Fullerene nanotubes in electric fields

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(Received 12 April 1995)

The electronic properties of fullerene nanotubes in strong electric fields are investigated using a density-functional cluster method. It is shown that the energy difference between the open-ended and the closed configurations decreases with increasing field. The field-induced stabilization is, however, not sufficient to make the energy of the open configuration lower than the energy of the capped structure. Nanotubes, including those with a finite band gap, are found to screen large external electric fields as do perfect conductors.

It is well known that fullerene nanotubes can be grown in a high-pressure plasma of ions and electrons generated by dc arcs between two carbon electrodes.[1] The mechanism of the arc growth of fullerene tubes is likely to be very complicated. Many factors, such as temperature gradients, pressure and plasma density, kinetic conditions, and electric field need to be taken into account. Among them, the role of the electric field is probably the least considered one, yet its interaction with fullerene tubules can be potentially significant due to the large fields present in the arc, which can be of the order of 10^8 V/cm in the small regions near the tube tips.[2] Such strong local electric fields are likely to influence both the geometric and electronic structure of the fullerene tubes, and hence the growth of the tubes in the arc. It has been speculated that, in such strong inhomogeneous fields, an open-ended fullerene tube might be stabilized relative to its closed-end isomeric configuration.[2] The dangling atoms at the open end of the graphitic structure would provide bases for direct precipitation of carbon ions, thereby facilitating the growth of uniform diameter nanotubes. Open-ended growth mechanisms emphasizing defects nucleation at the tube openings wider than 3 nm have very recently been proposed based on *ab initio* molecular dynamics calculations.[3]

In this paper, we present an investigation of the electronic structure of fullerene nanometer-diameter single-layer tubes in high electric fields. In particular, we compare the electronic properties of open-ended and closed fullerene tubes. An all-electron cluster approach is used in this work. The computational method used takes advantage of large parallel computers.

Our calculations show that the effects of electric field on stabilization of a fullerene tube with fully opened tip against that with a closed tip are rather weak. The calculations also show that fullerene nanotubes of different tip configurations and helical symmetry exhibit almost perfect metalliclike screening of external electric fields. The field-induced polarization of electrons in the tube results in charge accumulation at the tube tips. We speculate that the resulting Coulomb repulsion may introduce a potential barrier separating the open and closed tube configurations.

The cluster models for the fullerene tubes are formed by rolling a graphite sheet into a cylinder with the hexagons aligned parallel to the tube circumference and oriented to have flat-top openings for further growth.[4,5] Figure 1 shows two tubes with different forms of tips, one is open at both ends and one is capped by a fullerene hemisphere at the top end. To obtain the curvature for closing, six five-membered rings are used in the cap. The tubes are terminated at the bottom using hydrogen to saturate the carbon dangling bonds. The two tubes thus constructed have different electronic structures. A finite gap (~0.5 eV) exists between the highest occupied orbital level and the lowest unoccupied orbital level in the capped tube, but not in the open tube. The electron removal energies are also different for the two tube configurations. For a similarly constructed open tube with 108 carbon atoms, the ionization potential and electron affinity are 6.6 eV and 4.3 eV, respectively, compared to 6.7 eV and 3.6 eV for a capped one. These values can be further compared to those of the C_{60} molecule, which

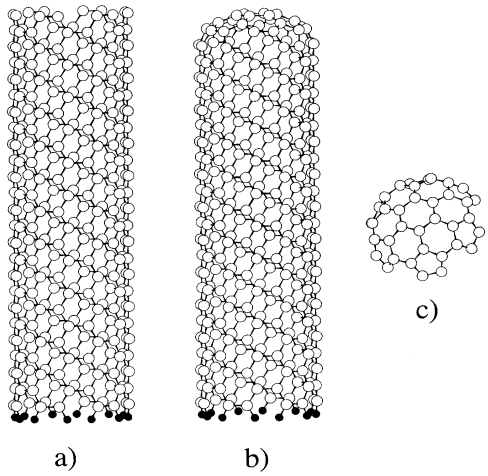

FIG. 1. The fullerene tube clusters. Each cluster contains 300 carbon atoms (large open circles) and 12 hydrogen atoms (small filled circles): (a) the open-ended configuration, (b) the capped-end configuration, and (c) the capping structure. The tubes shown here have a diameter of 0.8 nm. The electric field is applied in parallel with the tube axis, pointing to the hydrogen terminated end of the tube.

are calculated to be 7.8 eV and 3.0 eV.[6] The difference between an open tube and a capped tube is expected to vanish at large tube lengths; similarly formed infinite tubes would have metallic band structure.[4,7,8]

The electronic structure of the tube clusters are determined by all-electron local-density-functional (LDF) calculations. The coupled Kohn-Sham[9,10] equations and Poisson's equation are solved on a multicenter polar grid with efficient three-dimensional integrations.[11,12] Our computer program has been tested on several small cluster systems, which yielded results in good agreement with other LDF methods and experiment.[13] The exchange-correlation potential used in this calculation is the one derived by Hedin and Lundqvist.[14] The tube clusters are described by a set of double-ζ type numerical atomic orbital functions. The basis set for carbon contains the $1s$, $2s$, and $2p$ orbitals of the ground state carbon atom and the $2s$ and $2p$ orbitals of a C^{2+} ionic state. Adding a d function to carbon in smaller tube clusters has caused no qualitative change in the resulting electronic structure in the range of the external electric fields used in this calculation. The hydrogen basis contains two s functions and one p function. The computations are performed on the 512-node Intel Touchstone Delta parallel computer. The largest tube cluster (Fig. 1) used in this calculation contains approximately 2800 atomic orbitals. By taking advantage of the symmetry of the Hamiltonian, the demands for computational resources can be sufficiently reduced to make the calculation possible.

The total energy of a fullerene tube has been calculated in a uniform external electric field of various field strengths. The field is chosen parallel with the tube axis, pointing to the hydrogen-terminated end of the tube clusters. This arrangement corresponds to a negative potential bias for fullerene tubes growing from the carbon cathode surface. Positive bias is also possible and will be discussed later. Figure 2 shows the difference (in solid lines) between the calculated total energy of an open-ended tube and that of a capped tube. The tube clusters used here are constructed in the same way as those shown in Fig. 1, but composed of 204 carbon atoms.

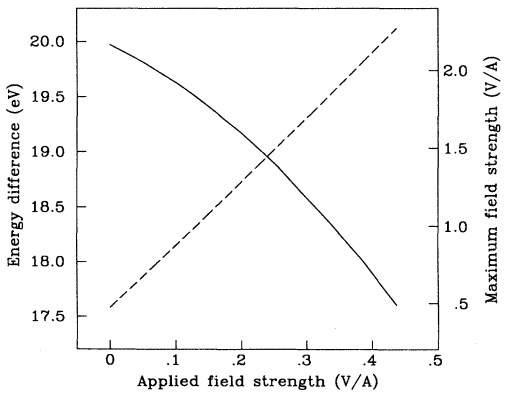

FIG. 2. The total-energy difference (solid) between two different configurations and the maximum field strength (dashed) outside the tip of an open-ended tube (see text). The tube clusters used here contain 204 carbon atoms and 12 terminating hydrogen atoms.

At zero applied field, the energy difference is at its maximum value, 20 eV. This difference is dominated by the binding energy of the closed structure of the cap [Fig. 1(c)]. The formation of the closed cap has added six additional C-C bonds to the capped tube (from joining 12 dangling bonds). The relatively small value of 3.3 eV per bond can be traced to the presence of five-membered rings in the cap, which can cause local stresses to lower the binding energy.

With increasing field strength, the energy difference decreases indicating the stabilization of the open-end configuration by the external field. The electrons in the open tube find themselves more easily polarized by the field due to the low-lying nonbonding orbitals originating from the dangling carbon atoms at the tube opening. In contrast, the finite band gap in the capped tube makes the promotion of electrons to higher energy levels more difficult. Intuitively, the less bonded electrons in the open tube can lower their potential energy by moving further away from the tip.

The small dimension of the tube tip can induce field concentrations. The local fields are enhanced around the tip. The maximum field strength outside the open tube end, calculated at various applied field strengths, is shown in Fig. 2 (in dashed lines). A near linear dependence can be seen. The local maximum field shown here has an upper bound $\sim$2 V/Å, beyond which the electrons become unbound. This limiting value can be increased by switching the potential bias or relaxing the tube structure. With the negative bias, the electrons are brought to the tip and become less bound. By reversing the direction of the applied field, the tip becomes positively charged and will bind electrons more tightly. The effects of structural relaxation have been studied using a linear carbon chain of approximately the same length as the tube clusters. It was found that the carbon chain undergoes a structural change in large electric fields, from a cumulene chain with double bonds to a polyacene chain with alternating single and triple bonds. The maximum induced field outside the terminal atom of the chain can be as large as $\sim$ 10 V/ Å before convergence problems arise. Considering that the carbon atoms in a fullerene tube are two-dimensionally connected, the maximum field strength that can be reached outside the tube end, after relaxing the tube structure, is expected to be smaller than 10 V/ Å. Simple extrapolation suggests that the external field alone would not stabilize the open structure to the level of the capped structure even at the 10-V/ Å field strength. However, it is more likely that the critical field strength for the onset of field emission from the highest occupied molecular orbital level would be reached between 2 and 10 V/ Å. In this new regime, the present computational approach, which employs a bound basis set, is no longer suitable.

In the presence of an external electric field, the electrons in the carbon structure of the nanotubes are redistributed. Figure 3 shows the electric field-induced charge densities in three different fullerene tube clusters. The contour plane cuts the tube along the axis. It can be seen that the electrons on the tube wall are polarized, leaving half of the tube charge rich and half

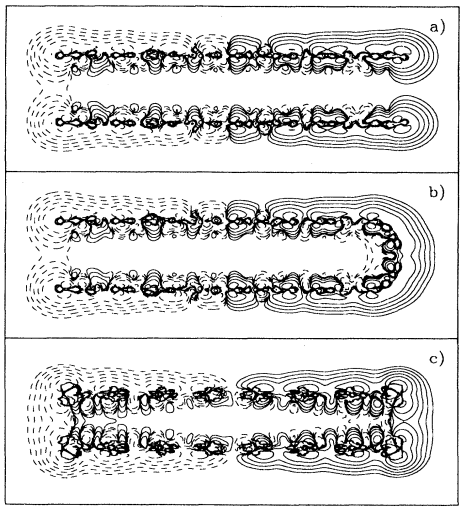

FIG. 3. The electric field-induced charge densities of (a) an open-ended and (b) capped 300 carbon atom tube with armchair structure (see Fig. 1) and (c) an open-ended 224 carbon atom tube with eight hexagons around the circumference and sawtoothlike openings. In the limit of infinite length, this tube is expected to have semiconducting band structure (see text). The applied field strength is 0.12 V/ Å. The contour levels begin with ± 0.2 Å^{-3} and increase subsequently by a factor of 3 in magnitude (negative values are represented by dashed lines). The dimensions of each plot are 40 Å wide and 20 Å high.

charge poor, while the electrons on the inner side of the tube are relatively unaffected. Note that the third tube [Fig. 3(c)] has a smaller diameter than the first two and a different helical symmetry (sawtooth) which will lead to semiconducting band structure in the limit of infinite tube length.[15] Hydrogen saturation is made at both ends of the tube to minimize the effects of dangling carbon orbitals.[16] The global charge polarization as shown in Fig. 3 can be attributed to the existence of delocalized π electrons in the carbon structure. Similar polarizations have also been obtained for fullerene tubes in weak external electric fields and with different tube lengths and diameters, implying that this may be a general property of fullerene nanotubes.

To further explore the screening properties of the fullerene tubes, we calculated the electrostatic potentials of a fullerene tube and a perfect conductor of similar dimensions placed in a uniform electric field. The upper and middle panels of Fig. 4 show the isopotentials for an open-ended and a capped fullerene tube cluster as in Figs. 3(a) and 3(b). The lower panel in Fig. 4 shows the isopotentials of a perfectly conducting hollow cylinder of the same aspect ratio. The similarities between the nanotubes and the perfect conductor indicate that the fullerene nanotubes can screen the external electric field much like a perfect metal. The fullerene tube in Fig. 3(c) (not shown here in Fig. 4), which has a different helical structure, screens the fields similarly. Figures 4(a) and 4(b) also reveal a distinct difference between the fullerene tube and a perfect conductor. The dipolarlike distribution of potential shows that charges are trapped at the

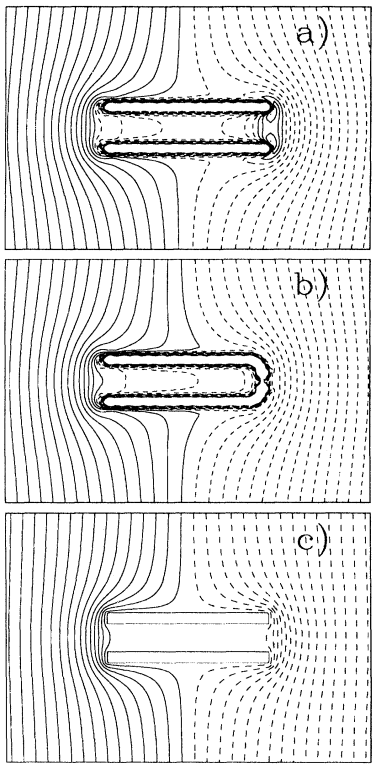

FIG. 4. The electrostatic potentials of a 300 carbon atom tube cluster with (a) an open and (b) a capped end configuration, in the same applied field as in Fig. 3. For comparison, the isopotentials of a perfect conductor hollow cylinder of similar aspect ratio in a uniform field are provided in (c). The contour levels are equally spaced (0.3 V per level) and the negative values are represented by dashed lines. The dimensions of each plot are 70 Å wide and 50 Å high.

atomic sites on the tube tip.

Since the nanotube remains basically isopotential, the potential drop over a short distance outside the tube tip will induce large local electric fields. To estimate the field enhancement around the tip of a long fullerene tube, we have performed an embedded cluster calculation in which the entire fullerene tube except the top segment is

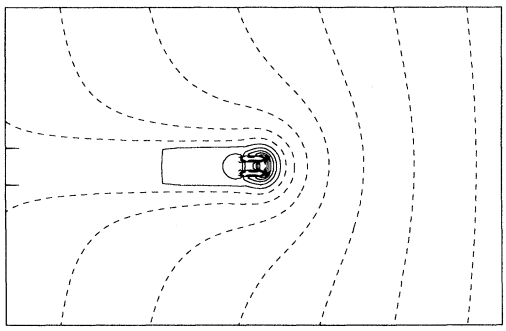

FIG. 5. The electrostatic potentials near the top of a long fullerene tube, as modeled by placing a tube cluster (of 120 atoms) on top of a metal post (see text). The contour spacings are 0.3 V. The dimensions of the plot are 300 Å wide and 200 Å high.

replaced by a perfectly conducting tube of similar size. The carbon cluster is thus embedded in the inhomogeneous fields induced by the substitute conductor tube in the presence of an external uniform field. In Fig. 5, we show the calculated electrostatic potential in a region around the embedded cluster simulating a long fullerene tube with an aspect ratio of 20. Our calculation shows that for a length-to-diameter ratio of 100, a factor of 80 enhancement of the local field strength at the tube tip can be obtained. To keep the electrons bound, positive potential bias has been used in these calculations.

In summary, we have studied the electronic structure of fullerene nanotubes in large external electric fields. We show that the electric field alone is not sufficient to make the open tube configuration more stable than the capped configuration. We also show that fullerene nanotubes can screen applied electric fields like perfect metals. This metalliclike screening occurs for tubes with electronically different structures and appears to be a general property of fullerene nanotubes. The strong charge accumulation at the tube tips may introduce a potential barrier that could prevent the tubes from closing.

This research was supported by the National Science Foundation, the Office of Naval Research, and the Robert A. Welch Foundation. The computations were performed using the Intel Touchstone Delta system operated by Caltech on behalf of the Concurrent Supercomputing Consortium. Access to this facility was provided by the Center of Research for Parallel Computation at Rice University.

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