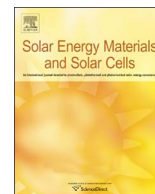




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Phosphorene as a promising anode material for (Li/Na/Mg)-ion batteries: A first-principle study

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ABSTRACT

The increasing interest in future energy storage technologies has generated the urgent need for alternative rechargeable batteries. Density functional theory calculations (DFT), including van der Waals interactions, have been carried out in order to evaluate the prospects of a novel 2D material named phosphorene as an anode material for Li, Na and Mg-ion batteries. We determined the binding energies and diffusion barriers on a phosphorene monolayer. Our results show that at low coverage, the adatoms bind strongly on phosphorene with a significant charge transfer. After lithiation of phosphorene, a semiconductor-to-conductor transition is observed. We also found that a single adatom diffuses more easily along the open channel (zigzag direction) than across channels (armchair direction). For example, our result for the diffusion of Na on phosphorene shows a low diffusion barrier value of 0.04 eV along the zigzag direction against 0.30 eV along the armchair direction. The findings of our study suggest that phosphorene could make a good candidate as an anode material for different rechargeable batteries.

1. Introduction

Since its discovery in 2004, graphene [1] has received enormous interest and drawn the attention of researchers around the world due to its extraordinary physical properties [2–5] that are found to be absent in its bulk counterpart, graphite, and which has opened the way into examining its potential in a variety of applications such as in solar cells [6], Li-ion batteries (LIBs) as both cathode and anode material [7,8], etc. Besides graphene, numerous 2D materials have gained the consideration of researchers like germanene [9,10], silicene [10,11] or borophene [12,13] and recently a new material named phosphorene joined the family of 2D nanostructures and was mechanically isolated [14–16] from its bulk parent black phosphorus (the most stable allotrope of phosphorus firstly discovered by Bridgman in 1914 [17]), receiving immediate interest. Unlike flat graphene, a stable phosphorene layer favors a puckered structure due to the sp^3 hybridization where its P atoms are arranged in a hexagonal form and exhibits a semi-conducting behavior with an intrinsic direct band gap that can be modulated by increasing the number of stacked layers [18]. The unique

anisotropic structure of phosphorene, presented in the armchair and zigzag orientations, is absent in graphene and seems to strongly influence the transport and optical properties of phosphorene [19,20]. This unique structural anisotropy may also lead to other intriguing physical properties as our study discusses its impact on the diffusion behavior of different elements on the surface of phosphorene as an anode material for battery applications. In fact, the usage of 2D materials as anodes in batteries has been extensively explored for graphene [21–23] and 2D-MoS₂ [24–26] in LIBs showing high reversible lithium storage capacity. However, the weak binding energy and the high diffusion barriers in those 2D materials are disadvantageous and are still preventing their further integration in batteries [27,28]. On the other hand, it was demonstrated that black phosphorus is a good anode material for LIBs with a high capacity of 1279 mAh.g⁻¹ and an excellent cycle of life of 100 cycles [29]. In this regard, we suggest that the intriguing properties of phosphorene, including its high carrier mobility up to 1000 cm² V⁻¹ s⁻¹ [14], could be of benefit to its performance in a battery as an anode material as compared to its bulk counterpart. We have investigated in this work, using first-principles calculations based on density functional

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theory, the adsorption and diffusion of three different elements: Li, Na and Mg on phosphorene monolayer in order to evaluate the pertinence of phosphorene as an anode material for different rechargeable batteries.

2. Computational details

All calculations were performed within the framework of density functional theory (DFT), implemented in the Quantum-espreso package [30]. The generalized gradient approximation (GGA) in the form of the Perdew – Burke – Ernzerhof (PBE) functional and projector augmented wave (PAW) potentials [31] are used to take into account the electron-ion interactions. Effect of van der Waals (vdW) interaction is accounted for by using a dispersion-corrected DFT method (DFT-D method) [32]. A plane wave cutoff of 40 Ry was used for all the calculations. All atomic positions and lattice vectors were fully optimized to obtain the unstrained configuration using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) method. Atomic relaxation was performed with an energy convergence of 10^{-5} Ry and a force convergence of 10^{-4} Ry per Bohr. The phosphorene monolayer is modeled using a 1×2 supercell in order to investigate the adsorption and diffusion properties. A periodic boundary condition is applied and the size in the perpendicular direction to the phosphorene plane is large enough (larger than 15 Å) to avoid interactions induced by periodic images. K-point samplings of $4 \times 3 \times 1$ were used for the structure relaxation, while denser meshes of $16 \times 12 \times 1$ were used to calculate the density of states (DOS) and electronic properties.

3. Results and discussion

From our calculations, we found that the lattice parameters for a phosphorene monolayer are $a = 4.63$ Å, $b = 3.29$ Å and $\Delta c = 2.10$ Å (thickness of a single layer), in agreement with previous studies [33,34]. In order to explore the binding of the phosphorene surface with Li, Na and Mg we firstly started by placing a single adatom at four different adsorption sites as shown in Fig. 1: hollow (H), top (T) and bridge (B1 and B2) and found that the most stable configuration for the three elements is the H-site (similar to previous studies [35]), which is above the center of the triangle consisting of three phosphorus atoms in the surface. Those results are summarized in Table 1 by giving binding energies (E_b), vertical distances (h) alongside with the bond lengths of the nearest P atoms to the adsorbed atom at the H-site as illustrated in Fig. 2. From the calculations, we can observe that the binding energies of Li and Na are inversely proportional to the atomic radii where the highest absolute E_b values are found to be for Li. Therefore, we can tell that the general trend of the adsorption of the alkali adatoms (Li, Na, K, etc.) on phosphorene can be predicted through their atomic radii; where a small radius indicates a higher absolute binding energy and thus a strong attachment of the adatom to the surface of phosphorene while a larger radius indicates the opposite. While for Mg, it is surprisingly observed that its binding energy does not follow the same trend in regards of the atomic radii. In fact, Mg has the lowest values of E_b of them all, which is clearly in contrast with its atomic size as in comparison with Na. This particularity was discussed by Banerjee S. et al. [36] where it was found that the P-Mg interaction is responsible of reducing the polarizability of Mg and thus resulting in a weak binding energy. The summarized results in Table 1 are found to be in very good agreement with other reported studies where larger supercell models were used. For example, Weifeng Li et al. [37] found a value of 1.97 eV on the adsorption of Li at the H-site against 1.94 eV in our case. In addition, Vadym V. Kulish et al. [38] (1.59 eV against 1.56 eV in our work) and Wei Jin et al. [39] (1.09 eV against 0.93 eV in our work) found similar results as we did for Na and Mg, respectively. An analysis on the charge transfer between phosphorene and a single adatom in the hollow site has been carried out by the Bader charge package [40] showing a large charge transfer to the surface especially in the case of Li

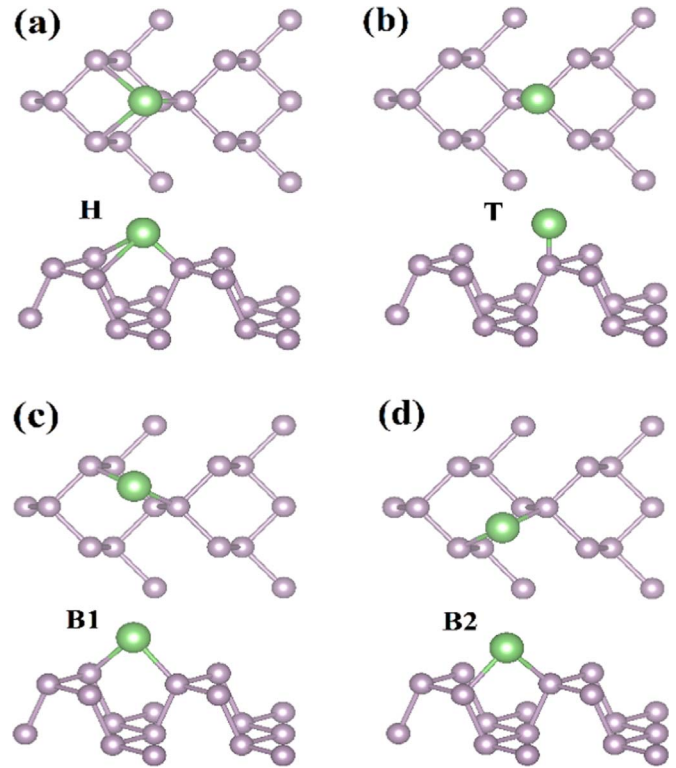


Fig. 1. Top and side views of Li adsorption on phosphorene surface in different adsorption sites (a) Hollow, (b) Top, (c) Bridge 1 and (d) Bridge 2. The purple and green spheres represent P and Li atoms, respectively.

Table 1

Absolute binding energies E_b at different adsorption sites, vertical distance (h) at the H-site and distance d_{P-A} between the adatoms and the nearest P atoms at the H-site.

atoms	$ E_b $ (eV)				h (Å)	d_{P-A} (Å)		
	H	T	B1	B2		P ₁ -A	P ₂ -A	P ₃ -A
Li	1.945	1.687	1.896	1.896	1.53	2.42	2.55	2.55
Na	1.568	1.032	1.499	1.499	2.34	2.89	3.01	3.01
Mg	0.931	0.930	0.924	0.924	2.10	2.73	2.90	2.90

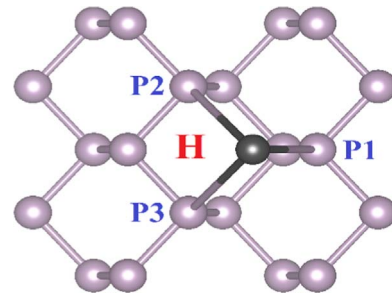


Fig. 2. Top view of the adsorption structure and bond lengths of an adatom on phosphorene at the H-site.

giving the value of 0.80 |e|, 0.53 and 0.68 |e| for Na and Mg respectively, which should be the reason for the strong binding energy. Furthermore, we gradually increased the number of the adsorbed atoms of the three elements on the surface of a 1×2 supercell of phosphorene (eight phosphorus atoms) in order to investigate the influence of the concentration of the adatoms on the surface. As a general trend, it is noticed from Fig. 3 that the adsorption energy keeps a negative value by increasing the adatoms concentration until reaching a value of $x = 1.0$ where both sides of phosphorene are fully covered with Li, Na or Mg, indicating that the maximum concentration of the adatoms is $x = 1.0$.

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