Enhanced Absorption and Diffusion Properties of Lithium on B,N,V$_C$-decorated Graphene

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Systematic first-principles calculations were performed to investigate the adsorption and diffusion of Li on different graphene layers with B/N-doping and/or C-vacancy, so as to understand why doping heteroatoms in graphene anode could significantly improve the performance of lithium-ion batteries. We found that the formation of single or double carbon vacancies in graphene are critical for the adsorption of Li atoms. While the N-doping facilitates the formation of vacancies, it introduces over binding issue and hinders the Li diffusion. The presence of B takes the excessive electrons from Li and N and reduces the energy barrier of Li diffusion on substrates. We perceive that these clear insights are crucial for the further development of graphene based anode materials for lithium-ion batteries.

With excellent characters of high energy density, long cycling life and environmental friendliness, lithium-ion batteries (LIBs) have been widely used in portable electronic devices$^{1-5}$. The performance of LIBs is mainly determined by the intrinsic properties of their electrodes. Therefore much attention has been paid in the recent years on exploring and developing novel electrode materials. Carbonaceous materials, such as graphite$^6$-$^7$, carbon nanofibers$^8$-$^9$, carbon nanotubes$^{10-12}$ and porous carbon$^{13,14}$, are promising anode materials in LIBs due to their high Li-storage capacity, high conductivity, decent electrochemical activity and low cost$^{15,16}$. In particular, graphene has attracted extensive research interests with a theoretical maximum lithium capacity of 784 mAh/g by forming Li$_2$C$_6$ structure$^{17}$, and an even higher capacity up to 1488 mAh/g for an isolated graphene flake that is only 0.7 nm in diameter$^{18,19}$. However, it was found that the Li capacity of some graphene samples can be even significantly lower than that of bulk graphite$^{20}$, possibly due to the formation of small Li clusters on graphene as the interaction between Li atoms$^{21-23}$ is much stronger than that between Li and pristine graphene$^{24-26}$.

Many approaches have been pursued to functionalize graphene as an anode material and doping graphene with nitrogen (N) and/or boron (B) atoms is one of the most effective ways. For example, Reddy et al. found that the Li capacity of N-doped graphene layers produced by chemical vapor deposition (CVD) technique is almost doubled compared to that of pristine graphene because of the appearance of a large number of surface defects$^{27}$. Wu et al. prepared N- and B-doped graphene samples by using a mixed gas of NH$_3$BCl$_3$ and Ar, which show a high reversible Li-capacity of >1040 mAh$^{-1}$ at a low rate of 50 mA$^{-1}$, meaning that they can be charged and discharged quickly$^{28}$. The significant enhancement in the performance of N-/B-doped graphene motivates active theoretical studies to understand the physical mechanism behind$^{29-32}$.

In the present work, we performed systematic density functional theory (DFT) calculations for the structures and energetics of different B/N/V$_C$-decorated graphene geometries, as well as the Li adsorption and diffusion
on them. We sorted out the roles of doping and vacancy decoration on the improvement of Li-adsorption on graphene, and identified several structures that have good adsorption energy, low diffusion barrier and easy preparation in experiments. Our theoretical results provide instructive guidelines for the further development of high performance C-based anode materials for LIBs.

Results and Discussions

The formation and Li-adsorption-performance of G_NxV_y substrates. We first studied the adsorption configurations and energies of one Li atom on the decorated graphene cells with x N-atoms and y V_C, G_NxV_y, (x = 0–4 and y = 0–2), corresponding to a N-concentration of ~1.4–5.6%, comparable with the experimental range for graphene samples synthesized via the thermal reaction between graphene oxide and NH_3 at high temperature. After structural optimization, we see that for y = 0, i.e., N-substituted graphene without V_C, N atoms prefer to stay far away from each other to minimize the perturbation to the graphene π-electron bonds, as depicted in Table S1 in the supplementary material (SM). The C-N bond length is about 1.40–1.43 Å, very close to the C-C bond length in the pristine graphene. For y = 1 and 2, i.e., N-doped graphene with V_C, the N dopants prefer to connect with two C atoms and form pyridine-like structure, which introduces a strongly localized donor states near the Fermi level. The corresponding C-N bond length reduces to ~1.34 Å, deviating away from the lattice position of pristine graphene.

For each system, we explored different Li adsorption sites (cf. Table S2 in SM) and those with the lowest adsorption energies, E_{ad}, are shown in Fig. 1. We see that the E_{ad} of Li on the hollow site (H) of a 6 × 6 graphene supercell, 0.27 eV, is lower than that on the top site (T), 0.57 eV. The distance between Li and substrate, d_{LG}, of the H-site, 1.72 Å, is also smaller than that of the T-site, 1.92 Å. These results indicate a single Li adatom prefers the hollow site on pristine graphene but Li atoms are more likely to form Li clusters since the value of E_{ad} is positive, in consistent with previous results (see details in Table S3 in SM). For the adsorption of one Li atom on the G_NxV_y systems, we found that Li prefers to stay on the H-site of graphene rather than any places near the N atoms. The E_{ad} of Li on G_NxV_y (G_NxV_y) systems, 0.39 (0.34) eV, are also positive, and the corresponding values of d_{LG} are 1.75(1.76) Å, indicating that pure N-dopings in graphene don’t improve the lithium adsorption. Strikingly, with the presence of V_C on pristine graphene, the E_{ad} decreases to negative values of ~1.36 eV for single V_C and ~0.73 eV for double V_C, as shown in Fig. 1, indicating that the adsorption of Li on the vacancy position is energetically preferred. The atomic positions in G_NxV_y have no obvious changes compared with perfect graphene due to the weak intraplanar relaxation, whereas a typical 5–8–5 defect can be found in G_NxV_y with decreased C-C bond lengths near vacancies from 2.46 Å to 1.81 Å, as depicted in the insets in Fig. 1.

For double vacancies in graphene, with a very low E_{ad} of ~2.89 eV for G_NxV_y. The formation energy of single N-dopant on graphene, E_{form}(N), is 0.91 eV, comparable with the previous DFT studies of 0.79 eV and 0.97 eV. Interestingly, this value doesn’t change significantly with the increase of N dopants, as depicted in the blue line in Fig. 2 and the red curve in Figure S1(a). Here the blue solid squares show the E_{form}(N) of single N-dopant on the G_NxV_y substrates (shown in the insets)
that were used in $E_{\text{for}}$ calculations of single C-vacancy, and the error bar illustrates the $E_{\text{for}}(N)$ window for different doping configurations of N on $G_{NxV0}$ (cf. more details in Table S1 in SM). Clearly, it is rather easy to insert N atoms in graphene, which serves as the precursor step for the formation of C-vacancies and consequently, enhances the Li adsorption. Considering the values of $E_{\text{for}}$ of VC and N-dopings and the values of $E_{\text{ad}}$ of Li, we believe that $G_{N3V1}$ and $G_{N4V2}$ configurations can be easily formed and they are responsible to the enhancement of lithium capacity of graphene anode materials.

**Adsorption and diffusion of Li on B- and N-codoped $G_{BxN3-xV1}$ substrates.** As we mentioned above, the graphite-like B/C/N layered materials prepared using CVD or other methods showed good performances as the anode matrix of LIBs. Various precursors were used in experiments to create B dopings, including $B_C$, NaBH$_4$, $B_2O_3$ and so on. So theoretically the $E_{\text{for}}$ of single B-doping on graphene, $E_{\text{for}}(B)$, changes from $-5.30$ eV under B-rich conditions to $+8.09$ eV under oxidation conditions, as shown in Figure S1(b) in SM. Although the average values of $E_{\text{for}}(B)$ under typical experimental conditions, ranging from $-0.23$ eV with $B_C$ precursor to $+1.47$ eV with NH$_3$BH$_3$ precursor, are a little higher than $E_{\text{for}}(N)$, the calculated $E_{\text{for}}(VC)$ of single C-vacancy on $G_{BxN3-xV1}$ is comparable with that of $G_{N3V1}$, and interestingly, its value for the B/N co-doped graphene, $G_{BxN3-xV1}$ ($x=0–3$), is even lower than the corresponding value for the pure N-doped graphene by $\sim 1.20$ eV, as presented by the green stars in Fig. 2.

Then we give the values of $E_{\text{ad}}$ for Li on several adsorption sites of $G_{BxN3-xV1}$ substrates, as depicted in Fig. 3. For Li on $G_{B1N2V1}$, we found that Li in the ground state is located at the vacancy site, close to the B dopant with a $d_{VG}$ of 1.65 Å. A similar adsorption structure was obtained for Li/$G_{B2N1V1}$, but the Li atom is much closer to the N dopant instead of B. Strikingly, the most stable adsorption site of Li on $G_{BxV1}$ substrate is on the hollow site of the hexagonal ring adjacent to the B atom. Overall, the B and N co-doped graphene substrates give negative adsorption energies, and the values of $E_{\text{ad}}$ of one Li atom on $G_{BxN3-xV1}$ are in the order: $G_{N3V1}$ ($-3.12$ eV).
< G_B1N2V1 (−1.77 eV) < G_B1V (−1.20 eV) < G_B1 (−0.99 eV). Obviously, all of them are more active toward the adsorption of Li, compared with pristine graphene. Using G_B1N2V0 as an example, we also studied the x-dependence of E_ad (see Table S4 in SM) and found that E_ad decreases with the doping concentration of B till it is smaller than 2.78%.

While adsorption energies determine the Li capacity, the energy barrier of Li diffusion dictates the efficiency of charge and discharge cycles. Using the G_B1 substrate as an example, we calculated the E_ad of Li on selected adsorption sites along the diffusion pathway of H→T→V→H, as shown in the inset in Fig. 4 highlighted by the blue arrow, and obtained the energy barrier of Li diffusion by using ΔE_ad = E_ad(site) − E_ad(H). For each adsorption site, we fixed the lateral coordinates of Li and optimized all the other atomic positions. The energy barrier for the movement of one Li atom on G_B1 is only 0.41 eV, and the largest difference in d_G→H is about 0.27 Å. The low energy barrier and the small change in d_G→H indicate a relatively flat potential energy surface of G_B1 for the Li movement. Similarly, we studied the diffusion of Li on G_B1N2V1 and obtained ΔE_ad of 0.80 eV and 0.48 eV along two different pathways, and the corresponding difference in d_G→H of 0.83 Å and 0.56 Å, respectively (see Figure S2 in SM). Note that without B, the ΔE_ad of Li diffusion on G_N3V1 is 2.62 eV, 6.5 times larger than that of G_B1V1. Clearly, the lithiation-delithiation process of Li on decorated graphene needs the joint effects of vacancy, B- and N-dopants.

**Electronic properties of decorated graphene substrates.** We performed detailed analyses on the electronic properties of various graphene substrates with/without Li adsorption, so as to understand the role of doping and/or vacancy on the Li adsorption. The total and partial density of states (DOS) of pristine graphene (G), G_B1, G_N1, and G_V1 are plotted in Fig. 5(a). The dashed line with shadow in the uppermost panel in Fig. 5(a) shows a perfect Dirac state of the pristine graphene at the Fermi level (E_F). The adsorption of Li atom keeps the DOS profile almost unchanged, but the E_F moves to the conduction states due to the addition of 1e from Li. As was well known, the E_F of B(N)-doped graphene is shifted to the valence(conduction) band, as shown in the middle panels in Fig. 5(a), indicating that G_B1 (G_N1) is a hole (electron)-rich material. The adsorption of Li on G_B1 substrate compensates the hole attraction and the Dirac state of Li/G_B1 moves back to ~2.1 eV above the E_F. The attractive/repulsive electrostatic interactions between Li and substrates lead to a negative/positive E_ad values. Strikingly, for G_V1 substrate, as shown in the lower panel in Fig. 5(a), there is a big peak around E_F caused by the hybridization of Li-p_z and C-p_z in-plane orbitals, and the adjacent peak at ~0.7 eV below the E_F is composed of the Li-s and C-p_y, orbitals. Thus the interaction between Li and G_V1 substrate is very strong, leading to a low E_ad value.

Interestingly, we found that the DOS profile of G_B1V1 substrate in Fig. 5(b) is very similar with that of G_B1, with peaks of B-p states near the E_F. The adsorption of Li makes the B-p states shift to lower energies, but the hybridization of Li-s,p and B-p states is still relatively weak near the E_F. Similar with G_V1, the DOS of G_N1V1 also has a big peak right at the E_F, coming from the dangling bonds at the N atom sites. The orbital hybridizations of N-p and Li-s,p orbitals can be observed around ~1.8 eV and ~3.5 eV, which are responsible for the lower E_ad of G_N1V1 than G_B1V1. The interaction between Li and substrate can be described more clearly by the electron redistribution, n(r) = n_i→ad(r) = n_a→ad(r) − n_r(r), obtained from electron densities of Li on substrates, pure substrates and Li atom. As displayed in the insets in Fig. 5(b) and (c), there are obvious electron transfer from Li to dopants which enhances the binding of Li on decorated graphene substrates. The contrast between G_B1V1 and G_N1V1 manifest through the influence of N extending to the second nearest neighbors of C atoms due to the symmetry breaking of the π-electron system, whereas B appears to only affect the nearest neighbor C atoms.

In summary, we performed systematic first-principles calculations to study the adsorption and diffusion of Li on decorated graphene with BP and/or N dopants and C vacancies. The adsorption energy of one VC on graphene is as high as 8.01 eV, the N-doping drastically decreases this value to as low as ~0.14 eV for G_N1V1. The co-doping of B keeps negative adsorption energies for Li, and significantly reduces...
the energy barrier of Li diffusion, e.g., 0.41 eV for Li/G_B3V1 and 0.48 eV for Li/G_B2N1V1. The electronic structure analyses show that the interaction between Li and B states is rather weak, whereas Li has a strong orbital hybridization with N-\(p\) states, causing a high diffusion barrier. Our theoretical studies provide clear insights for the understanding of the individual roles of doping and vacancy decorations for the performance of enhancement of N(B)-doped graphene as electrode materials in LIBs, and provide guidelines for the design of new battery materials.

Methods

Our density functional theory calculations were performed using the Vienna Ab initio Simulation Package (VASP)\textsuperscript{42,43}. Projector-augmented-wave (PAW) potential and the PW91 version of general gradient approximation (GGA)\textsuperscript{44} were employed to describe the electron-ionic core interactions and the exchange-correlation interaction among electrons, respectively. Our preliminary calculations by using the vdW-DF2 version of nonlocal van der Waals functional\textsuperscript{45,46} show that the inclusion of dispersion corrections in DFT don’t change the main features of Li adsorption on decorated graphene. We used an energy cutoff of 500 eV for the plane-wave basis expansion and a size-dependent Monkhorst-Pack \(k\)-points sampling in the Brillouin zone (BZ). The crystal constant and positions of the ions were fully relaxed until the final force on each atom is smaller than 0.01 eV/Å. The optimized in-plane lattice constant of graphene primitive cell is 2.47 Å, in good agreement with the experimental values of 2.46 Å derived from the X-ray crystallography of AB graphite and with previous theoretical predictions\textsuperscript{36}. For the adsorption and diffusion of one Li atom on decorated graphene, we used a periodic slab consisting of a 6 \(\times\) 6 graphene supercell and a vacuum layer of 12 Å along the normal direction to avoid the interaction between two adjacent images.

To assess the stability of Li adsorbed on graphene, we calculate the adsorption energy \((E_{ad})\) of a Li adatom as follows

\[
E_{ad} = (E_{tot} - E_{sub} - n_{Li}E_{Li})/n_{Li}
\]

Figure 5. The total and partial density of states (DOS) of (a) G, G_B1, G_N1, and G_V1 substrates, (b) G_B3V1, and (c) G_N3V1 substrates. The solid line and dashed line with shadow in each panel denote the DOS of substrates with and without Li adsorption, respectively. Zero energy gives the position of the Fermi level. Insets in (a) show the local atomic positions, where the gray sticks, green, blue and pink balls represent C, B, N and Li atoms, respectively. Insets in (b) and (c) are the electron redistributions within the range of \(\pm 2 \times 10^{-3}\) e/Å\(^3\), and the yellow and blue isosurfaces represent electron accumulations and depletions.
where $E_{\text{tot}}$ and $E_{\text{sub}}$ are the total energies of the graphene after and before lithium adsorption, respectively, $n_n$ is the number of Li adatoms, and $E_A$ is the energy of one Li atom in the body-centered cubic crystal phase. A negative value of $E_A$ implies a spontaneous adsorption of Li atoms.

The formation energies ($E_{\text{f}}$) of defects, including N-doping and C-vacancy, on graphene are calculated as follows:

$$E_{\text{f}} = (E_{\text{tot}} - n_nE_D + n_CE_C - E_A)n_C$$  \hspace{1cm} (2)$$

where $E_{\text{f}}$, $E_{\text{tot}}$, and $E_{\text{sub}}$ are the total energies of decorated graphene and pristine graphene, respectively; $E_D$ and $E_C$ are the energies of one N atom in N$_2$ gas and one C atom in graphene, respectively; and $n_n$ and $n_C$ are the numbers of N-dopants and C-vacancies in the supercell, respectively.

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Acknowledgements
Work was supported by the startup fund of China Thousand Young Talents, and National Basic Research Program of China (973 program, No: 2013CB934700). The calculations were supported by Tianhe2-JK in Beijing Computational Science Research Center.

Author Contributions
Mengting Jin, J.G. Deng and Y.N. Zhang wrote the main manuscript text, Mengting Jin and L.C. Yu prepared Figures 1, 2 and 5, and Mengting Jin and W.M. Shi prepared Figures 3–4. All authors reviewed the manuscript.

Additional Information
Supplementary information accompanies this paper at http://www.nature.com/srep

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Jin, M. et al. Enhanced Absorption and Diffusion Properties of Lithium on B,N,VC-decorated Graphene. Sci. Rep. 6, 37911; doi: 10.1038/srep37911 (2016).

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