Manipulation of Separation Selectivity for Alkali Metals Using Hydrated Single-Walled Carbon Nanotubes: A Theoretical Study

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Abstract

Alkali metal (Cs/Li/Na) adsorption on hydrated (5, 5)/(9, 0) single-walled carbon nanotubes (CNTs) with a capped edge had been investigated by first-principles calculations. For the hydrated indefective (5, 5)/(9, 0) CNT, adsorption energy ordering of the alkali-metal adatoms is Cs>Li>Na so that the Cs adsorption was energetically favored with respect to the Li/Na adatom. However, the adsorption energy ordering of the alkali-metal adatoms for the defective (5, 5) CNT was Li>Cs>Na. Therefore, the (5, 5)/(9, 0) P-CNT adsorbed Cs atoms preferentially, while the (5, 5)/(9, 0) D-CNT adsorbed Li atoms advantageously. The marked difference of the adsorption energy order was attributed to different electronegativities, different atomic radii of different alkali metals and influence of the vacancy defect. Therefore, separation selectivity for alkali metals could be actualized using the capped single-walled carbon nanotubes.

Keywords

First-principles calculation, Alkali metal, Carbon nanotube, Adsorption energy, Vacancy defect, Separation selectivity.

1. Introduction

Carbon nanotubes [1] (CNTs) have been considered to be one of the promising candidates because of its outstanding electrical and mechanical properties, vast surface area and large length-to-diameter ratio [2-5]. Especially in recent years, they have aroused scientific interests in different areas, and great achievements in scientific research have demonstrated far-ranging applications in nanometer-scale devices in future [6-8].

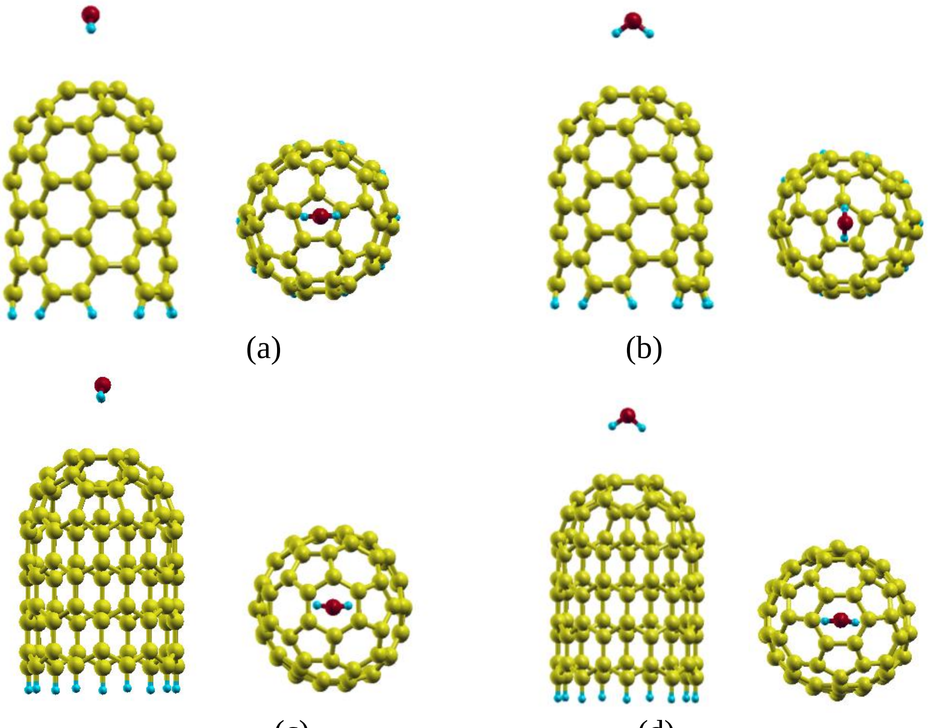
But most single-walled carbon nanotubes prepared in the laboratories are not indefective. In addition to vacancy defects, a crowd of more complicated defects can also be formed, e.g., pentagon/heptagon Stone-Wales (SW) defects, amorphous complexes, etc[9]. However, the behavior of these defects is strongly influenced by annealing and diffusion of original simple defects such as vacancy defects [10]. It has been demonstrated that most defects in the CNTs that appear under ion irradiation are vacancy defects [11-12]. The vacancy defects play a crucial role in determining electronic properties of the nanotubes [13-14].

Carbon nanotubes have potential applications in rechargeable Li ion batteries because of superior Li adsorption capabilities. The lithium ions can adsorb both on the channels between the nanotubes, and on the interior and exterior of the nanotubes [15]. The experimental reversible capacities of the Li-adsorbed pristine CNT system have been reported to be 20–25% larger than that of the graphitic carbon material [16-18]. Therefore, many theoretical and experimental studies have been devoted to investigate the adsorption of lithium and other alkali metals on single-walled CNTs or multi-walled CNTs [19-31].

However, some issues about the CNTs with alkali metal adatoms still remained. It is in particular need of understanding the effects of the humidity (H_2O) on the alkali metal adsorption. In this paper, we reported the theoretical results of separation selectivity for alkali metals (Li/Na/Cs) using hydrated (5, 5)/(9, 0) single-walled carbon nanotubes based on the first-principles calculations. The calculation results show that the H_2O molecule on the capped single-walled CNTs have a significant influence on the adsorption energy of alkali-metal adatoms. The adsorption positions of H_2O molecule adsorption on the capped CNTs different alkali metals (Li/Na/Cs) have also been investigated.

2. Theoretical Method

In Fig.1, the single-walled armchair (5, 5) and zigzag (9, 0) CNTs with a capped edge were constructed, because the capped CNTs were energetically favored with respect to opened CNTs even at strong electric fields [32]. The (5, 5)/(9, 0) CNT was simply simulated by a five-layer/seven-layer (50/63 carbon atoms) stem along the tube axis. Based on the experimental observation [33], the (5, 5) and (9, 0) CNTs were capped symmetrically by a hemisphere of C_{60} at one end, and the dangling bonds at the other end were saturated by hydrogen atoms. The two layers of carbon atoms at the bottom and the hydrogen atoms were fixed during the whole calculation in order to consolidate chemical stability and simulate infinite CNTs [34]. The similar models also had been employed by other researchers [35-37]. A vacancy defect was created by removing a carbon atom from the tip of the (5, 5)/(9, 0) CNT. We choose two symmetrical atomic configurations for hydrated CNT systems (atomic configuration I and II based on different adsorption orientations, which were shown in Fig. 1. The alkali-metal adatom (Li/Na/Cs) was initially located above the center of different pentagons or hexagons (from P_1 to P_5) on the caps.


(a) (b)

(c) (d)

Fig. 1. The side and top views of two atomic configurations for hydrated P-CNTs. (a) Atomic configuration I of (5, 5) P-CNT, (b) Atomic configuration II of (5, 5) P-CNT. (c) Atomic configuration I of (9, 0) P-CNT, (d) Atomic configuration II of (9, 0) P-CNT. Yellow, blue and red balls correspond to the C, H, and O atoms, respectively.

Our calculations are performed within first-principles DFT under the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) [38]. Ultrasoft pseudopotential with a plane-wave basis set up to a kinetic energy cutoff of 30 Ry for the wavefunctions were used. The Brillouin zone is sampled only at the Γ point. Atomic positions were optimized until the maximum force on any atom is less than 1.0×10^{-4} a. u.. The CNTs were constructed within a same tetragonal supercell employing a vacuum width of 20 Å in axial direction and a separation of 12 Å in radial direction to avoid interaction between the atoms of adjacent CNTs. The QUANTUM ESPRESSO suite of codes [39-40] was used to perform all calculations.

3. Results and Discussions

In this research, the adsorption energy is defined as

$$E_{\text{ad}} = E_{\text{nano}} + E_{\text{adso}} - E_{\text{nano+adso}}$$

where E_{nano}, E_{adso}, $E_{\text{nano+adso}}$ are the total energy of the CNTs, the alkali metal adatom (Li/Na/Cs), and the CNT with the alkali metal adatoms, respectively.

If we research the influence of the humidity on the adsorption, the H_2O molecule must be taken into account in the first-principles calculations. We investigate the effects of H_2O molecule on adsorption of different alkali metals (Li/Na/Cs). The structure of (5, 5) or (9, 0) carbon nanotube adsorbed with a H_2O molecule in Fig. 2 is stable, while the adsorption energy is quite small so that the water molecule is easy to be desorbed from the cap of the CNTs. The atomic configurations II is more stable than atomic configuration I, but there is little difference in the adsorption energy, so that the adsorption orientations of the H_2O molecule have little influence on the adsorption energy.

The hydrated P-CNTs/D-CNTs with the Li/Na/Cs adatom (Li/Na/Cs+H_2O@CNT) systems are listed in Fig. 2-3 and Tab. 1. For hydrated (5, 5)/(9, 0) P-CNT, the adsorption energy of atomic configurations II with the Li/Na/Cs adatom is more stable than that of atomic configuration I with adatoms, but there is little difference in the adsorption energy. The adsorption energy of hydrated (9, 0) P-CNT/D-CNT with Li/Na/Cs adatom is slightly higher than that of hydrated (5, 5) P-CNT/D-CNT with Li/Na/Cs adatom, which indicate that the interaction between the tip of the hydrated (9, 0) P-CNT and the alkali metals is more strong than that between the tip of the hydrated (5, 5) P-CNT and the alkali metals.

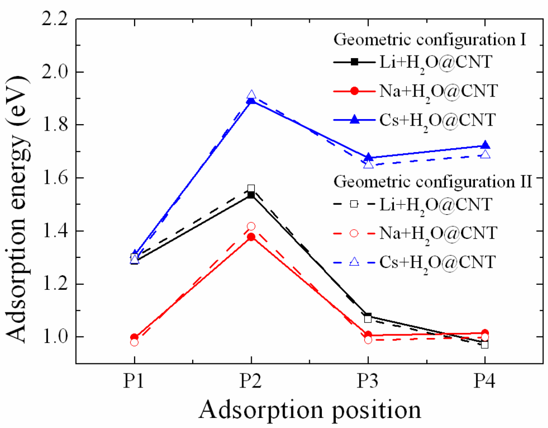


Fig. 2. The adsorption energy of hydrated (5, 5) P-CNT with Li/Na/Cs adatom on different adsorption positions P_1-P_4.

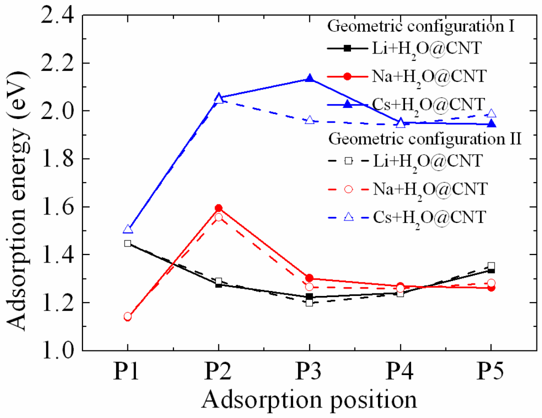


Fig. 3. The adsorption energy of hydrated (9, 0) P-CNT with Li/Na/Cs adatom on different adsorption positions P_1-P_5.

Table 1: The adsorption energy (in eV) of the Li/Na/Cs adatom on the hydrated (5, 5)/(9, 0) D-CNT.

	Adsorption energy
D-(9, 0) CNT-1+H_2O	0.1469/0.1428
Hydrated D-(9, 0) CNT-1+Li (p_1)	3.2218/3.1974
Hydrated D-(9, 0) CNT-1+Na (p_1)	2.9281/2.9294
Hydrated D-(9, 0) CNT-1+Cs (p_1)	2.8628/2.9294
D-(5, 5) CNT-1+H_2O	0.2258/0.2217
Hydrated D-(5, 5) CNT-1+Li (p_1)	3.0301/3.0423
Hydrated D-(5, 5) CNT-1+Na (p_1)	2.7880/2.8274
Hydrated D-(5, 5) CNT-1+Cs (p_1)	2.9702/3.0097

From adsorption on hydrated P-CNT to adsorption on hydrated D-CNT, the adsorption energy increases distinctly. For example, for the atomic configurations II, from the hydrated (5, 5)/(9, 0) P-CNT with the Cs adatom on P_1 to the hydrated (5, 5)/(9, 0) D-CNT with the Cs adatom on the same position, the adsorption energy increases distinctly (from 1.29eV/1.50 eV to 2.93 eV/3.01 eV). Therefore, the Li/Na/Cs adsorption on H_2O@D-CNTs is more stable than on H_2O@P-CNTs.

Similarly, For the hydrated (5, 5)/(9, 0) P-CNT, the Cs/Na atom has the largest/smallest adsorption energy. However, For the hydrated (5, 5)/(9, 0) D-CNT, the Li/ Na atom has the largest/smallest adsorption energy. This result indicate that the hydrated (5, 5)/(9, 0) P-CNT adsorb Cs atoms preferentially, while the hydrated (5, 5)/(9, 0) D-CNT adsorb Li atoms advantageously. Therefore, selective adsorption or separation selectivity for alkali metals (Li/Na/Cs) can be actualized using the hydrated capped single-walled carbon nanotubes in the seawater.

Due to the electronegativities of alkali metals are less than that of carbon atom, the alkali-metal adatoms on the CNTs are easily ionized, and transfer their electrons to CNTs. Here we use the Li atom as an example to analyze the adsorption. Fig. 4 illustrates the differential charge density distributions (DCDD) of the hydrated (5, 5) P-CNT adsorbed with the Li atom on the top position (P_1). The Li+H_2O@ (5, 5) P-CNT system has an symmetric DCDD, but the negative charges accumulate between the O atom and the H_2O molecule, and the five nearest-neighbor carbon atoms on the caps. The Li atom is therefore predicted to donate its major 2s electron to the hydrated P-CNT and form a Li cation on the tip surface. The charge transfer will lead to elevation of the Fermi levels and interplay among the energy states. Other alkali-metal atoms play similar roles as the Li atom.

Because diameter of the Li/Na/Cs atom is comparable with that of the hexagon or pentagon rings of CNTs, alkali metals can cut down the spatial extensions of p electrons into the vacuum by forming chemical bonds with CNTs and keep the electrons on CNTs, which results in repulsion among the energy states. Fig. 5 shows density of states (DOS) of the hydrated (5, 5) P-CNT before and after Li adsorption on the top position (P_1). The hydrated (5, 5) P-CNT shows metallic characteristics and the DOS near the Fermi level has been enhanced after Li adsorption. This phenomenon indicated that alkali metal adsorption can improve the electric conductivity of the hydrated (5, 5) P-CNT. There is little difference between the DOS of the (5, 5) P-CNT and hydrated (5, 5) P-CNT before and after Li adsorption.

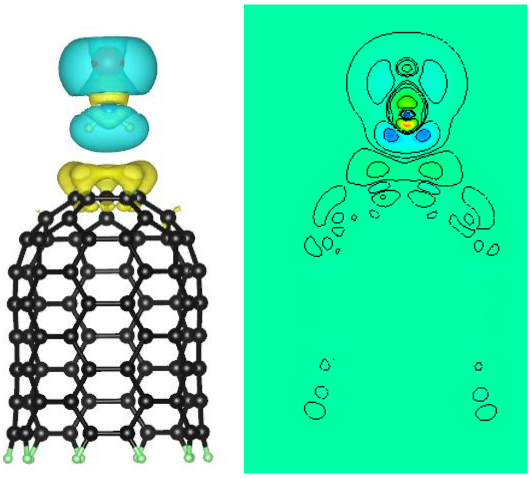


Fig. 4. The contour of differential charge density distribution (DCDD) of hydrated (5, 5) P-CNT with the Li adatom. Blue and yellow represent positive and negative charge distributions, respectively. The differential charge density distribution is defined as

$$C = C(\text{hydrated CNTs} + \text{Li}) - C(\text{hydrated CNTs}) - C(\text{Li}) .$$

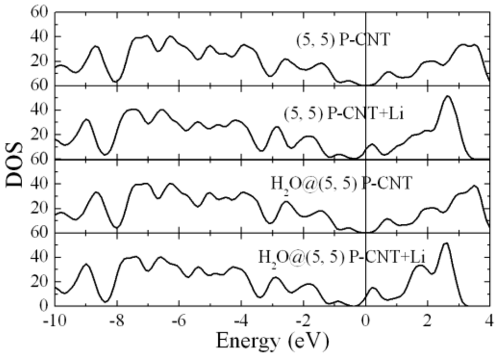
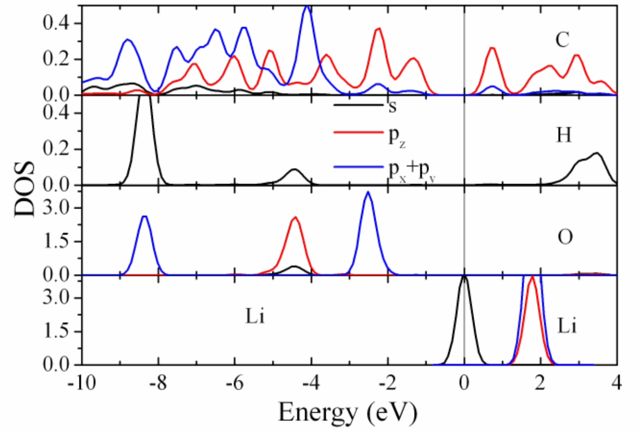
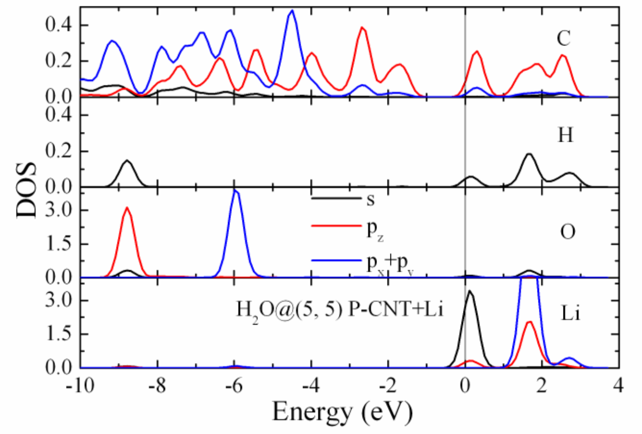


Fig. 5. the density of state (DOS) of (5, 5) P-CNT, (5, 5) P-CNT+Li, hydrated (5, 5) P-CNT, and hydrated (5, 5) P-CNT+Li . The Fermi levels are set to 0 eV.

The projected density of states (PDOS) offers the detailed information of electronic structure of the adsorption systems. Fig. 6 shows the projected density of states (PDOS) of the carbon atoms in the first layer, the oxygen atom, the hydrogen atom and the Li atom before and after adsorption for the hydrated (5, 5) P-CNT. When the Li atom is adsorbed on the hydrated (5, 5) CNT, its 2s state are partly occupied and there exists a broad resonance with its $2p_z$ orbital and $2p_z$ state of carbon atoms near the Fermi level. This result implies that the Li-CNT interaction and the augment of Fermi levels mainly originate from hybridization of these states. These characteristics are consistent with charge redistribution given in Fig. 4. The similar results are observed for other adsoption systems.



(a)



(b)

Fig. 6. the projected density of states (PDOS) of hydrated (5, 5) P-CNT+Li systems. PDOS of the carbon atoms in the first layer, the hydrogen atom, the oxygen atom and the Li atom (a) before adsorption and (b) after adsorption. The Fermi levels are set to 0 eV.

4. Conclusion

The first-principles calculations on hydrated (5, 5)/(9, 0) single-walled carbon nanotubes with the Cs/Li/Na adatom have been performed. The results have shown that the energy ordering of the alkali-metal adatoms on the hydrated (5, 5)/(9, 0) P-CNT is Cs>Li>Na. Therefore, the Cs adsorption is energetically favored on the hydrated P-CNTs with respect to other adatoms. The hydrated P-CNT prefers to adsorb Cs atoms, while the hydrated D-CNT prefers to adsorb Li atoms. The different electronegativities of the alkali metals and the emergence of the vacancy defect on the cap result in the dissimilarity. Therefore, selective adsorption or separation selectivity for alkali metals can be actualized using different capped single-walled carbon nanotubes in a humid environment (such as briny environment).

Acknowledgments

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