

# Ab-Initio Density Functional Calculations of the Growth and Structural Properties of Short Carbon Nanobells

**G L Zhao and D Bagayoko**

Department of Physics, Southern University and A & M College  
Baton Rouge, Louisiana 70813, USA

Corresponding author's e-mail address: zhao@grant.phys.subr.edu

**Abstract.** We performed ab-initio density functional calculations to study the structural and growth properties of short carbon nanobells. We used a real space approach and the linear combination of atomic orbitals (LCAO) formalism. In the nitrogen-doped carbon nanobells, the nitrogen atoms that are attracted to the open-edge sites of the carbon nanobells play an important role in the growth of the short carbon nanostructures. We present the calculated electronic structure of the short nanobells. The calculated local density of states of the nanobells revealed field emission characteristics that agree with experimental observations.

## 1. Introduction

Carbon nanostructures present interesting properties with a great potential of applications. Particularly, short carbon nanotubes or carbon nanobells present excellent field-emission properties that have attracted a great interest for applications.<sup>[1-8]</sup> Experiments demonstrated that the nitrogen-assisted synthesis can grow carbon nanofibers on a large scale.<sup>[9-12]</sup> Such carbon nanofibers exhibit a "bamboo-like" structure. Distinctively, a great part of the bamboo-like nanofibers consists of short carbon nanobells. Individual nanobells are self-contained and stack one on top of the other to create a long nanofiber. The carbon nanobells may be viewed as short nanotubes such that their lengths are of the same order as their diameters. The electronic structure of the short carbon nanobells is substantially different from that of the pure and long carbon nanotubes because of 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  $0.8 V / \mu m$ .<sup>[9,13]</sup> We performed ab-initio density functional calculations, aiming to understand the growth, structural, and electronic properties of short carbon nanobells.

## 2. Method

Although the experimental synthesis of carbon nanobells produced samples of various sizes, measurements revealed that the atomic structure of the bamboo-like morphology in thick nanobells is similar to that of the thinner ones.<sup>[9]</sup> 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 another. Single nanobells can be easily separated from other

parts of the nanofiber.<sup>[10]</sup> Hence, our ab-initio calculations will focus on single nanobells. The weak interaction between adjacent carbon nanobells may be included as a perturbation in further studies in modeling the bamboo-like morphology of the nanofibers. We constructed a prototypical carbon nanobell as a model to simulate the general structure of short carbon nanobells. Figure 1 presents the calculated images of the electron density distribution of a prototypical carbon nanobell in real space. The prototypical carbon nanobell includes 150 atoms and consists of half of the C<sub>240</sub> fullerene with 30 extra atoms on the bell. Its length and diameter are 8.5 and 7.4 Å, respectively. Although the size of this prototypical carbon nanobell may differ from that of fabricated samples, their fundamental features are similar. These features include the structural properties of the open-edge, the wall, and the closed cap of the nanobells.

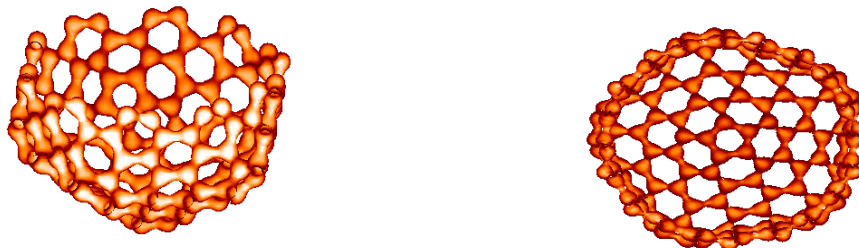


Figure 1. The calculated images of the electron density distribution in real space for a prototypical carbon nanobell that is viewed from different directions

Our ab-initio calculations are based on the density functional theory of Hohenberg-Kohn and Kohn-Sham.<sup>[14,15,16,17,18]</sup> In the linear combination of atomic orbitals (LCAO) method, we solved the Kohn-Sham equations self-consistently by employing the Rayleigh-Ritz variational process.<sup>[19,20]</sup> In the self-consistent calculations for the electronic structure of short CN<sub>x</sub> nanobells, we employed an extended basis set that includes atomic orbitals of C(1s2s3s 2p3p) and N(1s2s3s 2p3p). Here C(3s 3p) and N(3s 3p) are extra orbitals that are used to augment the basis set to account for possible charge diffusion and polarization in the short nanobells. The real space approach of the LCAO method enables us to complete the required computations using our SiliconGraphics Origin2000 that is equipped with 4 GB RAM (memory).

### 3. Results

#### 3.1. Relaxed Atomic Structure near the Open-Edge of the Short Carbon Nanobell

The open-edges of carbon nanobells play an important role in their electronic properties. The structure near the open edge of the carbon nanobell is different from that in the inner wall and the closed cap. We performed total energy minimization to identify the atomic structure near the open-edge of the prototypical carbon nanobell. The calculated C-C bond length on the

first atomic ring at the open-edge of the carbon nanobell is  $1.37 \text{ \AA}$ , which is much shorter than the C-C bond length of  $1.415 \text{ \AA}$  in 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 a result of the reduction in coordination number. The calculated bond length of the carbon atoms on the first atomic ring to the carbon atoms on the second ring is  $1.40 \text{ \AA}$ , 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.

### 3.2. A Possible Growth Mechanism of Carbon Nanobells

The growth mechanism of the carbon nanobells remains a difficult problem. There are probably two major growth models.<sup>[1]</sup> The first one assumes that the carbon atoms are added at the open-ends of the nanobells.<sup>[1,11]</sup> The second one involves the  $\text{C}_2$  absorption process that is assisted by the pentagonal defects on the closed caps.<sup>[1]</sup> Although both models are very interesting, we have technical difficulties 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 following two cases. In the first case, a ring of 20 carbon atoms attaches to the open-edge of the carbon nanobell at a bond-length of  $1.415 \text{ \AA}$ . In the second case, these 20 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  $4.7 \text{ eV/atom}$ . In this growth model, see Figure 1,  $\text{C}_2$  dimers are absorbed at the active dangling bond sites at the open end of the carbon nanobell. A  $\text{C}_2$  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 growth model is consistent with previous analysis of experimental results.<sup>[11,13,21]</sup> Although we cannot rule out the second growth model (growth on the closed cap of carbon nanobells), our calculations presented clear evidence that the first growth mechanism is highly possible.

### 3.3. Nitrogen-Doped Carbon Nanobell

Experimental results indicated that the growth of the short carbon nanobells is highly dependent on the nitrogen concentration in the gas mixture during the synthesis.<sup>[9,10]</sup> Without nitrogen atoms in the growth gas mixture under the same conditions, long and pure carbon nanotubes, without the “bamboo-like” morphology, are produced. However, it was not clear why the nitrogen atoms could turn the growth of the would-be long carbon nanotubes into that of short carbon nanobells. We performed total energy calculations to study the nitrogen-doped carbon nanobells ( $\text{CN}_x$  nanobells). Since nitrogen atoms can also form the planar  $\text{sp}^2$ -hybrid,<sup>[22]</sup> we studied the substitutional doping of nitrogen atoms in the  $\text{CN}_x$  nanobells. The substitutional doping of nitrogen atoms in  $\text{CN}_x$  nanobells was also proposed from the analysis of experimental results.<sup>[13]</sup>

We first replaced carbon atoms with nitrogen atoms at the open-edge of the prototypical 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 in the second case is lower than that in 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 total energy minimization. The calculated C-N bond length in the first atomic ring at the open-edge of the nanobell is  $1.376 \text{ \AA}$ . The bond-length, from the nitrogen atoms of the first atomic ring to the carbon atoms of the second atomic ring, is  $1.377 \text{ \AA}$ . They are close to the length of the partially double C-N bond ( $1.352 \text{ \AA}$ ) in heterocyclic systems.<sup>[23]</sup> The C-C bond length from the first atomic ring to the second ring is  $1.397 \text{ \AA}$ . 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 with nitrogen atoms (for carbon atoms) in the wall (away from the open-edge and the closed cap) of the prototypical carbon nanobell. We used the same computational 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 with nitrogen in the wall of carbon nanobells is not energetically favored.

These calculated results for the nitrogen-doped nanobells in the prototypical model 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 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  $\text{CN}_x$  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. This growth mechanism for the nitrogen-doped carbon nanobells and the effect of the nitrogen atoms in the growth process agree with the observations from experiments.<sup>[9,10,11,13]</sup>

We present the calculated local density of states (LDOS) of the  $\text{CN}_x$  nanobell in Figure 2. The dopant nitrogen atoms stay at the open-edge sites in the prototypical nanobell. The LDOS from the nitrogen and carbon atoms on the first atomic ring at the open-edge of the nanobell are shown in the first and the second panels of Figure 2, respectively. There is no N atom on other atomic rings away from the open-edge of the nanobell. Figure 2 clearly shows that 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 around the Fermi level. The LDOS at the Fermi level, from the N and C atoms on the first atomic ring at the open-edge, are 0.56 and 0.71 states per eV per atom, respectively. The contribution, from the second atomic ring near the open-edge, to the LDOS at the Fermi level 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 contribution to LDOS at the Fermi level, at about 0.08 states per eV per atom. Thus, electrons will be emitted from the atomic sites near the open-edge of the nanobell in field-emission experiments. The real nanobell samples in experimental studies mostly involve multilayers of graphite sheets and the nanobells stacked one on top of the other. The weak interactions between graphite layers in these nanobells and that between the bells may further broaden the electronic energy levels.

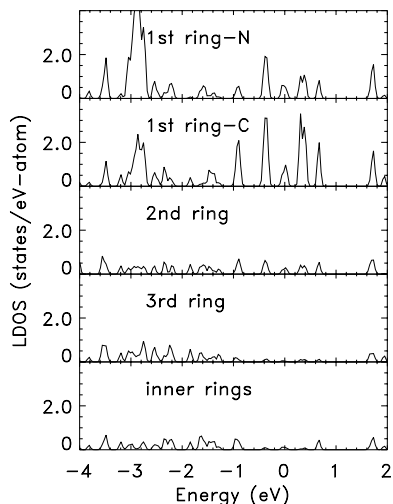


Figure 2. The calculated local density of states of electrons of a nitrogen-doped carbon nanobell. The 1<sup>st</sup> ring-N and -C refer to the nitrogen and carbon atoms on the first atomic ring at the open-edge of the nanobell. The 2<sup>nd</sup> and 3<sup>rd</sup> rings refer to the second and third atomic rings near the open-edge. The inner rings refer to the atomic sites away from the open-edge, including the closed cap. The Fermi level is at 0.0 eV.

#### 4. Conclusion

In conclusion, we performed ab-initio density functional calculations to simulate the growth, structural, and electronic properties of prototypical carbon nanobells. 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. The calculated local densities of states of the CN<sub>x</sub> nanobells indicate that electrons are most likely emitted from the atomic sites near the open-edge of the carbon nanobell in field-emission experiments. This result agrees with experimental observations.

**Acknowledgements:** This work was funded in part by the US Department of the Navy, Office of Naval Research (ONR Award No: N00014-05-1-0009), by US National Science Foundation (Award No. CCF-0508245), and by US NASA (Award No. NCC 2-1344).

---

#### References

- [1] Dresselhaus M S, Dresselhaus G, and Eklund P C 1996 *Science of Fullerenes and Carbon Nanotubes*, (Academic Press, New York).
- [2] de Heer W A, Châtelain A, Ugarte D 1995 *Science*, **270**, 1179.
- [3] Rinzler A G, et al 1995 *Science*, 269, 1550.
- [4] Wang Q H, et al 1997 *Appl. Phys. Lett.* **70**, 3308
- [5] Wang Q H, et al 1998 *Appl. Phys. Lett.* **72**, 2912.
- [6] Chen Y, et al 1998 *Appl. Phys. Lett.* **73**, 2119.
- [7] Dean K A and Chalamala B R 2000 *Appl. Phys. Lett.* **76**, 375.
- [8] Bonard J M, et al 1998 *Phys. Rev. Lett.* **81**, 1441.
- [9] Ma X, et al 1999 *Appl. Phys. Lett.* **75**, 3105.

- 
- [10] Ma X, et al 2000 Appl. Phys. Lett. **77**, 4136.
- [11] Ma X and Wang E G 2001 Appl. Phys. Lett. **78**, 978.
- [12] Wang E G , et al 2003 Carbon **41**, 1827.
- [13] Zhong D Y, Liu S, Zhang G Y, Wang E G 2001 J. of Appl. Phys. **89**, 5939.
- [14] Hohenberg P and Kohn W 1964 *Phys. Rev.* **136**, B864; Kohn W and Sham L J 1965 *Phys. Rev.* **140**, A1133.
- [15] Zhao G L, Bagayoko D, and Yang L 2004 Phys. Rev. B **69**, 245416.
- [16] Callaway J and March N H 1984 *Solid State Physics*, vol. 38, Edited by H. Ehrenreich, D. Turnbull, and D. Seitz, (Academic Press, New York), p.135.
- [17] Zhao G L, Bagayoko D, and Wang E G 2003 Modern Physics Letters B, **17**, 375.
- [18] Bagayoko D, Zhao G L, Fan J D, and Wang J T 1998 *Journal of Physics: Condensed Matter*, **10** , 5645.
- [19] Mikhlin S. G 1971 *The Numerical Performance of Variational Methods*, (Wolters-Noordhoff Publishing), ch.1, 2, & 7.
- [20] Gould S H 1957 *Variational Methods for Eigenvalue Problems*, (University of Toronto Press), Ch. 2.
- [21] Gavillet J, Loiseau A, Journet C, Willaime F, Daucastelle F, and Charlier J C 2001 Phys. Rev. Lett. **87**, 275504.
- [22] Harrison W A 1980 *Electronic Structure and the Properties of Solids*, (W. H. Freeman and Company, San Francisco), p. 91.
- [23] CRC Handbook of Chemistry and Physics, 1990 Edited by R. C. Weast. D. R. Lied, M. J. Astle, and W. H. Beyer, (CRC Press, Boca Raton, Florida), p. F-188.