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# First-principles study of alkali-atom doping in a series of zigzag and armchair carbon nanotubes

Y. W. Wen, H. J. Liu,<sup>a)</sup> X. J. Tan, L. Pan, and J. Shi

*Department of Physics and Key Laboratory of Acoustic and Photonic Materials and Devices (Ministry of Education), Wuhan University, Wuhan 430072, People's Republic of China*

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First-principles calculations are performed to study the Li doping in a series of carbon nanotubes with different diameters and chiralities. It is found that the Li–Li interaction inside or outside zigzag tubes is repulsive but strongly screened. Moreover, small diameter zigzag tubes are energetically more favorable than larger ones for Li doping. In contrast, almost all the armchair tubes have the same Li binding energy, especially for the outside doping. Our theoretical results suggest that small diameter zigzag tubes could be plausible candidates for Li-ion battery application. In addition, the doping of other alkali atoms in zigzag tubes is also investigated and the optimal binding distance between them are determined. © 2010 American Institute of Physics. [doi:10.1063/1.3291128]

## I. INTRODUCTION

The Li-ion rechargeable battery is an attractive power source for its wide applications in laptop computers, cellular telephones, and so on. Usually, the traditional Li-ion battery anode is made of carbon material, in which graphite is the most popular candidate.<sup>1–4</sup> However, the upper limit of the Li intercalation capacity for graphite is only 372 mAh/g, it is thus necessary to find new materials to replace it. Since their discovery in 1991,<sup>5</sup> carbon nanotubes (CNTs) have attracted a lot of attention from the battery industry due to their unique one-dimensional structure which offer an interesting channel for chemical doping. Indeed, the Li-doped CNTs were intensively investigated by a lot of experiments.<sup>6–11</sup> It was found that CNTs have high Li storage capacity and the Li intercalation could increase the electrical conductivity of nanotubes. Moreover, Shimoda *et al.*<sup>12</sup> reported that the Li storage capacity could be increased to LiC<sub>3</sub> when the single-wall CNT (SWNT) bundles were chemically etched to short segments and the corresponding cell voltages had been measured. Another work showed that the SWNT-zeolite complex can be doped with Li by about 10% in weight.<sup>13</sup> At the same time, many theoretical studies about the Li-doped CNTs were reported. Zhao *et al.*<sup>14</sup> investigated the (10, 0) and (10, 10) SWNT ropes and found that the Li intercalation density is significantly higher than that in graphite. Udomvech *et al.*<sup>15</sup> studied the intercalation energy of Li/Li<sup>+</sup> traveling across several types of zigzag SWNTs and predicted that small diameter nanotubes might be better than larger ones when used in Li batteries. Indeed, ultrasmall diameter (4 Å) SWNTs<sup>16,17</sup> were found to be much favorable for Li doped inside and there is a marked chirality dependence of the energies.<sup>18</sup> In addition, the calculations of Li doping outside these small tubes suggest that the binding energies are even more favorable, and the outer surface can significantly enhance the Li intercalation capacity.<sup>19</sup> Furthermore, the electrochemical properties of Li-doped SWNT-zeolite complex have been

studied, and high battery voltage could be obtained for the system with good cyclic stability.<sup>20</sup> All these works suggested that CNTs would be promising candidates for Li-ion battery material. However, only few CNTs have been studied up to now, such as (10, 0) and (10, 10). It is still unclear which type of CNTs would be the best choice for the Li-battery material. In this work, two series of SWNTs ( $n, 0$ ) and ( $n, n$ ) are intercalated with Li and other alkali atoms by density functional calculations. We will focus on the structures and total energies of the doped systems, and discuss their chirality and diameter dependence, as well as the effect of doping site and doping concentration. The results may help us determine the most favorable CNTs for alkali-atom doping and Li battery material.

## II. COMPUTATIONAL METHOD

Our calculations have been performed using a plane-wave pseudopotential method as implemented in the code of VASP.<sup>21–23</sup> The exchange-correlation energy is in the form of Perdew–Wang-91<sup>24</sup> and the cutoff energy is set to 286 eV. The  $k$ -points are sampled on a  $1 \times 1 \times 20$  grid for the (5, 0) primitive cell, and equivalent  $k$ -sets are used for other zigzag and armchair tubes. We choose a standard supercell geometry so that the tubes are aligned in a hexagonal array. The closest distance between adjacent tube walls is kept at 10 Å so that the interaction between the tube and its periodic images can be negligible. The atomic positions are fully relaxed until the magnitude of the forces acting on all atoms becomes less than 0.05 eV/Å, which also converge the total energy within 1 meV.

## III. RESULTS AND DISCUSSIONS

As mentioned above, two series of SWNTs are investigated in the present calculations, and they are the zigzag tubes ( $n, 0$ ) and armchair tubes ( $n, n$ ) with ( $3 \leq n \leq 10$ ). The alkali atoms are intercalated both inside and outside these tubes with different concentration. This is done by choosing one or more primitive cells along the tube axis and corre-

<sup>a)</sup>Author to whom correspondence should be addressed. Tel.: +86–27–68754613. Electronic mail: phlhj@whu.edu.cn.

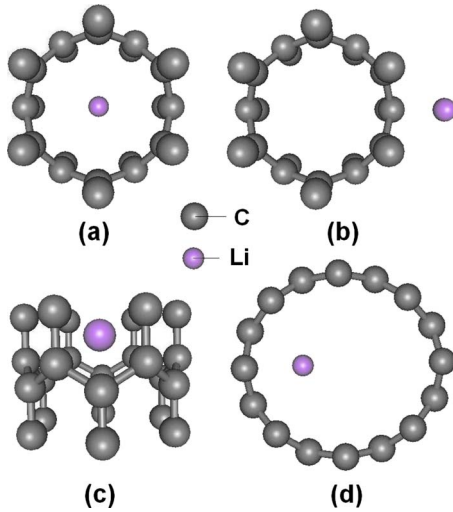


FIG. 1. (Color online) Ball-and-stick model of Li doped (a) inside and (b) outside a nanotube. (c) is a side view of outside doping. (d) indicates that the cross-section becomes elliptic when the Li is doped inside larger zigzag tube.

sponds to different distance between neighboring alkali atoms. Figure 1(a) and 1(b) schematically show the Li doping inside and outside a nanotube, respectively. For the latter case, the Li atom is facing the center of a hexagonal carbon ring [Fig. 1(c)]. We first focus on the zigzag  $(n,0)$  tubes. After geometry optimizations, we find that the inside Li prefer to reside in the axis of  $(n,0)$  tube when  $n < 6$ ; however, it will be off-centered located at a distance of about  $2.0 \text{ \AA}$  from the tube wall if  $n \geq 6$  and the corresponding tube becomes elliptic-like [see Fig. 1(d)]. Such observation is different from previous report where the doped Li still stay along the axis of  $(6,0)$  tubes.<sup>25</sup> This might be caused by a high-symmetry configuration used in their calculations. Similar trend can be found for the armchair  $(n,n)$  tubes. That is, the doped Li will reside in the axis of small diameter  $(n,n)$  tubes with  $n < 4$ , and be off-center positioned for larger ones ( $n \geq 4$ ). The off-center configurations suggest that there will be an optimal distance between the doped Li and the tube wall, which is found to be  $\sim 2.0 \text{ \AA}$  for both the zigzag and armchair tubes. If the radius of a tube is smaller than the optimal distance, there will be uniform repulsion between the tube and inside Li which makes it fixed at the tube center. Otherwise, the doped Li will be off-centered to find the optimal distance. Thus too large or too small nanotubes may not be

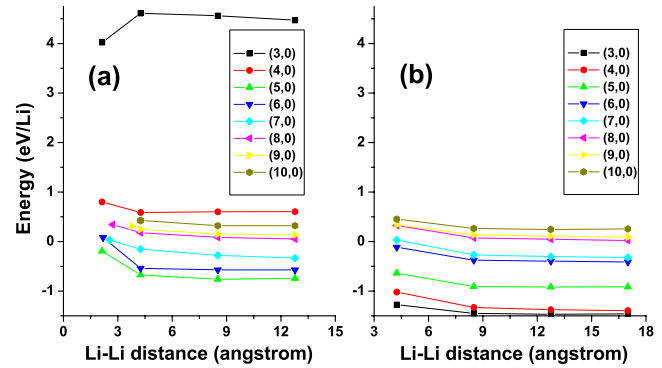


FIG. 2. (Color online) Calculated binding energies of Li-doped (a) inside and (b) outside a series of zigzag nanotubes with different Li–Li distance in the unit cell. The corresponding doping concentrations are given in Table I.

favorable for Li doped inside. For the outside doping, there will be no space restriction and the Li will always find the optimal distance which is about  $1.5$  and  $1.7 \text{ \AA}$  for the zigzag and armchair tubes, respectively.

Figure 2(a) and 2(b), respectively show the calculated binding energies for Li doped inside and outside a series of  $(n,0)$  tubes. We have considered a certain range of doping concentration which corresponds to different Li–Li distance in the unit cell (see Table I). Note that larger (smaller) Li–Li distance corresponds to lower (higher) doping concentration. The binding energy  $E_b$  is defined as

$$E_b = [E(\text{tube} + n\text{Li}) - E(\text{tube}) - nE(\text{Li})]/n,$$

where  $E(\text{tube} + n\text{Li})$  is the total energy of a Li-doped tube at particular concentration,  $E(\text{tube})$  is the total energy of a pristine tube, and  $E(\text{Li})$  is the total energy of Li in bulk structure (bcc). A negative number of binding energy means that doping is favorable if the chemical potential of Li is set at that of bulk Li. There are some interesting features of this figure. First, whether the Li is doped inside or outside the  $(n,0)$  tubes, the binding energies converge rapidly as the Li–Li distance is increased (or doping concentrations is decreased). As the Li atom will donate its  $2s$  electron to the CNT and become positively charged, this observation means that there is obvious Coulombic repulsion between the Li ions only when they are very close to each other, which suggests that the nanotubes may have strong screening effect for the Li doping. Second, when the Li is doped outside  $(n,0)$  tubes, we see from Fig. 2(b) that the calculated binding energies at

TABLE I. The Li doping concentrations ( $\text{LiC}_n$ ) for a series of zigzag tubes with different Li–Li distances  $D$  (in unit of  $\text{\AA}$ ) in the unit cell.

Tube	$D=2.13$	$D=4.25$	$D=8.50$	$D=12.75$	$D=17.00$
(3,0)	$\text{LiC}_6$	$\text{LiC}_{12}$	$\text{LiC}_{24}$	$\text{LiC}_{36}$	$\text{LiC}_{48}$
(4,0)	$\text{LiC}_8$	$\text{LiC}_{16}$	$\text{LiC}_{32}$	$\text{LiC}_{48}$	$\text{LiC}_{64}$
(5,0)	$\text{LiC}_{10}$	$\text{LiC}_{20}$	$\text{LiC}_{40}$	$\text{LiC}_{60}$	$\text{LiC}_{80}$
(6,0)	$\text{LiC}_{12}$	$\text{LiC}_{24}$	$\text{LiC}_{48}$	$\text{LiC}_{72}$	$\text{LiC}_{96}$
(7,0)	$\text{LiC}_{14}$	$\text{LiC}_{28}$	$\text{LiC}_{56}$	$\text{LiC}_{84}$	$\text{LiC}_{112}$
(8,0)	$\text{LiC}_{16}$	$\text{LiC}_{32}$	$\text{LiC}_{64}$	$\text{LiC}_{96}$	$\text{LiC}_{128}$
(9,0)	$\text{LiC}_{18}$	$\text{LiC}_{36}$	$\text{LiC}_{72}$	$\text{LiC}_{108}$	$\text{LiC}_{144}$
(10,0)	$\text{LiC}_{20}$	$\text{LiC}_{40}$	$\text{LiC}_{80}$	$\text{LiC}_{120}$	$\text{LiC}_{160}$

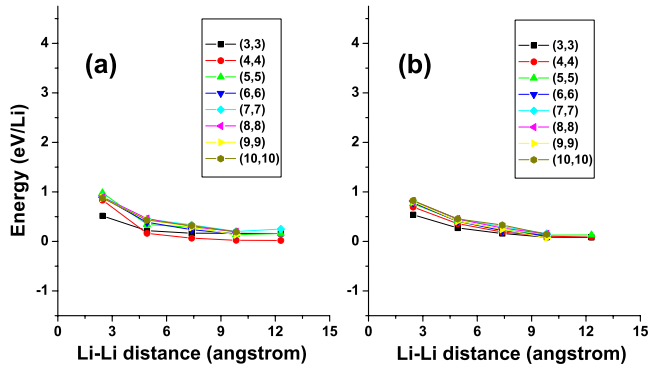


FIG. 3. (Color online) Calculated binding energies of Li-doped (a) inside and (b) outside a series of armchair nanotubes with different Li–Li distance in the unit cell. The corresponding doping concentrations are given in Table II.

low concentration limit decrease as the tube diameters are decreased. It is thus energetically more favorable for Li doped outside small diameter nanotubes than large ones. Similar results can be found when the Li is doped inside these tubes except for the (3, 0) and (4, 0) tubes which are too small for Li to be fitted into them. Indeed, the calculated Li binding energies for the (3, 0) and (4, 0) tubes are very high because of strong Pauling repulsions between the Li and tubes. The one with the lowest binding energy is thus (5, 0) tube, which matches the optimal Li-tube distance mentioned above. Third, if we compare Fig. 2(a) with Fig. 2(b), it is interesting that the converged binding energy of outside doping is lower than that inside for each smaller diameter tube ( $n < 6$ ); while there is little energy difference between these two sites for each larger one ( $n > 6$ ). The reason is that the radius of (6, 0) tube is close to the optimal distance mentioned above, and the Li atom inside tubes with radius larger than it can always find the effective binding distance as the case of outside doping.

In Fig. 3, we give the calculated binding energies for Li doped inside and outside a series of armchair nanotubes. The corresponding doping concentrations and Li–Li distances are summarized in Table II. In contrast to the zigzag tubes, the armchair tubes may not be favorable for Li doping since the binding energies indicated in Fig. 3 are all positive. At low concentration limit (or very large Li–Li distance), it is found that almost all the armchair tubes have the same binding energies for Li. Moreover, there is little energy difference between the inside and outside doping. All these indicate that

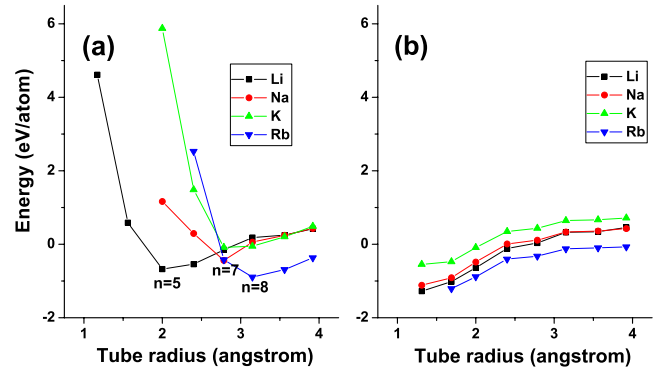


FIG. 4. (Color online) Calculated binding energies of different alkali atoms doped (a) inside and (b) outside a series of zigzag SWNTs.

the chirality of nanotube plays an important role in the Li doping. If we focus on the inside doping, we see from Fig. 3(a) that the (4, 4) tube have the lowest binding energy among all the armchair tubes. This is due to the fact that the radius of (4, 4) tube is very close to the optimal distance of  $\sim 2.0$  Å. In contrast, the Li binding energy of (3, 3) tube is larger since it is a bit narrow for Li to be fitted into.

To find the optimal distance between nanotubes and other alkali atoms, we have done a series of calculations where Na, K, and Rb atoms are introduced into zigzag tubes with different diameters. Figures 4(a) and 4(b) show the calculated binding energies for the inside and outside doping, respectively. We see that for each kind of alkali atom, there exists a particular tube to be fitted into it with the lowest binding energy [Fig. 4(a)], thus the radius of that tube is close to the optimal doping distance. When the size of alkali atom increases from Li to Rb, it is found that the optimal distance increases from the radius of (5, 0) tube to that of (8, 0) tube. If the radius of a tube is smaller than the optimal distance, there will be strong Pauling repulsion between the doped atom and the tube and the energy will be unfavorable, as indicated in Fig. 4(a). On the other hand, if the radius of a tube is too large, the doped alkali atom will move away from the tube center which also causes a weaker binding with the tube. However, the results are quite different when the alkali atoms are doped outside these tubes [Fig. 4(b)]. We see that the binding energy increases monotonously as the diameter of the nanotube is increased. This is reasonable since smaller curvature of larger tube will weaken the alkali binding.

TABLE II. The Li doping concentrations ( $\text{LiC}_n$ ) for a series of armchair tubes with different Li–Li distances  $D$  (in unit of Å) in the unit cell.

Tube	$D=2.46$	$D=4.92$	$D=7.38$	$D=9.84$	$D=12.30$
(3,3)	$\text{LiC}_{12}$	$\text{LiC}_{24}$	$\text{LiC}_{36}$	$\text{LiC}_{48}$	$\text{LiC}_{60}$
(4,4)	$\text{LiC}_{16}$	$\text{LiC}_{32}$	$\text{LiC}_{48}$	$\text{LiC}_{64}$	$\text{LiC}_{80}$
(5,5)	$\text{LiC}_{20}$	$\text{LiC}_{40}$	$\text{LiC}_{60}$	$\text{LiC}_{80}$	$\text{LiC}_{100}$
(6,6)	$\text{LiC}_{24}$	$\text{LiC}_{48}$	$\text{LiC}_{72}$	$\text{LiC}_{96}$	$\text{LiC}_{120}$
(7,7)	$\text{LiC}_{28}$	$\text{LiC}_{56}$	$\text{LiC}_{84}$	$\text{LiC}_{112}$	$\text{LiC}_{140}$
(8,8)	$\text{LiC}_{32}$	$\text{LiC}_{64}$	$\text{LiC}_{96}$	$\text{LiC}_{128}$	$\text{LiC}_{160}$
(9,9)	$\text{LiC}_{36}$	$\text{LiC}_{72}$	$\text{LiC}_{108}$	$\text{LiC}_{144}$	$\text{LiC}_{180}$
(10,10)	$\text{LiC}_{40}$	$\text{LiC}_{80}$	$\text{LiC}_{120}$	$\text{LiC}_{160}$	$\text{LiC}_{200}$

#### IV. SUMMARY

In summary, we have performed first-principles calculations to study the structural properties and binding energies of alkali-atom doped CNTs. Both the interior and exterior of these tubes are considered and the effect of tube diameter, chirality, and doping concentration are discussed in details. Our calculations give a valuable insight on the search for Li-ion battery materials, which needs further experimental and theoretical investigations.

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