Half metallicty in finite-length zigzag single walled carbon nanotube: A first-principle prediction

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Half metallicty in finite-length zigzag single walled carbon nanotube: A first-principle prediction

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We predict here from first-principle calculations that finite-length $(n,0)$ single walled carbon nanotubes (SWCNTs) with H-termination at the open ends displaying antiferromagnetic coupling when n is greater than 6. An opposite local gating effect of the spin states, i.e., half metallicity, is found under the influence of an external electric field along the direction of tube axis. Remarkably, boron doping of unpassivated SWCNTs at both zigzag edges is found to favor a ferromagnetic ground state, with the B-doped tubes displaying half-metallic behavior even in the absence of an electric field. Aside of the intrinsic interest of these results, an important avenue for development of CNT-based spintronic is suggested. © *2008 American Institute of Physics*.
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The emerging field of spintronics seeks to exploit electronic spin in addition to electronic charge and is igniting a revolution in computer science, information science, and many other areas.[1,2] A key challenge stimulating innovation in this area is how to efficiently manipulate the spin polarization of current. A half metal, i.e., a material which filters the current into a single spin channel without any external operation, fully meets this demand.[3,4] In the search for materials for spintronics applications, single walled carbon nanotubes (SWCNTs) have been proposed as promising candidates due to their peculiar electronic structure and properties.[5–7] Currently, most existing efforts have focused on metal doping of SWCNTs and gate control by connecting CNTs with ferromagnetic (FM) leads.[5,8,9] Recently, zigzag graphene nanoribbons (GNRs) have been reported to carry a spin current response to an external electric field,[10] which opens a pathway for the development of carbon-based spintronic devices. Finite-length open-ended zigzag SWCNTs can be considered to be rolled from finite-length zigzag GNRs.[11] An interesting question is whether half metallicity could be preserved in finite-length zigzag $(n,0)$ SWCNTs. Theoretically, magnetism in finite-length zigzag SWCNTs has been reported in earlier studies.[12–14] Higuchi *et al.* further confirmed that magnetism could possibly arise from zigzag edge effects and showed that the reactions to create hydrogenated (7, 0) or (8, 0) SWCNTs are exothermic.[15] Very recently, Likodimos *et al.* observed antiferromagnetic (AFM) behavior experimentally in SWCNTs.[16] However, antiferromagnetism and half-metallicity in finite-length SWCNTs has not yet been reported.

In this letter, we present ab initio density functional theory (DFT) calculations based on the local spin density approximation (LSDA) to explore whether there exists AFM coupling and half metallicty in zigzag SWCNTs. Remarkably, we find that finite-length hydrogenated zigzag $(n,0)$ SWCNTs have an AFM ground state if n is greater than 6. Similar to GNRs,[10] the opposite local gating effect of the spin states on the two ends of nanotube is seen to occur in the presence of external electric field along the direction of tube axis. Most interestingly, we find that an unpassivated SWCNT with B-dopants at both zigzag edges favors a FM ground state and shows half-metallic behavior even in the absence of electric field. These results suggest an avenue for the future development of nanotube-based spintronics devices.

The present magnetism calculations in finite-length and open-ended SWCNTs were performed using the plane-wave basis VASP code[17,18] implementing the LSDA exchange correlation functional.[19] An all-electron description, the projector augmented wave method[20,21] is used to describe the electronic-ion-core interaction. The cutoff energies for plane waves are chosen to be 500 eV and the vacuum space is at least 12 Å in x, y, and z dimensions of supercell, which is enough to separate the interaction between periodic nanotube images. Only the Γ point is used for sampling the one-dimensional Brillium Zone due to the large supercell used. All the atoms in the supercell were allowed to relax and the force tolerance was set at 0.01 eV/Å. To explore the effect of external electric field along tube axis, all-electron DFT calculations were performed at LSDA/6-31G level by using GAUSSIAN 03 program package.[22] Diffusion function was not included due to the limitation of computational feasibility in very large system.

The lengths of $(n,0)$ nanotubes are defined according to the number of carbon atoms along the tube axis (labeled L4, L6, etc.). A series of hydrogenated and open-ended $(n,0)$ zigzag SWCNTs with three different lengths (L4, L6, and L8) were built.[23] The structures were fully optimized in a large supercell by using a spin-unpolarized DFT calculation and the relaxed equilibrium nanotube structures were used as the initial configuration for further optimizing three magnetic

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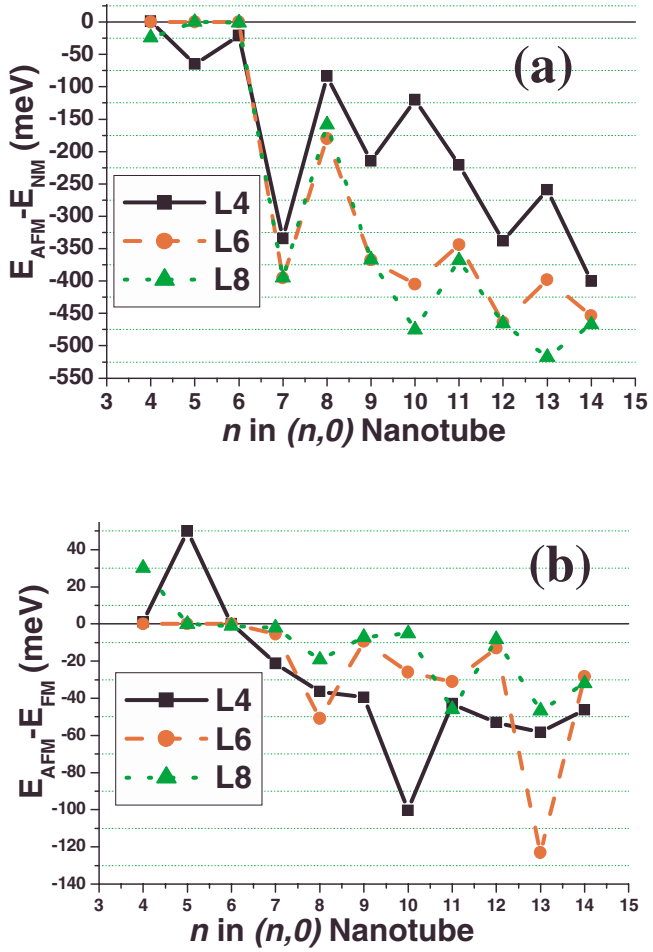

FIG. 1. (Color online) (a) The variation of energy difference between AFM and NM phases in finite-length open-ended $(n,0)$ nanotubes as a function of n. (b) Similarly, variation of energy difference between the AFM and FM phases.

phases, i.e., the nonmagnetic (NM), FM, and AFM states. The energy differences between AFM and NM and between AFM and FM (i.e., E_{AFM}-E_{NM} and E_{AFM}-E_{FM}) as a function of the dimensions of $(n,0)$ nanotubes were then calculated, as plotted in Figs. 1(a) and 1(b), respectively. Clearly, the stability of magnetic phases depends strongly on the specific diameter and length of finite nanotubes. FMs are more stable than AFM phase for a (5, 0) nanotube with length of L4 and (4, 0) nanotube with length of L8. As the diameter of the SWCNT increases, all the finite-length $(n,0)$ zigzag nanotubes will become magnetic and AFM phase appears in these calculations to be the ground state when the dimension of nanotube (n) is greater than 6. We should note that limitations of computational feasibility prevent us from pushing to sufficient lengths of nanotube. It would be expected that E_{AFM}-E_{FM} will decrease with increasing length of tube as that observed in zigzag GNRs.[10]

In Figs. 2(a) and 2(b), we present three-dimensional isosurfaces (the isovalue is 0.01 $e/\mathrm{Å}^3$) of spin charge density magnetization $(\rho_\uparrow$-$\rho_\downarrow)$ in an open-ended (8, 0) nanotube with a length of L6 for the FM and AFM phase, respectively. The corresponding densities of states were also plotted in Figs. 2(c) and 2(d). Apparently, the magnetic charge density is mainly localized at the zigzag edge of two open ends in the FM phase. In the AFM phase, spin-up and spin-down charge densities were distributed at each open end and decay from

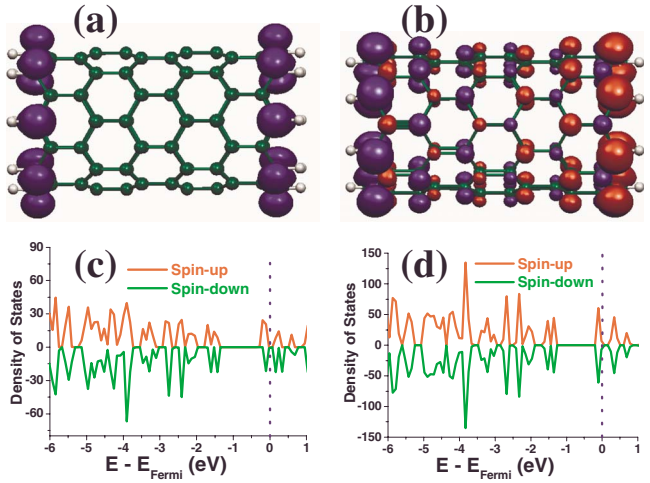

FIG. 2. (Color online) Three-dimensional isosurfaces of spin charge density magnetization $(\rho_\uparrow$-$\rho_\downarrow$, the isovalue is 0.01 $e/\mathrm{Å}^3$). for the (a) FM and (b) AFM phases in L6-(8, 0) nanotube. (c) and (d) represent the corresponding density of state for (a) and (b). Blue and red represent positive and negative, respectively.

the edges to the middle. The local magnetic moment in the middle is nearly zero, indicating that the magnetic moment arise from the zigzag edge.

The AFM coupling for the finite-length, open-ended $(n,0)$ SWCNT was further confirmed by full electron calculations using GAUSSIAN 03.[22] An (8, 0) SWCNT with three different lengths (L4, L6, and L8) was chosen as an example for study. The same functional (LSDA) as in the former plane-wave calculations is used for comparison. The stability of AFM state with respect to the above lying higher spin multiplicity state was verified by the calculation at LSDA/6-31G level. The energy differences, i.e., E_{AFM}-E_{NM} and E_{AFM}-E_{FM} for L6-(8, 0) nanotube are −216 and −63 meV, respectively. These are in good agreement with the plane-wave calculations, as shown in Fig. 1.[24]

Having explored the electronic properties for an open-ended zigzag (8, 0) nanotube with different lengths, we now turn to study the effect of external electric field. Figure 3 presents the spin-polarized highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gap dependence on an external field along the direction of tube axis for three different lengths (L4, L6, and L8). Clearly, all α and β spin energy gaps are degenerate in the absence of electric field. They are 0.38, 0.43, and 0.35 eV for L4, L6, and L8, respectively. With the application of the

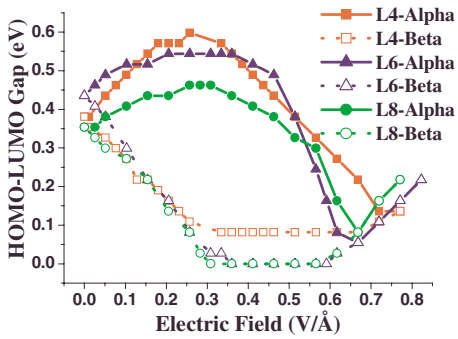

FIG. 3. (Color online) The dependence of spin-polarized HOMO-LUMO gap on the strength of an external electric field along the tube axis for (8, 0) nanotube for L4, L6, and L8, respectively.

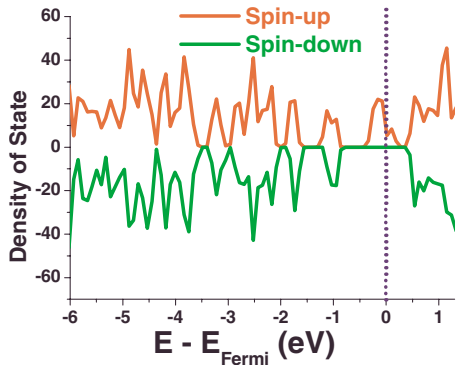

FIG. 4. (Color online) Up- and down-spin densities of state of L8-(8, 0) SWCNT with both edges doped by B atoms. Blue dot line represents the Fermi level.

external field, the spin-down HOMO-LUMO band gap decreases rapidly while the spin-up band gap experiences a steady increase. This trend is consistent for all nanotube lengths, until the spin-down band gap for the very short nanotube (L4) levels out at a finite value of 0.008 eV when the electric field ranges from 0.33 to 0.65 V/Å, whereas the spin-down band gap for the longer tubes decreases to zero. Both spin-up and spin-down channels meet together when the field reaches about 0.8 V/Å.[25,26] Clearly, the very short zigzag nanotube (L4) could not be half metallic at any field strength. For longer nanotubes (L6 and L8), the spin-down gaps vanish at intermediate field strength as described above, while the spin up channels remain semiconducting. This indicates that half metallicity is predicted in open-ended finite-length zigzag nanotubes (excepting the very short L4), as has been found in the GNRs. However, the half metallicity will be destroyed if the electric field along tube axis is too strong (around 0.65 V/Å in the present calculations). Hence, the finite-length zigzag nanotubes will only display half metallicity for a limited range of external electric field. The threshold of external field for appearance of half-metallicity (0.3 V/Å in the present calculations) is almost the same for the L6 and L8 nanotubes.

The three coordinated boron (B) atom is a common dopant in carbon materials. It may introduce holes in strongly correlated low-dimensional systems as proposed earlier.[27] In order to explore the potential effects of such doping on the magnetic and electronic properties discussed above, we have carried out additional calculations in which the edge C atoms in an L8-(8, 0) SWCNT are replaced by B atoms. We found that the system is predicted to be NM in the presence of H-passivation of the B edge atoms. However, in the absence of H-passivation, the edge B-doped finite-length SWCNT is FM and the energy difference between AFM and FM phases is only 2 meV. In Fig. 4, we plot the up- and down-spin densities of states for this system. Remarkably, even in the absence of any electric field, the unpassivated B-doped SWCNT shows metallic behavior for majority spin and insulating behavior for the minority spin, i.e., half metallicity.[28]

In summary, we have demonstrated by a systematic series of *ab initio* DFT calculations that the ground state of finite-length and open-ended $(n,0)$ zigzag nanotubes is AFM and exhibits half metallicity under the influence of an external electric field along the tube axis. The realization of antiferromagnetism and half metallicity is found to depend strongly on the diameter and length of the nanotube. Our calculations indicate that the necessity of an electric field aligned with the nanotube axis to create complete spin polarization can be circumvented by nonmetallic doping: unpassivated SWCNTs with B substitution at both zigzag edges are predicted to favor a FM ground state and exhibit half-metallic behavior even in the absence of an applied electric field. This suggests that the half metallicity in the case of the B-doped systems—in addition to being manifested in a field-free environment—is also likely to be less sensitive to physical dimensions such as length and diameter, potentially allowing greater tolerance limits in terms of device fabrication. These results highlight an intriguing avenue for future investigations in the development of nanotube-based nanospintronic devices.

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