Gold cluster beyond hollow cage: A double shell structure of Au_{58}

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It is well known that gold cluster can have planar or hollow cagelike structure due to the relativistic effect. In this study, by first principles calculation on the Au_{58} cluster, we propose that gold cluster of medium size can form a shell-like structure, which is demonstrated by the remarkable robustness of a double shell structure with a hollow inner shell of ten atoms. © *2010 American Institute of Physics*. [doi:10.1063/1.3324961]

I. INTRODUCTION

Gold clusters and nanoparticles have been attracting much attention for more than one decade due to their important application in nanotechnology and chemical catalysis.[1–5] Intensive theoretical and experimental efforts have been made to study their chemical and physical properties, and surveyed in recent reviews.[6] It was found that the structures of gold clusters are very different from those of other noble metals. The structures of small gold clusters with less than 13 atoms were proved to be planar, stabilized by relativistic effect (RE)-enhanced *s-d* hybridization.[7–12] The most fascinating structures of gold clusters might be the hollow cagelike structures,[13–18] which can be seen as a natural extension of small planar structure to larger size.

The cagelike structures cannot be favorable in energy for large gold clusters owing to the low coordination, which was confirmed by a recent study.[19] As the size increases, the cluster shows a more metallic behavior. The *s*-electrons become more delocalized, favoring more compact structures with higher coordination. When the cluster grows to a certain size range, the compromise of RE-enhanced *s-d* hybridization and the *s*-electrons' delocalization would give rise to structures in the core-shell configuration. In this configuration, the coordination is improved due to the existence of an inner core, while the outer shell may still be stabilized by the RE-induced *s-d* hybridization, which causes surface contraction.[20] Thus, the core-shell structure can be considered as an intermediate phase between cagelike structure of smaller cluster and compact structure of the bulk. The existence of the core-shell structures has been proven by recent studies on Au_{34}, Au_{58}, and ligand-protected gold clusters.[21–24]

For core-shell structures, the relative size of the inner core and outer shell is a fundamental aspect of structural property and would most probably dramatically influence the stability. Then, it is interesting to study the relation between this relative size and the stability of cluster. In this work, we show that for Au_{58}, the structures with ten inner atoms are most favorable in energy. Furthermore, we find that a double shell structure of Au_{58}, with ten inner atoms forming a hollow shell, is highly robust.

II. METHODOLOGICAL DETAILS

To reveal the effect of core-shell size on stability, it is crucial to find stable structure for each relative core-shell size. In our work, that is accomplished by using a genetic algorithm method implemented with empirical potential.[25,26] In detail, for each reasonable relative core-shell size, the possible structures of the outer shell were obtained by splitting and splicing the outer shells of parent structures, while the structures of the inner core were obtained through various symmetries and adopting the existing structure of small gold clusters. Competitive candidate structures were effectively acquired through this scheme, and their stabilities were then further examined by density functional optimization and calculation.

Structural optimization and total energy calculation were based on the density functional theory with the generalized gradient approximation (GGA) in the PW91 functional[27] implemented in the VASP code.[28] The $5d^{10}6s^1$ valence electrons were treated explicitly with scalar relativistic effects, and their interaction with the ionic cores was described by projector augmented wave potential.[29] Spin-orbit coupling and spin-polarization were not taken into account. The Kohn–Sham orbits were expanded in more than 210 000 plane waves with a cutoff energy of 230 eV. With periodic boundary condition, a simple cubic cell with edge length of 30 Å was used, which is large enough to neglect the interaction between periodic images. The Γ point approximation was used for Brillouin zone sampling. The self-consistent electronic structure calculation was converged in an energy scale of 1.0×10^{-6} eV, and the conjugate gradient method was adopted to optimize the structures with energy convergence of 1.0×10^{-5} eV. The reliability of the current computation for gold nanosystem was proved by our previous works.[14,21,22]

III. RESULTS AND DISCUSSION

To study the dependence of stability on core-shell size, the existing core-shell structures are important starting

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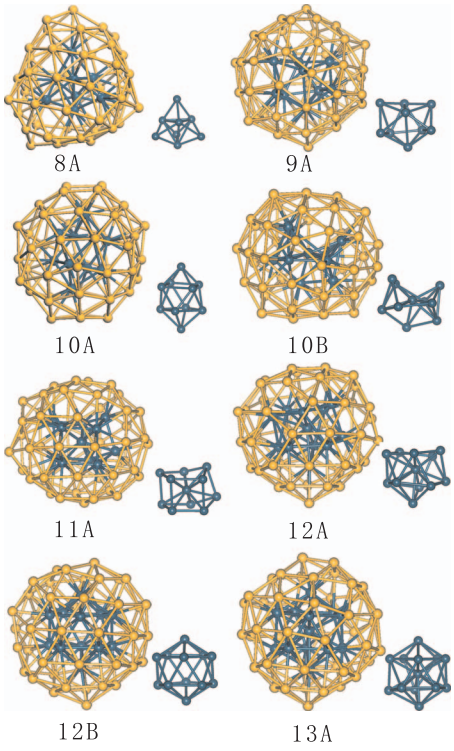

FIG. 1. Optimized low-energy structures of Au_{58}. The number below each cluster denotes the number of core atoms, while letters A and B attached to the number corresponding to the ground state and the first isomer. The inner cores are shown separately on the right of the cluster.

points. A spherical structure of Au_{58} was recently reported[22] and shown as 12A in Fig. 1. It consists of a 46-atom outer shell and a 12-atom inner core. The inner core can be roughly considered as a centered icosahedron with one corner atom missing. The region around the missing atom just below the outer shell forms a small *bubble*. Moving the center atom of 12A to the vacant corner site gives rise to structure 12B shown in Fig. 1, which is less stable than 12A with the total energy 0.45 eV higher. The outer shells of both 12A and 12B are composed of triangles like the Au(111) surface, with some local defects, such as pentagons and squares.

Starting with the 12A structure, we altered the size of inner core to see its effect. By using the genetic algorithm method described above, a structure with 11 inner atoms forming a centered pentagon prism was obtained, shown as 11A in Fig. 1. This 11A structure is more favorable by 0.11 eV than the 12A structure, which implies that structure with smaller core might be more stable. Carefully analyzing the 11A and 12A structures (see Fig. 1), it can be found that the whole structure of 11A is noncompact, while the lower hemisphere of 12A is highly compact and closely resembles the hemisphere of close-packed icosahedral Au_{55}. This observation explains the lower stability of 12A, as the icosahedral Au_{55} has been proven to be unfavorable in energy.[22] Also, as the 11A structure has one more atom on the surface, it has fewer surface defects (three square and one pentagon defects) than 12A (six square defects), which makes the 11A structure more stable.

Further reducing the inner core to ten atoms, two stable structures were obtained, shown as 10A and 10B in Fig. 1.

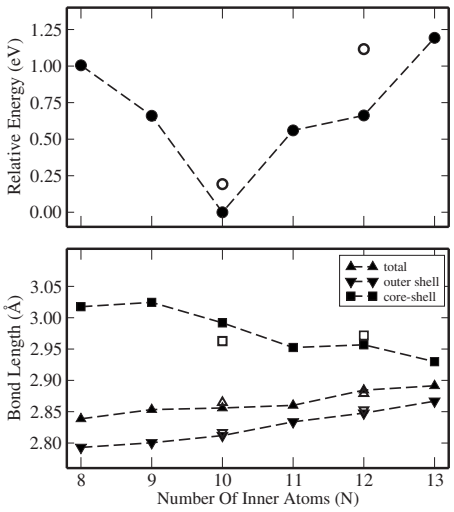

FIG. 2. Upper panel: relative energies of Au_{58} isomers vs the number of inner atoms. The minimum at ten inner atoms is prominent. Lower panel: average bond length of the Au_{58} isomers (upper triangle), average bond length of the outer shells (down triangle), and average length of bonds between inner core and outer shell(square). In each panel the hollow symbols denote the values for 10B and 12B.

The former has no center atom, while the latter has one center atom. For the 10A structure, the ten inner atoms form a hollow cage with rough D_{4d} symmetry. Thus, the whole cluster forms a novel double shell configuration with a hollow center. Compared with other structures, the 10A structure has the least defects and highest stability: only one square on the surface, and its total energy is 0.67 eV lower than that of 12A. The 10B structure has two square defects on the surface and is also 0.47 eV lower in energy than the 12A structure. Structures with other compact ten-atom inner cores were also considered in our calculation; however, they were proved to be unfavorable in energy.

We have also investigated structures with less than ten inner atoms, none of which is more favorable in energy than the 10A structure. The lowest-lying structures with eight and nine inner atoms are shown as 8A and 9A in Fig. 1. They are 1.00 and 0.66 eV higher in energy than 10A, respectively. The inner core of the 8A structure is a four-atom tetrahedral with each facet capped by one atom, while the core of 9A is a distorted hollow cage with no symmetry. The outer shells of these two structures are deformed severely from spherical profile.

The structures containing an inner core with more than 12 atoms are also investigated. The most stable 13-atom-core structure we found can be considered as the 12A structure with the bubble filled and one more pentagon defect left on the surface. Its total energy is 0.53 eV higher than that of 12A. This implies that the inner core with 13 or more atoms might be too large to be stable for Au_{58}.

The relative energies of all structures considered above are shown in the upper panel of Fig. 2 as a function of the number of the inner atoms. Apparently, the prominent minimum at ten inner atoms indicates that the Au_{58} cluster acquires the highest stability with an optimal relative core-shell size. The existence of an optimal relative core-shell size is easy to understand. Since the total number of atoms is fixed,

a larger core (shell) must lead to a smaller surface (shell). Structure with too large inner core and too small outer shell would undergo a large surface strain, whereas small core and large shell would sacrifice the core-shell binding due to the large difference between the radius of surface shell and the inner shell. Both cases make the cluster unstable. This is supported by the analysis of bond lengths. As shown in the lower panel of Fig. 2, the surface bonds are generally shorter than other bonds and particularly shorter than the bonds between inner atoms and outer ones. As the number of inner atoms increases, the average core-shell distance becomes shorter and the surface bonds longer. This leads to repulsion between the two shells and thus weakens the RE-induced strong bonding on the outer shell.

The recently developed TPSS functional (named after the initials of the authors of Ref. 31) has been claimed superior to others in describing Au–Au interactions.[30–32] The TPSS functional satisfies the exact constrains on exchange and correlation without empirical parameters, which is achieved by respecting two paradigms: the one- or two-electron ground state density and the slowly varying density limit. This makes the TPSS to well describe both molecules and solids. To confirm the reliability of our GGA results, we repeated some of the calculations using the TPSS functional for the exchange and correlation energy. Specifically, we relaxed the 10A, 11A, and 12A structures using the TPSS functional implemented in the CPMD package, and the calculated relative energies of these three structures are 0.0 eV (10A), 0.75 eV (11A), and 1.19 eV (12A), while the GGA results are 0.0 eV (10A), 0.56 eV (11A), and 0.67 eV (12A). So both functionals predicted the same energy order, although the relative energy is not the same.

The optimal relative core-shell size (10 inner atoms versus 48 outer atoms) can be actually predicted by a simple geometric model. Assuming that a hollow atomic shell is nearly spherical and is simply composed of equilateral triangle facets with lateral length of ~2.87 Å, the average Au–Au bond length of the 12A structure, its radius can be estimated using the number of atoms on the shell. For a double shell structure, the separation of the inner and outer shells is the difference between their radii,[33] and its variation with the number of atoms in the inner shell is shown in Fig. 3. The ten-atom inner shell corresponds to separation of 2.84 Å, very close to the optimized Au–Au interatomic distance, which indicates that inner shell with ten atoms corresponds to the best core-shell match.

To gain a deeper understanding of the core-shell structures, it is insightful to see the interaction between the inner core and the outer shell. The binding energies between the core and the shell are shown in Table I. Interestingly, for structures with same core-shell size, those with hollow inner core have a relatively weak core-shell binding, which can be seen through comparison between 10A and 10B, as well as between 12A and 12B. Moreover, the inner core and outer shell of 10A only slightly deform much without the support of each other. Upon relaxation, the outer shell and inner core of 10A well maintained their structures with only slight distortion and with energy lowered by 0.94 and 0.49 eV, respectively. While for the 10B structure, the outer shell also basically maintained itself with energy lowered by 1.30 eV, but the inner core deformed dramatically into a more compact configuration with energy lowered by 2.19 eV. So, in the 10A structure, the outer shell and the inner shell are each in an approximate local minimum of energy and comparably interact weak with each other. (see Table I).

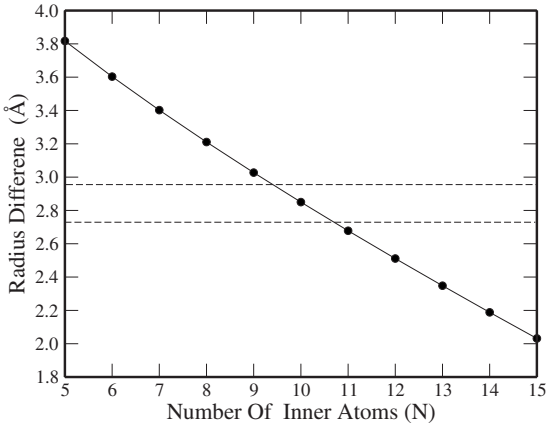

FIG. 3. The variation in the radius difference between the inner shell and the outer shell vs the number of inner atoms obtained by the geometry model. The dashed line shows the reasonable range of the Au–Au interatomic distance, which suggests the inner shell with ten atoms is optimal.

The photoelectron spectrum measurement[22] on Au_{58}^- ~ Au_{64}^- clusters suggested that Au_{58} is uniquely robust and Au_{59} appears to be formed by simply adding one extra atom to Au_{58}'s surface.[22] For all the structures considered in the present study, the energetic order for their anionic structures is exactly the same as their neutral ones, as shown in Fig. 2. So the stability anion of 12A is exceeded by other structures. Thus, although 12A was proposed to be the possible structure in the experiment, it is desirable to detect the existence of other structures rather than 12A. We calculated the density of states (DOS) for all the neutral Au_{58} structures, as well as for the Au_{59} structures formed by adding one atom to their surface, as shown in Fig. 4. The DOS of 10A and 12A, and also other structures such as 10B and 12B, have similar basic structure. Comparing the PES of Au_{58}^- with the DOS of 10A and 12A, it is hard to determine as to which gives the better agreement. Further considering their corresponding Au_{59} structures, it can be noticed that the gap between the first occupied state and the following states is around 0.5 eV for

TABLE I. Total energies for Au_{58} cluster isomers (E_{tot}), their separated inner core (E_c) and outer shell (E_{sh}), and the binding energies of the outer shell and the core ($E_{cs}=E_c+E_{sh}-E_{tot}$). The structures of the inner core and outer shell is just taken from the structures of Au_{58} without further relaxation. All values in eV.

Structure	E_{tot}	E_c	E_{sh}	E_{cs}
8A	−157.17	−16.54	−134.39	6.24
9A	−157.52	−18.23	−130.54	8.75
10A	−158.18	−20.76	−127.33	10.09
10B	−157.98	−19.50	−126.99	11.49
11A	−157.62	−21.80	−122.69	13.13
12A	−157.51	−24.18	−118.67	14.66
12B	−157.06	−24.73	−118.60	13.73
13A	−156.98	−26.75	−114.10	16.13

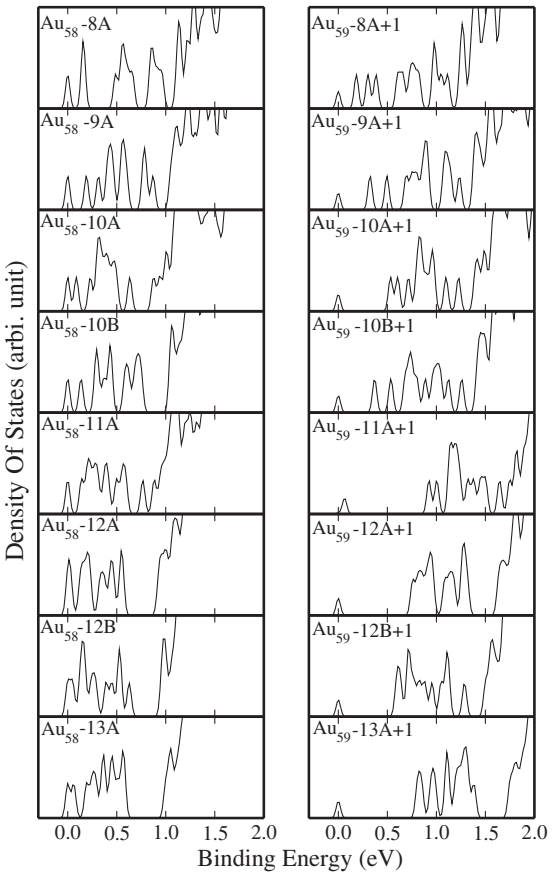

FIG. 4. DOS of the Au_{58} isomers and the corresponding Au_{59} isomers.

the 10A+1 structure; 0.78 eV for the 12A+1 structure, while the corresponding experimental gap of Au_{59}^- is nearly 0.62 eV.[34] In other words, the gaps of the 10A and 12A structures both deviate from the experimental data by only 0.1 eV, although in the opposite direction. The gap of other Au_{59} structures are also in the range of 0.50–1.0 eV. Thus, although the 12A structure is a competitive candidate, the electronic structure of 10A is also reasonably acceptable, and other structures' existence cannot be fully ruled out. Given the energetic advantage of 10A, it is reasonable to expect it is one of the candidates that should be considered (see Fig. 4).

IV. SUMMARY

In summary, we have demonstrated that structure composed of atomic shells can be an important candidate for gold cluster besides planar and hollow cagelike ones. For Au_{58}, a double shell structure consisting of a hollow inner shell of ten atoms is found to be highly stable. It is significant to consider this shell structure as an extension of the hollow cage structures, such as tetrahedral Au_{16}, icosahedral Au_{32}, tubular Au_{50}, and so on. Thus, the evolution of the structure of gold clusters can be from planar, to cage, to shells, and finally to the compact structure as the number of atoms increases. Following this understanding, the Au_{16} cage may be of special importance. The Au_{16} cage can be seen as the tetrahedral Au_{20} deprived of the four corner atoms, so it intrinsically remains the fcc-like stacking as Au_{20}. Thus, actually any cluster taking Au_{16} cage as the inner core would have a bulk kernel and may be an embryo of the bulk fcc phase. On the other hand, a self-stabilized outer shell provides a good chance to produce stable endohedral gold clusters, which would be a topic of future research.[19,35–40]

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[33] This model is to calculate the radius of a golden cage with certain number of atoms. First we approximately use the Euler's rule by assuming $N_{atom}+N_{facet}\simeq N_{bond}$, where N_{atom} is the number of atoms, N_{facet} the number of surface triangles, and N_{bond} the number of surface bonds. The atoms of a shell are either five coordinated or six coordinated, resulting in $2.5N_{atom}\leq N_{bond}\leq 3.0N_{atom}$. Set that $N_{bond}=gN_{atom}$, $2.5\leq g\leq 3.0$. Therefore, $N_{facet}=(g-1)N_{atom}$ and thus the cage radius r can be calculated as $4\pi r^2=N_{facet}S$, where S is the area of each surface triangle. All triangles are assumed to be equilateral with lateral length of 2.87 Å, the typical Au–Au distance in cluster. In this work, considering the deviation of the atomic shells from spherical profile, the value of g is taken as 2.98.
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