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First-principles study on the enhancement of lithium storage capacity in boron doped graphene

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The adsorption of Li ions on boron doped graphene was investigated using a first-principles method. Our results show that, as boron doping turns graphene into an electron-deficient system, more Li ions can be captured around boron doped centers than in pristine graphene. One boron atom doped into graphene (6C ring unit) can adsorb six Li ions, which indicates that boron doped graphene is an efficient Li-ion storage material for lithium batteries. Further investigations show that, under limited conditions, boron doped graphene (BC₅) can form Li₆BC₅ compound after Li-ion adsorption, corresponding to a lithium storage capacity of 2271 mAh/g which is six times that of graphite. © 2009 American Institute of Physics. [doi:10.1063/1.3259650]

Lithium ion batteries are the state-of-the art power sources for portable electronic devices and potentially for electric vehicles and hybrid electric vehicles. They use the chemistry of lithium transition metal oxide cathode and graphite anode.^{1,2} However, graphite is not an ideal anode material for lithium ion batteries due to its limited lithium storage capacity (372 mAh/g). Carbon nanotubes (CNTs) have been studied for use as high capacity lithium storage materials because CNTs can adsorb Li ions both on the outside and on the inside surfaces. Experimental investigations have shown that single-wall CNTs exhibit a reversible capacity of upto 500 mAh/g,³ significantly higher than that of graphite. The maximum capacity of CNTs can be increased to as high as 1000 mAh/g (in the form of Li_{2.7}C₆) by chemical etching⁴ or ball-milling,⁵ which open up paths allowing Li ions to diffuse inside the CNTs. Ever since boron doped CNTs with different B versus C ratios have been synthesized,^{6–8} they have been expected to have higher Li-ion storage capability than pristine CNTs, and this has been confirmed both experimentally⁹ and theoretically.¹⁰ Additionally, boron doped carbonaceous materials have exhibited higher reversible capacity and better cycling stability than their pure counterparts.^{11,12}

Recently, graphene or graphite in single-layer form, has attracted tremendous attention because of its excellent structural and electronic properties, such as chemical and thermal stability, high electrical conductivity, and mechanical strength.^{13,14} Graphene is a strictly two-dimensional, flat, and single-layer material. Unlike CNTs, graphene has two equal surfaces. Very recently, the Li ions storage capacity of graphene was found to be 784 mAh/g,¹⁵ which is twice the capacity of graphite. The reason may be that graphene adsorbs Li ions on its two equal surfaces, forming LiC₃ compound. As mentioned above, the Li ion storage capacity can be enhanced by doping boron into both graphite and CNTs.

In this letter, we dope boron into graphene to investigate the enhancement of Li-ion storage by inspecting the electronic structures of boron doped graphene and its Li ion storage capacity.

Density functional theory (DFT), as implemented in the Dmol³ package¹⁶ is used in our electronic structure calculations. The parameterization by Perdew, Burke, and Ernzerhof¹⁷ is used for exchange and correlation interaction in the generalized gradient approximation. A double numerical basis set and a polarized function were chosen for calculations. A supercell ($2\sqrt{3} \times 2\sqrt{3}$)R30° containing 24 atoms (SC₁) is used to investigate the interaction of the Li ions with a single boron doped defect. There are one boron and 23 carbon atoms in one boron doped SC₁, termed BC₂₃, in which the boron concentration is 4.17 at. %. The Brillouin zone of SC₁ is sampled by a $4 \times 4 \times 1$ Monkhorst and Pack grid.¹⁸ The interaction between the Li ions and the 16.7 at. % boron doped graphene, corresponding to BC₅ compound, is modeled in a ($\sqrt{3} \times \sqrt{3}$)R30° supercell containing six atoms (SC₂). The reciprocal space of this supercell is represented by an $8 \times 8 \times 1$ Monkhorst and Pack grid. The *z*-direction lattice constant is fixed at 20 Å. All structures are fully relaxed until the force is less than 0.054 eV/Å.

The optimized in-plane lattice constant of pristine graphene is 2.463 Å, which is close to the experimental value of 2.460 Å. The relaxed lattice constant of boron doped graphene is 2.484 or 2.536 Å, corresponding to the concentration of 4.17 or 16.7 at. %, respectively. Because the boron covalent radius is larger than that of its carbon counterpart, the lattice constant of doped graphene increases with increasing boron concentration. The average adsorption energy per Li ion (E_{ad}) is defined as follows:

$$E_{ad} = (E_{gra} + nE_{Li} - E_{Li-gra})/n, \quad (1)$$

where E_{Li} , E_{gra} , and E_{Li-gra} represent the total energy of a lithium atom, the pristine graphene, and the Li-graphene, respectively. n is the number of Li ions.

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FIG. 1. (Color) (a) The DOS of pristine and boron doped graphene. (b) A schematic map showing one Li ion adsorbed on boron doped graphene. The red line indicates the hexagon center, and 1, 2, and 3 represent the three high symmetry sites: the top, bridge, and hollow, respectively. Contour plots of the electron density along the graphene plane for pristine and boron doped graphene are shown in the left and right insets of (a), respectively.

First, the electronic properties of pristine and boron doped graphene were investigated using SC_1 . As shown in Fig. 1(a), after boron doping, as boron has one electron less than carbon, the Fermi level is depressed into the valence band, and the graphene becomes an electron-deficient system. The contour plots of the electron density of pristine and boron doped graphene are shown in the insets of Fig. 1(a). The graphics imply that the electron-deficient area of boron doped graphene is mainly distributed around the boron. Boron substitution may increase the electronic conductivity and Li ion adsorption of graphene.

As in pristine graphene, there are three high symmetry positions for Li ions adsorbed on boron doped graphene. As shown in Fig. 1(b), they are the top site (above the boron atom), the bridge site (above the bond center of the B-C bond), and the hollow site (above the center of the hexagon), respectively.¹⁹ After full relaxation, our calculated results show that the hollow site is the most favored site with the minimum total energy, while the top and the bridge sites are the second and third most stable positions. Also, we should note that the hollow site is the most stable site for Li ions in CNTs and pristine graphene as well.^{10,20–23} The final position of a single adsorbed Li ion is shown in Fig. 1(b), where it should be noted that the Li ion deviates slightly from the center of the hexagon and comes closer to the boron. After introducing boron into pristine graphene, the original symmetry is broken. Because boron atoms and Li ions are electron acceptors and donors, respectively, the Li ions and boron tend to attract each other.

We further investigated the case of the adsorption of two Li ions, as shown in Fig. 2. A, B, and C are used to represent the three nearest hollow sites around the boron. Up and down mark the upper and lower sides of the graphene. Using those signs, the position of one Li ion is well defined, for example, A_{up} corresponds to the configuration of one Li ion located on the top of the A site on the upper side. As mentioned above, Li ions prefer to be situated on the top of the hexagon center, and therefore, $A_{up}-B_{up}$, $A_{up}-A_{down}$, and $A_{up}-B_{down}$ are used for simulating the adsorption of two Li ions. From $A_{up}-B_{up}$ to $A_{up}-B_{down}$, the distance between Li ions increases gradually. The relaxed configurations and distances between two Li ions are shown in Figs. 2(a)–2(c), which indicates that the total energy decreases monotonically with increasing Li-Li distance. This fact tells us that Li ions tend to separate themselves as far as possible from each other around boron. In this way, additional Li ions are put around a nearby boron atom until the extreme case shown in Fig. 2(d), in which six Li ions are adsorbed around boron. After the Li ions are

adsorbed on boron doped graphene, Li ions transfer electrons to the host material. As shown in Fig. 3(a), the average net charge and adsorption energy of a Li ion decrease with increasing number of Li ions, which mean that the ability of doped graphene to adsorb Li ions is progressively weakened [Eq. (1)]. However, in the case of the adsorption of six Li ions, the average adsorption energy is as high as 1.976 eV, which indicates that one boron doped center can capture six Li ions. Density of states (DOS) analysis for the case where six Li ions are adsorbed [see Fig. 3(b)], shows that Li ion adsorption can raise the Fermi level of the graphene. As can be seen in Fig. 3(c), the contribution of Li ions to the total DOS around the Fermi level is from both *s* and *p* orbitals. It should be noted that the current boron concentration is 4.167 at. %.

Next, we increase the boron concentration to 16.7 at. %, corresponding to BC_5 compound, in which each hexagon has a boron neighbor. As discussed above, one boron can adsorb six Li ions in BC_{23} . However, can each hexagon accommodate two Li ions in BC_5 ? Six Li ions were put into SC_2 , forming Li_6BC_5 compound. The calculated results are given in Table I. The distance between the Li ion and the graphene

FIG. 2. (Color) Schematic map of two Li ions adsorbed on boron doped graphene: (a), (b), and (c) illustrate the $A_{up}-B_{up}$, $A_{up}-A_{down}$ and $A_{up}-B_{down}$ configurations, respectively. The numbers show the distance between the two Li ions. (d) The structure for adsorption of six Li ions. The purple and yellow balls represent Li ions located at up and down sites, respectively. The pink balls represent sites occupied by boron.

FIG. 3. (Color) (a) Average charge and adsorption energy of Li ion vs number of Li ions, (b) the total DOS of the case where six Li ions are adsorbed, and (c) the corresponding total, and the p and s contributions to the DOS from Li ions.

is 1.925 Å, and the average absorption energy is 0.759 eV. As there are two even Li layers in Li_6BC_5 and the Li-Li distance is 2.543 Å, hence, the calculated adsorption energy comes from the two following parts: one is the interaction between the Li ions and the graphene and the other is from the interaction among Li ions. In order to obtain the pure adsorption energy of Li ions on graphene, the graphene layer is removed from the Li_6BC_5 compound, and the bonding energy between the Li ions among Li layers is found to be 0.454 eV. Therefore, the pure average adsorption energy of Li ions on graphene is 0.305 eV, indicating that Li_6BC_5 compound can exist stably. Simultaneously, we did the calculations for the pristine graphene Li_6C_6 compound for a comparison, and the calculated results are shown in Table I. There is almost no

TABLE I. The relaxed Li-graphene distance, the average net charge, and adsorption energy of Li ions in Li_6C_6 and Li_6BC_5 compounds, respectively. The pure adsorption energy between Li ions and the host is shown in parentheses.

Composition	$D_{\text{Li-graphene}}$ (Å)	Li charge (e)	Adsorption energy (eV)
Li_6BC_5	1.925	0.066	0.759(0.305)
Li_6C_6	3.671	0.008	0.367(0.023)

interaction between Li ions and graphene in Li_6C_6 , implying that Li_6C_6 compound cannot exist stably.

In summary, the adsorption of Li ions on boron doped graphene has been investigated using DFT calculations. After boron doping, graphene becomes an electron-deficient system, and an electron-deficient center appears around each boron atom. Li ions tend to situate themselves on the top of hexagon centers with a boron neighbor. Our calculations indicate that the Li ion storage capacity can be dramatically improved to 2271 mAh/g by boron doping and that Li_6BC_5 can exist stably.

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