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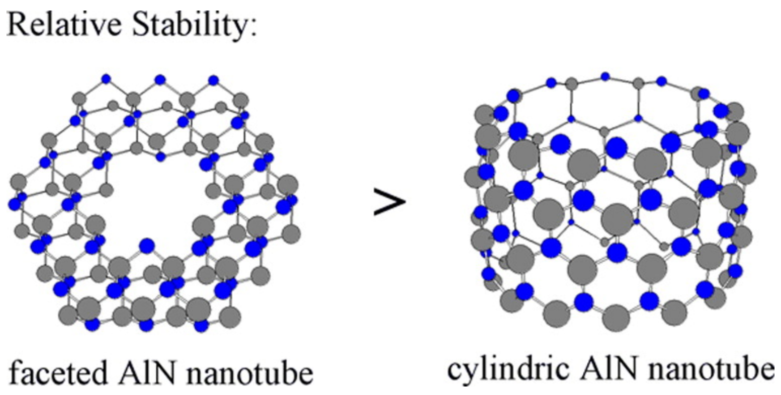

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AlN Nanotube: Round or Faceted?

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The unusual properties and wide potential applications of carbon nanotubes (CNTs), resulting from their unique tubular nanostructures, have been stimulating extensive explorations of nanotubes of various materials for over a decade.[1] For quite a long time, the nanotube formation is generally limited in layered materials,[2] which is easy to understand when regarding nanotube as the cylindric form rolled from the corresponding sheet, analogous to the case for CNTs.[3] The weak van der Waals forces between the molecular layers and the strong intralayer bonds are suggested to be necessary for the formation of these nanotubes.[2a] As for the nonlayered materials with strong interlayer interactions, template confinement is needed to obtain the corresponding nanotubes.[4] Very recently, the hexagonal AlN nanotubes with nonlayered structure have been synthesized without template.[5] We found that the AlN nanotubes are different from the nanotubes of layered materials and show the faceted geometry with hexagonal cross sections. Actually, similar features also exist in the few recently reported nanotubes of other nonlayered materials using template-free approaches,[6] which could be inferred from the electronic micrographs there, although such a geometrical specialty is often ignored in the literature.[6d,e] These new experimental progresses have extended the nanotubes from layered materials to nonlayered materials, and the faceted instead of cylindric geometry seems to be the characteristic feature of the latter.[7] Along with the experimental efforts, theoretical studies have also been devoted to the nanotubes of nonlayered materials such as GaN and AlN.[8] By analogy with CNTs, the theoretical models are built therein, which are intuitively different from the current experimental results. The theoretical study of faceted nanotubes still remains an open challenge, which is obviously urged by the experimental progresses for conceptional understanding of such structures. In this contribution, a theoretical study is performed for AlN nanotubes. In comparison with the cylindric model, a faceted model is proposed and verified as an energetically more favorable nanostructure. The correlation between the geometrical symmetry of the faceted AlN nanotube and the crystal symmetry of the corresponding bulk AlN is established, which should also be applicable to the cases for other nonlayered materials.

Carbon nanotubes have been closely associated with certain fullerenes.[9] Therefore, the investigation of AlN fullerenes is also expected to provide some useful information. Strain energy (SE) calculation has been performed for cagelike $(AlN)_n$ clusters as analogies of $(BN)_n$ fullerenes ($12 \leq n \leq 20$) at the Hartree−Fock (HF)/6-31G* level using the Gaussian98 package.[10] As shown in Figure 1, all $(AlN)_n$ clusters possess higher SE, indicating the relative instability of such structures. The geometry investigation shows that the SE difference for $(AlN)_n$ and $(BN)_n$ might result from the Al−Al bonding as shown in Figure 1, which might not be actually chemical bonding but arise from geometric factors as suggested by Timoshkin et al.[11] However, there could be another possibility. Within the $(AlN)_n$ clusters, N atoms possess the lone pair electrons while Al atoms offer the vacant d-type polarization functions. The electrons could hence be cyclic-delocalized to form the δ-bonding between Al atoms, which is similar to the case in disilaoxirane with ring structure.[12] The formation of these bonds eventually brings "Al−N−Al" triangles into the square−hexagon system, which might add to the strain energy. Instability of cagelike $(AlN)_n$ clusters hints that an AlN nanotube with similar structure of BN nanotube might also be energetically unfavorable based on the nanotube−fullerene correspondence.

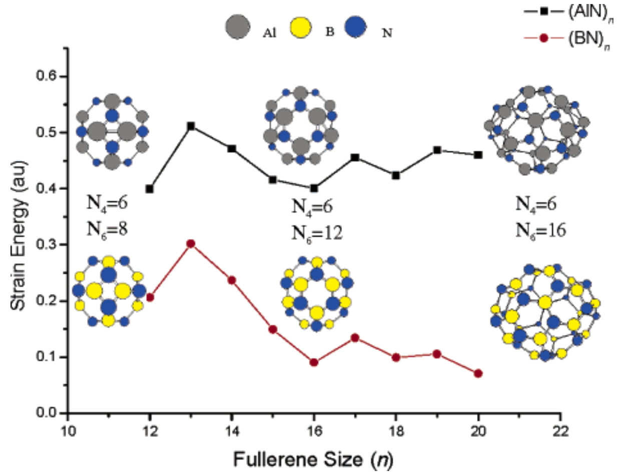

Figure 1. SE comparison between $(AlN)_n$ and $(BN)_n$ ($12 \leq n \leq 20$). Clusters with $n = 12$, 16, and 20 for $(AlN)_n$ and $(BN)_n$ are shown in parallel to show the geometry difference. Both $(AlN)_n$ and $(BN)_n$ have the identical numbers of squares (N_4) and hexagons (N_6) for the same size, as cited in the figure between two polyhedra.

As for the one-dimensional AlN system, three models as segments from the (1) faceted nanotube, (2) nanowire, and (3) single-walled nanotube are taken into account here. Each model possesses 48 Al and 48 N atoms, respectively. Hydrogen atoms are used to saturate all the dangling bonds to satisfy the four-coordinate configuration, which is proved to be the most favorable coordination state.[11] Optimized geometries at HF/6-31G* level are shown in Figure 2. Detailed parameters for the tetrahedral coordination of Al−N in different models are shown in Figure 3a−c, using mean values, with those of bulk AlN in Figure 3d for comparison. These models are also optimized using periodic boundary conditions (PBC) to test the boundary effects in the segment models.

Actually, both segment models and those with PBC converge to similar geometries. To simplify, we discuss segment models. Model 1 is geometrically similar to the experimentally obtained faceted nanotubular structure. It could be understood as a nanocrystal with a hollow interior, hence preserving the crystal symmetry. It also explains the single-crystal property of the AlN nanotubes[5] while excluding other possibilities, like twin joints for two adjacent facets.[7]

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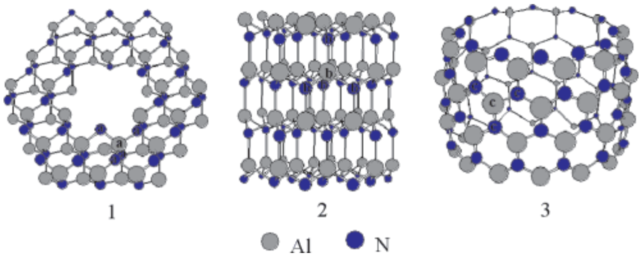

Figure 2. Optimized geometries of AlN (1) faceted nanotube, (2) nanowire, and (3) single-walled nanotube. Atoms marked with a, b, and c are chosen as representative atoms. H atoms are hidden for the sake of clarity.

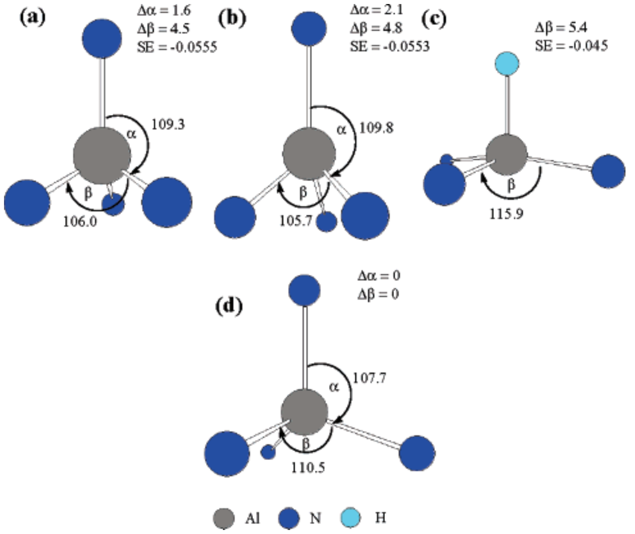

Figure 3. Tetrahedral coordination of Al−N (a−c) marked in Figure 2 and (d) in the bulk AlN. SE (au) and bond angle variations (deg) are listed on the upright to each model. $\Delta\alpha = |\alpha_{\text{modle}} - \alpha_{\text{bulk}}|$, $\Delta\beta = |\beta_{\text{model}} - \beta_{\text{bulk}}|$. Average SE calculated from the total SE divided by the number of Al−N bonds in each model.

As seen in Figure 3, the bonding configuration in bulk AlN, which could be taken as the most stable one, is altered in each nanostructure due to the inevitable strain. Hence, the distortion extent of the bonding configuration might reflect the relative value of the strain energy. Here we use bond angle variation, $\Delta\alpha$ and $\Delta\beta$, to describe the distortion, which is defined as the bond angle difference between the nanostructure and the bulk material. The total SE is averaged to each Al−N bond to describe the relative stability. For models 1 and 2, larger α and smaller β indicate a tetrahedron configuration sharper than that in the bulk material, which could be understood as radial compression due to the strain. As for model 3, the largest $\Delta\beta$ of 5.4° might correlate to the largest strain energy for this model, as is proved by the SE calculation.

As expected, the relative order of SE for the three models does agree well with that of the bond angle variations. Model 1 possesses the lowest SE of −0.0555 au per bond, and model 2 comes in second with a comparable average SE of −0.0553 au. The negligible disadvantage for model 2 might come from the smaller outer diameter compared to that of model 1. With the relatively easy synthesis of AlN nanowires, the appearance of the faceted nanotubes is also rather acceptable. As for model 3, the highest value of −0.045 au makes it energetically unfavorable. Actually, the cylindric AlN nanotube has not been observed to date.

Following the discussion above, one might expect that the most stable morphology of specific nanostructure would give the smallest bond angle variation. In crystallography, bond angle is a crucial parameter to determine the crystal symmetry. Therefore, similar bond angles should produce similar symmetry for both nanostructure and corresponding bulk material, which is the case for AlN system. In fact, such similarity could also be inferred from other faceted nanotubes synthesized without template,[8] for example, nanotubes with rectangular cross sections for cubic GaN or MgO and hexagonal cross sections for trigonal Se or Te. This could be helpful to predict the morphologies of the nanotubes from nonlayered materials.

In summary, theoretical studies on one-dimensional AlN nanostructures have been performed. For the first time, a faceted model is proposed and verified to be energetically more favorable in comparison with the normally used cylindric model. Close correlation has been established that the nanotube structure should possess similar symmetry to that of the corresponding bulk crystal. This is important to fully understand the geometrical specialty of AlN nanotubes and the few other recently reported faceted nanotubes, and could be used to predict the morphology for the increasing nanotubes from nonlayered materials.

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Supporting Information Available: Validation of basis sets and methods, optimized geometry of all $(\text{AlN})_n$ and $(\text{BN})_n$ clusters, modeling process, optimized segment models with H atoms shown, the optimized AlN nanostructures with PBC, the influence of saturated atoms, strain energy calculation, and full author list for ref 10. This material is available free of charge via the Internet at http://pubs.acs.org.

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