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First-Principles Study of Li Doping in a Double-Wall Carbon Nanotube *

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By performing first-principles calculations, we study Li doping in a double-wall carbon nanotube where a (5,0) tube is confined inside a (14,0) tube. There are three possible sites for Li doping and two of them are energetically favorable. The change of energy band structure is closely related to the doping sites and the charge transfer is investigated. Bader charge analysis indicates that Li prefers to donate its electron to the inner (5,0) tube. Moreover, the Li capacity of the system can reach $LiC_{4.75}$ which makes it a promising candidate for Li-ion battery materials.

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Due to their interesting quasi-one-dimensional character, carbon nanotubes have attracted much attention from the science community for more than ten years. The interior space of single-wall carbon nanotubes (SWNTs) can be used to encapsulate many molecules, which offers an opportunity to explore new one-dimensional systems with nanosizes. Recently, double-wall carbon nanotubes (DWNTs) have been synthesized by a high temperature coalescence of the C_{60} molecule confined inside SWNTs.[1,2] Similar to the SWNTs, DWNTs also exhibit characteristic breathing-like modes, which have been identified by Raman measurement.[3−8] The intertube distance of DWNTs is close to that of graphite and varies from 3.3 Å to 4.1 Å.[9] It is thus assumed that the tube-tube interactions in DWNTs are dominated by the van der Waals force. Bellarosa *et al.*[10] discussed the radius and chirality contributions to such interactions. Intertube charge transfer and electrical conductance have also been investigated in DWNTs,[11−15] and possible applications in fields such as quantum dots[16] and field-effect transistors[17] were discussed. Moreover, the additional interlayer space of DWNTs offers good opportunities to modify the physical properties of carbon nanotubes by means of doping. For example, the co-doping of K and Br in the inner and outer shell of (7,0)@(16,0) DWNT makes it an ideal candidate for p-n junction and diode applications.[18] On the other hand, it was found experimentally and theoretically that SWNTs are plausible candidates for Li-ion battery materials,[19−25] and ultra-small diameter (4 Å) carbon nanotubes confined in zeolite have a much higher Li capacity.[26] In this Letter, we consider the doping of Li into a related system where the 4 Å tube (5,0) is confined in a larger (14,0) tube. We choose (5,0) as the inner wall of DWNT since it is very favorable for Li doping,[21,27] and the outer wall is thus determined by the intertube distance.

Our calculations are performed using a plane-wave pseudopotential formulation.[28−30] The exchange-correlation energy is in the form of Perdew-Wang-91[31] with generalized gradient corrections (GGA). We use ultra-soft pseudopotentials for both the C and Li atoms. The cutoff energy is set to 286 eV and uniform k-points are used along the tube axis. We use a standard supercell geometry so that the DWNTs are aligned in a hexagonal array, and the center-to-center distance between the DWNT and its periodic image is set to 24 Å. Optimal atomic positions are determined until the magnitude of the forces acting on all atoms becomes less than 0.05 eV/Å.

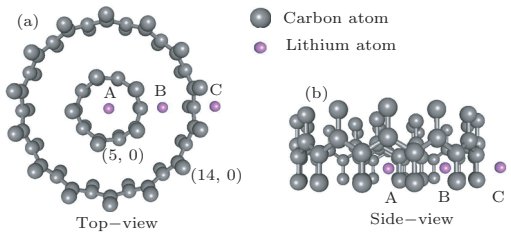


Fig. 1. Top and side view of possible Li doping sites in the DWNT (5,0)@(14,0). Note that each site may have many equivalent positions.

The unit cell of the chosen DWNT contains 76 carbon atoms where 20 come from the inner (5,0) tube and 56 from the outer (14,0) tube. Figure 1 schematically shows possible Li doping sites in the DWNT. In addition to the interior of the (5,0) tube (site A), the Li atom can be also intercalated into the area between the inner wall and outer wall (site B). It is also possible for Li to be doped outside the (14,0) tube (site C). Note that each site may have many equivalent po-

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sitions. We begin our investigation with one Li atom per unit cell. For all three configurations, we find that the DWNT keeps a very stable structure upon Li doping, and there is almost no change of the tube radius. Table 1 summarizes the calculated Li binding energies for the three doping sites in the DWNT. For comparison, the results for the individual (5,0) and (14,0) tubes are also given. The binding energy E_b is defined by the expression

$$E_b = E(\mathrm{DWNT} + \mathrm{Li}) - E(\mathrm{DWNT}) - E(\mathrm{Li}),$$

where $E(\mathrm{DWNT} + \mathrm{Li})$ is the total energy of the DWNT with one Li atom doped, $E(\mathrm{DWNT})$ is the total energy of the pristine DWNT, and $E(\mathrm{Li})$ is the total energy of one Li atom in bulk structure (bcc). A negative number for the binding energy corresponds to an exothermic reaction. For the individual SWNT, we can find from Table 1 that the Li atom would prefer to be doped into the interior of the smaller (5,0) tube rather than that of the larger (14,0) tube. This is also the case for the outside doping in the (5,0) and (14,0) tubes. For the DWNT, we can find from Table 1 that two of them are energetically favorable. One with the lowest energy is site B which can also be visualized as the outside of the (5,0) tube or the inside of the (14,0) tube. It should be noted that this energy value is significantly lower than those found at the corresponding sites of the individual (5,0) and (14,0) tubes. This is reasonable since at the intertube space, the Li binds to both the inner and outer walls of the DWNT, while only one wall is involved for the case of individual tubes. It is interesting to find that the interior of the DWNT has a higher binding energy than that of the (5,0) tube, while the exterior of the DWNT has a lower one than that of the (14,0) tube. This is probably due to small charge transfer from the outer shell to the inner shell.[13] Indeed, we have carried out an additional calculation which shows that for the un-doped DWNT about 0.29% of the π electrons of the (14,0) tube are given to the (5,0) tube. The transferred electrons will enhance the Li binding to the outer wall while reducing it to the inner one.

Table 1. Calculated Li binding energies (in units of eV) for three different doping sites in the DWNT (5,0)@(14,0) with a nominal formula of $C_{76}Li$. The calculated results for the individual (5,0) and (14,0) tubes are also given for comparison.

Sites	DWNT (5,0)@(14,0)	SWNT (5,0)	SWNT (14,0)
A	−0.67	−0.74	0.58
B	−0.96		
C	0.29	−0.68	0.59

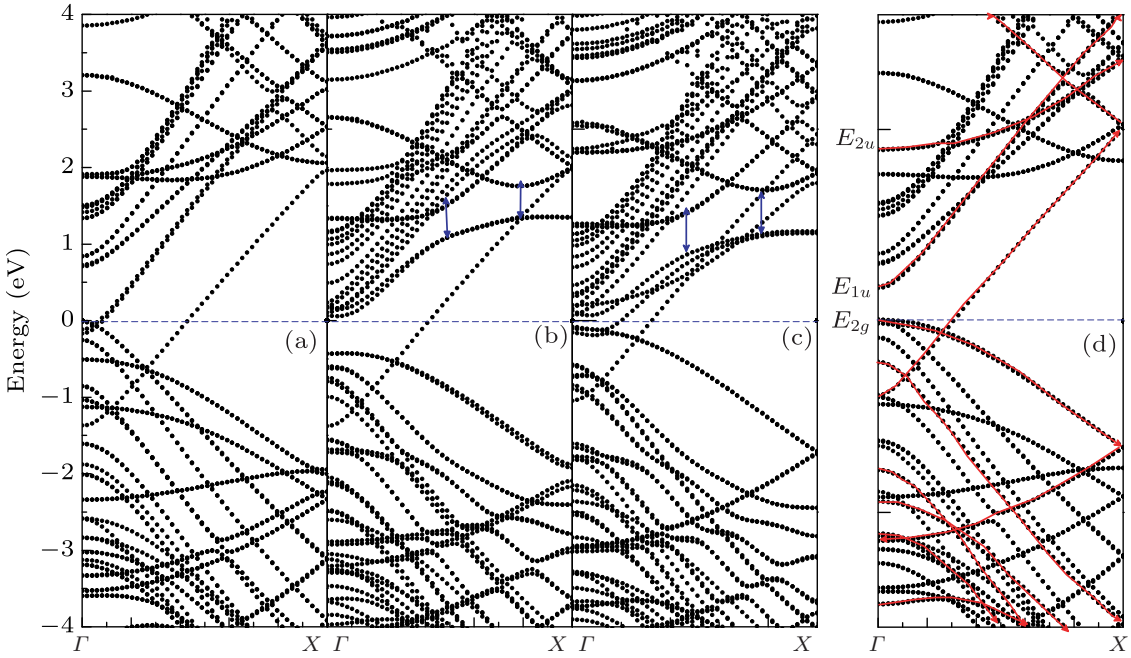


Fig. 2. Energy band structures of DWNT with Li doped at (a) site A, (b) site B, and (c) site C. Note that the system has a concentration of $C_{76}Li$. For comparison, the band structure of un-doped DWNT is shown in (d) where the bands from the (5,0) tube are marked as red curves. The Fermi levels are at 0 eV. The blue arrows indicate obvious band-splitting.

Figure 2 shows the calculated energy band structures for the DWNT with Li doping at different sites. Note there is only one Li atom per unit cell with the nominal formula of $C_{76}Li$. The band structure is plotted using 50 uniform k-points along the tube axis. For comparison, the result of the pristine DWNT is also presented. As the outer (14,0) tube is semiconducting while the inner (5,0) tube is metallic,[32] we see from Fig. 2(d) that the un-doped DWNT is metallic and those bands from the (5,0) tube (marked as red curves) and the (14,0) tube can still be identified. However, some degenerate bands are now separated

due to symmetry breaking caused by tube-tube interaction. Upon doping of Li, we see from Figs. 2(a)–2(c) that the overall topology of the band structure roughly follows a rigid band picture. That is, the Fermi level becomes up-shifted when the $2s$ electron of the Li atom is transferred to the DWNT. In addition, the Li doping may change the relative position and/or degeneracy of those bands coming from the (5,0) and (14,0) tubes. When Li is introduced inside the inner tube (site A), we see from Fig. 2(a) that there is almost no change of the outer (14,0) tube's bands. However, almost all the bands of the inner (5,0) tube are pushed down by about 0.35 eV. The doubly-degenerate E_{1u} bands even get down-shifted by 0.60 eV and become lower than the upper valence band of the (14,0) tube. The E_{2u} bands now coincide with the conduction band of (14,0) tube at about 1.95 eV. For the intertube doping (site B), the change of the (5,0) tube's bands is similar to the case of site A except that the degenerate E_{2u} bands are now separated by a small gap of 0.18 eV. On the other hand, the bands of the (14,0) tube get down-shifted by about 0.58 eV and the original degenerate bands at about 1.50 eV are now separated. In particular, we observe obvious band-splitting due to strong band-band repulsion, as indicated by the small blue arrows in Fig. 2(b). For the Li doping at site C, we see that the bands of the (5,0) tube are nearly the same as those found in the un-doped DWNT except that the E_{2g} bands are down-shifted slightly, while the change of the bands from the (14,0) tube is similar to the case of intertube doping. The differences among Figs. 2(a), 22(b) and 22(c) are due to the fact that when the Li atom is doped at sites A and C, its $2s$ electrons are mainly transferred to the inner (5,0) and outer (14,0) tubes, respectively; while at site B, the electrons are donated to both of them. This can be further confirmed by investigating the contour plot of differential charge density which is defined as the difference between the charge density of Li-doped DWNT and that of the pristine DWNT and Li:

$$\Delta\rho = \rho(\mathrm{DWNT} + \mathrm{Li}) - \rho(\mathrm{DWNT}) - \rho(\mathrm{Li}).$$

Figure 3 shows the differential charge density contours on the (001) plane for the three doping sites. It is obvious that at site A, the $2s$ electrons of Li are donated to the inner wall. For site B, there are charge accumulations in both the inner wall and outer wall, which indicates that the electrons are given to both tubes. For site C, we see that the charge is mostly transferred to the outer wall. To have a quantitative understanding, we have performed Bader charge analysis[33–35] for the three doping configurations (Table 2). We see that for interior doping, almost all the $2s$ electron (96%) of Li is transferred to the inner (5,0) tube. In the case of intertube doping, 63% of the charge is given to the inner (5,0) tube and the remaining 37% to the outer (14,0) tube. In the case of exterior doping, most of the charge (80%) is donated to the outer (14,0) tube, as is expected. It is interesting to find there is still a small fraction of the charge (21%) that is donated to the inner (5,0) tube even though it is a bit far away from the Li atom. Such long-distance charge transfer could only be realized via intertube interactions.

Table 2. Bader charge analysis for the charge transfer in the DWNT (5,0)@(14,0). The values (in units of electrons) indicate the net charge received upon Li doping.

Sites	Inner (5,0)	Outer (14,0)
A	0.962	0.038
B	0.634	0.366
C	0.207	0.793

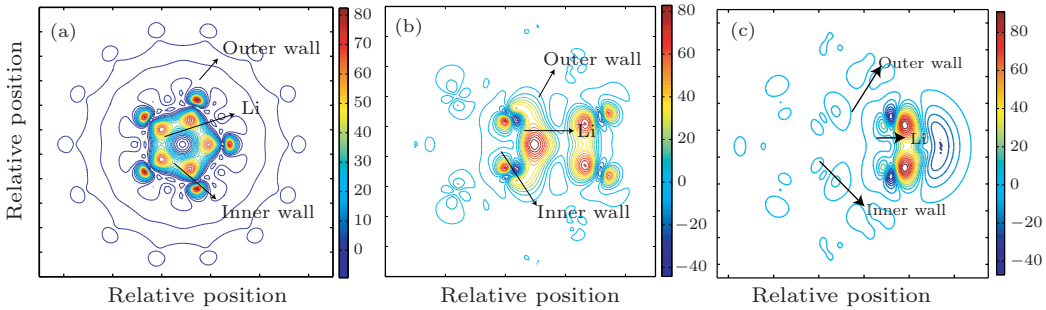


Fig. 3. Differential charge density contours on the (001) plane for Li doping in the DWNT at (a) site A, (b) site B, (c) site C.

We now consider the high concentration limit of Li doping. As site B is the most favorable and there are many equivalent positions between the inner and outer tubes, it is anticipated that the Li atoms can be doped with a large amount. To reach a high Li concentration, 14 Li atoms are introduced into the intertube space and arranged in two alternate layers. In each layer, there are 7 Li atoms which are initially positioned according to the symmetry of the outer (14,0) tube. The Li binding energy for such a configuration is calculated to be −1.17 eV, which means that the doping is still favorable at such high concentrations ($C_{76}Li_{14}$). It is interesting to note that the concentration can be further increased if one more Li atom is inserted into

the interior of the (5,0) tube and another is located outside the (14,0) tubes. The obtained configuration thus contains 16 Li atoms per unit cell with a nominal formula of C_{76} Li_{16} or $LiC_{4.75}$. This concentration corresponds to a Li intercalation capacity of 470 mAh/g, which is significantly higher than the upper limit of graphite intercalated compounds (372 mAh/g). We have examined the optimized structure of the DWNT with 16 Li atoms doped, and found that there is only a slight deformation of tube structure compared with the un-doped case. The good structural stability together with the enhanced Li capacity suggests that the (5,0)@(14,0) DWNT may have potential application in Li-ion batteries. It will be interesting to experimentally test this prediction when the (5,0)@(14,0) DWNT is formed by techniques such as coalescence of small C_{20} molecules confined inside a larger (14,0) tube.

In summary, we have used the first-principles pseudopotential method to study the binding energies and electronic properties of Li-doped DWNT (5,0)@(14,0). It is found that the area between the inner (5,0) tube and the outer (14,0) tube is quite favorable for Li doping, and the system has a Li storage capacity larger than the highest value of graphite intercalated compounds. It is mentioned that if bundled together, the interstitial channels between the DWNTs will offer additional room for Li storage, and this will be the subject of our future work.

References

[1] Bandow S, Takizawa M, Hirahara K, Yudasaka M, Iijima S 2001 *Chem. Phys. Lett.* **337** 48

[2] Pfeiffer R, Holzweber M, Peterlik H, Kuzmany H, Liu Z, Suenaga K, Kataura H 2007 *Nano Lett.* **7** 2428

[3] Rahmani A, Sauvajol J-L, Cambedouzou J and Benoit C 2005 *Phys. Rev.* B **71** 125402

[4] Barros E B, Son H, Samsonidze Ge G, Souza Filho A G, Saito R, Kim Y A, Muramatsu H, Hayashi T, Endo M, Kong J and Dresselhaus M S 2007 *Phys. Rev.* B **76** 045425

[5] Chen G, Bandow S, Margine E R, Nisoli C, Kolmogorov A N, Crespi V H, Gupta R, Sumanasekera G U, Iijima S and Eklund P C 2003 *Phys. Rev. Lett.* **90** 257403

[6] Cambedouzou J and Sauvajol J-L, Rahmani A, Flahaut E, Peigney A and Laurent C 2004 *Phys. Rev.* B **69** 235422

[7] Rauf H, Pichler T, Pfeiffer R, Simon F, Kuzmany H and Popov V N 2006 *Phys. Rev.* B **74** 235419

[8] Souza Filho A G, Endo M, Muramatsu H, Hayashi T, Kim Y A, Barros E B, Akuzawa N, Samsonidze Ge G, Saito R and Dresselhaus M S 2006 *Phys. Rev.* B **73** 235413

[9] Charlier J-C, Michenaud J-P 1993 *Phys. Rev. Lett.* **70** 1858

[10] Bellarosa L, Bakalis E, Melle-Franco M and Zerbetto F 2006 *Nano Lett.* **6** 1950

[11] Kang Y J and Chang K J, Kim Y H 2007 *Phys. Rev.* B **76** 205441

[12] Uryu S and Ando T 2007 *Phys. Rev.* B **76** 155434

[13] Zólyomi V, Koltai J, Rusznyák Á, Kürti J, Gali Á, Simon F, Kuzmany H, Szabados Á and Surján P R 2008 *Phys. Rev.* B **77** 245403

[14] Lu J and Wang S D 2007 *Phys. Rev.* B **76** 233103

[15] Uchida K, Okada S, Shiraishi K and Oshiyama A 2007 *Phys. Rev.* B **76** 155436

[16] Wang S D and Grifoni M 2008 *Phys. Rev.* B **77** 085431

[17] Wang S D and Grifoni M 2007 *Phys. Rev.* B **76** 033413

[18] Xiao Y, Yan X H, Ding J W 2007 *Chin. Phys. Lett.* **24** 3506

[19] Tarascon J M, Armand M 2001 *Nature* **414** 359

[20] Udomvech A, Kerdcharoen T, Osotchan T 2005 *Chem. Phys. Lett.* **406** 161

[21] Wen Y W, Liu H J, Miao L, Hu Y 2008 *J. Nanosci. Nanotechnol.* accepted

[22] Gao B, Kleinhammes A, Tang X P, Bower C, Fleming L, Wu Y and Zhou O 1999 *Chem. Phys. Lett.* **307** 153

[23] Frackowiak E, Gautier S, Gautier H, Bonnamy S and Beguin F 1999 *carbon* **37** 61

[24] Jouguelet E, Mathis C, Petit P 2000 *Chem. Phys. Lett.* **318** 561

[25] Shimoda H, Gao B, Tang X P, Kleinhammes A, Fleming L, Wu Y and Zhou O 2002 *Phys. Rev. Lett.* **88** 015502

[26] Liu H J, Li Z M, Liang Q, Tang Z K and Chan C T 2004 *Appl. Phys. Lett.* **84** 2649

[27] Yang J L, Liu H J and Chan C T 2001 *Phys. Rev.* B **64** 085420

[28] Kresse G and Hafner J 1993 *Phys. Rev.* B **47** R558

[29] Kresse G and Hafner J 1994 *Phys. Rev.* B **49** 14251

[30] Kresse G and Hafner J 1996 *Comput. Mater. Sci.* **6** 15

[31] Perdew J P, Wang Y 1992 *Phys. Rev.* B **45** 13244

[32] Liu H J and Chan C T 2002 *Phys. Rev.* B **66** 115416

[33] Henkelman G, Arnaldsson A and Jónsson H 2006 *Comput. Mater. Sci.* **36** 254

[34] Sanville E, Kenny S D, Smith R and Henkelman G 2007 *J. Comp. Chem.* **28** 899

[35] Tang W, Sanville E and Henkelman G 2009 *J. Phys.: Condens. Matter* **21** 084204