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M_4@Si_{28} (M=Al,Ga): Metal-encapsulated tetrahedral silicon fullerene

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It is known that silicon fullerenes cannot maintain perfect cage structures like carbon fullerenes. Previous density-functional theory calculations have shown that even with encapsulated species, nearly all endohedral silicon fullerenes exhibit highly puckered cage structures in comparison with their carbon counterparts. In this work, we present theoretical evidences that the tetrahedral fullerene cage Si_{28} can be fully stabilized by encapsulating a tetrahedral metallic cluster (Al_4 or Ga_4). To our knowledge, this is the first predicted endohedral silicon fullerene that can retain perfectly the same cage structure (without puckering) as the carbon fullerene counterpart (T_d-C_{28} fullerene). Density-functional theory calculations also suggest that the two endohedral metallosilicon fullerenes T_d-M_4@Si_{28} (M=Al and Ga) can be chemically stable because both clusters have a large highest occupied molecular orbital-lowest unoccupied molecular orbital energy gap (~0.9 eV), strong spherical aromaticity (nucleus-independent chemical shift value of −36 and −44), and large binding and embedding energies. © *2005 American Institute of Physics*.
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INTRODUCTION

Ever since the discovery of the buckminsterfullerene C_{60},[1] carbon fullerenes have been a subject of intense experimental and theoretical studies. In essence, fullerene structures can be viewed as hollow cages composed of 12 pentagons plus certain number of hexagons. Silicon is a group-IV neighbor element of carbon in the periodic table. However, structural properties of silicon, ranging from bulk to small clusters, can be quite different from the carbon largely because of unfavorable sp and sp^2 hybridizations of valence orbitals.[2–5] It is known that low-lying medium-sized silicon clusters do not show hollow-cage structures like carbon fullerenes.[6–9] In fact, first-principles calculations suggest that medium-sized silicon clusters beyond Si_{27} tend to form "stuffed-fullerene-like" structures with highly puckered and distorted outer cages.[8,9] To date, "bucky" silicon has not yet been observed nor synthesized in laboratory.

Since hollow-cage form of silicon fullerenes is intrinsically high energy, much attention has been devoted to chemical stabilization of silicon fullerenes through encapsulation.[10–17] For carbon, endohedral fullerenes have long been established.[18] However, for the silicon counterpart, the existence of endohedral fullerenes such as endohedral carbon fullerenes remains elusive. Some progress has been made in synthesizing metal-encapsulated cage structures. One cage structure that resembles the endohedral silicon fullerene is the metal-encapsulated silicon clusters M@Si_{16} (M=Ti, Zr, W, etc.),[11,17] whose silicon cage is composed of squares and pentagons. Density-functional theory (DFT) calculation, however, suggests that the Frank-Kasper polyhedron (composed of triangles) is more likely the correct cage structure for M@Si_{16} since it gives lower energy and larger highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gap compared to other cage structures.[13,15] A closer match to the endohedral fullerene is the silicon clathrate Na_8–Si_{46},[19] whose silicon backbone is composed of face sharing and somewhat distorted Si_{20}, Si_{24}, and Si_{28} fullerene cages.

On the theoretical side, much focus has been placed on seeking potential endohedral species that can fully stabilize the icosahedral (I_h) cage of the "silicon buckyball" Si_{60}.[14,16] A common strategy has been to encapsulate (metal or nonmetal) clusters also with the I_h symmetry, such as the "buckyball" C_{60}, or I_h-$Al_{12}X$ (X=Si, Ge, Sn, and Pb) and I_h-$Au_{12}W$ magic clusters. However, Sun *et al.*[14,16] have shown that none of these endohedral species are capable of stabilizing the icosahedral Si_{60} cage—the Si_{60} cage can easily break or become highly puckered and distorted even with the encapsulated species. Furthermore, the HOMO-LUMO gaps of these endohedral Si_{60} clusters are quite small ($Al_{12}X$@Si_{60}: <0.24 eV and $Au_{12}W$@Si_{60}: ~0 eV). A similar conclusion was drawn for the smallest icosahedral fullerene I_h-Si_{20}.[13]

In this article, we show the first-principles evidences of two highly stable metal-encapsulated silicon fullerenes M_4@Si_{28} (M=Al and Ga), both retaining identical tetrahedral (T_d) symmetry and cage structure as the T_d-C_{28} fullerene, and having a large HOMO-LUMO gap. The principle of the cluster design is similar to that applied to chemical stabilization of the open-shell structure T_d-C_{28} fullerene through encapsulating a tetravalent metal atom (U, Zr, Ti, or Hf),[20,21] which results in a closed-shell electronic configuration. If the Si_{28} fullerene can be stabilized with the same tetrahedral symmetry and geometric structure as C_{28} fullerene, its cage would have a larger size than the C_{28} cage. Consequently, a single metal atom is too small and thus unlikely to prevent the tetrahedral Si_{28} cage from puckering and distortion. To meet both the T_d symmetry and the closed-

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TABLE I. Calculated properties of $Al_4@Si_{28}$, $Ga_4@Si_{28}$, and $In_4@Si_{28}$ versus C_{40} and $Ti@C_{28}$.

Property	$Al_4@Si_{28}$[a]	$Ga_4@Si_{28}$[a]	$In_4@Si_{28}$[a]	C_{40}[a]	$Hf@C_{28}$[a]
Symmetry point group	T_d	T_d	T_d	D_2	T_d
HOMO/LUMO gap (eV)	0.92/0.95	0.84/0.90	0.52/0.54	0.87/0.87	2.23/2.26
Frontier-orbital configuration	$(t_1)^6(t_2)^6(a_1)^0$	$(t_1)^6(t_2)^6(t_2)^0$	$(t_1)^6(t_2)^6(a_1)^0$	$(b_1)^2(b_3)^2(b_2)^0$	$(t_2)^6(a_1)^2(e)^0$
Vibrational frequency (cm^{-1})					
Lowest	70.9/71.3	60.5/63.2	30.6/35.2	288.1/288.2	−44.5/−30.3
Highest	459.6/468.7	464.0/473.0	414.3/423.9	1540.6/1552.5	1364.7/1377.8
Binding energy (eV/atom)	−3.60/−3.74	−3.73/−3.86	−3.22/−3.43		−6.94/−7.11
Embedding energy (eV)	−10.6/−12.1	−13.7/−15.0	−3.4/−6.8		−8.2/−8.8
NICS	−36.5/−36.4	−44.7/−43.4	−51.6/−53.4	24.2/24.8	

[a]BP86/PBEPBE.

shell requirements, we have examined a variety of tetrahedral metal clusters T_d-M_4 as potential endohedral species to stabilize the T_d-Si_{28} cage. The metal clusters considered include the main group-I (Li_4,Na_4) and -III (Al_4,Ga_4,In_4) clusters, as well as the transition-metal group-I (Au_4) and -III (Sc_4) clusters. These metal clusters possess either "4" or "12" valence electrons. It is found that only the main group-III metal clusters can achieve a stable and closed-shell tetrahedral T_d-$M_4@Si_{28}$ clusters.

RESULTS AND DISCUSSIONS

Density-functional theory calculations were carried out to study the structural and chemical stabilities of the putative metal-encapsulated silicon fullerenes $M_4@Si_{28}$ (M=Al, Ga, and In). We optimized these cluster structures using two popular functionals: the generalized gradient approximation functional BP86 (Refs. 22 and 23) and PBE.[24] The 6-31G* basis set was applied to all elements considered (except In, Sc, and Au) for which we adopted the effective core potential (ECP) of LANL2DZ basis set.[25] Harmonic vibrational-frequency calculations were performed on the basis of the optimized structure. All calculations were done with using the GAUSSIAN03 software package.[26]

Some calculated properties of the three clusters are given in Table I ($Al_4@Si_{28}$ and $Ga_4@Si_{28}$). As shown in Fig. 1, the optimized cluster exhibits a perfect fullerene structure as the T_d-C_{28} fullerene—the outer cage is composed of 12 pentagons and four hexagons. Each of the four inner metal atoms is located near the center of the neighbor hexagon. The bond lengths between silicon atoms range from 2.360 to 2.460 Å, while the PBE values are slightly smaller (by ~0.01 Å). These calculated Si–Si bond lengths are a little longer than the fullerenelike $M@Si_{16}$ structure (2.27–2.36 Å) reported previously.[12] Note that a recent x-ray-diffraction measurement on silicon clathrate Ba_8Si_{46} shows that the Si–Si bond lengths are between 2.274 and 2.415 Å,[27] very close to our results. Furthermore, the four inner metal atoms all form six coordinations with nearest Si atoms, with three relatively short Si–M bond lengths (2.511–2.667 Å), and three long ones (2.804–2.862 Å). The bond length between the inner metal atoms is the shortest (2.619 Å) for $Ga_4@Si_{28}$ and longest (3.009 Å) for $In_4@Si_{28}$. Considering that the atomic radii of the Al, Ga, and In are 1.43, 1.22, and 1.63 Å, respectively, we can conclude that the larger the atomic radii, the longer M–M and Si–Si bond lengths, and the larger the cage dimension. Thus, one could modify the dimension of the bucky silicon via encapsulating atoms with different atomic radii.

The harmonic vibrational frequencies, calculated from both DFT methods (BP86 and PBE) are all positive, indicating that the three tetrahedral structures are all local minima. The lowest vibrational frequency of $Al_4@Si_{28}$ is 70.9 cm^{-1}

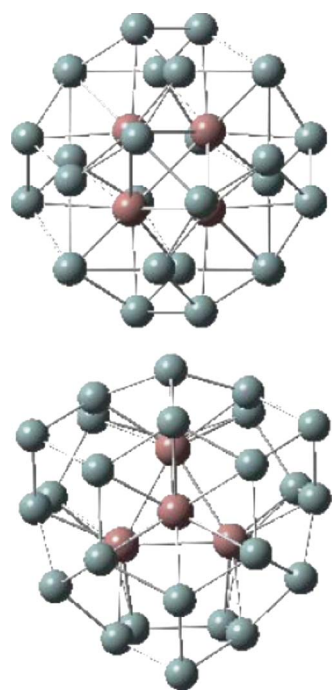

FIG. 1. (Color online). The top view (top) and side view (bottom) of the tetrahedral geometry for $M_4@Si_{28}$ (M=Al, Ga, and In) clusters. The silicon atoms are represented with gray color, and the encapsulated metal atoms are shown with pink color.

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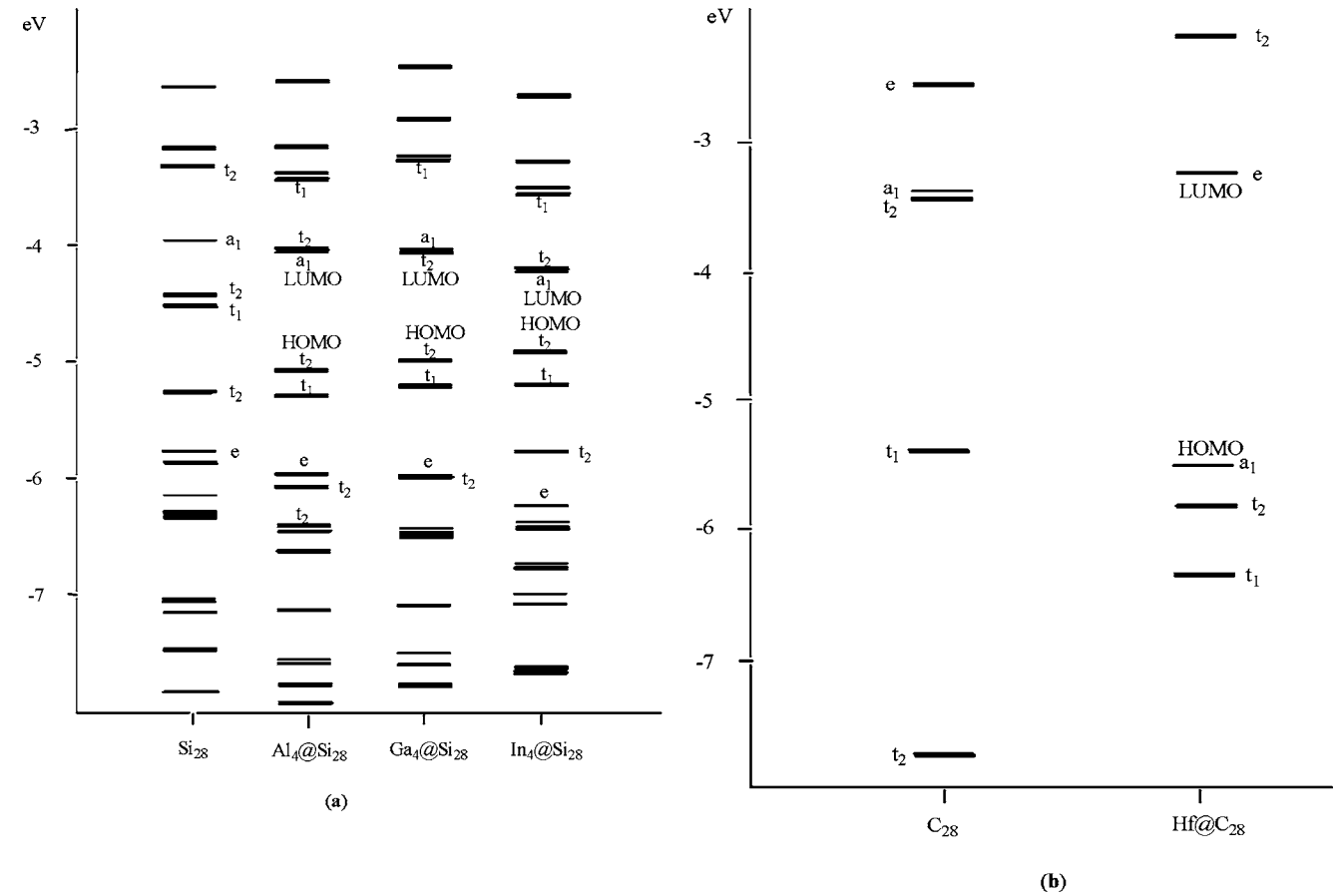

FIG. 2. The calculated energy-level diagram of (a) Si_{28}, $Al_4@Si_{28}$, $Ga_4@Si_{28}$, and $In_4@Si_{28}$, and (b) C_{28} and $Hf@C_{28}$ with the PBEPBE functional.

with the symmetry e, which is larger than 60.5 cm^{-1} of $Ga_4@Si_{28}$ and 30.6 cm^{-1} of $In_4@Si_{28}$. Thus, $Al_4@Si_{28}$ is the most rigid structure among the three clusters.

DFT calculations also show that two of the three tetrahedral clusters have quite large HOMO-LUMO energy gaps (Table I). The $Al_4@Si_{28}$ cluster has the largest gap (BP86: 0.92 eV and PBE: 0.95 eV) among the three, suggesting that it has the highest chemical stability. The HOMO-LUMO gap of $Al_4@Si_{28}$ (0.95 eV) is comparable to that of D_2-C_{40} fullerene (0.87 eV) but significantly less than T_d-$Hf@C_{28}$ endohedral fullerene[20,21] (2.26 eV). However, the calculated vibrational frequencies for the tetrahedral metal-encapsulated T_d-$Hf@C_{28}$ fullerene show three negative frequencies (the lowest frequency is given in Table I). In other words, T_d-$Hf@C_{28}$ fullerene structure is not a local minimum. Note that D_2-C_{40} fullerene also has a closed-shell electron configuration with 40 valence electrons if one assumes each C atom contributes one delocalized π electron.

Spherical aromaticity arising from electron delocalization is likely another important factor contributed to the chemical stability of the $M_4@Si_{28}$ (M=Al and Ga) clusters. The nucleus-independent chemical shift[28] (NICS) values at the cage centers can be used as a measure of the spherical aromaticity for various cage structures, for example, I_h-C_{60} (−2),[29] I_h-Au_{32} (−100),[29] Si_{60} (I_h: −1.4 and C_i: −7.8),[30] D_2-C_{40} (24) (Table I), and D_3-C_{32} (−47). The more negative the NICS value, the stronger the spherical aromaticity. Here, the calculated NICS values are −36 for $Al_4@Si_{28}$, −45 for $Ga_4@Si_{28}$, and −52 for $In_4@Si_{28}$. These large negative values suggest that the three endohedral silicon fullerenes are strongly aromatic, stronger than D_2-C_{40} and I_h-C_{60}, and comparable to a very stable fullerene D_3-C_{32} which has the "magic number" (32) of delocalized π electrons.[28]

The calculated binding energies (BEs) of $Ga_4@Si_{28}$ are −3.73 eV with BP86 and −3.86 eV with PBE, the largest among the three clusters, and this value is very close to the experimental measurement for the pure silicon clusters with a similar size.[31] Moreover, the embedding energies (EEs) of $Ga_4@Si_{28}$ are −13.7 eV with BP86 and −15.0 eV with PBE, which again are the largest among the three. This EE value is larger than the reported EE values (ca. −8 to −14 eV) of M-Si_{16} clusters.[12] The BE and EE values of $Al_4@Si_{28}$ are close to $Ga_4@Si_{28}$, while those of $In_4@Si_{28}$ are much smaller, which provides further evidence on the relatively high stability of $Al_4@Si_{28}$ and $Ga_4@Si_{28}$ clusters.

Finally, the energy-level diagrams of Si_{28}, $Al_4@Si_{28}$, $Ga_4@Si_{28}$, and $In_4@Si_{28}$ are shown in Fig. 2. It can be seen that the frontier-orbital configurations of $Al_4@Si_{28}$, $Ga_4@Si_{28}$, and $In_4@Si_{28}$ are nearly the same, and all [except $Ga_4@Si_{28}$ (HOMO: t_2 and LUMO: t_2^*)] resemble the configuration of Si_{28} shell whose HOMO and LUMO symmetries are t_2 and a_1^*, respectively. This frontier-orbital behavior of the $M_4@Si_{28}$ (M=Al, Ga, and In) clusters is very similar to that of endohedral carbon fullerene T_d-$Hf@C_{28}$, as shown in Fig. 2(b), where the frontier-orbital configurations of T_d-$Hf@C_{28}$ are mainly contributed by the C_{28} shell. Here,

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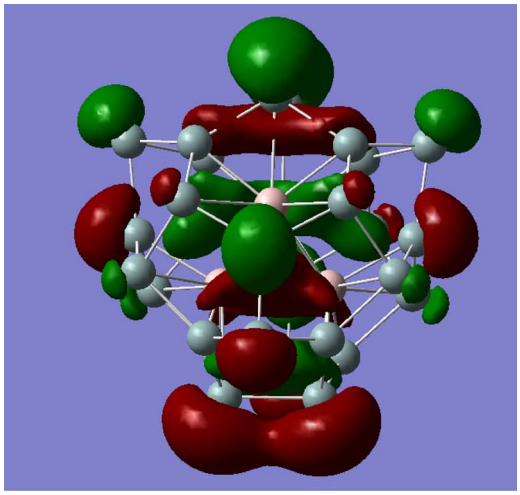
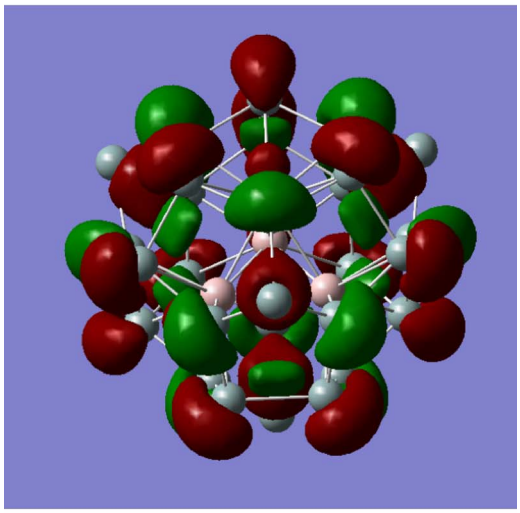


(a)



(b)

FIG. 3. (Color online). (a) The HOMO of the $Al_4@Si_{28}$ calculated with PBEPBE/6-31G* method. (b) The LUMO of the $Al_4@Si_{28}$.

the HOMO of $M_4@Si_{28}$ (M=Al, Ga, and In) is threefold degenerate, while the LUMO is nondegenerate for $Al_4@Si_{28}$ and $In_4@Si_{28}$ but threefold degenerate for $Ga_4@Si_{28}$. Combining the HOMO and LUMO orbital diagrams of $Al_4@Si_{28}$, respectively [Figs. 3(a) and 3(b)], can also show that the HOMO and LUMO orbitals are mainly contributed by the Si_{28} shell. The energy of HOMO increases with the order of $Al_4@Si_{28}$, $Ga_4@Si_{28}$, and $In_4@Si_{28}$ while the energy of LUMO decreases with the order of $Al_4@Si_{28}$, $Ga_4@Si_{28}$, and $In_4@Si_{28}$. As a result, the HOMO-LUMO gap of $In_4@Si_{28}$ is smaller than the other two.

In summary, we predict the existence of two highly stable metal-encapsulated silicon fullerenes, T_d-$Al_4@Si_{28}$ and T_d-$Ga_4@Si_{28}$, both having perfectly the same carbon fullerene geometric structure. The two endohedral silicon fullerenes exhibit a large HOMO-LUMO gap than any endohedral silicon fullerenes previously reported. They also have a large negative NICS value, large binding energies as well as embedding energies, all indicating that the two endohedral silicon fullerenes can be chemically and energetically stable. To our knowledge, this is the first theoretical evidence on the possible existence of highly stable metal-encapsulated silicon fullerene having the same cage structure (without puckering and distortion) and high symmetry (T_d) as the carbon fullerene counterpart. It is our hope that this theoretical prediction can stimulate future experiments on synthesizing the metal-encapsulated bucky silicon with cage structures resembling carbon fullerenes.

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