Effects of nitric acid doping on the adsorption properties and diffusion behavior of Li adsorption on graphene: A first-principles study

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Abstract. In order to study the influence of nitric acid doping on the adsorption of Li on the surface of graphene , the adsorption and diffusion behavior of Li adatoms at three high symmetry sites on graphene and NO_3^-−graphene were systematically investigated by the first-principles method based on density functional theory. The electronic properties of the adatoms were also calculated. The most stable adsorption of Li adatoms on the surface of graphene changed from H site to B site after nitric acid doping. Nitric acid doping enhanced the stability of adsorption of Li adatoms onto the graphene surface, the adsorption energies of H, B and T increased by 2.176eV, 2.816eV and 2.747eV, respectively. there were three charge transferafter after the adsorption of Li adatoms onto the surface of the NO_3^--graphene system.: Li→graphene, graphene→NO_3^- and Li→NO_3^-, respectively. The adsorption of Li adatoms onto the surface of the NO_3^--graphene system exhibited both N-type and P-type doping. Nitric acid treatment reduced the activation energy of Li adatoms on the surface of graphene and promoted the migration of Li adatoms on the surface of NO_3^--graphene.

Introduction

Lithium-ion (Li-ion) battery is currently the most widely used energy storage device. In most commercially available Li-ion batteries, graphite is used as the negative electrode material. However, graphite has a limited Li storage capacity (372 mAh/g) and Li ions diffuse slowly in graphite materials.

New 2D materials for Li-ion battery anode materials have gained increasing attention in recent years. Graphene is a monolayer of carbon atoms packed into a dense honeycomb crystal structure. The unique structure enables the internal carrier mobility to reach $2\times10^5 cm^2 \cdot V^{-1} \cdot s^{-1}$[1] and can be used as a conductive material. However, the carrier concentration of graphene is low, only $10^{12} cm^{-2}$[2], which cannot meet the requirements as a conductive thin film material. Many studies [3-4] have proven that graphene has a high Li storage capacity and cycling performance as the negative electrode material of Li-ion batteries. Theoretical studies have explored the adsorption properties [5-6] and migration behavior [7-8] of Li on graphene surface. Recent studies have found that nitric acid treatment can increase the carrier concentration of graphene and improve its conductivity [9-10]. In 2014, experiments by Guo et al. [11] showed that nitric acid treatment introduces P-type doping into graphene. Doping increases the carrier concentration by about 2.5 times, which significantly improves the graphene conductivity. In 2016, D'Arsié et al. [12] experimented that graphene can introduce stable P-type doping under high temperature and high nitric acid concentration conditions.

Although several studies have investigated the negative electrode material of graphene as a battery, the influence of nitric acid treatment on the adsorption and migration of Li on the surface of

graphene has yet to be explored. Thus, this study evaluated the adsorption properties, electrical properties, and migration behavior of Li adatoms on the surface of graphene before and after nitric acid treatment to provide a theoretical basis for the further development of energy storage devices with improved performance.

Computational methods

All calculations were performed by the first-principles method based on density functional theory [13] and Vienna Ab Initio Simulation package (VASP) [14] code. The Li–graphene system was modeled by placing one adatom on a 3×3 rectangle graphene supercell under periodic boundary conditions. The electronic exchange–correlation potential was obtained by generalized gradient approximation using the Perdew–Burke–Ernzerhof form. The interaction between the electron and the ion core displayed an ultra-soft pseudopotential [15]. Brillouin-zone integrations were performed using Monkhorst–Pack grids [16] (9×9×1 mesh). The plane wave cut-off energy was set to 500 eV. The atoms were relaxed until the internal forces were within 0.01 eV/Å. The total energy variation was smaller than 10^{-4} eV. The Nudged Elastic Band (NEB) method [17] was used to predict the minimum energy pathways for Li diffusion. The dimension of the supercell in the z direction was 15 Å, which used to simulate the adsorption and diffusion of Li on the graphene.

To determine the adsorption energies of the Li adatom in the highly symmetrical positions of graphene, the total energy of the configurations was calculated. Table 1 lists the total and adsorption energies of the Li−graphene and Li−NO_3^-–graphene systems. The adsorption energy E_{ad} is defined as follows:

$$E_{ad} = E_{Li} + E_{G/NO_3^--G} - E_{config} \qquad (1)$$

where E_{Li} is the free energy of a single Li adatom, E_{G/NO_3^--G} is the free energy of graphene and

NO_3^-–graphene sheet, and E_{config} is the total energy of configuration.

Charge distribution and charge transfer can be qualitatively observed based on the charge density difference. Charge density difference was defined as follows:

$$\Delta\rho = \rho_{config} - \rho_G - \rho_{Li} \qquad (2)$$

where ρ_{config} is the charge density difference of configuration, ρ_{Li} is the charge density of Li adatom,

and ρ_G is the charge density of graphene.

Results and discussion

Adsorption Properties of Li on Graphene Surface Before and After Nitric Acid Doping

The adatoms adsorbed onto the surfaces of the graphene and NO_3^-–graphene have three possible high-symmetry sites, namely, the H, B and T sites. The adsorption configuration is shown in Fig. 1 . By calculation, the most stable adsorption site of NO_3^- was B site on grapheme, and its adsorption height was 3.25Å. We studied the stable configurations of the Li–graphene and Li–NO_3^-–graphene systems. Table 1 shows the energy and structural parameters, where E_{config} represents the configuration energy, E_{ad} represents the binding energy ,and h represents the dsorption height .
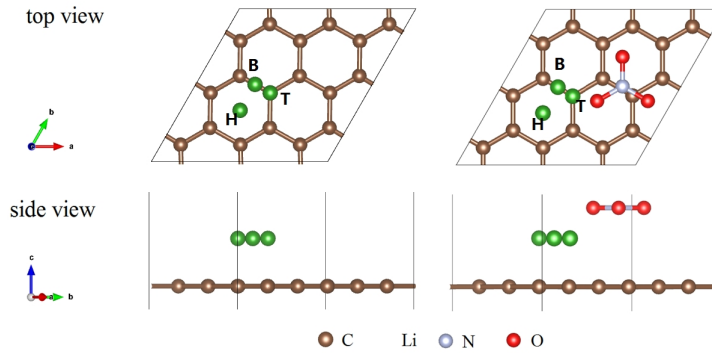
C   Li   N   O

Fig. 1 Top and side view of three possible adsorption sites

Table 1   Energetic and structural properties for the Li adsorption on surface of graphene and NO_3^--graphene.

Sheet	Site	E_{config}[eV]	E_{ad}[eV]	h[Å]
graphene	H	-167.206	<u>1.160</u>	1.659
	B	-166.909	0.863	1.953
	T	-166.893	0.847	1.967
NO_3^--graphene	H	-192.966	3.336	2.032
	B	-193.309	3.679	2.263
	T	-193.223	3.594	2.289

As shown in Table 1, in the Li–graphene system, H site → B sit → T site, the adsorption energy decreased gradually, the adsorption height increased gradually, and the stability of the Li–graphene system decreased gradually. Therefore, the H site is the most stable adsorption site for the Li adatom on the surface of graphene. In the Li-NO_3^-–graphene system, the greatest largest adsorption energy when adsorbed onto the B site of the NO_3^-–graphene surface, indicating that the system was the most stable at this time. In the B site → H site → T site system, the adsorption energy decreased gradually, and the stability of the Li–NO_3^-–graphene system decreased gradually. The most stable adsorption site of Li adatom on the surface of graphene changes from H site to B site after nitric acid treatment.

Nitric acid doping increased the adsorption height of Li adatom on the graphene surface, but increased the adsorption energy of Li adatoms on the graphene surface. The adsorption energy of Li adatom at the H site, B site, and T site of the NO_3^-– graphene system increased by 2.176 eV, 2.816 eV, and 2.747 eV, respectively, compared with the Li adatom at the intrinsic graphene surface. That is, Li adatoms were more easily adsorbed on the surface of graphene due to nitric acid treatment, and the ability of graphene to store Li was increased.

Electrical Properties of Li on Graphene Surface Before and After Nitric Acid Doping

To clarify the influence of nitric acid doping on the electrical properties of the Li–graphene system, the differential charge densities of the Li–graphene and Li–NO_3^-–graphene systems were calculated. The 3D differential charge density diagram (CDD) is shown in Fig. 2. The yellow color in the 3D plot denotes an increase in the charge density after bonding, and the cyan color represents a charge density loss.
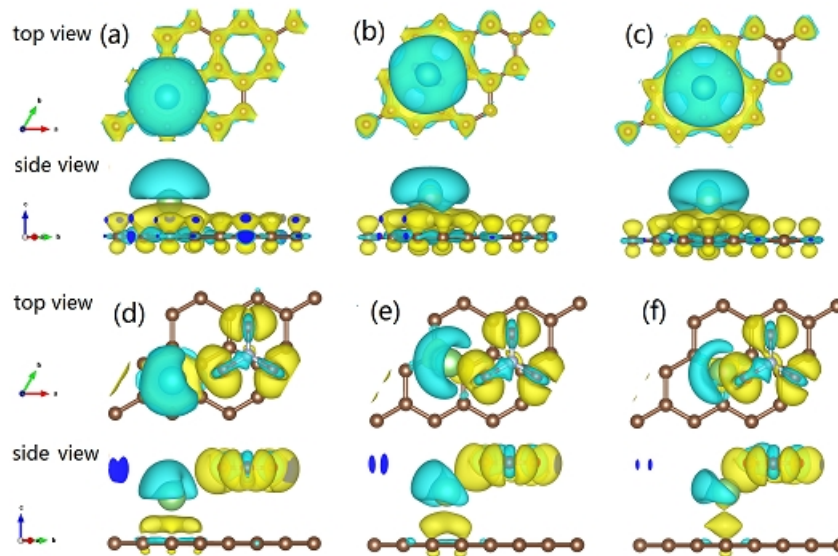
Fig. 2 Top view and side view of CDD induced by Li adatoms adsorption of graphene and NO_3^-–graphene.

Fig. 2 shows that after the Li adatom was adsorbed onto the surface of graphene, the Li adatom was bluish green   and a yellow color appeared around the graphene. This result indicated that the charge density around the Li adatom decreased, whereas that around graphene increased. That is, the Li adatom lost electrons, and the graphene gained electrons. The charges were transferred from the Li adatom to graphene. At this point, Li was the donor, and graphene was the acceptor, forming N-type doping.

After atomic adsorption of Li onto the surface of the NO_3^-–graphene system, the charge density was redistributed. First, a distribution of differential charge density was found between the Li adatom and the nearby graphene. After the Li adatom was adsorbed onto the surface of the NO_3^-–graphene system, the charge density around the Li adatom decreased, whereas that around the P atom around the Li adatom increased. That is charges transfer from the Li adatom to the nearby graphene. Secondly, a distribution of differential charge density was not found between the NO_3^- and the nearby grapheme, which is due to the higher adsorption height of NO_3^-. The surrounding NO_3^- was yellow. The graphene around NO_3^- was bluish green. That is, NO_3^- gained electrons, and the P atom near NO_3^- lost electrons, resulting in a charge transfer from the graphene to the near NO_3^-. Thirdly, after nitric acid doping, the electron cloud shape of Li over graphene changes significantly. The existence of the differential charge density between the Li adatom and NO_3^- can be judged by the color of the electron cloud, and the charge is transferred from the Li adatom to the nearby NO_3^-. In the adsorption process, the Li adatom loses electrons to the graphene near it, forming N-type doping. NO_3^- gets electrons from its surrounding graphene, forming P-type doping. The Li-NO_3^-–graphene system exhibited both N-type and P-type doping.

Migration Behavior of Li on Graphene Surface Before and After Nitric Acid Doping

The Li adatom on the surface of graphene have three possible migration paths: H → B → H, H → T → H, and H → T→ B → T → H. The Li adatom on the surface of the NO_3^-–graphene system have two possible migration paths: B → T→ B and B → H→ B. The NEB method was used to divide the location of migration transition states in the migration path, as shown in Fig. 3.
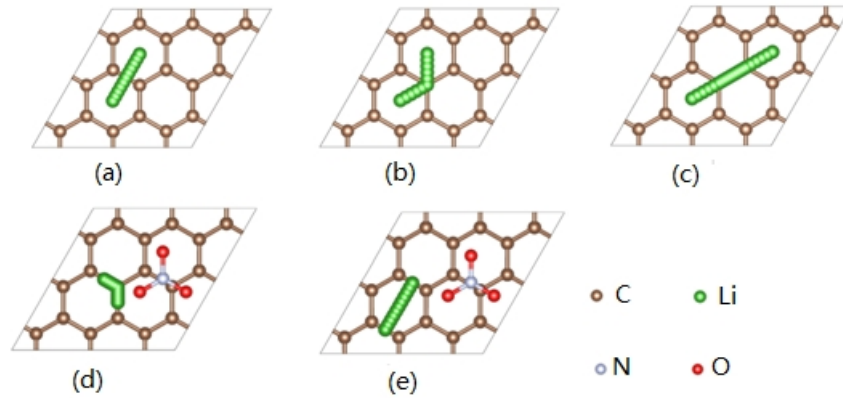
Fig.3   The schematic polts of diffusion pathways of Li adatoms on the grapheme and NO_3^-–graphene by the NEB methob

The first-principles method was used to calculate the total configuration energy and migration activation energy at different positions. The migration path and migration energy curve of Li adatom on the surface of graphene or NO_3^--graphene are plotted in Figs. 4 and 5.
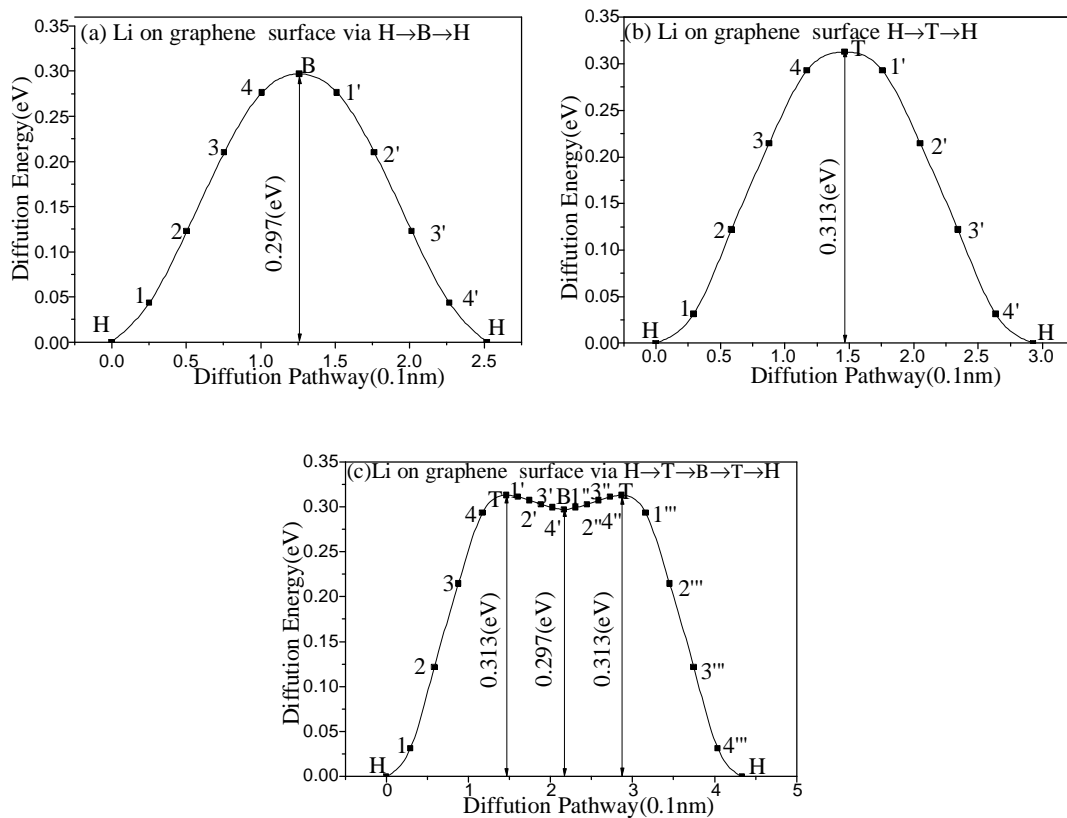

Fig.4   Diffusion pathway and diffusion energy curves of Li adatom on the surface of graphene via the (a)H→B→H, (b) H→T→H , (c) H→T→B→T→H diffusion passway , respectively
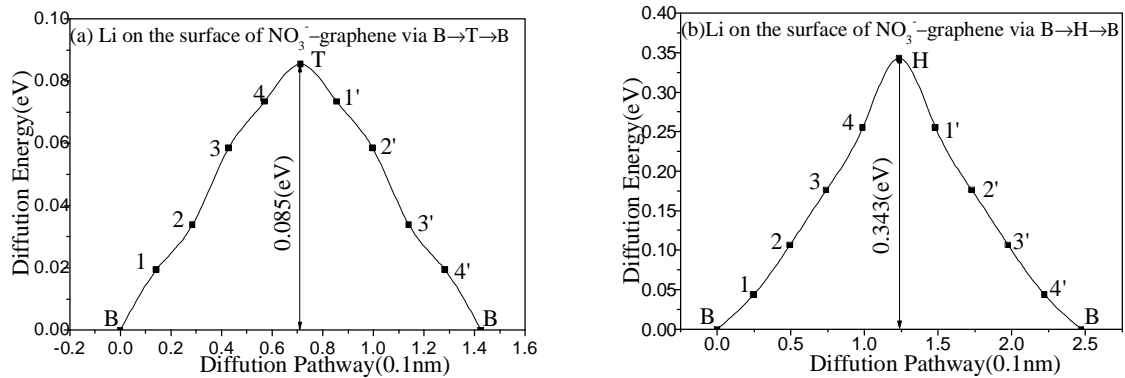
Fig.5　Diffusion pathway and diffusion energy curves of Li adatoms on the surface of NO_3^--graphene via the (a) B→T→B, and (b)B→H→B diffusion passway , respectively

As shown in Fig. 4, when the Li adatom migrated along the H→B path on the surface of graphene, the activation energy required for migration was 0.297eV, which was less than that required for migration along the H→T path (0.313eV). That is, the Li adatom migrated easily along the graphene surface along the H→B path with a lower migration activation energy. Figure 5 shows that the migration activation energy required for the Li adatom to migrate along the B→T path on the NO_3^--graphene surface was 0.085eV, which was less than that required for migration along the T→H path (0.343eV). That is, the Li adatom migrated easily along the B→T path with a lower migration activation energy on the NO_3^--graphene. This result indicated that nitric acid doping reduced the activation energy of Li adatom migration onto the surface of graphene. That is, the Li adatom migrated more easily on the surface of NO_3^--graphene than on the surface of graphene.

Conclusion

Adopting the pseudopotential plane wave method based on density functional theory, the adsorption properties, electrical properties and migration behavior of Li adatoms on the surface of graphene and NO_3^--graphene were calculated by VASP software package. In this study: (1) The most stable adsorption of Li adatoms on the surface of graphene changed from H site to B site after nitric acid doping. Nitric acid doping enhanced the stability of adsorption of Li adatoms onto the graphene surface. (2) there were three charge transferafter after the adsorption of Li adatoms onto

the surface of the NO_3^--graphene system: Li→graphene, grapheme→NO_3^- and Li→NO_3^-, respectively.

Li adatoms were adsorbed on the surface of graphene, only N-type doping was formed, and after nitric acid treatment, P-type doping was introduced. (3) Nitric acid treatment reduced the activation energy of Li adatoms on the surface of graphene and promoted the migration of Li adatoms on the surface of NO_3^--graphene.

Acknowledgements

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