Mechanism of sodium adsorption on *N*-doped graphene nanoribbons for sodium ion battery applications: A density functional theory approach

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ABSTRACT

Density functional theory (DFT) calculations were employed to investigate the adsorption and diffusion mechanisms of sodium on graphene nanoribbons (GNR). The calculated adsorption energy in the edge region (−1.096 eV) of pristine GNR was lower than that for the center region (−0.836 eV). In addition, the adsorption energies on GNRs with nitrogen-doped defects (4ND, 3NV, and pyrrolic: −3.794 to −1.837 eV) were lower than that for the pristine-GNR edge (−1.096 eV). The adsorption properties of sodium on GNRs were strongly affected by the introduction of nitrogen defects. Band structure analysis revealed that the *3s* valance orbital of sodium is raised in energy when sodium is strongly adsorbed on the GNR. Moreover, when the sodium is adsorbed in close proximity to the nitrogen atoms, the *p* orbital of nitrogen is lowered in energy due to strong interactions between the sodium and adjacent nitrogen atoms. Although improved adsorption of sodium on GNRs with nitrogen-doped defects was observed, the diffusion energy barrier obtained for sodium on the pyrrolic-GNR (0.009−0.021 eV) was lower than that for the pristine-GNR (0.019−0.079 eV). Therefore, the adsorption and diffusion properties of sodium on GNRs can be beneficially affected by the introduction of nitrogen-doped defects at the GNR edge.

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1. Introduction

Rechargeable batteries are essential components in a variety of industrial applications such as electronic vehicles (EVs), portable electronic devices, and energy storage systems (ESSs) [1–5]. Among rechargeable batteries, lithium ion batteries (LIBs) have been widely used in portable devices owing to their relatively high power densities and rate performance [5–8]. Although LIBs have

demonstrated good performance as rechargeable batteries, sodium ion batteries (SIB) have been in the spotlight in recent years due to their low cost and the natural abundance of sodium, which makes up approximately 2.6% of Earth's crust [4,9,10]. In addition, the low reduction potential of sodium (−2.71 V vs. the standard hydrogen electrode (SHE)) imparts safety to the SIBs [3,4,11].

However, the performance of SIBs needs to be improved in order to reach, or exceed, the power densities and reversible capacities of LIBs. Many researchers have been working toward enhancing the power densities, cycling stabilities, capacities, and rate performance of SIBs through the design of improved electrode materials [3,12–14]. Graphite has already been used as the anode material in LIBs, but it cannot be applied to SIBs [3,15–18]. Since the radius of the sodium ion is morphologically larger than the interplanar distance between graphite sheets, it is difficult to intercalate sodium

into graphite [19,20]. Among alternative carbonaceous materials, some researchers have focused on graphene nanoribbons (GNRs) because of their lower dimensionality and higher metal-ion adsorption ability than those of graphite [21–25].

GNRs are quasi-one-dimensional (1D) materials composed of nanosized strips of graphene-based materials. Many researchers have obtained GNRs by unzipping carbon nanotubes (CNTs) using various techniques such as chemical oxidation [23,24], physico-chemical [26], electrical [27], catalytic [28,29], and intercalation-exfoliation [30] methods. Unlike the morphologically symmetric graphene, GNRs show chiral edge states, and zigzag and armchair edge structures [31,32]. These morphological features impart unique electronic properties to electrochemical devices [21,33–37].

Using DFT, Uthaisar et al. [37] theoretically revealed that in-teractions between Li atoms and GNRs depend on the graphene edge structure, and confirmed that Li adsorption on zigzag GNRs is electronically advantageous over adsorption on an armchair type GNRs. They observed theoretically that Li atoms can easily diffuse toward the graphene edges [25]. For these reasons, they suggested that anodes made from zigzag GNRs could promote much higher discharge rates and power densities in LIBs. Research has been undertaken with the aim of enhancing the performance of SIBs through modification of the GNRs. Through the use of nitrogen-doping and edge effects in GNRs, Liu et al. [38] experimentally enhanced the performance of LIBs, and achieved high capacities, excellent cycling performance, and rate capabilities. In addition, researchers have investigated the ideal doping position for GNRs and observed that nitrogen doping at the edges was energetically favorable [35,39–41].

To the best of our knowledge, theoretical studies on sodium adsorption and the diffusion mechanism on nitrogen-doped GNRs (N-GNR) have not been performed. The effect of GNR nitrogen doping on sodium adsorption also remains unclear. Herein, we investigated the adsorption and diffusion behavior of sodium in zigzag GNRs using DFT. We mainly considered various types of nitrogen doping in these GNRs (N-GNRs) through chemical modi-fication [38,42], such as graphitic N, 4-nitrogen di-vacancy (4ND), 3-nitrogen vacancy (3NV), and pyrrolic nitrogen doping. We calculated the formation energies to check the thermodynamic stability of each N-GNR system considered. Adsorption energies (E_a) of sodium on these GNRs were then calculated to understand the effects of the edge, as well as the nitrogen-doped defects on adsorption. The electronic structure of the Na-GNR system was also investigated in order to identify the adsorption mechanism of so-dium. In addition, to check the diffusion behavior of sodium, diffusion energy barriers (ΔE_b) were calculated by means of the nudge elastic band (NEB) method.

2. Computational methods

All calculations presented here were performed by means of the Vienna Ab Initio Simulation Package (VASP) [43,44] using the projector augmented wave (PAW) method [45]. For electron ex-change and correlation terms, we employed a generalized gradient approximation (GGA) of the Perdew–Burke–Ernzerhof (PBE) functional [46] including spin polarization. The PBE functional has been successfully used for carbon-based systems [47–52]. To accurately describe the interactions between the sodium atoms and the GNR substrates, we considered dipole and dispersion correc-tions. In the energy and electronic property calculations, k-point samplings for the Brillouin zone were performed using the $2 \times 3 \times 1$ Monkhorst-Pack k-point mesh [53]. The unit cell size was 34.900 Å × 14.760 Å × 10.000 Å, and the energy cut-off was set at 500 eV. To avoid direct interaction between the original structure and its self-image, periodic boundary conditions (PBC) were

applied, with the vacuum separation distance set to 15 Å and 10 Å along the x- and z-directions, respectively. The atomic positions were optimized until the energy change was less than 1×10^{-6} eV per cell and the force on each atom was less than 0.01 eV Å^{-1}. The width of the zigzag GNR was classified by the number of zigzag chains across the nanoribbon. We considered a zigzag GNR with a width of 8 chains. Both edges were terminated with 12 hydrogen atoms [34], and this material was referred to as "pristine-GNR" (Fig. 1(a)). We selected four different nitrogen-doping models (graphitic N, 4ND, 3NV, and pyrrolic). The graphitic N-GNR struc-ture was obtained by substituting a specific single carbon atom in the pristine-GNR edge with one nitrogen atom, as depicted in Fig. 1(b). The 4ND-GNR structure was constructed by removing a C–C bond and replacing the four nearest neighbor carbon atoms with nitrogen atoms to create a di-vacancy defect, as depicted in Fig. 2(a). Similarly, the 3NV-GNR structure was obtained by substituting three carbon atoms with nitrogen atoms to create a
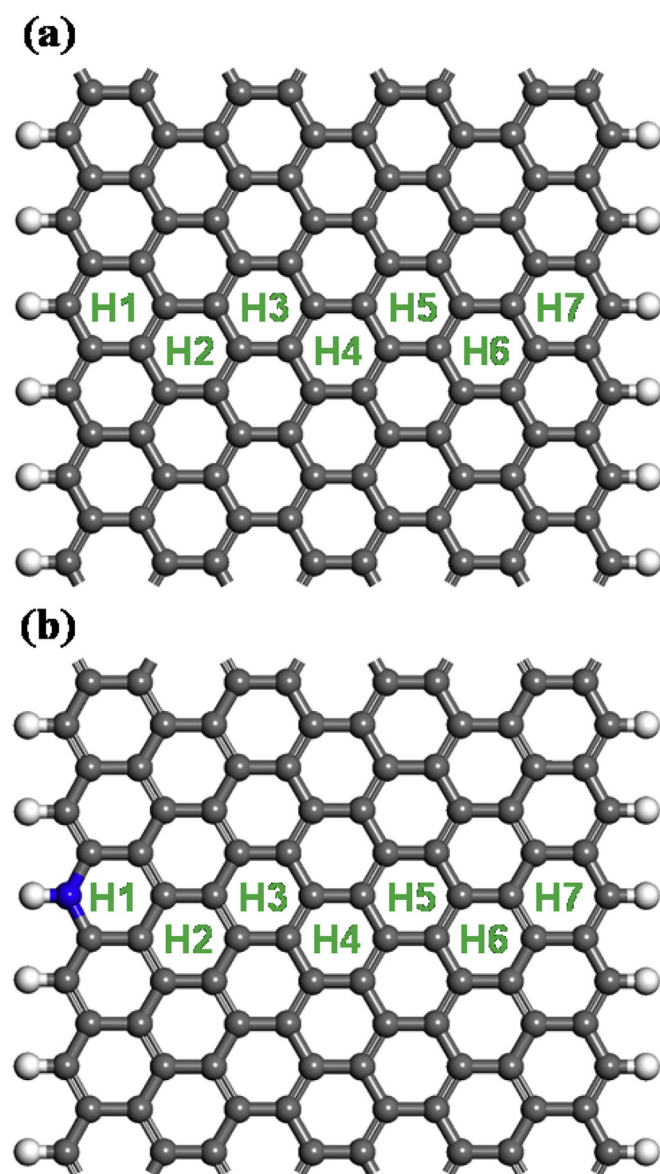

Fig. 1. Sodium adsorption on non-defective GNRs. A schematic structure and sodium adsorption sites for (a) pristine-GNR and (b) graphitic N-GNR. Grey, white, and blue spheres represent carbon, hydrogen, and nitrogen atoms, respectively. (A colour version of this figure can be viewed online.)