Adsorption and diffusion of sodium on graphene with grain boundaries

Xiaoli Sun [a], Zhiguo Wang [a, *], Yong Qing Fu [b, **]

[a] *School of Physical Electronics, Center for Public Security Information and Equipment Integration Technology, University of Electronic Science and Technology of China, Chengdu, 610054, PR China*
[b] *Faculty of Engineering and Environment, University of Northumbria, Newcastle upon Tyne, NE1 8ST, UK*

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 $0.09-0.35$ 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.

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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—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 MoS_2 [9], V_2O_5 [10], disordered graphene [11], C_3B [12], Ti_3C_2 [13], and hierarchical Fe_3O_4 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 MoS_2 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

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  * Corresponding author.
  ** Corresponding author.
    E-mail addresses: zgwang@uestc.edu.cn (Z. Wang), richard.fu@northumbria.ac.uk (Y.Q. Fu).

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 divancancy 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 Fig. 1a and b, 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 show 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.
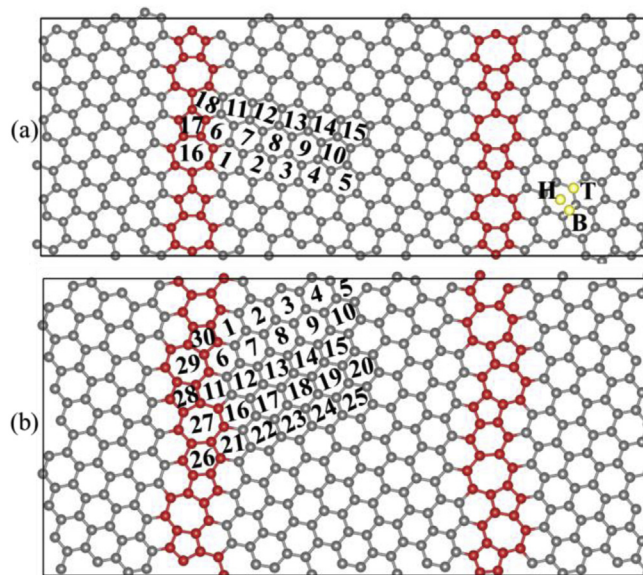

Fig. 1. Optimized atomistic configurations of graphene with (a) zigzag- and (b) armchair-oriented GBs. H, B and T sites are corresponding to the positions where sodium atom is positioned above the center of a hexagonal ring formed by carbon atoms, above a C-C bond, and on top of a carbon atom, respectively.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

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.

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

$$E_{ads}(Na/Li) = \left(E_{GBs+n\cdot Na/Li} - E_{GBs} - n \cdot E_{Na/Li} \right)/n \qquad (1)$$

where $E_{GBs+n\cdot Na/Li}$ 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. $E_{Na/Li}$ 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.