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# Reversible Hydrogen Storage in Metal-Decorated Honeycomb Borophene Oxide

Parsa Habibi, Thijs J. H. Vlugt, Poulumi Dey, and Othonas A. Moultos\*

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**ABSTRACT:** Two-dimensional (2D) boron-based materials are receiving much attention as  $H_2$  storage media due to the low atomic mass of boron and the stability of decorating alkali metals on the surface, which enhance interactions with  $H_2$ . This work investigates the suitability of Li, Na, and K decorations on 2D honeycomb borophene oxide ( $B_2O$ ) for  $H_2$  storage, using dispersion corrected density functional theory (DFT-D2). A high theoretical gravimetric density of 8.3 wt %  $H_2$  is achieved for the Li-decorated  $B_2O$ structure. At saturation, each Li binds to two  $H_2$  with an average binding energy of -0.24 $eV/H_2$ . Born–Oppenheimer molecular dynamics simulations at temperatures of 100, 300, and 500 K demonstrate the stability of the Li-decorated structure and the  $H_2$  desorption behavior at different temperatures. Our findings indicate that Li-decorated 2D  $B_2O$  is a promising material for reversible  $H_2$  storage and recommend experimental investigation of 2D  $B_2O$  as a potential  $H_2$  storage medium.



**KEYWORDS:** hydrogen, hydrogen storage, borophene oxide, physisorption, hydrogen binding energy, density functional theory, Born–Oppenheimer molecular dynamics, metal decoration

#### 1. INTRODUCTION

Conventional methods of hydrogen  $(H_2)$  storage, which include highly pressurized chambers or cryogenic cooling, are energy-intensive, lead to boil-off losses, and may require thick storage walls.<sup>1,2</sup> For these reasons, chemisorption and physisorption-based H<sub>2</sub> storage systems have emerged as an alternative.<sup>1,3,4</sup> Chemisorption-based H<sub>2</sub> storage in hydrides, such as MgH<sub>2</sub>, leads to high capacities but slow adsorption/ desorption kinetics due to strong covalent interactions with H atoms.<sup>4–7</sup> Physisorption-based  $H_2$  storage, for example in metal-organic frameworks (MOFs), leads to faster adsorption/desorption kinetics but lower H<sub>2</sub> capacities due to the weak (van der Waals) interactions of the porous framework with  $H_2$ .<sup>8–11</sup> Among physisorption-based  $H_2$  storage materials, two-dimensional (2D) structures exhibit great potential in reaching high H<sub>2</sub> capacities due to their large surface to volume  $^{-14}$  To achieve reversible H<sub>2</sub> storage, the binding of H<sub>2</sub> ratios.<sup>1</sup> on the 2D substrate generally needs to be enhanced. Several adjustments have been proposed to enhance the binding of  $H_2$  with 2D substrates.<sup>13,15–19</sup> Examples of such adjustments include external charge modulation,<sup>16,17</sup> and introduction of decorating atoms (mainly metals such as Li), which enhance interactions by polarizing  $H_2$ .<sup>13,18,19</sup> 2D boron sheets (borophene), which have been recently synthesized,<sup>20-22</sup> have shown a favorable affinity for different metal-decorating atoms, in contrast to graphene, in which clustering of metal atoms can occur.<sup>23,24</sup> Using a variety of metal decorations, such as Li,<sup>18,19,23</sup> Na,<sup>25</sup> Ca,<sup>26</sup> and Ti<sup>27</sup> on different borophene polymorphs, impressive H<sub>2</sub> gravimetric densities have been

obtained ranging from 6 to 15 wt %, exceeding the US department of energy (DOE) requirement for onboard storage of 6.5 wt %  $H_2$ .<sup>28</sup>

Experimental and theoretical studies on borophene have indicated that borophene is prone to oxidation when exposed to air.<sup>20,29-31</sup> For this reason, the protection of borophene polymorphs from air can be crucial for applications such as H<sub>2</sub> storage.<sup>31</sup> Although uncontrolled oxidation is undesirable, one can intentionally use the oxidation process to produce structures that are more chemically stable.<sup>32,33</sup> For this reason, researchers have been actively looking into a variety of 2D boron oxide structures.<sup>33,34</sup> Inspired by the recent synthesis of honeycomb borophene on an Al substrate,<sup>21,32</sup> a 2D honeycomb borophene oxide (B2O) structure has been theoretically proposed.<sup>32</sup> Phonon dispersion and ab initio molecular dynamics simulations have shown that the 2D honeycomb B<sub>2</sub>O structure is stable at temperatures up to 1000 K.<sup>32</sup> 2D honeycomb B<sub>2</sub>O has a high capacity for Li/Na functionalization, thereby being a promising anodic material.<sup>35</sup> In particular, B<sub>2</sub>O has been shown to have one of the highest capacities for Li storage.<sup>35</sup> The high affinity of 2D B<sub>2</sub>O to

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metal-decorating atoms, with its high stability hints at the suitability of this material for H<sub>2</sub> storage applications. Similar to other 2D boron-based structures, such as borophene,<sup>36</sup> 2D boron oxides can form different structural polymorphs.<sup>33,34,37</sup> Honeycomb B<sub>2</sub>O has lower formation energy compared to other 2D allotropes such as B<sub>4</sub>O, B<sub>5</sub>O, B<sub>6</sub>O, B<sub>7</sub>O, and B<sub>8</sub>O indicating its stability.<sup>32,33</sup> Other 2D polymorphs of boron oxide such as the recently reported B<sub>2</sub>O<sub>3</sub><sup>37</sup> may also be suitable for H<sub>2</sub> storage applications, however, the study of these materials is beyond the scope of this work.

In this work, the use of 2D B<sub>2</sub>O as an efficient H<sub>2</sub> storage material is investigated using first-principles calculations. Three different alkali metals (i.e., Li, Na, and K) are considered for enhancing the interactions of 2D B<sub>2</sub>O with H<sub>2</sub>. The addition of these metal-decorating atoms is found to be favorable as evident by negative adsorption energies. All three metal atom types increase the binding energy of H<sub>2</sub> compared to the pristine structure and result in binding energies suitable for reversible H<sub>2</sub> storage. Our density functional theory (DFT) calculations with the Li-decorated 2D B2O structure clearly show that a notable gravimetric density of 8.3 wt % H<sub>2</sub> can be achieved. By performing Born-Oppenheimer molecular dynamics (BOMD) simulations we show that the Li-decorated structure is stable at 100, 300, and 500 K. Finally, we used semi-empirical calculations to show that under adsorption conditions of 298 K and 30 atm and desorption conditions of 373 K and 3 atm, a practical gravimetric density of 5.2 wt % H<sub>2</sub> can be attained. Our findings strongly recommend further experimental investigation of 2D honeycomb B2O as a potential H<sub>2</sub> storage medium.

#### 2. COMPUTATIONAL DETAILS

2.1. Density Functional Theory. DFT calculations are carried out using plane-wave basis sets, as implemented in the Vienna ab initio simulation package (VASP 5.3.5).<sup>38,39</sup> The projected augmented wave method (PAW) is used and the generalized gradient approximation (GGA) is applied with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional.<sup>40</sup> Van der Waals forces are accounted for using a dispersion corrected framework (DFT-D2).41 This approach is commonly used in other studies of  $H_2$  storage on 2D metal-decorated substrates.<sup>13,15,18,27,42</sup> An inter-layer separation of more than 30 Å is used to prohibit inter-layer interactions.<sup>19</sup> Nevertheless, a smaller inter-layer spacing may also be applicable.<sup>15,18,42</sup> The cut-off energy is set to 700 eV for the plane-wave basis set and a  $\Gamma$ -centered Monkhorst-Pack kpoint mesh of  $3 \times 9 \times 1$  is used for the structural relaxations and binding energy calculations. The energy convergence criteria for the self-consistent electronic loop is set to  $10^{-6}$  eV. All lattice parameters and atomic positions are relaxed until the residual forces acting on each atom are below 1 meV/Å. Gaussian smearing with a  $\sigma$  of 0.02 eV is used for Brillouinzone integration. A  $2 \times 2$  conventional unit cell of borophene oxide, containing 16 B atoms and 8 O atoms, is used for the DFT simulations. The H<sub>2</sub> adsorption energies are calculated from<sup>18,43-46</sup>

$$E_{\rm b} = (E_{\rm S+qH_2} - E_{\rm S} - qE_{\rm H_2})/q \tag{1}$$

where  $E_{\rm b}$  is the average binding energy of H<sub>2</sub> with the 2D substrate,  $E_{\rm S+qH_2}$  and  $E_{\rm S}$  are the energies of the substrate with and without H<sub>2</sub> molecules,  $E_{\rm H_2}$  is the energy of a H<sub>2</sub> molecule in a vacuum, and *q* is the number of H<sub>2</sub> molecules. All energies

in eq 1 are computed using DFT. For simulations in which the 2D structure is functionalized with metals atoms, the average  $H_2$  binding energy is calculated using  $^{18,43-46}$ 

$$E_{\rm b} = (E_{\rm S+M+qH_2} - E_{\rm S+M} - qE_{\rm H_2})/q$$
(2)

where  $E_{S+M+qH_2}$  and  $E_{S+M}$  represent the energy of the 2D metaldecorated substrate with and without H<sub>2</sub>, respectively. The single H<sub>2</sub> removal energy,  $E_{r}$ , is calculated according to<sup>47</sup>

$$E_{\rm r} = E_{\rm S+M+qH_2} - E_{\rm S+M+(q-1)H_2} - E_{\rm H_2}$$
(3)

where  $E_{S+M+qH_2}$  and  $E_{S+M+(q-1)H_2}$  represent the energies of a 2D metal-decorated substrate containing q and (q-1) H<sub>2</sub> molecules, respectively. In the case of metal-decorated 2D B<sub>2</sub>O there is an intrinsic dipole in the direction normal to the 2D plane. For this reason, calculations are carried out to examine if there is a need for dipole corrections in this system. It is found that for single-metal (Li, Na, and K)-decorated B<sub>2</sub>O dipole corrections change the total energies by less than 0.02% and the metal adsorption energies on B<sub>2</sub>O by less than 2.5% (most different for K-decorated and the least for Li-decorated B<sub>2</sub>O). As the results do not show considerable change, dipole corrections were not accounted for the rest of the computations.

2.2. Born-Oppenheimer Molecular Dynamics (BOMD). To investigate the finite temperature stability of the structure, BOMD simulations are carried out using VASP. To create the BOMD simulation box, the DFT supercell is multiplied by a factor of 2 along its smallest side, thereby creating a 2  $\times$  4 supercell. The stability of the H<sub>2</sub>-saturated and Li-decorated B<sub>2</sub>O structure is examined at three different temperatures (i.e., 100, 300, and 500 K) using the Nosé-Hoover thermostat.<sup>48,49</sup> These simulations are performed in the canonical ensemble (NVT) and include only the  $\Gamma$ -point. Alternatively, the NPT ensemble can be used for the simulations. As the number of H<sub>2</sub> molecules is relatively small (32 in total), large pressure fluctuations are expected upon adsorption/desorption of H<sub>2</sub>. Due to this when using the NPT ensemble caution must be taken to adjust only the volume normal to the 2D plane, to avoid creating artifacts (e.g., artificial wrinkles) on the 2D structure. For this reason, the NVT ensemble is chosen. The same cut-off energy and smearing as in the DFT calculations are used. The "normal" precision mode is used for the BOMD simulations and the "accurate" precision mode is used for the DFT simulations. The BOMD simulations are carried out with a time-step of 1 fs, for a total time of 10 ps. The Verlet algorithm is used for integrating the equations of motion.<sup>50</sup> The variation of free energy (as defined by Kresse et al.<sup>38</sup>) as a function of simulation time is shown in Figure S1. In all BOMD simulations, an equilibration period of 5 ps is initially performed. Production runs of 5 ps are used for sampling the property of interest. VESTA is used for all atomic visualizations.<sup>51</sup>

#### 3. RESULTS AND DISCUSSION

**3.1. Pristine B<sub>2</sub>O Structure.** The planar 2D structure of honeycomb B<sub>2</sub>O is shown in Figure 1. Our results indicate that the relaxed lattice constants for the conventional unit cell are 2.76 and 7.37 Å, while the lattice constant for the primitive cell is 3.93 Å (both sides are equal). The optimal B–O and B–B bond lengths in our simulations are computed to be 1.34 and 1.71 Å, respectively. These results agree well with other DFT



**Figure 1.** Top and side view of the 2D honeycomb borophene oxide structure. The lattice constant for the primitive cell (shown with blue lines) is 3.93 Å, and the lattice constants for the conventional cell (shown with black lines) are 2.76, and 7.37 Å.

results from the literature.<sup>32,33</sup> A single  $H_2$  molecule is then added to the system to compute the binding to the 2D B<sub>2</sub>O structure. According to eq 1, a single H<sub>2</sub> adsorbs with a binding energy of -0.10 eV/H<sub>2</sub> to the 2D B<sub>2</sub>O structure. Figure S2 shows different initial configurations that are probed and the final relaxed configuration of H<sub>2</sub> on 2D B<sub>2</sub>O. All of the different initial configurations converged into the same final configuration after relaxing all atomic positions and the structural parameters. Although the binding energy of H<sub>2</sub> with the pristine borophene oxide structure is higher than that of striped borophene (c.a. -0.05 eV/H<sub>2</sub>),<sup>18</sup> this binding energy is not adequate for reversible storage of H<sub>2</sub>.<sup>52-55</sup> This illustrates the necessity for the addition of metal-decorating atoms.

**3.2. Metal Decoration.** Three different alkali metaldecorating atoms have been probed, i.e., Li, Na, and K. These alkali metal atoms have shown to be particularly adept at enhancing the interaction with H<sub>2</sub>, for other 2D structures such as striped borophene,<sup>18</sup> boron phosphide,<sup>15</sup> and boron hydride.<sup>42</sup> Other metal decorations such as Ca and Ti have also shown to be suitable for H<sub>2</sub> storage applications on 2D borophene structures,<sup>26,27</sup> but examining the applicability of these or other metal atoms as dopants on 2D B<sub>2</sub>O for H<sub>2</sub> storage is beyond the scope of this work. Before assessing the influence of the decorating atoms on the binding of H<sub>2</sub>, the adsorption energy of these metal atoms is calculated on the B<sub>2</sub>O surface according to<sup>35</sup>

$$E_{\rm ads} = E_{\rm S+M} - E_{\rm S} - E_{\rm M,C}$$
(4)

where  $E_{ads}$ ,  $E_{S+M}$ ,  $E_{M,C}$ , and  $E_S$  are the energy of adsorption, the energy of the substrate plus the metal atom, the cohesive energy of the bulk crystalline metal, and the energy of the substrate, respectively. A negative adsorption energy signifies the favorable adsorption of the metal atom on the 2D substrate

and a positive energy means that the metal atoms would preferentially cluster together.<sup>15</sup> The values of  $E_{ads}$  are -1.00, -0.71, and -1.11 eV for a single Li, Na, and K-decorated 2D B<sub>2</sub>O structure, respectively. All three metal-decorating atoms i.e., Li, Na, and K prefer the hollow position in the ring of honeycomb B<sub>2</sub>O (see Figure 2a for Li) and are situated at a distance of 1.40, 2.02, and 2.41 Å, respectively (see Figure S3 for different configurations). The charge density difference plot of a Li-decorated system is shown in Figure 2b. This charge density difference plot is calculated using<sup>15</sup>

$$\Delta \rho = \rho_{\rm S+M} - \rho_{\rm S} - \rho_{\rm M} \tag{5}$$

where  $\Delta \rho$ ,  $\rho_{S}$ ,  $\rho_{M}$ , and  $\rho_{S+M}$  represent the charge density difference, charge density of the substrate, the metal atom, and the combined structure, respectively.

In Figure 2b, it can be seen that the addition of the Li atom to the B2O substrate leads to the formation of a charge depleted region on top of Li (blue region as indicated in Figure 2b), while there is an enhancement of the charge density for the boron and oxygen atoms in the vicinity of Li (yellow region in Figure 2b). Bader charge analysis carried out on Li-, Na-, and K-decorated B<sub>2</sub>O (see Table S1) illustrates the loss of electronic charge by decorating the 2D substrate with alkali metals. A H<sub>2</sub> molecule that is added to this system interacts with the metal atom and is adsorbed in the charge depleted region as shown in Figure 2c. Figure S4 shows different configurations that are considered for H<sub>2</sub> adsorption on Li, Na, and K-decorated 2D B<sub>2</sub>O. For the Li-decorated structure, H<sub>2</sub> preferentially adsorbs on top of the O-atom, in the vicinity (top edge) of the Li atom (as seen in Figure 2c). The favourability of this position is attributed to H<sub>2</sub> maximizing its attractive interaction with the Li atom (and its periodic image) and the 2D B<sub>2</sub>O sheet. Similarly, for the Na and K-decorated system (see Figure S4) this site is found to be the most favorable, although the exact positioning of H<sub>2</sub> differs due to the different atomic sizes of Na and K compared to Li. The results for the adsorption of a single H<sub>2</sub> indicate a binding energy of  $-0.34 \text{ eV/H}_2$  in the case of the Li-decorated structure, and a binding energy of -0.25 and -0.28 eV/H<sub>2</sub> for Na- and K-decorated structures, respectively. These calculations show that all of the alkali metal (i.e., Li, Na, K)decorated B2O structures have resulted in an interaction energy in the range suitable for reversible H<sub>2</sub> storage (above -0.10 and below  $-0.60 \text{ eV/H}_2$ .<sup>52-55</sup> For further calculations of the H<sub>2</sub> gravimetric density, the Li-decorated structure is investigated in more detail because of its higher interaction



Figure 2. Top and side views of (a) a single Li-decorated 2D honeycomb  $B_2O$  structure, (b) the charge density difference of the Li-decorated structure, the isosurface value is set to 0.0015 e/Å<sup>3</sup> (blue areas represent charge density depletion, while yellow areas represent gain), and (c) an adsorbed  $H_2$  on the Li-decorated structure, with the  $H_2$  orientation parallel to the B–O–B bond.



**Figure 3.** (a) Top and side views of a structure containing 5 H<sub>2</sub> surrounding one Li atom. Two H<sub>2</sub> are within a 2.5 Å radius from Li (shown in gray), while the other three are further away due to repulsive forces (shown in pink). (b) The variation of the average H<sub>2</sub> binding energy ( $E_b$ ) and H<sub>2</sub> removal energy ( $E_r$ ) as a function of the number of adsorbed H<sub>2</sub> molecules per Li. The lines connecting the points are used to guide the eye.



**Figure 4.** (a–c) Different configurations of the half-covered Li structures shown from the top and the side. (d) Top and side view of  $H_2$  adsorption in structure (a). Each Li atom can successfully bind to two  $H_2$  leading to a gravimetric density of 8.3 wt %  $H_2$ . In the top view, the Li and H atoms that are at the bottom are given a darker shade for better readability of the figure.

energy with  $H_2$  and the lower atomic mass of Li compared to Na and K.

**3.3.** H<sub>2</sub> **Gravimetric Density.** To test the suitability of Lidecorated honeycomb  $B_2O$  for  $H_2$  storage, it is important to estimate the maximum theoretical gravimetric density of  $H_2$  in this structure. For this, both the number of  $H_2$  and Li atoms need to be systematically increased. Before increasing the

number of Li atoms it is useful to obtain an estimate of the number of  $H_2$  molecules one Li atom can bind to, and how the average binding energy between  $H_2$  and the metal-decorated structure changes with the addition of  $H_2$ .

To visualize how  $H_2$  molecules disperse around the Li atom, a structure containing five  $H_2$  surrounding one Li atom is shown in Figure 3a. Out of the five  $H_2$  that are shown in this



Figure 5. BOMD simulation snapshots of the Li-decorated  $B_2O$  structure at three different temperatures of (a) 100 K, (b) 300 K, and (c) 500 K.  $H_2$  molecules that are at a distance exceeding 2.5 Å from the closest neighboring Li atom are colored in purple while the ones within this range are colored in gray. The average H-atom distribution calculated over the last 5 ps of the BOMD simulations as a function of the distance perpendicular to the surface (d).

figure, two H<sub>2</sub> have a distance lower than 2.5 Å from Li, while the other three are positioned at a distance of more than 2.5 Å from the Li atom. In Figure 3b the average binding energy per  $H_2$  and the  $H_2$  removal energy is shown as a function of the number of H<sub>2</sub> molecules per Li atom. In a single Li-decorated system, when the number of  $H_2$  molecules is increased from 2 to 3, a large decrease in the magnitude of the  $H_2$  removal energy is observed from  $-0.27 \text{ eV/H}_2$  to around  $-0.10 \text{ eV/H}_2$ . Considering that  $-0.10 \text{ eV}/\text{H}_2$  is approximately the interaction energy of H<sub>2</sub> with borophene oxide in the absence of Li, it can be concluded that the 3rd to 5th H<sub>2</sub> molecules interact very weakly with Li. Based on the findings shown in Figure 3, it is evident that each Li atom can optimally interact with two H<sub>2</sub> molecules, with an average binding energy of  $-0.30 \text{ eV/H}_2$ . Considering that H<sub>2</sub> preferentially binds to the top sides of the Li atom, parallel to the B-O-B bond, it is not suitable to fully cover the structure with Li atoms (i.e., two Li atoms in each hexagonal hole, one at the top and the other at the bottom). Overloading the structure with Li atoms will reduce the number of H<sub>2</sub> that can be adsorbed per Li atom, and thus, lead to a lower H<sub>2</sub> gravimetric density. For this reason, a "halfcovered" structure of Li atoms (i.e., a structure containing half as many Li atoms as a fully covered structure) is deemed optimal.

Different half-covered Li configurations are shown in Figure 4a-c. From the three structures shown, structure (a) is the most energetically stable, while structure (b) has the highest energy (with a relative difference of 1.5% compared to the energy of structure (a)). Structure (c) has a relative energy difference of only 0.3% with respect to structure (a). Considering that structure (a) is the most energetically stable configuration, it is used for further calculations of  $H_2$  adsorption. The addition of two  $H_2$  on the top side of each

Li atom (as depicted in Figure 4d) resulted in an average binding energy of  $-0.24 \text{ eV/H}_2$ . The weakest H<sub>2</sub> binding energy (H<sub>2</sub> removal energy from the fully H<sub>2</sub> saturated structure shown in Figure 4d) is calculated to be  $-0.21 \text{ eV/H}_2$ , while the strongest H<sub>2</sub> binding energy (H<sub>2</sub> binding energy for the first H<sub>2</sub> added to the structure shown in Figure 4a) is  $-0.27 \text{ eV/H}_2$ . Each H<sub>2</sub> in this structure is located at a distance lower than 2 Å from a Li atom. The gravimetric density (GD) of H<sub>2</sub> can be calculated using<sup>18</sup>

$$GD = \frac{qM_{H_2}}{qM_{H_2} + nM_B + lM_O + kM_m}$$
(6)

where q, n, l, and k represent the number of H<sub>2</sub> molecules, B, O, and metal-decorating atoms in the simulation box, respectively, while M denotes their respective molar masses. Using eq 6, the H<sub>2</sub> gravimetric density of this structure equals 8.3 wt %, which exceeds the 6.5 wt % target set by the DOE.<sup>28</sup>

3.4. Finite Temperature Stability. To further check the stability and desorption of H<sub>2</sub> at finite temperatures, BOMD simulations are carried out at target temperatures of 100, 300, and 500 K. The results are shown in Figure 5. Figure 5a-c depicts the BOMD snapshots after 10 ps. From these subfigures, it can be seen that at 100 K, all of the H<sub>2</sub> molecules are bound to the Li-decorated B<sub>2</sub>O structure, at 300 K 50%, and at 500 K  $\sim$ 85% of the H<sub>2</sub> molecules are at distances larger than 2.5 Å from the Li atom. To obtain a more quantitative measure of the desorption process, the H-atom distribution in the simulation box is plotted as a function of the distance perpendicular to the 2D surface. The distribution plot is normalized such that the area under the curve equates to the number of H atoms in the simulation. Figure 5d shows two peaks, both at a distance of  $\sim$ 3 Å away from the 2D structure, which corresponds to the perpendicular distance of the  $H_2$ 

adsorption sites (above and below) from the 2D structure. The adsorption peak gradually decreases with the increase in the temperature, as  $H_2$  molecules begin to distribute evenly in the simulation box. The BOMD simulations also demonstrate that even at 500 K, no clustering of Li atoms is observed in the 10 ps simulation time frame, and the metal-decorated structure is found to be stable. This confirms the favorable Li adsorption energy as discussed in Section 3.2. No chemical reactions have occurred between  $H_2$  molecules and the 2D substrate, so the structure does not undergo irreversible changes and  $H_2$  molecules can be released without having to overcome a significant energy barrier (covalent bond formation/breaking). Therefore, the findings from the BOMD simulations indicate the stability of Li-decorated B<sub>2</sub>O for H<sub>2</sub> storage in the temperature range of 100–500 K.

**3.5.** Adsorption and Desorption Conditions. In the BOMD simulations, the pressure is not controlled and can vary considerably at different temperatures. In this section, semiempirical calculations are used to estimate the practical  $H_2$  storage capacity at finite temperatures and pressures. The occupation number (*F*), which represents the expected number of  $H_2$  molecules that can be adsorbed on the structure, can be calculated using<sup>56</sup>

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$$F = \frac{\sum_{n=0}^{N_{\max}} ng_n \exp\left[\frac{n(\mu - E_b)}{k_B T}\right]}{\sum_{n=0}^{N_{\max}} g_n \exp\left[\frac{n(\mu - E_b)}{k_B T}\right]}$$
(7)

where  $N_{\text{max}}$  is the maximum number of  $H_2$  molecules that can be adsorbed,  $g_n$  is the degeneracy of a state containing  $n H_2$ , and  $E_b$ , T,  $k_B$ , and  $\mu$  represent the average  $H_2$  binding energy (function of n), temperature, Boltzmann constant, and chemical potential of  $H_2$  in the gas phase, respectively. To simplify the expression, it is assumed that each adsorption site on the structure is independent of its neighboring sites. In this case, the situation simplifies to finding the occupation number of a single site (f), on which at most a single  $H_2$  can be adsorbed. In this case, the degeneracy of the occupied and unoccupied state are both 1 and the single site occupation number equates to <sup>13,47,54,57</sup>

$$f = \frac{1}{1 + \exp\left[\frac{-(\mu - E_{\rm b})}{k_{\rm B}T}\right]} \tag{8}$$

where the chemical potential of H<sub>2</sub> in the gas phase  $\mu$  is a function of temperature and pressure. The total occupation number *F* and the single site occupation number *f* are related by  $F = M_{\text{sites}}f$ , in which  $M_{\text{sites}}$  refers to the total number of H<sub>2</sub> adsorption sites on the structure.<sup>54</sup> The chemical potential  $\mu$  in our calculations is obtained using the empirical relation<sup>47,54,57,58</sup>

$$\mu(T, P) / [eV] = \mu_{ideal}(T, P) + 0.00015(T - 186.5) + 0.00065 \left[ (\log_{10} \frac{P}{P_0} - 0.5)^2 - 0.25 \right]$$
(9)

where the temperature (T) is in the unit of K, pressure (P) is in the unit of atm, and the reference pressure  $(P_0)$  is 1 atm.  $\mu_{\text{ideal}}$  is the ideal chemical potential and is calculated using<sup>56</sup>

$$\mu_{\text{ideal}}(T, P) = -k_{\text{B}}T \ln\left[\left(\frac{2\pi m_{\text{H}_{2}}k_{\text{B}}T}{h^{2}}\right)^{3/2}\frac{k_{\text{B}}T}{P}\right]$$
(10)

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where *h* is Planck's constant and  $m_{\rm H_2}$  is the mass of a single H<sub>2</sub> molecule. In our calculations, adsorption takes place at a temperature of 298 K and a pressure of 30 atm, while desorption occurs at 373 K and 3 atm. These adsorption/ desorption conditions are often used in the literature for calculating the practical gravimetric density.<sup>13,42,47,54,57</sup> Under these conditions, the chemical potential (as calculated by eq 9) and the ideal chemical potential are similar in value.<sup>57</sup> Under adsorption conditions, the ideal chemical potential is -0.21eV, while a value of -0.22 eV is obtained using eq 9. Under desorption conditions, the ideal chemical potential gives a value of -0.36 eV, while  $\mu$  is obtained as -0.38 eV using eq 9.<sup>57</sup> Calculating f under the adsorption conditions yields a value of 0.64, while under the desorption conditions *f* becomes 0.01. This gives a practical gravimetric density of around 5.2 wt % H<sub>2</sub> for the Li-decorated B<sub>2</sub>O under these capture/release conditions. Lowering the adsorption temperature and/or increasing the adsorption pressure can lead to higher gravimetric capacities. These findings indicate that the Lidecorated B<sub>2</sub>O structure can be used for reversible H<sub>2</sub> storage, under near-ambient conditions. To obtain the optimal release/ capture conditions and more accurate calculations of H<sub>2</sub> capacity at various temperatures and pressures, further simulations are encouraged.

#### 4. CONCLUSIONS

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The capability of 2D honeycomb borophene oxide for H<sub>2</sub> storage applications is assessed using DFT and BOMD simulations. This 2D structure has a favorable affinity with alkali metal atoms such as Li, Na, and K, as indicated by the negative adsorption energy of these metals. These alkali metaldecorated B<sub>2</sub>O structures have enhanced H<sub>2</sub> binding energies with respect to the pristine B<sub>2</sub>O structure. In particular, the Lidecorated structure reaches a gravimetric density of 8.3 wt %  $H_2$  with an average binding energy of  $-0.24 \text{ eV}/H_2$ , which exceeds the gravimetric density requirement set by DOE for onboard H<sub>2</sub> storage applications.<sup>28</sup> BOMD simulations at 100, 300, and 500 K and calculations of the occupation number show both the stability and reversible binding of H<sub>2</sub> on the Lidecorated borophene oxide structure. Our simulations strongly encourage experiments on borophene oxide and further simulations to accurately find the H<sub>2</sub> capacity at various pressures and temperatures.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c09865.

Free energy plots as a function of time during Born– Oppenheimer molecular dynamics simulations of  $H_2$ saturated, Li-decorated 2D honeycomb  $B_2O$ ; different configurations of a single Li, Na, and K atom on 2D  $B_2O$ and their respective energy differences; and Bader charge analysis of single Li, Na, and K-decorated 2D  $B_2O$ (PDF)

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#### Notes

The authors declare no competing financial interest.

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