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

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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. One bottleneck of using hydrogen for vehicular applications is the lack of safe and efficient hydrogen storage materials 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. 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. 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, as well as their boron-, nitrogen- and beryllium-substituted nanostructures, 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_{60}B_{12} may be as high as 9 wt% [13]. Yildirim et al. revealed that Ti-coated single-walled carbon nanotubes can store 8 wt% of H_{2} [23]. To avoid the clustering problem of transition metal atoms on the surface of carbon nanostructures, Yoon and co-workers 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 C_{60}[Ca,] with an AE of 0.2–0.4 eV/H_{2}. Through first-principles computations, Sun et al. predicted that Li-decorated fullerene C_{60}[Li,C_{60}] can store up to 9 wt% of H_{2} at 0.075 eV/H_{2}. Furthermore, Yoshida et al. measured the hydrogen absorption of Li_{12}C_{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_{12}C_{60}) and Li_{12}C_{60}-H_{2} 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 [15]. Subsequently, another experimental results 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.

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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 were studied, as were relevant model nanostructures, such as boron monolayer sheets, fullerenes, and nanotubes. In particular, following the proposal of the celebrated I$_{h}$ C$_{60}$ buckyball, 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 = Li, Na, K, Be, Mg, Ca, Sc, Ti, and V)\textsuperscript{25,31–33}. However, B$_{80}$ was subsequently found to favor core-shell type structures at various theoretical levels\textsuperscript{34,35}. 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, $D_{3d}$ B$_{40}$ and $D_{3d}$ B$_{40}$, were observed in a combined experimental and theoretical study, marking the onset of the borosphere chemistry, whose future development may be envisioned to parallel that of the fullerenes. Endohedral M@B$_{80}$ (M = Ca, Sr) and exohedral M&B$_{40}$ (M = Be, Mg) metalloborospherenes were also predicted, which further support the structural, electronic, and chemical robustness of the B$_{80}$ borosphere\textsuperscript{36}. Closely following B$_{80}$ chiral B$_{80}$, B$_{80}^{+}$, and B$_{80}^{2+}$ borospherenes were also studied\textsuperscript{37,38}, which expand the borosphere 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-pack B$_{3}$ 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.\textsuperscript{40} 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\textsuperscript{41,42}. 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\textsuperscript{28,29,43,44}. 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$_{m}$-B$_{40}$-nH$_{2}$, which have an AE value that is either rather small (0.075 eV)\textsuperscript{35} or too large (up to 0.82 eV)\textsuperscript{40} 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$_{Li}$&B$_{40}$(1), C$_{Li}$&B$_{40}$(2), up to $D_{3d}$ Li&B$_{40}$(3). The Li&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&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-pack, triangular B$_{3}$ 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\textsuperscript{36}, $D_{3d}$ B$_{40}$ (I$_{h}$), 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$_{60}$ (I$_{h}$) (3.02 eV) calculated at the same level. All the valence electrons in B$_{40}$ are either delocalized σ or π 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$_{2}$H$_{2}$, H$_{2}@$B$_{40}$ and 2H$_{2}@$B$_{40}$ are shown in Fig. 1. In the C$_{2}$ B$_{2}$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 exothermal 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$_{40}$ borosphere 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\textsuperscript{43}. As a comparison, our calculation results show that the dissociative AE of a single H$_{2}$ for C$_{60}$H$_{2}$ is only ~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 ~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 exothermal C$_{Li}$ Li&B$_{40}$(1), in which Li caps a heptagon, turns out to be more stable by 0.20 eV with respect to C$_{Li}$ 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, dimer (0.95 eV), and in the Li bulk (1.63 eV)\textsuperscript{15}. 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
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\(^1\).

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

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

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Li₆&B₄₀ 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 CsLi&B₄₀(1), C₂ᵥLi&B₄₀(2), and D₂dLi₆&B₄₀(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 B₄₀, it is obvious that charge transfer from Li atom to B₄₀ indeed takes place upon Li decoration.

Figure 4 shows the frontier canonical molecular orbitals (CMOs) of 1–3, which are compared with those of D₂dB₄₀. Upon attachment of the first Li atom on B₄₀, the lowest unoccupied molecular orbital (LUMO) of B₄₀ (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') of 1 and LUMO (b) of 2 correspond to the degenerate LUMO + 1 of D₂dB₄₀. In D₂dLi₆&B₄₀(3) (Fig. 4c), six electrons are transferred from Li to the B₄₀ cage, which successively occupy the LUMO and degenerate LUMO + 1 of D₂dB₄₀. 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 D₂d. As a consequence, the LUMO + 2 (b) of D₂dB₄₀ 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 B₄₀ 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 B₄₀.

![Figure 2](image2.png)

**Figure 2.** Top and side views of the optimized configurations of CsLi&B₄₀(1), C₂ᵥLi&B₄₀(2), and D₂dLi₆&B₄₀(3), in which one Li atom is coated on a heptagonal hole of B₄₀, 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|) |
|-----------------|------------|--------------|-----------------|
| CsLi&B₄₀(1)     | 3.08       | 2.34         | 0.88            |
| C₂ᵥLi&B₄₀(2)    | 2.88       | 2.33         | 0.87            |
| D₂dLi₆&B₄₀(3)   | 3.07       | 2.33         | 0.87            |

**Table 1.** Calculated Binding Energy (BE) of Li to B₄₀, Li–B Bond Distance, and Atomic Charge on Li Atom for Li&B₄₀(1), Li&B₄₀(2), and Li₆&B₄₀(3).

![Figure 3](image3.png)

**Figure 3.** Top views of the isosurface of charge density differences of CsLi&B₄₀(1), C₂ᵥLi&B₄₀(2), and D₂dLi₆&B₄₀(3). Yellow color represents the electron accumulation region, and blue represents the electron depletion region.
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_{40} (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$_2$ Adsorption on Li-Decorated B$_{40}$.** The C$_{2v}$ Li&B$_{40}$(1), C$_{2v}$ Li&B$_{40}$(2), and D$_{2d}$ Li$_6$&B$_{40}$(3) clusters are well-defined molecular systems for the adsorption of H$_2$ molecules. H$_2$ can be added successively to the systems, from one H$_2$ molecule up to six per Li site. The largest complex corresponds to the adsorption of 34 H$_2$ molecules to 3, that is, Li$_6$&B$_{40}$-34H$_2$. Tables S1 and 2 summarize the AEs and the equilibrium Li–B, Li–H, and H–H distances for the Li$_m$-B$_{40}$-nH$_2$ ($m=1, 6; n=1–34$) complexes.

When one H$_2$ molecule is introduced to 1, due to the polarization interaction between the charged Li atom and the H$_2$ 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$^+$ ion interacting with H$_2$.

The AE of the first H$_2$ to 1 is 0.25 eV, which is in quantitative agreement with that in Li$^+$H$_2$ (0.25 eV).

With more H$_2$ molecules being attached to 1, the average AE of H$_2$ decreases, the Li–B distance, and the distances between H$_2$ 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$_2$ molecules with an average AE of 0.11 eV/H$_2$. From one to six H$_2$, the average AE decreases from 0.25 to 0.11 eV/H$_2$, whereas the consecutive AE decrease from 0.25 to 0.05 eV/H$_2$. This effect may be partially due to the steric repulsion when the number of H$_2$ 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$_2$ 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$_2$ to 1–4 H$_2$, so that the first three H$_2$ are closer to the Li site than the next three. In other words, the adsorption of the first three H$_2$ molecules forms an inner core with Li, upon which the additional H$_2$ molecules adsorb loosely. The data of consecutive AE confirm this to be indeed the case: The first three H$_2$ 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$_2$ can be constructed on the basis of 1–3 H$_2$ by adding one H$_2$ on the top of Li. However, when the fifth and sixth H$_2$ are put on successively in 1–5 H$_2$ and 1–6 H$_2$, they flee away after structural optimization as shown in Fig. 5a. Therefore, the Li site in 1 may adsorb three H$_2$ molecules comfortably, whereas additional H$_2$ are only physisorbed.

Basically, the adsorption of H$_2$ on 2 is rather similar to that on 1. Up to five H$_2$ molecules may be adsorbed on the Li site in 2 (Fig. 5b). Again, the first three H$_2$ are located closely to Li, with the fourth H$_2$ being situated symmetrically on top of Li at a substantially larger distance. For the 2–5H$_2$ case, there is a structural rearrangement...
for the H₂ molecules, suggesting that this Li site can potentially adsorb up to four H₂ molecules at a reasonable strength. Nonetheless, the fifth H₂ only interact with Li loosely. On the basis of the consecutive AEs (0.22–0.17 eV for the first three H₂; Table S1), we conclude that the Li site in 2 is capable of adsorbing at least three H₂ molecules with further possibility for a fourth, whereas additional H₂ molecules should be considered physisorbed.

Based on the above results of H₂ adsorption on single Li-decorated B₄₀, we constructed and optimized the H₂ adsorption configurations on the Li₆&B₄₀ complex, which aims at exploring the hydrogen storage capacity. The starting configurations were constructed by attaching the corresponding H₂ molecules around Li atoms above the 4 heptagonal and 2 hexagonal holes on the B₄₀ cage. Successively, 6 H₂, 12 H₂, 18 H₂, 24 H₂, and up to 34 H₂ are adsorbed on Li₆&B₄₀(3), whose optimized structures are shown in Fig. S2 and 6. The former four cases correspond to the adsorption of one to four H₂ on each Li site. For the 34 H₂ case, that is, Li₆&B₄₀-34 H₂(4), 6 H₂ are adsorbed on each heptagonal Li site and 5 H₂ are on each hexagonal Li site, as depicted in Fig. 6. The total interaction energy of 34 H₂ in 4 is 3.43 eV, yielding an average AE of 0.10 eV/H₂. The calculated consecutive AEs are collected in Table 2, which reflects the adsorption nature more faithfully. Similar to 1 and 2, the first three H₂ for each Li in 4 are located close to the adsorption site, resulting in the 3–6 H₂, 3–12 H₂, and 3–18 H₂ complexes with reasonable AEs of 0.18–0.11 eV/H₂. Additional H₂ molecules in 3–24 H₂ and 4 complexes are farther away for the Li sites with relatively weak AEs of 0.03–0.05 eV/H₂, hinting physisorption in nature. In summary, up to 34 H₂ 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%.

**H₂ Adsorption on Li-Decorated B₄₀H₁₆** Borospherene B₄₀ as an electron-deficient system is generally considered to be more reactive than C₆₀, we can thus engineer and passivate B₄₀ at least partially with B–H bonds, which may benefit the adsorption and release of H₂ molecules. B₄₀ has 16 tetracoordinate and 24 pentacoordinate sites, where the former are anticipated to be more reactive. A model B₄₀H₁₆ cage cluster is readily constructed via
16 B–H bonds for the tetracoordinate B sites, which can also be decorated with six Li atoms, resulting in a $D_{2d}$ $Li_6&B_{40}H_{16}(5)$ 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 $Li_6&B_{40}(3)$.

$Li_6&B_{40}H_{16}(5)$ can also adsorb from 6 $H_2$, 12 $H_2$, 18 $H_2$, 24 $H_2$, and up to 34 $H_2$ molecules, resulting in a series of $5-nH_2$ complexes (Fig. S3). The optimized structure for $Li_6&B_{40}H_{16}-34H_2(6)$ 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 $5-nH_2$ species. For the first 6 $H_2$ molecules in $5-6H_2$, the average AE amounts to 0.22 eV/$H_2$. The average Li–B and Li–H distances, 2.33 and 1.97 Å, respectively, are almost the same as those in $Li_6&B_{40}-6H_2$ (that is, 3–6$H_2$). With further $H_2$ adsorption, the average AEs for the first 18 $H_2$ in $5-nH_2$ decrease slightly down to 0.17 eV/$H_2$, which are in the ideal thermodynamic range for reversible hydrogen storage.\textsuperscript{10,11} The $Li_6&B_{40}H_{16}(5)$ complex thus behaves rather similar to $Li_6&B_{40}(3)$ in terms of hydrogen storage properties, except for the B–H passivation in 5. The 18 “core” $H_2$ in $Li_6&B_{40}H_{16}-34H_2(6)$ represents a gravimetric density of 6.5 wt%, where an additional 8.6 wt% of dissociated H atoms and loosely physisorbed 16 $H_2$ are not counted.

### Table 2. Calculated Average and Consecutive Adsorption Energy (AE) of $H_2$, Bond Distances of Li–B, Li–H, and H–H in the $Li_6&B_{40}-nH_2 (n = 6, 12, 18, 24, 34)$ Complexes.

| System        | $AE/H_2$(eV) (average) | $AE/H_2$(eV) (consecutive) | $R_{Li-B}$ (Å) | $R_{Li-H}$ (Å) | $R_{H-H}$ (Å) |
|---------------|------------------------|----------------------------|----------------|----------------|----------------|
| $Li_6&B_{40}-6H_2$ | 0.18                   | 0.18                      | 2.34           | 1.99           | 0.75           |
| $Li_6&B_{40}-12H_2$ | 0.17                   | 0.17                      | 2.37           | 2.00           | 0.76           |
| $Li_6&B_{40}-18H_2$ | 0.15                   | 0.11                      | 2.41           | 2.08           | 0.76           |
| $Li_6&B_{40}-24H_2$ | 0.12                   | 0.03                      | 2.41           | 2.54           | 0.76           |
| $Li_6&B_{40}-34H_2$ | 0.10                   | 0.05                      | 2.42           | 2.94           | 0.76           |

#### Figure 7. Top and side views of the optimized configurations of $Li_6&B_{40}H_{16}(5)$ and $Li_6&B_{40}H_{16}-34H_2(6)$. The B atom is in orange, Li in purple, and H in white.

### On the Possibility of Doubling the $H_2$ Adsorption Sites: Li-Decorated Triangular $B_6$ Corners.

To further improve the hydrogen storage capacity of Li-decorated $B_{40}$, we also attempted to place Li atoms on top of the close-packing, triangular $B_6$ corner sites of the cube-like $B_{40}$ cage. As a test case, adsorption of a single $H_2$ molecule on a corner Li site is optimized (Fig. S4). The BE of Li is 1.87 eV, which is lower than those in $Li&B_{40}(1)$ and $Li&B_{40}(2)$, but the value still represents a reasonable strength. In fact, it is comparable to the corresponding value for $C_{60}$ (1.80 eV)\textsuperscript{13}. Moreover, the AE for the first $H_2$ amounts to 0.28 eV, which is comparable to and even slightly
gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional was adopted to treat the
consecutive AEs change from 0.17 to 0.36 eV/H₂, which are ideal for reversible hydrogen storage and release.

obtained. We do not exclude the possibility of further H₂ adsorption onto the

approach was used, where the B₄₀-based systems were placed at the center of a 25

tion corrected DFT (DFT-D) scheme was used to describe the van der Waals (vdW) interaction. The supercell

Figure 8. Optimized configurations of Li₁₄&B₄₀(7) and its H₂ adsorption complexes: Li₁₄&B₄₀-14H₂,
Li₁₄&B₄₀-28H₂, and Li₁₄&B₄₀-42H₂(8). The B atom is in orange, Li in purple, and H in white.

Concluding Remarks
In conclusion, we have carried out a comprehensive density-functional study on the lithium-decoration of B₄₀
borospherene and the potential utilization of Li-B₄₀ complexes as a novel nanomaterial for hydrogen storage.
We showed that all six heptagonal and hexagonal holes on B₄₀ surface can be decorated with Li atoms and each
Li site is capable of adsorbing up to six or five H₂ molecules. This results in an ultimate Li₆&B₄₀-34H₂ complex,
in which 18 H₂ are bound to Li sites with ideal adsorption energies of 0.11–0.18 eV per H₂, corresponding to a
gravimetric density of 7.1 wt%. The additional 16 H₂ are physisorbed in nature. We further showed that the eight
close-packaging, triangular B₅ corner sites on the B₄₀ cage are also readily decorated with Li, which more than
double the number of sites for Li-decoration from six in Li₅&B₄₀(3) and
Li₈&B₄₀H₂(5) to fourteen in Li₁₄&B₄₀(7), owing to the eight triangular B₅ corners (versus six hexagonal/heptagonal
holes). The optimized structure of Li₈&B₄₀(7) is shown in Fig. 8. Here, upon Li decoration, the boron
structure distorts considerably from the free-standing B₄₀ borospherene, but the cage motif maintains. The average
BE is 2.57 eV/Li. Following the strategy for Li₅&B₄₀(3) and Li₈&B₄₀H₂(5), we build a series of model complexes:
7–14 H₂, 7–28 H₂, and Li₈&B₄₀-42H₂(8), whose optimized structures are depicted in Fig. 8. The calculated average
AE for the first 14 H₂ in 7–14 H₂, is 0.32 eV/H₂, for the second 14 H₂ in 7–28 H₂, is 0.22 eV/H₂, and for the third
14 H₂ in Li₁₄&B₄₀-42H₂(8) is 0.12 eV/H₂, suggesting that all these H₂ molecules are thermodynamically favorable
for a hydrogen storage material. For the extreme case of 8, a maximum gravimetric density of 13.8 wt% is
obtained. We do not exclude the possibility of further H₂ adsorption onto the 8 complex, albeit those additional
H₂ are anticipated to interact rather loosely with the Li sites.

Methods
All calculations were based on DFT, using a plane-wave basis set with the Projector Augmented Wave (PAW)
pseudopotential method as implemented in the Vienna ab initio Simulation Package (VASP). Generalized
gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) 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 which is thus a suitable choice for our current system. The dispersioncorrected DFT (DFT-D) scheme was used to describe the van der Waals (vdW) interaction. The supercell
approach was used, where the B₄₀-based systems were placed at the center of a 25 × 25 Å³ vacuum space.
And only the Γ 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 10⁻⁶ eV/Å and a
tolerance in total energy was at least 10⁻⁸ eV.
of Li-decorated B40, $E_{\text{H2}}$ 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 $D_{\text{Li}}, B40$ in our previous work (ref. 36), the HOMO-LUMO energy gaps of 1, 2, and 3 were calculated using the Gaussian 09 package$^5$, 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$^{5,19}$, which has been benchmarked in prior works as a reliable method for boron clusters.

References

1. Schlaphach, L. & Züttel, A. Hydrogen-storage materials for mobile applications. Nature 414, 353–358 (2001).
2. Cortright, R. D., Davada, R. R. & Dumesic, J. A. Hydrogen from catalytic reforming of biomass-derived hydrocarbons in liquid water. Nature 418, 964–967 (2002).
3. Coontz, R. & Hanson, B. Not So Simple. Science 305, 957 (2004).
4. Lubitz, W. & Tumas, W. Hydrogen: an overview. Chem. Rev. 107, 3990–3903 (2007).
5. Dresselhaus, M. S. & Thomas, L. I. Alternative energy technologies. Nature 414, 332–337 (2001).
6. Crabtree, G. W., Dresselhaus, M. S. & Buchanan, V. The hydrogen economy. Phys. Today 57, 39–44 (2004).
7. Eberle, U., Felderhoff, M. & Schüth, F. Chemical and physical solutions for hydrogen storage. Angew. Chem., Int. Ed. 48, 6608–6630 (2009).
8. Cohen, R. L. & Wernick, J. H. Hydrogen storage materials: properties and possibilities. Science 214, 1081–1087 (1981).
9. Graetz, I. New approaches to hydrogen storage. Chem. Soc. Rev. 38, 73–82 (2009).
10. Meng, S., Kaxiras, E. & Zhang, Z. Metal-diboride nanotubes as high-capacity hydrogen storage media. Nano Lett. 7, 663–667 (2007).
11. Murray, L. J., Dincă, M. & Long, J. R. Hydrogen storage in metal–organic frameworks. Chem. Soc. Rev. 38, 1294–1314 (2009).
12. Chandrakumar, K. R. S. & Ghosh, S. K. Alkali-metal-induced enhancement of hydrogen adsorption in C$_60$ fullerene: an ab initio study. Nano Lett. 8, 13–19 (2008).
13. Sun, Q., Jena, P., Wang, Q. & Marquez, M. First-principles study of hydrogen storage on Li$_x$C$_{60}$. J. Am. Chem. Soc. 128, 9741–9745 (2006).
14. Wang, Q., Sun, Q., Jena, P. & Kawazoe, Y. Theoretical study of hydrogen storage in Ca-coated fullerenes. J. Chem. Theory Comput. 5, 374–379 (2009).
15. Teprovich, I. J. A. et al. Synthesis and characterization of a lithium-doped fullerane (Li$_x$C$_{60}$H). for reversible hydrogen storage. Nano Lett. 12, 582–589 (2012).
16. Mauron, P. et al. Hydrogen sorption in Li$_x$C$_{60}$. J. Phys. Chem. C 117, 22595–22602 (2013).
17. Yoshida, A. et al. Reversible hydrogen storage/release phenomena on lithium fulleride (Li$_x$C$_{60}$) and their mechanistic investigation by solid-state NMR spectroscopy. J. Mater. Chem. 21, 9480–9482 (2011).
18. Yoon, M. et al. Calcium as the superior coating metal in functionalization of carbon fullerenes for high-capacity hydrogen storage. Phys. Rev. Lett. 100, 206806 (2008).
19. Wang, Q. & Jena, P. J. Density functional theory study of the interaction of hydrogen with Li$_x$C$_{60}$. Phys. Chem. Lett. 3, 1084–1088 (2012).
20. Sun, Q., Wang, Q. & Jena, P. Storage of molecular hydrogen in BN cage: energetics and thermal stability. Nano Lett. 5, 1273–1277 (2005).
21. Kim, Y. H. et al. Non-dissociative adsorption of H$_2$ molecules in light-element-doped fullerenes. Phys. Rev. Lett. 96, 086102 (2006).
22. Zhao, Y. F. et al. Boron-based organometallic nanostructures: hydrogen storage properties and structure stability. Nano Lett. 8, 157–161 (2008).
23. Yildirim, T. & Ciraci, S. Titanium-decorated carbon nanotubes as a potential high-capacity hydrogen storage medium. Phys. Rev. Lett. 94, 175501 (2005).
24. Pajkó, P., Yurim, Y. & Veziroglu, T. N. A review of hydrogen storage systems based on boron and its compounds. Int. J. Hydrogen Energ. 29, 1371–1376 (2004).
25. Orimo, S. I. et al. Complex hydrides for hydrogen storage. Chem. Rev. 107, 4111–4132 (2007).
26. Hazrati, E., Brocks, G. & de Wijs, G. A. First-principles study of LiBH$_4$ nanoclusters and their hydrogen storage properties. J. Phys. Chem. C 116, 18038–18047 (2012).
27. Li, M. et al. CA-coated boron fullerenes and nanotubes as superior hydrogen storage materials. Nano Lett. 9, 1944–1948 (2009).
28. Er, S., de Wijs, G. A. & Brocks, G. DFT study of planar boron sheets: a new template for hydrogen storage. J. Phys. Chem. C 113, 18962–18967 (2009).
29. Wang, J., Zhao, H. Y. & Liu, Y. Boron-double-ring sheet, fullerene, and nanotubes: potential hydrogen storage materials. ChemPhysChem 15, 3453–3459 (2014).
30. Swocki, N. G., Sadrazilov, A. & Yakobson, B. I. B$_{40}$ fullerene: an ab initio prediction of geometry, stability, and electronic structure. Phys. Rev. Lett. 98, 166804 (2007).
31. Li, Y. C. et al. Alkali-metal-doped B$_{40}$ as high-capacity hydrogen storage media. J. Phys. Chem. C 112, 19268–19271 (2008).
32. Wu, G., Wang, J. L., Zhang, X. Y. & Zhu, L. Y. Hydrogen storage on metal-coated B$_{40}$ buckyballs with density functional theory. J. Phys. Chem. C 113, 7052–7057 (2009).
33. Li, J. L., Hu, Z. S. & Yang, G. W. High-capacity hydrogen storage of magnesium-decorated boron fullerene. Chem. Phys. 392, 16–20 (2012).
34. Li, F. Y. et al. B$_{40}$ and B$_{101–103}$ clusters: remarkable stability of the core-shell structures established by validated density functionals. J. Chem. Phys. 136, 074302 (2012).
35. Goedecker, S., Hellmann, W. & Lenosky, T. Global minimum determination of the boron–oppenheimer surface within density functional theory. Phys. Rev. Lett. 95, 055501 (2005).
36. Zhai, H. J. et al. Observation of all-boron fullerene. Nature Chem. 6, 727–731 (2014).
37. Bai, H., Chen, Q., Zhai, H. J. & Li, S. D. Endohedral and exohedral metalloborospherenes: M@B$_{40}$ (M = Ca, Sr) and M&B$_{40}$ (M = Be, Mg). Angew. Chem., Int. Ed. 54, 941–945 (2015).
38. Chen, Q. et al. Experimental and theoretical evidence of an axially chiral borospheren. ACS Nano 9, 754–760 (2015).
39. Chen, Q. et al. Cage-like B$_{12}^-$ and B$_{12}^{2-}$: new chiral members of the borospheren family. Angew. Chem., Int. Ed. 54, 8160–8164 (2015).
40. Dong, H. L., Hou, T. J., Lee, S. T. & Li, Y. Y. New Ti-decorated B$_{40}$ fullerene as a promising hydrogen storage material. Sci. Rep. 5, 09952 (2015).
41. Targets for onboard hydrogen storage systems for light-duty vehicles. US Department of Energy Office of Energy Efficiency and Renewable Energy and The FreedomCAR and Fuel Partnership. (2009).
42. Churchard, A. J. et al. A multifaceted approach to hydrogen storage. Phys. Chem. Chem. Phys. 13, 16955–16972 (2011).
43. Srinivasu, K. & Ghosh, S. K. An ab initio investigation of hydrogen adsorption in li-doped closo-boranes. J. Phys. Chem. C 115, 1450–1456 (2011).
44. Tai, T. B. & Nguyen, M. N. A three-dimensional aromatic B$_{40}$Li$_8$ complex as a high capacity hydrogen storage material. Chem. Commun. 49, 913–915 (2013).
45. Pupysheva, O. V., Garajian, A. A. & Yakobson, B. I. Fullerene nanocage capacity for hydrogen storage. *Nano Lett.* **8**, 767–774 (2008).
46. Rao, B. K. & Jena, P. Hydrogen uptake by an alkali metal ion. *Europhys. Lett.* **20**, 307–312 (1992).
47. Pophristic, V. & Goodman, L. Hyperconjugation not steric repulsion leads to the staggered structure of ethane. *Nature* **411**, 565–568 (2001).
48.Blochl, P. E. Projector augmented-wave method. *Phys. Rev. B* **50**, 17953–17979 (1994).
49. Kresse, G. & Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **59**, 1758–1775 (1999).
50. Kresse, G. & Hafner, J. Normal-conserving and ultrasoft pseudopotentials for first-row and transition elements. *J. Phys.: Condens. Matter* **6**, 8245–8257 (1994).
51. Kresse, G. & Furthmüller, J. Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **54**, 11169–11186 (1996).
52. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **77**, 3865–3868 (1996).
53. Gao, Y., Wu, X. J. & Zeng, X. C. Designs of fullerene-based frameworks for hydrogen storage. *J. Mater. Chem. A* **2**, 5910–5914 (2014).
54. Wu, Q. & Yang, W. Empirical correction to density functional theory for van der waals interactions. *J. Chem. Phys.* **116**, 515–524 (2002).
55. Ottmann, F., Bechstedt, F. & Schmidt, W. G. Semiempirical van der waals correction to the density functional description of solids and molecular structures. *Phys. Rev. B* **73**, 205101 (2006).
56. Johnson, E. R., Mackie, I. D. & DiLabio, G. A. Dispersion interactions in density-functional theory. *J. Phys. Org. Chem.* **22**, 1127–1135 (2009).
57. Frisch, M. J. *et al.* Gaussian 09, Revision B.01 Gaussian, Inc., Wallingford, CT (2010).
58. Adamo, C. & Barone, V. Toward reliable density functional methods without adjustable parameters: the PBE0 model. *J. Chem. Phys.* **110**, 6158–6170 (1999).
59. Krishnan, R., Binkley, J. S., Seeger, R. & Pople, J. A. Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions. *J. Chem. Phys.* **72**, 650–654 (1980).

**Acknowledgements**

This work was supported by the Key Projects of the National Natural Science Foundation of China (No. 21336006), the National Key Technology R&D Program (No. 2013BAC14B04), the National Natural Science Foundation of China (No. 21573138 and 21243004), the Shanxi Province Science Foundation for Youths (No. 201601D202017), the Youth Foundation of Taiyuan University of Technology (No. 1205-04020202), the Scientific Research Fund for the Introduction of Talents from Taiyuan University of Technology (No. tyut-rc201519a), and the State Key Laboratory of Quantum Optics and Quantum Optics Devices (No. KF201402).

**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**

Supplementary information accompanies this paper at http://www.nature.com/srep

Competing financial interests: The authors declare no competing financial interests.

**How to cite this article**: Bai, H. *et al.* Lithium-Decorated Borospherene B_{40}: A Promising Hydrogen Storage Medium. *Sci. Rep.* **6**, 35518; doi: 10.1038/srep35518 (2016).

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