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Enhanced Electron Field Emission in B-doped Carbon Nanotubes

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ABSTRACT

Field emission properties of B-doped carbon nanotubes are investigated from both theoretical and experimental standpoints. Using tight-binding and ab initio calculations, it is observed that B-saturating tip edges of carbon nanotubes induce the presence of large peaks within the local density of states (LDOS) located in an energy region close to the Fermi level (Ef). These localized states suggest a field emission enhancement for the B-doped tubes. In addition, ab initio theoretical results indicate that the work function for B-doped tubes is 1.7 eV lower when compared to pure carbon-terminated nanotubes. Experimentally, it is found that B-doped tubes, which are produced by arc discharge techniques and contain B mainly at the tips, exhibit stable electron field emission at lower turn-on voltages (1.4 V/μm) when compared to pure single- and multiwalled carbon nanotubes (2.8 and 3.0 V/μm, respectively) measured under the same conditions. We strongly believe our results will bring new insights in the fabrication of stable field emission sources.

Due to their unique tubular structure and dimensions, carbon nanotubes[1] exhibit fascinating mechanical and electronic properties.[2] Ten years after their identification,[1] these tubules continue to display intriguing properties and novel applications. Among these, the usage of nanotubes is found in the fabrication of (a) electron field emitters,[3−5] (b) STM tips,[6] (c) gas storage devices,[7−10] (d) actuators,[11] (e) high power electrochemical capacitors,[12] (f) sensors,[13−14] nanotransistors,[15,16] (g) nanothermometers,[17] (h) Fe-filled nanotubes as magnetic storage devices,[18] etc.

Controlling the growth of carbon nanotubes has been a great challenge in tailoring their electronic properties, because the nanotubes may behave as metals or semiconductors depending on the chirality and diameter.[19,20] However, it is possible to circumvent this problem by doping carbon nanotubes with different atoms, which can be incorporated within the hexagonal carbon network. In this context, it has been demonstrated that B (or N) can greatly modify the electronic properties of nanotubes so that acceptors (or donors) dominate the electronic structure of the system (e.g., from semiconductor to metallic).[21,22]

In this account, we demonstrate that B doping also influences significantly the field emission performance of carbon nanotubes. In particular, we have carried out tight-binding and ab initio calculations on armchair and zigzag tubes, demonstrating that B atoms, located at the tip edges of the tubules, are responsible for an enhancement in the electron field emission. The latter is caused by the presence of electronic states in the valence and conduction bands close to the Fermi energy, Ef. In addition, we have used arc techniques to produce multiwalled B-doped tubes saturated with B, which revealed excellent field emission at low voltages. To the best of our knowledge, this is the first time that doped nanotubes exhibit notable electron emission properties at extremely low turn-on voltages.

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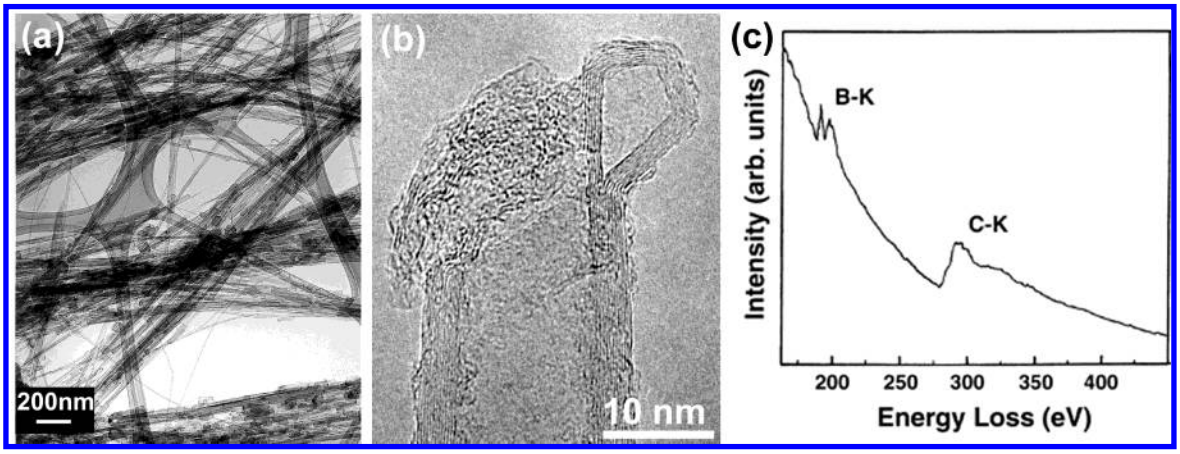

Figure 1. (a) TEM image of B-doped carbon nanotubes produced by arc techniques. These tubes are much longer (<100 μm) than those produced in a standard carbon arc apparatus. (b) HRTEM image of a B-doped carbon nanotube. In these samples is usually found the presence of ill formed caps, which exhibit larger concentrations of B. It is believed that B acts as a surfactant during growth, which results in the formation of long tubules. (c) Typical EEL spectrum revealing the presence of B (ionization K-shell edge at ca. 188 eV) and C (ionization K-shell edge located at ca. 284.5 eV) mainly at the tip.

To obtain the local densities of states (LDOS) of various types of B-doped and undoped tubes, we have performed tight-binding (TB) calculations using a recursion approach,[23] which has proved to model accurately carbon nanotube tips[24] and to capture the essential features associated with composite $B_xC_yN_z$ nanotube heterojunctions.[25] Ab initio calculations were carried out using standard multigrid-based real space.[26]

B-doped carbon nanotubes were prepared by DC arcing BN/graphite electrodes in an inert atmosphere (e.g., He, N_2) at 500 Torr. The tubes were collected from the inner core deposit formed on the cathode. A detailed description of the synthesis of this material can be found elsewhere.[27−28]

Field emission measurements were performed by creating a nanotube cathode, using B-doped carbon nanotubes dispersed in an SDS solution.[29] The dispersion was then centrifuged, and the liquid phase filtered with a 0.4 μm pore size filter. Subsequently, the deposits on the filter were washed and dried in air for several days in order to give a conducting film comprising pathways of randomly oriented nanotubes. Only the optimally oriented nanotubes contribute to the field emission current. Using randomly oriented nanotube films with even quantities of nanotube material ensures that the averaged local screening effects are constant from sample to sample. Assuming a random distribution of nanotube orientations, we estimate an emission site density $>10^9$ cm^2. Electrical contacts were made directly on the nanotube film. The measurements were performed using a parallel plate configuration with an area of 0.25 cm^2. The field emission performance was also recorded for single- and multiwalled carbon nanotubes for comparison using the same configuration.

The B-doped carbon nanotubes used in the present study usually consist of nested tubules, which are crystalline and long ($\leq$ 100 μm). In various occasions these tubes also exhibit ill-formed caps, opened or with negative curvature regions (Figure 1), in which higher B concentrations are also present, as observed by electron energy loss spectroscopy (EELS) analyses,[27−28] (Figure 1). The fact that the tubes are long suggests that boron acts as surfactant and catalyst during formation. In this context, it has been demonstrated, using ab initio calculations, that B can indeed catalyze the growth of long tubes of zigzag chirality, in which B is preferentially located at the tube tips.[30] EELS studies have also shown that only minute B traces (<1%) are present within the tube bodies[31] and that B is often located at the tube tips with concentrations as high as 10%.

To investigate the effect of boron doping localized mainly at the end of carbon nanotubes, TB simulations were performed and local densities of states (LDOS) were calculated for different tip topologies and tube chiralities. We first studied the presence of B atoms within the carbon network of a perfectly closed nanotube. A regular (10,10) armchair nanotube is thus constructed with a capping C_{240} hemifullerene. For such a nanostructure made solely of carbon atoms, sharp localized electronic states, associated with the presence of pentagons, are known to appear close to the Fermi energy,[24] (Figure 2 red curve). When B is randomly substituted at the tip apex (~10%), some modulations of the LDOS are observed, mainly at the onset ($\leq$8 eV) of the π-valence bands region (Figure 2 green curve). However, only minor changes appear at the Fermi region.

We also investigated the electronic properties of open-ended zigzag and armchair tubes containing B saturating the edges at the tips. Figure 3a shows the LDOS for a (5,5) tube (Figure 3a black curve) with open nonsaturated edges (Figure 3a red curve) and B dimer terminated tip (Figure 3a green curve). It is clear from these curves that the B-doped tube exhibits huge LDOS nearly at the Ef (0.2 eV) as well as large localized electronic peaks close below (at ca. −1.2 and −1.5 eV) and above (at ca. 1.0 eV) the Fermi energy, and which can be clearly associated with the presence of B atoms at the nanotube edge.

The large signal located at Ef indicates that these tubes may behave as metals, as demonstrated by microwave conductivity,[32] scanning tunneling spectroscopy measurements,[21] and transport measurements.[33] In addition, the presence of large localized peaks close to Ef suggests good

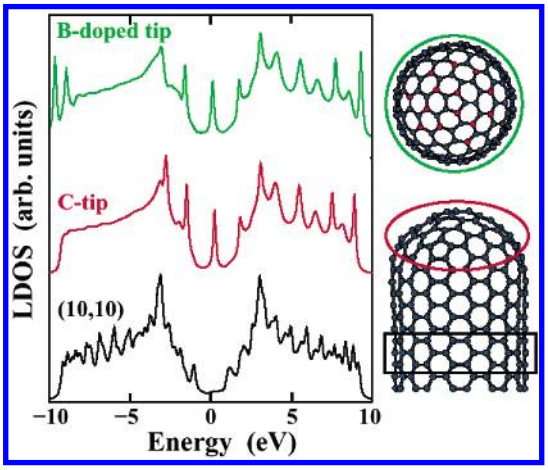

Figure 2. Tight-binding densities of states of B-doped and undoped armchair (10,10) nanotubes capped by half a C_{240}. The DOS of the perfect (10,10) tube is shown in black. The LDOS averaged over the tip region for a pure carbon structure and for a random B doping (∼10% − red spheres) are shown in red and green, respectively.

emission properties, as the Fermi region is completely filled by Boron electronic states.

Electron diffraction studies have indicated that B-doped carbon nanotubes exhibit a preferred zigzag chirality.[30] Therefore, calculations were also carried out on B-terminated zigzag tubes. Figure 3b shows the LDOS for an open (10,0) tube with B at the edges. In this case, localized states are located only on the valence region at ca. −0.5 and −1.0 eV (Figure 3b green curve). Again, these huge intensities suggest a good field emission performance of the doped tubes. For an undoped open zigzag tube, the LDOS shows only a single localized peak at the Ef (Figure 3b red curve). This result is in perfect agreement with recent ab initio calculations which demonstrate that dangling bond states localized at the clean edges of zigzag graphitic ribbons are major contributors to the field emission current,[34] with the peaks being located exactly at the Fermi energy. On the other hand, armchair graphitic ribbons display dangling bond states at ±3.0 eV around the Fermi level,[34] as also observed in Figure 3a (green curve). Again, we believe that for the zigzag case, the electron emission of the B-doped material may be superior due to the numerous states located close to the Ef. Similar DOS for the B-doped carbon nanotubes, exhibiting large intensities close to the Ef, have also been calculated in this study using ab initio techniques. Some of these localized states associated with boron dopants at the tip of the open tubes are illustrated in Figure 4.

The enhancement in the field emission properties can also be predicted by investigating the modification of the work function due to the presence of the boron atoms at the nanotube edges. For example, ab initio calculations indicate that the work function for a small (9,0) carbon nanotube, terminated with B, is reduced by 1.7 eV when compared to the analogue undoped carbon nanotube. This confirms that the presence of B indeed improves the electron emission properties of the system.

We have performed measurements on thin films of B-doped tubes in order to verify the predicted enhancement

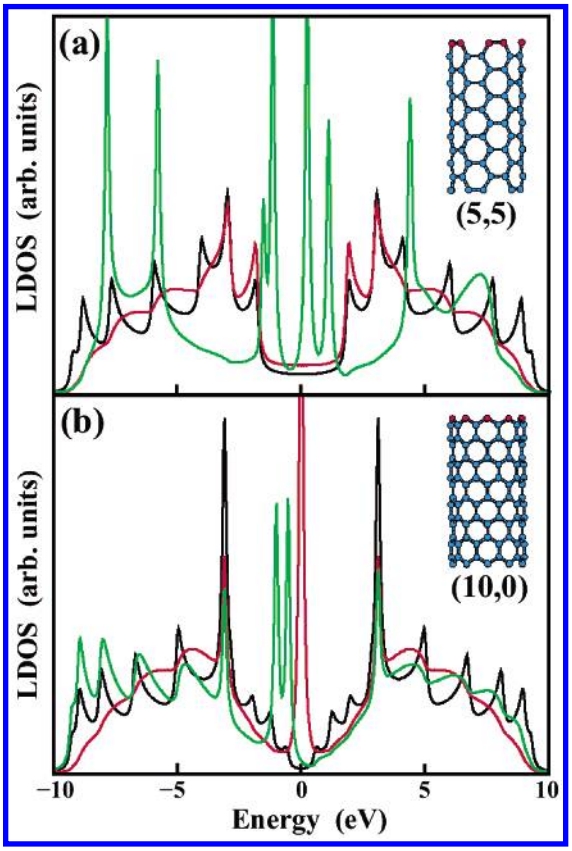

Figure 3. Tight-binding electronic properties of B-doped and undoped open-edged armchair (a) and zigzag (b) nanotubes. The effect of B-doping is illustrated by comparing the LDOS averaged over the edges of a pure carbon structure − undoped tube (a,b red curve) and B dimers (red spheres) at the armchair edges (a, green curve) or B dangling atoms (red spheres) at the zigzag edges (b, green curve). The B-doped material exhibits numerous localized states in the Fermi energy region, suggesting good field emission properties. Black curves indicate the DOS of perfect infinite (5,5) and (10,0) tubes in (a) and (b), respectively, which are shown for comparison.

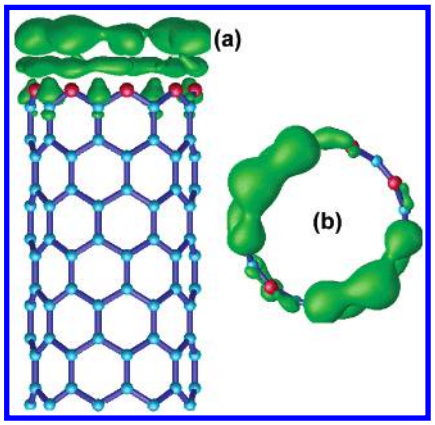

Figure 4. Side (a) and top (b) views of localized states at the edges of a boron saturated zigzag (9,0) carbon nanotube computed using ab intio calculations. The work function of this tube is 1.7 eV lower than that of the same nanotube made exclusively of carbon atoms.

for field emission. We also compared the results with the corresponding values obtained for SWNTs and MWNTs. Figure 5 shows current density, *J*, vs applied field, *E*, emission characteristics for B-doped and pure carbon MWNT

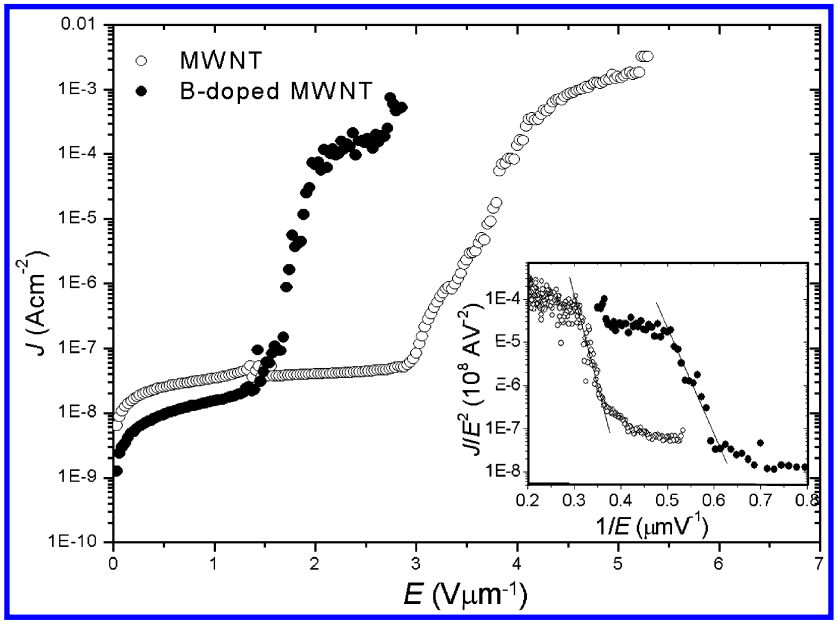

Figure 5. $J-E$ emission characteristics measured in parallel plate configuration of the B-doped nanotube films and comparable films of pure carbon arc-produced MWNTs. The plate area was 0.25 cm^2. Inset shows the Fowler−Nordheim plots for each curve. The calculated field enhancement factor β was found to be ca. 1000.

thin films. These films were prepared under identical conditions with the same concentration of nanotubes using the method outlined in ref 29. It is clear that the B-doped material exhibits a low turn-on field (1.4 V/μm), whereas comparable films of pure carbon MWNTs require higher applied fields in order to observe the onset of electron emission (3 V/μm). These results indicate an enhanced emission from the B-doped tubes when compared to MWNTs. In this context, it is also important to note that the turn-on field we observed for SWNTs was ca. 2.8 V/μm. We should also note that our results with B-doped tubes are comparable to the best results obtained for other carbon-based cold cathodes (e.g., amorphous carbon, diamond-like carbon, N-doped diamond, fullerene-like carbon).[35]

In Figure 5, we observe that the field emission current density tends to saturate for B-doped nanotubes for fields >2 V/μm, a common feature of carbon-based cold cathodes. The corresponding Fowler−Nordheim (FN) plots shown on the inset of Figure 5 indicate the linear region of an FN-type emission mechanism. The field enhancement factor, i.e., the ratio of the microscopic field at the nanotube tip to the average applied macroscopic field, can be extracted from the linear region, and it was found to be ca. 1000 assuming a work function of 5 eV that is common to carbon nanotubes, C_{60}, and graphite. If the aspect ratio of the B-doped carbon nanotubes is 10000, and used as a field enhancement factor, the FN plot reveals a work function of 16 eV; an unphysical high value for the low B-dopant concentration. This measurement by itself cannot determine whether enhanced field emission is the result of a field enhancement factor and/or reduced work function. However, ab intio calculations demonstrate that the work function for B-doped nanotubes is 1.7 eV smaller than that of undoped carbon nanotubes. This indicates that B at the tips of the tubes is mainly responsible for an enhanced field emission response, but the fact that the tubes are long will enhance even further the electron emission. Because the conditions for field emission are not fully optimized, it should be possible to improve the emission performance. Thus we believe this doped material has great potential in the development of stable field emission flat panel displays.

Very recently, Zhang et al.[36] and Meunier et al.[37] have reported on the electron field emission enhancement for capped B-doped carbon nanotubes and composite BCN nanotubes. However, none of these accounts reported on the effects of an open carbon nanotube saturated with B atoms. Our results indicate that open tubes terminated with B atoms exhibit considerable lower work functions when compared to those reported in these works.

In summary, we have computed the LDOS for B-doped open-edged nanotubes of zigzag and armchair chiralities using a tight-binding Hamiltonian. In both cases, we observed numerous localized states close above and below the Ef, indicating good field emission performance. Ab initio calculations have confirmed these findings and provided an explanation of the field emission enhancement by a reduction of the work function due to the presence of boron atoms at the nanotube edge. From the experimental point of view, B-doped carbon nanotubes do indeed exhibit electron emission at low turn on fields (e.g., ca. 1 V/μm). These results demonstrate for the first time that B-doped tubes show great potential as building blocks for stable and intense field emission sources, thus opening new avenues in vacuum microelectronics. Furthermore, N-doped nanotubes[22] could also exhibit enhanced electron emission: possibly a new branch of research with the prospect of ultralow field emission sources.

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