-walled nanotubes as a function of *n* varying in the range 10–40. The radii of these nanotubes are up to ~19 Å, *i.e.*, close to the radii of experimentally observed AlO(OH) nanotubes.[12,13] For the calculations the density-functional-based tight-binding (DFTB) method with full geometry optimization was employed.[16,17] This method gives reliable data for structural, energetic and electronic characteristics of $Al(OH)_3$ and Al_2O_3, consistent with experimental and theoretical *ab initio* results.[18]

The results of the geometry optimization show that the final topologies of AlO(OH) cylindrical nanotubes can essentially change depending on the type of the tube. The initial structures of the (0, *n*) nanotubes were found to be unstable and have disintegrated into bundles of planar nanostripes after geometry optimization (Figure 1, structure **3**). The small (*n*, 0) nanotubes are also unstable up to *n* = 17. This behaviour can be explained taking into account the large thickness of an AlO(OH) layer and the corresponding high strain energy E_{str} of the nanotubes (the energy of a nanotube relative to the energy of an infinite monolayer). The strain energies for all stable (*n*, 0) AlO(OH) tubes, whose morphology has been kept tubular after geometry optimization, are shown in Figure 2. The values of E_{str} can be approximated by a $1/R^2$ curve, as for the most nanotubes of other compounds. However, as one could see, these values are very high, as compared to E_{str} of other nanotubes. For instance, at R = 10 Å, E_{str} of carbon tubes is close to 0.01 eV per atom;[19] for MoS_2 tubes based on hexagonal three atomic layer S–Mo–S E_{str} is ~0.15 eV per atom;[20] and for AlO(OH) tubes, it is ~0.22 eV per atom. Evidently, the (0, *n*) and small (*n*, 0) AlO(OH) nanotubes have so high values of strain energies, that in spite of appearance of dangling chemical bonds the formation of bundles of nanostripes is more preferable in this case.

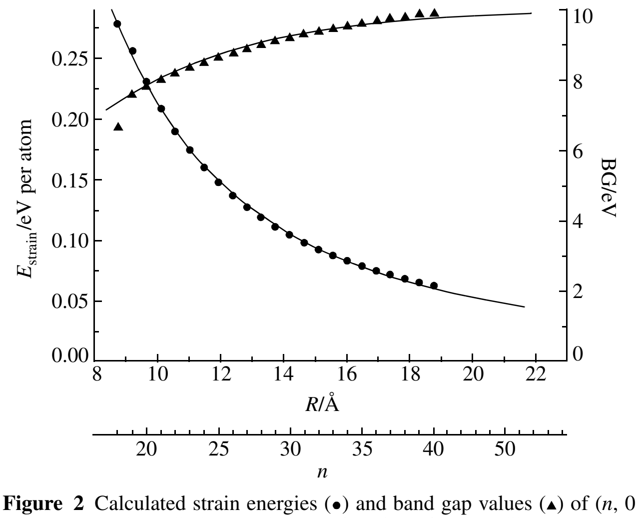

Figure 2 Calculated strain energies (●) and band gap values (▲) of (*n*, 0) AlO(OH) single-walled nanotubes as a function of their radii *R*.

The chemical bonding in AlO(OH) nanostructures, as well as in bulk AlO(OH), has a mixed covalent-ionic character. Charge transfer from aluminium (Q ≈ +0.7e) to oxygen (Q ≈ –0.4e) in the bulk material changes for nanotubular AlO(OH) (Table 1). It is remarkable that charge transfer between O and H in OH groups does not depend so much on the radius of the tube as charge transfer between Al and O atoms of OH groups. One can see that, with decreasing radii, the absolute charge values of Al and O atoms on the outer side of AlO(OH) nanotubes are increased by 25–30%. It means that with decreasing radii the Al–OH bonds of the outer walls are more ionic and their basicity

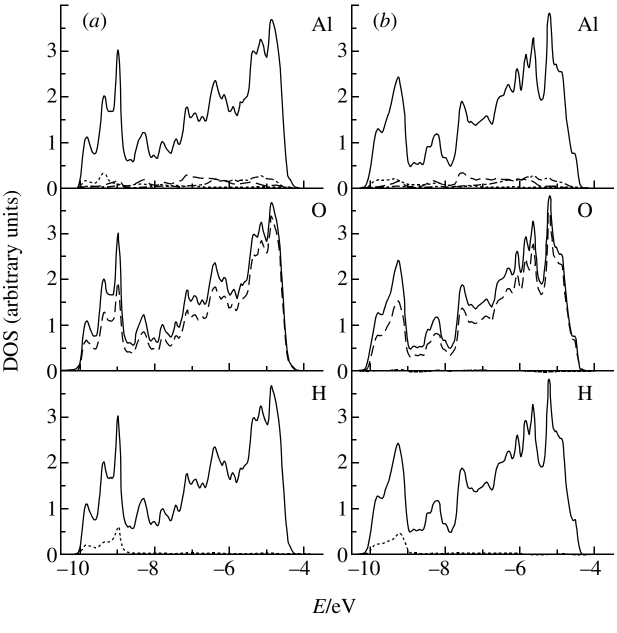

Figure 3 Total (solid line) and partial densities of valence states for (*a*) (25, 0) and (*b*) (0, 25) nanotubes after geometry optimization: *s* states (dot lines), *p* states (dash lines), *d* states (dash-dot lines) are shown. All energies are given relative to the Fermi level.

Table 1 Mulliken charges of outer (out) and inner (in) walls of AlO(OH) nanotubes.

Nanotube		Charge/e					
Index	*R*/Å	H^{in}	H^{out}	O^{in}	O^{out}	Al^{in}	Al^{out}
(18, 0)	8.74	+0.30	+0.29	–0.43	–0.48	+0.62	+0.92
(20, 0)	9.66	+0.30	+0.29	–0.43	–0.46	+0.65	+0.76
(30, 0)	14.20	+0.30	+0.29	–0.40	–0.41	+0.64	+0.70
(40, 0)	18.78	+0.30	+0.30	–0.39	–0.40	+0.68	+0.64
monolayer	—	+0.30	+0.30	–0.39	–0.39	+0.67	+0.67

could be higher, which can change the AlO(OH) catalytic activity. In the case of Al and O atoms of the inner walls, the atomic charges change insignificantly, and in the case of Al atoms they are even smaller than in a monolayer.

All of the AlO(OH) systems considered here are insulators with a wide band gap. Independent from the specific topology of the optimized (0, *n*) and (*n*, 0) nanotubes their band gaps approach the band gap of the bulk material (~10 eV) (Figure 2). The calculated densities of states (DOS) of nanostructures are shown in Figure 3. The differences between the band structures of stable (*n*, 0) nanotubes and final bundle-like structures of (0, *n*) nanotubes are insignificant. The valence band of both types of nanostructures is composed mainly by 2*p* O states, the lower part of conduction band is formed by 3*p* Al and 3*d* Al states. The 2*p* O and 1*s* H states responsible for the O–H bonding are 8–9 eV below the Fermi level. This picture clearly expresses the nature of chemical bonding in hydroxyalumina: mainly ionic character of Al–O (and Al–OH) and covalent character of O–H bonds.

In summary, the models of γ-AlO(OH) single-walled nanotubes were constructed and their stability and electronic properties were studied using a DFTB approach. We discovered the stability of only one type of nanotubular AlO(OH) – (*n*, 0) nanotubes with $R > 8.5$ Å, whereas (0, *n*) and thinner (*n*, 0) nanotubes decompose into the bundles of nanostripes. Our calculations demonstrate that nanostructured AlO(OH) is an insulator independent of diameter and type. Based on the comparison of atomic charges of bulk and nanotubular forms of γ-AlO(OH) an increase of the basicity of hydroxyl groups at the outer walls by decreasing the nanotube radii is predicted.

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References

1 R. Tenne, *Chem. Eur. J.*, 2002, **8**, 5296.
2 C. N. R. Rao and M. Nath, *Dalton Trans.*, 2003, 1.
3 G. R. Patzke, F. Krumeich and R. Nesper, *Angew. Chem., Int. Ed. Engl.*, 2002, **41**, 2447.
4 G. S. Zakharova, V. L. Volkov, V. V. Ivanovskaya and A. L. Ivanovskii, *Usp. Khim.*, 2005, **74**, 651 (*Russ. Chem. Rev.*, 2005, **74**, 587).
5 A. L. Chernozatonskii, P. B. Sorokin and A. S. Fedorov, *Phys. Solid State*, 2006, **48**, 1903.
6 A. N. Enyashin, V. V. Ivanovskaya, Yu. N. Makurin and A. L. Ivanovskii, *Phys. Lett. A*, 2004, **326**, 152.
7 V. V. Ivanovskaya, A. N. Enyashin and A. L. Ivanovskii, *Mendeleev Commun.*, 2003, 5.
8 A. N. Enyashin and G. Seifert, *Phys. Stat. Sol. (b)*, 2005, **242**, 1361.
9 A. N. Enyashin, V. V. Ivanovskaya and A. L. Ivanovskii, *Mendeleev Commun.*, 2004, 94.
10 A. N. Enyashin, G. Seifert and A. L. Ivanovskii, *Phys. Solid State*, 2006, **48**, 751.
11 M. Linnolahti and T. A. Pakkanen, *Inorg. Chem.*, 2004, **43**, 1184.
12 D. Kuang, Y. Fang, H. Liu, C. Frommen and D. Fenske, *J. Mater. Chem.*, 2003, **13**, 660.
13 H. Hou, Y. Xie, Q. Yang, Q. Guo and C. Tan, *Nanotechnology*, 2005, **16**, 741.
14 P. Raybaud, M. Digne, R. Iftimie, W. Wellens, P. Euzen and H. Toulhoat, *J. Catal.*, 2001, **201**, 236.
15 P. P. Reichertz and W. J. Yost, *J. Chem. Phys.*, 1946, **14**, 495.
16 D. Porezag, T. Frauenheim, T. Köhler, G. Seifert and R. Kashner, *Phys. Rev. B*, 1995, **51**, 12947.
17 G. Seifert, D. Porezag and T. Frauenheim, *Int. J. Quantum Chem.*, 1996, **58**, 185.
18 J. Frenzel, A. F. Oliveira, H. A. Duarte, T. Heine and G. Seifert, *Z. Anorg. Allg. Chem.*, 2005, **631**, 1267.
19 D. H. Robertson, D. W. Brenner and J. W. Mintmire, *Phys. Rev. B*, 1992, **45**, 12592.
20 G. Seifert, H. Terrones, M. Terrones, G. Jungnickel and T. Frauenheim, *Phys. Rev. Lett.*, 2000, **85**, 146.

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