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Density functional theory study of potassium atom adsorbing on the interior and exterior of a series of carbon nanotubes

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ABSTRACT

Density functional theory was applied to study the adsorption of potassium atoms on the interior and exterior of a series of carbon nanotubes. It is found that K atoms can stably adsorb on the interior and exterior of a carbon nanotube. A K atom adsorbs at the center or near the sidewall on the interior of a carbon nanotube, but a K atom will only adsorb near the sidewall on the exterior of a carbon nanotube. The interior of a small-radius carbon nanotube is not favorable for K-atom adsorption, due to repulsive interaction. The interior of a medium-radius carbon nanotube is more favorable for K atom adsorption because of the interaction of the K atom with multiple carbon rings. We also investigate the K atom in regard to adsorption distance, Mulliken population, and the redistribution of electron density.

1. Introduction

A single-walled carbon nanotube (SWNT) is a one-dimensional material that possesses novel mechanical, electronic, magnetic [1], and chemical properties [2]. So carbon nanotubes (CNTs) have been applied in many fields [3–5]. The intrinsic electronic and mechanical properties of CNTs can be modified by the introduction of foreign atoms. Potassium, as a kind of typical electrondonor dopant, can be doped in SWNTs to enhance the physical and chemical properties of the SWNT. Many studies have focused on the electronic, optical, and emission properties of potassium-intercalated carbon nanotubes [6–15]. Theoretical calculations [16,17] have revealed that potassium doping is not a simple charge transfer. The nearly free electron state of the nanotube couples with the K 4 s orbital. Kang et al. [18,19] investigated structural phases of potassium in carbon nanotubes. As the radius of the carbon nanotubes is increased, various structural phases may be formed, ranging from an atomic strand to multi-shell packs. Gao et al. [20] used molecular dynamics to predict structures and properties of potassium doping a single-wall carbon nanotube, finding the optimum stoichiometry to be KC_{16}. Yang et al. [21,22] showed that the curvature of a carbon nanotube surface enhances the stability of high-coverage structures of potassium adsorbate. Yang et al. [23] reported that the frequency of high-frequency Raman mode and the specific heat curves vary with the saturation of K atoms. Kotakoshi et al. [24] found that ion irradiation could be used to introduce K ions into different types of CNTs. Early in 2005, Yang and Ni [25] showed that K atoms intercalating can induce semiconductor–semiconductor transitions for carbon nanotubes. Farajian et al. [26] investigated the stationary as well as the dynamic effective potentials for inserting typical alkali metals into carbon nanotubes, the height of the potential barrier of K is higher than that of Na. Kang and Hwang [27] used carbon nanocapsules to encapsulate potassium ions for nano-memory-element applications.

The investigation of interactions between K atoms and different types of carbon nanotubes is necessary to understand the effects of chirality. Therefore, we investigated the adsorption energy, adsorption distance, and charge transfer of K atoms on the interior and exterior for a series of carbon nanotubes. We also investigated the redistribution of electron density induced by the adsorption of K atoms. We found that the interiors of medium-radius carbon nanotubes are more suited for K atom adsorption than the interiors of smaller-radius CNTs.

2. Method

Our calculations were based on density functional theory (DFT) as implemented in the SIESTA package [28], which is based on the generalized gradient approximation (GGA) of the Perdew–Burke–Emzerhof (PBE) exchange–correlation functional [29]. The interactions between valence electrons and ions were treated by norm-conserving pseudopotentials [30] with separable non-local operators [31]. Atomic orbitals with double-ζ were used to expand the electron wave functions [28,32]. An energy cutoff of 150 Ry was applied to the real-space mesh with a single *k* point, and 0.02 Ry

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was the confinement energy shift that defined the cutoff radii of the atomic orbitals. All geometries were optimized using the CG method [33]. The convergence criterion for structure optimization was that all forces be less than 0.05 eV/Å. The energies were converged to 1×10^{-4} eV.

3. Results and discussion

A series of $(n,0)$ single wall carbon nanotubes are investigated in the present calculations, where $n = 8, 10, 12, 14, 16, 18, 20, 22$. All edge carbon atoms on the two ends of a carbon nanotube having dangling bonds are passivated by hydrogen atoms. The vacuum region extends 15 Å in three directions in order to eliminate the interaction between the carbon nanotube and its image. We consider that there are three typical sites on the carbon nanotube that could adsorb K atom, namely, the hollow site (H) at the center of a hexagon, the bridge site (B) at the center of a carbon–carbon bond, and the top site (T) directly above a carbon atom (see Fig. 1a). The K atom was therefore put on these three typical sites of the interior and exterior of a carbon nanotube. The adsorption conformations of a K atom in the interior and exterior of a (14,0) carbon nanotube are shown in Fig. 1.

Firstly, we calculate the adsorption energy of the K atom on the interior and exterior of the carbon nanotube. At each site, a K atom could adsorb on the carbon nanotube stably. To study the stability of the adsorption, the adsorption energy is calculated using the formula

$$E_{ads} = E_{CNT+K} - E_{CNT} - E_K \quad (1)$$

where E_{CNT+K} is the total energy of the carbon nanotube together with the adsorbed K atom, E_{CNT} is the energy of the independent carbon nanotube, and E_K is the energy of the single K atom. The calculated adsorption energies are shown in Table 1. The adsorption energies are negative, which signifies an exothermic process. The K atom could adsorb stably on the interior or exterior of the carbon nanotube. Comparing the adsorption energy of a K atom in the three typical sites, we found that the adsorption energy was almost the same at all three sites. Here, a K atom close to the hollow site is analyzed as an example of adsorption configuration.

The adsorption energies of a K atom at a hollow site on the interior and exterior of a carbon nanotube are shown in Fig. 2. The adsorption energies of a K atom in the interior are almost stronger than the exterior for a given type of carbon nanotube. In the interior of the carbon nanotube, the adsorption energies of the K atom increase, then decrease to −1.03 eV, as the carbon nanotube radius increases. The strongest adsorption energy for a K atom is in the interior of (10,0); the weakest adsorption energy for a K atom is in the interior of (8,0). On the exterior of the carbon nanotube, the adsorption energies of the K atom increase with increasing radius, finally reaching −0.93 eV. The difference in adsorption energies between interior and exterior gradually decreases with increasing carbon nanotube radius.

The adsorption distances of a K atom on the interior and exterior of a carbon nanotube for a hollow site are shown in Fig. 3. In the interior of the carbon nanotube, the shortest adsorption

Table 1
The adsorption energies of a K atom on the interior and exterior of a carbon nanotube for various sites. In and Ex represent the interior and exterior of the carbon nanotube. The letters H, B, and T represent the hollow, bridge, and top sites of the carbon nanotube. Energy is presented in units of (eV).

	H(In)	H(Ex)	B(In)	B(Ex)	T(In)	T(Ex)
(8,0)	−0.53	−0.59	−0.53	−0.56	−0.51	−0.58
(10,0)	−1.40	−0.69	−1.40	−0.67	−1.41	−0.68
(12,0)	−1.22	−0.75	−1.22	−0.73	−1.23	−0.73
(14,0)	−1.15	−0.82	−1.16	−0.80	−1.16	−0.80
(16,0)	−1.09	−0.84	−1.09	−0.82	−1.10	−0.83
(18,0)	−1.08	−0.88	−1.08	−0.85	−1.08	−0.86
(20,0)	−1.06	−0.91	−1.07	−0.88	−1.07	−0.89
(22,0)	−1.03	−0.93	−1.03	−0.89	−1.03	−0.90

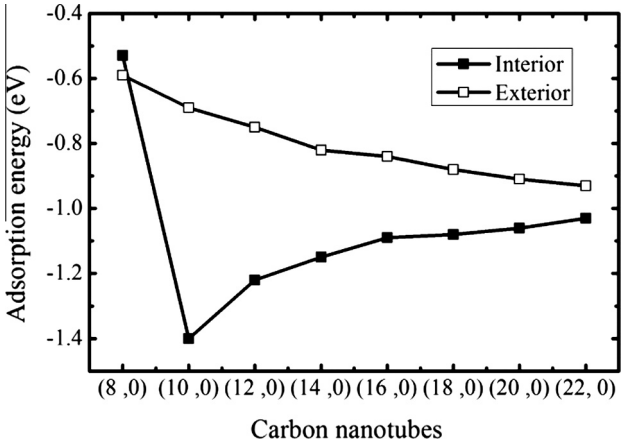

Fig. 2. The adsorption energies of a potassium atom on the interior and exterior of a carbon nanotube at a hollow site.

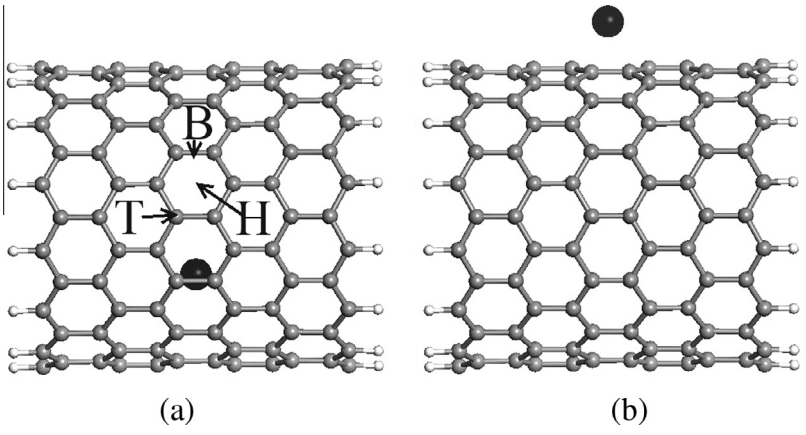

Fig. 1. The conformations of a K atom adsorbed on the interior and exterior of a (14,0) carbon nanotube. The grey, white, and black balls represent carbon, hydrogen, and potassium atoms, respectively. (a) The letters H, B, and T represent the hollow, bridge, and top site of the carbon nanotube, with a K atom adsorbed stably in the interior of the carbon nanotube, (b) K atom adsorbed stably on the exterior of the carbon nanotube.