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Adsorption and Diffusion of Sodium on Graphene with Grain Boundaries

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ABSTRACT

Effects of grain boundaries (GBs) in graphene on adsorption and diffusion of sodium were investigated using first principle calculations. Results showed that the presence of GBs in graphene enhanced the adsorption of sodium, with their adsorption energies in the range of -1.32~-0.79 eV, which were lower than the value of -0.67 eV for sodium adsorbed on pristine graphene. The diffusion energy barriers were in the range of 0.09 to 0.35 eV when sodium was diffused along GBs of graphene, whereas they were decreased when sodium was gradually diffused into the GBs. Results showed that graphene with GBs had a larger energy storage capacity for sodium than the pristine one, indicating that it can be used as a good anode material for sodium ion batteries.

Keyword: Graphene; Grain boundaries; Adsorption and diffusion; Diffusion batteries; first principle calculations

1. Introduction

Comparing with three-dimensional materials which are commonly used as electrode materials in batteries, two dimensional (2D) materials show better electrochemical properties, such as excellent charge capacity retention, higher charge/discharge rates and longer cycling life time [1-5]. Commercialized graphite anode for lithium ion batteries (LIBs) has an energy capacity of 372 mAh/g [6], and this capacity can be increased up to values of 600 to 1000 mAh/g by reducing graphite into a monolayer, i.e., using graphene [7, 8]. Other 2D materials have also been studied as the potential electrode materials for LIBs, such as MoS₂ [9], V₂O₅ [10], disordered graphene [11], C₃B [12], Ti₃C₂ [13], and hierarchical Fe₃O₄ microsphere/graphene nanosheets [14]. There are various types of defects in these 2D materials [15-21], which can affect their electrochemical performance. Effects of these defects on adsorption and diffusion of lithium atoms on graphene [22-26] and silicene [27] have previously been investigated. Point defects, edges and grain boundaries (GBs) in graphene can enhance adsorption of lithium atoms on graphene [26, 28-30], which can improve the charge storage capacities [22]. It was also found that a monolayer of MoS₂ with defects showed better adsorption and diffusion properties of lithium atoms compared to those of its perfect counterpart [31].

Due to the limited lithium resources, LIBs are insufficient for the increasing demands of energy storage [32, 33]. As sodium is located below lithium in the periodic table and these two elements show similar chemical properties in many aspects, sodium ion batteries (NIBs) have recently received much interest to be used as a low cost alternative to LIBs [34]. Various 2D materials have been investigated to be used as the electrode materials for NIBs, and some of them showed better electrochemical properties as the electrodes for NIBs than those for

LIBs [3,6,35,36]. For example, the diffusion energy barriers for lithium and sodium atoms on silicene were found to be 0.21 and 0.12 eV, respectively [5]. The diffusion energy barriers for sodium atom diffusing along zigzag and armchair directions of monolayer black phosphorene were 0.04 and 0.38 eV, respectively [35,36], whereas the corresponding diffusion energy barriers for the lithium atom to diffuse along zigzag and armchair directions were 0.08 and 0.68 eV, respectively [35, 36]. Using these 2D materials as the electrodes, NIBs showed faster charging/discharging rates than those using LIBs [37].

Inspired by the findings that point defects or GBs in the graphene can enhance the adsorption and diffusion of lithium atoms [25, 26], there were previous studies to understand the effects of these defects in graphene on the adsorption and diffusion of sodium atoms. Graphene with vacancies could strengthen the Na-C interactions [38]. Using graphene as the anode for NIBs, the energy capacities were found to be 1450 and 1071 mAh/g for the graphene with divacancy and Stone-Wales defects, respectively [22, 39]. The GBs can induce defect states close to the Fermi level of graphene [40, 41] and can interact with sodium atoms, therefore, the adsorption and diffusion of sodium atoms could be tuned by GBs in graphene.

As far as we know, there are no reports to investigate the effects of GBs in graphene on adsorption and diffusion of sodium. In the present work, using a density functional theory (DFT), we systematically studied the adsorption and diffusion of sodium on graphene with two types of commonly observed GBs, i.e., zig-zag and armchair ones [26, 42]. The adsorption and diffusion behaviors of sodium atoms were also compared with those of lithium ones.

2. Computational details

All the DFT calculations were performed with SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) codes [43]. We chose a local density approximation (LDA) for exchange-correction functions parameterized by the Ceperley-Alder (CA) [44]. The valence electron wave functions were expanded using a double- ζ basis set plus polarization functions. The cut-off energy was set to be 180 Ry for the calculation of self-consistent Hamiltonian matrix. Larger cut-off energy of 250 Ry was also tested. The results are listed in Table S1, which shows that the adsorption energies of Li and Na on pristine graphene are same with that calculated with cut-off energy of 180 Ry. The pseudopotential generation was performed using the ATOM program within the SIESTA package, and electronic configurations for pseudopotentials generation and cut-off radii are listed in Table S2. The pseudopotentials were successfully used to calculate lattice constants of ionic compounds of Li_2O and Na_2O (see the supporting information).

A 6×6 hexagonal supercell was used to model pristine graphene, and a $3\times 3\times 1$ k-point mesh including the Γ -center was used to sample the Brillouin zones. Larger hexagonal supercells were also tested, and the results show that this does not apparently affect the adsorption energies (see Table S3). The simulation models used in this work were two parallel and equally spaced GBs in a rectangular simulation supercell in order to satisfy periodic boundary conditions. A vacuum thickness of 30 Å above graphene sheet was used to avoid the influence of the interlayer. Two types of GBs, i.e. zig-zag and armchair ones [40, 45] shown in Figs. 1a and 1b, were considered. The initial structures of graphene with GBs were obtained by relaxing the positions of carbon atoms along with the lattice parameters until the

force on each atom was less than 0.02 eV/Å. The Brillouin zones were sampled using a $2 \times 4 \times 1$ k -point mesh. Results listed in Table S4 showed that using a denser k -point mesh with $4 \times 6 \times 1$ and a larger cut-off energy of 250 Ry achieved similar results, indicating that the $2 \times 4 \times 1$ k -point mesh and cut-off energy of 180 Ry we used was good enough. The zig-zag GBs were composed of pentagon/heptagon/hexagon (5-7-6), whereas the armchair ones were composed of pentagons/heptagons/pentagons/heptagons/hexagon (5-7-5-7-6). There are generally three possible adsorption sites for a single sodium atom on graphene considering the hexagonal symmetry of graphene: the hollow site (H) at the center of a hexagon; the bridge site (B) at the midpoint of a carbon-carbon bond; and the top site (T) directly above a carbon atom. All these sites are illustrated in Fig. 1a. Previous analysis showed that the hollow site (H) is normally the most stable adsorption position for lithium and sodium atoms [25, 28, 38, 39]. Our calculation results also showed that sodium prefers to occupy the H site.

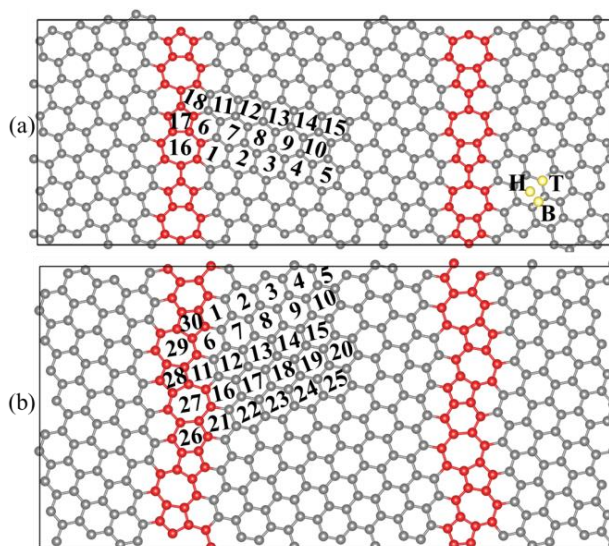


Figure 1 Optimized atomistic configurations of graphene with (a) zigzag- and (b) armchair-oriented GBs. H, B and T sites are corresponding to the positions where sodium atom is positioned above the center of a hexagonal ring formed by carbon atoms, above a C-C

bond, and on top of a carbon atom, respectively. The sequential numbers denote the adsorption sites at graphene with GBs investigated.

To investigate the stability of sodium/lithium atoms on graphene with GBs, the adsorption energy $E_{\text{ad}}(\text{Na/Li})$ of sodium/lithium atoms was calculated based on equation (1):

$$E_{\text{ads}}(\text{Na/Li}) = (E_{\text{GBs}+n\cdot\text{Na/Li}} - E_{\text{GBs}} - n \cdot E_{\text{Na/Li}}) / n \quad (1)$$

where $E_{\text{GBs}+n\cdot\text{Na/Li}}$ and E_{GBs} are the total energies of the supercell with and without adsorption of number of n sodium/lithium atoms, respectively. The adsorption energy can be calculated using an isolated Li/Na atom or bulk metal as the reference states. $E_{\text{Na/Li}}$ is the energy of an isolated Na/Li atom or half of the energy body center cubic Li/Na bulk metal. The basis set superposition error (BSSE) [46] induced by the artificial shortening of distances and strengthening of the interactions was corrected by applying the counterpoise corrections [47] using "ghost" atoms. The BSSE was calculated to be -0.15 eV (for Na) and -0.17 eV (for Li). The BSSE was considered for all the adsorption energies in the whole work. According to equation (1), a larger negative value of adsorption energy indicates a more favorable exothermic reaction occurring between graphene and adopted atoms.

Several methods, such as Nudged Elastic Band (NEB) method, dimer method, and constrained method, can be used to determine the diffusion energy barriers of atoms in the condensed matters [48]. The NEB method is often considered as the most efficient one, whereas when the final state is unknown, the dimer method was often used [48]. The constrained method is the simplest and the most intuitive one. Because there could be a large computational effort needed when using the NEB method for the parallel computation, we used the constrained method and compared with the results from the NEB method with

several cases, and results indicate that the constrained method is reliable to be used to calculate the diffusion behavior of sodium atoms on graphene. With the constrained method, one degree of freedom of the sodium/lithium atom was fixed, whereas all the other $n-1$ degrees of freedom were allowed to relax, i.e. the energy of the system was minimized in an $n-1$ dimensional hyperplane.

The sodium/lithium atom was diffused from one stable H site to a nearest one by passing through the B site on graphene. The sodium/lithium atom was pushed along the H-B-H path but constrained in the direction along the path. It was free to move in the directions perpendicular to the path for sodium/lithium atom, and all other atoms are allowed to move freely.

3. Results and Discussion

3.1 Adsorption of sodium/lithium on graphene with GBs

The calculated adsorption energies for sodium atoms adsorbed at H, B and T sites on pristine graphene are -0.67, -0.49 and -0.48 eV, respectively. The sodium atom was found to stay preferably at H site, which agrees with the previous reported result [38, 49]. The distance between sodium atom and graphene is 2.08 Å, and the bond length of the Na-C atoms is 2.52 Å.

Several adsorption sites for sodium on graphene with zig-zag oriented GB were calculated. The results are shown in Fig. S1, and the calculated adsorption energies are listed in Table S5. The sodium atom was found to stay preferably at H site. Therefore, we will focus on the H sites in the following part of the paper. The adsorption energies of sodium atoms on

graphene with zig-zag and armchair-oriented GBs, obtained using **an isolated sodium atom as the reference** state are shown in Figs. 2a and 2b, respectively. The corresponding adsorption sites are presented in Figs. 1a and 1b, respectively. The adsorption energies are increased as sodium atom is adsorbed at H sites which are far away from GBs, indicating that sodium atom prefers to be adsorbed near GBs. The adsorption energies are -1.20 and -1.32 eV for sodium atoms adsorbed at site 16 on graphene with zigzag-oriented GBs and site 27 on graphene with armchair-oriented GBs, respectively. These readings are smaller than the adsorption energy of -0.67 eV for sodium atom on pristine graphene, which indicates that the adsorption of sodium atom is enhanced by the existence of GBs. Comparing the adsorption energies of sodium atoms on different hollow sites above the center of the polygonal rings (i.e., pentagon, heptagon and hexagon) of GBs, the stability data of the sodium atoms from high to low can be summarized in the following order: heptagon>hexagon>pentagon. At the hollow site for the heptagon, the distance between sodium atom and graphene is 1.96 Å. For the heptagon, sodium atom is 2.10 Å away from graphene, whereas for the pentagon, the sodium atom is 2.19 Å away from graphene. The adsorption energies of sodium atoms adsorbed **on graphene** with the armchair-oriented GBs are larger in the absolute values than those with zigzag-oriented GBs. To compare with, the adsorption behavior of the lithium atoms on graphene with GBs shows the similar trend as that of sodium atoms, which can be seen from Figs. 2c and 2d. The existence of the GBs in graphene can enhance the adsorption of lithium atoms, which consists with the previously reported results [25, 26]. **The adsorption energies of sodium/lithium on graphene with GBs using the bulk metal as a reference state are shown in Fig. S2, which reveals the same trend with that using isolated atoms as a reference state.**

Results also reveal that sodium atom shows the same adsorption behavior with those from LDA and generalized gradient approximation (GGA) calculations expect for the absolute values (see Fig. S3 in the supporting information). We can conclude that the calculations using LDA do not apparently affect the conclusion of this work.

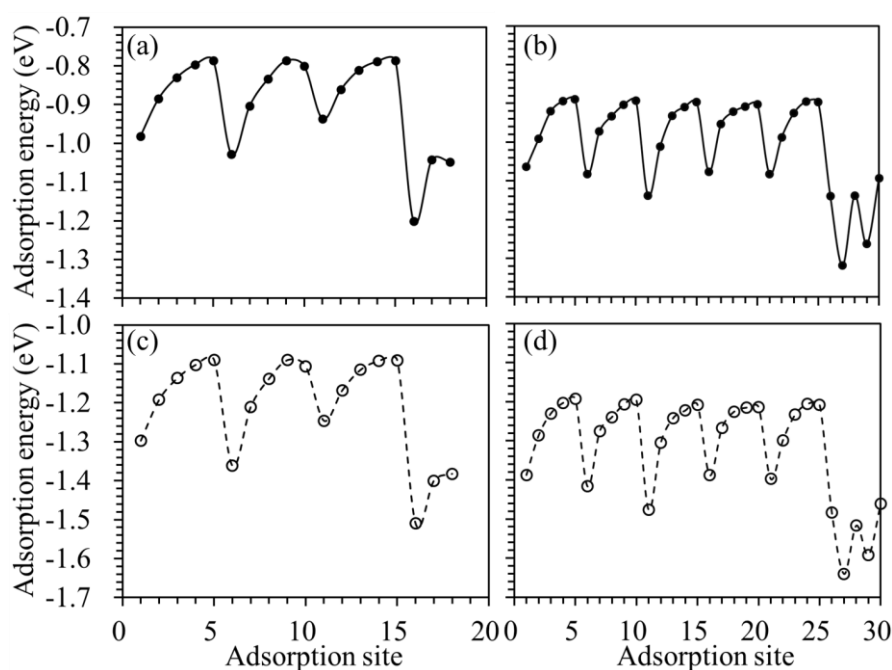


Figure 2 Adsorption energies of sodium/lithium on graphene with (a)/(c) zigzag- and (b)/(d) armchair-oriented GBs. The corresponding adsorption sites are presented in Fig. 1a and 1b, respectively.

With increasing the Na content, Na clusters may form. It is known that the formation of Na cluster would seriously reduce the charge/discharge capacity of the batteries. Also the formation of Na cluster will induce dendrite growth of sodium, which is harmful for the safety of NIBs. We have investigated more sodium atoms adsorbed on graphene and compared the binding energies and adsorption energies with those of small Na_n clusters (see the supporting information). The results indicate that graphene with GBs can store more sodium atoms with a

larger Na/C ratio, and the existence of GBs could prevent formation of Na clusters on graphene.

3.2 Diffusion of Na/Li on graphene with GBs

The charging rate of NIBs depends on the diffusion behavior of sodium atoms on graphene. Smaller values of the diffusion energy barriers will lead to a faster charging rate. The diffusion energy barriers of sodium and lithium atoms on the pristine graphene are 0.19 and 0.25 eV, respectively. The diffusion energy barrier of lithium atom is close to the value of 0.26 eV calculated using the NEB method [50].

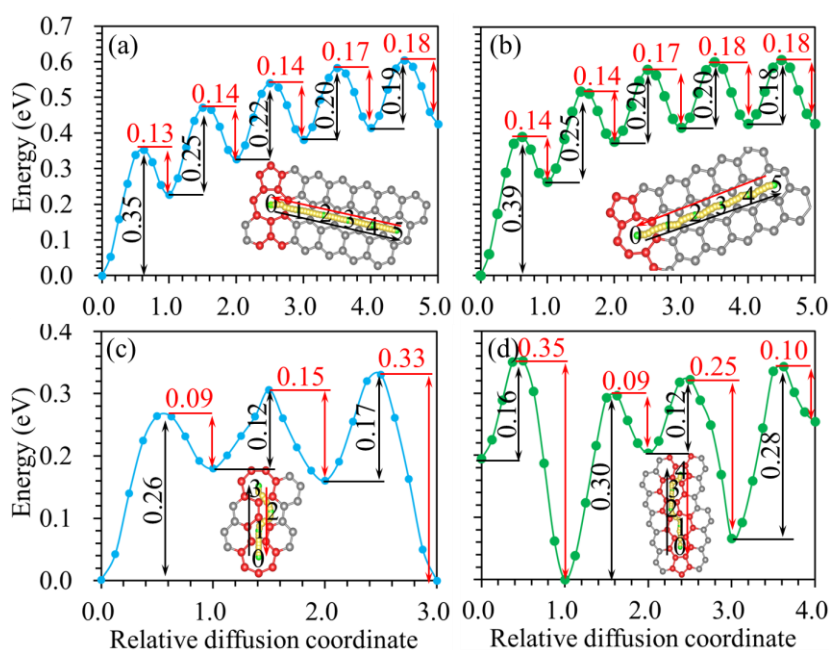


Figure 3 Energy curves for sodium diffusion on graphene with (a)/(c) zigzag-oriented GBs and (b)/(d) armchair-oriented GBs. Inset show the corresponding diffusion paths.

Two possible paths were investigated for sodium atom diffusion on graphene with GBs, i.e., one is along GBs and the other is perpendicular to GBs. When sodium atom diffuses towards GBs as shown in Figs. 3a and 3b, the calculated diffusion energy barrier is 0.18 eV at

the sites far away from GBs ($>10 \text{ \AA}$), which is similar to the value on a pristine graphene. The diffusion energy barrier decreases with the decrease of distance of sodium atom to the GBs. The diffusion energy barriers are 0.18, 0.17, 0.14, 0.14 and 0.13 eV as the sodium atom diffuses along the path of $5 \rightarrow 4 \rightarrow 3 \rightarrow 2 \rightarrow 1 \rightarrow 0$ (see Fig. 3) on graphene with zigzag-oriented GBs. However, when sodium atom diffuses backward from GBs, i.e. along the path $0 \rightarrow 1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \rightarrow 5$, the diffusion energy barriers are 0.35, 0.25, 0.22, 0.20 and 0.19 eV. This clearly indicates that GBs behave as potential traps for sodium atoms. These traps can increase the adsorption energy of sodium atoms. The diffusion behavior of sodium atom on graphene with armchair-oriented GBs shows the similar characteristics. The diffusion energy barriers are in the ranges of 0.09-0.33 and 0.09-0.35 eV when sodium atoms diffuse along zig-zag and armchair-oriented GBs, respectively, as shown in Figs. 3c and 3d. **The diffusion behaviors of the sodium atoms calculated using LDA and GGA show similar results except for the absolute values (see Fig. S4 in the supporting information).**

The energy curves for sodium atoms diffusing from site 0 to site 1 and from site 4 to site 5 calculated using climbing image nudged elastic band (CI-NEB) theory [51] are shown in Fig. S4a. In the calculation five images were involved to determine the saddle point through a linear interpolation from the fixed initial and final configurations. The CI-NEB calculation was done using codes from Vienna ab initio Simulation Package (VASP) [52]. The projector augmented wave (PAW) method [53] was used to describe electron-ion interactions, and the generalized gradient approximation with the Perdew-Burke-Ernzerhof (PBE) function was used to describe the electron exchange-correlation.

The calculated diffusion energy profiles of lithium on graphene with GBs are shown in

Fig. 4, which shows similar characteristics with those for sodium diffusion. The diffusion energy barriers decrease with the decrease of distance from lithium to GBs as it diffuses along the path which is moving towards to GBs. The diffusion energy barriers are in the ranges of 0.16-0.40 and 0.17-0.41 eV when the lithium diffuses along zig-zag and armchair-oriented GBs, respectively.

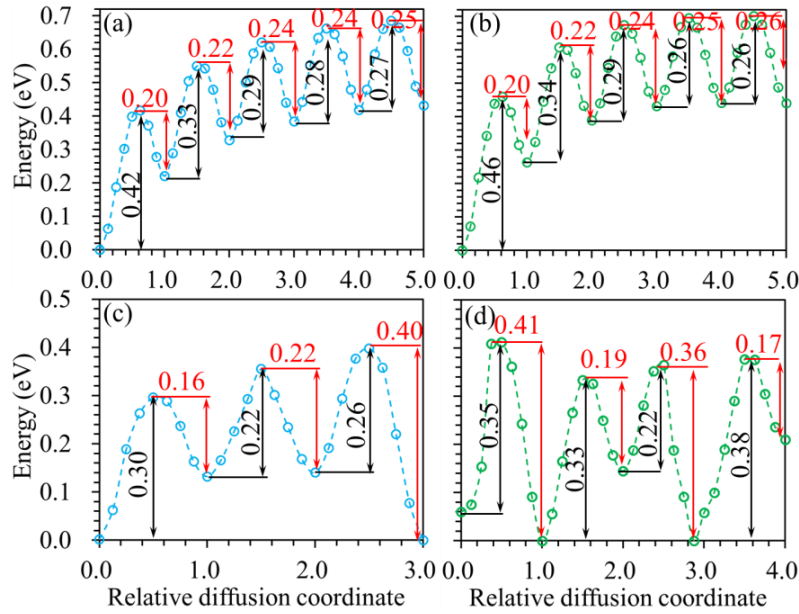


Figure 4 Energy curves for lithium diffusion on graphene with (a)/(c) zigzag-oriented GBs and (b)/(d) armchair-oriented GBs.

3.3 Density of states

To calculate the density of states (DOS), dense k-point meshes with $21 \times 21 \times 1$ and $15 \times 21 \times 1$ were used to sample the Brillouin zones for pristine graphene and graphene with GBs. The DOS results of pristine graphene with and without adsorption of a **sodium atom** are shown in Figs. 5a and 5b, respectively. The Fermi level was set to be zero. The adsorption of a **sodium atom** does not apparently change the DOS of graphene except for an upshift of the Fermi energy level into the conduction band. Na 3s state (green line in Fig. 5b) is located at 0.36 eV, which is higher than the Fermi energy level, indicating that Na atom will donate its

electron to graphene. Because of the existence of GBs in graphene, the Dirac point is destroyed and a localized band is formed near Fermi level [54], as the peaks marked with red dashed lines in Figs. 5c and 5e for graphene with zigzag- and armchair-oriented GBs, respectively. Interference of defect states of the GBs results in different adsorption behavior of Na on pristine graphene. When a sodium atom is adsorbed at the hollow site of the heptagon in GBs, a charge transfer from Na to graphene occurs and results in an upshift of Fermi level into the conduction band as shown in Figs. 5d and 5f. Because of the increased DOS values near the Fermi level, the up-shift of the Fermi level is smaller than that of pristine graphene with the adsorbed Na. Na 3s states are located at energy position higher than the Fermi energy level when they are adsorbed at the sites far away from the GBs, as shown in in Figs. 5g and 5h for Na adsorbed at sites 5 and 10, respectively. Na 3s states are located at lower energy positions as they are adsorbed at sites far away from the GBs compared with at the GBs, which results in a strong interaction between Na and graphene as they are adsorbed at the GBs. The charge-transfer of Li/Na adsorbed on the graphene was analyzed using the Mulliken population analysis [55, 56]. As the Li/Na is adsorbed at H site in the pristine graphene, the charges transferred from Li and Na to the graphene are 0.862 and 0.849 $|e|$, respectively. As the Na is adsorbed at the hollow site of the heptagon in GBs, the charges transferred from Na to the graphene are 0.831 and 0.822 $|e|$ for the graphene with zigzag- and armchair-oriented GBs, respectively. The charges transferred from Na to the graphene are 0.854 $|e|$ as the Na is adsorbed at site 5 of graphene with zig-zag oriented GB and site 20 of graphene armchair-oriented GB. The results indicate that the Li and Na atoms are in ionic state as they are adsorbed on the graphene.

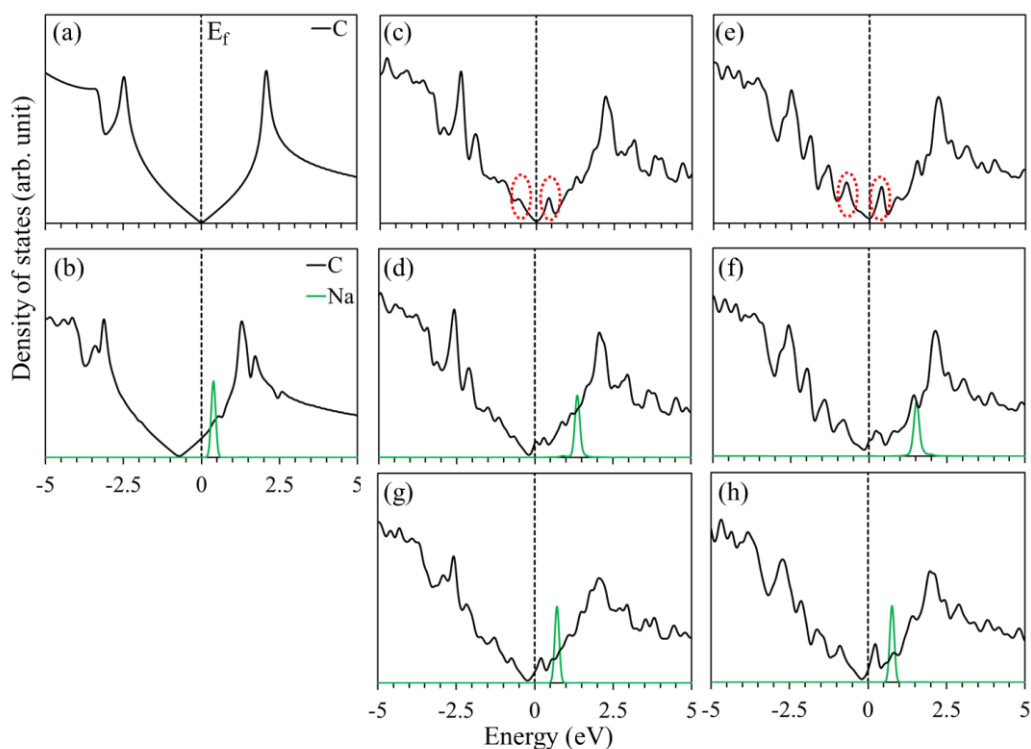


Figure 5 Density of states (DOS) of (a) pristine graphene and graphene with (c) zigzag- and (e) armchair-oriented GBs; DOS of Na adsorbed (b) pristine graphene and graphene with (d/g) zigzag- and (f/h) armchair-oriented GBs. The Na 3s state is denoted with green lines. The Fermi level is set to be zero.

3.4 Discussion

To be used as good anode materials for NIBs, the anode materials should have large values of exothermic reaction energy with sodium atoms so that anode materials have large storage capacities [57]. The presence of GBs enhances the adsorption of sodium atoms on graphene, indicating that a more favorable exothermic reaction occurs between graphene and sodium atom. The graphene with GBs should be better to store sodium atoms than those of pristine ones. The calculated diffusion energy barriers of sodium on graphene with GBs are in the range of 0.09-0.35 eV, which are smaller than the diffusion energy barriers values of 0.16-0.41 eV for Li on the same atomically structured graphene. The smaller diffusion energy

barrier for sodium than that of the lithium indicates that graphene might have better charging rate properties for NIBs than LIBs. The results agree with the reports that some of 2D materials show better electrochemical properties as the electrodes for NIBs than those for LIBs [3,6,35,36].

The dependence of the diffusivity on the diffusion energy barrier (E_A) obeys the Arrhenius equation [58]:

$$D = D_0 \exp(-E_A / k_B T) \quad (2)$$

in which k_B is the Boltzmann constant and T is the temperature. Based on equation (2), a 60 meV increase (or decrease) in the diffusion energy barrier results in ten times of decrease (or increase) in the diffusivity. From Figs. 4a and 4b, the diffusion barriers are not affected when the sodium diffuses at sites far away from the GBs, whereas the diffusion energy barriers decrease from 0.19 eV to 0.13 eV as sodium atoms diffuse near the GBs. Based on this result, the diffusivity of the sodium atom on graphene with GBs can be enhanced for the fast charging process. The reverse diffusion barriers near GBs are larger than those of sodium diffusion on pristine graphene; however they are much smaller than the diffusion barriers of 0.55-0.59 eV for the Li diffusion in silicon [59, 60]. Therefore, graphene with GBs is good to be used for discharge process of NIBs, and a good anode material for NIBs.

Above results also show that existence of GBs in graphene can prevent the formation of clustering of sodium atoms effectively, and thus inhibit dendrite growth of sodium, which is helpful to improve the safety of NIBs. GBs are likely to be introduced into graphene during chemical vapor deposition (CVD) growth process. Therefore, CVD growth can be used to fabricate low-cost, high-quality, and large area graphene as the anode for NIBs [61, 62].

4. CONCLUSION

In summary, the adsorption and diffusion of sodium atom on graphene with GBs were systematically studied using the DFT calculations. The sodium atom prefers to be adsorbed at GBs with large adsorption energies. The diffusion energy barriers decrease with the decrease of distance from sodium atom to GBs as it diffuses along the path which is moving towards to GBs. The diffusion energy barriers are in the ranges of 0.09-0.33 and 0.09-0.35 eV as the sodium atom diffuses along both zigzag- and armchair-oriented GBs, respectively. Therefore, the existence of GBs in graphene can enhance the adsorption and diffusion of sodium atoms, indicating that graphene with GBs is a promising anode material for NIBs.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at

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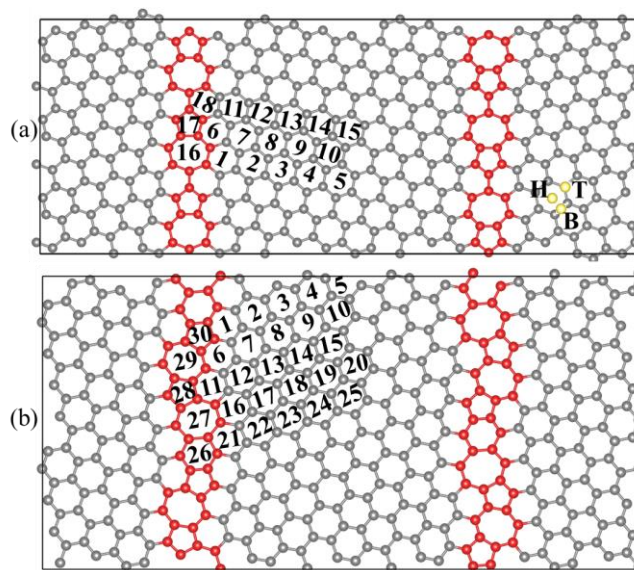
Figure 1 Optimized atomistic configurations of graphene with (a) zigzag- and (b) armchair-oriented GBs. H, B and T sites are corresponding to the positions where the sodium atom is positioned above the center of a hexagonal ring formed by carbon atoms, above a C-C bond, and on top of a carbon atom, respectively. The sequential numbers denote the adsorption sites at the graphene with the GBs investigated.

Figure 2 The adsorption energies of sodium/lithium in graphene with (a)/(c) zigzag- and (b)/(d) armchair-oriented GBs. The corresponding adsorption sites are presented in Fig. 1a and 1b, respectively.

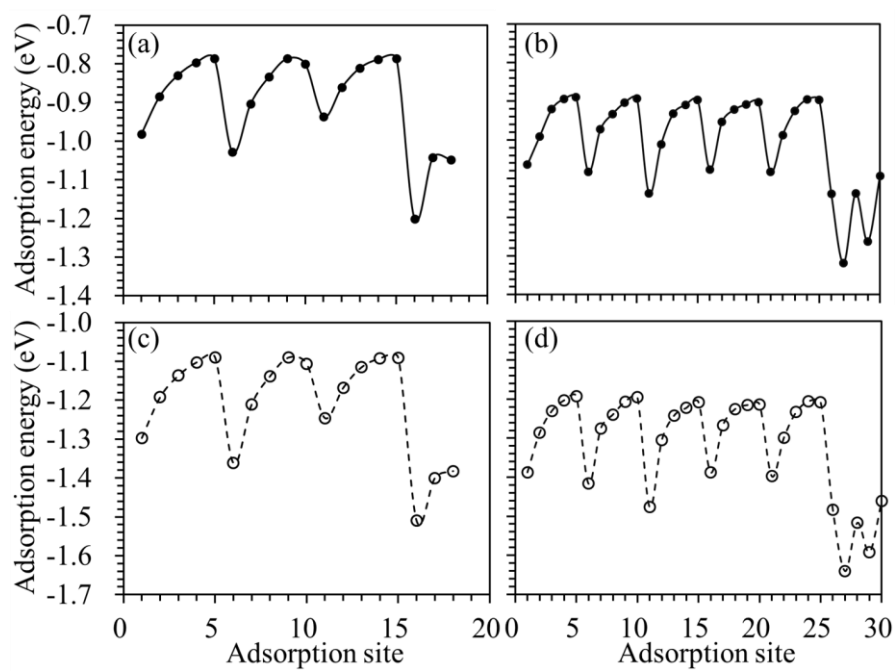
Figure 3 Energy curves for sodium diffusion in graphene with (a)/(c) zigzag-oriented GBs and (b)/(d) armchair-oriented GBs. Inset show the corresponding diffusion paths.

Figure 4 Energy curves for lithium diffusion on graphene with (a)/(c) zigzag-oriented GBs and (b)/(d) armchair-oriented GBs.

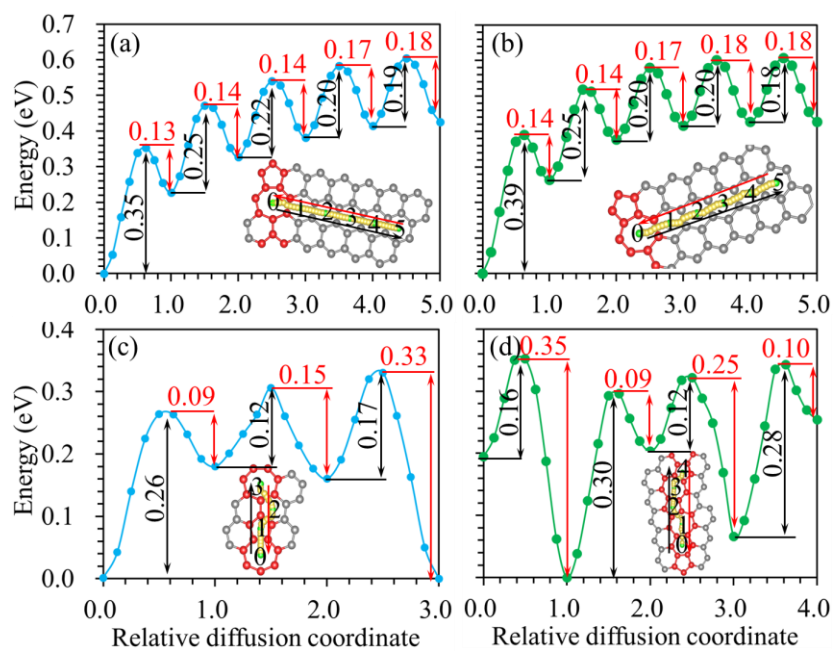
Figure 5 Density of states (DOS) of (a) pristine graphene and graphene with (c) zigzag- and (e) armchair-oriented GBs; DOS of the Na adsorbed (b) pristine graphene and graphene with (d/g) zigzag- and (f/h) armchair-oriented GBs. The Na 3s state is denoted with green lines. The Fermi level is set to be zero.



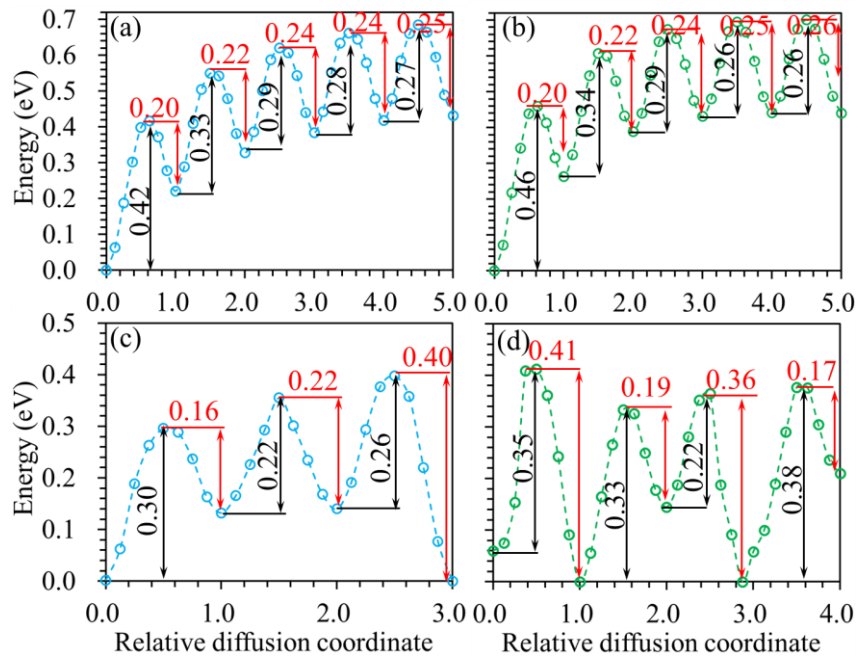
Sun et al. Figure 1



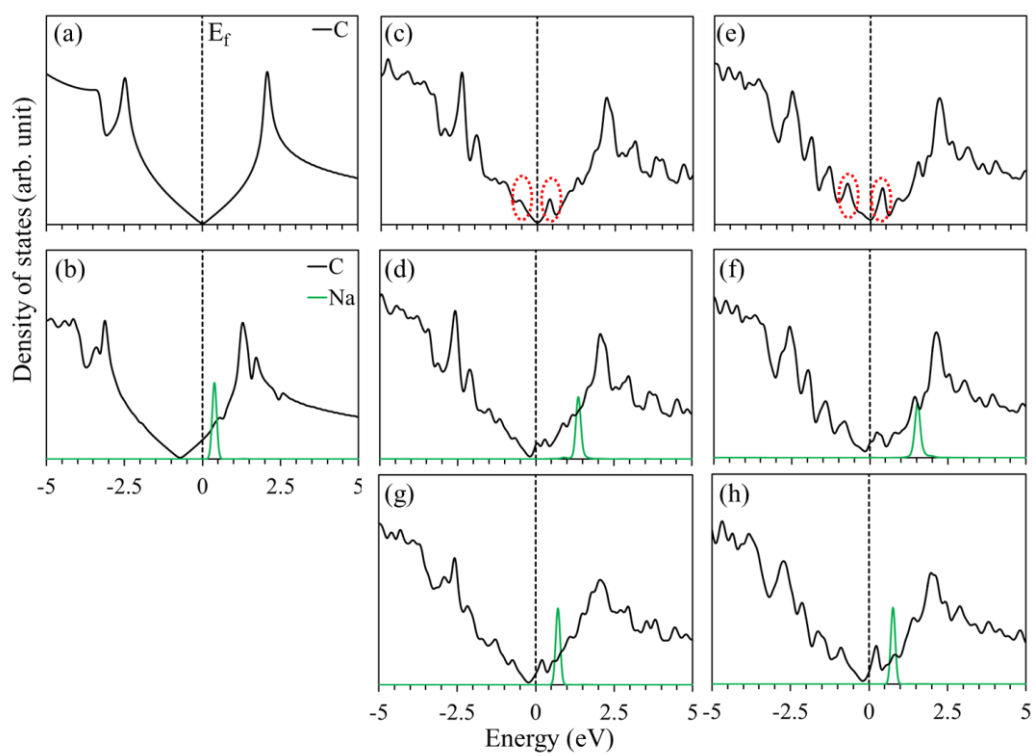
Sun et al. Figure 2



Sun et al. Figure 3



Sun et al. Figure 4



Sun et al. Figure 5