

ELECTRONIC STRUCTURE OF SHORT CARBON NANOBELLS

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We performed local density functional calculations for the electronic structure of short carbon nanobells. The calculated local density of states of the nanobells revealed field emission characteristics that agree with experimental observations. We also performed total energy calculations to study the structural stability and a related possible growth mechanism of the nanobells. In the nitrogen-doped carbon nanobells, nitrogen atoms that are attracted to the open-edge sites of the carbon nanobells appear to stop the growth of the nanostructures.

Keywords: Carbon nanobells; carbon nanostructures; electronic structure; carbon nanotubes; growth mechanism.

1. Introduction

Carbon nanotubes (CNTs) show a range of electronic properties that are potentially useful for electronic devices.¹ In particular, the excellent field-emission properties attracted great interest for applications.^{2–7} It has also been found that field-emission can be enhanced dramatically when the nanotube tips are open³ and that the emission depends on the electronic structure of the CNTs.⁸ Recent experiments demonstrated that the nitrogen-assisted synthesis of carbon nanofibers or nanotubes can support growth on a large scale.^{9–11} Such carbon nanofibers exhibit a “bamboo-like” structure. Distinctively, a great part of the bamboo-like nanofibers consists of open ends of short carbon nanobells. Individual nanobells are weakly stacked one on top of the other to create a long nanofiber. The carbon nanobells may be viewed as short carbon nanotubes such that their lengths are of the same order as their diameters, or as carbon quantum dots. Nonetheless, the electronic structure of the short carbon nanobells is substantially different from that of the pure and long nanotubes due to the quantum effects inherent to their sizes. The nanobells exhibit novel electron field emission properties with a turn-on field of electron emission as low as $0.8 \text{ V}/\mu\text{m}$.^{9,12}

Over the last twenty years, local density functional calculations have been successfully implemented to study various properties of materials, including various surfaces and interfaces. It has been demonstrated that local density functional computation is a reliable tool to study the electronic structure of materials. Although much progress has been made in understanding theoretically the electronic properties of fullerenes, carbon nanotubes, and other related nanostructures,^{1,13} we are not aware of a report of density functional calculations of the electronic structure and related properties of short carbon nanobells. The large number of atoms, 150 in the case we considered, that enter into the local density functional calculations presents some technical challenges. In this article, we present the first report on the calculated electronic structure of short carbon nanobells. Our computations employed local density functional computation and a real space approach. From the total energy calculations, we confirm an intuitively plausible growth mechanism of the nanobells.

Although the experimental synthesis of carbon nanobells produced samples of various sizes, measurements revealed that the surface atomic structure of the bamboo-like morphology in thick nanobells is similar to that of the thinner ones.⁹ Experiments also revealed that adjacent nanobells do not have a firm contact, but instead the closed end of one nanobell is weakly inserted into the open end of the other. Single nanobells can be easily separated from other part of the nanofiber.¹⁰ Hence, this work focuses on local density functional calculations on single nanobells. The weak interaction between adjacent carbon nanobells may be included as a perturbation in further studies including a modeling of the bamboo-like structures. We first constructed a prototypical model of the carbon nanobell to simulate the general structure of carbon nanobell samples that were used in experiments. We utilized a computer code for fullerene generations that was obtained from Michigan State University (Dr. David Tomanek's group). Our prototypical carbon nanobell includes 150 atoms that consist of half of the C₂₄₀ fullerene with 30 extra atoms on the bell. Its length and the diameter are 8.5 and 7.4 Å, respectively. Although the size of this prototypical carbon nanobell may differ from that of fabricated samples in experiments, their fundamental futures are similar. These features include the open-edge structure, the wall, and the closed cap of the bells. The density functional calculations of the prototypical carbon nanobell can reveal the information relevant to the understanding of the basic properties of carbon nanobells.

In these calculations, we utilized a local density functional potential and the linear combination of atomic orbitals (LCAO) formalism.^{14,15} We first relaxed the atomic structure of the carbon nanobell by using various bond lengths and by identifying the minimum of the calculated total energies. In the total energy calculations, we employed an extended basis set of atomic orbitals of C(1s2s3s 2p3p). Here, C(3s 3p) are the extra orbitals that are used to augment the basis set to account for possible charge diffusion and polarization in the carbon nanobell. The atomic orbitals were obtained from self-consistent, local density functional computations, using the linear combination of Gaussian orbitals (LCGO) method. We expanded the

atomic orbitals in terms of 13 Gaussian orbitals. We utilized a set of even-tempered Gaussian exponentials with a minimum of 0.124 and a maximum of 0.1365×10^5 . The total number of atomic orbitals that were included in the total energy calculations for the carbon nanobell is 1200. We employed a real space approach in the LCAO method to evaluate the electron wave function, the electron density, and the potentials. The real space approach enables us to complete the required computations using our SiliconGraphics Origin2000 that is equipped with 1 GB RAM (memory). From the total energy minimization, our calculated C-C bond length in the inner atomic rings of the carbon nanobell is 1.415 Å, which is close to the C-C bond length of 1.421 Å in graphite¹⁶ and to the commonly observed C-C bond length in carbon nanotubes of large sizes.

As identified by experimental studies,^{9,10} the open-ends of carbon nanobells play a particular role in their electronic properties. The structural property near the open edge of the carbon nanobell is different from those in the inner wall, due to the existence of some dangling bonds of the carbon atoms at the open-edge sites. We further employed the total energy minimization to identify the atomic positions of the relaxed structure near the open-edge of the carbon nanobell. The calculated C-C bond length in the first atomic ring at the open-edge of the carbon nanobell is 1.37 Å, which is shorter than the C-C bond length of 1.42 Å of the inner atomic rings of the bell. This reduction of the C-C bond length for the carbon atoms at the open-edge sites is mainly due to the absence of atoms on the empty side. The calculated bond length of the carbon atoms from the second atomic ring to the first atomic ring near the open-edge of the nanobell is 1.40 Å, which is not much different from that in the inner rings, away from the open-edge of the nanobell. This result indicates that the effect of further relaxation of the third atomic ring and inner rings would be insignificant. We retained the bond-length of the C atoms at the third atomic ring and inner rings as the one discussed above. This option is warranted, considering the large computational effort in performing the local density functional calculations for these systems.

We present in Fig. 1 the calculated three-dimensional (3-D) image of the electron density distribution in real space. From Fig. 1, we can identify the atomic structure of the carbon nanobell as well as the presence of covalent bonds, which is attributed to the sharing of electrons by two neighboring atoms in the nanobell.

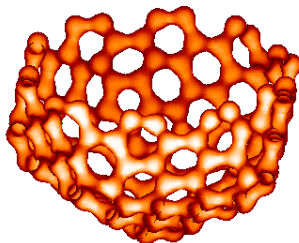


Fig. 1. The three-dimensional image of the calculated electron density of a short carbon nanobell.

Isolated pentagons are formed around the closed cap of the bell to curve the graphite sheet without disrupting the short-range order of the three-fold coordinated nearest-neighbors. In the wall of the bell, away from the closed cap, there are only hexagons.

We calculated the local density of states (LDOS) from the contributions of various atomic rings near the open-edge of the nanobell. We calculated the density of states using a Gaussian broadening method, which approximates the delta-function by a Gaussian function, with a Gaussian width of 0.04 eV. Such a Gaussian broadening may, in some senses, reflect the effects of defects, impurities, and of thermal vibrations of atoms in the real samples of carbon nanobells. In Fig. 2, we present the results of LDOS in an energy range of from -4 eV to 2 eV around the Fermi level ($E_F = 0$). The unit of LDOS in Fig. 2 is in states per eV per atom. We used this unit for convenient comparisons of the electronic properties of various atomic rings of the nanobell. A very interesting feature can be identified from the calculated local density of states. Figure 2 clearly shows that the C atoms of the first atomic ring at the open-edge of the nanobell have the dominant contribution to the electronic states at the Fermi level, with a value of 1.19 states per eV per atom. The contribution from the second atomic ring near the open-edge to the LDOS at the Fermi level is smaller than that of the first atomic ring at the open-edge. The LDOS at E_F from the C atoms of the second ring is only 0.55 states per eV per atom. The third and higher atomic rings, including the atomic sites of the closed cap of

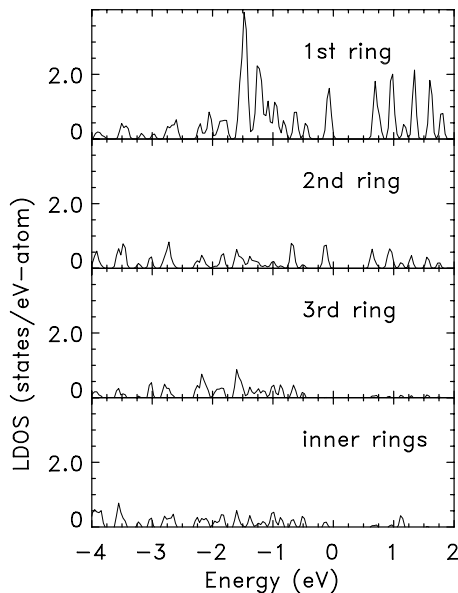


Fig. 2. Calculated local density of states (LDOS) of electrons of a carbon nanobell. The 1st, 2nd and 3rd rings in the figure refer to the first, second, and third atomic rings near the open-edge of the nanobell. The inner rings refer to the atomic sites away from the open-edge of the bell and include that of the closed cap. The Fermi level is at 0.0 eV.

the bell, have a much smaller contribution to the LDOS at the Fermi level, with an average value of 0.1 states per eV per atom. Consequently, electrons will most likely be emitted from the first and the second atomic rings near the open-edge of the nanobell in field-emission experiments. In order to obtain continuous emission in experiments, the closed cap of one nanobell is weakly inserted into the open end of another to form a nanofiber that is connected to a current source. A great part of the nanofiber then consists of open-ends on the side. The electron field emission is enhanced because each of the open-ends can contribute to electron emission. This feature is consistent with the observations of a side-emission in experimental studies.^{9,10}

The growth mechanism of the carbon nanobells is an important issue and remains a difficult problem. There are mainly two possible growth models. The first one assumes that the carbon atoms are added at the open-ends of the nanobells.^{1,11} The second one involves the C₂ absorption process that is assisted by the pentagonal defects on the closed caps.¹ Although both models are very interesting, we have technical difficulties up to the present in using density functional computations to simulate the second growth model. We successfully performed local density functional computations to test the first growth mechanism. Because of the active dangling bonds of carbon atoms at the open-edge of nanobells, there is a high possibility that carbon atoms can be attracted to these sites for growth to occur. We calculated the total energies in the two cases. In the first case, a ring of 20 carbon atoms attaches itself to the open-edge of the carbon nanobell at a bond-length of 1.415 Å. In the second case, these carbon atoms are free. The calculated total energy in case I is substantially lower than the corresponding value in case II. The total energy difference, which may also be defined as the cohesive energy of the carbon atoms in the first growth model, is 4.7 eV/atom. In this growth model (also see Fig. 1), C₂ dimers are absorbed at the active dangling bond edge sites at the open end of the carbon nanobell. A C₂ dimer that deposits on the open-edge of the bell forms one covalent bond on the same atomic ring. Each of the C atoms also forms one covalent bond with the C atom of the next atomic ring and remains an active dangling bond towards the open-space. This grow model is consistent with previous analysis of experimental results.^{11,12} Although we cannot rule out the second growth model (growth on the closed cap of carbon nanobells), our total energy calculations utilizing the local density functional method presented clear evidence that the first growth mechanism is highly possible.

Experimental results have indicated that the growth of the short carbon nanobells is highly affected by the nitrogen concentration in the gas mixture in the growth process.^{9,10} Without nitrogen atoms in the growth gas mixture, long and pure carbon nanotubes can otherwise be produced in the same condition (including the utilization of catalytic nanoparticles). However, it was not clear why the nitrogen atoms could turn the growth of the would-be long carbon nanotubes into that of short nanobells. We performed total energy calculations utilizing the local density functional method to study the nitrogen-doped carbon nanobells. Since

nitrogen atoms can also form the planar sp^2 -hybrid,¹⁷ we studied the substitutional doping of nitrogen atoms in the carbon nanobells.

We first replaced carbon atoms by nitrogen atoms at the open-edge of the nanobell. We compared the total energies in the two cases. In the first case, computations are carried out for the pristine carbon nanobell in the presence of ten free atoms of nitrogen. In the second case, ten nitrogen atoms replace ten carbon atoms on the open-edge and the substitutionally N-doped nanobell is in the presence of ten free atoms of carbon. The calculated total energy of the second case is lower than that of the first case by an amount of 0.5 eV per atom, without relaxing the structure. We then performed total energy calculations and identified the atomic positions of the relaxed structure of the nitrogen-doped nanobell from the minimum of the total energies. The calculated C-N bond length in the first atomic ring at the open-edge of the nanobell is 1.376 Å. The bond-length from the nitrogen atoms of the first atomic ring to the carbon atoms of the second atomic ring is 1.377 Å. The C-C bond length from the first atomic ring to the second ring is 1.397 Å. The total energy of the nitrogen-doped nanobell, in the relaxed structure, is lower than that of the undoped one by 0.72 eV per atom.

We also studied the substitutional doping of nitrogen atoms for carbon atoms in the wall of the carbon nanobell. We used the same computation procedure as discussed above. The calculated total energy of the N-doped nanobell at the wall position is much higher than that of the undoped bell, by an amount of 5 eV per atom. This result indicates that the substitutional doping of nitrogen atoms for carbon atoms in the wall of carbon nanobells is not energetically favored.

These calculated results of the nitrogen-doped nanobells thus indicate that the dopant nitrogen atoms prefer to stay at the open edge of the nanobell as opposed to being in the wall (i.e. lower atomic rings) of the nanobell. Once there are enough nitrogen atoms on the open edge of the nanobell, carbon atoms cannot attach to the open-edge of the nanobell. Such an attachment will result in nitrogen atoms being in inner rings other than that at the open-edge, resulting in a configuration that is not favored energetically. Consequently, nitrogen atoms act as the stopper of the growth of the carbon nanobell.

We present the calculated LDOS of the nitrogen-doped carbon nanobell in Fig. 3. There are ten N atoms on the first atomic ring at the open-edge of the nanobell. The N atoms form covalent bonds with C atoms of the first and the second atomic rings. There is no N atom on the other atomic rings of the nanobell. Similar to the LDOS of the undoped carbon nanobell in Fig. 2, the N and C atoms on the first atomic ring at the open-edge of the nanobell have the dominant contribution to the electronic states at the Fermi level. The LDOS at E_F from N and C atoms on the first atomic ring at the open edge are 0.56 and 0.71 states per eV per atoms, respectively. The contribution to the LDOS at the Fermi level, from the C atoms of the second atomic ring near the open-edge, is 0.23 states per eV per atom. The third atomic ring and the inner rings that include the closed cap have a much smaller

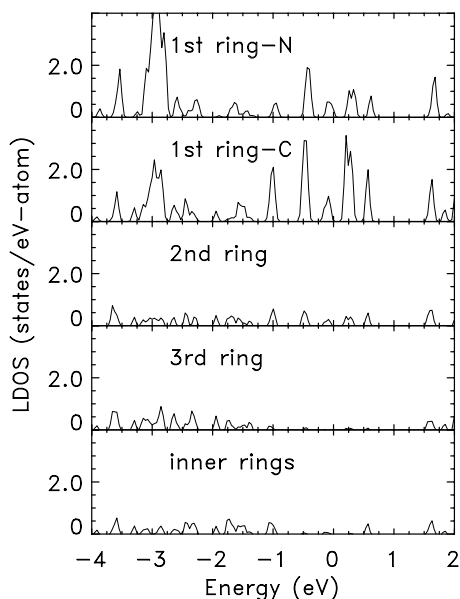


Fig. 3. Calculated local density of states of a nitrogen-doped carbon nanobell. The 1st ring-N and -C refer to the nitrogen and carbon atoms on the first atomic ring near the open-edge of the nanobell. The meanings of other notations in the figure are the same as those in Fig. 2.

contribution to LDOS at the Fermi level, with an average value of 0.08 states per eV per atoms. Thus, electrons will most likely be emitted from the atomic sites near the open-edge of the nanobell in field-emission experiments. There are also noticeable differences between the results in Figs. 2 and 3. The unoccupied electron states in Fig. 3 shift down considerably as compared to the results in Fig. 2. The energy gap between the occupied and unoccupied electron states in the N-doped nanobell is only 0.07 eV.

In conclusion, we successfully performed local density functional calculations for the electronic structure of carbon nanobells. The calculated local densities of states of the carbon nanobells indicate that electrons are most likely emitted from the atomic sites near the open-edge of the nanobell in field-emission experiments. We also performed total energy calculations to study the structural stability of the carbon nanobells and discussed a possible growth mechanism for the nanostructures. In the nitrogen-doped carbon nanobells, nitrogen atoms that are attracted to the open-edge of the nanobells may play a role of stopper of the growth of the nanostructures.

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References

1. M. S. Dresselhaus, G. Dresselhaus and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic Press, New York, 1996).
2. W. A. de Heer, A. Châtelain and D. Ugarte, *Science* **270**, 1179 (1995).
3. A. G. Rinzler, J. H. Hafner, P. Nikolaev, L. Lou, S. G. Kim, D. Tománek, P. Nordlander, D. T. Colbert and R. E. Smalley, *Science* **269**, 1550 (1995).
4. Q. H. Wang, T. D. Corrigan, J. Y. Dai, R. P. H. Chang and A. R. Krauss, *Appl. Phys. Lett.* **70**, 3308 (1997).
5. Q. H. Wang, A. A. Setlur, J. M. Lauerhaas, J. Y. Dai, E. W. Seelig and R. P. H. Wang, *Appl. Phys. Lett.* **72**, 2912 (1998).
6. Y. Chen, S. Patel, Y. Ye, D. T. Shaw and L. Guo, *Appl. Phys. Lett.* **73**, 2119 (1998).
7. K. A. Dean and B. R. Chalamala, *Appl. Phys. Lett.* **76**, 375 (2000).
8. J. M. Bonard, T. Stockli, F. Maier, W. A. de Heer, A. Chatelain, J. P. Salvetat and L. Forro, *Phys. Rev. Lett.* **81**, 1441 (1998).
9. X. Ma, E. Wang, W. Zhou, D. A. Jefferson, J. Chen, S. Deng, N. Xu and J. Yuan, *Appl. Phys. Lett.* **75**, 3105 (1999).
10. X. Ma, E. G. Wang, R. D. Tilley, D. A. Jefferson and W. Zhou, *Appl. Phys. Lett.* **77**, 4136 (2000).
11. X. Ma and E. G. Wang, *Appl. Phys. Lett.* **78**, 978 (2001).
12. D. Y. Zhong, S. Liu, G. Y. Zhang and E. G. Wang, *J. of Appl. Phys.* **89**, 5939 (2001).
13. There is a wealth of publications for the theoretical studies of carbon nanotubes and other nanostructures. Some of the recent publications also include, J. C. Charlier and G. M. Rignanese, *Phys. Rev. Lett.* **86**, 5970 (2001); G. Zhou, W. Duan and B. Gu, *ibid.* **87**, 5504 (2001); L. Yang and J. Han, *ibid.* **85**, 154 (2000); D. H. Oh, J. M. Park and K. S. Kim, *Phys. Rev.* **B62**, 1600 (2000).
14. G. L. Zhao and J. Callaway, *Phys. Rev.* **B50**, 9511 (1994).
15. G. L. Zhao, D. Bagayoko D and T. D. Williams, *Physical Review* **B60**, 1563 (1999).
16. CRC Handbook of Chemistry and Physics, eds. R. C. Weast, D. R. Lied, M. J. Astle and W. H. Beyer (CRC Press, Boca Raton, Florida, 1990), p. F-188.
17. W. A. Harrison, *Electronic Structure and the Properties of Solids* (W. H. Freeman and Company, San Francisco, 1980), p. 91.