Hydrogen storage capacity of Si-decorated B80 nanocage: first-principles DFT calculation and MD simulation

Masoud Darvish Ganji a* and Nasim Ahmadian b

a Department of Nanochemistry, Faculty of Pharmaceutical Chemistry, Pharmaceutical Sciences Branch, Islamic Azad University, Tehran - Iran (IAUPS)
b Department of Chemistry, Qaemshahr Branch, Islamic Azad University, Qaemshahr, Iran

Abstract
Hydrogen storage capacity of Si-coated B80 fullerene was investigated based on density functional theory calculations within local density approximation and generalized gradient approximation. It is found that Si atom prefer to be attached above the center of pentagon with a binding energy of -5.78 eV. It is inferred that this binding is due to the charge transfer between the Si atom and B80 cage, such as B80AM, B80Ca and B80Mg complexes. The media produced by 12 Si atoms coating on B80, i.e. Si12B80, which Si atoms do not cluster on the B80 surface, can store up to 96 hydrogen molecules resulting in the gravimetric density of 13.87 wt %. Binding of 96 H2 molecules adsorbed on Si12B80 is found to be -0.03 eV/H2 based on the first-principles van der Waals density functional calculations being an indication of the weak interaction (physisorption) between H2 molecules and B80. Furthermore, the adsorption behavior of 96 H2 molecules around the Si12B80 complex was studied through ab initio molecular dynamics simulation at room temperature. Our finding shows that hydrogen molecules escape from the cage, which highlights that the corresponding system easily releases the hydrogen molecules at ambient conditions.

Keywords: Adsorption; Hydrogen storage; MD simulation; B80 fullerene; DFT

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1. Introduction
Skyrocketing fossil fuel prices highlight the critical need for the development of new and renewable energy sources. Due to its environmental merits such as effortless synthesis, nonpolluting nature and rich sources, hydrogen has gained popularity as an energy carrier for fossil fuels in recent years [1-7]. Subsequent use of hydrogen necessitate a safe, stable and feasible storage system, which should be capable of storing hydrogen with high gravimetric/volumetric densities and leading absorbing-releasing process of hydrogen reversibly with fast kinetics and favorable thermodynamics, without dissociation its structure at near room temperature and ambient pressure [1-3, 8-10]. Furthermore, the binding energy in the range of 0.2-0.4 eV/H2, which is intermediate between physisorption and chemisorption, can supply an ideal storage system [11, 12]. Since using classical storage techniques such as metal hydrides, compressed hydrogen or such hydrogen cannot guarantee (make or produce) a suitable storage because of low capacity, non-reversibility or safety problems [13, 14]. To receive an effective storage media many interests have been recently directed to carbon nanostructures as potential adsorbents for hydrogen storage, due to their high specific surface area [1, 15-18]. The obtained results have demonstrated that

* Corresponding Author. Tel.: +98 911 113 7150; E-mail address: ganji_md@yahoo.com
adsorption take places based on van der Waals forces via weak interactions at ambient conditions [14, 19-21]. In addition, previous experimental results were found to be different for hydrogen storage capacity, highlighting the adsorption in pure carbon nanomaterials is not appropriate to be applied for sufficiently storing hydrogen molecule, and for satisfying the US Department of Energy (DOE) target of 6.5 wt% at ambient condition [13]. On the other hand, the isolated transition metal (TM) and alkali metal (AM) atoms or ions have been theoretically and experimentally examined toward hydrogen-storing media [22-24]. Although hydrogens bind molecularly, their aggregation into cluster after releasing hydrogen is not favorable for hydrogen storage reversibly [25, 26]. In recent years, surface functionalized carbon nanomaterials with TM have been examined in order to achieve the hydrogen uptake-release system exhibiting good reversibility and superior adsorption capacity at ambient conditions [27-29]. Based on density functional theory (DFT) calculations, Yildirim et al. [30] and Zhao et al. [27], respectively, have shown that Ti-coated single walled carbon nanotubes and Sc-coated B-doped fullerenes are able to store up to 8 wt % hydrogen with - 0.3 eV/H\textsubscript{2} binding energy, while Weon et al. [31] reported that fullerenes coated with Ni can store up to 6.8 wt % H\textsubscript{2} molecule. However, because of some serious problems associated with such systems such as: the first hydrogen dissociation due to extreme charge transfer between considered species [27], the reduction of the adsorbed hydrogen numbers at each site due to heavy-weight material (TM) used in the media, practical application of TM-decorated carbon nanostructures as suitable hydrogen storage system has deeply been a question for scientists. More importantly, because of high cohesive energy, TM atoms prefer to aggregate on the carbon nanostructures surface and form a cluster around the related surface, and hence result in considerably low hydrogen storage capacity [32-36]. To meet practical targets, Shevlin and Guo [37] reported that the defected (8, 0) nanotube-modulated Ti can adsorb five H\textsubscript{2} molecules with binding energies in the range from −0.2 to −0.7 eV/H\textsubscript{2}, which is typically desirable for hydrogen binding. Additionally, substantial efforts have been devoted to modify the carbon nanomaterials via functionalization with alkali metals (AM) and alkaline earth metals (AEM) having smaller cohesive energy than TM atoms, and being coated uniformly [14, 38, 39]. For instance, Sun et al. [29] have suggested that Li-uniformly coated C\textsubscript{60} fullerene, the larger binding energy than the cohesive energy of the bulk Li metal though it may have, due to weak H\textsubscript{2} adsorption energy cannot significantly ensure the desirable hydrogen storage for practical storage. Yoon et al. [40] employing DFT calculations have also illustrated that Ca-coated C\textsubscript{60} fullerene (Ca\textsubscript{32}C\textsubscript{60}) can adsorb 2.7 H\textsubscript{2} per Ca metal, and can be capable of a hydrogen uptake of ~ 8.4 wt %. On the other hand, doping of Si atoms, as the most common metalloid, onto the surface of carbon nanostructures appears to be useful to enhance the hydrogen storage capacity [41, 42], since it was found that Si atoms achieving suitable energy can be adsorbed on the surface of C\textsubscript{60} as impurities in industrial synthesis of C\textsubscript{60} fullerene [43]. In addition, Ni and Si possess a similar electronegativity which encourage researchers to evaluate the hydrogen storage of considered media [13]. Very recently, using first-principles theory based on DFT and Canonical Monte Carlo calculations (CMCS), Naghshineh and co-worker [13] have proposed that Si atoms decorated C\textsubscript{60} can adsorb one H\textsubscript{2} molecule with the binding energy of ~ 0.15 eV/H\textsubscript{2} highlighting Si-doped C\textsubscript{60} could be an appropriate choice as hydrogen storage material. Because of having empty p\textsubscript{z} orbital, boron (B) atoms can also play an important role as a charge acceptor in adsorption process. Thus, nanostructures including B atoms are good candidates to be investigated as hydrogen storage system. Ongoing research efforts have focused on using boron nanostructures (fullerenes and nanotubes) to develop the reversible hydrogen uptake-release as well as desirable binding energy at ambient conditions [1-3]. Meng et al. [44], through DFT computations, were encouraged to investigate metal–diboride nanotubes as novel nanomaterials. Using the TiB\textsubscript{2} (8,0) and (5,5) nanotubes, they have illustrated that in such system each Ti atom are capable of adsorbing two H\textsubscript{2} molecule reversibly, without metal clustering, which results in a storage capacity of 5.5 wt.% and the wanted binding energies in the range of 0.2−0.6 eV per H\textsubscript{2} molecule at ambient conditions. Discovered by Szwacki et al. [45] and named B\textsubscript{80}, structurally similar to the C\textsubscript{60} fullerene except for extra atoms placed in the centers of all hexagons was theoretically found to be the most stable boron cage. B\textsubscript{80}, however, have several pentagonal and hexagonal rings as active adsorption sites, which is suitable substrate to attract other atoms. In recent times, scientific efforts have been providing evidence indicating B\textsubscript{80} can be favorable in reversible hydrogen storage process at ambient conditions [1-3, 46, 47]. According to the theoretical study of Li et al [1], using Na/K-doped B\textsubscript{80} fullerenes (B\textsubscript{80}Na\textsubscript{12} and B\textsubscript{80}K\textsubscript{12}) as a storage medium for hydrogen results in gravimetric of 11.2% and 9.8% with the
adsorption energy of 1.67 and 1.99 kcal/mol, respectively. Although problems associated with clustering phenomena have been disappeared, the weak H\textsubscript{2} adsorption energy generates an unstable state at the room temperature. In recent study, Li et al. [2] proposed to theoretically serve Ca atoms to coat on B\textsubscript{80} fullerene and B nanotube homogeneously. They obtained an average binding energy of 0.10-0.30 eV with a hydrogen storage capacity of 7.6 wt % for Ca-coated (9, 0) B nanotube system. Superior results were found for Ca\textsubscript{12}B\textsubscript{80} having adsorption energy in the range of 0.12-0.40 eV and consequently being capable of storing 8.2 wt % H\textsubscript{2}. In an interesting work, Yang et al. [3] have theoretically suggested Mg-coated B\textsubscript{80} (Mg\textsubscript{12}B\textsubscript{80}) as novel media for hydrogen storage. They reported that Mg\textsubscript{12}B\textsubscript{80} can store 8 H\textsubscript{2} per Mg, resulting in a gravimetric capacity of 14.2 wt %, with the binding energy of 0.2 eV/H\textsubscript{2} at GGA and 0.5 eV/H\textsubscript{2} at LDA. In the calculations reported here, we first focused on the binding mechanism of Si-coated B\textsubscript{80} and then examined the adsorption of hydrogen on this novel media through GGA and LDA levels of theory. The obtained results indicate that 12Si-coated B\textsubscript{80} is capable of storing 96 H\textsubscript{2} molecules, resulting in a storage capacity of 13.87 wt % with the binding energy of -0.12 eV/H\textsubscript{2} at GGA, -0.29 eV/H\textsubscript{2} at LDA. Since van der Waals (vdW) interaction can revise adsorption geometries and energies, and intermolecular interactions [48, 49], we have also considered hydrogen storage behavior of the Si-B\textsubscript{80} media by employing first-principles vdW density functional (vdW-DF) calculations.

1.1 Computational details
All calculations were performed using the ab initio DFT code SIESTA [50, 51]. The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional was employed for the exchange correlation potential [52]. The core electrons are replaced by improved Troullier–Martins pseudopotentials [53], and a numerical atomic orbital basis set with polarization is used for the valence electrons. All total energies were calculated with a double-\(\zeta\) plus polarization (DZP) basis set. An equivalent kinetic energy cutoff of 125 Ry for the grid interaction was used to describe the charge density in real space. Geometrical optimisations were obtained by means of the conjugate gradient (CG) algorithm within Hellmann–Feynman forces including Pullay-like corrections until the residual forces were smaller than 0.02eV/Å. Moreover, the obtained results of binding energies of the hydrogen molecules approaching the theoretically produced media for GGA were compared with those of the local density approximation (LDA) with the Perdew-Zunger (PZ) parametrization [54]. Considering previous investigations demonstrate that GGA underestimates the H2 binding energy, while LDA overestimates them [55-57]. On the other hand, using these approximations based on DFT calculations is still controversial to illustrate van der Waals contributions [14]. Therefore, we have reoptimized the related configuration by employing the molecular mechanical potentials based on Grimme type for calculating vdW interactions [58].

2. Results and discussion
To design a suitable hydrogen storage media using Si atoms coated on B\textsubscript{80} fullerene, we first considered initial sites of B\textsubscript{80} for adsorption a Si atom. As illustrated in Figure 1, five possible adsorption sites were selected for one Si atom doping on the B\textsubscript{80} nanocage, namely, the top site directly above the boron atom of the cage (B-top) as A\textsubscript{1} site, the bridge sites above two different B-B bonds between hexagon-hexagon boron rings and between pentagon-hexagon boron rings as A\textsubscript{2} and A\textsubscript{3} sites respectively, the top sites directly above the center of pentagon and hexagon, as A\textsubscript{4} and A\textsubscript{5} sites, respectively.

We employed the optimized B\textsubscript{80} fullerene for the Si adsorption. After full structural optimization of the considered configurations, we calculated the binding energies, \(E_b\), of Si-doped B\textsubscript{80} fullerene for all five sites through the subsequent equilibrium to find the favorable energetically configuration.

\[
E_b = [E (B_{80} - Si)] - E (B_{80}) - E_{Si}
\]

Where \(E (B_{80} - Si)\), \(E_{B80}\) and \(E_{Si}\) are the total energies of the B\textsubscript{80} fullerene with an adsorbed Si atom, the pure B\textsubscript{80} fullerene and the Si atom, respectively. Considering the calculated results reveals that all binding energies are negative in the range of -4.66 eV (-107.46 Kcal/mol) – -5.78 eV (-133.29 Kcal/mol) that in comparison with those of C\textsubscript{60}Si [13] confirm the more strong interaction between Si atom and B\textsubscript{80} and also suggest the stability of this doped system by one Si atom, see Table 1.
Figure 1. Model for five possible adsorption sites for Si atom: (a) the top site directly above the boron atom of the cage (B-top), A1-site, (b-c) the bridge sites above two different B-B bonds between hexagons-hexagons boron rings and between pentagon-hexagon boron rings, A2-site and A3-site, respectively, (d-e) the top sites directly above the center of pentagon and hexagon, A4 and A5 sites, respectively. Atom colors: grey—silicon and pink —boron.

Table 1. Calculated binding energies ΔEb (eV) of all five optimized configurations of Si-doped B80 complexes.

<table>
<thead>
<tr>
<th>Considered sites</th>
<th>A1-site</th>
<th>A2-site</th>
<th>A3-site</th>
<th>A4-site</th>
<th>A5-site</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binding energy (eV)</td>
<td>-4.66</td>
<td>-4.67</td>
<td>-5.78</td>
<td>-5.77</td>
<td>-5.41</td>
</tr>
</tbody>
</table>

Furthermore, A3 site produces the most stable configuration in which Si atom placed above the B-B bond between a five and a six-member ring move upon the center of pentagonal ring after relaxation, as depicted in Figure 2. Similar optimized configuration was found to be energetically favorable complex in all AM, Ca and Mg doped on B80 [1-3]. The calculated binding energy for this configuration is -5.78 eV (-133.29 kcal/mol) and the equilibrium distance between Si atom and the closest boron atom of the cage is 2.201 Å, suggesting the strong interaction between two corresponding species and emphasizing the involvement of chemisorption in the adsorption process. For further understanding the interaction nature in the adsorption phenomenon, we analyze electronic properties of the most stable configuration. First, we investigate the total electron density maps of electronic density. Considering isosurface map for corresponding complex reveals that strong hybridization takes place between two respective molecules, and also the chemically doping a single atom on B80 changes the electronic charge distribution of boron atoms of the cage, resulting in a considerable charge transfer in the media, see Figure 3(a). The Mulliken charge analysis for this configuration shows that Si atom carries 0.35 e positive charge, which such positively charged Si atom at the tip upon the center of a pentagon of B80 cage promotes the hydrogen adsorption possibility due to the electronic field produced between Si and B80 fullerene.
Additionally, the highest occupied molecular orbital and the lowest unoccupied molecular orbital (HOMO-LUMO) electron density were obtained for the complex by employing OpenMX [59] computer codes based on the Troullier-Martine Pseudo-Potentials. As illustrated in Figure 3 (b) and (c), both HOMO and LUMO are distributed throughout the complex supporting electron conduction through this produced novel media for hydrogen adsorption. Due to strong potential of the Si-doped B₈₀ fullerene, there is a strong accumulation of charge density around the media.

To further investigate the effect of Si doping on B₈₀ in the hydrogen storage, we also pay attention to the total density of state (DOS) of pristine B₈₀ and Si doped on B₈₀ systems. As illustrated in Figure 4(a), after Si doping on B₈₀ the DOS around the Fermi level is depressed into the valence and conduction bands indicating a decrease in HOMO-LUMO energy gap hence leads system to a higher reactivity in comparison to pristine B₈₀. Such charge density at the Fermi level increases the charge transfers between two considered species. In addition, the difference in the Fermi level of Si-doped B₈₀ and the bare B₈₀ is 0.2 eV due to the electric field induced by Si atom above the cage. These results imply a strong orbital mixing near the Fermi level and involvement of covalent adsorption between Si atom and B₈₀, thus, Si doping on B₈₀ may promote the electronic conductivity in the media and provide a suitable condition for H₂ adsorption process. Furthermore, the stronger interaction between a single Si atom and constitutive boron atoms of corresponded pentagon can be extracted from the partial density of state (PDOS). As depicted in Figure 4(b), it is obvious that both HOMO and LUMO is localized on the Si atom and B₈₀ cage being consistent with the obtained results of considering HOMO and LUMO electron densities of this configuration. Considering PDOS of Si doped on B₈₀ significantly confirms the substantial contribution of the Si 3p and B 2p orbitals in the vicinity of the Fermi level. The bonding originates from the significant overlap between 3p orbitals of Si atom and 2p orbitals of boron atoms leading to a strong hybridization in bonding, i.e. the p-p hybridization, generating the high binding energy in the system.

Inspired by these results, we investigated the adsorption behavior between H₂ molecules and Si-doped B₈₀ system. As one H₂ molecule approaches the single Si-doped B₈₀ complex, an interaction is appeared between H₂ molecule and Si-doped B₈₀ system due to the polarization. The bond length of H₂ extended to 0.776 Å and 0.798 Å according to GGA and LDA levels of theory, respectively, which has significant difference than to an isolated H₂ molecule (0.75 Å). Meanwhile, the binding energy is -0.16 eV (3.69 Kcal/mol) for GGA and -0.23 eV (-5.31 Kcal/mol) for LDA. According to previous studies [55-57], we are aware of the apparent tendency of LDA and GGA to overestimate and underestimate the dispersion interaction, respectively. With regard to these effects, it is not surprising that the real adsorption energy can be positioned between the calculated results of GGA and LDA. The binding energy of B₈₀Si(H₂)₁ complex based on vdW-DF calculations within the PBE-GGA level of theory is found to be -0.22 eV, which indeed persuade us to follow our investigation.
To show the binding nature between H₃ and Si-doped B₈₀ molecule, we have performed the calculations of DOS for B₈₀Si(H₂)₁ system compared with the corresponding DOS for the Si-doped B₈₀ media. As represented in Figure 5, the DOS for B₈₀Si(H₂)₁ system is almost closely the superposition of the DOS of Si-doped B₈₀ and the DOS near the Fermi level is not modified by approaching one H₂ molecule on the outside surface of Si-doped B₈₀. Moreover, there is no difference in the Fermi level of two considered species (E_F = ~ 4.22 eV). These strongly indicate that there exists a weak orbital mixing near the Fermi level and confirm the association of noncovalent adsorption between H₂ molecule and Si-doped B₈₀ media. Figure 6 (a, b) illustrates HOMO and LUMO distributions for B₈₀Si(H₂)₁ system. It can be seen that approaching one H₂ molecule onto the Si-doped B₈₀ has no considerable effect on the HOMO and LUMO isosurfaces when compared to those of the pristine Si-doped B₈₀, see Figure 3 (b, c), implying the impossibility of modification of the electronic properties of the related system by H₂ adsorption process. Thus, it is really not unexpected that no charge accumulation could be seen between two corresponding species. In practice, adsorbing more H₂ molecules is determined based on the adsorption of else H₂ molecule by the host Si on the one hand and the repulsion effect by the earlier attracted H₂ molecules, on the other hand. Our results show that a single Si on B₈₀ can adsorb up to eight H₂ molecules with an adsorption energy of ~ -0.15 eV/H₂ at GGA and ~ -0.26 eV/H₂ at LDA. The average binding energies between GGA and LDA were found to be 0.19-0.24 eV/H₂, for all B₈₀Si(H₂)ᵈ complexes, n=1-8. These binding energies point out that our theoretically designed SiB₈₀ system is a suitable media for storing hydrogen molecules. Optimized configurations of B₈₀Si(H₂)₁ and B₈₀Si(H₂)₈ are demonstrated in Figs. 7(a) and (b), respectively.

To achieve a more decisive answer that such a system can be applied for practical applications, we have performed the binding energies of B₈₀Si(H₂)ᵈ, n=2-8, complexes by means of vdW-DF calculations. The results reveal that as the more H₂ molecules approaches the related system, the binding energy decreases from -0.15 eV/H₂ for B₈₀Si(H₂)₂ to -0.08 eV/H₂ for B₈₀Si(H₂)₈. This decrease in binding energy can be derived from the repulsion effect by the prior adsorbed H₂ molecules. Table 2 displays the values of binding energies at GGA, LDA and vdW-DF levels of theory, and the equilibrium Si-H distances and the bond length of H-H after full optimization at GGA and LDA levels of theory.
Figure 4. (a) The DOS for a pristine B$_{80}$ nanocage and a single Si-doped B$_{80}$ complex. The Fermi level is localized in zero. (b) PDOS of Si-doped B$_{80}$ with contributions from the five boron atoms of corresponded pentagon and Si atom. The energy at Fermi level is represented by the dashed vertical line.

Table 2. The adsorption energies of (H$_2$)$_n$, $n$=1-8, on Si-doped B$_{80}$ fullerene at the GGA-PBE, LDA-PZ and vdW-DF levels of theory, and the equilibrium Si-H distances and the bond length of H-H after full optimization computed at the GGA-PBE and LDA-PZ levels of theory.

<table>
<thead>
<tr>
<th>$n$</th>
<th>Ea (eV/H$_2$)</th>
<th>d$_{Si-H}$ (Å)</th>
<th>d$_{H-H}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>GGA</td>
<td>LDA</td>
<td>average $E_h$</td>
</tr>
<tr>
<td>B$_{80}$Si(H$_2$)$_1$</td>
<td>-0.16</td>
<td>-0.23</td>
<td>-0.20</td>
</tr>
<tr>
<td>B$_{80}$Si(H$_2$)$_2$</td>
<td>-0.13</td>
<td>-0.25</td>
<td>-0.19</td>
</tr>
<tr>
<td>B$_{80}$Si(H$_2$)$_3$</td>
<td>-0.17</td>
<td>-0.28</td>
<td>-0.23</td>
</tr>
<tr>
<td>B$_{80}$Si(H$_2$)$_4$</td>
<td>-0.14</td>
<td>-0.27</td>
<td>-0.21</td>
</tr>
<tr>
<td>B$_{80}$Si(H$_2$)$_5$</td>
<td>-0.19</td>
<td>-0.28</td>
<td>-0.24</td>
</tr>
<tr>
<td>B$_{80}$Si(H$_2$)$_6$</td>
<td>-0.14</td>
<td>-0.30</td>
<td>-0.22</td>
</tr>
<tr>
<td>B$_{80}$Si(H$_2$)$_7$</td>
<td>-0.15</td>
<td>-0.27</td>
<td>-0.21</td>
</tr>
<tr>
<td>B$_{80}$Si(H$_2$)$_8$</td>
<td>-0.15</td>
<td>-0.26</td>
<td>-0.21</td>
</tr>
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</table>

Figure 5. The DOS for one Si-doped B$_{80}$ system and B$_{80}$Si(H$_2$)$_1$ complex. The Fermi level is localized in zero.

Motivated by the obtained results of a single Si-doped B$_{80}$ for hydrogen storage, we decided to examine the possible and stable coating of B$_{80}$ fullerene by maximum Si atoms for the attachment of more capacity in hydrogen storage. Since B$_{80}$ fullerene has 12 pentagonal rings, we placed one Si atom above the center of each pentagon to design Si$_{12}$B$_{80}$ media, as illustrated in Figure 8. Our results reveal that after full optimization, the binding energy of such system is -6.02 eV/Si (-138.8 Kcal/mol), very stable even more than that of one SiB$_{80}$ with -5.78 eV/Si. Such an increase in binding energy is basically originated from the interaction among Si atoms.
Such trend has been also observed in Ca-coated B$_{80}$ for doping of B$_{80}$ by one Ca atom and 12 Ca atoms [2]. The next step is to investigate the clustering problem determining the reversible hydrogen storage. Hence, we calculated the binding energy of a Si$_{12}$ cluster on B$_{80}$ to compare the relative stability of this configuration with that of separated 12 Si atoms coated-B$_{80}$ fullerene, see Figure 8(b). Considering our calculations exhibits that the separated Si atoms on B$_{80}$ is the favorable energetically configuration than to the compact Si$_{12}$ cluster on B$_{80}$. Obviously, 7.31 eV (168.57 Kcal/mol) energy gap between two species not only reflects in fact that cluster formation does not occur during the storage but also introduce Si$_{12}$B$_{80}$ system as superior media comparing with Ca$_{12}$B$_{80}$ [2] and Mg$_{12}$B$_{80}$ [3].

Now we evaluate hydrogen storage capacity of Si$_{12}$B$_{80}$ complex using GGA, LDA and vdW-DF calculations. Si$_{12}$B$_{80}$ media was coated by 96 hydrogen molecules, as shown in Figure 9. Interestingly, the gravimetric density of H$_2$ in this media can reach 13.87 wt %, which can provide superior efficiency than to the obtained values for many of theoretically produced medias for hydrogen storage such as 11.2, 9.8 and 8.2 wt % for B$_{80}$Na$_{12}$ [1], B$_{80}$K$_{12}$ [1] and Ca$_{12}$B$_{80}$ [2], respectively, and comparable with the recent discovered Mg$_{12}$B$_{80}$ [3] system. After fully optimization the binding energy for each hydrogen molecule in Si$_{12}$B$_{80}$ (H$_2$)$_{96}$ system was found to be -0.12 eV (-2.76 Kcal/mol) for GGA, -0.29 eV (-6.69 Kcal/mol) for LDA and -0.03 eV (-0.69 Kcal/mol) for vdw-DF. Binding results based on vdw-DF show that this theoretically designed system is not an appropriate media to store H$_2$ molecules for practical applications.
Figure 8. Two isomers of $\text{Si}_{12}\text{B}_{80}$ as: (a) $12$ Si atoms coated on pentagonal rings of $\text{B}_{80}$, and (b) a $\text{Si}_{12}$ cluster on $\text{B}_{80}$.

Figure 9. Optimized configurations of $\text{B}_{80}\text{Si}_{12}(\text{H}_2)_{96}$ system at the GGA level of theory.

Figure 10. Snapshots of first-principles MD simulations of the $\text{Si}_{12}\text{B}_{80}(\text{H}_2)_{96}$ system at 300K for 3ps (a) GGA without vdW corrections and (b) GGA with vdW corrections.
We also studied the stability of the Si$_{12}$B$_{80}$(H$_2$)$_{96}$ system through the *ab initio* molecular dynamics (MD) simulation at GGA (PBE) with and without vdW corrections. We have carried out 3.0 ps MD simulations with a Nosé-Hover thermostat at 300 K. MD results reveal that in comparison with pure GGA, a large number of H$_2$ molecules escape from the media with accounting vdW interactions. This shows that the Si$_{12}$B$_{80}$ system can easily release H$_2$ molecules at room temperature, see Figure 10 (a, b).

3. Conclusion
In the present study, the possibility of hydrogen storage on Si-coated B$_{80}$ nanostructures has clearly been investigated. It is found that the most stable configuration of a single Si doped on B$_{80}$ surface among all possible configurations can store up to eight H$_2$ molecules. Although doping of a Si atom changes the electronic properties of B$_{80}$, does not destroy its structure. Such properties have directed us to examine the hydrogen storage capability of 12 Si-coated B$_{80}$ nanostructures. Our results indicate that theoretically produced Si$_{12}$B$_{80}$ media does not deal with the clustering problem. The hydrogen storage capacity of the Si$_{12}$B$_{80}$ is 13.87%, which is higher than the target of the U.S. Department of Energy (9 wt % by the year 2015). This system can store up 96 H$_2$ molecules with the binding energy of -0.03 eV/H$_2$ which does not meet suitable adsorption behavior required for practical applications. MD simulation is also performed to consider hydrogen storage behavior of Si$_{12}$B$_{80}$ at ambient temperature. MD simulation confirms the feasibility of easily desorption of H$_2$ molecules on B$_{80}$ surface at ambient temperature. Such results can reflect in fact that our theoretically designed system is a poor media for storing hydrogen molecules.

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[59] DFT OpenMX code is available on the web site http://staff.aist.go.jp/t-ozaki/openmx/.