High stability of the goldalloy fullerenes: A density functional theory investigation of M_{12}@Au_{20} (M=Na, Al, Ag, Sc, Y, La, Lu, and Au) clusters*

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Discovering highly stable metal fullerenes such as the celebrated C_{60} is interesting in cluster science as they have potential applications as building blocks in new nanostructures. We here investigated the structural and electronic properties of the fullerenes M_{12}@Au_{20} (M=Na, Al, Ag, Sc, Y, La, Lu, and Au), using a first-principles investigation with the density functional theory. It is found that these compound clusters possess a similar cage structure to the icosahedral Au_{32} fullerene. La_{12}@Au_{20} is found to be particularly stable among these clusters. The binding energy of La_{12}@Au_{20} is 3.43 eV per atom, 1.05 eV larger than that in Au_{32}. The highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) gap of La_{12}@Au_{20} is only 0.31 eV, suggesting that it should be relatively chemically reactive.

Keywords: nanostructures, gold fullerenes, density functional theory

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1. Introduction

Since the discoveries of fullerene C_{60},[1] highly symmetrical clusters with cagelike structures composed of non-carbon elements, especially of metal elements have inspired physicists and chemists with great interest, because it can exhibit unusual stability and reactivity, which are very important as the building blocks for novel nanomaterials. Gold is one of the most unique elements in the periodic table with very large relativistic effects. The strong relativistic effects of gold cause the Au_n clusters to exhibit unique structures that isolate them from other metallic clusters. Gold clusters exhibit a variety of structures from two-dimensional (2D) to three-dimensional (3D), including planar, pyramidal, shell-like "flat cage", and tubelike structures.[2–19] The most intriguing research in Au_n clusters is the prediction of a highly stable Au_{32} cage cluster with the same icosahedral (I_h) symmetry as C_{60} in 2004 by Johansson *et al.*[20] and by Gu *et al.*[21] In 2005, Ji *et al.*[22] investigated the Au_{32} cage-hollow structure using a photoelectron spectroscopy (PES) experiment combined with quantum mechanical calculations and they found the Au_{32} fullerene is the most stable one at zero temperature. These new discoveries have generated considerable interest in theoretical research of the Au_{32} fullerene to explore the properties and potential applications.[23–31]

In order to enhance the stability of gold clusters and improve their chemical activities, a considerable amount of experimental and theoretical work has been carried out on gold clusters doped with the impurity atoms.[32–41] For example, it is found that the M@Au_{12} cluster indeed has a highly symmetric icosahedral structure with significant stability.[42–45] Since the Au_{32} fullerene is predicted to be highly stable, it is intriguing to know whether a compound goldalloy fullerene with an endohedral cage structure is more stable than the pure Au_{32} fullerene. Recently, Kumar[46] found that coating 20 Au atoms on an Al_{13} cluster leads to high stability of the icosahedrally symmetric endohedral Al@$Al_{12}Au_{20}$ compound fullerene. Wang *et al.*[47] showed that a 22 karat nanogolden cage consisting of 12 Al and 20 Au atoms can be stabilized by embedding a Mn_4 cluster. Those two groups con-

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centrated the investigations on the combined Al–Au clusters. Is it possible that mixing of other different metal atoms (M_{12}) on Au_{20} magic clusters leads to a hollow cage fullerene with high stability? In this paper, we performed a first-principles study on the nanogolden M_{12}@Au_{20} (M=Na, Al, Ag, Sc, Y, La, Lu, and Au) clusters to explore their structural and electronic properties. It is found that the average binding energy of La_{12}@Au_{20} is 3.43 eV, which is much larger than 2.38 eV for a pure Au_{32} cage, suggesting that the stable La_{12}@Au_{20} has potential utility in new nanomaterials as building blocks.

2. Computational methods

All the calculations in this work are carried out by using the density functional theory (DFT)[48,49] implemented in the DMol^3 package.[50] The electron density functional is treated by the generalized gradient approximation (GGA) with the PW91 exchange-correlation functional parametrized by Perdew and Wang.[51] A relativistic semi-core pseudopotential (DSPP)[52] and double-numerical basis set that included de polarization functions (DND)[53] are employed in this work. The direct inversion in iterative subspace (DIIS) approach is used to speed up self-consistent field (SCF) convergence. The quality of SCF convergence tolerance is set as "fine" with a convergence criterion of 1×10^{-5} Hartree (1 Hartree=27.2113845 eV) on total energy and electron density, 2×10^{-3} Hartree/Å on the gradient, and 5×10^{-3} Å on the displacement in our calculation. The atomic distance cutoff in real space is set as 4.2 Å. Equilibrium geometries of M_{12}@Au_{20} are obtained from symmetry unrestricted optimization. Harmonic vibrational frequencies were computed to confirm that the low energy isomers are true minima. There is no imaginary frequency for structures reported here.

Table 1. Calculated vibrational frequency ω_e, vertical electron detachment energies VDE, adiabatic electron detachment energies ADE, and adiabatic electron affinity energies AEA of the Au_7, Au_7^- and Au_{20} clusters.

System	Property	This work	Experiment[4,5,15]
Au_7	ω_{e1}/cm^{-1}	153.8	165
	ω_{e2}/cm^{-1}	174.1	185
	ω_{e3}/cm^{-1}	186.2	203
Au_7^-	VDE/eV	3.42	3.46
	ADE/eV	3.32	3.40
Au_{20}	ω_e/cm^{-1}	133.6	146
	AEA/eV	2.741	2.745

In order to check the validity of the computational method, we performed the calculation on Au_7, Au_7^-, and Au_{20} clusters, respectively, and the results are summarized in Table 1. All of the properties of these clusters computed using PW91 functional, DND basis and DSPP pseudopotential in our work are in excellent agreement with available experiment data. For example, the computed vertical and adiabatic detachment energies of Au_7^- are 3.42 eV and 3.32 eV, which are well consistent with the experimental results,[4] 3.46 eV and 3.40 eV, respectively. Additionally, the computed adiabatic electron affinity energy of Au_{20} is 2.741 eV, in good agreement with the experimental results of 2.745 eV.[5] This indicates that our methods are reliable and accurate enough to describe the structures and properties of M_{12}@Au_{20} clusters.

3. Results and discussion

Figure 1 gives the optimized geometries of the lowest energy structure for pure Au_7, Au_{20}, Au_{32}, and M_{12}@Au_{20} clusters (M=Na, Al, Ag, Sc, Y, La, and Lu) using the computation scheme described in Section 2. Au_{20} forms a highly stable tetrahedral structure with T_d symmetry as shown in Fig. 1. This structure has been previously unambiguously assigned by comparing the experimental spectrum (Far-IR multiple-photon dissociation (FIR-MPD) spectroscopy in the gas phase) with the calculated vibrational spectra for multiple isomers.[15] We found the lowest-energy geometry of the Au_{32} cluster forms a cagelike structure with high I_h symmetry, in agreement with the previous theoretical results.[20–27] The energy of this structure is much lower than that of any other isomers in our computations. It can be seen that the hollow golden fullerene Au_{32} consists of twenty hexagons and twelve pentagons. We replace the Au atom at the center of each pentagon of Au_{32} with another metal atom to construct M_{12}@Au_{20} clusters which can be regarded as I_h symmetry 12-atom icosahedron combined with I_h symmetry Au_{20} dodecahedron (see Fig. 1). Table 2 gives the calculated parameters and properties of optimized M_{12}@Au_{20} clusters. Data on a pure Au_{32} cluster and the relative binding energy per atom (ΔE_b) compared with the ground state Au_{32} are included. From Table 2 we can see all the M_{12}@Au_{20} cages have high I_h symmetry.

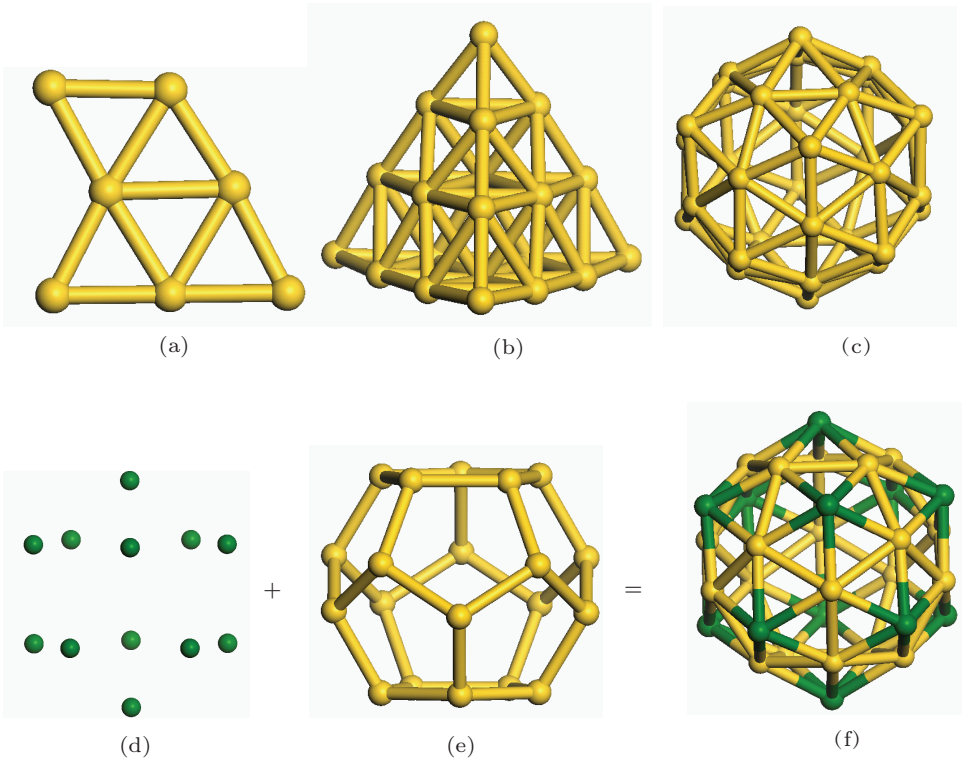


Fig. 1. (colour online) Geometries of the Au_7, Au_{20}, Au_{32}, and M_{12}@Au_{20} clusters (M=Na, Al, Ag, Sc, Y, La, and Lu) obtained from symmetry unrestricted optimization using density functional theory with the PW91 functional, DND basis, and DSPP pseudopotential (see text for details). The M atom is represented by green spheres. See Table 2 for the corresponding energetic and structural information.

Table 2. The symmetry type, the mulliken charge (a.u.) per M atom, the binding energy per atom (E_b), the dissociation energies (E_d), and the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) energy gap E_{gap} of the ground-state M_{12}@Au_{20} clusters (M=Na, Al, Ag, Sc, Y, La, and Lu).

Cluster	Symmetry	E_b/eV	ΔE_b/eV	E_d/eV	E_{gap}/eV	Charge/a.u.
Au_{32}	I_h	2.38	0	3.58	1.56	0
Na_{12}@Au_{20}	I_h	2.23	–0.15	3.19	0.80	0.722
Al_{12}@Au_{20}	I_h	2.96	0.58	3.30	0.68	0.805
Ag_{12}@Au_{20}	I_h	2.27	–0.11	3.35	1.50	0.138
Sc_{12}@Au_{20}	I_h	3.20	0.82	3.23	0.45	0.733
Y_{12}@Au_{20}	I_h	3.28	0.90	3.82	0.38	0.877
La_{12}@Au_{20}	I_h	3.43	1.05	4.40	0.31	0.940
Lu_{12}@Au_{20}	I_h	3.15	0.77	4.23	0.39	0.700

Generally, the binding energy of a given cluster is a measure of its thermodynamic stability. The calculated binding energy per atom (E_b) of the Au_{32} fullerene calculated using the following formula: $E_b = [E(M_{12}Au_{20}) - 12E(M) - 20E(Au)]/32$ is 2.38 eV, in good agreement with the previous results.[24,27,46] Table 2 shows that the binding energies of Na_{12}@Au_{20} and Ag_{12}@Au_{20} are lower than that of the pure Au_{32} cluster. And the E_b of Al_{12}@Au_{20} is 2.96 eV, which is 0.58 eV higher than that of Au_{32}. Kumar reported that their *ab initio* pseudopotential calculation for E_b of Al_{12}@Au_{20} is 3.017 eV,[46] which is in agreement with our result. From Sc to Lu, the E_b of these clusters are larger than that of Al_{12}@Au_{20}, and La_{12}@Au_{20} reaches the maximum of 3.43 eV, which is much larger than 2.38 eV for the Au_{32} fullerene as shown in Fig. 2. These largest relative binding energies compared with pure Au_{32} by 1.05 eV suggest that La_{12}@Au_{20} is relatively more stable than the neighboring clusters. To further study the stabilities of M_{12}@Au_{20} clusters, we also investigated the dissociation energies (E_d), which is defined as:

$E_d = [E(M_{12}Au_{20}) - E(M_{12}Au_{19}) - E(Au)]$. It is found that $La_{12}@Au_{20}$ also has the largest E_d of 4.40 eV, 0.82 eV higher than that of pure Au_{32}, suggesting it is most difficult to separate the Au atom from the $La_{12}@Au_{20}$ cluster. Thus, $La_{12}@Au_{20}$ should be the most stable one among these clusters.

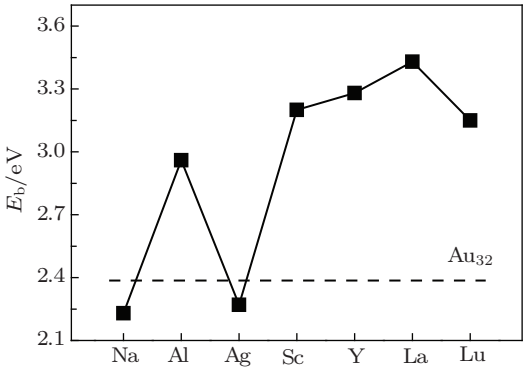


Fig. 2. The average binding energy (E_b) of the $M_{12}@Au_{20}$ clusters (M=Na, Al, Ag, Sc, Y, La, and Lu). The dotted horizontal line is for the Au_{32} cluster.

The HOMO–LUMO energy gap (E_{gap}) of the $M_{12}@Au_{20}$ clusters is given in Table 2 and displayed in Fig. 3. Earlier theoretical studies[20,21,24,27] on Au_{32} in I_h symmetry have shown that it has a large HOMO–LUMO gap. It has been stated that this gold fullerene is expected to be chemically inert. The energy gap of 1.56 eV of Au_{32} in our computations is in good agreement with these previous results.[20,21,24,27] A large energy gap corresponding to a high strength is required to perturb the electronic structure. Figure 3 shows the E_{gap} of the assembled fullerene $M_{12}@Au_{20}$ is smaller than the gap of Au_{32}. Interestingly, $La_{12}@Au_{20}$ has the smallest HOMO–LUMO gap of only about 0.31 eV, suggesting that it should be relatively chemically reactive. Because $La_{12}@Au_{20}$ has the large binding energy, this fullerene is more stable in structure but more chemically reactive as compared with the icosahedral Au_{32} fullerene. We would like to mention the 1.77 eV HOMO–LUMO gap of C_{60} determines that the bulk or solid-state material composed of C_{60} is a nonconductor. There are interesting possibilities that $La_{12}@Au_{20}$ may serve as a dynamical system in catalysis and nanostructured material science.

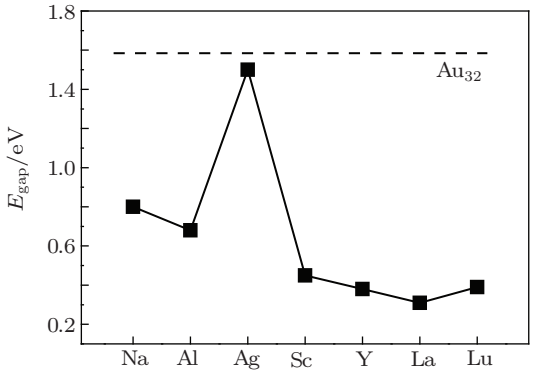


Fig. 3. The HOMO–LUMO energy gap (E_{gap}) of the $M_{12}@Au_{20}$ clusters (M=Na, Al, Ag, Sc, Y, La, and Lu). The dotted horizontal line is for the Au_{32} cluster.

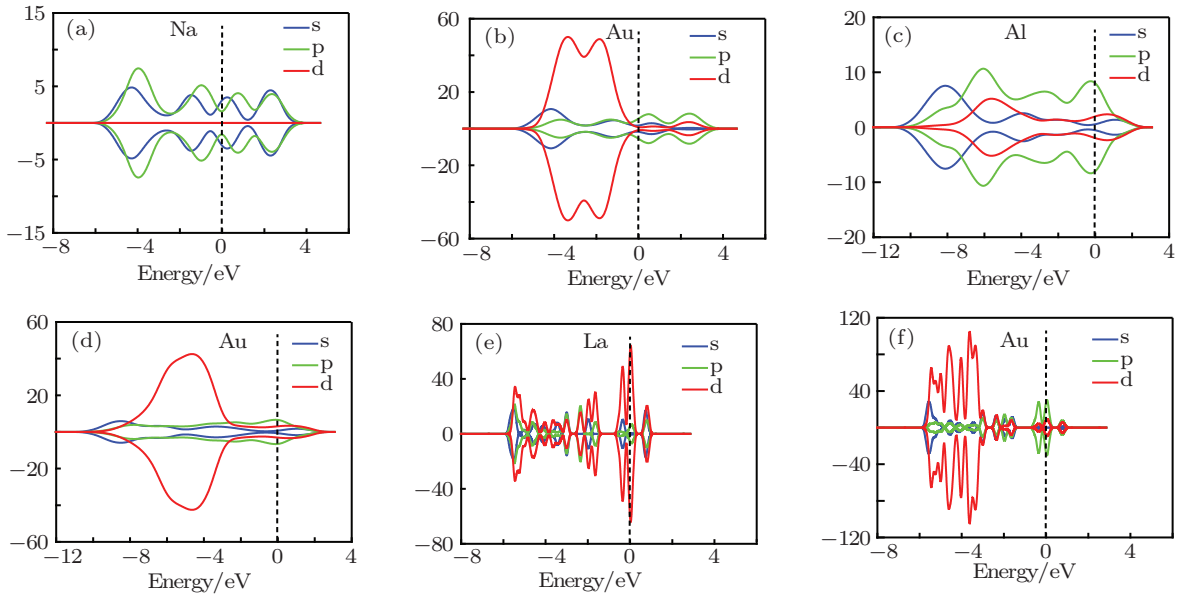


Fig. 4. (colour online) The partial density of states (PDOS) of s, p, and d orbitals for (a) Na atom and (b) Au atom in $Na_{12}@Au_{20}$ cluster; (c) Al atom and (d) Au atom in $Al_{12}@Au_{20}$ cluster; (e) La atom and (f) Au atom in $La_{12}@Au_{20}$ cluster. Spin up (positive) and spin-down (negative) densities are given in each case. The dashed lines indicate the location of the HOMO level.

We carried out Mulliken population analysis for the M_{12}@Au_{20} clusters. The atomic charge of per M atom is also listed in Table 2. Mulliken charge analysis indicates that M atoms entail some negative charge to the Au atoms in all M_{12}@Au_{20} clusters. There is an apparently strong charge transfer in La_{12}@Au_{20} by 0.940 (a.u.), which indicates strong interactions between Au and La atoms occur in this cluster through the charge transfers.

To explore the hybridization between the M atom and the Au atom in the M_{12}@Au_{20} cluster, we plot the partial densities of states (PDOS) of the Na atom and the Au atom in Na_{12}@Au_{20}, the Al atom and the Au atom in Al_{12}@Au_{20}, and the La atom and the Au atom in La_{12}@Au_{20} as three examples in Fig. 4. The PDOS is obtained by Gaussian extension applied to the eigenvalues and the broadening width parameter is chosen to be 0.1 eV. Figure 4 shows that the gold atom has strong s–d hybridization due to the strong relativistic effect and there is obviously strong hybridization between the atomic orbitals of the La atom and Au atom. That is the reason why the La_{12}@Au_{20} cluster is more stable than the other clusters.

4. Conclusion

In summary, we carried out a first-principles investigation with the density functional theory (DFT) to study the nanoalloy M_{12}@Au_{20} (M=Na, Al, Ag, Sc, Y, La, Lu, and Au) clusters. There are new examples of highly stable fullerenes formed between gold and other metal atoms. La_{12}@Au_{20} is highly stable with the large binding energy, 1.05 eV larger than that of the pure icosahedral Au_{32} fullerene. The HOMO–LUMO gap of La_{12}@Au_{20} is much smaller, compared with that in the Au_{32} cluster, suggesting that it should be relatively chemically reactive. The PDOS for M_{12}@Au_{20} clusters are studied to explore the interaction between the M atom and the Au atom. The stable M_{12}@Au_{20} guest–host bimetallic clusters may have potential utility in new nanomaterials as building blocks. We hope that our results will stimulate the experimentalist to validate our theoretical prediction.

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