Constructing silicon nanotubes by assembling hydrogenated silicon clusters

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Abstract

The search or design of silicon nanostructures similar to their carbon analogues has attracted great interest recently. In this work, density functional calculations are performed to systematically study a series of finite and infinite hydrogenated cluster-assembled silicon nanotubes (SiNTs). It is found that stable one-dimensional SiNTs with formula $Si_{m(3k+1)}H_{2m(k+1)}$ can be constructed by proper assembly of hydrogenated fullerene-like silicon clusters $Si_{4m}H_{4m}$. The stability is first demonstrated by the large cohesive energies and HOMO-LUMO gaps. Among all such silicon nanotubes, the ones built from $Si_{20}H_{20}(m = 5)$ and $Si_{24}H_{24}(m = 6)$ are the most stable due to the silicon bond angles that are most close to the bulk $sp^3$ type in these structures. Thermostability analysis further verifies that such tubes may well exist at room temperature. Finally, both finite nanotubes and infinite nanotubes show a large energy gap. A direct-indirect-direct band gap transition has been revealed with the increase of the tube radius. The existence of direct band gap may make them potential building blocks for electronic and optoelectronic devices.

Keywords: hydrogenation, silicon clusters, cluster-assembled nanotubes

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I. INTRODUCTION

Since the discovery and application of carbon fullerenes and carbon nanotubes (CNTs) [1], stable cage and tube-like structures have attracted a great deal of attention. Silicon and carbon are members of the same group in the periodic table, suggesting a potential probability to form similar structures. Furthermore, due to the fundamental importance of silicon in present-day integrated circuits, substantial efforts have focused on investigating nano-scale forms of silicon, both for the purpose of further miniaturizing the current microelectronic devices and in the hopes of unveiling new properties that often arise at the nano-scale level [2]. However, it is difficult to form cages or tubes like carbon fullerenes or nanotubes purely with Si atoms because silicon does not favor the $sp^2$ hybridization that carbon does. Carbon normally forms strong $\pi$ bonds through $sp^2$ hybridization, which can facilitate the formation of two-dimensional spherical cages (or planar structures such as benzene and graphene). Silicon, on the other hand, usually forms covalent $\sigma$ bonds through $sp^3$ hybridization, which favors a three dimensional diamond-like structure.

Interestingly, it has been reported that Si cage clusters can be synthesized by encapsulating suitable foreign atoms to terminate the dangling Si bonds that inherently arise in cage-like networks. Many researchers [3–5] reported that transition metal (TM) atoms are the most suitable elements for cage formation due to their $d$ band features. In addition, rare earth atoms have also been doped into silicon cages [6–9]. Another way to stabilize the Si cages is to terminate the cluster surface by hydrogen [10–13], which is similar to the dodecahedral $C_{20}H_{20}$.

Meanwhile, tube-like silicon nanostructures have also attracted great attention. Thus far, a few hollow and nonhollow silicon nanotube structures have been proposed based on intuition or the behavior of similar materials and theoretically characterized in recent years [12–40]. Nevertheless, most of these structures have the instability problem arising from the unsaturated dangling bonds. Among all the present schemes for constructing silicon nanotubes, one is of great interest in which metal atoms are encapsulated in the tubes. This scheme has two advantages. On one hand, the metal atom is able to support the tube wall so as not to collapse. On the other hand, it can saturate the dangling bonds and further stabilize the structure. However, this scheme is limited to tubes with very small radii ($R \leq 1$ nm) since for larger tubes, the tube becomes metallic, then the above two advantages will disappear.
In comparison, hydrogen saturation outside the tubes should also be a very good way for the construction of silicon tubes for three reasons. At first, each dangling bond can be saturated by one hydrogen atom. Thus the instability caused by the dangling bonds would be removed and this scheme is not limited to small size tubes. Moreover, compared with the metal encapsulation scheme, the intrinsic features of silicon dominate in the properties of the tubes with no interference of metal atoms. More importantly, in geometry, it is a “real” empty tube, instead of a filled one. In fact, the effect of outside saturation of dangling bonds has been already demonstrated in experiments, where the surfaces of silicon nanowires (SiNWs) are always passivated by hydrogen atoms [27, 41] or by silicon oxide layers [42–45].

Therefore, hydrogen terminated silicon cages will be perfect building blocks for Si nanotubes and in this work, we present our design of hydrogenated cluster assembled single wall silicon nanotubes and systematically investigate their stabilities and electronic properties using density functional theory (DFT) calculations. We find that stable one-dimensional silicon nanotubes (SiNTs) with formula \( \text{Si}_{m(3k+1)}H_{2m(k+1)} \) can be constructed by proper assembly of hydrogenated fullerene-like silicon clusters \( \text{Si}_{4m}H_{4m} \) and these tubes can even exist at room temperatures.

II. COMPUTATIONAL DETAILS AND MODEL DESIGN

All theoretical computations are performed with the DFT approach implemented in the Dmol\(^3\) package [46, 47], using all electron treatment and the double numerical basis including the \( d \)-polarization function (DNP) [46]. The exchange-correlation interaction is treated within the generalized gradient approximation (GGA) using BLYP functional. Self-consistent field calculations are performed with a convergence criterion of \( 2 \times 10^{-5} \) Hartree on total energy. The convergence thresholds are set to 0.002 Hartree/Å for forces and 0.005 Å for the displacement.

The single \( \text{Si}_{4m}H_{4m} \) \( (m = 4, 5, 6, 7, 8) \) cage-like clusters are optimized first, and some of the initial structures are based on the results reported in Refs. 10 & 11. Then the optimized stable single clusters are taken as basic units (keep them as original) and stacked together along the axis of symmetry to construct finite nanotubes, with the adjacent two units sharing the same bottom surface. One dimensional infinite nanotubes are also investigated by including the smallest repeated unit cell in the supercell, with the size chosen as
25Å×25Å×L_z, where the direction of z is defined as the axial direction of the nanotubes, and L_z is the length of the supercell in the z direction. Meanwhile, in order to avoid interaction from the adjacent tubes, a sufficiently large vacuum region is introduced along the radial directions. The Brillouin zone was sampled with a 1×1×20 irreducible Monkhorst-Pack k-point grid for structural relaxation and band structure calculations.

Thermal stability of the hydrogenated silicon nanotubes is studied within ab initio quantum molecular dynamics framework performed by heating at 400K by using NVT(constant volume and temperature) dynamics with a massive Noseé-Hoover thermostat. Time step is set as 1.0 fs, total simulation time was set as 4.0 ps.

III. RESULTS AND DISCUSSIONS

A. Structures of Si_{4m}H_{4m} clusters and finite nanotubes

The fully optimized structures of Si_{4m}H_{4m} (m=4, 5, 6, 7, 8) clusters are shown in Fig. 1. All these structures share the following common characteristics: 1. All of them are fullerene-like hollow structures; 2. Each Si atom has three Si neighbors, with one H atom saturating the dangling bond outside the cage and thus an sp^3 type hybridization is satisfied; 3. All these structures consist of 2m polygons and two other polygons at the two ends, with the edge number of these two polygons as m. Meanwhile, these two polygons are parallel to each other, but with a relative angle of \( \frac{\pi}{m} \) between them. Thus each vertex atom of one polygon falls exactly on the perpendicular bisector of one edge in the other polygon. Specifically, for Si_{20}H_{20}(m=5), the cage is composed of 12 pentagons, which is very similar to the structure of carbon fullerene C_{20}H_{20}. In addition, structures of Si_{16}H_{16}(m=4), Si_{24}H_{24}(m=6) and Si_{28}H_{28}(m=7) have been widely discussed in very recent years [10, 11, 13] and the structural information we obtained is consistent with these reports.

Taking these original clusters as basic units, we stack them along the central axis of the cage to form finite nanotubes. The two adjacent cages share the same bottom polygon. We note that for the shared polygon, there is no need for hydrogen saturation because each Si atom already has four Si neighbors and thus the sp^3 hybridization bond type is fulfilled. The molecular formula of the finite tube can be written as Si_{m(3k+1)}H_{2m(k+1)}, where the number of units k defines the length of the nanotube, while the number of atoms m in
the bottom polygon defines the size in the directions vertical to the axis and can be taken as a measurement of the radius. Consequently, each group of \( m \) and \( k \) uniquely defines a nanotube with different radius and length therefore such a nanotube can be denoted as \( \text{NT}(m, k) \). After full optimization, for one certain value \( m(m = 4, 5, 6, 7) \), and for \( k \) ranging from 2 to 4 concerned in the present work, the tubes are always straight and stable. Furthermore, if the number of repeated units \( k \) is fixed, the length of the tubes decreases with the increasing \( m \). The angles of H-Si-Si and Si-Si-Si inside the repeated units are all about 109°, which is very close to the 109.5° of \( sp^3 \), but the Si-Si-Si angle between two units becomes smaller and smaller with the increase of tube radius (from 127.8° of \( m=4 \) to 99.0° of \( m=8 \)).

**B. Electronic structures**

In order to measure the relative stability of the tubes as well as the influence of the length and width, we have calculated the cohesive energy \( (E_{coh}) \). The \( E_{coh} \) are defined by the following formula[48–50]:

\[
E_{coh} = \frac{BE[\text{NT}(m, k)] + \mu_H N_H}{N_{Si}}
\]  

(1)

where \( BE[\text{NT}(m, k)] \) is the binding energy of finite nanotube(\( Si_{m(3k+1)}H_{2m(k+1)} \)), \( N_{Si} \) and \( N_H \) are the number of Si and H atoms, respectively, \( \mu_H \) is the chemical potential of H, and thus the comparison of relative stability of different systems becomes straightforward. This effectively removes the energy contribution of all Si-H bonds in every system.

As illustrated in Fig. 2(a), the cohesive energy \( E_{coh} \) of the finite tubes is above 2.95eV and increases gradually as the length \( k \) increases for each fixed \( m \), which indicates that the tube becomes increasingly stable as it gets longer. On the other hand, the stability of the tube does not depend monotonously on the tube radius as measured by \( m \). Particularly, the \( E_{coh} \) curves of \( m=5 \) or \( m=6 \) are very close and are obviously higher than the others, which means that, for any length \( k \), the tubes with radius \( m=5 \) or \( m=6 \) are the most stable.

In addition, Fig. 2(b) shows the variation of energy gaps between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the finite tubes. When \( m \) (radius of the tube) is fixed, the HOMO-LUMO gap decreases as the length \( (k) \) of the nanotube increases. Comparing the gaps of the tubes with different radius (or \( m \),
see Fig. 2(b)), we find that the tubes NT(4, k), NT(5, k) and NT(6, k) always have similar HOMO-LUMO gaps due to the analogous structural parameters characterized by bond angle and length. With the further increase of the tube radius \( m = 7, 8 \), the HOMO-LUMO gap decreases rapidly.

The spatial resolved local density of states (LDOS) of HOMO and LUMO states of cage clusters and finite nanotubes are plotted in Fig. 3 for the understanding of the bonding properties. For the convenience of descriptions, we define the atoms of two opposite polyhedron as bottom atoms, and the other atoms lying between the two polyhedrons as side atoms. For small size clusters \( m = 4, 5 \), both bottom atoms and side atoms have contributions on HOMOs, but for large size clusters \( m = 6, 7, 8 \), HOMOs are almost localized on the side silicon atoms. On the other hand, The LUMO states of small size clusters \( m = 4, 5, 6 \) are mainly localized inside the cage (Fig. 3(a)) while for bigger size clusters \( m = 7, 8 \), the LUMO states are localized around the bottom atoms. For finite nanotubes NT\((m, 4)\) with small size \((m = 4, 5)\), both the HOMO and LUMO are distributed on the side atoms and the shared bottom atoms (see (Fig. 3(b))). However, for finite tubes with large sizes \((m = 6, 7, 8)\), the HOMO is localized on the side atoms while the LUMO is localized on the shared bottom atoms, which are very similar to their building units, namely, the cage clusters. Furthermore, with the increase of the radius, both the HOMO and LUMO tend to be localized on the middle atoms while the contributions from the end atoms become negligible.

### C. Infinite nanotubes

The increased stability of finite nanotubes with increasing length leads to our interest in examining further the stability of infinite nanotubes. The smallest repeated unit cell of the infinite nanotubes can be obtained by removing the Si and H atoms of one bottom polygon and the H atoms of the other bottom polygon of a finite tube NT\((m, 2)\) or \(Si_{7m}H_{6m}\), and thus it can be described by a formula \(Si_{6m}H_{4m}\), where \( m \) is again the number of atoms in the bottom or connecting polygon. Note that the repeated unit cell should not be based on NT\((m, 1)\) but on NT\((m, 2)\) to produce a periodic system. Therefore we can define these infinite tubes as NT\((m, \infty)\) \((m = 4, 5, 6, 7, 8)\). Two repeated cells of the infinite tubes are shown in Fig. 4 with different radii concerned in this work.

Full structure relaxation indicates that the infinite nanotubes have similar geometric
structures to finite ones, but the length of the smallest repeated cell is slightly changed. The lengths of the smallest repeated cell of the \( m = 4 \) tube and the \( m = 5 \) tube become 0.08Å and 0.11Å longer than those of the finite ones for producing these repeated cells. But for \( m = 6, m = 7 \) and \( m = 8 \), the lengths become 0.075Å, 0.212Å and 0.365Å shorter. The diameter of tubes and Si-H bond lengths are almost the same as those of the finite ones. The average Si-Si bond length is 2.401Å, and the Si-H bond length is 1.497Å, which are similar to the 2.36Å and 1.50Å in Ref. 37, and the exohydrogenated carbon nanotube like structures (2.34Å and 1.51Å in Ref. 34, 2.335Å and 1.521Å in Ref. 33).

In order to study the stability of the infinite tubes \( \text{NT}(m, \infty) \), their cohesive energies are calculated and included in Fig. 2(a). By comparison, we find that the cohesive energies of them are larger than those of finite ones, which means that it is possible to synthesize long tubes. Further, thermal stability of the hydrogenated silicon tubes has been checked within \textit{ab initio} quantum molecular dynamics framework performed by heating at 400K for 4.0 ps with the time step of 1.0 fs using NVT(constant volume and temperature) dynamics with a massive Nose-Hoover thermostat. The cluster model is implemented for these tubes without any symmetry constraints so that all atoms are allowed to move freely. No collapse is found at this time scale, indicating that these hydrogenated silicon nanotubes may survive at room temperature.

Another concern about the structural stability of the proposed hydrogenated silicon tubes comes with whether multiple tubes will be collapsed and merged into a large cluster when they are put together. Our calculations on NT(5, \( \infty \)) and NT(7, \( \infty \)) show that when two, three or four nanotubes are placed together in parallel, with very small initial distance between them, after full optimization, all of these tubes separate away from each other with no collapse or distortion. The separation is largely due to the mutual repulsion of the surface hydrogen atoms. It gives another proof that single hollow silicon nanotubes can well exist and they will not be combined together with the “protection” from the surface hydrogen atoms between the tubes.

Finally, the band gaps (\( \Delta_g \)) of the infinite tubes are analyzed and exhibit large values from 2.3eV of NT(8, \( \infty \)) to 2.8eV of NT(4, \( \infty \)), which implies that they are wide gap semiconductors. Particularly, the band gaps of NT(5, \( \infty \)) and NT(6, \( \infty \)) are obtained as 2.69 eV and 2.71 eV, respectively, which agree very well with the 2.65 eV and 2.70 eV reported in Ref. 37 for the same structures. The band gap of the tube is inversely
proportional to the radius, which is similar to the gap changes in exohydrogenated single-wall carbon nanotubes (SWCNT)[51] and exohydrogenated single-wall silicon nanotubes[34]. Meanwhile, seen from Fig. 5, the type of the band gaps can be controlled by tuning the tube radius. The smallest tube NT(4, ∞) (Fig. 5(a)) has a direct band gap at Z-point, while NT(5,∞)(Fig. 5(b)) has an indirect band gap. When m in NT(m, ∞) goes to m = 6, 7, 8, these tubes all display a direct band gap at Γ-point. From Fig. 5, we see that for m = 4, both the bottom of the conduction band (BC) and the top of the valence band (VT) lie at Z point, thus the m = 4 tube is a semiconductor with a direct gap at Z point. Interestingly, with the increase of the radius, both the BC and TV move toward the Γ point. However, the BC moves much faster than TV, thus an indirect gap is observed with m = 5. After m = 6, both BC and TV arrive at Γ point and a direct gap is always observed. We believe such an band evolution is related to the structure changes with the radius, and the nanotubes have a one-dimension-like to three-dimension-like transition as the increasing radius. For the thinnest nanotube NT(4, ∞), the confinement along Z direction is smaller than that along vertical directions because of the one dimension feature. Consequently the band gap at Γ is larger than that at Z, then the effective gap opens at Z point. On the other hand, for the largest radius tube NT(8, ∞), three dimensional feature is apparently shown and the confinement along vertical directions is relatively smaller than that of small tubes. This makes the band gap at Γ be small, so that the effective gap opens at Γ point. Accordingly, as the radius of tube changes from NT(4, ∞) to NT(8, ∞), the confinement along vertical directions changes evidently. This variation leads to a transition between direct band gap and indirect band gap. Larger tubes NT (9, ∞) and NT (10, ∞) are tested, and the band structures of the tubes are shown in supplementary materials. We can find that they are also both semiconductors with a direct band gap at Γ point. Our results also show that band gap open at Γ is more sensitive to the change of diameter than that at Z point. The reason for this is that the size of basic repeated unit cell keeps almost unchanged in building nanotube, hence the physical phenomena close to the size of basic repeated unit cell are not sensitive to the size change of nanotube. In fact, such a size induced change is also observed in the HOMO-LUMO gap and the cohesive energy in the finite tubes (see Fig. 2). In Fig. 2, we see that m = 5 is a special size, since after m = 5, both the HOMO-LUMO gap and the cohesive energy changes monotonously with the radius. The existence of direct band gap in hydrogenated silicon nanotubes is quite important for the utilization of these nanosturctures
in building nanoscale optoelectronic devices.

IV. CONCLUSIONS

A series of finite and infinite hydrogenated silicon nanotubes are systematically studied by performing first-principles calculations. Our results reveal that one-dimensional stable SiNTs $Si_{m(3k+1)}H_{2m(k+1)}$ can be built by stacking $Si_{4m}H_{4m}$ cagelike clusters along the central axis of the cage. These tubes have large cohesive energies and HOMO-LUMO gaps. Among all the tubes, those with the sizes of $m=5$ and 6 are the most stable, because their $sp^3$ bond angle is most close to 109.5°. Thermodynamics analysis shows that these tubes may exist at room temperature, which further confirms the stability of the proposed silicon nanotubes. The infinite silicon nanotubes have also been investigated and it is found that there is a direct-indirect-direct band gap change with the increasing radius. For $m = 4$, the direct gap opens at Z point, while for $m \geq 6$, the direct gap opens at Γ point. In the $m = 5$ case, an indirect gap is observed.

We want to note that, although single wall silicon nanotubes have attracted great attention recently, such silicon nanotubes have not been synthesized yet experimentally due to the $sp^3$ hybridization of silicon and the subsequent unsaturated dangling bonds. Our study indicates that hydrogen passivation may be a good way to stabilize hollow single wall silicon nanotubes. Particularly, necklace-like hollow structures built from single cage-like clusters are proposed in our work. These findings may provide some useful suggestions for experimental fabrications of hollow single wall silicon nanotubes.

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Figure captions

Fig. 1. (Color online) Top view of the optimized $Si_{4m}H_{4m}$ ($m=4, 5, 6, 7, 8$) clusters (the 1st row) and side view of cluster-assembled nanotubes $Si_{m(3k+1)}H_{2m(k+1)}$ ($m=4, 5, 6, 7, 8; k=1, 2, 3, 4$) (all the rest).

Fig. 2. (Color online) (a) The cohesive energy of finite $Si_{m(3k+1)}H_{2m(k+1)}$ ($m=4, 5, 6, 7, 8; k=1, 2, 3, 4$), (b) HOMO-LUMO gaps of finite $Si_{m(3k+1)}H_{2m(k+1)}$ ($m=4, 5, 6, 7, 8; k=1, 2, 3, 4$) tubes. For comparison, the binding energies of infinite nanotube NT($m, \infty$) are also put at the ending of (a).

Fig. 3. (Color online) The spatial resolved local density of states (LDOS) with the level of 0.015e/Å$^3$ of highest-occupied molecular orbital (HOMO) and lowest-unoccupied molecular orbital (LUMO) of (a) $Si_{4m}H_{4m}$ ($m=4, 5, 6, 7, 8$) clusters and (b) $Si_{m(3k+1)}H_{2m(k+1)}$ ($m=4, 5, 6, 8; k=4$) tubes.

Fig. 4. (Color online) Side views of two unit cells of $Si_{6m}H_{4m}$ infinite nanotubes NT($m, \infty$) ($m=5, 6, 7, 8$).

Fig. 5. Electronic band structures of the infinite nanotubes (a) NT($4, \infty$), (b) NT($5, \infty$), (c) NT($6, \infty$), (d) NT($7, \infty$), (e) NT($8, \infty$).
Fig. 1 Guo et al.

$Si_{m(3k+1)}H_{2m(k+1)}$

$(m=4, 5, 6, 7, 8; k=1, 2, 3, 4)$
Fig 2: Guo et al.
Fig. 3  Guo et al.

(a)

HOMO

LUMO

\( \text{Si}_{18}H_{16} \)
\( \text{Si}_{22}H_{20} \)
\( \text{Si}_{26}H_{24} \)
\( \text{Si}_{28}H_{32} \)

(b)

NT(4, 4)

NT(5, 4)

NT(6, 4)

NT(8, 4)

HOMO

LUMO
Fig. 4 Guo et al.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4}
\caption{NT(5, \infty), NT(6, \infty), NT(7, \infty), NT(8, \infty)}
\end{figure}
FIG. 5:

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increasing radius

Energy (eV)

Gamma (Γ) Z

(a) (b) (c) (d) (e)