J|A|C|S
COMMUNICATIONS

Published on Web 02/15/2007

Energy Optimum Chiralities of Multiwalled Carbon Nanotubes

Wanlin Guo* and Yufeng Guo

Institute of Nano Science, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, China

Received August 25, 2006; E-mail: wlguo@nuaa.edu.cn

The exceptional physical, mechanical, and biochemical properties of carbon nanotubes (CNTs) are strongly dependent on the tube chirality. Although carbon nanotubes have so far been synthesized by various methods, the chiralities of CNTs including single- and multiwalled tubes are generally found in random distributions.[1] Recently, some reports showed that multiwalled CNTs (MWNTs) obtained by different synthesized methods have identical or nearly identical chiralities when the growth temperatures are relatively low.[2−7] However, the growth mechanism and synthesis conditions for achieving such monochirality have not been understood until now.[7] Chirality control of CNTs is still the most challenging problem in nanotube research.

In this communication, we report a study of the energetically favored chiral configurations of two neighboring tubes in a MWNT by extensive calculations for the energy differences in different MWNT models. Nearly identical chiralities give the lowest energy for MWNTs with a large inner diameter. For small inner tubes, the optimum chiral angle for each outer layer deviates to a smaller value depending on tube diameter, with the combination of zigzag to zigzag tubes always optimum. The relatively small energy difference (less than about 30 K in equivalent temperature between the optimum and arbitrary chiralities) suggests that low temperature control is necessary for achieving the optimum chiralities. The energy difference could also play an important role in the layer by layer growth process of a MWNT.[4]

Recently, a chirality dependent potential was specially parametrized for layered carbon structures by Kolmogorov and Crespi (the K−C potential) which can predict the chirality dependent interlayer interaction of MWNTs more effectively and precisely than other potentials[4,8−10] (see Supporting Information for details). In this work, we use a double-wall CNT (DWNT) model for simplicity, to model the interaction in MWNTs.[11] The DWNT model is appropriate because the interaction between two nonadjacent layers is at least 50 times lower than those between two neighboring layers.

Systematical statics calculations of energy are conducted for a DWNT of different chiralities based on the revised K−C potential.[8,10] It is found that for a selected inner tube (n, m) with chiral angle θ_i, except one or a few specific outer tubes with significantly lower interlayer energy, all other outer tubes have the interlayer energy above a certain minimum, or a threshold energy E_t, as shown in Figure 1. When the diameter d of the inner tube is small (less than about 3 nm; see Figure 1A), only one outer tube with the index ($n + 9$, m) has the lowest energy. For larger tubes of diameter in the range of 3 nm $< d <$ 10 nm, the outer tube of ($n + 10$, m) may replace ($n + 9$, m) as the optimum configuration. However, when the inner tube is large (i.e., with a diameter larger than 12 nm), outer tubes of (n, $m + \Delta m$) with $\Delta m \geq 10$ can also have the lowest energy (see Figure 1B).

According to the lowest interlayer energy, the best matched outer/inner helical angle ratios, θ_o/θ_i, for all inner tubes with $\theta_i > 2.1°$ included in the calculation are drawn in Figure 2A for a large range

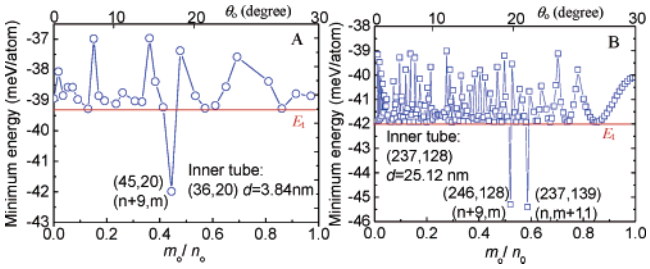

Figure 1. The minimum interlayer potential energy for all of the possible matched outer tubes. (A) For inner tube (36, 20), except for the outer tube ($n + 9$, m), all of the remaining matched tubes have energy higher than the threshold value $E_t = -39.3$ meV/atom. (B) For a larger inner tube (237, 128), E_t is lower and there are two outer tubes ($n + 9$, m) and (n, $m + 11$) having exceptional low energy.

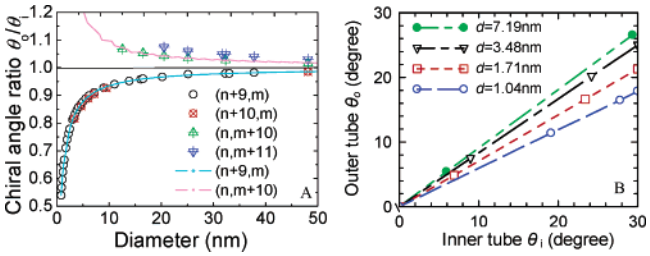

Figure 2. (A) The chiral angle ratio of the optimum matched outer tubes to the selected inner tubes (n, m) with different tube diameters and chiral angles. The marks represent the energy optimum matching pairs. The curves for the ideal ($n + 9$, m) and (n, $m + 10$) outer tubes are drawn as guiding lines. (B) The variation of the optimum chiral angle of the outer tube with that of the inner tube for given diameters ranging from 1 to 7 nm.

of diameters (d = 0.7−48 nm) and m/n ratios (m/n = 0−1). The figure clearly shows that ($n + 9$, m) or ($n + 10$, m) is always the optimum matched outer tube for $d <$ 10 nm, and the chiral angle ratio θ_o/θ_i decreases with decreasing d. For a given diameter of less than 10 nm, θ_o increases linearly with θ_i from zigzag to armchair, and the ratio θ_o/θ_i is constant (see Figure 2B). It is interesting to note that the zigzag to zigzag matching pair is always energetically favored independent of d.

For large tubes with $d >$ 12 nm, (n, $m + \Delta m$) with $\Delta m \geq 10$ in addition to the ($n + 9$, m) or ($n + 10$, m) configuration can also have exceptional low energy, as shown in Figure 1B. This is also included in Figure 2A. The $n + 9$ and $n + 10$ tubes have similar angle ratios, which smoothly and monotonically approach the unity with increasing d. In comparison, the (n, $m + 10$) and (n, $m + 11$) curves are less smooth but also show a general trend of approaching unity with increasing d. When $d >$ 20 nm, $n + 9$ and $m + 10$ lead to a chiral angle ratio within 4% of unity. Therefore, nearly identical chiralities can be expected for tubes with large diameters based on energy. This can be shown more clearly by the first and second optimum matched inner/outer tubes in Figure 3A for the tubes with $d >$ 20 nm, in which the difference of chiralities is within 1.8°. In summary, nearly identical chiralities for tubes of zigzag to armchair

10.1021/ja0662063 CCC: $37.00

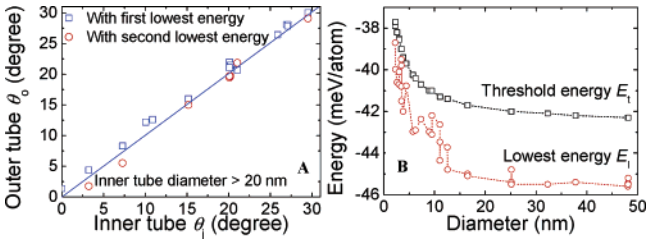

Figure 3. (A) For tubes with large diameter (d > 20 nm), the first and second lowest energy matched tube pairs with an energy increment of <0.5 meV/atom are all plotted in the figure. All the energy optimum chiral angles are within 1.8° of the identical chiral angle. (B) The variation of the lowest energy E_l and the threshold energy E_t with tube diameter.

are favored for large DWNTs. The chirality of the outer tube depends on the chirality of the inner tube.

The energy gap between the lowest energy of the optimum tube pairs and the threshold energy, E_t, is shown in Figure 3B as a function of the tube diameter. At a given diameter, the chiral angle also influences the energy gap. When tube diameter is larger than about 12 nm, the effect of chiral angle is small and the energy gap is about 3.5 meV/atom (about 30 K in equivalent temperature). However, when the tube diameter is less than about 10 nm, the gap becomes much smaller and sensitive to the chiral angle. The temperature difference in this case changes from 20 K to very low value of several kelvin. On the other hand, the threshold energy increases remarkably with decreasing diameter when the tube diameter is smaller than about 10 nm. The higher threshold energy and smaller energy gap for a small tube means difficulties in synthesizing such small nanotubes with the optimum chiralities, but it will be much more tolerant to control the chiralities of large tubes with low temperature growth techniques. When the diameter is large enough, the threshold value is approaching the experimental value of interlayer energy for planar graphite (−42.6 meV/atom; see Supporting Information).

Experimentally, MWNTs of similar chirality have been reported. The most dramatic is the carbon tubular cones of nearly identical chirality obtained by plasma-assisted chemical vapor deposition (CVD) at the substrate temperature of 600 °C (the local temperature of the sample holder on the graphite substrate was about 870 °C),[3,4] where the inner most seed tube has diameter about 2 nm. Layer by layer growth mechanism was proposed for these cones. In another recent experiment with careful low temperature study,[7] ∼80% of as-prepared MWNTs at the substrate temperature of 600 °C were found to be of nearly identical chiralities. The chiral angle ranges from zigzag to armchair. At slightly higher temperature (>650 °C), however, the synthesis usually resulted in multichiral MWNTs. The reported monochiral MWNTs are synthesized with a temperature lower than 900 °C (see refs 2−7). Above 900 °C, the chiralities of MWNTs are generally reported as randomly distributed.[1,7] DWNTs of arbitrary chiralities and small diameter (1.4−5.3 nm) grown by CVD at 700−900 °C were also reported recently,[12] where the growth temperature for a mixture of SWNTs and DWNTs was ∼700 °C, and the growth of DWNTs becomes dominated over 800 °C.

These experimental results demonstrate that the intertube interaction energy, which is considered here, plays a significant role at low growth temperature. Although the growth temperature for MWNTs is ∼600 °C or above, the experiments show that the products are very sensitive to a small temperature difference (less than 100 K).[7,12] In comparison, the energy difference of ∼30 K for the optimum chiralities can be dominant in the case of low temperature growth. Of course, the dominance of the optimum energy difference should be understood in view of probability.

In conclusion, the energetically optimum chiral configurations exist in MWNTs, as shown by systematical analyses of the chirality dependent intertube interaction energy. For large tubes with a diameter >12 nm, nearly identical chiralities have the lowest energy and therefore are the energy optimum, while arbitrary chiralities have energy above a threshold value about 3.5 meV/atom (with equivalent temperature ∼30 K) higher. For small nanotubes with a diameter <10 nm, the energy optimum chiral angle for each outer layer deviates to a value smaller than that of the inner one, depending on the tube diameter, but with a much smaller energy gap between the lowest and the threshold energies. Independent of tube size, the combination of zigzag to zigzag tubes is always energy favored. It is proposed that low growth temperature is a necessary requirement for synthesizing MWNTs with the energy optimum chiralities. The diversified observations in all available experiments are in agreement with the present energy calculations.

Acknowledgment. The work is supported by National NSF (No. 10372044), Jiangsu Province NSF, the PCSIRT, and the Cultivation Fund of the Key Scientific and Technical Innovation Project of the Ministry of Education of China (No. 705021). We wish to thank Professor Enge Wang for helpful discussions since 2004, and Professor J.M. Zuo for helpful discussions as well as providing their unpublished experimental data.

Supporting Information Available: Calculation method and the details of energy calculations of the DWNTs. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Liu, M.; Cowley, J. M. *Carbon* **1994**, *32*, 393. (b) Ge, M.; Sattler, K. *Science* **1993**, *260*, 515. (c) Feng, L.; Chou, S. G.; Ren, W.; Gardecki, J. A.; Swan, A. K.; Ünlü, M. S.; Goldberg, B. B.; Cheng, H. M.; Dresselhaus, M. S. *J. Mater. Res.* **2003**, *18*, 1251. (d) Bacsa, R. R.; Peigney, A.; Laurent, C. H.; Puech, P.; Bacsa, W. S. *Phys. Rev. B* **2002**, *65*, 161404. (e) Kociak, M.; Suenaga, K.; Hirahara, K.; Saito, Y.; Nakahira, T.; Iijima, S. *Phys. Rev. Lett.* **2002**, *89*, 155501.
(2) Ruland, W.; Schaper, A. K.; Hou, H.; Greiner, A. *Carbon* **2003**, *41*, 423.
(3) Zhang, G. Y.; Jiang, X.; Wang, E. G. *Science* **2003**, *300*, 472.
(4) Zhang, G. Y.; Bai, X. D.; Wang, E. G.; Guo, Y.; Guo, W. *Phys. Rev. B* **2005**, *71*, 113411.
(5) Zuo, J. M.; Vartanyants, I.; Gao, M.; Zhang, R.; Nagahara, L. A. *Science* **2003**, *300*, 1419.
(6) Koziol, K.; Shaffer, M.; Windle, A. *Adv. Mater.* **2005**, *17*, 760.
(7) Xu, Z.; Bai, X. D.; Wang, Z. L.; Wang, E. G. *J. Am. Chem. Soc.* **2006**, *128*, 1052.
(8) Kolmogorov, A. N.; Crespi, V. H.; Schleier-Smith, M. H.; Ellenbogen, J. C. *Phys. Rev. Lett.* **2004**, *92*, 085503.
(9) Kolmogorov, A. N.; Crespi, V. H. *Phys. Rev. Lett.* **2000**, *85*, 4727.
(10) Guo, W.; Gao, H. J. *Comput. Model. Eng. Sci.* **2004**, *7*, 19.
(11) For a (n, m) inner tube ($n \geq m$) with a radius R, there are many possible outer tubes with different indexes of ($n + \Delta n$, $m + \Delta m$), ($n + \Delta n \geq m + \Delta m$). According to the experimental results which yield the average interlayer space of 3.38 Å,[2,3] we set the outer tubes' radius to satisfy the condition $R + 3.23$ Å $\leq R_{outer} \leq R + 3.53$ Å. A large amount of cases are considered with m/n ranging from 0 to 1 and with a diameter of $d = 2R$ ranging from <1 to 50 nm. For each given inner tube, total energy calculations by use of the revised K−C potential for all of the possible outer tubes with a radius falling in this range are performed. For each matched inner/outer tube pair, interlayer static sliding and rotation with enough small steps are simulated to find the stable interlayer energy of the system.
(12) Gao, M.; Zuo, J. M.; Zhang, R.; Nagahara, L. A. *J. Mater. Sci.* **2006**, *41*, 4382.

JA0662063