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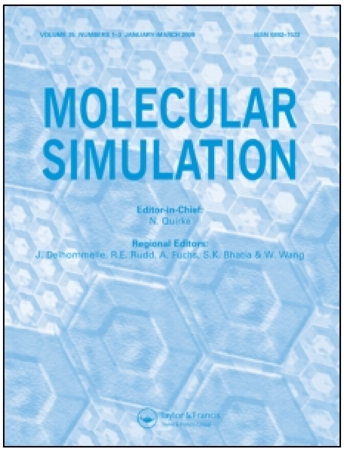

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Fully exohydrogenated Si_{60} fullerene cage

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Fully exohydrogenated Si_{60} fullerene cage

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Using first-principles calculations based on density functional theory, we demonstrate that Si_{60} fullerene cage can be stabilized by exohydrogenated method. In contrast to previous theoretical studies that Si_{60} fullerene geometry construction will be seriously distorted when it is bare or encapsulated by metal atom clusters, exohydrogenated scheme shows that $Si_{60}H_{60}$ cage will be able to keep perfect fullerene structure similar to C_{60}.

Keywords: Si_{60}; Fullerene; Exohydrogenate; Stability

1. Introduction

Nanoscale silicon (Si) clusters are currently of great interest because they play an important role not only on the fabrication of advanced microelectronic devices, but also on the understanding of nanomaterial foundation physical principle. Recently, with the development of C_{60} fullerene research and applications, more interests have been drawn in exploring the Si_{60} fullerene cage since both of Si and carbon are isovalent. However, Si prefers sp^3 hybridization while C prefers sp^2 hybridization, leading to that tube or cage structure are stable for C clusters but highly unstable for Si ones. Although some new theoretical and experimental developments have been achieved in stabilizing little Si cage clusters [1–3], the Si_{60} fullerene cage still keep illusive and has not been found in experiment. It was reported that little Si or Ge cages could be stabilized by endohedral encapsulation of transition metal atoms, which have been verified by the experimental and theoretical results [2–4]. But, this method seems not valid for Si_{60} fullerene cage because the diameter of Si_{60} fullerene cage is so large that it is difficult for all Si sites to be encapsulated by single metal atom in the cage. Another trial way to stabilize the Si_{60} fullerene cage is to form a $C_{60}@Si_{60}$ structure suggested by Harada *et al.* [5]. Unfortunately, the $C_{60}@Si_{60}$ has not been synthesized experimentally so far for the reason that C_{60} has a so large diameter and it stretches the Si–Si bond to induce the higher cluster energy, which can not be compensated by relatively weak Si–C bond energy [6]. Recently, a theoretical study have tried to stabilize Si_{60} cage by including small magic cluster $Al_{12}X(X = Si, Ge, Sn, Pb)$ in it [6]. Although its results showed that Si_{60} cage could be stabilized by this method, the embedded clusters of $Al_{12}X$ were all decomposed and the optimized geometries of the Si cage showed that the fullerene geometry structure was seriously distorted.

Another way to stabilize Si cage structure is hydrogenated method, which has been proved effective for little Si cage [1]. Small Si cage adsorbed by H such as $Si_{20}H_{20}$ shows high symmetries with all Si atoms nearly tetrahedrally bonded, which suggests that hydrogenated method may be applied in Si_{60} fullerene cage. Especially Si_nH_x such as $Si_{29}H_{24}$ could emit light in the visible range [7], which also makes it possible to apply hydrogenated Si_{60} cage for photoluminescence. But, up to now, the synthesis of hydrogenated Si_{60} cage is still a challenge whatever in experiment and theory.

Since carbon nanostructures such as nanotubes have been found the promise application for the storage of hydrogen due to large effective surface. Many researches have been performed to investigate the hydrogen–carbon cage interactions such as $C_{20}H_{20}$ [8], $C_{60}H_{36}$ [9]. In comparison with the carbon cages, the Si cage materials probably attract H more effectively, most likely due to the stronger interaction between H and Si dangling bond from sp^3 hybridization.

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2. Details of calculations

In this letter, we reported the Si_{60} fullerene cage stabilized by adsorbed H atoms using first-principles calculations based on density functional theory. The calculation code was $Dmol^3$ from Accelrys Inc. [10], in which each electronic wave function is expanded in a localized atom-centered basis set defined on a numerical grid. All-electron calculations were performed with a double numeric polarized basis set (DNP) and the gradient-corrected PBE functional. A finite basis-set cut-off of 4.6 Å was used to reduce computational time without any significant loss in accuracy.

3. Results and discussion

We have carried out a systematic study of the stability of Si_{60} fullerene cage with or without H exohydrogenate. The geometry calculation was carried out without any symmetry constraint and all atoms were relaxed until a minimum energy structure was obtained. The tolerances of energy, gradient and displacement convergence were 10^{-5}Hartree, 0.002 Hartree/Å and 0.005 Å, respectively. Since the pure Si_{60} fullerene structure has not been observed in experiment, the beginning Si_{60} cage was made by pentagon and the hexagon with perfect icosahedral fullerene cage. So Si_{60} model is similar to C_{60} except larger cage diameter. Exohydrogenated Si_{60} fullerene cage is based on the bare Si_{60} model just adding H atom adsorbed to each Si site. The cluster model for hydrogenated Si_{60} cage contains 60 Si atoms and 60 H atoms, so called as $Si_{60}H_{60}$.

At first, the structural optimization calculations were performed for bare Si_{60} cage (Si_{60}). Because Si_{60} cluster has many isomers, the initially used model will determine the optimized geometry. In this paper, we focus on the fullerene cage model as shown in figure 1a. The optimized result (figure 1b) shows the distorted spherical structure which has some different bond lengths ranging from 2.23 to 2.35 Å (some bond length labeled in the figure). The binding energy of the cluster is 229.36 eV. The highest occupied-lowest unoccupied molecular orbital (HOMO–LUMO) gap is 0.62 eV. The optimized Si_{60} cage was found a lower C_{2h} symmetry geometry with a tolerance of 0.1 Å, in agreement with Ref. [11], which suggests that the initial configuration with I_h symmetry is unstable.

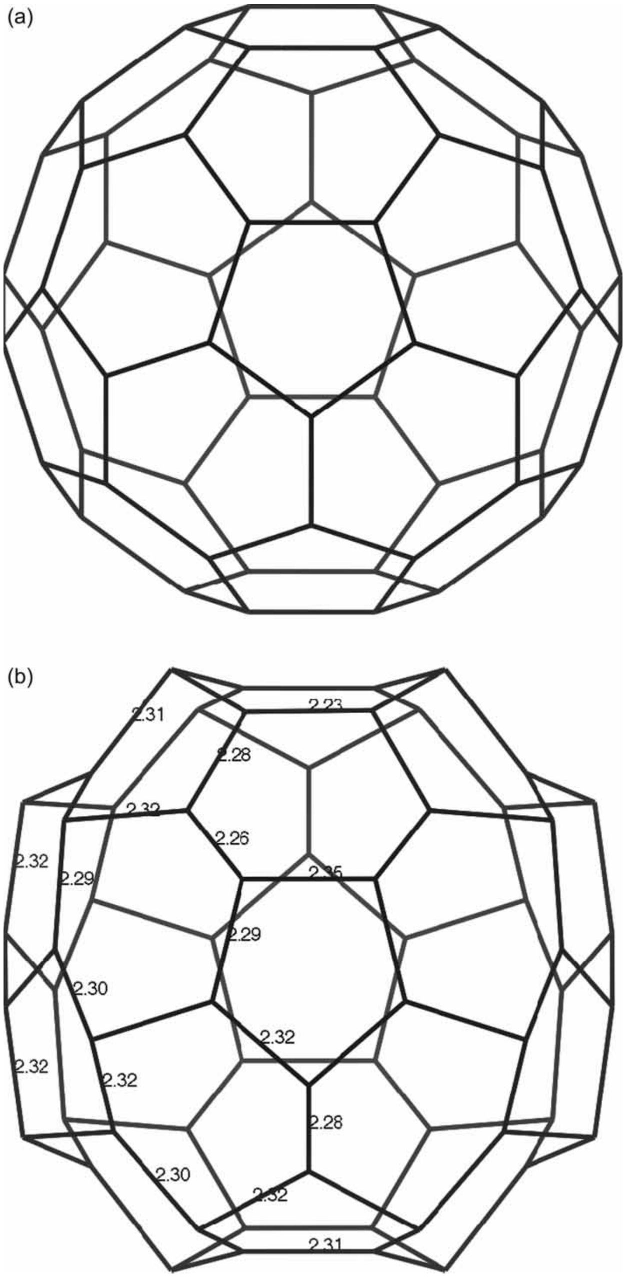

Figure 1. Starting (a) and optimized (b) geometries of Si_{60} obtained from fullerene cage. The labels show some bond length of the Si–Si bond for optimized Si_{60} structure.

Then exohydrogenated Si_{60} cage ($Si_{60}H_{60}$) has been studied. In the initial model the Si sites are same as the initial bare Si_{60} cage structure mentioned above. The difference is that every Si atom is adsorbed with hydrogen atom from outside of the cage as shown in figure 2a. The final optimized $Si_{60}H_{60}$ structure is shown in figure 2b. Obviously we can find that the optimized one remains spherical-like geometry, which suggests that the adsorbed H atoms stabilize the structure of Si_{60} cage. The hydrogenated Si_{60} cage make that all four valence electrons of Si could participate covalent bonding so all Si atoms nearly tetrahedrally bonded (figure 2b). Si–H bond length is 1.50 Å for all the 60 Si–H bonds. In addition, the Si–Si bond length for $Si_{60}H_{60}$ was uniform to two different values after optimization. The bond length of pentagon is 2.37 Å, while the Si–Si bond connecting two neighboring pentagon is 2.36 Å. The $Si_{60}H_{60}$ has a large HOMO–LUMO gap of 3.57 eV. Noting the previous study [1], in which Vijay Kumar *et al.* calculated empty cage of Si_nH_n such as $Si_{12}H_{12}$, $Si_{16}H_{16}$ and $Si_{20}H_{20}$, we found their Si_nH_n cages had large HOMO–LUMO gaps and the gap increased with n(2.564, 2.881 and 2.911 eV for $n = 12$, 16, 20). Our calculated $Si_{60}H_{60}$ cage agree well with this rule by a larger gap value of 3.57 eV with the larger

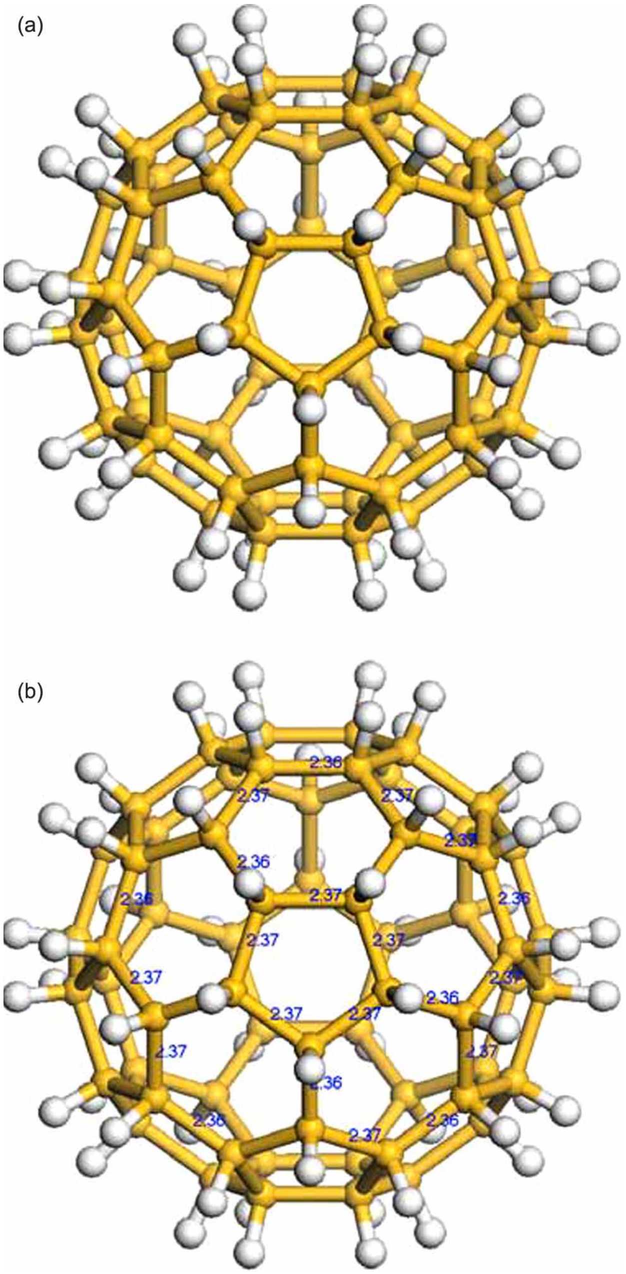

Figure 2. Starting (a) and optimized (b) geometries of $Si_{60}H_{60}$. The labels show some bond length of the Si–Si bond for optimized $Si_{60}H_{60}$ structure.

$n = 60$. The optimized $Si_{60}H_{60}$ cage was found an I_h symmetry geometry with a tolerance of 0.01 Å. In contrast to many previous studies for Si_{60} cage which always seriously distorted and lower symmetry than C_{60} fullerene, the $Si_{60}H_{60}$ does still keep spherical-like geometry similar to C_{60} fullerene cage. The $Si_{60}H_{60}$ also keeps a high I_h symmetry same as C_{60} fullerene.

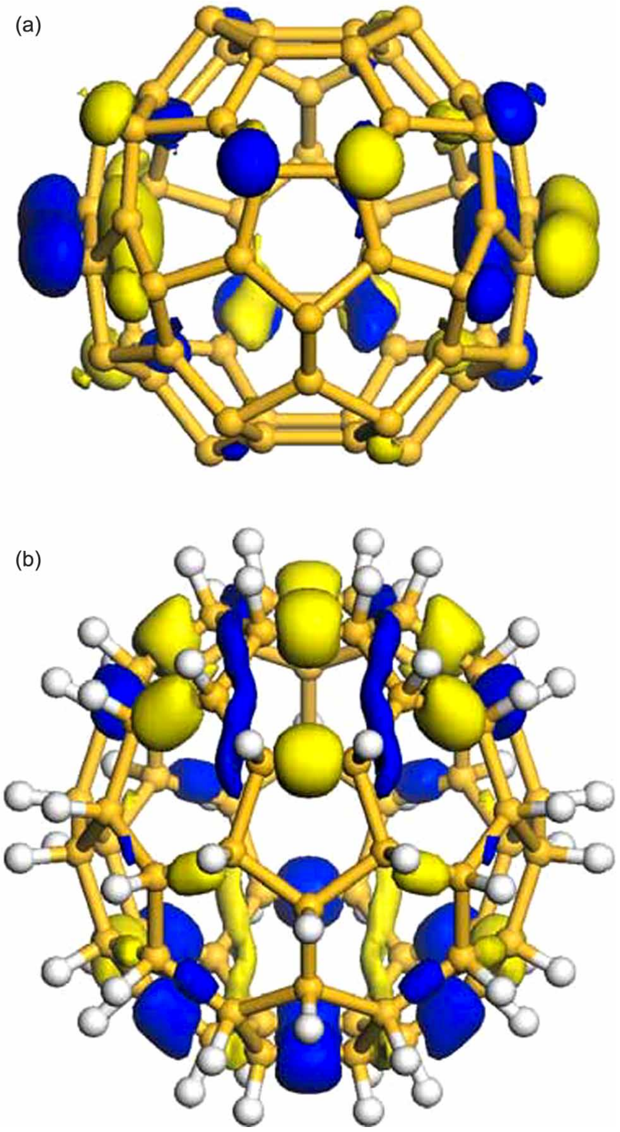

Figure 3. Isosurfaces at fixed value (2% of max. amplitude) of highest occupied molecular orbital (HOMO) for the following: (a) bare Si_{60} and (b) hydrogenated $Si_{60}H_{60}$. The HOMO is affected much by the H.

Table 1 shows some differences between bare Si_{60} and $Si_{60}H_{60}$. It can be found that the HOMO–LUMO gap of $Si_{60}H_{60}$ is very larger than that of bare Si_{60}. The average Si–Si bond length of $Si_{60}H_{60}$ is also longer than that of bare Si_{60}. This elongated bond could be due to the adsorbed H atom that makes covalence bond with Si atom, resulting in that some electrons between Si–Si bonds transferred to Si–H bonds. This kind of electron transfer will weaken Si–Si bond energy and elongate its bonds. The loss of binding energy of Si_{60} could be compensated by Si–H binding energy, so the whole cage will keep more

Table 1. Symmetry, binding energy, Si–Si bond length, HOMO, LUMO and HOMO–LUMO gap calculated for $Si_{60}H_{60}$ cage and bare Si_{60}.

Cluster	*Symmetry*	*Binding energy (eV)*	*Si–Si bond length (Å)*	*HOMO (eV)*	*LUMO (eV)*	*Gap (eV)*
Si_{60}	C_{2h}	− 229.36	2.23 ~ 2.35	− 5.05	− 4.43	0.62
$Si_{60}H_{60}$	I_h	− 400.08	2.36 ~ 2.37	− 6.54	− 2.97	3.57

energy favorable state than bare Si_{60}. In order to have an idea of the electron state affected by adsorbed H, we have analyzed the HOMO orbital for the before and after hydrogenated cluster (Si_{60} and $Si_{60}H_{60}$). Figure 3 gives the plots of the HOMO for the two cases. When it is bare Si_{60}, the HOMO orbitals concentrate at the top site of some Si atoms, meaning some dangling bond. These orbitals are distributed at two sides of the cage (see left and right sides of figure 3a). When it is $Si_{60}H_{60}$, the Si dangling bonds are saturated by H and the HOMO orbitals concentrate at the middle of some Si bonds. These orbitals in $Si_{60}H_{60}$ are distributed at the top and bottom sides of the cage (figure 3b).

To investigate the charge transfer between H and Si atoms, we computed partial charge on each atom in $Si_{60}H_{60}$ using the Mulliken population analysis. The results show that every H atom should transfer 0.033 electrons to the Si atom, which was directly bonded. A little transferred electrons suggest the covalence bonding for Si–H.

It is difficult to compare the stability of this two clusters by comparing their binding energy because the $Si_{60}H_{60}$ add additional 60 H to the Si_{60}, which results in that its binding energy is larger than bare Si_{60}'s one naturally. Now we investigate one bare Si_{60} cluster and 30 hydrogen molecules as a whole system which has the same atom type and atom number as $Si_{60}H_{60}$ cluster. By calculating the total energy respectively for two clusters, we find the total energy of the $Si_{60}H_{60}$ cage is 36.07 eV lower than that of bare $Si_{60} + 30H_2$ cluster, which indicates that the $Si_{60}H_{60}$ is very stable and Si_{60} easily attract hydrogen in the surrounding environment. This characterization makes Si_{60} fullerene a possible candidate material for hydrogen storage. We also compare $Si_{60}H_{60}$ with the cluster including 60 Si atoms in crystal Si and 30 H_2, which has the same atom type and atom number as $Si_{60}H_{60}$. The calculation results show that the total energy of the $Si_{60}H_{60}$ cage is 12.09 eV larger than this artificial isomer (about 0.1 eV/atom difference). Due to the 60 Si atoms in crystal should bind surrounded Si atoms, it's energy may be underestimated. So the $Si_{60}H_{60}$ should be relative stable. Since there are many isomers for the large clusters and the optimization structure depends on the initial model we choose, it should be emphasized that this stable cluster configuration does not mean the obtaining of $Si_{60}H_{60}$ cluster ground state geometry. Anyway, it can be safely concluded that $Si_{60}H_{60}$ fullerene structure should be a metastable state of this cluster.

In summary, systemic calculations are performed on $Si_{60}H_{60}$. The results show that $Si_{60}H_{60}$ is an energetically favorable state. Sixty H atoms adsorbed to Si_{60} make Si fullerene cage keep high symmetry to I_h, longer Si–Si bond length and larger HOMO–LUMO gap to 3.57 eV. So it is possible to synthesize $Si_{60}H_{60}$ if one uses exohydrogenated method to Si cluster and this $Si_{60}H_{60}$ cage maybe a candidate material for the storage of hydrogen.

Acknowledgements

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