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Abstract

The lowest-energy structure of the Si_{60} cluster has been determined from an unbiased search using a genetic algorithm (GA) with the tight-binding model followed by local optimization of 'hand-made' structures using density-functional theory (DFT). GA simulations show that Si_{60} tends to adopt endohedral fullerene configurations. A large number of isomers with different stuffing/cage ratio and cage configuration were then constructed and optimized at DFT level. An endohedral fullerene of $Si_{12}@Si_{48}$ was found to be most stable; it is energetically preferred to the hollow I_h cage by 12.371 eV and to a previously proposed lowest-energy structure by 4.841 eV. The competition between different structural growth patterns at Si_{60} is discussed.

Since the discovery of the C_{60} cage with high symmetry (I_h) [1], there have been considerable efforts concentrating on its analogue, the Si_{60} cluster [2–14]. One may naturally ask a simple question: does Si_{60} prefer the same football-like cage configuration as C_{60}? If the answer is no, what is the lowest-energy structure of Si_{60}?

In some early studies [2–7], a perfect I_h cage in complete analogy with C_{60} was assumed for Si_{60}, and the associated structural and electronic properties were computed. However, other investigations revealed that the spheroidal hollow I_h cage of Si_{60} is indeed unstable under finite-temperature molecular dynamics relaxation and will transform into other low-symmetry cages [8–13]. For example, Chen compared four Si_{60} cages with different symmetries (I_h, T, T_h, C_i) and found that the C_i cage is the most stable one. Moreover, other types of structure, either relaxed bulk-like fragments [9] or endohedral structures [10, 13], were found to be energetically preferred to the hollow Si_{60} cages. For instance, based on the endohedral fullerene $Si_{20}@Si_{40}$, Sun *et al* proposed two possible low-energy configurations for Si_{60} [13]. However, the true global minimum structure of Si_{60} is still unclear since an unbiased search is lacking.

Experimentally, it is almost impossible to directly determine the geometrical structure of a free cluster. The structural information can be only inferred from the physical and chemical properties of the clusters. For Si_n clusters with size around $n = 60$, the ionic mobilities [15], binding energies [16], ionization potentials [17], photoelectron spectra [18], and chemical reactivity [19] were obtained in previous experiments. Most of the measured properties exhibit smooth size dependence, implying that the cluster structure follows a given growth pattern and that the addition of one more atom will not induce dramatic structural reconstruction. Ionic motilities of the Si_n clusters reveal a structural transition from prolate shapes to spherical-like ones around $n = 27$, and the spherical shape of the clusters lasts up to at least $n = 60$ [15]. This non-spherical to spherical transition of cluster geometry coincides well with recent theoretical simulation of the Si_n clusters ($n = 27$–39) [20]. It was also found that Si_n clusters with $n = 30$–70 are much less reactive than bulk silicon [19], implying that these clusters have well-reconstructed surfaces with minimum dangling bonds.

From a chemical bonding point of view, although silicon and carbon belong to the same group in the periodic table, there is a fundamental difference between them. It is well known that carbon atoms may undergo either sp^2 or sp^3 hybridization, while the valence orbitals of silicon only allow sp^3 hybridization. To stabilize a silicon fullerene cage, some endohedral atoms are needed to form sp^3 hybridization and to saturate the surface dangling bonds. Recently, using a combined scheme of an unbiased search at the semi-empirical tight-binding level and biased local optimization using density-functional theory, Zeng, Zhao, and co-workers have systematically studied the structural properties of Si_n clusters with $n = 27$–50 and revealed that the endohedral silicon cages are the general structural motif of medium-sized Si_n clusters up to $n = 50$ [20–25]. An empirical rule [21, 22] within the space-filling picture has been proposed to estimate the stuffing/cage ratio of a silicon endohedral fullerene cage. Assuming a nearly spherical shape, the maximum number p of the atoms that can be stuffed inside a fullerene cage with q surface atoms ($q = 26$–60) is given by

$$p \simeq -1.5525 + 0.03071q + 0.00515q^2. \tag{1}$$

Hence, the possible stuffing/cage combinations for Si_{60} cluster within $p + q = 60$ are $Si_{14}@Si_{46}$, $Si_{12}@Si_{48}$, and $Si_{10}@Si_{50}$, while $Si_{12}@Si_{48}$ fits equation (1) best. However, it is still questionable whether the structural growth pattern of endohedral fullerene will continue up to Si_{60}.

To validate the structural motif of endohedral fullerene for Si_{60} and to find the possible lowest-energy structures, in this work we performed a comprehensive study of the Si_{60} cluster using a two-step strategy. First we performed an unbiased search using a genetic algorithm (GA) [26, 27] incorporated with a non-orthogonal tight-binding (NTB) model [28]. The same GA-NTB scheme has been used in previous studies of medium-sized Si_n clusters with $n = 27$–50 [20, 21]. To further locate the lowest-energy endohedral fullerene configuration, we examined a large number of structural isomers of Si_{60} by considering different combinations of outer fullerene cages and filling atoms, i.e., $Si_{14}@Si_{46}$, $Si_{12}@Si_{48}$, and $Si_{10}@Si_{50}$. These 'hand-made' structural isomers were optimized using all-electron density-functional theory implemented in the DMol package[3]. We used a double numerical basis including the d-polarization function (DND) and adopted the generalized gradient approximation with the Perdew–Burke–Ernzerhof (PBE) functional to describe the exchange–correlation interaction [30]. The accuracy of the present PBE/DND scheme has been validated for Si_2 dimer and silicon solid in a previous paper [22].

In the GA simulation, a number of initial configurations were generated from scratch. Any two individuals in this population were then chosen as parents to produce a child cluster via a

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[3] DMol is a density-functional theory (DFT) package based on atomic basis distributed by Accelrys Inc. [29].

'cut and splice' crossover operation [26], followed by an optional mutation operation of 30% probability. The child cluster was relaxed using tight-binding molecular dynamics simulation, while the potential energy surface (PES) of the silicon clusters was described by an NTB total energy model [28]. The locally stable child was then selected to replace its parents if it had lower energy. In this work, we kept 128 parents in the population and performed over 10 000 GA iterations to ensure the global minimum on the PES.

Similar to previous results on smaller Si_n clusters ($n = 27$–50), an unbiased GA search revealed a strong tendency of forming the endohedral fullerene structure in a Si_{60} cluster. Almost all the final configurations from the GA simulation can be viewed as endohedral fullerene cages, including both classical fullerenes (containing only five-membered and six-membered rings) and non-classical fullerenes (also containing four-membered and/or seven-membered rings) [31]. Among the top 28 lowest-energy isomers from the GA search (within energy span of 1 eV), we found ten isomers of $Si_{12}@Si_{48}$ configurations and thirteen isomers of $Si_{10}@Si_{50}$ configuration. Although the NTB model is not highly accurate for describing the PES of silicon clusters, the unbiased GA search incontestably demonstrated that the endohedral fullerene is the dominant structural motif of Si_{60}. Moreover, the present results support the empirical estimation of stuffing/cage ratio by equation (1).

To further explore the lowest-energy configuration of Si_{60}, we have systematically examined all isomers belonging to the three possible combinations of endohedral fullerenes, $Si_{14}@Si_{46}$, $Si_{12}@Si_{48}$, and $Si_{10}@Si_{50}$. The initial structures of the fullerene cages were taken from the fullerene structure library [32], and the coordinates were uniformly rescaled by a factor of 1.7 to produce the silicon cages. For the classical fullerene cages with 46, 48, and 50 surface atoms, there are 116, 199, and 271 isomers, respectively. In this work, we used the same number indexes as in the fullerene structure library [32] to identify them. Similar to previous works [22, 23], we stuffed silicon atoms uniformly inside the fullerene cage only by space-filling consideration. After full geometry optimization, the lowest-energy ('best') isomers for each stuffing/cage combination of endohedral fullerenes are No. 104 for $Si_{14}@Si_{46}$, No. 199 for $Si_{12}@Si_{48}$, and No. 266 for $Si_{10}@Si_{50}$, respectively. Among them, the best $Si_{12}@Si_{48}$ endohedral fullerene based on the No. 199 cage of Si_{48} was found to be most stable. Other endohedral fullerenes with alternative stuffing/cage ratio lie higher in the PES, for example, $\Delta E = 0.851$ eV for the best $Si_{10}@Si_{50}$ isomer and $\Delta E = 1.525$ eV for the best $Si_{14}@Si_{46}$ isomer. These energy differences are in qualitative agreement with the GA-NTB results that Si_{60} tends to adopt an endohedral fullerene structure with $Si_{12}@Si_{48}$ and $Si_{10}@Si_{50}$ configurations. The top 28 isomers from the GA-NTB simulation were also optimized using the same PBE/DND scheme, but none of them are energetically comparable to the most stable 'hand-made' endohedral fullerenes. Thus, these GA-generated structures are not given in figure 1.

For comparison, we considered hollow cages configurations with different symmetries (I_h, T, T_h, C_i) [12], as well as the previously proposed endohedral fullerenes (SF1 and SF2) of $Si_{20}@Si_{40}$ [13]. In addition, we constructed a supercluster configuration using Si_{10} with tetracapped trigonal prism as building units, in the spirit of [25], and constructed a bulk-like fragment by cutting from a piece of diamond structure of silicon and slightly adjusting the position of a few surface atoms to reduce the dangling bonds. All of these structural isomers and their relative energies with respective to the lowest-energy configuration (of No. 199 for $Si_{12}@Si_{48}$) are shown in figure 1.

Most importantly, the energy of the current lowest-energy configuration of $Si_{12}@Si_{48}$ is significantly lower than the previously proposed ones [13], i.e., $\Delta E = 4.84$ eV for SF1 and $\Delta E = 5.04$ eV for SF2. Compared to the hollow cages, the current endohedral fullerenes with well-reconstructed surface are energetically more favourable by about 8–12 eV. Among those
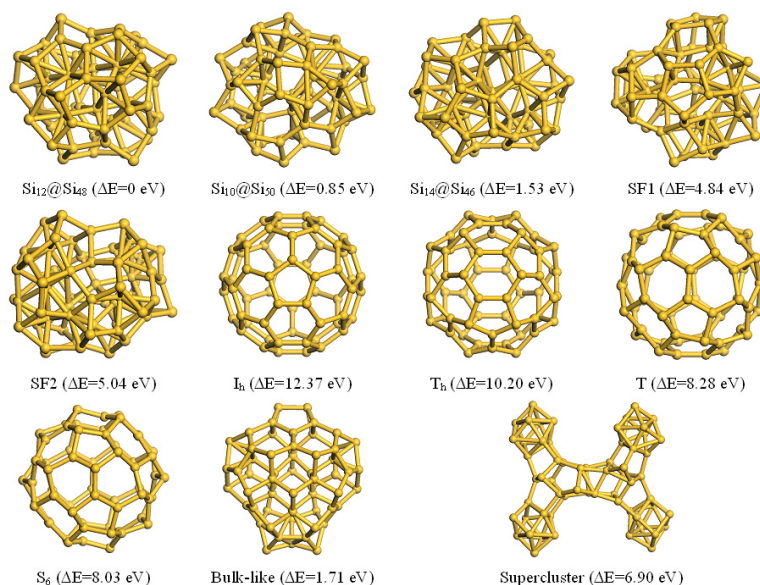
Figure 1. Structure and relative energy for representative isomers of Si_{60}. For each combination of the endohedral fullerenes, such as $Si_{14}@Si_{46}$, $Si_{12}@Si_{48}$, and $Si_{10}@Si_{50}$, only the best isomers with lowest energy are shown as representative.

(This figure is in colour only in the electronic version)

hollow cage configurations, the C_i cage proposed by Chen [12] transforms into S_6 symmetry after optimization, which has lower energy than other cages. From our calculation, the energy differences between the high-symmetry I_h cage and the low-symmetry T_h, T, S_6 (C_i) cages are 2.171, 4.096, and 4.338 eV, respectively, in reasonable agreement with the previously reported values of 1.522, 3.755, and 3.959 eV, at the B3LYP/6-31G* level [12].

In figure 1, it is noticeable that the Si_{10}-based supercluster configuration is not quite energetically favourable, with $\Delta E = 6.9$ eV, whereas the energy of a bulk fragment with a diamond-structured core and a reconstructed fullerene-like surface is rather closer to the lowest-energy configuration with $\Delta E = 1.71$ eV. In the medium-sized silicon clusters, there are several competitive structural growth patterns, such as a supercluster based on Si_9 or Si_{10} units of [14, 24, 33], endohedral fullerene [20–25], and bulk-like structure with diamond lattice [14]. The former one is the continuation of the structural motif of the smaller Si_n clusters [24, 33], while the silicon clusters will eventually become a piece of bulk solid with diamond structure when the cluster size is large enough [14]. The present results imply that the Si_n clusters in the size regime around $n = 60$ have already deviated from the molecule-like behaviour of small clusters, but the transition into bulk solid has not completed yet. In other words, the structural motif adopted by endohedral fullerene represents an intermediate state between molecule-like and bulk-like sides. Using a cutoff distance 2.65 Å for the Si–Si bond [23], the average coordinate number (CN) of the lowest-energy configuration of $Si_{12}@Si_{48}$ is 4.03, comparable to the bulk value. The average CN for the endohedral atoms is 5.25, while that for the surface atoms on the cage is 3.73.

The validity of our theoretical calculations can be also affirmed by comparing with the available experimental data. The theoretical binding energy of the Si_{60} cluster with the lowest-energy configuration is 3.943 eV, which reproduces the experimental value (4.13 eV) well [16].

The adiabatic ionization potential (IP) from our calculations is 5.621 eV, in close agreement with the experimental IP of 5.4 eV [17]. The electronic gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) is 0.333 eV, compared to the gap of 0.65 eV for the I_h cage and 0.731 eV for the S_6 cage.

Recently, Ona *et al* [14] coupled GA with the semiempirical MSINDO method to search stable structures of medium-sized Si_{60} clusters and the structures selected by the GA-MSINDO global search were further optimized at the DFT level. For Si_{60}, they also obtained an endohedral cage-like configuration as the most stable structure, which is very similar to the SF1 structure reported by Sun *et al* [13]. However, since the coordinates of their structure are not available, it is impossible to make a direct comparison between our lowest-energy structure and theirs.

So far, we have mainly focused on the classical fullerenes. Our calculations show that the non-classical endohedral fullerenes with four-member rings or seven-member rings on the surface are usually less favourable than the classical fullerenes. However, it is not possible to entirely rule out the existence of non-classical endohedral fullerenes since there are limitless possibilities of them.

To summarize, the lowest-energy structure of Si_{60} was determined using a genetic algorithm and density-functional theory. An unbiased GA search at the NTB level suggested that the endohedral fullerene is the general structural motif of Si_n clusters in the size regime around $n = 60$. Careful examinations of all possible endohedral fullerene configurations with stuffing/cage ratio of 14@46, 12@48, 10@50 show that the No. 199 cage of $Si_{12}@Si_{48}$ is the lowest-energy one, which is energetically preferred to previously reported structures. Other types of structure, including hollow cages, Si_{10}-based superclusters, and diamond-like bulk fragments, have been compared. Our present results suggest that Si_{60} is in the intermediate stage of the transition from molecule-like to bulk-like behaviour.

Acknowledgments

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