Hollow Li$_{20}$B$_{60}$ Cage: Stability and Hydrogen Storage

Jing Wang$^{1,2}$, Zhi-Jing Wei$^3$, Hui-Yan Zhao$^3$ & Ying Liu$^{4,3}$

A stable hollow Li$_{20}$B$_{60}$ cage with $D_{2}$ symmetry has been identified using first-principles density functional theory studies. The results of vibrational frequency analysis and molecular dynamics simulations demonstrate that this Li$_{20}$B$_{60}$ cage is exceptionally stable. The feasibility of functionalizing Li$_{20}$B$_{60}$ cage for hydrogen storage was explored theoretically. Our calculated results show that the Li$_{20}$B$_{60}$ molecule can adsorb a maximum of 28 hydrogen molecules. With a hydrogen uptake of 8.190 wt% and an average binding energy of 0.336 eV/H$_2$, Li$_{20}$B$_{60}$ is a remarkable high-capacity storage medium.

Boron is an element of fascinating chemical complexity due to the multicenter bonds, which yield a wide range of boron structures from the usual three dimensional (3D) polyhedral geometries$^1$ to one-dimensional (1D) nanotubes$^{2,3}$ and the recently discovered B$_{96}$ cage$^4$, which is structurally analogous to C$_{60}$, with 12 pentagonal and 20 hexagonal rings. The B$_{96}$ cage has an additional boron atom at the center of each hexagon, and has the same icosahedral point group symmetry as does the C$_{60}$ fullerene. Based on first-principles calculations, several other fullerenes and stuffed fullerene-like structures have been proposed. Yan et al.$^5$ constructed a series of stable B$_{60+k}$ (0 ≤ $k$ ≤ 5, $k$ = 1) fullerenes by using the modified leapfrog algorithm. Zope et al.$^6$ demonstrated the existence of a family of stable boron fullerenes containing 80$n^2$ ($n$ = 1–5) atoms. Prasad et al.$^7$ found that for B$_{98}$, B$_{100}$, B$_{101}$, and B$_{102}$ clusters, the stuffed fullerenes built on icosahedral-B$_{12}$ units, are more stable than the fullerene-like boron clusters.

In the course of ongoing studies of the geometric structures of B$_n$ clusters, the design of boron-based nanomaterials is being closely examined for their applications in hydrogen storage$^{8-12}$. Using first-principles calculations, the buckyball B$_{96}$ coated with various metals $M$ = Li, Na, K, Be, Mg, Ca, Sc, Ti, and V has been investigated for hydrogen storage$^{8,9,12}$. It has been found that Na and Ca appear to be the best candidates for hydrogen storage. The B$_{96}$Na$_{12}$ fullerene can store up to 72 H$_2$ molecules with a gravimetric density of 11.2% while Ca$_{12}$B$_{90}$ can bind up to 66 H$_2$ molecules with a hydrogen storage capacity of 9.0 wt%$^8$. The hydrogen storage properties of planar boron sheets coated with alkali metals have also been investigated, and the boron–Li system was found to be a good candidate for hydrogen storage purposes$^8$. Ab initio studies of hydrogen adsorption in Li-doped hexagonal (B$_6$H$_6$Li$_2$) were carried out by Srinivasu et al.$^{11}$. They found each Li site can adsorb a maximum of three hydrogen molecules which corresponds to a gravimetric density of 12 wt%. More recent investigations of boron nanostructures have shown that Li-decorated boron sheets and nanotubes based on the boron double ring are potential hydrogen storage media$^{12}$. These studies indicate that there is an exciting future for boron-based nanomaterials, specifically in low dimensional structures, which might lead to novel devices with diverse and unique properties$^{13}$.

In the present work, we report that our first-principles calculations within density functional theory (DFT) have identified a stable Li$_{12}$B$_{60}$ cage. We have explored the feasibility for hydrogen storage, and the results show that the hydrogen uptake of the Li$_{12}$B$_{60}$ molecule is 8.190 wt%, making it an attractive candidate as a high-capacity hydrogen storage material.

A large Li$_{12}$B$_{60}$ cage was constructed based on a Li-B sheet as shown in Fig. 1, which is stable and can maintain its original 2D configuration. After full relaxation, it was found that the Li$_{12}$B$_{60}$ cage obtained had robust stability and a nearly spherical shape with a D$_2$ point group symmetry, as shown in Fig. 2(a). The binding energy of Li$_{12}$B$_{60}$ cage is −4.888 eV/atom, which is closely related to that of the Li-B sheet (−4.957 eV/atom). In this cage structure, the B atoms can be seen to form “truncated octahedrons” with the 20 Li atoms capping the fourteen faces. For the Li atoms, there are three different positions: six “face-centered” sites (Li$^I$), four top sites on the “truncated faces” formed by the boron hexagons (Li$^II$), and four top sites on the “truncated faces” formed by boron triangles (Li$^III$).

$^1$Department of Physics and Hebei Advanced Thin Film Laboratory, Hebei Normal University, Shijiazhuang 050024, China. $^2$State Key Laboratory for Superlattices and Microstructures, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, China. $^3$National Key Laboratory for Materials Simulation and Design, Beijing 100083, China. Correspondence and requests for materials should be addressed to Y.L. (email: yliu@hebtu.edu.cn)
On each “face-centered” site, there exists a Li₂ dimer with an average Li-Li distance of 2.635 Å. Four Li atoms are located on the top sites of the “truncated face” formed by the boron hexagons. The remaining 4 Li atoms are located on the top sites of the boron triangles. We refer to these atoms below as Li_I, Li_{II}, and Li_{III}, respectively, as shown in Fig. 2. The relative stability of this Li₂₀B₆₀ cage was discussed by comparing with other structures, which arose during the high-temperature dynamic simulations, but no lower-energy structures were found (see Figures S2 and S3 in the Supplementary Information).

The stability of Li₂₀B₆₀ was further checked using vibrational frequency analysis and molecular dynamics (MD) simulations. The vibrational frequency analysis of the Li₂₀B₆₀ cage indicates no imaginary frequencies and the highest intensity frequency was 687.9 cm⁻¹. For more details see Section IV of the Supplementary Information, as well as some low-frequency modes. Therefore, the Li₂₀B₆₀ cage is kinetically stable. We also carried out ab initio molecular dynamics simulations with the constant-temperature, constant-volume (NVT) ensemble in a Massive Nosé-Hoover thermostat. The total simulation time was set to be 1.0 ps with 1000 dynamics steps. It was found that the structure of the D₂⁻Li₂₀B₆₀ cage was not disrupted up to a temperature of ~600 K. These results indicate that D₂⁻Li₂₀B₆₀ cage has good thermodynamic stability.

It is natural to explore the electronic structure of the Li₂₀B₆₀ cage. To this end, we calculated the deformation electron density, partial density of states (PDOS), and frontier molecular orbitals, including the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) as shown in Figs 2(b) and 3. From the deformation electron density, one can see an alternation of three-center and two-center bonds on each of the six centered-faces of the “truncated octahedron”. On the “truncated faces” formed by the boron hexagons, there is obvious sp²-like bonding between B atoms, while on the “truncated faces” formed by the boron triangles, the Li atoms contribute parts of their 2s electrons to the neighboring B atoms. From the point of view of doping, the three-center triangular regions could be regarded as donors and the two-center hexagonal regions could be
regarded as acceptors\textsuperscript{14}. Thus it is the mixing of the two-center and three-center bonding that promotes the stability of the D\textsubscript{2}-Li\textsubscript{20}B\textsubscript{60} cage. As for the case of the HOMO and LUMO orbitals, it was found that the HOMO orbitals are mostly localized on the B atoms and have a predominantly s-p hybridization characteristic. The LUMO orbitals are also mostly localized on the B atoms and the hybridization is also predominantly of s-p character, which is consistent with the hybridization of Li-B sheet\textsuperscript{15}. The energy level features show that the LUMO orbital is doubly degenerate. Close examination of the PDOS (see Fig. 3) further confirms the hybridization characteristics of the HOMO and LUMO orbitals.

We next investigated the interaction between the Li\textsubscript{20}B\textsubscript{60} cage and hydrogen molecules. It was found that hydrogen can bind to the Li sites with a binding strength reflecting typical van der Waals interactions. The hydrogen binding energy (\(E_b\)) for Li\textsubscript{20}B\textsubscript{60} is defined as \(E_b = (E(\text{Li}_{20}\text{B}_{60}) + n \times E(H_2) - E[\text{Li}_{20}\text{B}_{60}(H_2)_n])/n\). We first added one H\textsubscript{2} molecule near each Li atom. After energy minimization, it was found that the H\textsubscript{2} molecule tends to occupy a position above the Li atom and with its axis parallel to the boron hexagonal or triangle plane. The average distance of the H\textsubscript{2} molecule from the Li atom is 2.270 Å indicating a van der Waals interaction between the H\textsubscript{2} molecules and the Li\textsubscript{20}B\textsubscript{60} cage. The average adsorption energy of the first adsorbed H\textsubscript{2} molecule of each Li is 0.460 eV which lies within the range 0.1–0.6 eV suggested as a criterion for a hydrogen storage medium.

A second and third H\textsubscript{2} were then added. The results indicated that the Li atoms in different positions can adsorb different numbers of H\textsubscript{2} molecules. Each Li\textsuperscript{I} or Li\textsuperscript{II} atom can only adsorb one H\textsubscript{2}, and the H\textsubscript{2} prefers to be located right above the Li atom. The Li\textsuperscript{III} atom can absorb a maximum of three H\textsubscript{2} molecules. Thus, a total of 28 hydrogen molecules can be adsorbed onto the surface of the Li\textsubscript{20}B\textsubscript{60} system as shown in Fig. 4, corresponding to a hydrogen uptake of 8.190 wt% with an average binding energy of about 0.336 eV/H\textsubscript{2}. The binding energies of all 28 H\textsubscript{2} molecules have also been counted and the values distribute in the range 0.1–0.4 eV/H\textsubscript{2} (see Figure S1

---

Figure 3. (a) Partial density of states (PDOS), (b) HOMO and (c) LUMO orbitals for Li\textsubscript{20}B\textsubscript{60} cage. In part (a), the positive and negative DOSs represent spin up and spin down. In parts (b,c), different colors represent the phases of wave functions: blue for positive and yellow for negative. The isosurface is set at a value of 0.015 e/Å\textsuperscript{3}. 

---

\[ E_b = \frac{E(\text{Li}_{20}\text{B}_{60}) + n \times E(H_2) - E[\text{Li}_{20}\text{B}_{60}(H_2)_n]}{n} \]
of Supplementary Information). This hydrogen storage capacity is in excess of 6 wt%, the U. S. Department of Energy target and is comparable to some similar systems, such as the alkali-metal (Li, Na, K) -doped B$_{80}$ fullerenes, the Li-doped boron sheet, and boron nanotubes. All these results suggest that the Li-B cage is a potential candidate for hydrogen storage.

In summary, our first-principles studies have identified a stable Li$_{20}$B$_{60}$ molecule. The results of vibrational frequency analysis and molecular dynamics simulations demonstrate that this Li$_{20}$B$_{60}$ cage is exceptionally stable. The Li$_{20}$B$_{60}$ cage can adsorb a maximum of 28 H$_2$ molecules, resulting in a hydrogen gravimetric density of 8.190 wt% with an average adsorption energy of 0.336 eV/H$_2$. This is a remarkable result indicating another application for the Li-B cage as a potential high-capacity storage medium.

Methods

Our calculations were carried out with the exchange-correlation potential described by the Perdew-Burke-Ernzerhof version (PBE) of the general gradient approximation (GGA) as implemented in the DMol package. The double-numerical basis plus polarized functions (DNP) was chosen. When discussing the adsorption of hydrogen molecules onto the Li$_{20}$B$_{60}$ cage, the van der Waals (vdW) interactions, which are crucial for the formation, stability, and function of molecules were taken into account. Here, the hybrid semi empirical dispersion-correction approach of Tkatchenko and Scheffler (TS) scheme was used in the process of structure optimization. Some previous studies have investigated the hydrogen capacity of metal-decorated 2D sheets or 1D nanotubes using the semi-empirical dispersion-correction approach. All structures were fully relaxed and geometric optimizations were performed with convergence thresholds of $10^{-6}$ Ha/Å for forces, and $5 \times 10^{-3}$ Å for the atomic displacements. In the self-consistent field calculations, the convergence threshold was set to $10^{-6}$ Ha on the total energy. Geometry optimizations were performed with unrestricted spin and without any symmetry constraints.

References

1. Oganov, A. R. et al. Ionic high-pressure form of elemental boron. Nature 457, 863 (2009).
2. Yang, X., Ding, Y. & Ni, J. Ab initio prediction of stable boron sheets and boron nanotubes: structure, stability, and electronic properties. Phys. Rev. B 77, 041402(R) (2008).
3. Singh, A. K., Sadrazadeh, A. & Yakobson, B. I. Probing properties of boron α-tubes by ab initio calculations. Nano Lett. 8, 1314 (2008).
4. De, S. et al. Energy landscape of fullerene materials: a comparison of boron to boron nitride and carbon. Phys. Rev. Lett. 106, 225502 (2011).
5. Sowacki, N. G., Sadrazadeh, A. & Yakobson, B. I. B$_{3}$ fullerene: An Ab initio prediction of geometry, stability, and electronic structure. Phys. Rev. Lett. 98, 166804 (2007).
6. Yan, Q. B., Sheng, X. L., Zheng, Q. R., Zhang, L. Z. & Su, G. Family of boron fullerenes: General constructing schemes, electron counting rule, and ab initio calculations. Phys. Rev. B, 78, 201401(R) (2008).
7. Zope, R. R. et al. Boron fullerenes: From B$_{3}$ to hole doped boron sheets. Phys. Rev. B 79, 161403(R) (2009).
8. Prasad, D. L. V. K. & Jemmis, E. D. Stuffing improves the stability of fullerene-like boron clusters. Phys. Rev. Lett. 100, 165504 (2008).
9. Li, Y., Zhou, G., Li, J., Gu, B. L. & Duan, W. Alkali-metal-doped B$_{80}$ as high-capacity hydrogen storage media. J. Phys. Chem. C 112, 19268 (2008).
10. Li, M., Li, Y., Zhou, Z., Shen, P. & Chen, Z. Ca-coated boron fullerenes and nanotubes as superior hydrogen storage materials. Nano Lett. 9, 1944 (2009).
11. Er, S., Wij, G. A. de & Brocks, G. DFT study of planar boron sheets: a new template for hydrogen storage. J. Phys. Chem. C 113, 18962 (2009).
12. Srinivasu, K. & Ghosh, S. K. Tuning the metal binding energy and hydrogen storage in alkali metal decorated MOF-5 through boron doping: A theoretical investigation. J. Phys. Chem. C 115, 1450 (2011).
13. Wang, J., Zhao, H. Y. & Liu, Y. Boron-double-ring sheet, fullerene, and nanotubes: Potential hydrogen storage materials. Chem. Phys. Chem. 15, 3453 (2014).
14. Peney, E. S., Bhownick, S., Sadrazadeh, A. & Yakobson, B. I. Polymorphism of two-dimensional boron. Nano Lett. 12, 2441 (2012).
15. Zhang, H., Wang, J., Tian Z. X. & Liu, Y. Lithium boride sheet and nanotubes: structure and hydrogen storage. Phys. Chem. Chem. Phys. 17, 13821 (2015).

Figure 4. Optimized structure of Li$_{20}$B$_{60}$ cage with hydrogen molecules adsorbed by the Li atom. (a,b) view from different angles.
16. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **77**, 3865 (1996).
17. Delley, B. Fast calculation of electrostatics in crystals and large molecules. *J. Chem. Phys.* **92**, 508 (1990).
18. Kaplan, I. G. *Intermolecular Interactions* (Wiley, Chichester, England, 2006).
19. Tkatchenko, A. & Scheffler, M. Accurate molecular Van Der Waals interactions from ground-state electron density and free-atom reference data. *Phys. Rev. Lett.* **102**, 073005 (2009).
20. Yang, H. C., Wang, J. & Liu, Y. Metal-silicane: Stability and properties. *J. Appl. Phys.* **116**, 083501 (2014).

**Acknowledgements**

We thank Dr. N. E. Davison for his help with the language. This work was supported by the National Natural Science Foundation of China (Grant Nos 11274089, 11304076, and U1331116), the Natural Science Foundation of Hebei Province (Grant Nos A2012205066 and A2015205179), the Science Foundation of Hebei Education Award for Distinguished Young Scholars (Grant No. YQ2013008), and the Program for High-level Talents of Hebei Province (Grant No. A201500118). We also acknowledge partial financial support from the 973 Project in China under Grant No. 2011CB606401.

**Author Contributions**

Y.L. designed the initial structures and performed the theoretical calculations. J.W. and Y.L. analyzed the results and wrote the manuscript. All authors discussed the results and commented on 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: Wang, J. *et al.* Hollow Li_{20}B_{60} Cage: Stability and Hydrogen Storage. *Sci. Rep.* **6**, 24500; doi: 10.1038/srep24500 (2016).

This work is licensed under a Creative Commons Attribution 4.0 International License. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder to reproduce the material. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/