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Is borophene a suitable anode material for sodium ion battery?

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ABSTRACT

2D Boron is an atomically thin layer of boron with both light weight and metallicity, two kinds of potential structures are proposed, namely, a close-packed triangular B layer(denoted $B_{\triangle}$ hereafter) and a hexagonal voids or vacancies (○) in B layer(denoted $B_{○}$ hereafter) (Evgeni S. et al. Nano Lett. 2012, 12, 2441−2445). Here, we use first-principles calculations to investigate the potential of borophene as an anode material for sodium-ion batteries. It is found that borophene has an adsorption energy to sodium atoms of −1.448 eV for all boron atoms in the plane ($B_{○}$) and −1.731 eV for $\mathbf{B_{\Delta}}$. The fully sodiated phase of borophene is $Na_{0.083}B$ and $Na_{0.1}B$ for $\mathbf{B_{\Delta}}$ and $B_{○}$, respectively, which corresponds to a theoretical specific capacity of 248 mAh g^{-1} (496 mAh g^{-1} for two sides) for $\mathbf{B_{\Delta}}$ and 298 mAh g^{-1} (596 mAh g^{-1} for two sides) for $B_{○}$. The energy barrier along the furrow of corrugated borophene is only 12 meV for $\mathbf{B_{\Delta}}$, which suggests that sodium diffusion on borophene can be extremely fast for $\mathbf{B_{\Delta}}$. In addition, a strong directional anisotropy is observed for sodium diffusion with a 352.5 meV barrier perpendicular to the furrow of $\mathbf{B_{\Delta}}$. Finally, both exhibit metallic characteristics during the entire sodiation process, which indicates that the material has excellent electronic conductivity. The findings in this work suggest that as an anode material for sodium-ion batteries, borophene can drastically boost the energy and power density of batteries.

1. Introduction

With the rapid development of consumer electronics, such as mobile devices and electric vehicles, rechargeable batteries that have a high capacity and rate capability have attracted great attention in both academia and industry. The lithium ion battery (LIB), one of the most widely studied rechargeable batteries, plays a critical role in next-generation energy technology because of its advantages of battery capacity and energy efficiency [1]. The growing interest in LIBs has significantly promoted the development of electrode materials. Despite the wide-spread use of Li-ion cells, batteries based on alternative carrier ions, such as sodium ions, can be more suitable for large-scale energy storage systems. Although the higher gravimetric capacity of Li-ion cells is critical for portable applications, the relative abundance and low cost of Na-ion batteries now make them an attractive alternative for grid storage. Recently, new electrodes using two-dimensional (2D) nanomaterials have been widely explored. In particular, graphene, which is the most well studied 2D material, exhibits a unique capacity in LIBs because of its high charge carrier mobility, large surface area and broad electrochemical window [2]. In recent years, many studies have proven that graphene can be used as both anode and cathode materials with great success. Molybdenum disulfide (MoS_2), which is another typical layered material, has also been demonstrated to be an ideal anode material for Na batteries and exhibits a high reversible sodium storage capacity and superior rate capability [3]. Substantial research efforts have been invested during previous decades to produce electrode materials for sodium batteries that will enable facile intercalation of Na ions at suitable potentials [4]. SIB and LIB have identical important problems regarding their electrolytes, cathode and anode. However, a full SIB does not use elemental sodium as the negative electrode; it is composed of hard carbon or metal oxide intercalation compounds. The negative electrode is one of the most urgent problems to solve because the typical graphite carbons used in LIBs do not intercalate

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Na^+ ions. The discovery of good anode materials is a major challenge. Finding good anode materials is urgent for the improvement of Na-ion batteries [5].

Recently, a new 2D material has been successfully synthesized on silver surfaces under ultrahigh-vacuum conditions using borophene as a star material [6]. Borophene is a crystalline 2D boron sheet on silver surfaces under ultrahigh-vacuum conditions. Unlike bulk boron allotropes [7], borophene shows consistent metallic characteristics with the predictions of significant anisotropy [8,9]. However, several structures have been theoretically proposed. Mannix et al. suggest that the borophene monolayer consists of B atoms stacked in puckered sub planes. Each B atom is bonded with two adjacent atoms in the same plane and one B atom from a different plane [6]. However, several other researchers noted that a new unit cell of borophene, in which all B atoms are in one plane, is metallic, flat and composed of mixtures of hexagons and triangles. Various 2D boron sheets can be described as $B_{1-x}V_x$ pseudoalloys, where V is the vacancy in a parent triangular lattice (for example, $x = 1/3$ corresponds to a hexagonal sheet), and these sheets can be obtained by removing atoms from a flat triangular sheet. Most recently, Liu et al. [10] reported that two-dimensional boron with different structures might be superconductors, but some proposed structures might be thermally unstable. As a new member of the 2D material family, an interesting question is: is monolayer borophene a promising anode material for use in ion batteries? [11,12] To answer this question, a detailed study on the Na adsorption and diffusion process in monolayer borophene is indispensable.

Here, we report our theoretical studies of the adsorption and diffusion of Na atom in two types of borophene: all of the boron atoms are in a plane, which is denoted as $B_\bigcirc$ and a buckled structure with the boron atoms distributed in two layers, which is denoted as $\mathbf{B_\Delta}$. Our studies show that Na ions can intercalate into $B_\bigcirc$ atoms with a binding energy of approximately −1.488 eV, which indicates a strong interaction between two elements, whereas for $\mathbf{B_\Delta}$, the binding energy is approximately −1.731 eV. Na is present in the cationic state, the $2s^1$ electrons of which are completely transferred to borophene. Modulated by its puckered structure, Na diffusion in borophene shows strong directional anisotropy; along the **F3** direction, the migration barrier is only 0.06 eV for Na on the borophene surface, whereas in the **F1** direction, the barrier is 0.198 eV for $\mathbf{B_\Delta}$. For the $B_\bigcirc$ sheet, the migration barrier is 0.300 eV. The extremely small energy barrier along the F3 direction in B_Δ guarantees rapid diffusion of Na atoms with an estimated diffusivity of 10^2~10^4 times faster than that of other 2D anode candidates, such as graphene and MoS2. Moreover, the estimated average voltage of the Na intercalation into borophene is 1.33 V and 1.45 V for the $B_\bigcirc$ and B_Δ structures, respectively, which is higher than that other types of commercial anode materials. Based on our present findings, borophene are expected to be used in promising SIB electrodes that have a high rate capacity.

2. Computational details

All of the calculations were performed using the Vienna ab initio simulation package (VASP) [13]. Projector-augmented-wave (PAW) potentials were used to consider the electron-ion interactions, whereas the electron exchange-correlation interactions were treated using the Perdew–Burke–Ernzerhof exchange correlation functional in the scheme of generalized gradient approximation (GGA) [14]. A plane wave cutoff of 500 eV was used for all calculations. Because the interaction between the ion atoms and substrate belongs to the vdW interaction, the effect of van der Waals

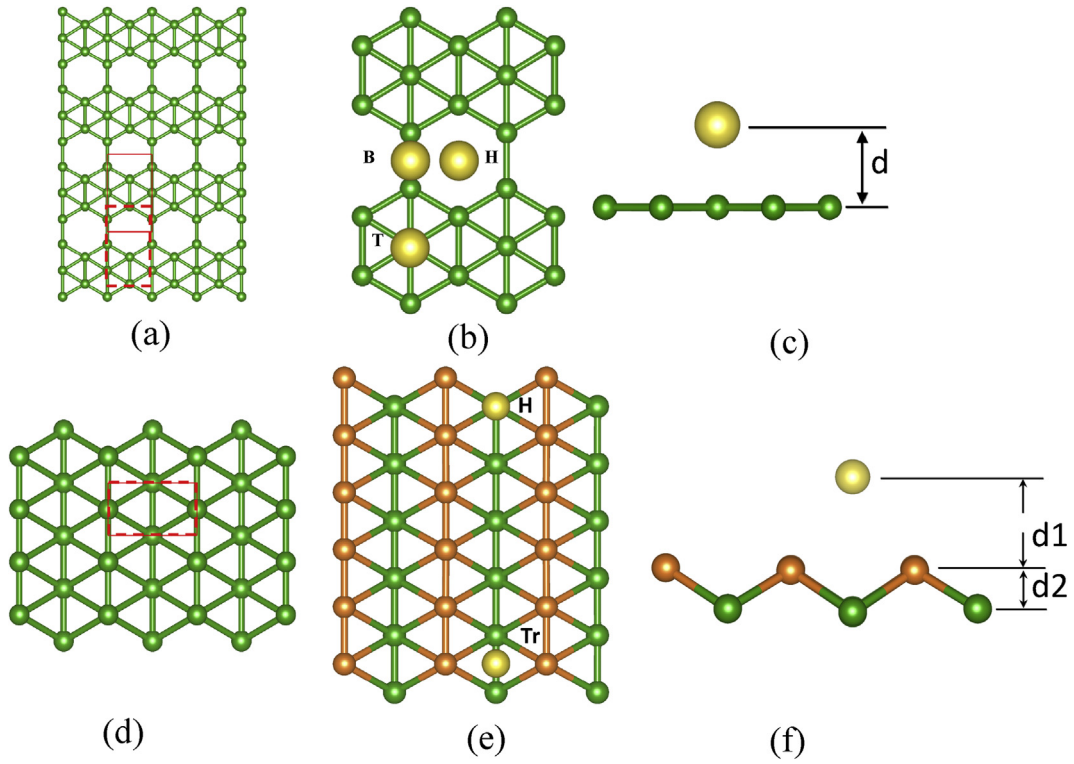

Fig. 1. (a) Atom structure of $\mathbf{B_\bigcirc}$; the red region is the primitive cell; (b) possible absorption position in $\mathbf{B_\bigcirc}$ (top view); (c) side view of $\mathbf{B_\bigcirc}$, where **B** denotes the bridge site, **H** denotes the hollow site and **T** denotes the top site; (d) atom structure of $\mathbf{B_\Delta}$; the red region is the primitive cell; (e) a possible absorption position in $\mathbf{B_\Delta}$ (top view); (f) side view of $\mathbf{B_\Delta}$, where **Tr** denotes the center of two hollow boron atoms, **H** denotes the hollow site and **T** denotes the top site. In this figure, the green atom denotes the boron atom. In figures (e) and (f), the orange and yellow atoms denote the boron atom in the hollow sites and the sodium atom, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)