

Structure of SiAu₁₆: Can a silicon atom be stabilized in a gold cage?

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Nanostructures of Au and Si as well as Au–Si hybrid structures are topics of great current interest from both scientific and technological points of view. Recent discovery of Au clusters having fullerene-like geometries and the possibility of endohedral complexes with Si atoms inside the Au cage opens new possibilities for designing Au–Si nanostructures. Using *ab initio* simulated annealing method we have examined the stability of Si–Au₁₆ endohedral complex. Contrary to what we believed, we find that the endohedral configuration is metastable and the structure where Si atom binds to the exterior surface of the Au₁₆ cage is the lowest energy structure. The bonding of Si to Au cluster mimics its behavior of that in bulk and liquid phase of Au. In addition, doping of Si in high concentration would cause fracture and embrittlement in gold nanostructures just as it does in the bulk phase. Covalent bonding between Au–Au and Au–Si is found to be a dominant feature in the stability of the Au–Si nanostructures. Our study provides insight that may be useful in fabricating hybrid Au–Si nanostructures for applications microelectronics, catalysis, biomedicine, and jewelry industry. © 2007 American Institute of Physics. [DOI: 10.1063/1.2804872]

Gold and silicon are two of the most important elements in the Periodic Table. Gold is the noblest of all metals and is prized throughout history for its beauty and resistance to corrosion.¹ Silicon, on the other hand, forms the basis for electronics. The interaction of Si and Au exhibits some unique features: Although Au and Si do not form any stable crystalline alloys at any concentration and temperature, SiAu₄ (Ref. 2) commonly known as aurosilane is a very stable structure where four of the Au atoms behave just like hydrogen atoms. This raises the following question: Can Si be incorporated into nano gold? This is particularly important as novel nanoelectronic devices can be envisioned by creating Au–Si interface. In addition, the discovery³ of reactive gold nanoparticles has caused a great deal of interest in exploring the synthesis of gold at the nanoscale.⁴ It was recently demonstrated⁵ that the Au₁₆ cluster can form a cage structure similar to that of carbon fullerenes. The possibility of having pure metal cage that can be functionalized with endohedral atoms opens a new area research with potential for technological breakthroughs. For example, Au can be used for catalysis⁶ and can be easily functionalized for biomedical applications in drug delivery, hyperthermal treatment, and magnetic separation.^{7–9}

It was recently suggested that Au₁₆ which has a cage structure with a distorted T_d geometry can be endohedrally doped with Si making a Si–Au₁₆ cluster.¹⁰ Such cluster, analogous to Si–Al₁₂ (Ref. 11) can have 20 delocalized electrons and mimic a magic cluster due to electronic shell closure. The study of Si–Au₁₆ raises the following interesting

question: Does the interaction of Si with Au₁₆ resemble that in aurosilane or bulk phase? Recall that the former is a very stable species while the later does not form any stable crystalline alloy. The predicted stability¹⁰ of endohedral Si–Au₁₆ cluster would suggest that the interaction is dominated by the sp^3 bonding characteristics of Si and a nanoalloy of Si–Au is possible even though its bulk counter part does not exist.

We have examined the stability of endohedral Si–Au₁₆ by carrying out *ab initio* simulated annealing calculation with different starting geometries. We show that the endohedral doping belongs to a metastable configuration. The lowest energy structure is that of the Si atom bonding on the surface site of the Au₁₆ cluster and is 0.457 eV lower in energy than the metastable endohedral complex. Thus, the outer surface of nanogold structure is more reactive for Si doping than its interior, similar to that of gold bulk. The results indicate that the bonding between Si and gold is not the same as that between Si and Al and that the electronic shell closure may not be the leading contributor to the stability of the Si–Au₁₆ complex.

Our calculations are based on spin-polarized density functional theory with generalized gradient approximation (GGA) for exchange and correlation potentials. We have used the Perdew–Burke–Ernzerhof form for the GGA and a plane-wave basis set with the projector augmented plane wave method as implemented in the Vienna *ab initio* simulation package (VASP).^{12,13} Supercells with 15 Å vacuum spaces along the x , y , and z directions for all the calculated structures are used. Due to the large supercell the Γ point is used to represent the Brillouin zone. The geometries of the structures are optimized without symmetry constraint. The energy cutoff was set to 300 eV and the convergence in en-

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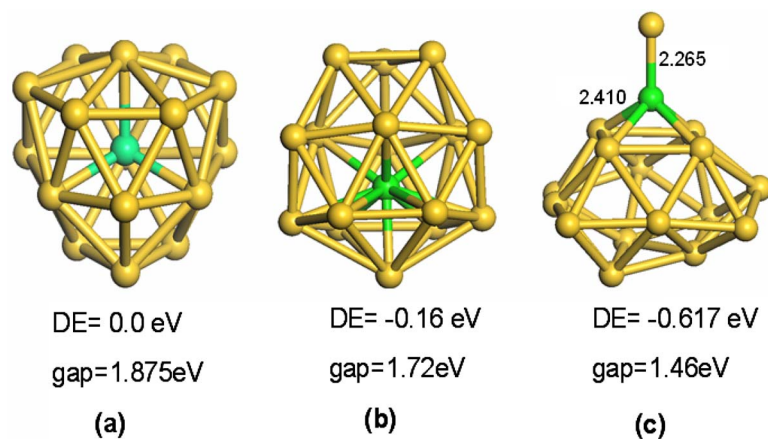


FIG. 1. (Color online) Three configurations of SiAu_{16} : (a) on-center, (b) off-center, and (c) on-surface obtained from (a) and (b) using simulated annealing. The relative energy (DE) and energy gap (gap) are specified.

ergy and force were 10^{-4} eV and 1×10^{-3} eV/Å, respectively. The accuracy of our numerical procedure was tested for Au_2 and AuSi dimers. The calculated bond lengths for Au_2 and AuSi are 2.526 and 2.251 Å, respectively, which agree very well with corresponding experimental values^{14,15} of 2.500 and 2.257 Å. For larger gold nanostructures, readers can refer to our previous studies.¹⁶ Tests were also carried out for Si-Au_{16} with on-center and off-center configurations, as shown in Figs. 1(a) and 1(b), the latter is found to be 0.16 eV lower in energy, in agreement with the results in Ref. 10. Although these two isomers have nearly the same energy, frequency calculations indicate that the on-center configuration [Fig. 1(a)] is unstable. The reason is the following: SiAu_4 is found to be a closed shell with T_d symmetry and the bond length of Au-Si being 2.299 Å.² Although the T_d symmetry in the on-center configuration of Si-Au_{16} [Fig. 1(a)] can make Si to be sp^3 -like, the Au-Si bond length is 2.51 Å, more than 0.2 Å ($\sim 9.2\%$) larger than that in SiAu_4 .² Therefore, the cavity of Au_{16} cage is too big for encapsulating the Si atom at the center. Consequently, the off-center configuration is more preferable, similar to that in La-C_{60} .

To study the stability of the off-center configuration further, we carried out simulated annealing. The simulation lasted for 15 ps with a time step of 1 fs. The temperature was gradually reduced from 800 to 0 K as the simulation proceeded. Finally it was found that the Si atom emerges from the cage and resides on its surface with one Au atom forming a Au-Si bond, as shown in Fig. 1(c). Starting from the on-center configuration in Fig. 1(a) and following the same procedure, we still found the geometry to converge to that of Fig. 1(c), which is 0.617 and 0.457 eV lower in energy than that of on-center and off-center configurations, respectively.

Due to the lower symmetry as compared to the other two structures, the energy gap between highest occupied and lowest unoccupied molecular orbitals (HOMO-LUMO gap) is reduced, but still having a value of 1.46 eV that is comparable to that of C_{60} (1.57 eV).¹⁷ To further check the stability of the complex in Fig. 1(c), we switched the positions of Si and the Au atom it is bonded to, and reoptimized the geometry with the Si atom inside the cage. However, after simulated annealing, the Si atom again came out of cage. These simulations clearly indicate that intrinsically Si impurity prefers to reside on the cage surface rather than in its interior.

The HOMO and LUMO are shown in Figs. 2(a) and 2(b). Si atom contributes more to LUMO than to HOMO. Figure 2(c) shows the charge difference isosurface with positive value, defined as the difference between the total density and the isolated atoms. We clearly see that charge accumulates on bonds between Au-Au and Au-Si. Therefore, covalent bonding is dominant in this structure. Similar features are also found for on-center and off-center configurations, as shown in Fig. 3. Inside the cage, Si-Au bonding is also found to be more covalentlike. The dominant covalent bonding features make it questionable to apply jellium model to the stability of Si-Au_{16} , as the jellium model essentially requires metalliclike bonding so that the valence electrons are freelike.

Up to now we have demonstrated that the on-surface geometric configuration is much more stable in energy than that of off-center endohedral complex. Unfortunately, there are no experimental techniques that can verify the predicted structures directly. It is customary to compare the computed properties of various isomers with experiments and a good

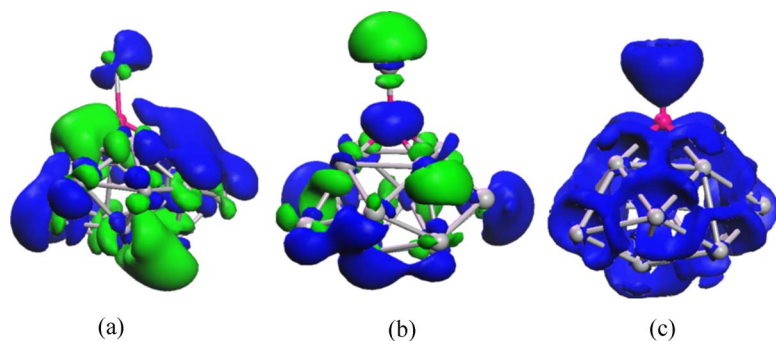


FIG. 2. (Color online) (a) HOMO and (b) LUMO of SiAu_{16} . (c) The difference charge distribution corresponding to the geometry of Fig. 1(c).

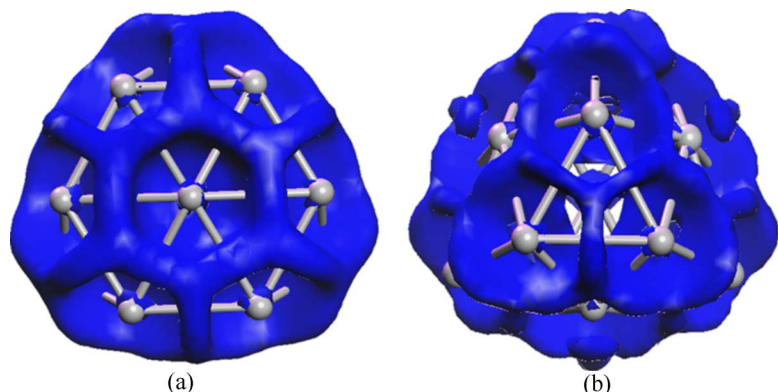


FIG. 3. (Color online) Difference charge density distribution of SiAu₁₆ corresponding to the geometry of Figs. 1(a) and 1(b), respectively.

agreement between theory and experiment serves as an indirect evidence for the predicted geometry. These experiments include photoelectron spectroscopy (PES) as well as infrared (IR) spectroscopy. The PES measures among other features the HOMO-LUMO gap. We find this gap for the two isomers to be 1.72 and 1.46 eV, respectively. The difference is rather small and one has to find other characteristic features that can distinguish between the two isomers. We have calculated the frequency and IR intensity of these isomers and find rather large differences. For the off-center geometry, as shown in Fig. 1(b), there are three peaks of IR intensity with values of 2.59, 8.49, and 8.49 km/mol located at 220, 248, and 251 cm⁻¹, respectively. These three vibrational modes are mainly contributed by the Si atom. However, for the on-surface geometry [see Fig. 1(c)], there are only two modes with the IR intensities of 2.26 and 45.85 km/mol located at 137 and 453 cm⁻¹. The first mode originates from the Au atom directly bonding with Si atom, and the second mode is from the Si atom. The IR intensity of the later is 20 times larger than that of the former. Compared to the off-center geometry, the IR intensity is five times larger. Therefore, infrared spectroscopy would be an effective means to detect these two isomers: high IR intensity and high frequency corresponding to the on-surface configuration, while low IR intensity and low frequency corresponding to the endohedral configuration.

As we see from above, the off-center configuration is a metastable state. How can then one put a Si atom inside the cage to form a Si–Au₁₆ complex? After comprehensive simulation, we came to the conclusion that once Au₁₆ is formed, it is extremely difficult to introduce a Si impurity from outside to the inside of the cage. As Si atom attempts to pass through the cage surface, it always sticks on the surface. So one possible way to form Si–Au₁₆ is to use Si impurity as

a nucleation center, and then introduce Au atoms. However, the synthesis temperature should not be too high, otherwise due to the much smaller atomic mass of Si atom, it may diffuse to the surface. In addition, one needs to control the doping concentration of Si since the cage structure may break if there are too many Si atoms. We demonstrate this by replacing two Au atoms in Fig. 1(c) with two Si atoms to form Si₂Au₁₅ cluster. The optimized geometry is shown in Fig. 4. Note that it has a sheetlike structure where the Au cage is completely broken. This is in agreement with the fact¹⁸ that silicon causes fracture and embrittlement in gold jewelry during the manufacturing process where silicon is added to increase the fluidity of molten gold. It is also interesting to note that the two-dimensional-like Au–Si structure as shown in Fig. 4(b) is similar to what happens in eutectic liquid surface where a crystalline monolayer is formed.¹⁹

In summary, using *ab initio* simulated annealing method we studied the stability of Si–Au₁₆ and find that the endohedral configuration is metastable. Instead, Si atom prefers bonding on the surface site of gold cluster, similar to what happened between Si₆₀ and Au₁₂W clusters,²⁰ sharing some features found in bulk and liquid phases. Doping of Si in high concentration would cause fracture and embrittlement in gold nanostructure. Our study provides insight on the interactions of Au–Si at nanoscale which can be important in the design of new hybrid Au–Si nanostructures for applications in microelectronics, catalysis, biomedicine, and jewelry industry.

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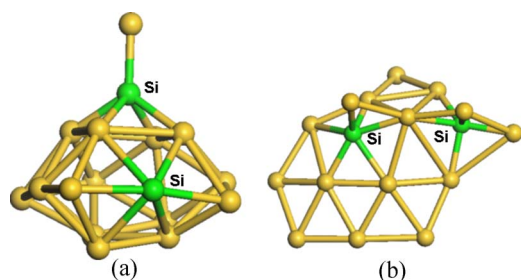


FIG. 4. (Color online) Initial (a) and final (b) structures of Si₂Au₁₅.

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