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Effect of electric field on the electronic structures of carbon nanotubes

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We have investigated the electronic structures of a capped single-walled carbon nanotube under the applied electric field using density functional calculations. The capped tube withstands field strengths up to 2 V/Å. When the electric field is applied along the tube axis, charges are transferred from the occupied levels localized at the top pentagon of the cap, and not from the highest occupied level localized at the side pentagon, to the unoccupied levels. We find that the charge densities at the top of the armchair cap show two- or five-lobed patterns depending on the field strength, whereas those of the zigzag cap show a three-lobed pattern. The interpretation for the images of the field emission microscope is also discussed. © *2001 American Institute of Physics.*
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The superb chemical and mechanical stabilities and little tip degradation of the carbon nanotubes (CNTs) make them one of the promising candidates for field emitters. In addition, the high aspect ratio and small diameter of the CNT tip can lower the threshold voltage.[1] Recently, a flash lamp using CNT tips was developed,[2] and large size CNT-based field emission displays with full color have been demonstrated.[3] The emission currents from the CNT tips have been intensively studied and interpreted in terms of the Fowler–Nordheim equation, which fails at high field region.[3–5] The origin of current saturation at high fields has been attributed to the gas adsorbates. Yet, the effects of tip morphologies to the work function and turn-on voltage are not clearly understood.

Several groups reported field emission microscopy (FEM) images,[6,7] that are useful to the analysis of the field emission properties and tip structures of CNTs. The observed FEM patterns showed up to six-fold symmetries. While some symmetries in the FEM images are interpreted in terms of gas adsorbates, no clear relationship between the FEM images and nanotube tip structures has been demonstrated. The main difficulty arises from the absence of the reliable theoretical prediction of such patterns in relation to the surface morphologies. These FEM patterns are neither fully incorporated in previous theoretical calculations of the electronic structures of local tip,[8] nor the electronic structures of different surface morphologies.

In the present report, we present density functional calculations for the electronic structures of capped single-walled CNTs. We find that the two-lobed pattern can be observed in the FEM particularly at armchair cap even without the presence of gas adsorbates, and furthermore, the symmetry can be changed under different field strengths. We predict that in the case of the armchair cap, the FEM image with five-fold symmetry, originating from the degenerate lowest unoccupied molecular orbital (LUMO) and the next level from the LUMO, should be observed at low field strength, whereas the FEM image with a two-lobed pattern, originating from the highest occupied molecular orbital (HOMO) or the LUMO, should be observed at high field strength. We also predict that three-lobed pattern can be also observed in case of the zigzag cap.

In this study, we considered single-wall (5,5) and (9,0) nanotubes with a capped edge. The armchair (5,5) nanotube is modeled by five layers of carbon rings (50 carbon atoms) along the tube axis, whose one end is capped with C_{30} and the dangling bonds at the other end are saturated by hydrogen atoms to emulate an infinite tube.[9] The zigzag (9,0) nanotube is similarly constructed, again with six layers of carbon rings (54 carbon atoms) along the tube axis and further capped by C_{30}. The two carbon layers at the bottom in addition to hydrogen atoms are fixed during the whole simulations.

Our total energy calculations and the corresponding structure optimizations are based on the density functional formalism within the local density approximation and the generalized gradient approximation, as implemented in DMOL3 code.[10] All-electron Kohn–Sham wave functions are expanded in a local atomic orbital basis. In the double-numerical basis set, the $2s$ and $2p$ carbon orbitals are represented by two wave functions each, and a $3d$ type wave function on each carbon atom is used to describe the polarization. The forces on each atom to be converged during each relaxation are less than 10^{-3} a.u.

The optimized geometry of a capped (5,5) nanotube at neutral state shows that the top pentagon has equivalent bond lengths of 1.44 Å, longer than those of hexagons (1.42 Å) on the tube wall. We now apply the electric field along the tube axis. Figure 1 shows the total binding energies as a function of the field strength. The binding energy is approximately

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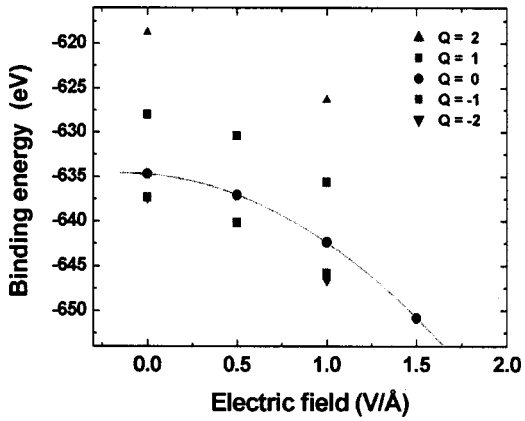

FIG. 1. The binding energy of a capped (5,5) nanotube carrying a charge Q, as a function of the strength of the applied electric field is shown.

proportional to the square of the strength of the applied electric field. The binding energy decreases when one more electron is added, and saturates at $Q=-2e$. This phenomenon is similar to that observed in C_{60} and attributed to the strong electron affinity of carbon species.

Figure 2 shows the energy levels of a capped (5,5) nanotube under different electric field strengths for a neutral state. The energy gap between the HOMO and LUMO is 1.4 eV, a little smaller than 1.9 eV of C_{60}. The corresponding local charge densities are shown in Fig. 3. The electron densities of the HOMO [Fig. 3(c)] and LUMO [Fig. 3(e)] are localized mostly at the side of the cap. This suggests that even though we used metallic tubes, the field emission can no longer be explained by the metal model because of the existence of the local band gap formation near the cap. For instance, the field emission currents from such capped metallic tubes cannot be fully explained by the Fowler–Nordheim equation.

The HOMO–LUMO gap decreases with increasing field strengths, suggesting the change of effective work functions. The degenerate states marked by filled diamonds move towards the Fermi level and finally become nondegenerate under high field strengths because of the increase of the Coulomb repulsion near the Fermi level. When the direction of the electric field is changed to 45° from the tube axis, the degeneracies are fully released compared to the same field

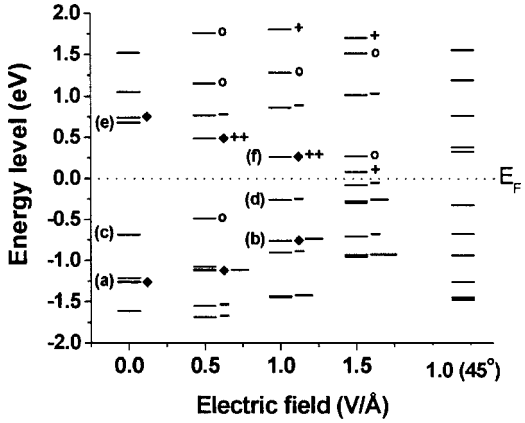

FIG. 2. The energy levels of a capped (5,5) nanotube with different field strengths for a neutral state are shown. The Fermi level E_F is set to zero. The degree of local charge transfer is illustrated as (+, 0, and −) and the degenerate states are marked by filled diamonds. The corresponding local charge densities of (a)–(f) levels are shown in Fig. 3.

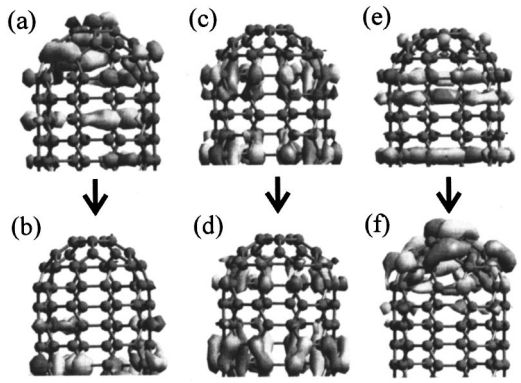

FIG. 3. Changes of local charge densities of a capped (5,5) nanotube are shown. The first row [(a), (c), and (e)] are local charge densities under no applied electric field. The second row [(b), (d), and (f)] are those under the electric field of 1 V/Å. The corresponding energy levels are indicated in Figs. 2(a) and (b) are the second energy levels from the HOMO, (c) and (d) are the HOMO, and (e) and (f) are the LUMO.

strength of 1 V/Å applied to the tube axis, as shown in the last panel in Fig. 2. In this field direction, the charge densities are shifted asymmetrically along the *xz* direction. Here, we note that the charge transfer does not occur directly from the HOMO to the LUMO. This is related to the local charge densities of the pentagons located at the side of the cap, as will be discussed in the following.

Figures 3(a) and (b) illustrate the local charge densities of the second level from the HOMO, where the localized charge densities at the top of the cap leak out completely. The HOMO states are localized at the pentagons located at the side of the cap, where the charge densities also leak out but relatively less than those at the top pentagon. This can be understood in terms of the different alignments of the π orbitals. While the π orbitals at the top pentagon site are well polarized, because they are parallel to the field direction, those at the side pentagon sites are less polarized, being almost perpendicular to the field direction.[11] When the electric field is applied, the LUMO is always filled first, as can be seen in Fig. 2. Figures 3(e) and (f) clearly demonstrate the charge densities of the LUMO, which is localized at the cap under the high electric field.

We now consider the charge density of the top cap,

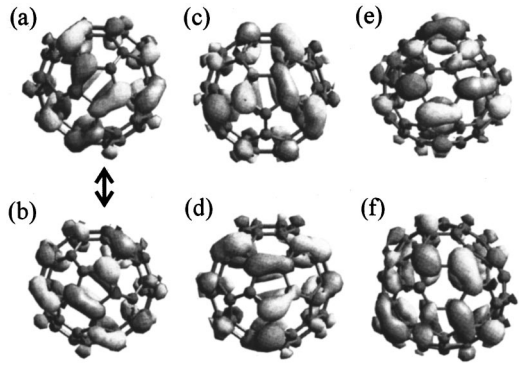

FIG. 4. Top view of local charge densities of a capped (5,5) nanotube is shown. The first column [(a) and (b)] is the case of low electric field ($F=0$ V/Å and $Q=-1e$). (a) is the LUMO and (b) is the next level from LUMO and these levels are degenerate. The second column [(c) and (d)] is the case of high electric field ($F=1$ V/Å and $Q=-1e$). (c) is the HOMO and (d) is the LUMO. The third column [(e) and (f)] is a capped (9,0) nanotube under the electric field ($F=1$ V/Å and $Q=0$).

which may be compared with the FEM image. Figures 4(a) and (b) show the top view of the charge densities of the LUMO and the next level from the LUMO at zero field (or low field limit in practice), where the charge densities are shown only at the cap sites. Although each state shows two lobes, both are degenerate states and hence a five-fold symmetry can be shown by the superposition of two images. The situation, however, is different in the high field region.[12] Both the HOMO and LUMO states show two lobes and cannot be superposed, because they are nondegenerate. Therefore, a two-lobed pattern should be observed in the FEM under a high electric field. Dean and Chalamala have observed two lobes in the FEM images, although these are interpreted in terms of gas adsorbates.[6] Five- and six-fold symmetries are shown only after high-temperature annealing (900 K). However, the chances of breaking the cap structure upon such an annealing were not discussed. Saito *et al.* also observed a five-fold symmetry in the FEM images.[7] Our calculations suggest that two-lobed pattern can be obtained at the high field region even without the presence of gas adsorbates.

So far, we have calculated the charge densities at different field strengths for a given capped armchair tube. Since the symmetries of the charge densities are expected to be strongly dependent on the cap structure, here, we provide another example of a capped zigzag tube which shows different symmetry in the charge density. Figures 4(e) and (f) show the HOMO and LUMO states that exhibit three-lobed pattern for both cases, revealing different symmetries from the capped armchair tube. Among all other states near the Fermi level, the HOMO and LUMO are localized exclusively at the cap. A six-fold symmetry may be observable from the deeply occupied states at higher field strength.

In summary, we found charge transfer mechanism of CNTs under the applied electric field using density functional calculations. We note that the charge transfer does not occur directly from the HOMO to the LUMO, but from occupied levels localized at the top pentagon of the cap to the unoccupied levels. This is related to the alignment of π orbitals and the local charge densities of the pentagons located at the cap. We explained lobed patterns of a FEM of CNTs in terms of charge densities localized at the top of the capped structure. The armchair cap showed two- or five-lobed patterns depending on the field strength, whereas the zigzag cap showed a three-lobed pattern.

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[10] DMO13 is a registered software product of Molecular Simulations Inc.; B. Delley, J. Chem. Phys. **92**, 508 (1990).
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[12] The FEM images were usually observed in field strength of a few hundreds V/cm (low field limit). The local field is expected to be amplified by the field enhancement factor due to the sharpness of the CNT tip. So, field emission typically occurs when the actual field at the tip is ~0.5 V/Å in an experimental situation (see Ref. 11).