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# Hydrogen storage in Li, Na and Ca decorated and defective borophene: a first principles study

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Recently synthesized two-dimensional (2D) borophene possesses unique structural, mechanical, electrical and optical properties. Herein, we present a comprehensive study of H<sub>2</sub> storage in alkali metal decorated and defect containing 2D borophene using density functional theory calculations. While the adsorption of H<sub>2</sub> over pristine borophene was found to be weak with a binding energy of  $-0.045$  eV per H<sub>2</sub>, metal decoration and point defects enhanced the adsorption strength significantly. Interestingly, the magnitudes of binding energy for a single H<sub>2</sub> molecule over Li, Na and Ca decorated borophene were found to increase up to  $-0.36$ ,  $-0.34$ , and  $-0.12$  eV per H<sub>2</sub>, respectively. On the other hand, while the binding energy of one H<sub>2</sub> molecule over the borophene substrate containing a single vacancy (SV) was only  $-0.063$  eV per H<sub>2</sub>, similar to that of phosphorene, the binding energy increased to an enormous  $-0.69$  eV per H<sub>2</sub> over borophene containing a double vacancy (DV). To gain further insight into the H<sub>2</sub> adsorption process and identify sources of charge transfer, differential charge densities and projected density of states were calculated. Significant charge accumulation and depletion caused strong polarization of the H<sub>2</sub> molecules. Finally, Na, Li and Ca decorated borophene yielded the gravimetric densities 9.0%, 6.8%, and 7.6%, respectively. The gravimetric density of the borophene containing a DV was found to be the highest, a staggering 9.2%, owing to increased interactions between DV borophene and the H<sub>2</sub> molecules. These results suggest that borophene can be an effective substrate for H<sub>2</sub> storage by carefully engineering it with metal decoration and point defects.

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## 1. Introduction

Borophene, a two-dimensional (2D) form of boron, offers intriguing structural, electronic, and optical properties. For example, the monolayer is inherently metallic, has a puckered structure, possesses excellent in-plane mechanical properties, with a Young's modulus of up to 398 GPa nm, and exhibits Dirac transport properties and superconductivity.<sup>1-3</sup> Due to these unique properties, monolayer borophene can be used for heterogeneous catalysis and H<sub>2</sub> evolution,<sup>4</sup> as electrodes in rechargeable metal-ion batteries,<sup>5</sup> and in photoelectronic devices.<sup>6</sup> In 2015 Mannix *et al.* reported for the first time the successful synthesis of borophene by physical vapor deposition on a Ag(111) surface.<sup>7,8</sup> *Ab initio* molecular dynamics (AIMD) based simulations have confirmed its thermodynamic stability.<sup>9</sup> Recently, Pekoz *et al.*<sup>10</sup> have shown that borophene is both dynamically and thermodynamically stable. The phonon dispersion curve at the ground state does not contain imaginary frequencies and the structure is also intact at temperatures as

high as 1000 K. These facts raise the following question: can borophene be used for H<sub>2</sub> storage?

Molecular hydrogen is a renewable and green energy source which is used in fuel cells and for chemical hydrogenation. While it is an excellent candidate as a fuel, conventional storage methods like high pressure cylinders or cryogenic tanks pose practical limits on its efficient and safe storage and transportation.<sup>11</sup> The primary targets for effective H<sub>2</sub> storage based on a physisorption mechanism are (a) a high gravimetric density; the target of 7.5 wt% system gravimetric density has been decided as the revised target by the United States Department of Energy (US DOE)<sup>12</sup> for ultimate full fleet applications, and (b) easy recycling of hydrogen at ambient pressure and temperature.<sup>13,14</sup> Since the discovery of graphene, 2D materials, by virtue of their high surface to volume ratio, have been identified as providing an advanced route for hydrogen storage by physical adsorption.<sup>11,15</sup> In the recent past, first principles based density functional theory (DFT) calculations have been extensively used to computationally investigate H<sub>2</sub> storage over 2D substrates. For reversible H<sub>2</sub> storage (*i.e.* adsorption and release under near ambient conditions), a binding energy in the range between  $-0.1$  and  $-0.2$  eV per H<sub>2</sub> is considered acceptable.<sup>16,17</sup>

Experimental advances in fabricating 2D materials have expedited their practical realization in current day progress in

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H<sub>2</sub> storage and the potential to adopt modern methods for H<sub>2</sub> storage applications. During the quest for potential substrates for H<sub>2</sub> storage several 2D materials have been studied *e.g.* boron nitride sheets,<sup>18–20</sup> graphene,<sup>21–25</sup> phosphorene,<sup>26–28</sup> C<sub>2</sub>N<sup>29</sup> and MOS<sub>2</sub>.<sup>17</sup> Among 2D materials, graphene has been predicted to offer a 7% gravimetric density in H<sub>2</sub> storage and phosphorene has shown a gravimetric density of more than 5%. In the studies of H<sub>2</sub> storage over 2D materials, it has been found that metal decoration and defects enhance the H<sub>2</sub> storage capacity compared to that over pristine materials. Decorating 2D surfaces using metallic adatoms is an effective way to increase the interactions between the substrate and the H<sub>2</sub> molecules, thereby increasing the gravimetric density. For example, Li decorated graphene has been reported to have a binding energy of  $-0.35$  eV per H<sub>2</sub> compared to  $-0.114$  eV per H<sub>2</sub> in pristine graphene.<sup>30</sup> Yu *et al.*<sup>27</sup> reported that Li decoration in pristine phosphorene increased the gravimetric density to 4.4% compared to the negligible storage capacity of pristine phosphorene. Hashmi *et al.*<sup>29</sup> reported a gravimetric density of 13 wt% over Li decorated C<sub>2</sub>N. Putungan *et al.*<sup>17</sup> reported a gravimetric density of 4.4 wt% over Li decorated MOS<sub>2</sub>. Another avenue for improving the storage capacity of potential substrates is defect engineering.<sup>31</sup> Yadav *et al.* demonstrated that using defective graphene, it was possible to achieve a gravimetric density of 7%. Recently, Halder *et al.*<sup>28</sup> combined these two methods, *i.e.* Li decoration and defect engineering, to improve the adsorption energy and gravimetric density of H<sub>2</sub> over phosphorene. They demonstrated that defective phosphorene possessed a binding energy of  $<0.1$  eV per H<sub>2</sub>, while Li-decorated single vacancy phosphorene had an enhanced adsorption energy of  $-0.48$  eV per H<sub>2</sub> leading to a gravimetric density of 5.3 wt%.

In the recent past several authors have attempted to study the H<sub>2</sub> storage capacity of pristine and metal decorated monolayer borophene. For example, Li *et al.*<sup>32</sup> reported that Li decorated borophene possessed a gravimetric density of 13.7 wt%. Chen *et al.*<sup>33</sup> reported a gravimetric density of 1.3 wt% in Ca decorated borophene. However, these studies have approached the metal decoration aspect on a case by case basis. Therefore, there is a need to carry out studies with several alkali atoms for better comparison and an in-depth understanding. Additionally, to the best of our knowledge, the effect of point defects on the H<sub>2</sub> storage capacity of borophene has not been studied yet. Only a few reports are available on the H<sub>2</sub> storage capacity of borophene and they are limited to metal decoration.<sup>33–35</sup> In this manuscript, we attempt to fill the gaps in our understanding with a comprehensive study of H<sub>2</sub> storage over metal decorated and defective borophene using extensive first principles based density functional theory (DFT) calculations. We have investigated H<sub>2</sub> storage in Li, Na and Ca decorated and single and double vacancy defective borophene. All the cases have been simulated in the same DFT-D framework with a similar type of pseudopotential to compare the performance of different decorations and defects. The results from our simulations have been compared with the data available in the literature. To gain insight into H<sub>2</sub> adsorption onto borophene, projected density of states (PDOS) have been computed to show the charge transfers and interactions among the elements.

## 2. Material and computational details

First principles based DFT calculations were performed using Quantum Espresso, an open source package available under a GNU license.<sup>36</sup> For all the elements, a Vanderbilt ultrasoft type pseudopotential was used along with the Perdew–Burke–Ernzerhof (PBE) exchange correlation functional.<sup>37,38</sup> The van der Waals correction was accounted for by adopting a dispersion corrected DFT (DFT-D) framework.<sup>39</sup> A spacing of around 20 Å was used in the direction normal to the 2D substrate to avoid interlayer long range van der Waals interactions between the periodic images. The cut-off energies for the wave functions and charge densities were set to be 60 Ry and 480 Ry, respectively. Self-consistent field (SCF) calculations were performed using a convergence threshold of  $1e^{-5}$  Ry for the total system energy to obtain the charge densities of the systems. A Monkhorst–Pack grid with  $4 \times 4 \times 1$  *k*-points was used for the Brillouin zone integrations.<sup>40</sup> The simulations were performed using Methfessel–Paxton smearing with a degauss value of 0.02.<sup>41</sup>

The binding energy of H<sub>2</sub> over borophene can be calculated as:

$$E_b = (E_{\text{boro}+i\text{H}_2} - E_{\text{boro}} - E_{i\text{H}_2})/i, \quad (1)$$

and

$$E_b = (E_{\text{boro}+M+i\text{H}_2} - E_{\text{boro}+M} - E_{i\text{H}_2})/i, \quad (2)$$

where  $E_b$  represents the binding energy of the hydrogen (eV per H<sub>2</sub>).  $E_{\text{boro}+i\text{H}_2}$ ,  $E_{\text{boro}}$ , and  $E_{i\text{H}_2}$  are the total energies (eV) of the borophene supercell and the hydrogen molecules, only the borophene substrate, and only the H<sub>2</sub> molecules, respectively. Similarly,  $E_{\text{boro}+M+i\text{H}_2}$  and  $E_{\text{boro}+M}$  represent the total energy of the full metal (M) decorated H<sub>2</sub> adsorbed borophene, and the metal decorated borophene, respectively. As per the above relation, a negative binding energy implies that adsorption is energetically favorable and spontaneous, while a positive binding energy indicates desorption. Smaller values of  $E_b$  imply stronger binding of H<sub>2</sub> with the substrate. The projected density of states (PDOS) has also been calculated for the systems to understand the charge transfer among the elements in the system.

For studying the H<sub>2</sub> adsorption capacity, at first the borophene substrate was relaxed at its ground state. To calculate the binding energy of hydrogen molecules over adatom decorated borophene, first, metal adatoms were relaxed over borophene for a range of initial positions. Most of the energetically favorable adatom configurations were chosen for further H<sub>2</sub> adsorption. Several initial positions for the H<sub>2</sub> molecules were considered over metal decorated borophene and the structures were energetically optimized.

## 3. Results and discussions

### 3.1. H<sub>2</sub> adsorption over pristine borophene

The optimized structure of the monolayer borophene supercell (4·3) is shown in Fig. 1(a) and the projected density of states



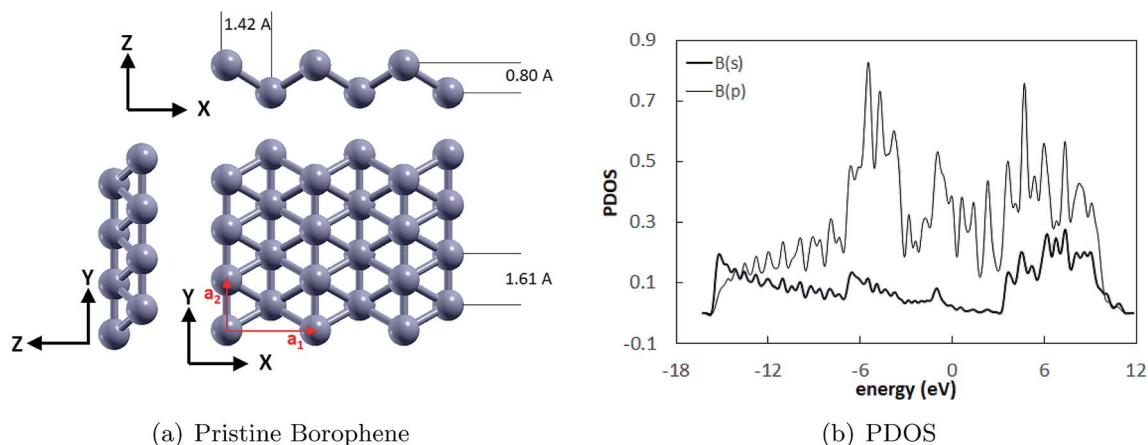


Fig. 1 (a) The pristine borophene substrate with its unit cell vectors and dimensions ( $a_1 = 2.85 \text{ \AA}$  and  $a_2 = 1.61 \text{ \AA}$ ), and (b) PDOS of the unit cell of borophene with the Fermi energy shifted to zero.

(PDOS) is shown in Fig. 1(b). It can be seen that borophene has a puckered structure wherein the B atoms belong to two different atomic planes in the out-of-plane direction. The lattice parameters of the unit cell are  $a_1 = 2.85 \text{ \AA}$  and  $a_2 = 1.61 \text{ \AA}$ , and are shown by the red arrows. The lattice parameters reported here are in excellent agreement with those reported before. For example, DFT calculations performed by Jiang *et al.*<sup>5</sup> predicted lattice parameters of  $2.861 \text{ \AA}$  and  $1.641 \text{ \AA}$  for borophene. Similarly, the lattice parameters of the borophene supercell reported by Xiang *et al.*,<sup>42</sup> *i.e.*,  $2.85 \text{ \AA}$  and  $1.62 \text{ \AA}$ , also match with our calculations. The pucker height of  $0.8 \text{ \AA}$  reported here is in excellent agreement with the results obtained by Mannix *et al.*<sup>7</sup> Additionally, the PDOS shows that borophene is inherently metallic at the ground state due to the absence of a finite bandgap, which agrees well with that previously reported in ref. 32.

To find the adsorption energies, as shown in Fig. 2(a), several geometrically unique sites in borophene were selected.  $\text{H}_2$

molecules were placed at a distance of  $3 \text{ \AA}$  away from the borophene substrate along the out-of-plane direction and the structures were optimized. The binding energies obtained from the DFT calculations are listed in Table 1. It was observed that the binding energies were in the range  $-0.032$  to  $-0.045 \text{ eV}$  per  $\text{H}_2$ , with position A (Fig. 2(b)) the best site with a binding energy of  $-0.045 \text{ eV}$  per  $\text{H}_2$ . The stable position of the  $\text{H}_2$  molecule was measured at a vertical distance of around  $2.95 \text{ \AA}$ . However, this binding energy of well below  $-0.1 \text{ eV}$  per  $\text{H}_2$  is not sufficient for hydrogen storage. The PDOS of the system with the  $\text{H}_2$  molecule at position A is shown in Fig. 3. A comparison of the projected density of states presented in Fig. 1(b) and those in 3 shows that the electrons in the p shells of boron and the s shell of the  $\text{H}_2$  molecule are hybridized close to  $-5 \text{ eV}$  and  $5 \text{ eV}$ .

### 3.2. $\text{H}_2$ adsorption over Li, Na and Ca decorated borophene

To evaluate the effect of alkali metal decoration on the hydrogen adsorption capability of borophene, first, isolated metallic

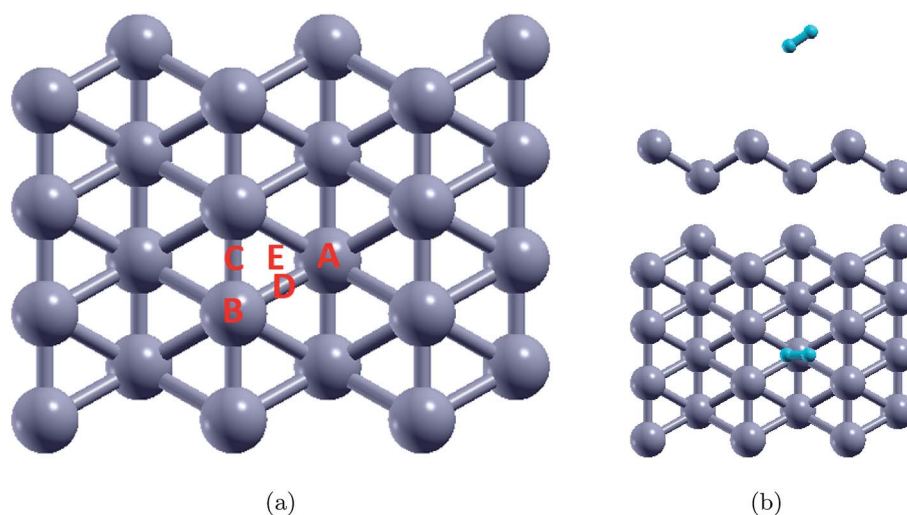
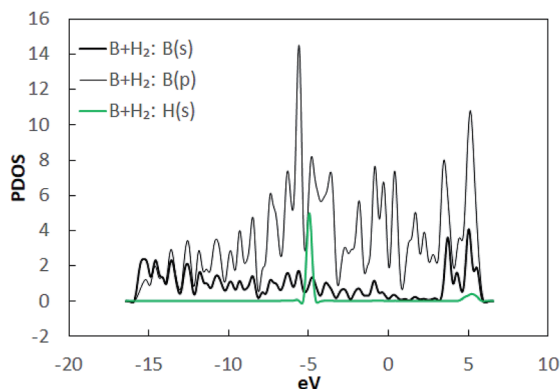


Fig. 2 (a) Different initial locations of the  $\text{H}_2$  molecules over pristine borophene substrate and (b) the best adsorption site in terms of binding energy.



**Table 1** Binding energies of H<sub>2</sub> over pristine borophene for different adsorption sites (Fig. 2(a))

H <sub>2</sub> position	A	B	C	D	E
$E_b$ (eV per H <sub>2</sub> )	-0.045	-0.032	-0.034	-0.039	-0.045



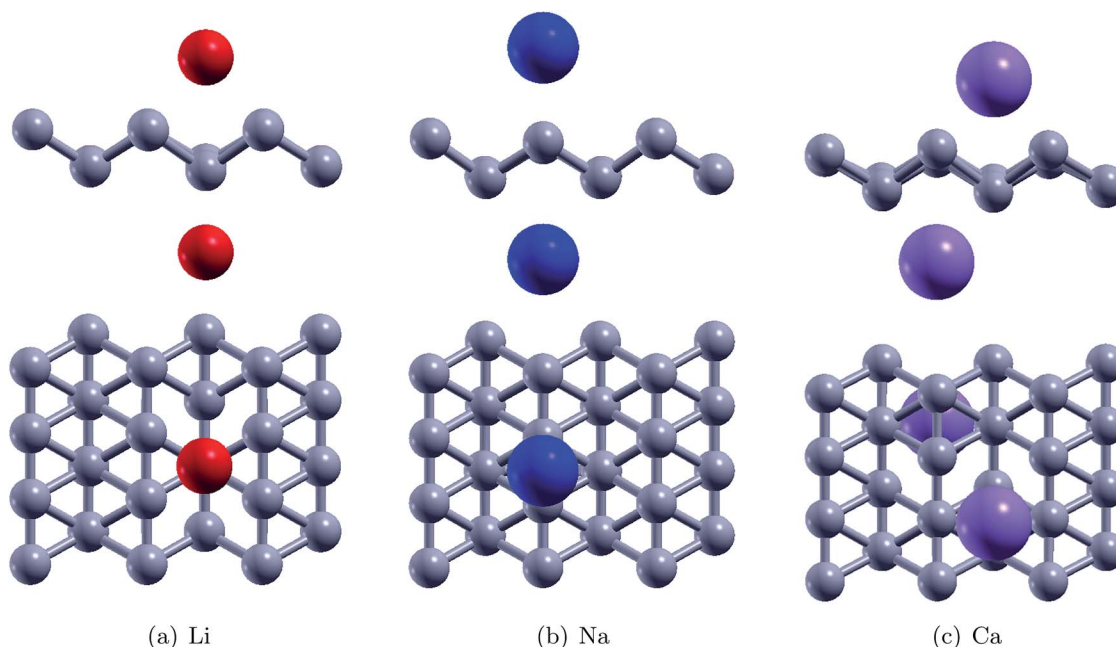
**Fig. 3** Projected density of states (PDOS) of the constituents in H<sub>2</sub> adsorbed pristine borophene.

adatoms (Li, Na and Ca) were adsorbed over borophene. Several initial positions for the adatoms were chosen at a distance of 3 Å away from borophene on both sides, and the structures were energetically minimized. The stability of borophene decorated (by physisorption) with alkali metal atoms on both sides has been studied in a host of research articles.<sup>5,42–45</sup> These studies have performed ground state DFT and finite temperature AIMD simulations and have reported these structures to be stable. Additionally, the gravimetric density of H<sub>2</sub> storage for various

2D materials (graphene and phosphorene) has been evaluated for double-sided metal decoration.

Fig. 4 shows the relaxed configurations after adatom decoration on both sides, which are consistent with those reported in ref. 32. It can be noted that Li and Na are stable at symmetric positions with respect to borophene, however, the Ca atoms have stable positions which are oblique with respect to the borophene sheet. This fact can be attributed to the electronegativity of the adatoms: due to the Ca atom being more electronegative, the two Ca atoms interact with each other. The binding energies of the Li, Na and Ca atoms onto the substrate were determined using the relation  $E_b^M = E_{B+2M} - E_B - E_{2M}$  and were found to be 2.47 eV, 2.50 eV, and 3.64 eV, respectively (Table 2). In the fully relaxed state, the vertical distances of Li, Na and Ca from the substrate were measured to be 1.80 Å (top) and 2.0 (bottom); 2.0 Å (bottom) and 2.35 Å (top); and 1.80 Å (both top and bottom), respectively, in the relaxed configurations. The cohesive energies of bulk Li, Na and Ca are 1.63 eV per atom, 1.11 eV per atom, and 1.84 eV per atom, respectively.<sup>46</sup> The binding energies of the adatoms over the borophene substrate are stronger than the cohesive energy of the bulk material and thus, can be adsorbed as single atoms over borophene instead of coalescing into their bulk forms.

Thereafter, H<sub>2</sub> molecules were adsorbed over metal decorated borophene by placing the H atoms facing the adatoms (Fig. 5). In the stable configuration, the H<sub>2</sub> molecules were at a distance of 1.95 Å, 2.35 Å, and 2.65 Å away from the Li, Na, and Ca adatoms, respectively. The binding energies of the H<sub>2</sub> molecules were calculated to be -0.36 eV per H<sub>2</sub>, -0.34 eV per H<sub>2</sub>, and, -0.12 eV per H<sub>2</sub> for Li, Na and Ca decoration, respectively. It can be deduced that Li decoration offers better adsorption of the H<sub>2</sub> molecule to the substrate. The projected density of states (PDOS) of pristine borophene for the substrate

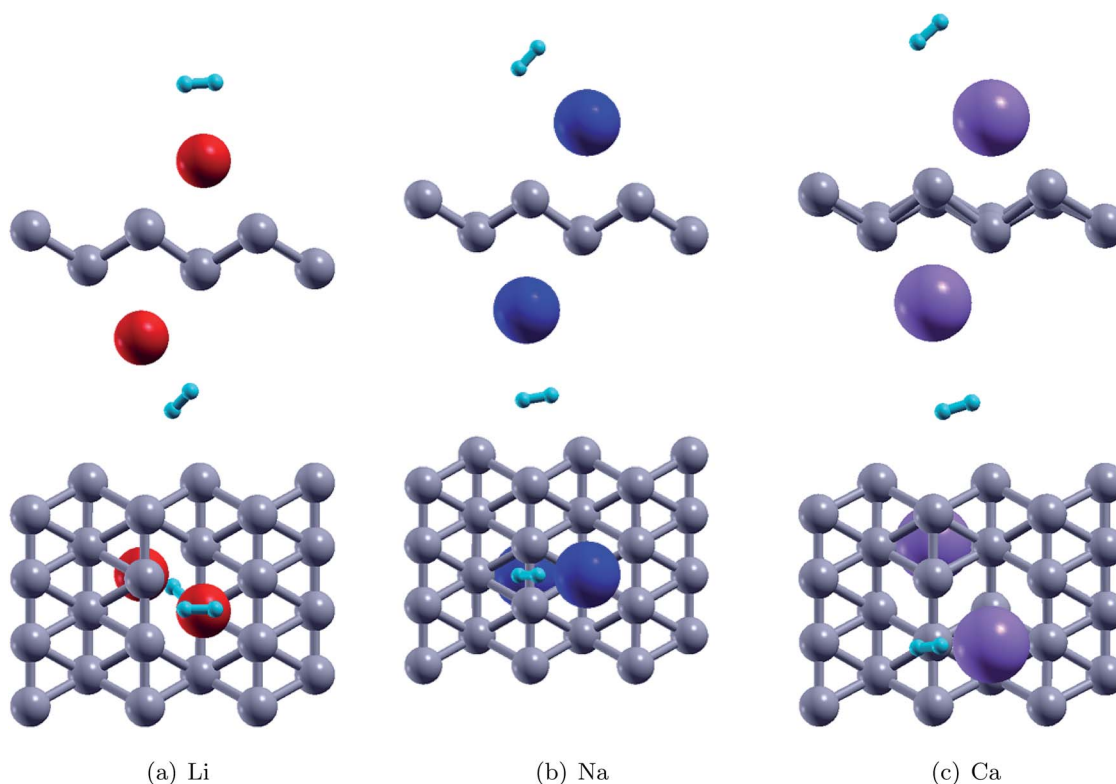


**Fig. 4** The relaxed configurations of Li, Na and Ca decorated pristine borophene



**Table 2** The binding energies of the different elements ( $E_b^M$ ) over pristine borophene and the binding energies of  $H_2$  ( $E_b^{H_2}$ ) over metal decorated borophene

Adatom	Atomic mass (amu)	$Z_{\text{sub-M}}$ (Å)	$E_b^M$ (eV per atom)	$R_{M-H_2}$ (Å)	$E_b^{H_2}$ (eV per $H_2$ )
2Li	6.94	1.80	-2.47	1.95	-0.36
2Na	22.99	2.35	-2.50	2.35	-0.34
2Ca	40.08	1.80	-3.64	2.65	-0.12



**Fig. 5** The stable configurations of  $H_2$  adsorbed on Li, Na and Ca decorated borophene

alone and those of borophene in the  $H_2$  adsorbed system are shown in Fig. 6 to elucidate the interactions. It can be observed that the peak in the PDOS for borophene is reduced in the  $H_2$  adsorbed system compared to that in the PDOS for borophene with the substrate alone. Furthermore, in metal decorated systems significant hybridization can be observed between the metal atoms and the boron and H atoms. For example, in Li-decorated borophene, an additional H peak is seen at 3 eV, and electrons in the valence band of hydrogen are pulled down to the -9 eV level by the electrons in the valence band of Li and hybridization can be observed between the Li(s) electrons and the H(s) electrons. In the case of Na, the density of the H peak in the valence band is significantly smaller than that for the Li and Ca decorated borophene samples. Additionally, the valence band peak for H can be seen to be split into two peaks, unlike that for Li and Ca decorated borophene. In the case of Ca decorated borophene, the H peak in the valence band is pulled to the -10 eV energy level, and hybridization can be seen to take place between the H(s) and Ca(s) and Ca(f) electrons.

### 3.3. $H_2$ adsorption over defective borophene

Single vacancy (SV) and double vacancy (DV) defects were created by removing atoms from the supercell. Different unique SV and DV defects created by removing the atoms are shown in Fig. 7. It should be noted that one SV defect and two unique DV defects could be created (Fig. 7). The defective borophene substrates were then relaxed at their ground state by energy minimization. The formation energies of the defects were calculated using the relation,  $E_f = E_{\text{defect}} - \frac{N-n}{N} E_{\text{pristine}}$ , where  $E_{\text{defect}}$  and  $E_{\text{pristine}}$  are the total energies of defective and pristine borophene, respectively,  $N$  is the number of atoms in the pristine substrate, and  $n$  is the number of atoms removed from the pristine supercell to create the defects ( $n = 1$  for SV, and  $n = 2$  for DV). As summarized in Table 3, the calculated formation energy for the SV defect is 0.12 eV and those for the DV defects are 1.31 eV (DV-1) and 1.26 eV (DV-2).

Herein, we have studied  $H_2$  adsorption over borophene containing SV and DV-2 defects (since the formation energy of



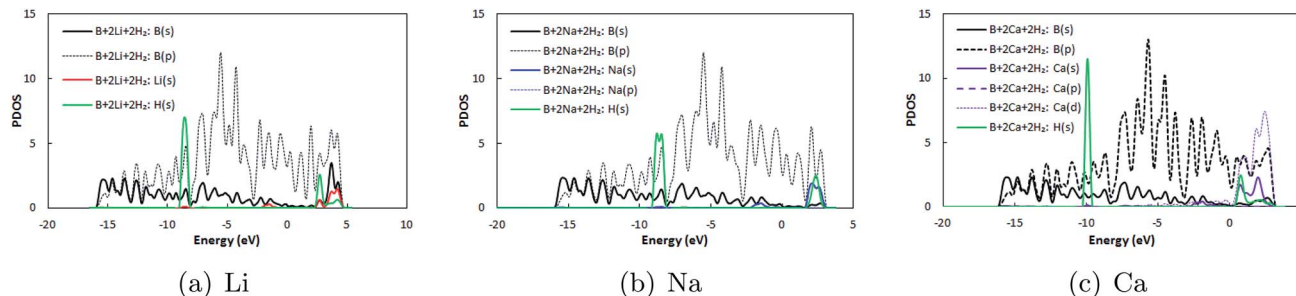


Fig. 6 Projected density of states (PDOS) of borophene in  $H_2$  adsorbed (a) Li, (b) Na, and (c) Ca decorated pristine borophene. In the legends, B represents the borophene substrate only and B + 2Li + 2 $H_2$  represents the  $H_2$  adsorbed Li decorated borophene system.

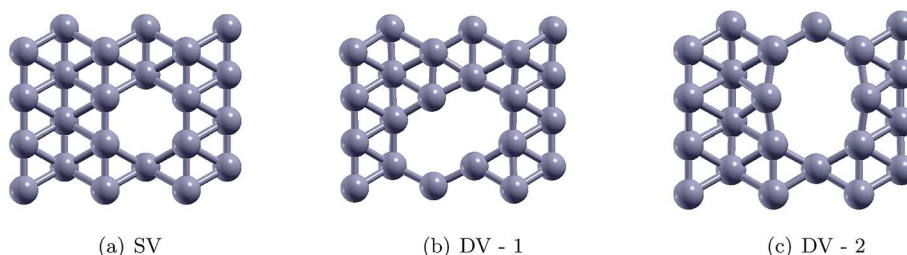


Fig. 7 Schematics for the single vacancy (SV) and double vacancy (DV) defects in borophene.

Table 3 Formation energies for the different single vacancy (SV) and double vacancy (DV) defects in borophene

Defect	SV	DV-1	DV-2
Formation energy (eV)	0.12	1.31	1.26

DV-2 is lower than that of DV-1).  $H_2$  molecules were placed at several locations facing the defects at a distance of 3 Å away from the substrate and the systems were energetically optimized. The atomic configurations corresponding to the best adsorption energies are shown in Fig. 8. The stable distances for the  $H_2$  molecules from the defective substrate were measured as

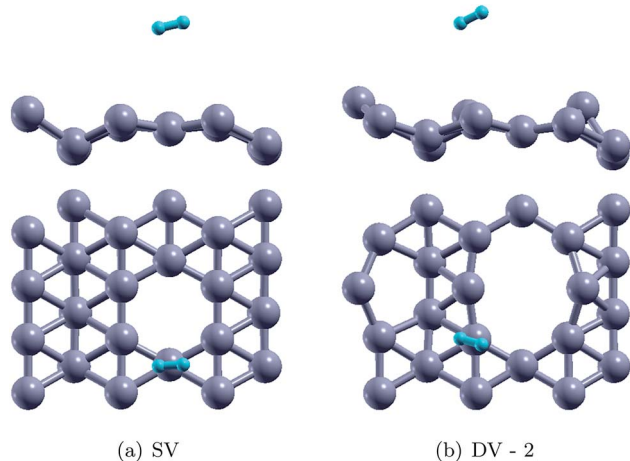


Fig. 8 The stable configurations of  $H_2$  adsorbed SV and DV defective borophene.

3.08–3.09 Å for SV and DV defective borophene. The binding energies of the  $H_2$  molecule over defective borophene were calculated to be  $-0.063$  eV per  $H_2$  for the SV defect and a staggeringly large  $-0.69$  eV per  $H_2$  for the DV defect (Table 4). It is worth noting that the binding energy of the  $H_2$  molecule over DV defective borophene is better than those obtained by decorating borophene with alkali metals. To visualize the interactions between the  $H_2$  molecules and the borophene substrate, the projected density of states (PDOS) was calculated, as shown in Fig. 9. The PDOS indicates the interaction of the  $H_2$  molecules with the defective substrate around the peak at 5 eV above the Fermi energy level. A comparison between Fig. 3 and 9 indicates that the density of the H peak close to the 5 eV level is much more pronounced in the defective substrates than in the pristine substrate. This indicates a transfer of charge from the defective substrates to the  $H_2$  molecules leading to greater interaction and a larger binding energy for the  $H_2$  molecules.

#### 3.4. Gravimetric densities for $H_2$ storage in borophene

In order to estimate the maximum capacity for  $H_2$  storage, gravimetric densities have been calculated for the metal

Table 4 The binding energy ( $E_b^{H_2}$ ), distance ( $R_{sub-H_2}$ ) of  $H_2$  from the substrate, and bond length ( $R_{H-H}$ ) of  $H_2$  in borophene with different defects. The binding energies correspond to the adsorption of one  $H_2$  molecule. The distance is measured from the closest boron atom in defective borophene

System	$E_b^{H_2}$ (eV)	$R_{sub-H_2}$ (Å)	$R_{H-H}$ (Å)
SV	$-0.063$	3.08	0.7523
DV	$-0.690$	3.09	0.7519



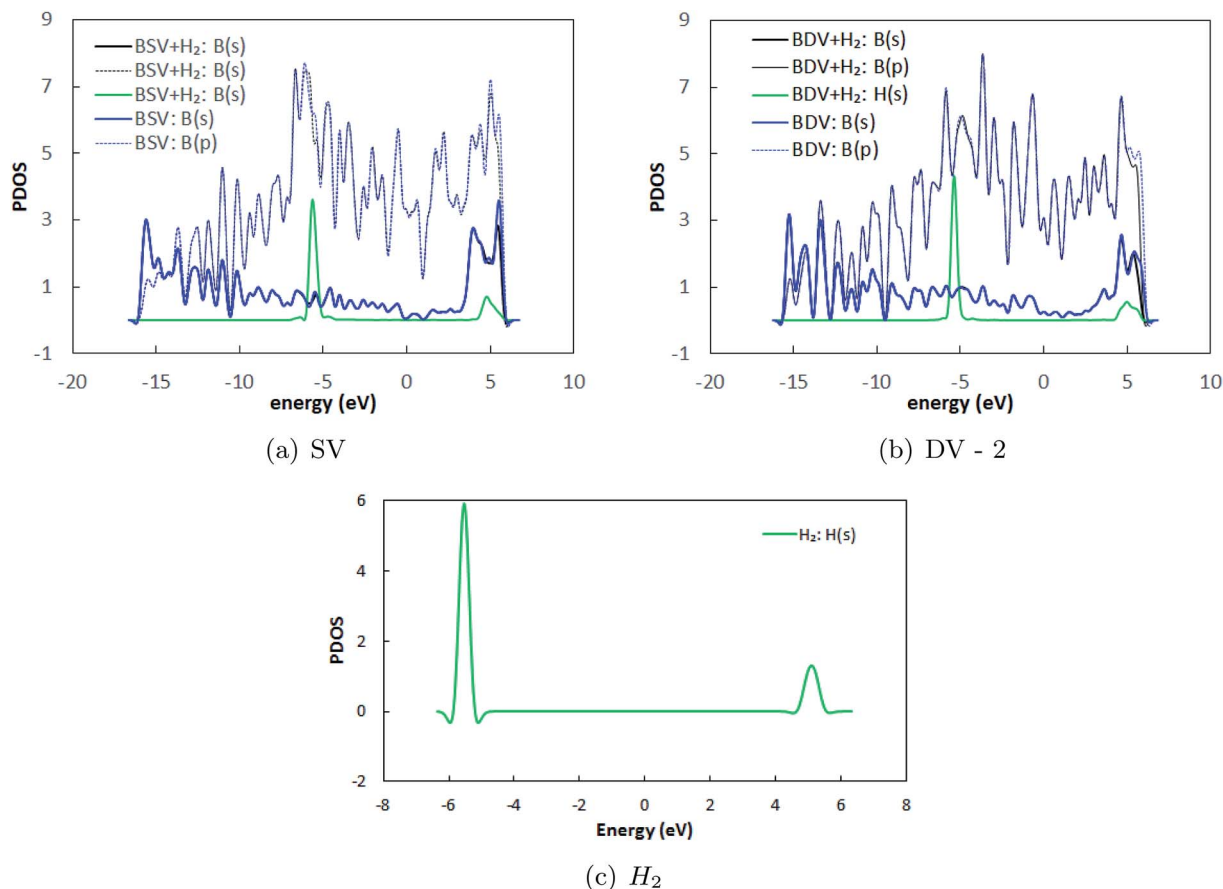


Fig. 9 Projected density of states (PDOS) of borophene in (a) SV and (b) DV defective borophene, and (c) only  $H_2$  with the Fermi energy shifted to zero. BSV and BDV represent single vacancy and double vacancy defective borophene. Similarly BSV +  $H_2$  and BDV +  $H_2$  represent  $H_2$  adsorbed systems.

decorated and DV defective borophene. The gravimetric density of  $H_2$  storage is given by:

$$C_g = \frac{pm_{H_2}}{qm_B + rm_M + pm_{H_2}}, \quad (3)$$

where  $m_{H_2}$ ,  $m_B$ ,  $m_M$  and  $p$ ,  $q$  and  $r$  represent the atomic mass and the total number of  $H_2$ , B, and the metal, respectively. To study the gravimetric density, the number of  $H_2$  molecules was sequentially increased and the binding energy was calculated using eqn (1) and (2). To determine the energy of the system, the structures with the three initial positions have been relaxed. It was observed that the total energies of the systems were very close to each other. The values obtained from the best case among the different initial positions have been reported. In all cases, the number of  $H_2$  molecules was increased till the binding energy had decreased to around  $-0.1$  eV per  $H_2$ .

Metal decoration on both sides of the substrate significantly enhanced the  $H_2$  storage capacity of pristine borophene. While Li yielded the highest binding energy of  $-0.36$  eV per  $H_2$ , for Na and Ca, the binding energies of  $-0.34$  eV per  $H_2$  and  $-0.12$  eV per  $H_2$  were calculated. Among the decorating elements Li, Na and Ca, Li yielded the best binding energy of  $-0.36$  eV per  $H_2$ . To show the relation between the  $H_2$  coverage and binding energy, the evolution in the binding energy of the  $H_2$  molecules

during the sequential adsorption of the  $H_2$  molecules over the borophene substrate is depicted in Fig. 10. The average binding energy of the  $H_2$  molecules with respect to the number of  $H_2$  molecules adsorbed over the substrate is shown. As can be observed in the figure image, the binding of the  $H_2$  molecules became weaker when more  $H_2$  molecules were adsorbed. The results show that the Li decoration on both sides could adsorb 10  $H_2$  molecules per Li atom yielding a gravimetric density of 6.8%. In the case of Na decoration, the number of adsorbed  $H_2$  molecules was 15 per Na atom and the gravimetric density was 9.0%. Furthermore, 14  $H_2$  molecules could be adsorbed per Ca atom on both sides of borophene while the binding energy per  $H_2$  molecule was around  $-0.1$  eV. This yielded a gravimetric density of 7.6%. The gravimetric density of  $H_2$  in DV defective borophene is shown in Fig. 11. Since DV defective borophene showed a better binding energy than SV defective borophene, the gravimetric density was only evaluated for DV defective borophene. It was found from the simulations that DV defective borophene could adsorb as many as 14  $H_2$  molecules on both sides of the substrate leading to a gravimetric density of 9.2%. It should be noted that the gravimetric density obtained was for one value of defect density. A decrease in the defect density in the borophene substrate may alter the gravimetric density.



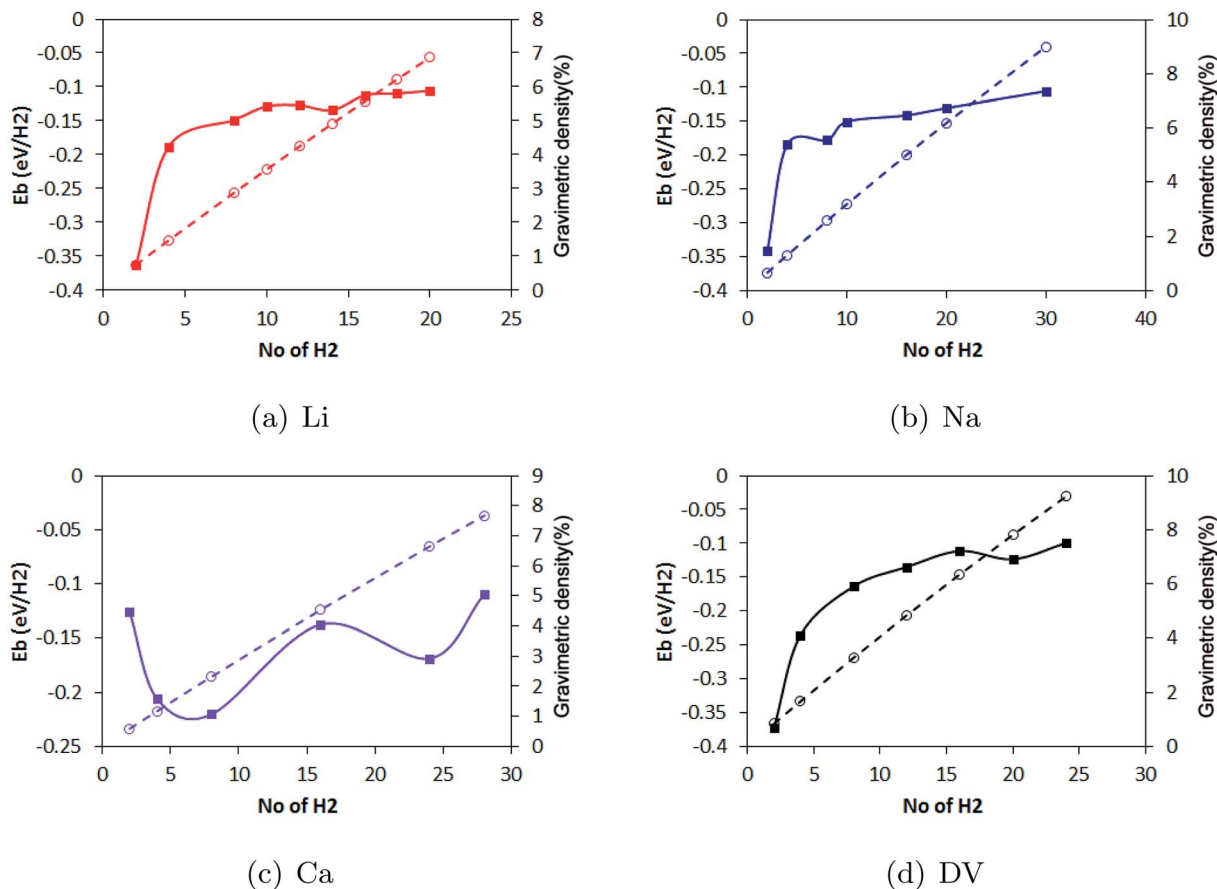


Fig. 10 The evolution in binding energy (continuous line) and gravimetric density (dashed line) during the sequential addition of H<sub>2</sub> molecules to (a) Li, (b) Na and (c) Ca decorated pristine borophene and (d) DV defective borophene.

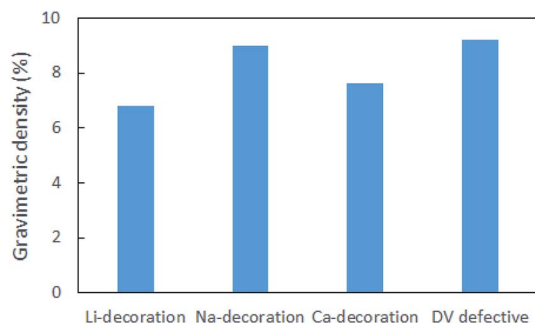


Fig. 11 Gravimetric densities for Li, Na and Ca decorated and defective borophene

Therefore, the values presented in this work can be considered as the upper limit for borophene with a great number of defects. The gravimetric density of DV defective borophene was found to be better than that of metal decorated pristine borophene (Fig. 11).

In the recent past, first principles based calculations have predominantly been used to screen 2D materials for H<sub>2</sub> storage purposes by characterising their adsorption strengths, gravimetric densities, *etc.* In all these studies, the methods used for calculation have varied, (for example, density functional theory,

*ab initio* and molecular dynamics). Additionally, the choice of pseudopotential (PAW or norm-conserving) and computational parameters (van der Waals corrections and energy and force cutoffs) is also erratic. We start our discussion by comparing the performance of borophene with that of graphene. Yadav *et al.*<sup>23,31</sup> reported that Ni decorated pristine and defective graphene (with Stone–Wales and single vacancies) can achieve gravimetric densities of 5.81% and 7.02%, respectively. Wang *et al.*<sup>47</sup> and Muthu *et al.*<sup>48</sup> found that while h-BN possesses a gravimetric density of 2.6%, h-BN nanoparticle modified MWCNTs can store 2.3% H<sub>2</sub>. On the other hand, while metal decorated pristine phosphorene had a gravimetric density of 3.6%,<sup>27</sup> calculations performed by Haldar *et al.*<sup>28</sup> predicted a gravimetric density of 5.3% for metal decorated phosphorene containing single vacancies. Additionally, another 2D material, Cr<sub>2</sub>C, also possesses a gravimetric density of 7.6%.<sup>49</sup> Therefore, the results of this first principles based study show that borophene can be a very competitive system for H<sub>2</sub> storage.

## 4. Conclusions

First principles based density functional theory (DFT) calculations have been performed to study H<sub>2</sub> storage in Li, Na and Ca decorated pristine and single vacancy (SV) and double vacancy





(DV) defective borophene. The DFT calculations were performed using the Vanderbilt ultrasoft pseudopotential along with the PBE exchange correlation functional in a DFT-D framework accounting for van der Waals interactions. While the binding energy of the H<sub>2</sub> molecule over pristine borophene was  $-0.045$  eV per H<sub>2</sub>, alkali metal decoration significantly enhanced the binding energy to be in the range  $-0.12$  to  $-0.36$  eV per H<sub>2</sub>, increasing the binding energy to acceptable values for reversible H<sub>2</sub> storage. The binding energies of the alkali metal were also found to be higher than their cohesive energies, thus decoration over the substrate was favored. The gravimetric densities of H<sub>2</sub> were found to be 6.8%, 9.0%, and 7.6% in Li, Na and Ca decorated borophene, respectively. Next, single vacancy (SV) and double vacancy (DV) defects were created in the borophene substrate. The formation energies of the SV and DV defects were determined to be 0.12 eV and 1.26 eV. Though the SV defect had a very low formation energy compared to that of the DV defect, the binding energy of the H<sub>2</sub> molecule over SV defective borophene was only  $-0.063$  eV per H<sub>2</sub>. On the other hand, DV defective borophene offered a binding energy of  $-0.69$  eV per H<sub>2</sub> for the first H<sub>2</sub> molecule. DV defective borophene yielded a gravimetric density of 9.2%, which was higher than that of metal decorated pristine borophene. Our simulation results show that borophene could be used as a substrate for H<sub>2</sub> storage. Defective borophene can offer competing H<sub>2</sub> storage capacity compared to that obtained with metal decoration.

## Conflicts of interest

There are no conflicts to declare.

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