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Ab initio study of Li adsorption in carbon nanotubes functionalized with amine and carboxyl groups

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ABSTRACT

The lithium adsorption energies and electronic structures of pristine ((8,0)) single-walled carbon nanotube (SWCNT) and functionalized carbon nanotubes with amine and carboxyl groups (NH_2/((8,0)) and COOH/((8,0))) were studied using density functional theory. The results show that the adsorption energies of lithium inside and outside of ((8,0)) SWCNT differ very little from each other. When the lithium is doped in carbon nanotubes, charge transfer takes place from the lithium to the nanotubes. After functionalization of carbon nanotubes with amine (—NH_2) and carboxyl (—COOH) groups, various positions for lithium adsorption around the functional groups can be served. The adsorption energy of lithium in these positions is greater than that of lithium in pure ((8,0)) SWCNT. When the lithium was doped in NH_2/((8,0)) and COOH/((8,0)), an energy gap between valence and conduction bands is observed, and the conductivity is reduced relative to lithium-doped non-functionalized carbon nanotubes.

1. Introduction

Rechargeable lithium ion batteries have been used extensively as compact power sources for various devices. A number of different types of lithium intercalation materials have been applied to increase the saturation density of Li adsorption and the transport of current [1].

Different carbonaceous materials in which lithium can intercalate reversibly are exploited as the anode materials for secondary lithium-ion batteries. Intercalated graphite is safe and is efficiently recycled so that it is considered as a viable alternative to metallic Li electrodes. However graphite can be intercalated to only a limited extent of up to one lithium per six carbon atoms, forming the first stage graphite intercalation compound (GIC), LiC_6[2,3]. To increase the adsorption capacity of the carbon-based electrode, carbon nanotubes (CNTs) have been proposed as a promising candidate to replace the Li-GIC negative electrode because of their distinguished electrical and mechanical properties as well as their large surface area [4–6].

A wide variety of theoretical and experimental studies have been carried out to investigate the adsorption capacity and the physical consequences of the intercalation of Li in single-walled carbon nanotubes (SWCNTs) [7–10]. Experiments have indicated that the maximum capacity for SWNTs can be raised up to $Li_{2.7}C_6$ via chemical etching or the ball-milling of nanotubes [11,12]. In simulation studies of Li intercalation in SWNT bundles, Zhao et al. demonstrated the possibility of attaining a high saturation density of around 3 lithium atoms per 6 carbon atoms (Li_3C_6) in nanotube bundles [13].

Many theoretical investigations have been carried out to determine the energetic consequences of lithium adsorption in single-walled nanotubes. These studies have reported a variety of useful quantities, such as the adsorption energy of Li in nanotubes of differing diameters and chiralities [13–20]. These studies demonstrate that for a single Li atom, the energies of absorption inside and outside the tube are similar. Charge transfer is also observed to take place from the Li atom to the walls of the nanotube.

To obtain strong Li adsorption and to accomplish other nanoscale engineering features, further progress in controlling material properties has been made through utilizing various chemical and structural modifications to carbon nanotubes, including doping impurities, forming structural defects, and hybridizing the nanotubes with fullerenes (C_{60}s). Zhou et al. investigated the lithium adsorption energy and electronic structure of boron- and nitrogen-doped single-walled carbon nanotubes using *ab initio* electronic structure calculations. Their calculations indicate that B-doping in SWCNT improves the capacity of the nanotubes to adsorb lithium atoms [21]. In other work Li et al. studied the

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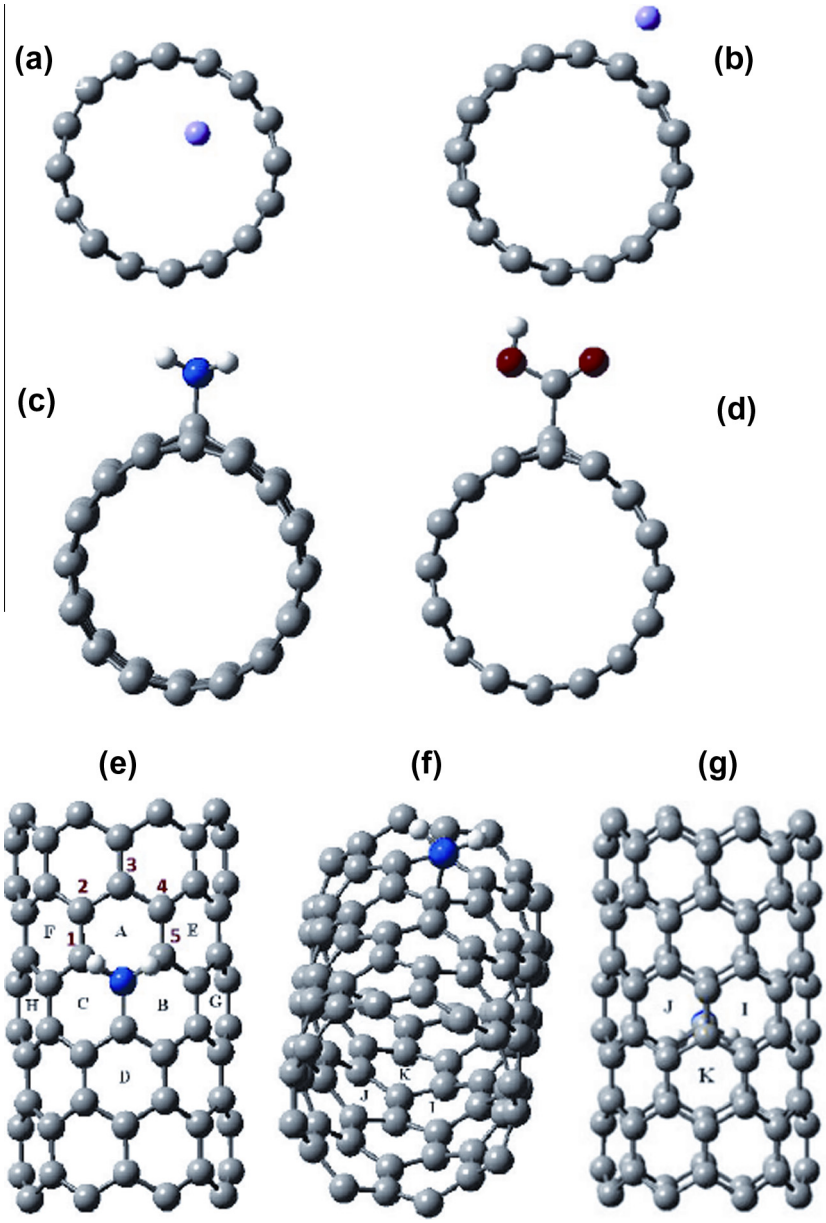

Fig. 1. Optimized structures for (a) Li@((8,0)), (b) Li-((8,0)), (c) NH_2/((8,0)) and (d) COOH/((8,0)) SWCNTs. (e), (f) and (g) label the different position for adsorption of Li in NH_2/((8,0)) SWCNT. Corresponding structures for COOH/((8,0)) SWCNT are similar.

adsorption energy of lithium at the pyridine-like defect of a (10,0) carbon nanotube and found that the Li adsorption energies at the pyridine-like defects of carbon nanotubes are much more than those in pristine CNTs, while the energy barrier of Li penetrating pyridine-like defects is much less than that of perfect SWCNTs [22]. Koh et al. investigated the Li adsorption of a CNT–C_{60} hybrid system using first-principle methods [23]. They observed that charges are transferred from the CNT to C_{60} to form positively carbon nanotubes and negatively charged C_{60}. As a consequence of the charge transfer, the Li adsorption energy of the hybrid system is larger than that of the pure SWCNT.

The doping of single-walled carbon nanotubes by Li is also known to increase the hydrogen storage capacity [24,25] of the nanotubes and to improve chemical reactivity by increasing reaction energies [26].

In addition to these potential benefits to nanotube engineering, the functionalization of SWCNT functionalizing provides a useful means to control features of the electronic structure, a crucial consideration in the manufacture of practical devices. For instance, Veloso et al. investigated the effect of functionalizing of SWCNT by —COOH, —NH_2 and —$CONH_2$ functional groups on the electronic and structural properties using *ab initio* calculations [27]. They showed that the functional groups have stabilizing interactions with the nanotubes which act as an electron donor. A common aspect for the electronic structures of these groups is a half-filled level in the gap region.

Like doping impurities or defects in carbon nanotubes, functionalizing carbon nanotubes may also have the potential to create high capacity Li storage materials.

In this article, density functional theory (DFT) calculations performed to study the adsorption energy of Li on the functionalized SWCNT are reported. Here the nanotubes are based on a ((8,0)) carbon nanotube framework, while amine and carboxyl groups are used as functional groups. There are a variety of sites in the vicinity