

High-coverage stable structures of potassium adsorbed on single-walled carbon nanotubes

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We have investigated the structures of potassium adsorbate on single-walled carbon nanotubes and graphite using the first-principles approach. We show that the curvature of carbon nanotube surface enhances the stability of high coverage structures of adsorbate. We predict that two types of high coverage structures ($x = 1/2, 2/3$) are stable for adsorption on the (6,0) carbon nanotube in addition to low coverage structures of adsorbate on graphite. The dependence of the stability on the size of carbon nanotubes is analyzed.

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The adsorption of atoms on carbon nanotubes has attracted much attention recently.¹⁻¹¹ The adsorbate formed on carbon nanotubes has the potential of revolutionizing gas storage technology²⁻⁵ and affects the electronic conductance of nanotubes.⁶⁻¹¹ The adsorption can be on individual single-walled carbon nanotubes and single-wall carbon nanotube (SWNT) bundles. Potassium, as a kind of typical electron-donor dopants, can be doped in SWNT's to enhance conductivity.^{6,7} Jo *et al.* calculated the energies for K-doped SWNT bundles with different doping concentrations, assuming that the doped potassium atoms are located at interstitial channel sites.⁸ Gao *et al.* performed molecular dynamics calculation using a parametrized potential to discuss the structure stability of adsorbate in nanotube crystals.⁹ Miyamoto *et al.* studied cohesion properties of potassium atoms inside the carbon nanotubes, determining the most stable structure according to the heats of formation.¹⁰ Miyake and Saito found that the effect of potassium doping inside carbon nanotubes is highly sensitive to the size of nanotube.¹¹ It is, however, unclear what kind of structures of potassium adsorbate outside the SWNT is most stable.

A single-walled nanotube can be considered as a rolled graphite sheet. The adsorption of atoms on the graphite with center of carbon hexagon as adsorption site can be described by a triangular lattice gas model, whose possible ground state has been investigated using different methods.^{12,13} When the graphite sheets are rolled into nanotubes, the effects of the size confinement on the ground-state structures are studied using the Monte Carlo method.¹⁴ In K adsorption on graphite surface, ordered structures with coverage of 1/4 and 1/3 were found and the phase transitions between $(2 \times 2)R 0^\circ$ and $(\sqrt{3} \times \sqrt{3})R 30^\circ$ were observed.^{15,16} Total-energy calculations have been carried out to investigate the ground states and discuss the stability of different phases.¹⁷ 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 much smaller than diameter of K atoms. For K adsorbate outside of the nanotube, the surface is curved and the distance between K atoms is enlarged due to the surface curvature and can also vary with the change of 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.

In this paper, we predict that structures with coverage of 1/4, 1/2, and 2/3 are stable for adsorption on carbon nanotubes, while in a flat graphite surface, only structures with coverage less than 1/2 are stable. The curvature effect is shown to be important for the stability of adsorbate structures. The dependence of the structure parameters on the diameters of the carbon nanotubes is analyzed.

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

$$E_b = E_d - E_0 - x\mu_K, \quad (1)$$

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. The width of chemical potential region where structures are stable is denoted as E_w . The maximum of the absolute value of E_b is denoted as $|E_b|_m$.

We performed the calculations of total energies of adsorbate structures using VASP (Vienna *ab initio* simulation package).¹⁸ The approach is based on an iterative solution of the Kohn-Sham equations of density-functional theory in a plane-wave basis set with Vanderbilt ultrasoft pseudopotentials.¹⁹ The exchange correlation given by Ceperley and Alder²⁰ is used in the parametrization of Perdew and Zunger.²¹ We set the plane-wave cutoff energy to be 400 eV. Monkhorst-Pack scheme²² is used to sample the Brillouin zone and the optimizations of the lattice constants and the atom coordinates are made by conjugate gradient minimization of the total energy. The tolerance of energy convergence is 10^{-4} eV.

We have calculated the energies of different types of adsorbate structures on the SWNT, graphite surface, and monolayer. For the adsorption on the $(n,0)$ nanotubes, when n can be divided by six, the possible ground-state structures of adsorbate on the $(n,0)$ tubes are the same with those on graphite.¹⁴ We have calculated the total energies of possible ground-state structures of adsorbate for the (6,0) tube as shown in Fig. 1. In the calculations, $1 \times 1 \times 11 k$ mesh is used. In Fig. 1, we have only listed the low coverage structures. The high coverage structures of $(2 \times 2)R 0^\circ$ and $(\sqrt{3} \times \sqrt{3})R 30^\circ$ types are counterparts of the low coverage

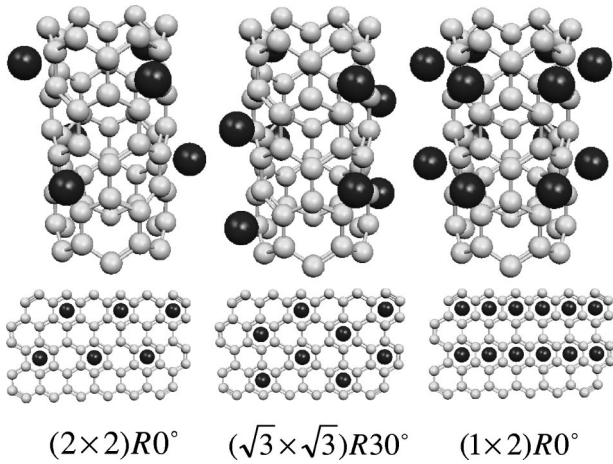
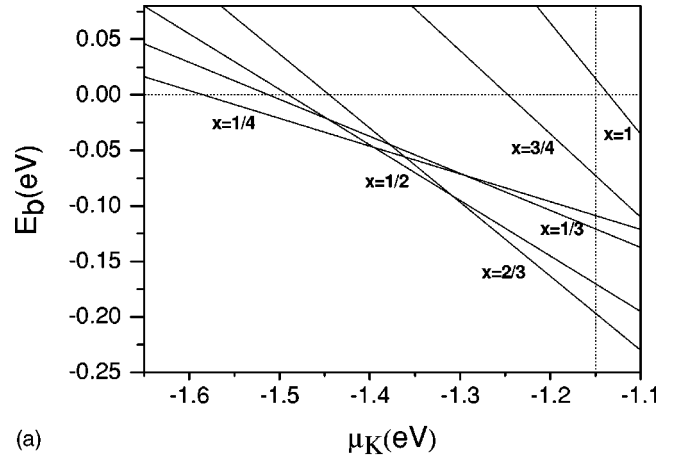
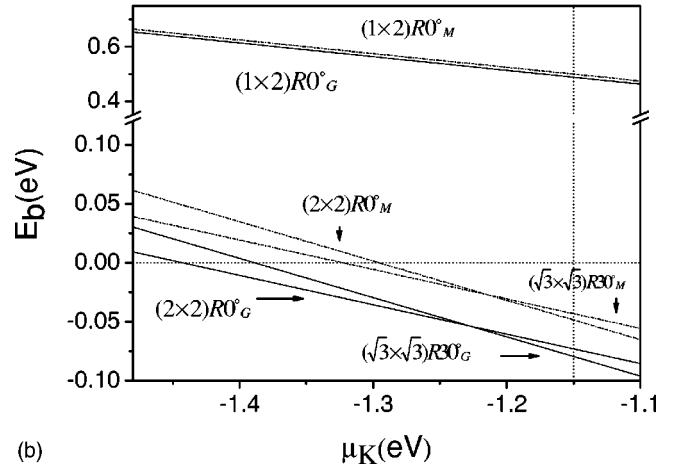


FIG. 1. The adsorbate structures on carbon nanotubes and graphite surface. Gray balls represent carbon atoms and black balls represent K atoms. High coverage structures of $(2 \times 2)R 0^\circ$ and $(\sqrt{3} \times \sqrt{3})R 30^\circ$ type are the counterparts of low coverage structures by exchanging atoms with vacancies.

structures by exchanging atoms with vacancies. In Fig. 2, we show the formation energies as functions of the chemical potential of K atoms for different adsorbate structures. For stable adsorbate structures, $E_b < 0$ determines the minimum value of μ_K . μ_K should also be less than the formation energy μ_0 of bulk K metal. μ_0 has been calculated on bcc K metal with a $11 \times 11 \times 11$ mesh. We find that the optimized lattice constant $a = 5.04 \text{ \AA}$ and $\mu_0 = -1.15 \text{ eV}$. $E_b = 0$ and $\mu_0 = -1.15 \text{ eV}$ are drawn in dashed line. Chemical potential μ_K for stable adsorbate structures varies between the two dashed lines. Figure 2(a) is the result for SWNT. The $(2 \times 2)R 0^\circ$ structure with $x = 1/4$ is most stable structure when $-1.585 \text{ eV} < \mu_K < -1.396 \text{ eV}$. This is the same type of structure which has been predicted by Gao *et al.* in nanotube crystals.⁹ The $(1 \times 2)R 0^\circ$ structure with $x = 1/2$ is most stable one when $-1.396 \text{ eV} < \mu_K < -1.309 \text{ eV}$ and the $(\sqrt{3} \times \sqrt{3})R 30^\circ$ structure with $x = 2/3$ is most stable one when $-1.309 \text{ eV} < \mu_K < -1.150 \text{ eV}$. For the K chain inside the $(n, 0)$ nanotube, the structure is stable only for $n \geq 7$.¹⁰ For $n = 6$, the K chain inside nanotube is unstable. Thus for the $(6, 0)$ tube the adsorption should occur outside of nanotube and the stable adsorbate structures are the $(2 \times 2)R 0^\circ$ structure with $x = 1/4$, the $(1 \times 2)R 0^\circ$ structure with $x = 1/2$, and the $(\sqrt{3} \times \sqrt{3})R 30^\circ$ structure with $x = 2/3$. The structural parameters of the stable structures are shown in Table I. Similar calculations have been performed on graphite surface and monolayer. As is shown in Fig. 2(b), the $(2 \times 2)R 0^\circ$ structure with $x = 1/4$ and $(\sqrt{3} \times \sqrt{3})R 30^\circ$ structure with $x = 1/3$ are most stable for graphite and monolayer. Changing chemical potential, the most stable adsorbate structure will change from the $(2 \times 2)R 0^\circ$ structure to the $(\sqrt{3} \times \sqrt{3})R 30^\circ$ structure, which agrees with the experiment results showing phase transition between $(2 \times 2)R 0^\circ$ and $(\sqrt{3} \times \sqrt{3})R 30^\circ$.¹⁶ The calculations show that the $(1 \times 2)R 0^\circ$ structure and higher coverage structures are not energy stable for adsorbate on graphite surface nor on graphite monolayer. For the $(1 \times 2)R 0^\circ$ structure on graphite, the nearest distance of K atoms is 2.441 \AA while the diameter of



(a)



(b)

FIG. 2. Formation energies for different types of adsorbate structures as functions of μ_K (a) on the $(6, 0)$ tube. Structures are represented by coverage; (b) on graphite surface and monolayer. Subscripts G and M correspond to graphite surface and monolayer, respectively.

$\times 2)R 0^\circ$ structure with $x = 1/4$ and $(\sqrt{3} \times \sqrt{3})R 30^\circ$ structure with $x = 1/3$ are most stable for graphite and monolayer. Changing chemical potential, the most stable adsorbate structure will change from the $(2 \times 2)R 0^\circ$ structure to the $(\sqrt{3} \times \sqrt{3})R 30^\circ$ structure, which agrees with the experiment results showing phase transition between $(2 \times 2)R 0^\circ$ and $(\sqrt{3} \times \sqrt{3})R 30^\circ$.¹⁶ The calculations show that the $(1 \times 2)R 0^\circ$ structure and higher coverage structures are not energy stable for adsorbate on graphite surface nor on graphite monolayer. For the $(1 \times 2)R 0^\circ$ structure on graphite, the nearest distance of K atoms is 2.441 \AA while the diameter of

TABLE I. Structural parameters for the stable structures on the $(6, 0)$ tube and graphite: h is the adsorption height and d is the nearest distance of K atoms. Subscript G corresponds to graphite. The results for monolayer is given in the bracket for comparison.

Type	$(2 \times 2)R 0^\circ$ $x = 1/4$	$(1 \times 2)R 0^\circ$ $x = 1/2$	$(\sqrt{3} \times \sqrt{3})R 30^\circ$ $x = 2/3$	$(2 \times 2)R 0_G^\circ$ $x = 1/4$	$(\sqrt{3} \times \sqrt{3})R 30_G^\circ$ $x = 1/3$
$h(\text{\AA})$	2.327	2.448	2.561	2.678(2.701)	2.776(2.732)
$d(\text{\AA})$	6.355	4.246	4.027	4.882(4.895)	4.228(4.246)

K atom in bulk structure is 4.544 Å.²³ The difference between the atom diameter and nearest distance of K atoms is large. Therefore the strong repulsion between K atoms makes the structure unstable. For the $(1 \times 2)R 0^\circ$ structure adsorbed on the (6,0) nanotube, the nearest-neighbor distance (4.858 Å) of K atoms along the rolling direction is larger than that (4.246 Å) along the unrestricted direction which corresponds to the second nearest-neighbor distance for adsorbate on graphite. Thus the nearest-neighbor distance for adsorbate on the SWNT is much larger than that on graphite. For the $(\sqrt{3} \times \sqrt{3})R$ structure with coverage of $2/3$ on the SWNT, the nearest-neighbor distance which is on a line 60° tilted with the rolling direction is 4.027 Å. It is also much larger than that on graphite. Thus the $(1 \times 2)R 0^\circ$ structure with coverage of $1/2$ and the $(\sqrt{3} \times \sqrt{3})R 30^\circ$ structure with coverage of $2/3$ on the (6,0) tube are stable. The $(\sqrt{3} \times \sqrt{3})R 30^\circ$ structure with $x=1/3$ is not the most stable one for SWNT, because the $(1 \times 2)R 0^\circ$ structure with $x=1/2$ and the $(\sqrt{3} \times \sqrt{3})R 30^\circ$ structure with $x=2/3$ have replaced the $(\sqrt{3} \times \sqrt{3})R 30^\circ$ structure with $x=1/3$ as more stable structures in the region of large chemical potential. The reason that high coverage structures of adsorbate are stable on the SWNT is as follows: For the same adsorption height h , the nearest-neighbor distance of adsorbate atoms on the nanotube is larger than that on the graphite due to the curvature of nanotube. The nearest-neighbor distance is also dependent on h . When h is increased, the distance of nearest-neighbor pairs unparallel to the tube will also increase. Thus the adsorbed atoms have one more degree of freedom to adjust the structure parameters. For a stable structure, the bonding length should not be much smaller than the diameter of adsorbed atoms. When atoms are adsorbed on graphite, the bonding length is only determined by the adsorbate structure. When the nearest-neighbor distance is much smaller than the diameter of the adsorbed atoms, there will be strong repulsion force, which will lead the adsorbate structures with high coverage unstable. For adsorbate on the SWNT, nearest-neighbor distance can be increased by the curvature and the increase of adsorption height h . This leads to the stability of high coverage structures ($x=1/2, 2/3$).

In the following, we will investigate the dependence of the stability of adsorbate structures on the nanotube size. When the nanotube size is changed, the adsorbate structures can be changed due to the confinement.¹⁴ Since $(1 \times 2)R 0^\circ$ type is the common ground state of adsorbate structure for all $(n,0)$ nanotubes, we will discuss the stability of high coverage structures $(1 \times 2)R 0^\circ$ with the increase of nanotube size and the curvature effect on stability of adsorbate. The distance of K atoms has strong effect on the structure stability. For the $(1 \times 2)R 0^\circ$ structure on graphite, the distance of K atoms is too small and the structure is unstable. When this type of structure is formed on carbon nanotubes, there are two kinds of nearest-neighbor pairs. One is along nanotube whose distance is denoted as d_z . The other is perpendicular to nanotube, whose distance is denoted as d_r . We have $d_r = \sqrt{3}d_C + 2\pi h/n$, where d_C is the nearest-neighbor distance between two carbon atoms. d_r varies with the diameter of the nanotube and the adsorption height h . In Fig. 3,

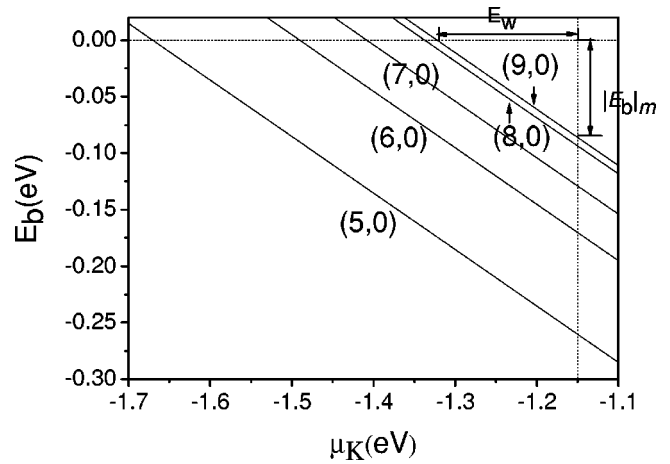


FIG. 3. Formation energy diagram for the $(1 \times 2)R 0^\circ$ structure on the $(n,0)$ nanotubes with different size n .

we show the variation of formation energy of the $(1 \times 2)R 0^\circ$ structure on $(n,0)$ nanotubes with the increase of n . E_w and $|E_b|_m$ measures the stability of structures. As is shown in Fig. 3, both E_w and $|E_b|_m$ are reduced with the increase of the size n , indicating that the structures become less stable. Figure 4 shows the variation of d_r and the adsorption height h with the increase of the size n of nanotubes. It can be seen that d_r decreases with the increase of the size of nanotubes, which leads to less stability of adsorbate structures. But even for the case of $n=9$, the nearest-neighbor distance d_r (4.206 Å) is still close to the bonding length of the K bulk bcc structure and thus the adsorbate structure remains stable. From Fig. 4, it can be also seen that the adsorption height increases with the increase of the size of nanotube. Since the nearest-neighbor distance d_r is reduced as the size n increases, this leads to a repulsion between K atoms. Thus h is increased with the increase of n to reduce the repulsion between K atoms. However, d_r is still reduced slightly with the increase of the size n which makes the structures less stable.

For the adsorption of K atoms inside the SWNT, it is found that linear K chains inside carbon nanotubes are stable

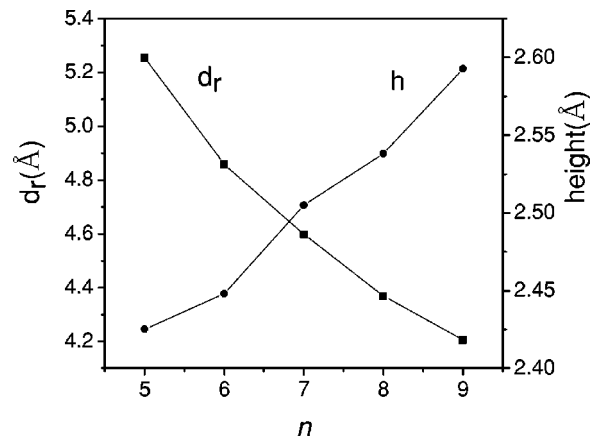


FIG. 4. The variation of d_r and adsorption height h with size n of nanotubes.

for the (7,0) and (8,0) tubes while the formation energy for the (6,0) tube is almost zero.¹⁰ We have found similar results for the K adsorption inside the nanotube. A stable structure of K atoms inside nanotube demands that the radii of nanotube should match the bonding length between K and C atoms. We have compared relative stability between the K chain inside nanotube and the $(1 \times 2)R 0^\circ$ structure outside nanotube. The K adsorption inside the nanotube has low coverage and corresponds to the small chemical potential, while the $(1 \times 2)R 0^\circ$ structure outside nanotube has high coverage and corresponds to the large chemical potential. We find that for the (7,0) tube, K chain is stable for $\mu_K < -1.228$ eV, otherwise $(1 \times 2)R 0^\circ$ is more stable. For the (8,0) tube, K chain is stable for $\mu_K < -1.190$ eV and otherwise $(1 \times 2)R 0^\circ$ is more stable.

In summary, we have investigated the stability of structures of K adsorbate on the SWNT and graphite. The formation energies of different adsorbate structures are calculated by the first-principles approach. We find that the adsorbate structures on the curvature surface of carbon nanotubes are

different with that on the flat surface of graphite. For adsorbate on graphite, the $(2 \times 2)R0^\circ$ structure ($x=1/4$) and the $(\sqrt{3} \times \sqrt{3})R 30^\circ$ structure ($x=1/3$) are stable structures, which agree with experimental results. For adsorbate on the SWNT, we predict that there are two types of high coverage stable structures ($x=1/2, 2/3$) in addition to the low coverage $(2 \times 2)R 0^\circ$ ($x=1/4$) structure that is stable for adsorbate on graphite. The stability of high coverage structures on the SWNT is due to the curvature structure of carbon nanotube surface. The curvature structure of carbon nanotubes leads to the dependence of nearest-neighbor distance d_r on the adsorption height h . d_r can be increased by the curvature and the change of the adsorption height h . This leads to stable high coverage structures $(1 \times 2)R 0^\circ$ ($x=1/2$) and $(\sqrt{3} \times \sqrt{3})R 30^\circ$ ($x=2/3$) for adsorbate on SWNT despite that the structures are not stable for graphite.

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