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## Lithium-Decorated Borospherene $B_{40}$ : A Promising Hydrogen Storage Medium

Hui Bai<sup>1</sup>, Bing Bai<sup>1</sup>, Lin Zhang<sup>1</sup>, Wei Huang<sup>1</sup>, Yue-Wen Mu<sup>2</sup>, Hua-Jin Zhai<sup>2,3</sup> & Si-Dian Li<sup>2</sup>

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The recent discovery of borospherene  $B_{40}$  marks the onset of a new kind of boron-based nanostructures akin to the  $C_{60}$  buckyball, offering opportunities to explore materials applications of nanoboron. Here we report on the feasibility of Li-decorated  $B_{40}$  for hydrogen storage using the DFT calculations. The  $B_{40}$  cluster has an overall shape of cube-like cage with six hexagonal and heptagonal holes and eight close-packing  $B_6$  triangles. Our computational data show that  $Li_m \& B_{40}(1-3)$  complexes bound up to three  $H_2$  molecules per Li site with an adsorption energy (AE) of 0.11–0.25 eV/ $H_2$ , ideal for reversible hydrogen storage and release. The bonding features charge transfer from Li to  $B_{40}$ . The first 18  $H_2$  in  $Li_6 \& B_{40}(3)$  possess an AE of 0.11–0.18 eV, corresponding to a gravimetric density of 7.1 wt%. The eight triangular  $B_6$  corners are shown as well to be good sites for Li-decoration and  $H_2$  adsorption. In a desirable case of  $Li_{14} \& B_{40}-42 H_2(8)$ , a total of 42  $H_2$  molecules are adsorbed with an AE of 0.32 eV/ $H_2$  for the first 14  $H_2$  and 0.12 eV/ $H_2$  for the third 14  $H_2$ . A maximum gravimetric density of 13.8 wt% is achieved in 8. The Li- $B_{40}-nH_2$  system differs markedly from the previous Li- $C_{60}-nH_2$  and Ti- $B_{40}-nH_2$  complexes.

Due to its merits of cleanness, renewability, abundance in nature, and high energy density per unit mass, hydrogen has been recognized as an appealing energy carrier for the future world. It has the potential to reduce our dependence on fossil fuels, which are limited in resource and harmful to the environment<sup>1–4</sup>. One bottleneck of using hydrogen for vehicular applications is the lack of safe and efficient hydrogen storage materials<sup>5–7</sup> that store molecular  $H_2$  reversibly with high gravimetric density and fast kinetics for adsorption, as well as desorption, under the conditions of moderate temperature and pressure<sup>8,9</sup>. An ideal  $H_2$  storage system would be one that binds hydrogen in molecular form and with an adsorption energy (AE) in the regime of 0.1–0.5 eV per  $H_2$ , that is, intermediate between the physisorbed and chemisorbed states<sup>10,11</sup>. Although advances have been made towards meeting the U.S. DOE's targets for hydrogen storage, an ideal system is yet to be designed and synthesized. Therefore, seeking novel hydrogen storage materials has remained an important issue.

Previous experiments and theoretical calculations have shown that metal-decorated carbon fullerenes and nanotubes<sup>12–19</sup>, as well as their boron-, nitrogen- and beryllium-substituted nanostructures<sup>20–22</sup>, might be good candidates for the storage of  $H_2$  molecules. For instance, Zhang and co-workers showed that the reversible hydrogen storage of transition-metal-coated  $C_{60}$  and  $C_{48}B_{12}$  may be as high as 9 wt%<sup>21</sup>. Yildirim *et al.* revealed that Ti-coated single-walled carbon nanotubes can store 8 wt% of  $H_2$ <sup>23</sup>. To avoid the clustering problem of transition metal atoms on the surface of carbon nanostructures, Yoon and co-workers<sup>18</sup> found that Ca can achieve homogeneous monolayer coating, which is superior to other metal elements. They concluded that up to 8.4 wt% of hydrogen can be stored in  $Ca_{32}C_{60}$  with an AE of 0.2–0.4 eV/ $H_2$ . Through first-principles computations, Sun *et al.*<sup>13</sup> predicted that Li-decorated fullerene  $C_{60}$  ( $Li_{12}C_{60}$ ) can store up to 9 wt% of  $H_2$ , albeit with a rather weak AE of 0.075 eV/ $H_2$ . Furthermore, Yoshida *et al.*<sup>17</sup> measured the hydrogen absorption of  $Li_5C_{60}$  based on experiments and confirmed that up to ~2.6 wt %  $H_2$  can be stored at 250 °C and 30 bar  $H_2$ . For lithium-doped fullerenes ( $Li_x-C_{60}-H_y$ ) with a Li: $C_{60}$  mole ratio of 6:1, a reversible uptake of 5 wt%  $H_2$  at 350 °C and 105 bar  $H_2$  and desorption onset temperature of ~270 °C was observed<sup>15</sup>. Subsequently, another experimental results<sup>16</sup> showed that up to 9.5 wt % deuterium ( $D_2$ ) are absorbed in  $Li_{12}C_{60}$  under a pressure of 190 bar and a temperature below 100 °C.

<sup>1</sup>Key Laboratory of Coal Science and Technology of Ministry of Education and Shanxi Province, Taiyuan University of Technology, Taiyuan 030024, Shanxi, China. <sup>2</sup>Nanocluster Laboratory, Institute of Molecular Science, Shanxi University, Taiyuan 030006, Shanxi, China. <sup>3</sup>State Key Laboratory of Quantum Optics and Quantum Optics Devices, Shanxi University, Taiyuan 030006, Shanxi, China. Correspondence and requests for materials should be addressed to W.H. (email: huangwei@tyut.edu.cn) or H.-J.Z. (email: hj.zhai@sxu.edu.cn)

Boron is the lighter neighbor of carbon in the periodic table, which possesses the similar merit as carbon in terms of light weight and potential applications for hydrogen storage. For this purpose, its chemical hydrides<sup>24–26</sup> were studied, as were relevant model nanostructures, such as boron monolayer sheets, fullerenes, and nanotubes<sup>27–29</sup>. In particular, following the proposal of the celebrated  $I_h B_{80}$  buckyball<sup>30</sup>, which is built upon the  $C_{60}$  motif by capping all 20 surface hexagons, a number of papers were devoted to hydrogen storage using  $B_{80}$  coated with metals ( $M = \text{Li, Na, K, Be, Mg, Ca, Sc, Ti, and V}$ )<sup>27,31–33</sup>. However,  $B_{80}$  was subsequently found to favor core-shell type structures at various theoretical levels<sup>34,35</sup>. It is thus not feasible to pursue any realistic technological applications of  $B_{80}$  buckyball as hydrogen storage materials.

Very recently, the first all-boron fullerenes or borospherenes,  $D_{2d} B_{40}$  and  $D_{2d} B_{40}^-$ , were observed in a combined experimental and theoretical study<sup>36</sup>, marking the onset of the borospherene chemistry, whose future development may be envisioned to parallel that of the fullerenes. Endohedral  $M@B_{40}$  ( $M = \text{Ca, Sr}$ ) and exohedral  $M\&B_{40}$  ( $M = \text{Be, Mg}$ ) metalloborospherenes were also predicted, which further support the structural, electronic, and chemical robustness of the  $B_{40}$  borospherene<sup>37</sup>. Closely following  $B_{40}$ , chiral  $B_{39}^-$ ,  $B_{41}^+$ , and  $B_{42}^{2+}$  borospherenes were also studied<sup>38,39</sup>, which expand the borospherene family and may eventually lead to new boron-based nanomaterials.

Borospherene  $B_{40}$  possesses a cube-like cage structure, whose six hexagonal and heptagonal holes each occupy a face of the cube. It also has eight triangular, close-packing  $B_6$  structural blocks, each on an apex of the cube. All B atoms are on the surface of the cage, which is an ideal, well-defined system for chemistry.  $B_{40}$  differs from carbon fullerenes in terms of structure and bonding, and the pursuit of borospherene-based nanomaterials for hydrogen storage is thus intriguing from a fundamental point-of-view. Furthermore, borospherenes are lighter than carbon fullerenes, which make the former systems better candidates to reach a higher gravimetric capacity for hydrogen storage. Relevant to this topic, Dong *et al.*<sup>40</sup> predicted on the basis of density-functional theory (DFT) calculations that Ti-decorated  $B_{40}$  fullerene ( $Ti_6 B_{40}$ ) is capable of storing up to 34  $H_2$  molecules with a maximum gravimetric density of 8.7 wt% and a reversible storage capacity of 6.1 wt%. To our knowledge, the U.S. DOE has set a target of 7.5 wt% for hydrogen storage capacity for the year of 2015<sup>41,42</sup>.

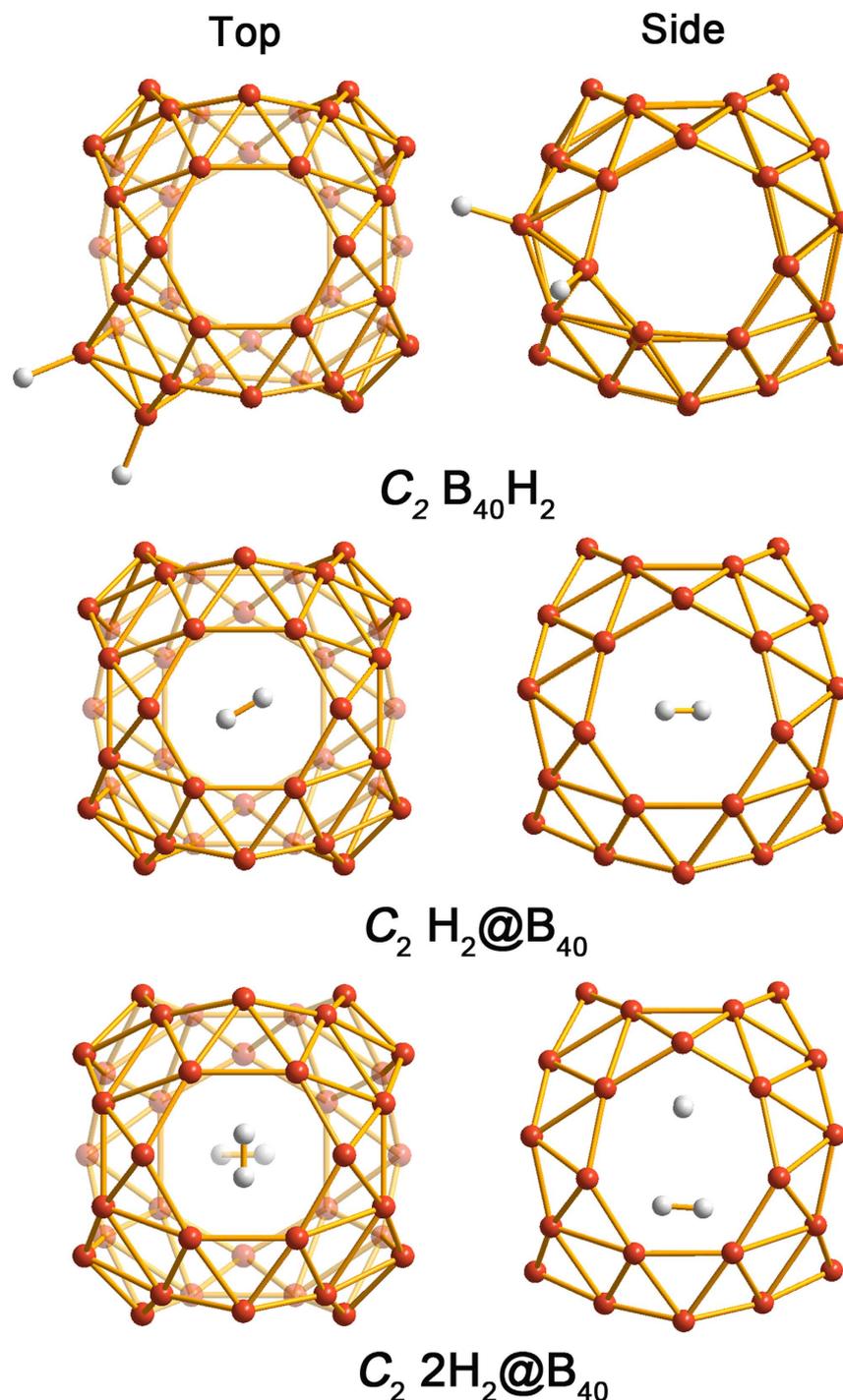
In this work, we choose to study lithium-decorated borospherene  $B_{40}$  as a potential candidate for hydrogen storage via extensive DFT calculations. Since boron-based nanomaterials are also candidates for lithium storage, the current ternary B-Li-H system is quite unique<sup>28,29,43,44</sup>. Compared to transition metal, Li as the lightest metal definitely will facilitate the improvement of hydrogen storage capacity for the metal-decorated  $B_{40}$  system. The  $Li_m-B_{40}-nH_2$  system differs markedly from  $Li_m-C_{60}-nH_2$  or  $Ti_6-B_{40}-nH_2$ , which have an AE value that is either rather small (0.075 eV)<sup>13</sup> or too large (up to 0.82 eV)<sup>40</sup>. Even the recently proposed  $Li_8-B_6-nH_2$  system<sup>44</sup> only has an AE of less than 0.1 eV. Our computational data show that Li-decorated  $B_{40}$  appears to be a promising medium for hydrogen storage. The Li atoms readily attach to the top of hexagonal and heptagonal holes on  $B_{40}$ , forming a series of charge-transfer complexes from  $C_s Li\&B_{40}(1)$ ,  $C_{2v} Li\&B_{40}(2)$ , up to  $D_{2d} Li_6\&B_{40}(3)$ . The  $Li_m\&B_{40}$  complexes can adsorb three  $H_2$  molecules per Li site with a moderate AE of 0.11–0.25 eV/ $H_2$ . The  $Li_6\&B_{40}(3)$  complex stores up to 34  $H_2$  with an average AE of 0.10 eV/ $H_2$ . The first 18  $H_2$  of these possess ideal AEs, which suggest a gravimetric density of 7.1 wt%. Furthermore, the eight close-packing, triangular  $B_6$  corner sites of  $B_{40}$  are also suitable for Li-decoration and  $H_2$  adsorption. In a desirable  $Li_{14}\&B_{40}(7)$  complex, up to 42  $H_2$  molecules can be stored with AEs of 0.12–0.32 eV/ $H_2$ , which corresponds to a gravimetric density of 13.8 wt%.

## Results and Discussion

**Isolated  $B_{40}$  Borospherene for  $H_2$  Adsorption.** The first all-boron fullerene called as borospherene<sup>36</sup>,  $D_{2d} B_{40}$  ( $^1A_1$ ), possesses a very large HOMO–LUMO gap of 3.13 eV at the PBE0 level that indicates its overwhelming stability, which is comparable to that of  $I_h C_{60}$  ( $^1A_g$ ) (3.02 eV) calculated at the same level. All the valence electrons in  $B_{40}$  are either delocalized  $\sigma$  or  $\pi$  bonds and there is no localized 2c–2e bond, unlike the  $C_{60}$  fullerene. In fact, the surface of  $B_{40}$  is not perfectly smooth and exhibits unusual heptagonal faces which may play a role that release the surface strains, in contrast to  $C_{60}$  fullerene whose surface makes up of pentagons and hexagons and presents the least strain. And the diameter of  $B_{40}$  is 6.2 Å, slightly smaller than the value of  $C_{60}$  (7.1 Å), which makes  $B_{40}$  more comfortable to accommodate a range of small molecules inside the cage.

We initially studied  $H_2$  adsorption on the isolated  $B_{40}$  borospherene. The optimized structures of  $B_{40}H_2$ ,  $H_2@B_{40}$  and  $2H_2@B_{40}$  are shown in Fig. 1. In the  $C_{2v} B_{40}H_2$  dihydride, the  $H_2$  molecule tends to form two B–H covalent bonds with the tetracoordinate-B sites, which dissociate  $H_2$ . The dissociative AE of a single  $H_2$  is up to 1.30 eV. For  $H_2$  storage inside the cage, only one  $H_2$  molecule can be encapsulated into  $B_{40}$ , which is marginally exothermic with an AE of 0.24 eV. Interestingly, once such an encapsulation is completed, the  $H_2$  molecule cannot escape due to substantial energy barriers ( $>3$  eV). The AE of a second  $H_2$  inside the cage is found to be endothermic by 1.32 eV, which is thus not feasible experimentally. In short, the above results show that an isolated  $B_{40}$  borospherene is not a good candidate for hydrogen storage directly. The  $B_{40}-H_2$  interactions appear to be different from the case of  $C_{60}$ . The latter is known to interact with  $H_2$  via weak van der Waals forces<sup>45</sup>. As a comparison, our calculation results show that the dissociative AE of a single  $H_2$  for  $C_{60}H_2$  is only  $\sim 0.18$  eV at the same level. However, similar to  $B_{40}$ , only one hydrogen molecule can reside inside the  $C_{60}$  cage with a negative AE value of  $\sim 0.22$  eV.

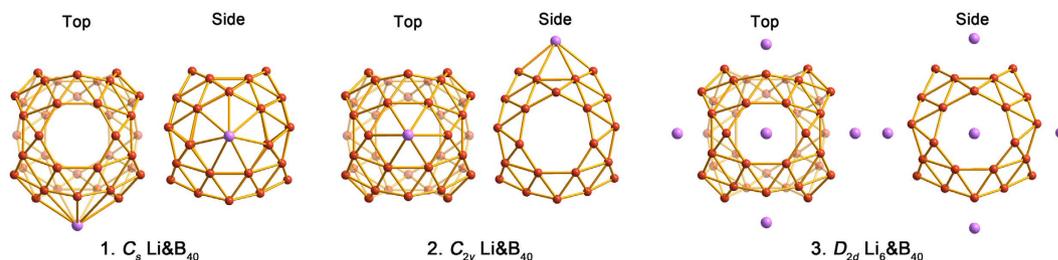
**Configurations of Li-Decorated  $B_{40}$ .** As shown in Fig. 2, we start with a single Li atom interacting with  $B_{40}$ . Relative stability of Li atom bound on heptagonal and hexagonal holes were considered. The exohedral  $C_s Li\&B_{40}(1)$ , in which Li caps a heptagon, turns out to be more stable by 0.20 eV with respect to  $C_{2v} Li\&B_{40}(2)$ . In the latter species, Li caps a hexagon. The BE for Li is 3.08 and 2.88 eV in **1** and **2**, respectively. Thus, Li prefers to bind on top of the heptagonal hole of  $B_{40}$ . The Li–B distance in **1** is 2.34 Å, compared to 2.33 Å in **2** (Table 1). Clearly, the BE of Li on the center of heptagon or hexagon in  $B_{40}$  is substantially higher than those on the pentagon of  $C_{60}$  (1.80 eV), in  $Li_2$  dimer (0.95 eV), and in the Li bulk (1.63 eV)<sup>13</sup>. This should help suppress the potency of Li aggregation to form clusters on  $B_{40}$  surface, suggesting that Li is a suitable adsorbate to decorate  $B_{40}$ . As shown



**Figure 1.** Top and side views of optimized configurations of  $B_{40}H_2$ ,  $H_2@B_{40}$  and  $2H_2@B_{40}$ .

in Table 1, electron transfer occurs from Li to borospherene  $B_{40}$  cage in **1** and **2**, resulting in a positive charge of 0.87–0.88  $|e|$  on Li as revealed in the Bader charge analysis. The ionized Li atom hints a possibility for  $H_2$  adsorption via the polarization mechanism<sup>18</sup>.

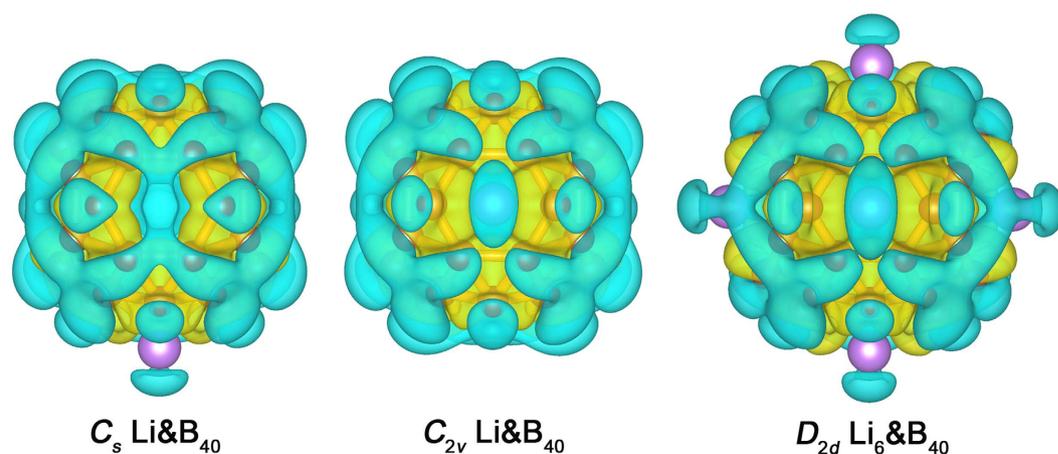
To increase the coverage of Li on  $B_{40}$ , we place one Li atom on top of every hexagon and heptagon hole and reach exohedral  $D_{2d}$   $Li_6@B_{40}$ (**3**) (Fig. 2). In complex **3**, six Li atoms remain isolated on the surface holes, resulting in a highly symmetric  $D_{2d}$  geometry. The average BE of Li in **3** is 3.07 eV/Li, which is comparable to that in  $Li@B_{40}$ (**1**) (3.08 eV) and is slightly larger than that in  $Li@B_{40}$ (**2**) (2.88 eV). There appears to be a collective effect for Li adsorption because six Li atoms in **3** have a higher total BE (18.48 eV) than six individual Li atoms in **1** and **2** combined (18.08 eV). This fact suggests that  $Li_6@B_{40}$ (**3**) is a favorable configuration for Li-decoration. Remarkably but not surprisingly, our computational data indicate that **3** is at least 6.29 eV more stable than  $B_{40}$  attached by a compact  $Li_6$  cluster (Fig. S1). Therefore, surface aggregation of Li for island clusters is unlikely in the



**Figure 2.** Top and side views of the optimized configurations of  $C_s$  Li&B<sub>40</sub>(1),  $C_{2v}$  Li&B<sub>40</sub>(2), and  $D_{2d}$  Li<sub>6</sub>&B<sub>40</sub>(3), in which one Li atom is coated on a heptagonal hole of B<sub>40</sub>, one Li atom is on a hexagonal hole, and six Li atoms are on the heptagonal/hexagonal holes, respectively. The B atom is in orange and Li is in purple.

system	BE/Li (eV)	$R_{Li-B}$ (Å)	charge on Li ( e )
$C_s$ Li&B <sub>40</sub> (1)	3.08	2.34	0.88
$C_{2v}$ Li&B <sub>40</sub> (2)	2.88	2.33	0.87
$D_{2d}$ Li <sub>6</sub> &B <sub>40</sub> (3)	3.07	2.33	0.87

**Table 1.** Calculated Binding Energy (BE) of Li to B<sub>40</sub>, Li–B Bond Distance, and Atomic Charge on Li Atom for Li&B<sub>40</sub>(1), Li&B<sub>40</sub>(2), and Li<sub>6</sub>&B<sub>40</sub>(3).

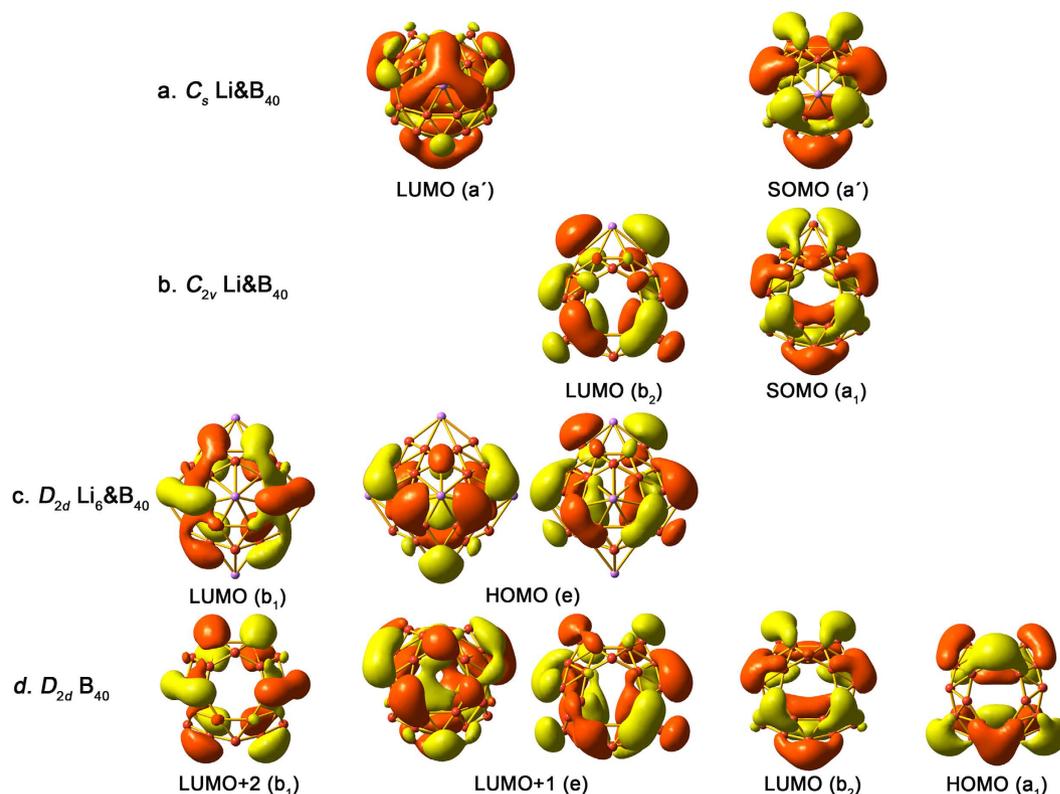


**Figure 3.** Top views of the isosurface of charge density differences of  $C_s$  Li&B<sub>40</sub>(1),  $C_{2v}$  Li&B<sub>40</sub>(2), and  $D_{2d}$  Li<sub>6</sub>&B<sub>40</sub>(3). Yellow color represents the electron accumulation region, and blue represents the electron depletion region.

Li<sub>6</sub>&B<sub>40</sub> system. The Li–B distance in 3 is 2.33 Å, nearly identical to those in 1 and 2. Bader charge analysis shows that the atomic charge on each Li atom in 3 is +0.87 |e|.

We further analyzed the isosurfaces of charge density differences in complexes  $C_s$  Li&B<sub>40</sub>(1),  $C_{2v}$  Li&B<sub>40</sub>(2), and  $D_{2d}$  Li<sub>6</sub>&B<sub>40</sub>(3), as depicted in Fig. 3. Here the yellow and blue colors represent electron accumulation and depletion regions, respectively. From the charge density variations of 1–3, which are induced by the adsorption of Li atoms onto B<sub>40</sub>, it is obvious that charge transfer from Li atom to B<sub>40</sub> indeed takes place upon Li decoration.

Figure 4 shows the frontier canonical molecular orbitals (CMOs) of 1–3, which are compared with those of  $D_{2d}$  B<sub>40</sub>. Upon attachment of the first Li atom on B<sub>40</sub>, the lowest unoccupied molecular orbital (LUMO) of B<sub>40</sub> (Fig. 4d) becomes half-filled due to charge transfer, which are the singly occupied molecular orbitals (SOMOs) in 1 and 2 (Fig. 4a,b). Note these three CMOs are virtually identical. Likewise, in line with their lower symmetry, LUMO (a<sub>1</sub><sup>′</sup>) of 1 and LUMO (b<sub>2</sub>) of 2 correspond to the degenerate LUMO + 1 of  $D_{2d}$  B<sub>40</sub>. In  $D_{2d}$  Li<sub>6</sub>&B<sub>40</sub>(3) (Fig. 4c), six electrons are transferred from Li to the B<sub>40</sub> cage, which successively occupy the LUMO and degenerate LUMO + 1 of  $D_{2d}$  B<sub>40</sub>. The latter LUMO + 1 become the highest occupied molecular orbital (HOMO) in 3, which are also doubly degenerated due to the same high symmetry of  $D_{2d}$ . As a consequence, the LUMO + 2 (b<sub>1</sub>) of  $D_{2d}$  B<sub>40</sub> becomes the LUMO in 3. The spatial distributions of the frontier CMOs in these four species are remarkably similar, demonstrating the electronic robustness of the B<sub>40</sub> cage motif along this series. The calculated Wiberg bond indices associated with Li are all less than 0.30 in 1–3, which further indicate that Li does not participate in the covalent bonding of B<sub>40</sub>.



**Figure 4.** Molecular orbital pictures of the LUMOs and HOMOs (or SOMOs) of  $C_s$  Li&B<sub>40</sub>(1),  $C_{2v}$  Li&B<sub>40</sub>(2), and  $D_{2d}$  Li<sub>6</sub>&B<sub>40</sub>(3), as compared with those of borospherene  $D_{2d}$  B<sub>40</sub>. The orbitals are aligned according to their shapes.

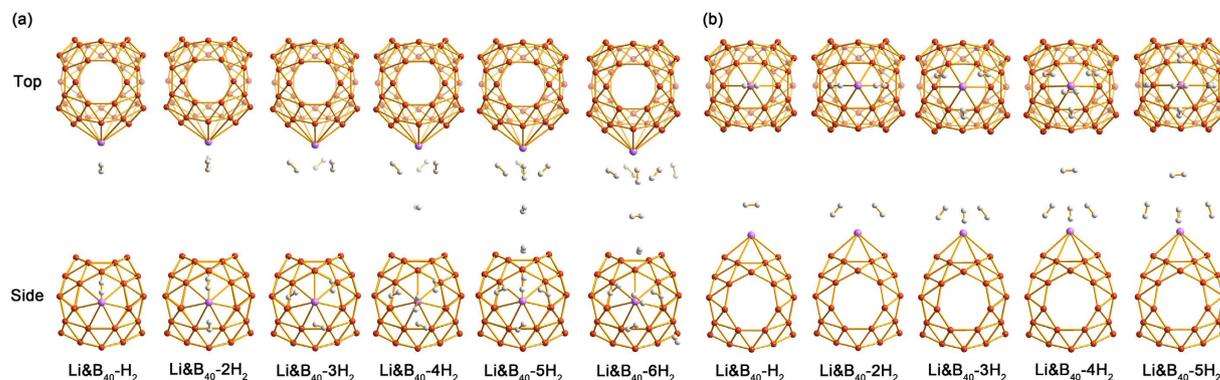
The calculated HOMO-LUMO energy gaps of **1**, **2**, and **3** are 1.39, 1.41, and 1.42 eV, respectively, which differ from that of  $D_{2d}$  B<sub>40</sub> (3.13 eV at the same level), suggesting the possibility to tune the electronic properties of borospherenes via metal-decoration, similar to the case of  $C_{60}$  buckyball.

**H<sub>2</sub> Adsorption on Li-Decorated B<sub>40</sub>.** The  $C_s$  Li&B<sub>40</sub>(**1**),  $C_{2v}$  Li&B<sub>40</sub>(**2**), and  $D_{2d}$  Li<sub>6</sub>&B<sub>40</sub>(**3**) clusters are well-defined molecular systems for the adsorption of H<sub>2</sub> molecules. H<sub>2</sub> can be added successively to the systems, from one H<sub>2</sub> molecule up to six per Li site. The largest complex corresponds to the adsorption of 34 H<sub>2</sub> molecules to **3**, that is, Li<sub>6</sub>&B<sub>40</sub>(**3**)-34 H<sub>2</sub>. Tables S1 and 2 summarize the AEs and the equilibrium Li-B, Li-H, and H-H distances for the Li<sub>*m*</sub>-B<sub>40</sub>-*n*H<sub>2</sub> (*m* = 1, 6; *n* = 1–34) complexes.

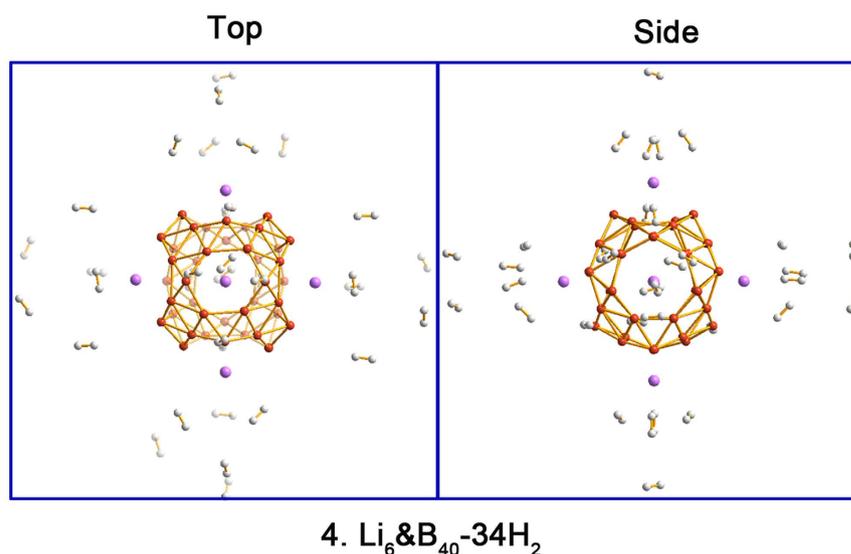
When one H<sub>2</sub> molecule is introduced to **1**, due to the polarization interaction between the charged Li atom and the H<sub>2</sub> molecule, the Li-B bond distance is slightly enlarged (by 0.01 Å) to 2.35 Å. The H-H distance is found to be 0.76 Å. The equilibrium Li-H distance is 1.97 Å, which is comparable to the value of 2.04 Å in the case of a free Li<sup>+</sup> ion interacting with H<sub>2</sub><sup>46</sup>. The AE of the first H<sub>2</sub> to **1** is 0.25 eV, which is in quantitative agreement with that in Li<sup>+</sup>H<sub>2</sub> (0.25 eV)<sup>46</sup>.

With more H<sub>2</sub> molecules being attached to **1**, the average AE of H<sub>2</sub>, consecutive AE of H<sub>2</sub>, the Li-B distance, and the distances between H<sub>2</sub> and Li change accordingly. As shown in Table S1 and Fig. 5a, a single Li atom in **1**, coated on a heptagonal hole, can adsorb up to six H<sub>2</sub> molecules with an average AE of 0.11 eV/H<sub>2</sub>. From one to six H<sub>2</sub>, the average AE decreases from 0.25 to 0.11 eV/H<sub>2</sub>, whereas the consecutive AE decrease from 0.25 to 0.05 eV/H<sub>2</sub>. This effect may be partially due to the steric repulsion<sup>47</sup> when the number of H<sub>2</sub> molecules increases. In line with this trend, the Li-B distances are elongated gradually from 2.35 to 2.43 Å. However, the H-H bond distance is nearly constant in the range of 0.75–0.76 Å, which is the value of free H<sub>2</sub> molecule, consistent with the nature of molecular adsorption. The Li-H distances span a rather wide range from 1.97 to 2.91 Å. Notably, there is an abrupt increase in the Li-H distances from 1–3 H<sub>2</sub> to 1–4 H<sub>2</sub>, so that the first three H<sub>2</sub> are closer to the Li site than the next three. In other words, the adsorption of the first three H<sub>2</sub> molecules forms an inner core with Li, upon which the additional H<sub>2</sub> molecules adsorb loosely. The data of consecutive AE confirm this to be indeed the case: The first three H<sub>2</sub> possess an AE of 0.25–0.11 eV, in contrast to 0.04–0.05 eV for the next three (Table S1). In fact, the structure of 1–4 H<sub>2</sub> can be constructed on the basis of 1–3 H<sub>2</sub> by adding one H<sub>2</sub> on the top of Li. However, when the fifth and sixth H<sub>2</sub> are put on successively in 1–5 H<sub>2</sub> and 1–6 H<sub>2</sub>, they flee away after structural optimization as shown in Fig. 5a. Therefore, the Li site in **1** may adsorb three H<sub>2</sub> molecules comfortably, whereas additional H<sub>2</sub> are only physisorbed.

Basically, the adsorption of H<sub>2</sub> on **2** is rather similar to that on **1**. Up to five H<sub>2</sub> molecules may be adsorbed on the Li site in **2** (Fig. 5b). Again, the first three H<sub>2</sub> are located closely to Li, with the fourth H<sub>2</sub> being situated symmetrically on top of Li at a substantially larger distance. For the 2–5 H<sub>2</sub> case, there is a structural rearrangement



**Figure 5.** Top and side views of the optimized configurations for successive addition of  $H_2$  molecules on (a)  $Li_6B_{40}(1)$  with a Li-coated heptagonal hole and (b)  $Li_6B_{40}(2)$  with a Li-coated hexagonal hole.



**Figure 6.** Top and side views of the optimized configuration of  $Li_6B_{40}-34H_2(4)$ . The B atom is in orange, Li in purple, and H in white.

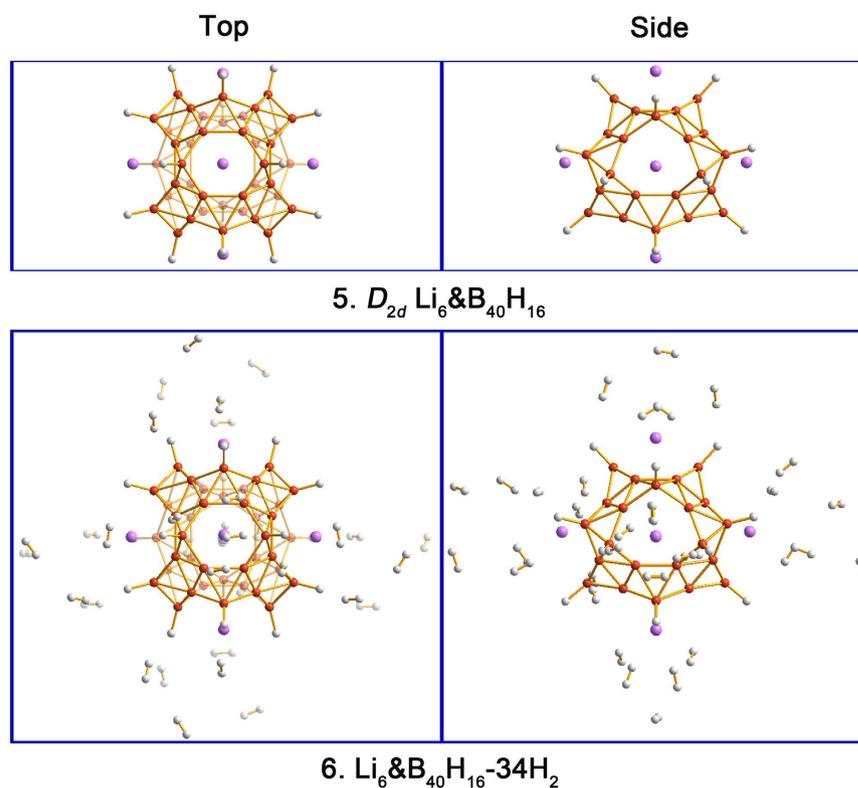
for the  $H_2$  molecules, suggesting that this Li site can potentially adsorb up to four  $H_2$  molecules at a reasonable strength. Nonetheless, the fifth  $H_2$  only interact with Li loosely. On the basis of the consecutive AEs (0.22–0.17 eV for the first three  $H_2$ ; Table S1), we conclude that the Li site in **2** is capable of adsorbing at least three  $H_2$  molecules with further possibility for a fourth, whereas additional  $H_2$  molecules should be considered physisorbed.

Based on the above results of  $H_2$  adsorption on single Li-decorated  $B_{40}$ , we constructed and optimized the  $H_2$  adsorption configurations on the  $Li_6B_{40}(3)$  complex, which aims at exploring the hydrogen storage capacity. The starting configurations were constructed by attaching the corresponding  $H_2$  molecules around Li atoms above the 4 heptagonal and 2 hexagonal holes on the  $B_{40}$  cage. Successively, 6  $H_2$ , 12  $H_2$ , 18  $H_2$ , 24  $H_2$ , and up to 34  $H_2$  are adsorbed on  $Li_6B_{40}(3)$ , whose optimized structures are shown in Fig. S2 and 6. The former four cases correspond to the adsorption of one to four  $H_2$  on each Li site. For the 34  $H_2$  case, that is,  $Li_6B_{40}-34H_2(4)$ , 6  $H_2$  are adsorbed on each heptagonal Li site and 5  $H_2$  are on each hexagonal Li site, as depicted in Fig. 6. The total interaction energy of 34  $H_2$  in **4** is 3.43 eV, yielding an average AE of 0.10 eV/ $H_2$ . The calculated consecutive AEs are collected in Table 2, which reflects the adsorption nature more faithfully. Similar to **1** and **2**, the first three  $H_2$  for each Li in **4** are located close to the adsorption site, resulting in the 3–6  $H_2$ , 3–12  $H_2$ , and 3–18  $H_2$  complexes with reasonable AEs of 0.18–0.11 eV/ $H_2$ . Additional  $H_2$  molecules in 3–24  $H_2$  and **4** complexes are farther away for the Li sites with relatively weak AEs of 0.03–0.05 eV/ $H_2$ , hinting physisorption in nature. In summary, up to 34  $H_2$  molecules may be adsorbed in **4**, among which the first 18 interact in moderate strength with the Li site, corresponding to a gravimetric density of 7.1 wt%.

**$H_2$  Adsorption on Li-Decorated  $B_{40}H_{16}$ .** Borospherene  $B_{40}$  as an electron-deficient system<sup>36</sup> is generally considered to be more reactive than  $C_{60}$ , we can thus engineer and passivate  $B_{40}$  at least partially with B–H bonds, which may benefit the adsorption and release of  $H_2$  molecules.  $B_{40}$  has 16 tetracoordinate and 24 pentacoordinate sites, where the former are anticipated to be more reactive. A model  $B_{40}H_{16}$  cage cluster is readily constructed via

system	AE/H <sub>2</sub> (eV) (average)	AE/H <sub>2</sub> (eV) (consecutive)	R <sub>Li-B</sub> (Å)	R <sub>Li-H</sub> (Å)	R <sub>H-H</sub> (Å)
Li <sub>6</sub> &B <sub>40</sub> -6H <sub>2</sub>	0.18	0.18	2.34	1.99	0.75
Li <sub>6</sub> &B <sub>40</sub> -12H <sub>2</sub>	0.17	0.17	2.37	2.00	0.76
Li <sub>6</sub> &B <sub>40</sub> -18H <sub>2</sub>	0.15	0.11	2.41	2.08	0.76
Li <sub>6</sub> &B <sub>40</sub> -24H <sub>2</sub>	0.12	0.03	2.41	2.54	0.76
Li <sub>6</sub> &B <sub>40</sub> -34H <sub>2</sub>	0.10	0.05	2.42	2.94	0.76

**Table 2.** Calculated Average and Consecutive Adsorption Energy (AE) of H<sub>2</sub>, Bond Distances of Li–B, Li–H, and H–H in the Li<sub>6</sub>&B<sub>40</sub>-*n*H<sub>2</sub> (*n* = 6, 12, 18, 24, 34) Complexes.

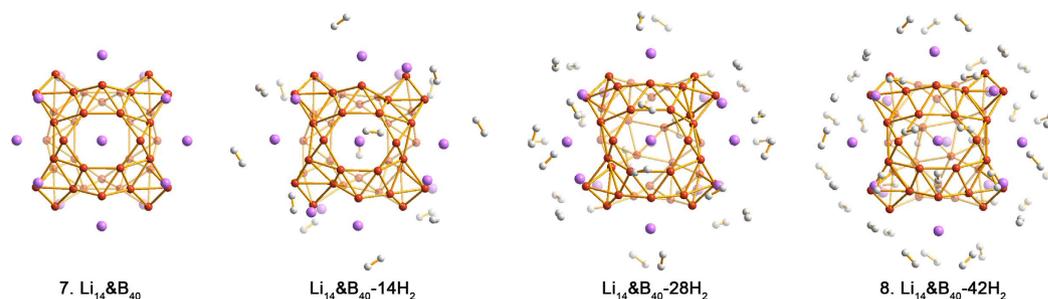


**Figure 7.** Top and side views of the optimized configurations of Li<sub>6</sub>&B<sub>40</sub>H<sub>16</sub>(5) and Li<sub>6</sub>&B<sub>40</sub>H<sub>16</sub>-34H<sub>2</sub>(6). The B atom is in orange, Li in purple, and H in white.

16 B–H bonds for the tetracoordinate B sites, which can also be decorated with six Li atoms, resulting in a *D*<sub>2d</sub> Li<sub>6</sub>&B<sub>40</sub>H<sub>16</sub>(5) complex as depicted in Fig. 7. The Li–B distance in 5 remains to be 2.33 Å, which is very close to that in 3. In complex 5, each Li atom carries a charge of 0.88 |e|. Interestingly, the B–H bonds markedly alter the Li-decoration properties in 5 and the average BE of Li atom now increases to 4.17 eV per Li, compared to 3.07 eV in Li<sub>6</sub>&B<sub>40</sub>(3).

Li<sub>6</sub>&B<sub>40</sub>H<sub>16</sub>(5) can also adsorb from 6 H<sub>2</sub>, 12 H<sub>2</sub>, 18 H<sub>2</sub>, 24 H<sub>2</sub>, and up to 34 H<sub>2</sub> molecules, resulting in a series of 5-*n*H<sub>2</sub> complexes (Fig. S3). The optimized structure for Li<sub>6</sub>&B<sub>40</sub>H<sub>16</sub>-34H<sub>2</sub>(6) is shown in Fig. 7. Note that hydrogen remains in the molecular state with a uniform H–H distance of 0.75 Å in all 5-*n*H<sub>2</sub> species. For the first 6 H<sub>2</sub> molecules in 5-6H<sub>2</sub>, the average AE amounts to 0.22 eV/H<sub>2</sub>. The average Li–B and Li–H distances, 2.33 and 1.97 Å, respectively, are almost the same as those in Li<sub>6</sub>&B<sub>40</sub>-6H<sub>2</sub> (that is, 3-6H<sub>2</sub>). With further H<sub>2</sub> adsorption, the average AEs for the first 18 H<sub>2</sub> in 5-*n*H<sub>2</sub> decrease slightly down to 0.17 eV/H<sub>2</sub>, which are in the ideal thermodynamic range for reversible hydrogen storage<sup>10,11</sup>. The Li<sub>6</sub>&B<sub>40</sub>H<sub>16</sub>(5) complex thus behaves rather similar to Li<sub>6</sub>&B<sub>40</sub>(3) in terms of hydrogen storage properties, except for the B–H passivation in 5. The 18 “core” H<sub>2</sub> in Li<sub>6</sub>&B<sub>40</sub>H<sub>16</sub>-34H<sub>2</sub>(6) represents a gravimetric density of 6.5 wt%, where an additional 8.6 wt% of dissociated H atoms and loosely physisorbed 16 H<sub>2</sub> are not counted.

**On the Possibility of Doubling the H<sub>2</sub> Adsorption Sites: Li-Decorated Triangular B<sub>6</sub> Corners.** To further improve the hydrogen storage capacity of Li-decorated B<sub>40</sub>, we also attempted to place Li atoms on top of the close-packing, triangular B<sub>6</sub> corner sites of the cube-like B<sub>40</sub> cage. As a test case, adsorption of a single H<sub>2</sub> molecule on a corner Li site is optimized (Fig. S4). The BE of Li is 1.87 eV, which is lower than those in Li&B<sub>40</sub>(1) and Li&B<sub>40</sub>(2), but the value still represents a reasonable strength. In fact, it is comparable to the corresponding value for C<sub>60</sub> (1.80 eV)<sup>13</sup>. Moreover, the AE for the first H<sub>2</sub> amounts to 0.28 eV, which is comparable to and even slightly



**Figure 8.** Optimized configurations of  $\text{Li}_{14}\text{B}_{40}$  (7) and its  $\text{H}_2$  adsorption complexes:  $\text{Li}_{14}\text{B}_{40}-14\text{H}_2$ ,  $\text{Li}_{14}\text{B}_{40}-28\text{H}_2$ , and  $\text{Li}_{14}\text{B}_{40}-42\text{H}_2$  (8). The B atom is in orange, Li in purple, and H in white.

greater than that in  $\text{Li}\text{B}_{40}(1)-\text{H}_2$  (0.25 eV) or  $\text{Li}\text{B}_{40}(2)-\text{H}_2$  (0.22 eV; Table S1). The above data hint that a triangular  $\text{B}_6$  corner site on  $\text{B}_{40}$  is as promising as, if not better than, a hexagonal/heptagonal site for hydrogen storage. The calculated consecutive AEs of  $\text{Li}\text{B}_{40}-n\text{H}_2$  ( $n = 1-3$ ) with  $\text{H}_2$  molecules adsorbed on a corner Li site are at the range of 0.22–0.28 eV/ $\text{H}_2$ . For  $\text{Li}_8\text{B}_{40}-n\text{H}_2$  ( $n = 8, 16, 24$ ) with  $\text{H}_2$  molecules adsorbed on eight corner Li site, the consecutive AEs change from 0.17 to 0.36 eV/ $\text{H}_2$ , which are ideal for reversible hydrogen storage and release.

In this way, one can more than double the number of sites for Li-decoration from six in  $\text{Li}_6\text{B}_{40}(3)$  and  $\text{Li}_6\text{B}_{40}\text{H}_{16}(5)$  to fourteen in  $\text{Li}_{14}\text{B}_{40}(7)$ , owing to the eight triangular  $\text{B}_6$  corners (versus six hexagonal/heptagonal holes). The optimized structure of  $\text{Li}_{14}\text{B}_{40}(7)$  is shown in Fig. 8. Here, upon Li decoration, the boron structure distorts considerably from the free-standing  $\text{B}_{40}$  borospherene, but the cage motif maintains. The average BE is 2.57 eV/Li. Following the strategy for  $\text{Li}_6\text{B}_{40}(3)$  and  $\text{Li}_6\text{B}_{40}\text{H}_{16}(5)$ , we build a series of model complexes: 7–14  $\text{H}_2$ , 7–28  $\text{H}_2$ , and  $\text{Li}_{14}\text{B}_{40}-42\text{H}_2(8)$ , whose optimized structures are depicted in Fig. 8. The calculated average AE for the first 14  $\text{H}_2$  in 7–14  $\text{H}_2$  is 0.32 eV/ $\text{H}_2$ , for the second 14  $\text{H}_2$  in 7–28  $\text{H}_2$  is 0.22 eV/ $\text{H}_2$ , and for the third 14  $\text{H}_2$  in  $\text{Li}_{14}\text{B}_{40}-42\text{H}_2(8)$  is 0.12 eV/ $\text{H}_2$ , suggesting that all these  $\text{H}_2$  molecules are thermodynamically favorable for a hydrogen storage material<sup>10,11</sup>. For the extreme case of 8, a maximum gravimetric density of 13.8 wt% is obtained. We do not exclude the possibility of further  $\text{H}_2$  adsorption onto the 8 complex, albeit those additional  $\text{H}_2$  are anticipated to interact rather loosely with the Li sites.

## Concluding Remarks

In conclusion, we have carried out a comprehensive density-functional study on the lithium-decoration of  $\text{B}_{40}$  borospherene and the potential utilization of  $\text{Li}-\text{B}_{40}$  complexes as a novel nanomaterial for hydrogen storage. We showed that all six heptagonal and hexagonal holes on  $\text{B}_{40}$  surface can be decorated with Li atoms and each Li site is capable of adsorbing up to six or five  $\text{H}_2$  molecules. This results in an ultimate  $\text{Li}_6\text{B}_{40}-34\text{H}_2$  complex, in which 18  $\text{H}_2$  are bound to Li sites with ideal adsorption energies of 0.11–0.18 eV per  $\text{H}_2$ , corresponding to a gravimetric density of 7.1 wt%. The additional 16  $\text{H}_2$  are physisorbed in nature. We further showed that the eight close-packing, triangular  $\text{B}_6$  corner sites on the  $\text{B}_{40}$  cage are also readily decorated with Li, which more than double the number of sites for hydrogen storage. The corresponding  $\text{Li}_{14}\text{B}_{40}-42\text{H}_2$  complex can store all 42  $\text{H}_2$  molecules at adsorption energies of 0.12–0.32 eV per  $\text{H}_2$ , suggesting a maximum gravimetric density of 13.8 wt%. The  $\text{Li}-\text{B}_{40}-\text{H}_2$  complexes as a hydrogen storage material differ markedly from the prior  $\text{Li}-\text{C}_{60}-\text{H}_2$  and  $\text{Ti}-\text{B}_{40}-\text{H}_2$  systems. The  $\text{Li}-\text{C}_{60}-\text{H}_2$  complex<sup>13</sup> adsorbs  $\text{H}_2$  rather loosely and is thus not efficient for hydrogen storage, whereas the  $\text{Ti}-\text{B}_{40}-\text{H}_2$  complex<sup>40</sup> bounds  $\text{H}_2$  too strongly, for which a substantial portion of  $\text{H}_2$  stored are not reversible for release. In fact, preliminary attempts also suggest that the structural integrity of  $\text{B}_{40}$  unit is maintained when they are allowed to interact with each other. Considering the presence of chemical bondings between them, we forecast it is possible to construct boron-based nanomaterials for hydrogen storage using lithium-decorated  $\text{B}_{40}$  unit as a building block or connecting the exohedral metalloborospherene with organic linkers. And the hydrogen storage capacity of the boron-based nanomaterials could be better than previously reported carbon-based counterparts.

## Methods

All calculations were based on DFT, using a plane-wave basis set with the Projector Augmented Wave (PAW)<sup>48,49</sup> pseudopotential method as implemented in the Vienna *ab initio* Simulation Package (VASP)<sup>50,51</sup>. Generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE)<sup>52</sup> functional was adopted to treat the electron exchange correlation. The GGA-PBE method has been previously utilized to treat Li-decorated fullerenes and heterofullerenes for hydrogen storage<sup>19,53</sup> which is thus a suitable choice for our current system. The dispersion corrected DFT (DFT-D) scheme<sup>54–56</sup> was used to describe the van der Waals (vdW) interaction. The supercell approach was used, where the  $\text{B}_{40}$ -based systems were placed at the center of a  $25 \times 25 \times 25 \text{ \AA}^3$  vacuum space. And only the  $\Gamma$  point was used to sample the Brillouin zone. The energy cutoff for the plane-wave basis set was set to 500 eV. All structures were fully relaxed until the force acting on each atom was less than  $10^{-2} \text{ eV/\AA}$  and a tolerance in total energy was at least  $10^{-4} \text{ eV}$ .

The binding energies (BEs) for the Li-decorated  $\text{B}_{40}$  are defined as  $E_b = -(E_{\text{Li-B}_{40}} - E_{\text{B}_{40}} - mE_{\text{Li}})/m$ , where  $E_{\text{Li-B}_{40}}$  is the total energy of Li-decorated  $\text{B}_{40}$ ,  $E_{\text{B}_{40}}$  and  $E_{\text{Li}}$  are the total energies of an isolated  $\text{B}_{40}$  and a Li atom, respectively, and  $m$  is the number of Li atoms. Similarly, the average AE for  $\text{H}_2$  is defined as  $E_a = -(E_{\text{Li-B}_{40}-n\text{H}_2} - E_{\text{Li-B}_{40}} - nE_{\text{H}_2})/n$  and the consecutive AE is defined as  $\Delta E = -(E_{\text{Li-B}_{40}-n\text{H}_2} - E_{\text{Li-B}_{40}-(n-1)\text{H}_2} - E_{\text{H}_2})$ , where  $E_{\text{Li-B}_{40}-n\text{H}_2}$  and  $E_{\text{Li-B}_{40}-(n-1)\text{H}_2}$  are the total energies of  $n$  and  $(n-1)$   $\text{H}_2$  adsorbed on the Li-decorated  $\text{B}_{40}$ , respectively.  $E_{\text{Li-B}_{40}}$  also represents the total energy

of Li-decorated  $B_{40}$ ,  $E_{H_2}$  is the total energy of isolated  $H_2$  molecule, and  $n$  stands for the number of adsorbed  $H_2$  molecules.

We note that for comparison with  $D_{2d}B_{40}$  in our previous work (ref. 36), the HOMO-LUMO energy gaps of **1**, **2**, and **3** were calculated using the Gaussian 09 package<sup>57</sup>, which is usually used for calculations on the isolated molecules. And the corresponding structures were optimized at the PBE0 levels with the 6-311 + G\* basis set<sup>58,59</sup>, which has been benchmarked in prior works as a reliable method for boron clusters.

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## Author Contributions

H.B., W.H., H.-J.Z. and S.-D.L. designed the project. H.B., B.B., L.Z. and Y.-W.M. constructed the structures and performed the electronic structure calculations. B.B. and L.Z. prepared all the figures and tables. H.B., W.H., H.-J.Z. and S.-D.L. analysed the data and wrote the paper. All authors discussed the results and made comments and edits to the manuscript.

## Additional Information

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