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Dependence of in-tube doping on the radius and helicity of single-wall carbon nanotubes

Liu Hong(刘 红)[a)b)†], Dong Jin-Ming(董锦明)[c)],
Qian Mei-Chun(钱湄杶)[c)], and Wan Xian-Gang(万贤纲)[c)]

[a)] *Department of Physics, Nanjing University, Nanjing* 210093, *China*
[b)] *Department of Physics, Nanjing Normal University, Nanjing* 210097, *China*
[c)] *Group of Computational Condensed Matter Physics, State Key Laboratory of Solid State Microstructures, Department of Physics, Nanjing University, Nanjing* 210093, *China*

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Using the Lennard–Jones interaction potential between the impurity atom and carbon atom, we have studied the dependence of in-tube impurity doping on the radius of a single-wall carbon nanotube (SWNT), as well as its helicity. The obtained results show that the radius of the most stably doped SWNT is different for different kinds of impurity atoms. This is useful for producing the required doped SWNT. In addition, it is found that the helicity of tube has a strong effect on the potential energy of the atoms doped in the SWNT.

Keywords: single-wall carbon nanotube, impurity atom, Lennard–Jones potential
PACC: 6148, 6170, 3420

1. Introduction

The discovery of carbon nanotubes (CNTs) by Iijima[1,2] and subsequent observations of unique mechanical and electronic properties of CNTs have initiated intensive research on these quasi-one-dimensional structures.

The conductive properties of nanotubes depend drastically on both the diameter and helicity of the CNT.[3−7] As is well known, the geometrical structure of a nanotube can be uniquely determined by its circumference vector $\boldsymbol{R} = n\boldsymbol{a}_1 + m\boldsymbol{a}_2$, where $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$ are the unit vectors of the graphite sheet, and n and m are integers.[8] The pair number (n, m) defines the radius and helicity of each tube, and is crucially important for the electronic properties of nanotubes. If $n - m = 3k$, with k an integer, the tubes are metallic; and all others are semiconducting.

It appears possible to improve the conductance of CNTs by doping. Lee *et al*[9] and Rao *et al*[10] found that the single-wall carbon nanotube (SWNT) rope can be doped to increase its conductance and even to become a metallic conductor. These reports give further hope for a new generation of nanoscale devices. However, the origin of the large increase of conductance is still unclear. On the other hand, it is difficult to use many standard techniques in the nanoscale region (10 to 100nm). Therefore, it is important to use a computer simulation method to study the relationship between structures and properties of a system. Recently, Gao *et al*[11] have studied the structure of the potassium-doped SWNT crystals by using the molecular dynamics method, in which the van der Waals interaction is adopted to represent the interaction between the doped atoms and the carbon atoms on the tube. Miyamoto *et al*[12] also predicted the structure and properties of a linear potassium-atom chain doped into a CNT by the density functional method. But these authors have not studied the influence of the tube helicity and radius, they only considered the achiral tubes, i.e. (10,10) armchair tube in Ref.[11] and $(n,0)$ zigzag tube in Ref.[12]. Furthermore, they studied only potassium-doping, but not other alkali atoms.

In this paper, we investigate the doping effect of different impurity atoms in the SWNT having different radii and helicities by analysing the dependence of the doped atom potential energy on the tube radius, as well as on the tube helicity. We hope to obtain results that will be useful for characterizing the doped SWNT.

†Author to whom any correspondence should be addressed. E-mail: liuhong@email.njnu.edu.cn

2. Theoretical method and results

For the alkali atom or the carbon atom in-tube doped into SWNT, the doped atom can be placed from outside to inside of a SWNT. The most stable structure of a system should be determined by minimizing its total energy. In our calculations, we employ the force fields method developed for studying the K-intercalated fullerenes.[13] Because there is still a debate in the literature about charge transfer in graphite intercalation compounds (GICs),[14] we assume that the charge of the alkali atom has not been transferred to the SWNT. Therefore, the following Lennard–Jones potential is adopted in our calculation

$$V(r) = 4\varepsilon\left[\frac{\sigma^{12}}{r^{12}} - \frac{\sigma^6}{r^6}\right], \qquad (1)$$

where r is the distance between the impurity and the carbon atoms on the tube surface. ε and σ are the parameters of this type of potentials shown in Table 1, which were used to determine the equilibrium position of the alkali atom in the C_{60} cage.[15] Using Eq.(1), an equilibrium distance of about 0.329nm between individual K and C atoms can be obtained, and the corresponding interaction energy for them is only –0.028eV. On the other hand, the energy of CNT has been calculated by using the models of Tersoff[16] and Brenner,[17] which are suitable to simulate the graphite structure as well as the fullerene. It is found that the lowest potential energy between two C atoms obtained by the Tersoff potential is –10.33eV with an equilibrium distance between two C atoms being 0.1447nm. Compared with that between the K and C atoms obtained above, the energy of CNT is very large and contributed mainly by the covalent bonds of C—C, leading to a great difficulty of changing structure of CNT by doping. So, it is reasonable in our calculation to assume that the structure of SWNT is rigid and not influenced by the in-tube doping. This means that we need only to include the potential energy between the impurity and the carbon atoms on the SWNT when we study the in-tube doping.

Table 1. Parameters of Lennard–Jones potential between the doped atom and the carbon atom.

Doped atom	C	Li	Na	K	Rb	Cs
ε/meV	2.10	78.40	43.60	28.00	16.90	8.53
σ/nm	0.350	0.220	0.250	0.293	0.319	0.338

2.1. Simple model

In order to consider the influence of the radius of SWNT on in-tube doping, we firstly adopt a simple model, in which the carbon atoms on SWNT are assumed to distribute uniformly on the surface of a nanotube with its density $\rho = 4/(3^{3/2}a^2)$ (a is the length of C—C bond).

So, the total potential energy between the doped atom and SWNT can be represented by an integral over the surface of SWNT

$$V(r) = \int_0^L \int_0^{2\pi} 4\rho\varepsilon\left[\frac{\sigma^{12}}{r^{12}} - \frac{\sigma^6}{r^6}\right] R\mathrm{d}\theta\mathrm{d}z,$$
$$r = \sqrt{R^2 + (z - z_0)^2 + x_0^2 + y_0^2 - 2R(x_0\cos\theta + y_0\sin\theta)}\,, \qquad (2)$$

where L and R are the length and radius of the SWNT, respectively. r is the distance between the doped atom at x_0, y_0, z_0 and the surface unit of SWNT. In our coordinate system, z-axis is taken along the axis of SWNT, and the origin point of z-axis is chosen at the tip of SWNT. When x_0=0 and y_0=0, the doped atom is placed on the axis of SWNT. So the coordinates of the centre of SWNT are x_0=0, y_0=0 and $z_0 = L/2$.

In calculation, we find that the potential energy of a doped atom placed at the centre of the SWNT is lower than that of the impurity atom at other positions in the tube. Also, the potential energy of the doped atom at the centre of SWNT is different for different tube radius.

The dependences of the potential energies of various alkali atoms and carbon atom at the centre of the nanotube on the tube radius are shown in Fig. 1, from which it is seen that when the tube radius is decreased to a value, e.g., 0.274nm for K atom, the total potential energy changes from negative to positive. This means that a K atom could not be doped into a nanotube with smaller radius than 0.274nm. That is because with decreasing tube radius the repulsive part in the potential energy is increased faster than the attractive part. So the total potential energy

is increased rapidly. The minimal value of each curve corresponds to the potential energy of the most stable state for this doped atom in SWNT, and its numerical value is shown in Table 2. When the tube radius is very large, the total potential energies for all different doped atoms will approach the same value, i.e. zero.

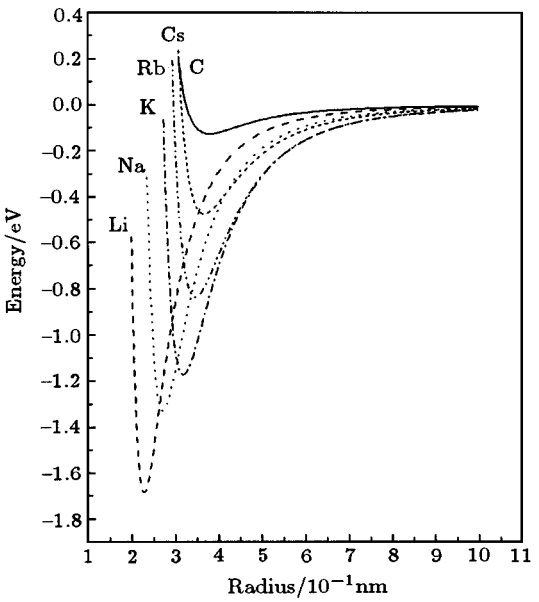


Fig.1. The dependence of the lowest potential energies for different doped atoms on tube's radius obtained by using the simple model.

Table 2. For the most stable state of doped system the potential energy and tube radius obtained by using the simple model.

Doped atom	C	Li	Na	K	Rb	Cs
Radius/nm	0.380	0.228	0.272	0.318	0.346	0.367
Energy/eV	–0.125	–1.686	–1.329	–1.172	–0.838	–0.475

Analysing the data in Table 2 and also Fig.1, it is easy to see that the tube radii and the potential energies corresponding to the most stable alkali doped SWNTs are increased with increasing the size of the doped atom. For example, the minimal potential energy of the most stable Li-doped SWNT is the lowest because the size of Li atom is the smallest among all the alkali atoms. Also, the tube radius is the smallest among these doped SWNTs, which equals to 0.228nm. However, the carbon-doped SWNT is an exceptional case, since the repulsive part in its potential energy is much larger than that of the alkali-doped SWNT, causing the radius of the most stable carbon-doped SWNT to reach a value of 0.380nm, which is larger than those of all the alkali-doped SWNT. Obviously, compared with those of the alkali atoms, the most stable carbon-doped SWNT has also the largest total potential energy, i.e. up to -0.125eV.

2.2. True carbon nanotube

Now, we turn to see the doping effect on the real geometric structures of SWNT. In this case, the potential energy of the doped atom in tube should be represented by the following summation

$$V(r) = \sum_i^N V_i(r_i) = \sum_i^N 4\varepsilon\left[\frac{\sigma^{12}}{r_i^{12}} - \frac{\sigma^6}{r_i^6}\right], \qquad (3)$$

where N is the total number of carbon atoms on the tube. r_i is the distance between the doped atom and the ith carbon atom on the tube. Because the z-axis is taken along the tube axis, and its zero point is taken at the tip of the tube, the z-coordinate z_0 of the position of the doped atom will represent its distance from the tube's tip.

In the process of calculation by using the simple model (in section 2.1), there exists a potential barrier before the doped atom entering into the tube with very small radius. This shows that it needs to apply a force to make the doped atom enter into this tube. So the existence of this barrier is very important for producing an in-tube doped-SWNT. Now, in this section, the potential barrier will be influenced by the helicity and radius of the real tube. Firstly, we take the potassium atom as an example, and the related results are shown in Figs.2(a), 2(b), and 2(c) for (n,0), (3,n) and (n,n) tubes (where n is taken from 4 to 10), respectively. From Fig.2, we can conclude:

1) When the K atom is far away from the tube's tip, its potential energy approaches zero.

2) When the tube radius (the number n) becomes very large, the potential energy of the K atom inside the tube approximately equals the value at outside, which is especially obvious in (n, n) tubes [see Fig.2(c)] because the radius of the (n, n) kind of SWNT is increased more rapidly with increasing n than other kinds of tubes. For example, the radius of (10,10) tube is larger (0.678nm), but in contrast, the radius of (10,0) tube is only 0.3914nm.

3) When the K atom becomes gradually close to the tube's tip from outside of tube, and for tubes with very small radii, e.g., the (4,0) tube with a radius of 0.1566nm, there always exists a position, at which the potential energy is lower than the values at outside or inside of the tube. With increasing radius, the position of this minimal potential energy goes to the right-hand side, and its absolute value is increased and be-

comes equal to the value at the tube centre, which is easily seen in Figs.2(a) and 2(b). This character also exists in the simple model. This minimal potential energy is caused by the interaction between the doped K and the carbon atoms not near the tube's tip. For different kinds of tubes, the position, and the value of this minimal potential energy are different.

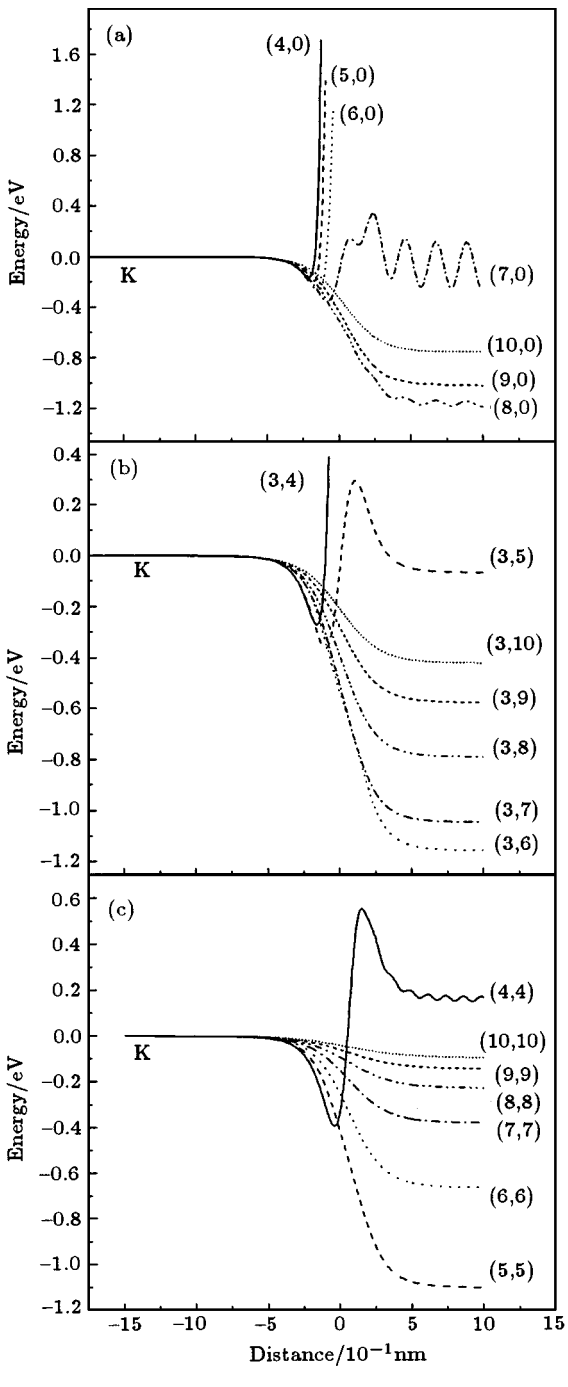


Fig.2. Variation of the potential energy of doped K atom with its distance from the tip of: (a) $(n, 0)$ tube; (b) $(3,n)$ tube; and (c) (n, n) tube.

4) Furthermore, let the K atom be closer to the tube's tip. For very small tube radius, there is a potential barrier (a peak), which is higher than the potential outside the tube. With increasing tube radius, the peak position is closer to the tube's tip, and its height is decreased rapidly and finally this peak disappears.

5) For $(n,0)$ tube, there are two peaks before the K atom completely going into the tube, which is different from the cases of (n, n) and $(3,n)$ tubes. For example, in (7,0) tube, the value of the first peak is 146.791meV, lower than the peak value 296meV in (3,5) tube, but the second one is 342.069meV. The position of the first peak is at 0.078nm inside the tube and the second one is at about 0.236nm. However, the peak position in (3,5) tube is at 0.1081nm. Obviously, these differences are caused by the structure of $(n,0)$ tube (zigzag tube).

6) It is seen that for $(n,0)$, $(3,n)$ and (n, n) tubes (n=4–10), there is a unique value of n, for which the corresponding potential energy at the centre of the tube is the lowest among the tubes of the same kind with the same kind of impurity atoms. For example, for $(n,0)$ kind of tube doped by K atom, the most stable SWNT is the (8,0) tube, which has the lowest potential energy, –1185.44meV. When $n > 8$ or < 8, its potential energy will be increased [see Fig.2(a)]. But for (n, n) kind of tube doped by K atom, the most stable SWNT is (5,5) tube, which has the lowest potential energy, –1100.21meV. When $n > 5$ or < 5, its potential energy will be increased [see Fig.2(c)].

Miyamoto found that the maximum heat of formation for doping K atom chain into $(n,0)$ tube is produced in the case of (7,0) tube.[12] In our calculation, the heat of formation is just the absolute value of the potential energy between K and all carbon atoms on SWNT. For the $(n,0)$ kind of SWNT, the heat of formation for doping K atom into (8,0) tube is the maximum, up to 1.185eV, which is in good agreement with the value 1.12eV/K atom for (7,0) tube obtained by Miyamoto, in which he considered the tube doped by a K atom chain. The n values for different kinds of tubes and different doped atoms are shown in Table 3, in which the corresponding potential energies and radii are also listed. Analysing the data in Table 3, we know that the most stable doped SWNT for different doped atoms are (3,8) tube for C-doped, (6,0) for Li-doped, (7,0) for Na-doped, (8,0) for K-doped, (9,0) for Rb-doped and Cs-doped.

Table 3. The potential energies of the most stable doped SWNT in different kinds of tube for different doped atoms.

Doped atom	Radius/nm	Potential/meV	Tubes
C-doped	0.3914	–123.80	(10,0)
	0.4070	–116.85	(6,6)
	0.3855	–124.89	(3,8)
Li-doped	0.2349	–1700.63	(6,0)
	0.2712	–1206.85	(4,4)
	0.2381	–1634.04	(3,4)
Na-doped	0.2740	–1355.89	(7,0)
	0.2712	–1329.93	(4,4)
	0.2740	–1325.97	(3,5)
K-doped	0.3132	–1185.44	(8,0)
	0.3390	–1100.21	(5,5)
	0.3107	–1156.08	(3,6)
Rb-doped	0.3523	–838.28	(9,0)
	0.3390	–828.43	(5,5)
	0.3413	–833.41	(4,6)
	0.3479	–837.23	(3,7)
Cs-doped	0.3523	–460.76	(9,0)
	0.4068	–410.70	(6,6)
	0.3855	–456.14	(3,8)

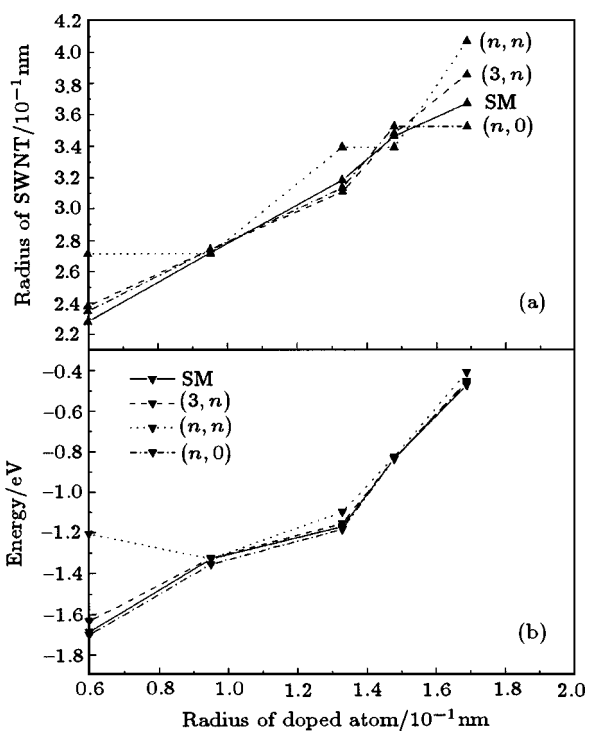


Fig.3. The effect of the size of alkali-atom on: (a) the radii of the most stable doped SWNTs; and (b) the potential energies of the most stable doped SWNTs. Dotted, dashed and dot-dashed lines correspond to (n,n), $(3,n)$ and $(n,0)$ tubes, respectively. Solid line represents the results of the simple model.

For the most stable doped SWNTs, their tube radii and the dependence of potential energy on the size of doped alkali-atom are shown in Fig.3. The $(n,0)$ tube (zigzag) seems to be easy to produce the alkali doped SWNT according to the above data and Fig.3. From Fig.3 it is obvious that the results obtained by using the simple model is in good agreement with that by taking into account the geometric structures of real CNTs when we study the dependence of the potential energy on tube radius. So, the simple model is a useful and effective one to select the tube radius for different sizes of doped atoms.

We have found that in addition to the tube radius effect, the tube's helicity has also strong influence on the potential energy of doped atom. For example:

1) the potential energies of the doped atoms in $(n,0)$ and (n,n) tubes vary periodically with varying positions of the doped atoms in these two kinds of achiral tubes (see Figs.2(a) and 2(c)). Among all tubes calculated above, there are no similar characteristics in other kinds of tubes. The peak height of periodical potential energy is decreased with increasing tube radius. So in Fig.2(c), when $n > 4$, the peak height is very small, which is not shown clearly in it. Furthermore, the peak–peak distances for different doped atoms are equal to 0.123nm in (n,n) armchair tubes, and 0.213nm in $(n,0)$ zigzag tubes. Having noted that half of the lattice constants along the axes of the (n,n) and $(n,0)$ tubes are 0.123 and 0.213nm, respectively, we believe that these periodic variations in potential energy are caused only by the periodic structures in these two kinds of tubes.

2) On the other hand, for (3,5) and (7,0) tubes, although their radii are the same, but their potential energies for the same doped atom are different. For instance, the potential energy for K atom at the centre of the (3,5) tube is only –67.469meV, but for the doped (7,0) tube it is –250.876meV, much lower than that of the former. Also, the minimal potential energy of the K-doped (7,0) tube is –350.656meV and that of the K-doped (3,5) tube is –363.551meV. The valley positions of their potential energies before entering into their tubes are at –0.082nm for the (7,0) tube and –0.09795nm for the (3,5) tube.

3) For the (4,4) tube, its radius is 0.2712nm, i.e. 0.0028nm smaller than that of (7,0) tube, but the potential energy of the K atom at the tube centre is very high, up to 150.706meV.

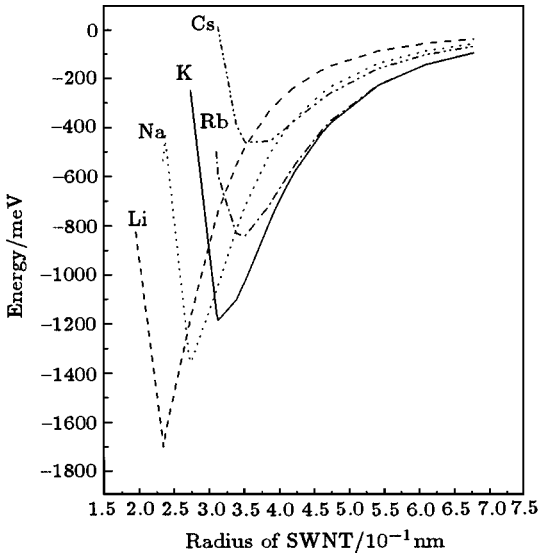


Fig.4. The dependence of the lowest potential energies for different doped atoms on tube's radius obtained by using the ture carbon nanotube model.

4) Letting the tube radius change from small to large, we show the relationship between the potential energies at the centre of the tube and the tube radius in Fig.4. It is found that the potential energies for Rb and Cs atoms are decreased when the radius increases from 0.2349nm of the (6,0) tube to 0.2381nm of the (3,4) tube. On the contrary, the potential energy for Li, Na, K atoms is increasing, which is an unusual result for Na and K atoms (the data are given in Table 4). Because in this range of tube radius the potential energy for Na and K atoms should be decreased with the tube radius (see Fig.1). Therefore, we believe that the potential energy of a doped tube is closely related to the tube helicity. Comparing Fig.4 with Fig.1, we can see that the variation of potential energy in Fig.4 is basically similar to that in Fig.1 except for the points discussed above.

Table 4. For different doped atoms the radii of the (6,0) and (3,4) tubes and the corresponding potential energy (eV).

Doped atom	C	Li	Na	K	Rb	Cs
(6,0) 0.2349nm	7.731	−1.701	−0.535	7.921	17.561	19.661
(3,4) 0.2381nm	7.677	−1.634	−0.452	7.966	17.504	19.545

In our calculations, the tube length is usually taken as 20nm. However, for a longer tube, e.g., the tube with a length of 80nm, we have obtained the same results. Thus, we can conclude that our calculated results are not sensitive to the effect of tube's tip.

3. Summary

In summary, we have calculated the potential energies of the atoms doped into CNTs with different helicities and radii. The obtained results show that for different doped atoms, the radius of the most stable doped SWNT is different, which will be useful to produce different kinds of doped SWNTs. In addition, the potential energy of the in-tube doped atom depends on the helicity and radius of the tube. We also demonstrate that the simple model with an assumed uniform distribution of the carbon atoms on the tube surface works well if we study only the tube radius effect on the in-tube doping.

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