

# Density functional theory study on Na, K metals and Na<sup>+</sup>, K<sup>+</sup> metallic ions adsorption on Nitrogen and Boron doped graphene for water desalination

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**ABSTRACT**— Doping graphene with foreign elements is an effective way to tune its physicochemical properties, thus paving a new way to enhance its practical application. Nitrogen (N) and Boron (B) are one of the most frequently used dopants, especially in water purification, desalination, and electrocatalysis. Despite its importance, the interaction between N and B-doped graphene and alkaline metals (Na and K) and their ions (Na<sup>+</sup> and K<sup>+</sup>) that must be captured to purify the water remains ambiguously. In this work, we use the density functional theory with the dispersion correction to systematically study the interaction of graphene doped with the graphitic N and B-structures with Na, K, Na<sup>+</sup> and K<sup>+</sup>. Alkali metals and ions interact repulsively with the N site; whereas they interact attractively with the B site. Energetically, Na and K tend to desorb on N-doped graphene while B-doped graphene further strengthens the Na and K adsorption. Electronic structure analysis implies that the adsorbates tend to donate an electron to the graphene substrate. The origin leading to the different adsorption behavior upon N and B doping is attributed to the fact that a lower perturbation of the  $\pi$ -electrons of graphene strengthens the alkali metals-graphene interaction. B doping or p-typed doping has great implications for doped graphene's electronic properties and the enhanced alkaline capture ability, thus would be helpful in desalination for water purification.

**KEYWORDS:** Graphene Water Desalination Density Functional Theory Calculation Cation Capture Membrane

## 1. INTRODUCTION

In industrial application of water purification, desalination, electrocatalysis, graphene and its functional derivatives are promising candidates due to their frictionless properties and high fluid permeability [1], [2]. The water and cations-graphene interface has been intensively investigated by experimental and computational studies [3- 10]. In practice, the interface can be studied by measuring static water contact angles (WCA), and different values of WCA are reported for water droplets on graphene [1- 4]. The discrepancy of the reported data originates from several factors, *i.e.* number of graphene layers, underlying substrate, effects of doping. Hong et. al. indicates underlying substrate or physical doping by applying a voltage which can unambiguously affect the hydrophilicity of graphene and later confirmed by [2- 4]. Both studies claimed that the origin of doping-induced wettability of graphene is due to the shift of the Dirac point away from the Fermi level of graphene. To provide an atomistic understanding, density functional theory (DFT) calculations have been widely employed to investigate the adsorption of water on graphene [6- 10]. Nevertheless, the different

computational parameters result in a difference in binding energy ( $E_b$ ) of a water monomer on graphene, which is mainly due to the lack of the van der Waals interaction treatment. By using the conventional GGA-PBE method, the  $E_b$  is 30 meV, whereas vdW-DF2<sup>C09x</sup> result [6] is 80 meV, which is consistent with the quantum chemistry method [8], with the random-phase approximation (RPA) (98 meV) and the diffusion Monte Carlo (DMC) method (100 meV). The variance between the GGA-PBE and vdW inclusive methods is 50 meV; however, [8] found that a change of  $E_b$  of H<sub>2</sub>O on graphene by 50 meV results in a change of graphene surface from hydrophobic to hydrophilic. This highlights the importance of using van der Waals inclusive DFT method to study water and cations - graphene interaction [7], [8].

Regarding to water desalination, graphene or graphene oxide monolayer are practically considered owing to the formation of a dense and delocalized electron cloud from the  $\pi$ -orbitals of graphene which have orders of magnitude higher than permeability and selective with different size, density, and functionality [11]. However, the industrial challenge for monolayer is to scale-up at a high efficiency and enhance capability of capture cations. One solution for those challenges is the fabrication of desalination membranes based on stacked of graphene oxide and/or functionalized graphenes by doping [12]. By making stacked functionalized graphene (*i.e.* a membrane), it shows not only extraordinary chemical and thermal stabilities but also flexibility and solution processibility [12]. N-doped graphene as a membrane to remove toxic organic compounds, contaminations, and cations (even heavy metals) from water was synthesized and investigated initially [13], [14]. In theoretical calculation of a non-equilibrium molecular dynamics study in electric field assisted desalination of water using B- and N-doped graphenes, it shows ion separation increase whereas ion hydration decreases under increasing field strength [15]. From the microscopic viewpoint, we are interested in understanding the inter- action between cations with functionalized graphenes (B- and N-doped graphenes).

In this paper, we report the Na, Na<sup>+</sup>, K and K<sup>+</sup> adsorption on graphitic N- and B-doped graphene using the vdW-DF method. First, we revisited the water on pristine graphene to validate our DFT results with the other state-of-the-art computational works. The structural properties and adsorption strength of water adsorbed on graphitic N-, B- doped graphene are then elucidated. The graphitic type doping by replacing C atoms with N or B atoms is more attractive because it exhibits interesting properties for fuel cells, Li-ion batteries, photocatalysis, and electrochemical sensing [16]. Moreover, graphitic doping also has higher stability than other doping configurations [17], [18]. In this context, we consider the single substitution of dopants (N, B) [19- 21]. Finally, the origin of cations adsorption is discussed based on electronic structure analysis.

## 2. Computational details

We performed all DFT calculations within the periodic supercell approach using the Quantum ESPRESSO package [22]. We used the standard Perdew-Burke-Ernzheof (PBE) exchange-correlation functional [23] with the pair-wise dispersion correction for the long-range van der Waals interaction proposed by Grimme [24] (PBE+D2). Core electrons are represented by optimized norm-conserving Vanderbilt pseudopotentials with the ONCVSP library generated by PBE [25]. The valence states were expanded in plane-wave basis set truncated with cut-off energies of 90 and 360 Ry for wave functions and augmented charge densities, respectively. All atoms are optimized with the residual force threshold of  $< 0.02$  eV/Å. The  $3 \times 3 \times 1$  k-points mesh is used for Brillouin-zone sampling [26] in structural optimizations. To accurately calculate the density of states (DOS), the  $\Gamma$ -centered  $21 \times 21 \times 1$  k-points mesh is employed.

Pristine, N-, and B-doped graphene is modeled by  $p(4 \times 4)$  supercell separated by a vacuum region with a length of 18 Å in the surface normal direction. To accurate modelling the alkali metal and ions - graphene interfaces, the solvent effect should be considered [27]. However, due to its huge computational requirement, we do not consider the solvation effect and focus on the interaction between graphene and alkali metals in the

vacuum condition. To discuss the stability of doping graphene, formation energy ( $E_{\text{form}}$ ) is calculated as,

$$E_{\text{form}}(\text{A}) = E_{\text{tot}}(\text{A}) - N_i E_{\text{tot}}(\text{M}_i) \quad (1)$$

where  $E_{\text{tot}}(\text{A})$  is total energy of the system we considered. Here,  $N_i$  and  $E_{\text{tot}}(\text{M}_i)$  denote the number of atoms and total energy of the M component ( $\text{M} = \text{C}, \text{B}, \text{N}, \text{K}, \text{and Na}$ ), respectively. Total energies of the C, B, N, K, and Na are estimated from the graphene,  $\alpha\text{-B}$ , solid-phase  $\text{N}_2$ , fcc-K, and fcc-Na, respectively, taken from Material Projects.

To estimate the binding strength of alkaline metals (M) with graphene surfaces, adsorption energy ( $E_{\text{ads}}$ ) is calculated by

$$E_{\text{ads}}(\text{M/gra}) = E_{\text{tot}}(\text{M/gra}) - E_{\text{tot}}(\text{gra}) - E_{\text{tot}}^{\text{iso}}(\text{M}) \quad (2)$$

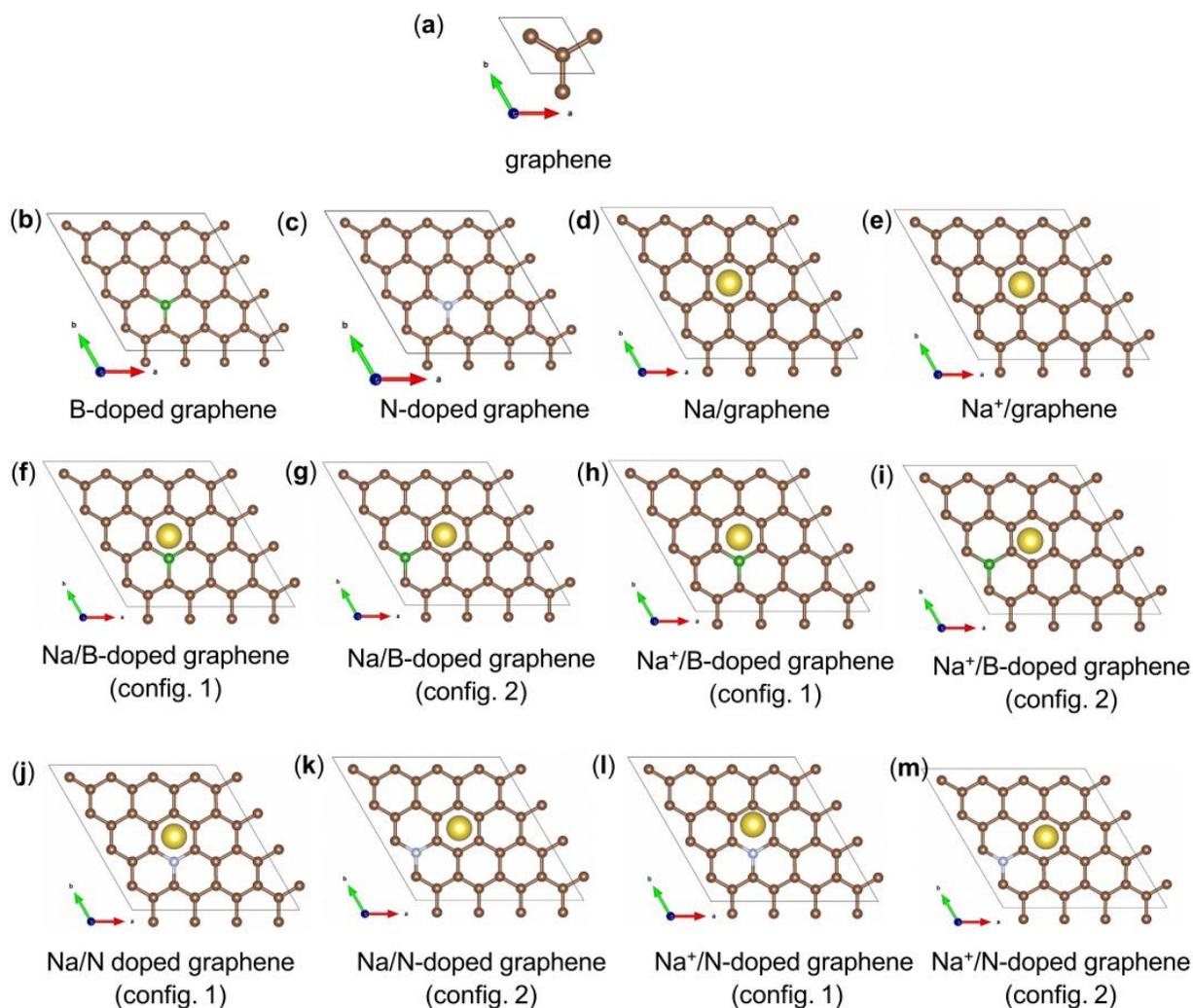
Here  $E_{\text{tot}}(\text{M/gra})$ ,  $E_{\text{tot}}(\text{gra})$ , and  $E_{\text{tot}}^{\text{iso}}(\text{M})$  are total energies of M adsorbed graphene surface, clean surface, and isolated M ( $\text{M} = \text{Na}$  and  $\text{K}$ ), respectively. With our definition, more negative adsorption energy implies stronger adsorbate - surface interaction.

### 3. Results and discussion

#### 3.1 Adsorption geometry of Na and K metals and ions on graphene

We begin with the adsorption of Na and K on pristine graphene. The hollow site is the most stable site for both cases, with the vertical bond distance of 2.318 and 2.616 Å for Na and K adsorbed on pristine graphene, respectively. Our finding is consistent with previous results [28]. Estimated adsorption energies for Na and K/graphene are -0.972 and -1.213 eV, respectively, indicating that K interacts with pristine graphene stronger than Na. To simulate the  $\text{Na}^+$  and  $\text{K}^+$ , we perform calculations with a deficit electron, starting from neutral geometries. From Table 1, upon the removal of an electron, vertical binding distance increases for both cases, indicating that metallic ions have more repulsive interactions with graphene surfaces.

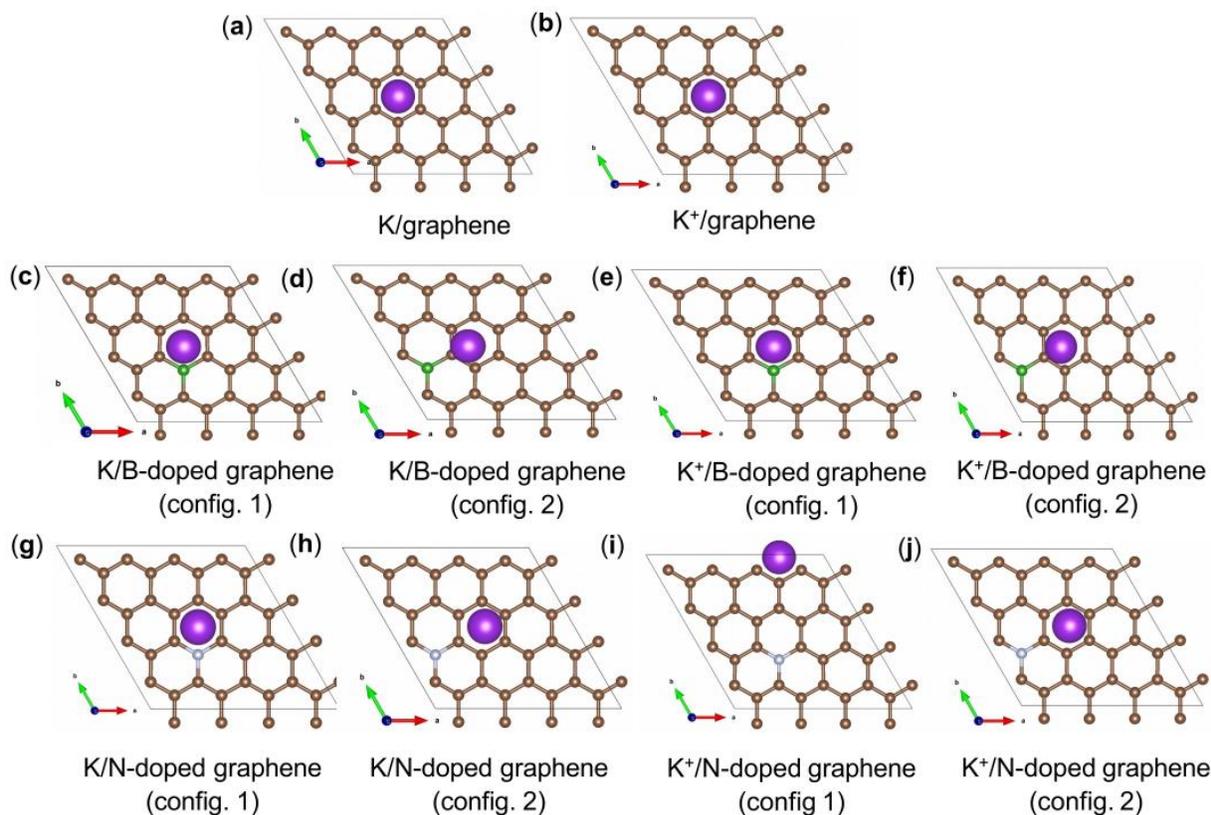
For Na adsorbed on N-doped graphene, we find that Na interacts repulsively with the N site. From Table 1, the calculated  $E_{\text{ads}}$ 's are 0.547 and 0.459 eV for config. 1 and 2, respectively, implying that config. 2 is more stable than config. 1. From positive adsorption energies for both configurations, Na atom tends to desorb near N sites.



**Figure 1:** Atomic models of Na and Na<sup>+</sup> adsorbed on pristine, N-doped, B-doped graphene. Color codes: grey (C), green (B), blue (N), yellow (Na).

In contrast, we find that upon the B doping, the  $E_{\text{ads}}$ 's further decreases to 1.126 eV for config.1, indicating that B doping strengthens Na-graphene interaction. We find that Na interacts attractively with B site as a result from a more negative  $E_{\text{ads}}$  of config. 1 compared to that of config. 2. Moreover, the vertical binding distance is further decreased in the case of Na adsorbed on B-doped graphene comparing to pristine and N-doped graphene. Upon the removal of an electron, Na<sup>+</sup> also interact repulsively with N site but attractively with B site.

For K adsorbed graphene, a similar trend also can be realized: K also interacts repulsively (attractively) with N (B) site. From Table 1, N doping results in the desorption of K atom while B doping strengthens K-graphene interaction by 0.372 eV. Compared to the adsorption geometry, one can see that binding distance in the case of K is larger than that of Na. It can be explained by larger atom radius of K.



**Figure 2:** Atomic models of K and K<sup>+</sup> adsorbed on pristine, N-doped, B- doped graphene. Color codes: grey (C), green (B), blue (N), yellow (Na).

From our result, one can see that B doping results in an enhancement of alkaline metals - graphene interaction. In contrast, N doping leads to the desorption of alkaline metals. This phenomenon is opposite with the enhancement of water - graphene interaction upon the N and B doping [29]. We expect that tailoring graphene by B dopants is beneficial for an enhancement of the alkaline metals capture, which could be used in desalination or water purification.

**Table 1:** Formation energies ( $E_{form}$ ), the vertical binding distance ( $d$ ) from the adsorbate to the graphene surface, adsorption energy ( $E_{ads}$ ), and effective Löwdin charge ( $\Delta q$ ) of Na, K adsorbed on pristine, N-doped, B- doped graphene. The effective Löwdin charge is estimated by  $\Delta q = Z - q$ , where  $q$  and  $Z$  are the total Löwdin population and valance electron of the adsorbate ( $Z = 9e$ )

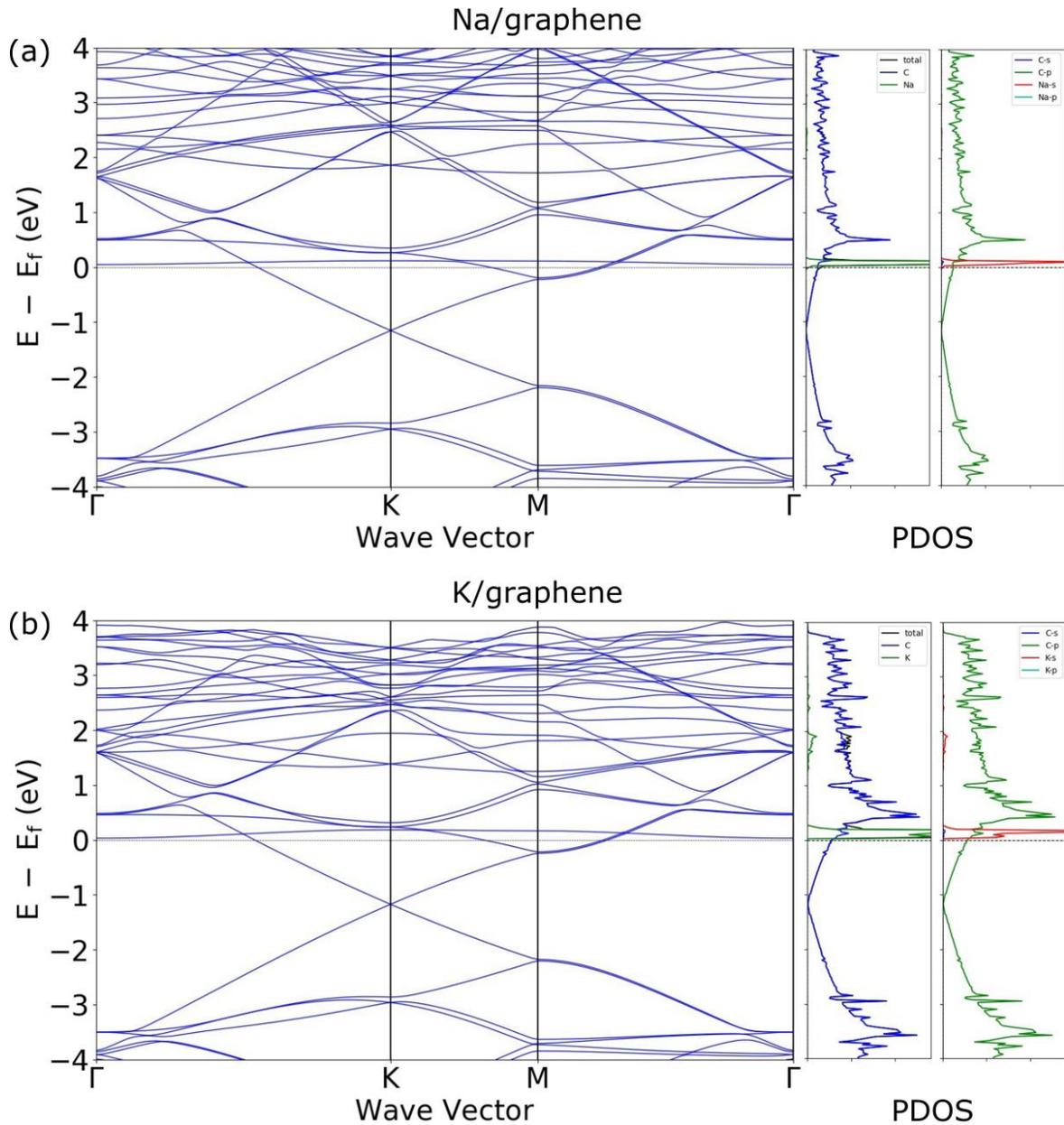
System	config.	$E_{\text{form}}$ (eV)	$d$ (Å)	$E_{\text{ads}}$ (eV)	$\Delta q$ (e)
Na/graphene		-1.520	2.318	-0.972	0.96
Na <sup>+</sup> /graphene		1.953	2.371		
Na/N-doped graphene	1	-0.182	2.309	0.547	0.68
	2	-0.269	2.310	0.459	0.78
Na <sup>+</sup> /N-doped graphene	1	3.031	2.411		
	2	2.878	2.384		
Na/B-doped graphene	1	-1.782	2.158	-1.126	0.93
	2	-1.584	2.161	-0.928	0.94
Na <sup>+</sup> /B-doped graphene	1	2.790	2.367		
	2	2.919	2.375		
K/graphene		-2.003	2.626	-1.213	0.97
K <sup>+</sup> /graphene		1.107	2.806		
K/N-doped graphene	1	-0.694	2.853	0.035	0.87
	2	-0.764	2.599	-0.035	0.92
K <sup>+</sup> /N-doped graphene	1	1.958	2.794		
	2	2.027	2.801		
K/B-doped graphene	1	-2.240	2.497	-1.584	0.96
	2	-2.121	2.496	-1.584	0.96
K <sup>+</sup> /B-doped graphene	1	2.007	2.803		
	2	2.083	2.815		

### 3.2 Electronic structure properties

We then analyze the electronic structure properties of Na and K adsorbed on graphene. From Löwdin population analysis in Table 1, one find that both Na and K is positively charged upon the adsorption on all graphene surfaces. It indicates that the electron is transferred from Na atom to graphene surfaces. For Na adsorption on pristine and B doped graphene,  $\Delta q$  of the Na atom are almost similar (0.96, 0.94 for Na/graphene and Na/B-doped graphene config. 1, respectively). All the charge value is nearly 1, indicating that even though the system is neutral, the Na atom tends to become Na<sup>+</sup> due to the electron exchange with the substrate. In contrast, on N doped graphene,  $\Delta q$  of the Na atom is 0.78 e for config 2, which is less than other cases, thus a less electron exchange with the surfaces upon the N doping appears. As a result, the interaction between Na and N-doped graphene is significantly destabilized, and Na interacts repulsively with the N site.

Similar trends for the electron exchange appears in the case of the K adsorption. However,  $\Delta q$ 's of K/N-doped graphene are 0.87 and 0.92 e for config. 1 and 2, respectively. These are larger than that of Na/N-doped graphene (0.68 and 0.78 e), indicating K atom can interact stronger with N-doped graphene compared to Na atom. Overall, we always find that the K atom tend to have larger electron transfer with graphene substrates comparing to the Na atom for all cases. Therefore, stronger K-graphene interactions over Na-graphene ones can be explained by the better electron exchange with the surfaces of the K atom. Energy band structures and atomic orbital projected density of states of Na/graphene and K/graphene systems are shown on Figure 3. Upon the Na and K adsorption on pristine graphene, the Dirac cone of graphene is downshifted below Fermi level, corroborating that the electron is donated from adsorbate to substrate. The *s* orbitals of Na and K becomes unoccupied because the PDOS's of 3*s* and 4*s* locate above Fermi levels for Na and K, respectively. Even though the electronic structures, namely energy band dispersion and PDOS of Na/graphene and K/graphene are quite similar,  $\Delta q$  of K is 0.97 e, which is slightly larger one of Na (0.96 e), indicating that

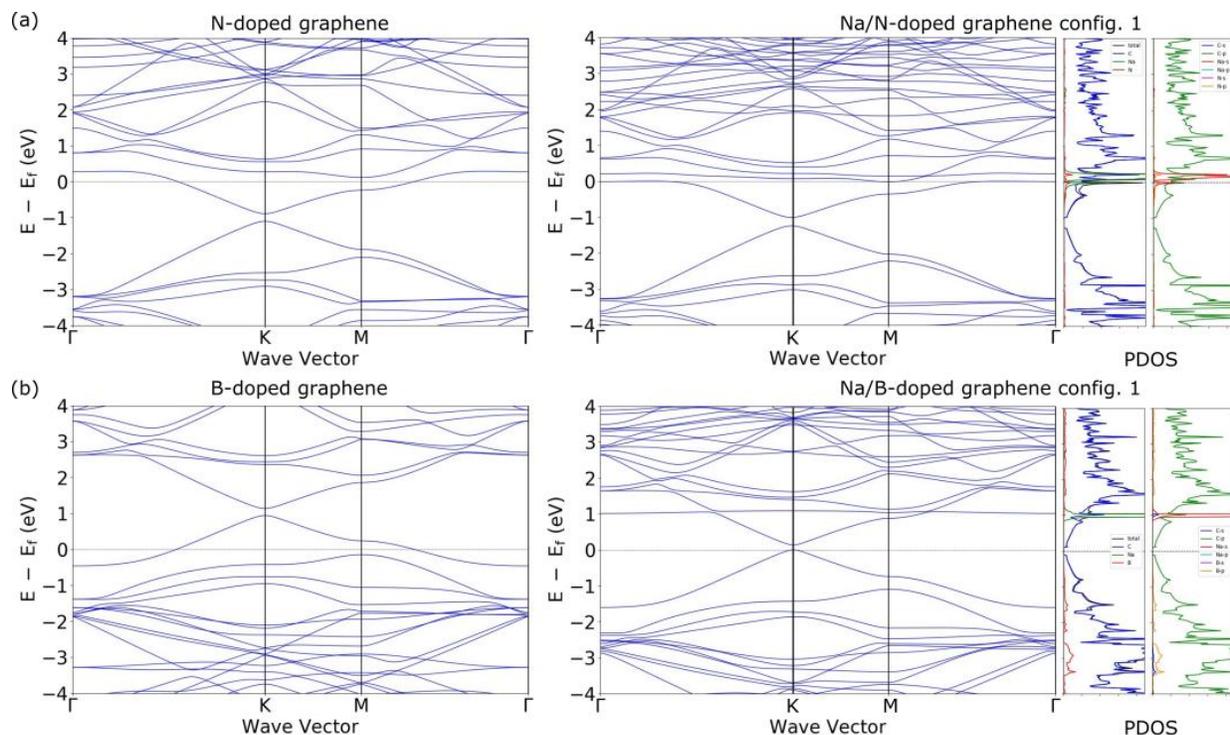
slight larger electron exchange appears for K, enhancing K-graphene interaction.



**Figure 3:** Energy band structures and atomic orbital projected density of states of Na (a) and K (b) adsorbed on graphene.

Energy band structures and atomic orbital projected density of states of Na adsorbed on N- and B- doped graphene systems are shown on Figure 4. First, from energy band structures, one can see that upon the N (B) doping, the Dirac cone is downshifted (upshifted) to below (above) Fermi levels. Therefore, N-doped and B-doped graphene are *n*- and *p*-type doping, respectively. Upon the Na adsorption, an electron is donated from Na to the doped graphene substrate, affecting the electronic structure of the doped graphene. As discussed in the Na adsorption on pristine, the electron transfer downshifts the energy band structure of graphene, acting like a *n*-type doping. From Figure 4 (a), the Dirac cones of graphene does not alter upon the Na adsorption, indicating that N-doped graphene interact repulsively with Na to decrease the electron donation. In contrast, the Dirac cones of graphene downshifted to Fermi levels upon the Na adsorption on B doped graphene (Figure

4 (b)), thus B-doped graphene tend to receive the electron donation from Na. As a result, the Na/B-doped graphene interaction is appealing, and  $E_{\text{ads}}$  of Na/B-doped graphene is more negative than one of Na/graphene. Our results suggest that the lower perturbation of the  $\pi$ -electrons of graphene strengthens the Na - graphene interaction [19].



**Figure 4:** Energy band structures and atomic orbital projected density of states of Na adsorbed on N-doped (a) and B-doped (b) graphene.

#### 4. Conclusions

We have investigated the interaction between Na, K metals as well as  $\text{Na}^+$ ,  $\text{K}^+$  metallic ions adsorption on Nitrogen and Boron doped graphene using dispersion-corrected DFT calculations. We have found that Na and K interact repulsively (attractively) with N- (B-) doped graphenes. Energetically, Na and K tends to desorb on N-doped graphene while B-doped graphene further strengthens the Na and K adsorption. Electronic structure analysis indicates that the alkaline metals tends to donate an electron to graphene surfaces. Moreover, a lower altering the  $\pi$ -electrons of graphene strengthens the alkaline metals - graphene interaction. Our result suggests that by B-doping or p-type doping can enhance the ability of alkaline metal capture due to the enhancement of alkaline metal- graphene interaction, which maybe helpful in desalination.

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