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REVIEW ARTICLE

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Adsorption on the carbon nanotubes

Abstract Adsorption on single walled carbon nanotubes (SWCNTs) is a subject of growing experimental and theoretical interest. The possible adsorbed patterns of atoms and molecules on the single-walled carbon nanotubes vary with the diameters and chirality of the tubes due to the confinement. The curvature of the carbon nanotube surface enlarges the distance of the adsorbate atoms and thus enhances the stability of high coverage structures of adsorbate. There exist two novel high-coverage stable structures of potassium adsorbed on SWCNTs, which are not stable on graphite. The electronic properties of SWCNTs can be modified by adsorbate atoms and metal-semiconductor and semiconductor-semi- conductor transitions can be achieved by the doping of alkali atoms.

Keywords SWCNT, adsorption, ground state, electronic property, transition, Monte Carlo, ab initio

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1 Introduction

Carbon nanotubes, since their first discovered in 1991 [1], have been seen as promising materials due to their unique physical, optical and mechanical properties [2]. The structure of an individual SWCNT is specified in terms of a vector $\boldsymbol{C}_h$ joining two equivalent points on the original lattice. The nanotube is produced by rolling up the graphite sheet so that the two end points of the vector are superimposed. The vector $\boldsymbol{C}_h$ can be expressed as $\boldsymbol{C}_h = n\boldsymbol{a}_1 + m\boldsymbol{a}_2$ and $\boldsymbol{a}_1$, $\boldsymbol{a}_2$ are the unit vectors of graphite, thus each pair of integers (n,m) represents a possible tube structure [3]. When $n - m$ is the multiple of 3, the corresponding (n,m) SWCNT is metallic, otherwise the SWCNT is semiconducting [4]. Those relations between the electronic properties and chiral structures of the (n, m) SWCNTs have been directly tested in experiments [5－7].

Adsorption on SWCNTs is a subject of growing experimental and theoretical interest. The adsorption can be on individual SWCNT and SWCNT bundles [8－22]. The adsorption sites of small molecules on the SWCNT bundles have been studied both in the experiments and theories [9,10]. Gases adsorbed on the groove sites where two nanotubes meeting on the external surface of SWCNTs bundles, can realize a one-dimensional (1D) physical system [11－14]. The adsorption of various gas molecules on different SWCNTs have been studied, and equilibrium position, adsorption energy, charge transfer, and electronic band structures can been obtained using first principles methods [15－17]. The physisorption and chemisorption of H_2 on SWCNTs have been studied both in theories and experiments, and the results show that the adsorbate formed on carbon nanotubes have the potential of revolutionizing gas storage technology [18－22].

It is found that the stable positions of the most metal adatoms are above the center of the carbon hexagon units when they are adsorbed on the outside of an individual SWCNT [23]. An investigation on the interactions of 3d transition metal with a single-walled armchair carbon nanotube was carried out to find adsorption geometries and magnetic properties of the adsorbed atoms and dimers [24]. In the experiment, the Au, Pd, Fe, Al, and Pb metal coat on carbon nanotubes with the help of a Ti buffer layer [25]. The researches on the Li and carbon nanotubes suggest not only a potential for the Li battery applications [26－28], but also an enhancement of hydrogen physisorption [29,30]. The adsorption of metal atoms on the carbon nanotubes will affect the electronic conductance of nanotubes [31－34]. Potassium, as a kind of typical electron-donor dopants, can be

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doped in SWCNTs to enhance conductivity [32,33]. A transition from a Tomonaga-Luttinger liquid to a Fermi-liquid behavior in potassium-intercalated mats of single-wall carbon nanotubes has been directly observed in experiment [34].

In this paper, firstly we discuss the possible adsorbed patterns of adsorbates on the single-walled carbon nanotubes for the atoms and molecules. Secondly, we describe the high-coverage stable structures of potassium adsorbed on SWCNTs. Then we show metal-semiconductor and semiconductor-semiconductor transitions in carbon nanotubes induced by intercalating alkali atoms.

2 Ground states of adsorbates on SWCNTs

A single-walled nanotube can be considered as a rolled graphite sheet. The adsorption sites on the center of carbon hexagons of the graphite sheet form a two-dimensional triangular lattice. A triangular lattice gas model has been used to describe the behavior of submonolayers of adsorbates on the graphite with centers of carbon hexagons as adsorption sites [35]. When the graphite sheet is rolled into a nanotube, the system is confined in the rolling direction, so the lattice of the adsorption sites on a carbon nanotube has a periodic condition along the rolling direction.

We consider the adatoms adsorbed on the center of carbon hexagons of SWCNT as a single-site adsorption, and use the Ising model to describe it [36]. Under the Ising model, spin $s_i = 1$ corresponds to atom occupying lattice site i, and $s_i = -1$ corresponds to vacancy occupying lattice site i. The Hamiltonian of system is given as:

$$H = J_1 \sum_{nn} s_i s_j + J_2 \sum_{nnn} s_i s_j + \mu \sum_i s_i$$

where J_1 is the nearest-neighbor interaction, J_2 is the next nearest-neighbor interaction, and μ is the chemical potential. The first sum runs over all the nearest-neighbor atom pairs, the second sum runs over all the next nearest-neighbor atom pairs, and the last sum runs over all the sites.

We discuss the case of $m = 0$ which is $(n, 0)$ zigzag type of SWCNTs, and use the Monte Carlo simulation to get all the possible ground states of the system. The ground state phase diagram for the case of $n = 6$ with $J_1 > 0$ is shown in Fig. 1 (a). There are nine different ground states and the corresponding structures are shown in Fig. 1 (b). By calculations on different $(n,0)$ SWCNTs, we find the relationship between the ground state structures and nanotube sizes n: the variation periodicity of the ground states with the increase of n is six [36], which is affected by the confinement along the rolling direction of SWCNTs. When n can be divided exactly by six, the ground state structures for the $(n,0)$ zigzag-type carbon nanotubes are the same as those of the planar triangular lattice. Otherwise, new ground state structures are found as a result of the size confinement of the system. If n cannot be divided exactly by two, there are eight new ground states. If n cannot be divided exactly by three, there are six and eight new ground states, respectively, depending on the remainder being one or two.

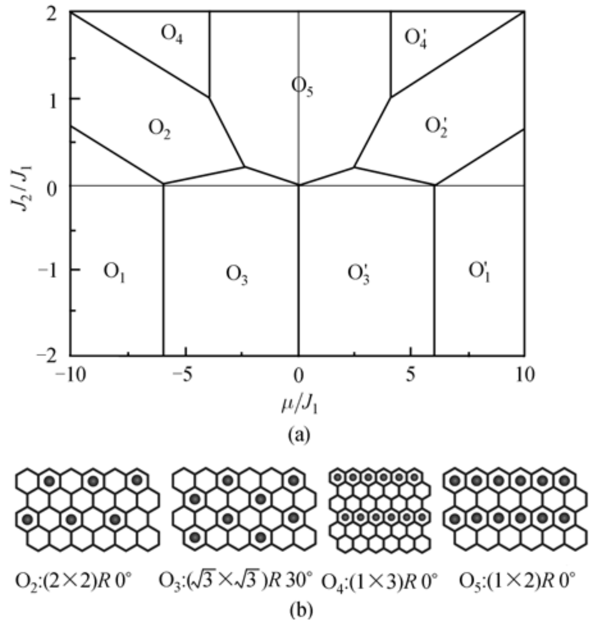


Fig. 1 (**a**) The ground state phase diagram for single-site adsorption on the (6,0) SWCNTs. The O_1 phase is a full structure with coverage $x = 1$, and the adsorbate patterns of O_2 - O_5 phases are shown in (**b**). The structures of the O_i' (i = 1, 2, 3, 4) phases are complementary to those of the O_i phases, and the black balls represent vacancies for the O_i phases or adatoms for the O_i' phases (from Ref. [36]).

Since the 2D triangular lattice exhibits a strong frustration effect for the antiferromagnetic Ising model [37], several different ground states may exist. The frustration effect can be measured by frustration function defined on closed contours [38]. For the SWCNTs, the system is confined in the rolling direction and new closed contours are formed along the the rolling direction. These lead to an additional frustration effect and new ground states. The ground states structures of adsorption on the SWCNTs can be composed of some basic substructures which are the primite cells of adsorption on the graphite plus derived substructures which are derived from the confinements of the SWCNTs, and the variation rules of the ground state structures accord with these facts [36].

We have also studied the two-site adsorption of diatomic molecules on the graphite and the carbon nanotubes [39]. The adsorbed diatomic molecules are modelled as dimers, which occupy two neighboring lattice sites, and we use the dimmer model to describe it [40—42]. The Hamiltonian of the System is given as:

$$H = J_1 \sum_{nn} s_i s_j + J_2 \sum_{nnn} s_i s_j + \mu \sum_i s_i - N J_1$$

It should to be notice that $s_i = 1$ means the corresponding site i is occupied by a unit of the dimer, and the occupation of the given lattice site demands one of its neighboring sites is also occupied. N is the number of adsorbed dimers. The term

NJ_1 is subtracted in the Hamiltonian since the summation over all the nearest-neighbor site pairs overestimates the total energy by including N bonds belonging to the N adsorbed dimmers [40—42].

By the Monte Carlo annealing, we obtained twelve different types of ground states of dimer adsorption on the (6, 0) SWCNT, more than the single-site adsorption. The structures of dimer adsorption on the $(n,0)$ SWCNTs are more complex than those of the singular-site adsorption due to addition frustration and confinement for the dimers. There is no general variation periodicity of the ground states with the increase of n for the different coverage. Compared with single-site adsorption, several helical structures are formed for the dimer adsorption on the $(n,0)$ nanotubes due to the confinement of nanotubes when the site number does not match with that of the basic substructure along the rolling direction [39].

3 High coverage adsorbate on SWCNTs

Since we have studied the ground states of adsorbates on SWCNTs with the effects of the size confinement, a total energy calculation has been carried out to investigate the ground states and discuss the stability of different phases. We have studied the adsorption of potassium on the SWCNTs [43,44]. For the K adsorption on graphite, the structures with coverage higher than 1/2 do not exist because of strong repulsion between K atoms in high coverage structures, where the nearest-neighbor bonding is smaller than diameter of K atoms [45]. When K atoms are adsorbed on outside of the nanotubes, the curved surface will enlarge the distance between K atoms, which can also be changed by the height of adsorbed atoms. This could lead to high coverage stable structures of adsorbate on carbon nanotubes although these structures are not stable for the case of adsorbate on graphite.

The stability of structures is determined by the formation energies. We define formation energy E_b as follows:

$$E_b = E_d - E_0 - x\mu_{\mathrm{K}}$$

where E_d and E_0 are energies per lattice site with and without K atoms doped. x denotes the coverage of K atoms. μ_{K} is the chemical potential of K atoms which should be less than the formation energy μ_0 of bulk K metal. For structure to be stable, E_b should be minus. The structure with minimum formation energy corresponds to the most stable structures. We perform the calculations of total energies of adsorbate structures using VASP (Vienna *ab initio* simulation package) [46—49]. The approach is based on an iterative solution of the Kohn-Sham equations of DFT in a plane wave basis set with Vanderbilt ultrasoft pseudopotentials [50]. The exchange-correlation given by Ceperley and Alder [51] is used in the parametrization of Perdew and Zunger [52].

We have calculated the total energies of possible ground-state structures of K adsorbate for the (6, 0) nanotube as shown in Fig. 1. We show the formation energies as functions of the chemical potential of K atoms for these different adsorbate structures in Fig. 2 (a). For stable adsorbate structures, $E_b<0$ determines the range of μ_{K}. μ_{K} should also be less than the formation energy μ_0 of bulk K metal, which is calculated on bcc K metal and found $\mu_0 = -1.15$ eV. Fig. 2 (a) shows that the $(2\times2)R\ 0^\circ$ structure with $x=1/4$ is most stable structure when $-1.585\ \mathrm{eV} < \mu_{\mathrm{K}} < -1.396$ eV, the $(1\times2)R\ 0^\circ$ structure with $x=1/2$ is most stable one when $-1.396\ \mathrm{eV} < \mu_{\mathrm{K}} < -1.309$ eV and the $(\sqrt{3}\times\sqrt{3})R\ 30^\circ$ structure with $x = 2/3$ is most stable one when $-1.309\ \mathrm{eV} < \mu_{\mathrm{K}} < -1.150$ eV [43]. Under the ideal gas model, μ_{K} depends on the temperature (T) and the pressure (p) of the environment, which is given as:

$$\mu_{\mathrm{K}} = k_{\mathrm{B}}T\ln p - \frac{5}{2}k_{\mathrm{B}}T\ln(k_{\mathrm{B}}T) - k_{\mathrm{B}}T\ln\left(\frac{2\pi m}{h^2}\right)^{\frac{3}{2}}$$

where k_{B} is the Boltzmann constant, m is the mass of potassium atom and h is the Planck constant. So the phase diagram of temperature and pressure which presents the exis-

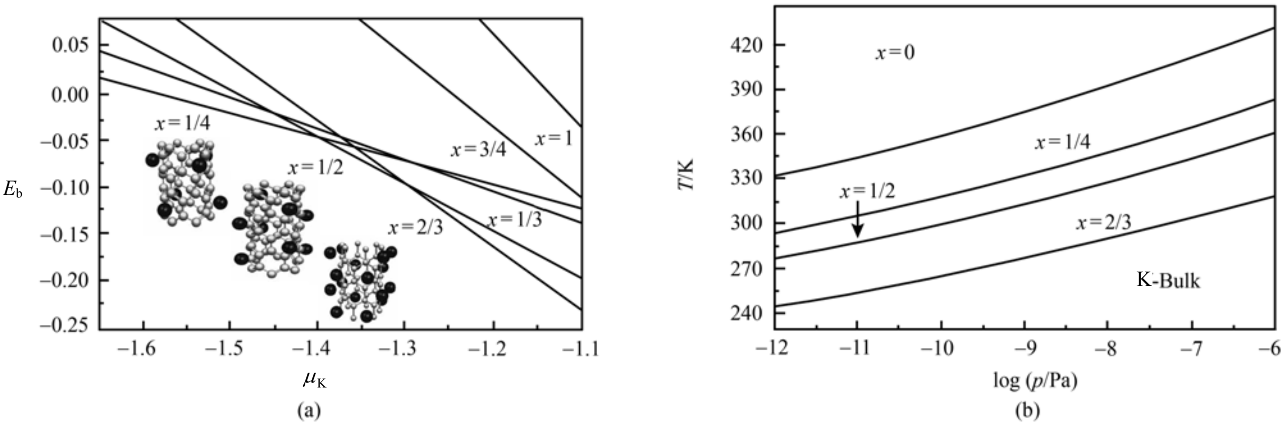


Fig. 2 (**a**) Formation energies for different types of adsorbate structures as functions of μ_{K} on the (6, 0) nanotube. The three most stable structures with coverage x =1/4, 1/2, 2/3 are also shown (from Ref. [43]). (**b**) The temperature and pressure areas where these three structures exist (from Ref. [44]).

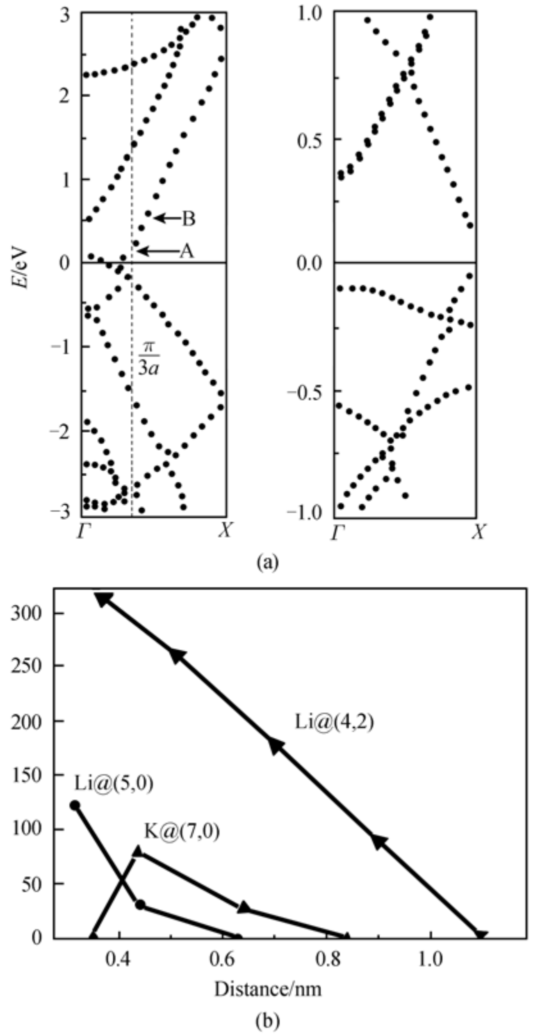
tent areas for stable structures is shown in Fig. 2 (b) [44]. It shows there are three different coverage (x=1/4, 1/2, 2/3) possible appearance for the potassium adsorbate on SWCNTs.

The nearest-neighbor K adatoms distance d_r on the (n,0) SWCNTs is larger than that of on the graphite for the same coverage [43]. When K atoms are adsorbed on graphite, the length of nearest-neighbor K adatoms distance is only determined by the adsorbate structure. Because the distance between centers of two nearest-neighbor carbon hexagons is smaller than the diameter of the adsorbed K atoms, the high coverage adsorbate structures with x>1/2 are unstable. While for the adsorption on the (n,0) SWCNTs, the d_r of one adsorbate structure can be increased by the decrease of nanotubes diameter n or by the increase of adsorption height h. An approximation for the distance of nearest-neighbor K adatoms along the rolling direction is $d_r = \sqrt{3}\, d_{C\text{-}C} + 2\pi h/n$, where $d_{C\text{-}C}$ is the length of C-C bonds. So these two adjustable parameters n and h are combined to elongate the d_r and cause the high coverage structures stable. So for adsorbate on the SWCNTs, we predict that there are two types of high coverage stable structures (x=1/2, 2/3) in addition to the low coverage $(2\times2)R\ 0^\circ$ (x=1/4) structure that is stable for adsorbate on graphite, due to the curvature structure of carbon nanotube surface. These results and mechanism are in accordant with the experiments that coverage of Li atoms in the SWCNTs bundles can be high [26,28].

4 Electronic properties of metal-adsorbed SWCNTs

When we study the K adsorbate outside of the nanotube, it is found that DOS near the Fermi level is increased as a result of potassium absorption, which may enhance the conductance of the tube [44]. When the metal atoms are adsorbed inside of SWCNTs, the intercalating dope can change the electronic property of nanotubes. Meunier *et al.* found that Li ions can enter tubes through topological defects or through the ends of open-ended nanotubes by ab initio simulations [53]. Jeong *et al.* used the plasma-ion irradiation method to insert metal atoms into nanotubes [54]. For K-intercalated single walled carbon nanotubes, the intercalating can enhance the conductance [32] and shift up the Fermi energy [55,56].

We show that intercalating of alkali atoms could transform a metal tube into a semiconductor tube or a semiconductor tube into a semiconductor tube with different band gaps due to a unique feature of band structures in some SWCNTs as quasi-one-dimensional materials [57]. We have performed the calculations of total energies and band structures of alkali-intercalated SWCNTs using VASP [46—49]. The sets of calculations are the same as those of K adsorbed on SWCNTs [43,44], except that we use the exchange correlation with the generalized gradient approximation given by Perdew and Wang [58]. For the pristine (5,0) carbon nanotube, there is a single band (from A to B) near the Fermi energy in the band structure as shown in Fig. 3 (a). The unit cell of the nanotubes can be changed by atom intercalating. For example, if the unit cell of the nanotube is enlarged three times, then due to the band folding, this single energy band is folded to the boundary of the Brillouin zone. The energy degeneracy is generally eliminated by the structure perturbation due to the intercalating and a gap in the band structures will appear. When the electrons from dopant atoms fully fill in all the energy bands below the gap, the nanotube becomes a semiconductor.



(a)

(b)

Fig. 3 (**a**) The band structure of pristine metal (5,0) SWCNT and the band structure of Li-doped semiconductor (5,0) SWCNT with Li_2C_{60} (from Ref. [57]). (**b**) The gaps of the alkali atoms doped SWCNTs with the distances of neighboring intercalated atoms.

We focus on the case that the alkali atoms are located along the axis of the tube. For Li-intercalated graphite, the distance between Li atoms and the sheet is 1.85 Å, while the radius of (5,0) tube is 2.04 Å, thus the (5,0) tube is suitable for Li intercalating. There are three kinds of possible structures for Li_2C_{60} in the (5,0) tube. Li intercalating makes the band structure [shown in Fig. 3 (a)] be folded at at $k = \pi/(3a)$, and the Fermi energy be shifted up to the ending point of the band at the boundary of the Brillouin zone. For the structure Li_2C_{60} where the two distances between the neighboring Li atoms are 3.10 Å and 9.62 Å respectively, there is a gap of 123 meV at the *X* point of the band structure as is shown in Fig. 3 (b). The nearest distances between the alkali atoms in the three structures are different. The band gaps decreases from 123 meV to 0 meV as the distances increases. Results of Li, K atoms in the (4,2) and (7,0) carbon nanotubes are also shown in the Fig. 3 (b).

This transition mechanism is quite general and there are possibilities to induce metal-semiconductor transitions and semiconductor-semiconductor transitions in various nanotubes by the intercalating of alkali atoms. Using this mechanism, one can transform semiconductor nanotubes with an indirect band energy gap into those with a direct energy gap, which is very important for fabricating the light-emitting devices. At the same time, this would also lead to a new method for forming the heterojunctions and be useful and important in the applications of nanodevices.

5 Summary

In summary, we have investigated the adsorption on the SWCNTs. Using the Monte Carlo simulation, we first obtained the possible adsorbed patterns of atoms and molecules on the single-walled carbon nanotubes and the ground state phase diagrams of single-site and two-sites (dimer) adsorption. For single-site adsorption on (*n*,0) SWCNTs, the variation periodicity of ground state structures with the increase of nanotube size *n* is obtained. For two-sites adsorption, the phase diagrams and variety of ground state structures are more complex. The curvature of carbon nanotube surface enlarge the distance of adsorbate atoms and thus enhances the stability of high coverage structures of adsorbate. By the first principle calculations, we have determined the energies of different types of potassium adsorbate structures on the SWCNTs and graphite surface. Two novel high-coverage ($x = 1/2, 2/3$) stable structures of *K* atoms adsorbed on SWCNTs, in addition to the low coverage ($x = 1/4$) structure which is stable for adsorbate on graphite, have been found. The electronic properties of SWCNTs can be modified by adsorbate atoms and metal-semiconductor and semiconductor-semiconductor transitions are achieved. Those results show the adsorption of carbon nanotubes have great potential of applications.

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