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

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Abstract
Hydrogen storage capacity of Si-coated B_{80} 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 B_{80} cage, such as $B_{80}AM$, $B_{80}Ca$ and $B_{80}Mg$ complexes. The media produced by 12 Si atoms coating on B_{80}, i.e. $Si_{12}B_{80}$, which Si atoms do not cluster on the B_{80} surface, can store up to 96 hydrogen molecules resulting in the gravimetric density of 13.87 wt %. Binding of 96 H_2 molecules adsorbed on $Si_{12}B_{80}$ is found to be -0.03 eV/H_2 based on the first-principles van der Waals density functional calculations being an indication of the weak interaction (physisorption) between H_2 molecules and B_{80}. Furthermore, the adsorption behavior of 96 H_2 molecules around the $Si_{12}B_{80}$ 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

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/H_2, 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

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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_2 binding energy, while Weon et al. [31] reported that fullerenes coated with Ni can store up to 6.8 wt % H_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_2 molecules with binding energies in the range from −0.2 to −0.7 eV/H_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_{60} fullerene, the larger binding energy than the cohesive energy of the bulk Li metal though it may have, due to weak H_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_{60} fullerene ($Ca_{32}C_{60}$) can adsorb 2.7 H_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_{60} as impurities in industrial synthesis of C_{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_{60} can adsorb one H_2 molecule with the binding energy of ∼ 0.15 eV/H_2 highlighting Si-doped C_{60} could be an appropriate choice as hydrogen storage material. Because of having empty p_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_2 (8,0) and (5,5) nanotubes, they have illustrated that in such system each Ti atom are capable of adsorbing two H_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_2 molecule at ambient conditions. Discovered by Szwacki et al. [45] and named B_{80}, structurally similar to the C_{60} fullerene except for extra atoms placed in the centers of all hexagons was theoretically found to be the most stable boron cage. B_{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_{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_{80} fullerenes ($B_{80}Na_{12}$ and $B_{80}K_{12}$) 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_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_{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 $Ca_{12}B_{80}$ having adsorption energy in the range of 0.12-0.40 eV and consequently being capable of storing 8.2 wt % H2. In an interesting work, Yang et al. [3] have theoretically suggested Mg-coated B_{80} ($Mg_{12}B_{80}$) as novel media for hydrogen storage. They reported that $Mg_{12}B_{80}$ can store 8 H_2 per Mg, resulting in a gravimetric capacity of 14.2 wt %, with the binding energy of 0.2 eV/H_2 at GGA and 0.5 eV/H_2 at LDA. In the calculations reported here, we first focused on the binding mechanism of Si-coated B_{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_{80} is capable of storing 96 H_2 molecules, resulting in a storage capacity of 13.87 wt % with the binding energy of -0.12 eV/H_2 at GGA, -0.29 eV/H_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_{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-ζ 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 optimizations 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_{80} fullerene, we first considered initial sites of B_{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_{80} nanocage, namely, the top site directly above the boron atom of the cage (B-top) as A_1 site, the bridge sites above two different B-B bonds between hexagon-hexagon boron rings and between pentagon-hexagon boron rings as A_2 and A_3 sites respectively, the top sites directly above the center of pentagon and hexagon, as A_4 and A_5 sites, respectively.

We employed the optimized B_{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_{80} fullerene for all five sites through the subsequent equilibrium to find the favorable energetically configuration.

$$E_b = [E (B_{80-Si})] - E (B_{80}) - E_{Si} \qquad (1)$$

Where E (B_{80-Si}), E_{B80} and E_{Si} are the total energies of the B_{80} fullerene with an adsorbed Si atom, the pure B_{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 $C_{60}Si$ [13] confirm the more strong interaction between Si atom and B_{80} and also suggest the stability of this doped system by one Si atom, see Table 1.
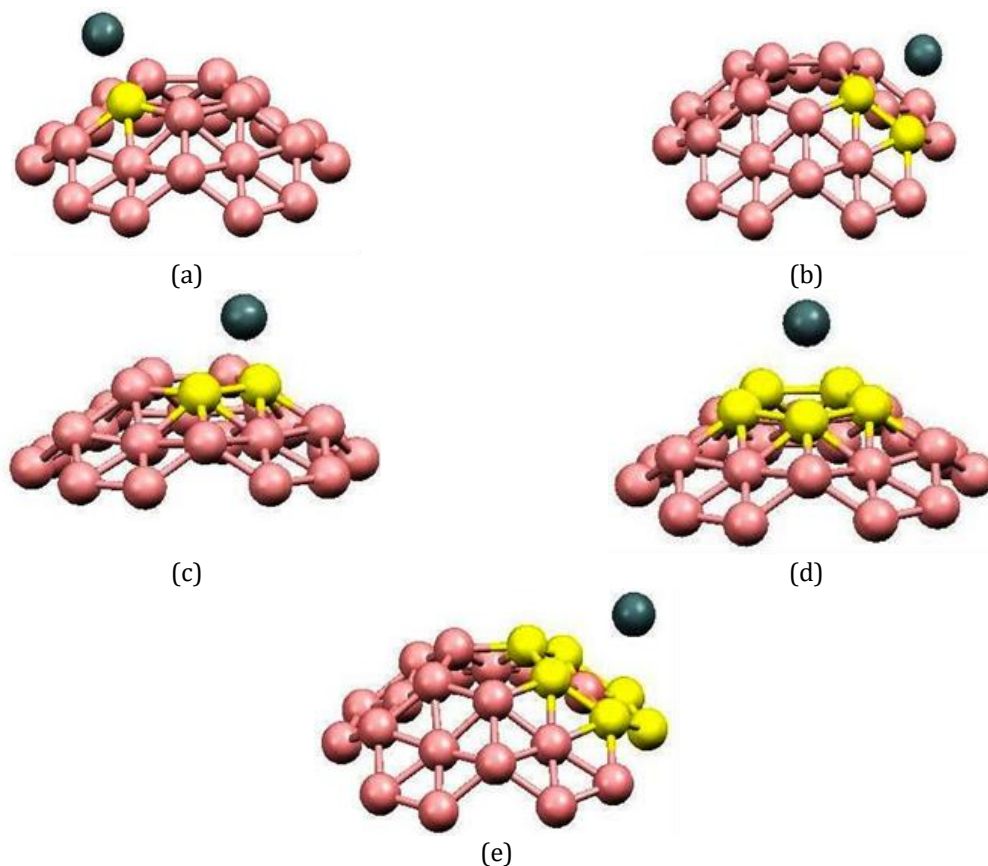
(a)

(b)

(c)

(d)

(e)

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), A_1-site, (b-c) the bridge sites above two different B-B bonds between hexagons-hexagons boron rings and between pentagon-hexagon boron rings, A_2-site and A_3-site, respectively, (d-e) the top sites directly above the center of pentagon and hexagon, A_4 and A_5 sites, respectively. Atom colors: grey—silicon and pink —boron.

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

Considered sites	A1-site	A2-site	A3-site	A4-site	A5-site
Binding energy (eV)	-4.66	-4.67	-5.78	-5.77	-5.41

Furthermore, A_3 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 B_{80} [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 B_{80} 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 B_{80} cage promotes the hydrogen adsorption possibility due to the electronic field produced between Si and B_{80} fullerene.
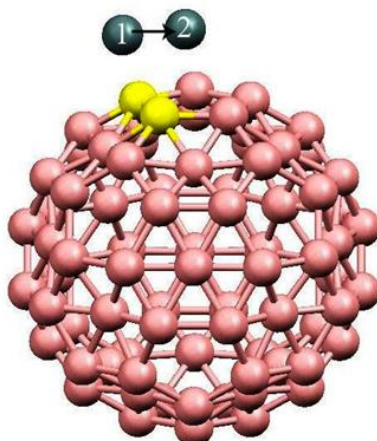
Figure 2. The position of a Single Si atom adsorbed on the A_3-site of B_{80} fullerene before full structural optimization (number 1) and after full structural optimization (number 2) at the GGA level of theory.

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 B_{80} fullerene, there is a strong accumulation of charge density around the media.

To further investigate the effect of Si doping on B_{80} in the hydrogen storage, we also pay attention to the total density of state (DOS) of pristine B_{80} and Si doped on B_{80} systems. As illustrated in Figure 4(a), after Si doping on B_{80} 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 B_{80}. 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 B_{80} and the bare B_{80} 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 B_{80}, thus, Si doping on B_{80} may promote the electronic conductivity in the media and provide a suitable condition for H_2 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 B_{80} cage being consistent with the obtained results of considering HOMO and LUMO electron densities of this configuration. Considering PDOS of Si doped on B_{80} 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 H_2 molecules and Si-doped B_{80} system. As one H_2 molecule approaches the single Si-doped B_{80} complex, an interaction is appeared between H_2 molecule and Si-doped B_{80} system due to the polarization. The bond length of H_2 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 H_2 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 $B_{80}Si(H_2)_1$ 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.
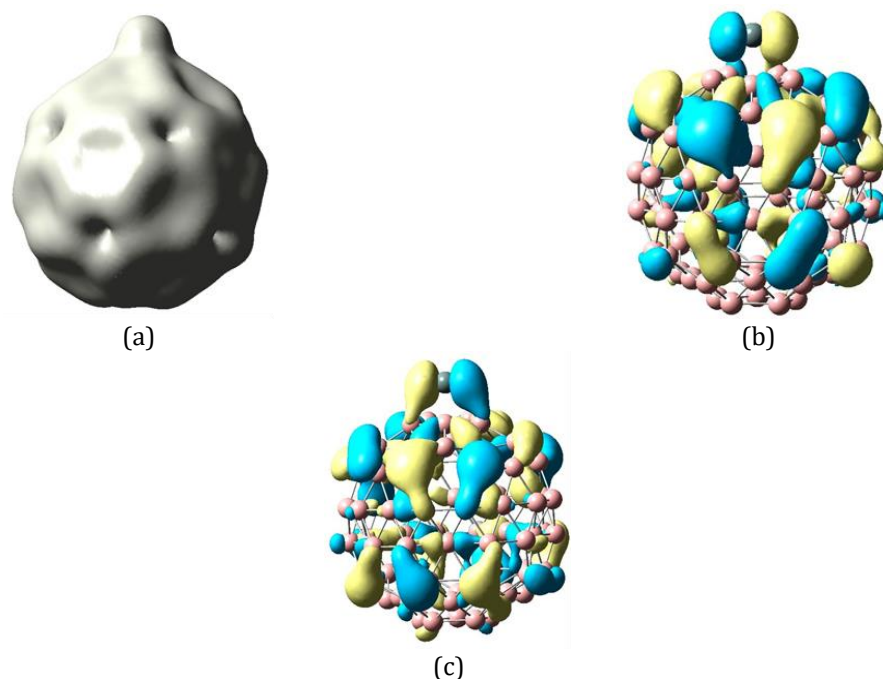
(a)

(b)

(c)

Figure 3. (a) Isosurface of the total electron density for corresponding Si-doped B_{80} system (the isovalue is 0.03). (b) Highest occupied (HOMO) and (c) lowest unoccupied (LUMO) molecular orbitals of system (the absolute values of the isosurfaces of the wave functions are 0.03). Yellow and blue colors donate the positive and negative sign of the wavefunction, respectively.

To show the binding nature between H_2 and Si-doped B_{80} molecule, we have performed the calculations of DOS for $B_{80}Si(H_2)_1$ system compared with the corresponding DOS for the Si-doped B_{80} media. As represented in Figure 5, the DOS for $B_{80}Si(H_2)_1$ system is almost closely the superposition of the DOS of Si-doped B_{80} and the DOS near the Fermi level is not modified by approaching one H_2 molecule on the outside surface of Si-doped B_{80}. 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 H_2 molecule and Si-doped B_{80} media. Figure 6 (a, b) illustrates HOMO and LUMO distributions for $B_{80}Si(H_2)_1$ system. It can be seen that approaching one H_2 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 $B_{80,}$ see Figure 3 (b, c), implying the impossibility of modification of the electronic properties of the related system by H_2 adsorption process. Thus, it is really not unexpected that no charge accumulation could be seen between two corresponding species.

In practice, adsorbing more H_2 molecules is determined based on the adsorption of else H_2 molecule by the host Si on the one hand and the repulsion effect by the earlier attracted H_2 molecules, on the other hand. Our results show that a single Si on B_{80} can adsorb up to eight H_2 molecules with an adsorption energy of ~ -0.15 eV/H_2 at GGA and ~ -0.26 eV/H_2 at LDA. The average binding energies between GGA and LDA were found to be 0.19-0.24 eV/H_2, for all $B_{80}Si(H_2)_n$ complexes, n=1-8. These binding energies point out that our theoretically designed SiB_{80} system is a suitable media for storing hydrogen molecules. Optimized configurations of $B_{80}Si(H_2)_1$ and $B_{80}Si(H_2)_8$ 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 $B_{80}Si(H_2)_n$, n=2-8, complexes by means of vdW-DF calculations. The results reveal that as the more H_2 molecules approaches the related system, the binding energy decreases from -0.15 eV/H_2 for $B_{80}Si(H_2)_2$ to -0.08 eV/H_2 for $B_{80}Si(H_2)_8$. This decrease in binding energy can be derived from the repulsion effect by the prior adsorbed H_2 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.
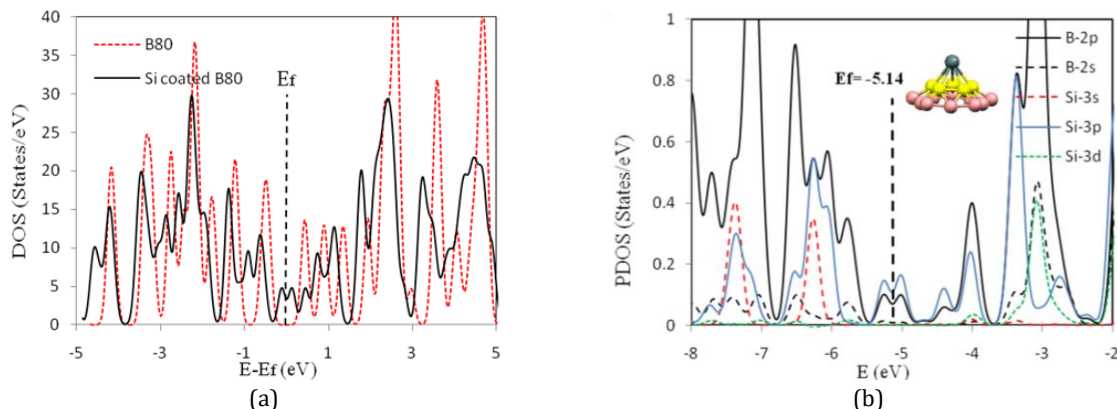
(a)   (b)

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.

|	E_a (eV/H_2)				d_{Si-H} (Å)		d_{H-H} (Å)	
	GGA	LDA	average E_b^a	vdW-DF	GGA	LDA	GGA	LDA
$B_{80}Si(H_2)_1$	-0.16	-0.23	-0.20	-0.21	3.13	2.89	0.776	0.798
$B_{80}Si(H_2)_2$	-0.13	-0.25	-0.19	-0.15	3.14-3.18	3.0-3.60	0.776	0.797-0.798
$B_{80}Si(H_2)_3$	-0.17	-0.28	-0.23	-0.09	3.15-3.34	2.9-3.27	0.776-0.777	0.797-0.800
$B_{80}Si(H_2)_4$	-0.14	-0.27	-0.21	-0.10	3.21-3.36	3.04-3.50	0.776-0.777	0.796-0.798
$B_{80}Si(H_2)_5$	-0.19	-0.28	-0.24	-0.07	3.34-3.60	3.04-3.40	0.775-0.777	0.797-0.798
$B_{80}Si(H_2)_6$	-0.14	-0.30	-0.22	___	3.04-3.28	2.8-3.48	0.776-0.777	0.797-0.799
$B_{80}Si(H_2)_7$	-0.15	-0.27	-0.21	___	2.8-3.37	2.64-3.28	0.776-0.778	0.797-0.799
$B_{80}Si(H_2)_8$	-0.15	-0.26	-0.21	-0.08	3.13-3.28	2.56-2.94	0.775-0.776	0.797-0.799
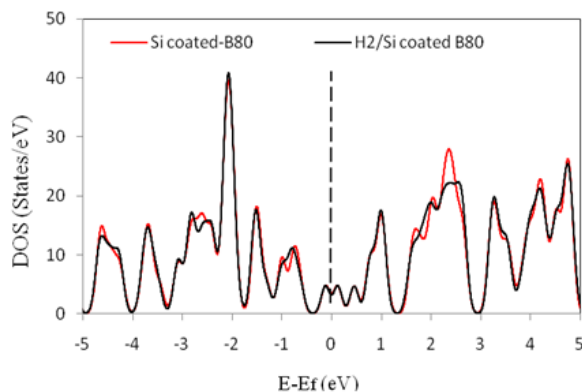
Figure 5. The DOS for one Si-doped B_{80} system and $B_{80}Si(H_2)_1$ complex. The Fermi level is localized in zero.

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.
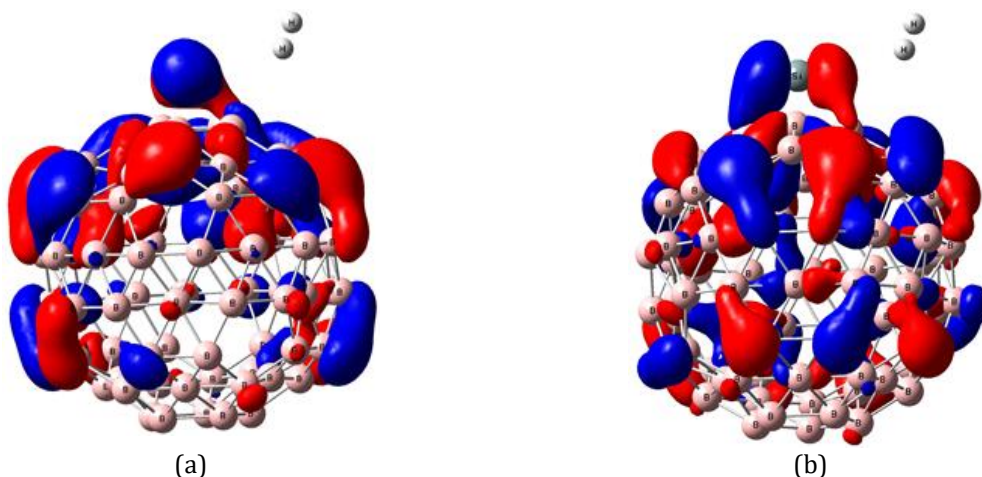
| (a) | (b) |

Figure 6. (a) HOMO and (b) LUMO of $B_{80}Si(H_2)_1$ complex. (The absolute values of the isosurfaces of the wave functions are 0.03).

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 $Ca_{12}B80$ [2] and $Mg_{12}B80$ [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.
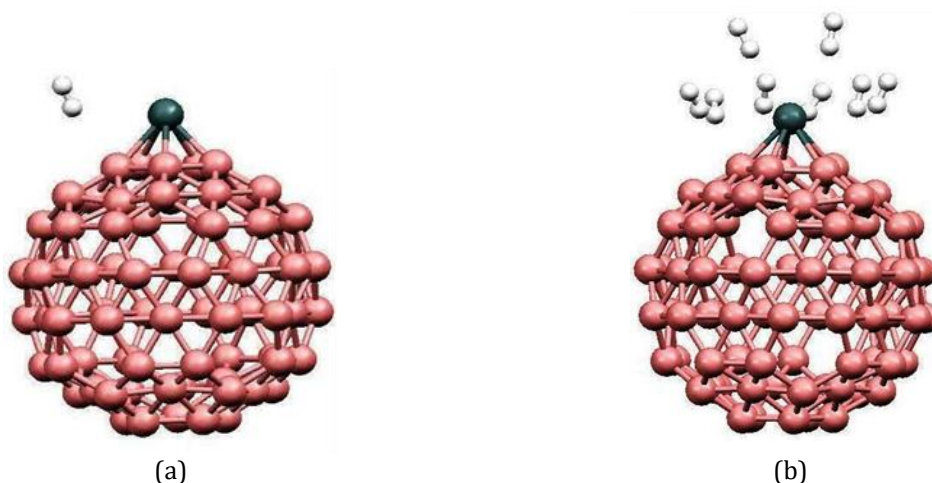

| (a) | (b) |

Figure 7. Optimized configurations of a Si-doped B_{80} (a) with a single H_2 molecule, (b) with 8 H_2 molecules at the GGA level of theory.
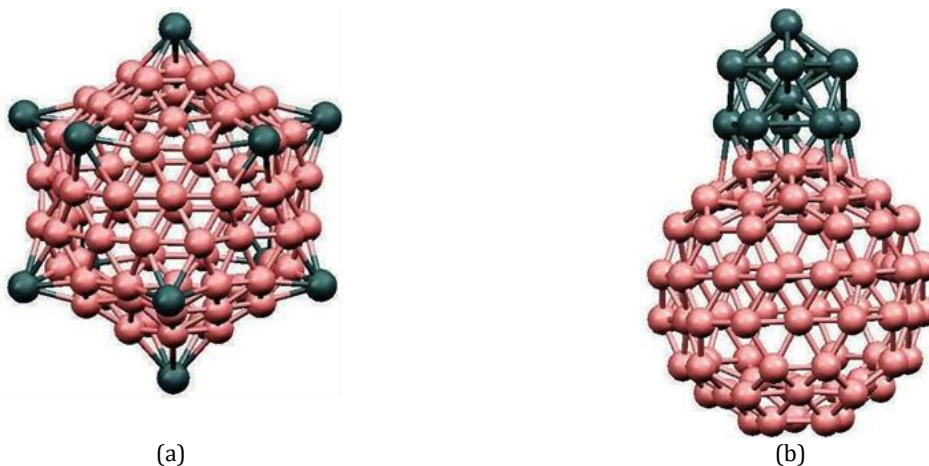
(a)   (b)

Figure 8. Two isomers of $Si_{12}B_{80}$ as: (a) 12 Si atoms coated on pentagonal rings of B_{80}, and (b) a Si_{12} cluster on B_{80}.
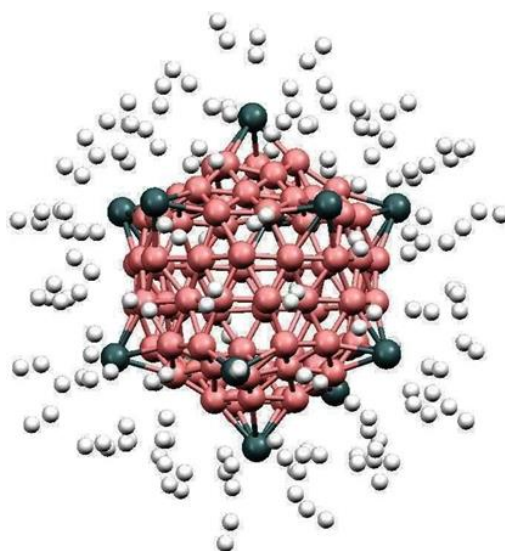

Figure 9. Optimized configurations of $B_{80}Si_{12}(H_2)_{96}$ system at the GGA level of theory.

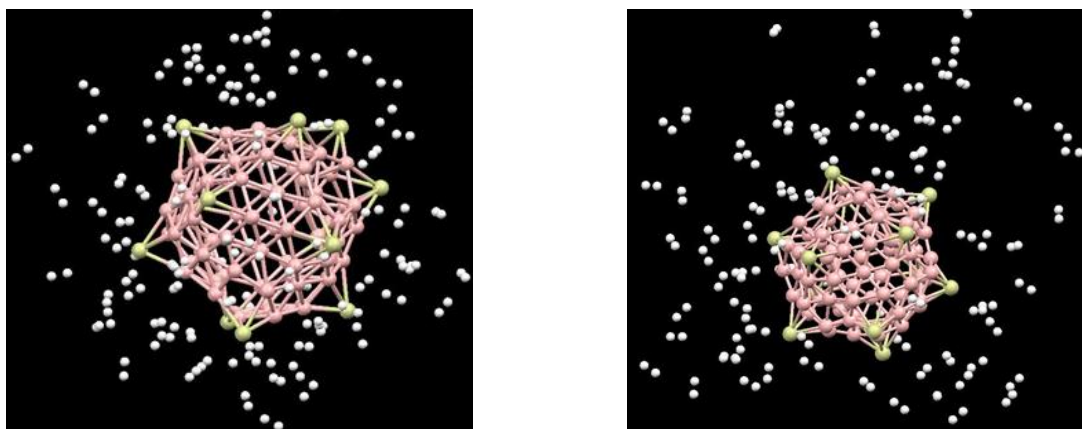**Figure 10**. Snapshots of first-principles MD simulations of the $Si_{12}B_{80}(H_2)_{96}$ system at 300K for 3ps (a) GGA without vdW corrections and (b) GGA with vdW corrections.

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.

4. Acknowledgement

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