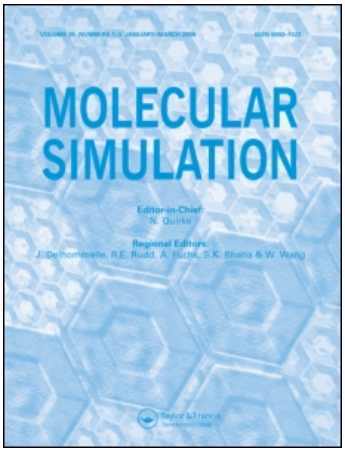

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Si_{60} fullerene-like cage passivated by F and Cl

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Si_{60} fullerene-like cage passivated by F and Cl

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It is generally considered that a bare Si_{60} fullerene-like cage is geometrically unstable. In this paper, a Si_{60} fullerene-like cage passivated by F or Cl atoms is investigated by the use of *ab initio* calculations based on density functional theory. The results show that passivated Si_{60} cage can be stabilised in a perfect fullerene structure. The geometry, stability and electronic properties for the passivated Si_{60} cage are discussed.

Keywords: Si_{60}; fullerene; passivation; stability

1. Introduction

Semiconductor cage structures have stimulated considerable interest in recent years due to their particular properties that are different from those of general semiconductor crystal materials [1]. Especially, the development of buckyball, C_{60}, greatly motivates researchers to investigate the possibility of forming silicon (Si) fullerene-like cages, since both silicon and carbon are isovalent. However, different electric characteristics between Si and C (e.g. Si prefers sp^3 hybridisation while C prefers sp^2 hybridisation) lead to the fact that tube or cage structures are stable for C clusters but highly unstable for Si clusters. Up to now, Si_{60} fullerene-like cages have not been found in nature or synthesised in laboratories. The stabilities of Si_{60} fullerene-like cages are mainly the focus of theoretical researches [2–4]. Since all-silicon Si_{60} molecules with a perfect fullerene-like structure were considered to be unstable by many computational studies [2,3], several structures were theoretically studied to stabilise Si_{60} fullerene-like cages, such as (a) Si fullerene encapsulation of $Ba@Si_{20}$ to form a $Ba@Si_{20}@Si_{60}$ structure [2], (b) Si fullerenes which include a C_{60} molecule to form a $C_{60}@Si_{60}$ structure [5], (c) Si fullerene encapsulation of a cluster, $Al_{12}X$ ($X = Si, Ge, Sn, Pb$) [2], (d) Si fullerene encapsulation of a metal atom to form $X@Si_{60}$ ($X = Zn, Pd, Be$) [6–8]. However, all of the cages mentioned above tended to be distorted. There was no valid structural form for Si_{60}, which can keep the high I_h symmetry of fullerenes. Recently, the hydrogenation method suggested by our group gives a possible way to realise fullerene-like $Si_{60}H_{60}$ cages [9]. The key idea of our method is to passivate the Si dangling bond to form stable sp^3 hybridisation. A similar exohedral doping method has also been reported to stabilise small Si cages [10,11]. In addition to H, strong electronegative elements such as F and Cl are usually employed to passivate Si dangling bonds in semiconductor technology. They form stable and strong F—Si or Cl—Si polar covalent bonds. Therefore, it is interesting to study whether F and Cl are excellent candidates for passivating Si_{60} cages.

2. Details of calculations

The atom models of Si_{60} cages passivated by F or Cl are investigated using first-principles calculations based on density functional theory. The calculation code was Dmol^3 from Accelrys Inc. (San Diego, CA, USA) [12], in which each electronic wave function is expanded in a localised atom-centred basis set defined on a numerical grid. All-electron calculations were performed with a double numeric polarised basis set and the gradient-corrected Perdew–Burke–Ernzerhof (PBE) functional. A finite basis-set cut-off of 4.6 Å was used to reduce computational time without any significant loss in accuracy. The geometry calculation was carried out without any symmetry constraint until the forces dropped below a threshold value of 0.002 Hartree/Å and the energy convergence below a threshold value of 10^{-5} Hartree. All atoms were relaxed until a minimum energy structure was obtained.

3. Results and discussion

The bare Si_{60} cage and H-passivated Si_{60} cage (called as $Si_{60}H_{60}$) have been investigated in our previous study [9]. Here, we carry out a systematic study on the stability of F-passivated and Cl-passivated Si_{60} cages (called as $Si_{60}F_{60}$ and $Si_{60}Cl_{60}$, respectively). The initial Si cage for geometry calculation is made by pentagon and hexagon with perfect icosahedral fullerene cage. Hence, the Si_{60}

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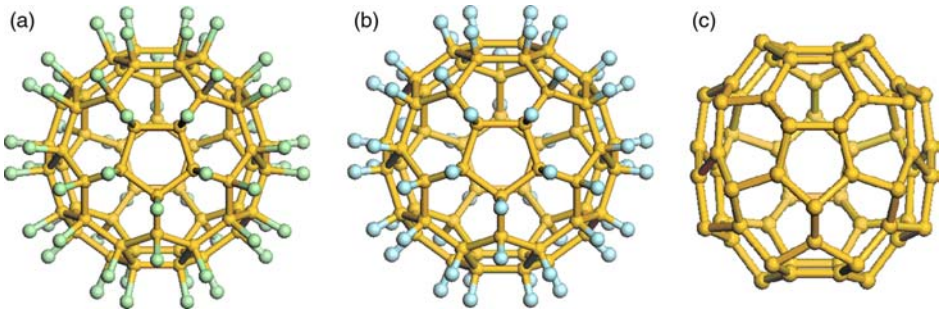

Figure 1. Optimised geometries for (a) $Si_{60}Cl_{60}$, (b) $Si_{60}F_{60}$ and (c) bare Si_{60}. The Si, Cl and F atoms are represented by yellow, green and blue balls, respectively (colour online).

model is similar to C_{60} except for larger cage diameter. Passivated Si_{60} cages by F or Cl are obtained by adding one F or Cl atom bonded to each Si atom. The energy-relaxed geometries for $Si_{60}Cl_{60}$ and $Si_{60}F_{60}$ are shown in Figure 1(a) and (b), respectively. The relaxed model of bare Si_{60} cage is shown in Figure 1(c) for comparison. The calculation results show that the $Si_{60}F_{60}$ and $Si_{60}Cl_{60}$ clusters are still in the fullerene-like geometry. Both possess the I_h symmetry with a tolerance of 0.01 Å. However, the bare Si_{60} cluster shows a distorted spherical structure and a lower C_{2h} symmetry geometry with a tolerance of 0.1 Å, in agreement with [3] which suggests the same C_{2h} symmetry for the bare Si_{60} by tight-binding molecular dynamics method.

The structure details and some characteristics for $Si_{60}F_{60}$ and $Si_{60}Cl_{60}$ are listed in Table 1. In spite of the similar structures for $Si_{60}F_{60}$ and $Si_{60}Cl_{60}$, there are some distinct differences for these two models. The Si—Si bond lengths range from 2.405 to 2.416 Å for $Si_{60}F_{60}$ and from 2.432 to 2.436 Å for $Si_{60}Cl_{60}$. The bond length is 1.626 Å for Si—F and 2.07 Å for Si—Cl. The highest occupied–lowest unoccupied molecular orbital (HOMO–LUMO) gap is 1.39 eV for $Si_{60}F_{60}$ and 2.03 eV for $Si_{60}Cl_{60}$. All of these differences can be attributed to the different interaction for F—Si and Cl—Si bonds. Different HOMO and LUMO orbital energy levels for bare Si_{60}, $Si_{60}H_{60}$, $Si_{60}Cl_{60}$ and $Si_{60}F_{60}$ are shown in Figure 2. It can be found that the energy gap of $Si_{60}Cl_{60}$ is the largest (2.03 eV). Figure 3 shows the HOMO and LUMO for the $Si_{60}Cl_{60}$ cage. The localisation of HOMO at Si—Si bonds and LUMO near Cl atoms signifies the nature of highly reactive sites. The orbital distribution for $Si_{60}F_{60}$ (not shown) is similar to that for $Si_{60}Cl_{60}$.

In order to investigate the charge population state for Si cages, we computed partial charge on each atom in $Si_{60}F_{60}$ and $Si_{60}Cl_{60}$ by the use of Mulliken population analysis. It is found that every Si atom transfers 0.48 electrons to the F atom in $Si_{60}F_{60}$, and that every Si atom transfers 0.24 electrons to the Cl atom in $Si_{60}Cl_{60}$. It is natural for F to obtain more electrons than Cl, due to the

Table 1. Symmetry, bond length and HOMO–LUMO gap calculated for $Si_{60}F_{60}$ and $Si_{60}Cl_{60}$ clusters.

Cluster	Symmetry	Si—Si bond length (Å)	Si—F (Cl) bond length (Å)	Gap (eV)
$Si_{60}F_{60}$	I_h	2.405–2.416	1.63	1.39
$Si_{60}Cl_{60}$	I_h	2.432–2.436	2.07	2.03

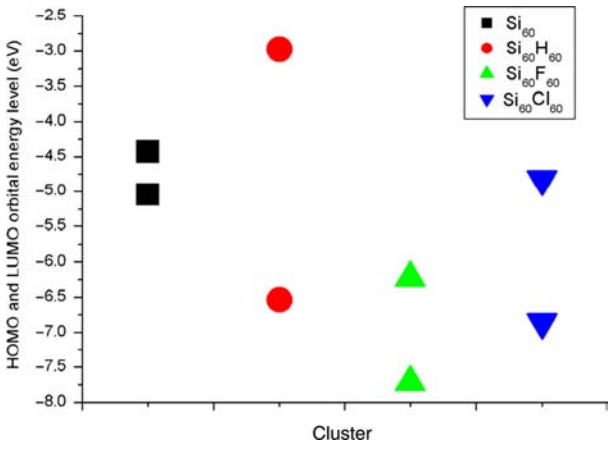

Figure 2. The HOMO and LUMO orbital energy levels for bare Si_{60}, $Si_{60}H_{60}$, $Si_{60}Cl_{60}$ and $Si_{60}F_{60}$.

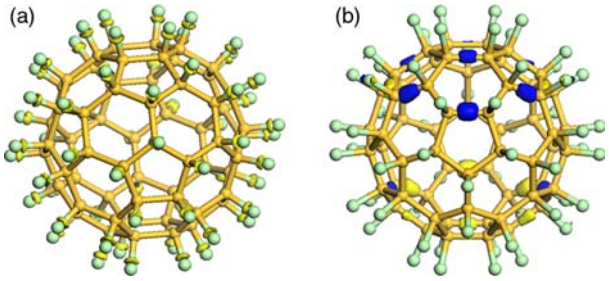

Figure 3. The orbital isosurfaces at fixed value for the $Si_{60}Cl_{60}$ cluster: (a) LUMO (1.8% of the maximum amplitude) and (b) HOMO (3% of the maximum amplitude).

Table 2. Binding energies for different clusters.

Cluster	Si_{60}	$Si_{60}F_{60}$	$Si_{60}Cl_{60}$	$Si_{60}H_{60}$
Binding energy (eV/atom)	3.83	4.54	3.58	3.33

fact that F is more electronegative than Cl. The electron transferring makes the cage similar to an electropositive ball wrapped by an electronegative shell. This should induce some interesting electromagnetism characteristics.

As mentioned above, the cage structure for Si with a perfect I_h symmetry can be obtained owing to adsorbed F or Cl atoms. The passivated Si_{60} cages make all four valence electrons of Si to participate in covalent bonding so that all Si atoms are nearly tetrahedrally bonded. This results in the considerably stable structure and low total energy. It can be concluded that the $Si_{60}Cl_{60}$ or $Si_{60}F_{60}$ fullerene structure should be a metastable state of this type of cluster. Table 2 shows the binding energy values for different clusters. It can be found that the binding energy for $Si_{60}F_{60}$ is 4.54 eV/atom, and this energy is the largest among the binding energies for all the clusters. The high binding energy for $Si_{60}F_{60}$ indicates that the interaction between Si—Si bond and Si—F bond is strong, and that this fullerene-like structure should be relatively stable.

In summary, systematic calculations are performed on $Si_{60}F_{60}$ and $Si_{60}Cl_{60}$. We show that $Si_{60}F_{60}$ and $Si_{60}Cl_{60}$ are energetically stable states. Both are able to keep the high symmetry of I_h.

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