

Doping of Different Geometries of Gold clusters - A Perspective

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Abstract

Gold clusters are known to form many cage like geometries such as Au₂₀, Au₂₄, Au₃₂. The shape of these clusters varies from Tetrahedral (Au₂₀) cage to Fullerene like (Au₃₂) and tubular form (Au₂₄). These geometries provide favorable positions for both exohedral and endohedral doping. We present Density Functional (DFT) study of stability cage like geometries of gold clusters with different dopants like Si, Ge. It is found that same dopant behaves differently for different shape of gold cage. For Au₃₂, Silicon atoms preferred exohedral position while for tubular Au₂₄ it preferred endohedral arrangement. In both cases the dopant tends to increase the stability of Gold cage.

Index Terms—Nanoparticles, Doped Gold clusters, DFT, Structural Properties

I. INTRODUCTION

Nanometer sized gold particles, opposed to the bulk gold, are not noble. Gold clusters are intensively studied both computationally and experimentally for their catalytic activity and the reactivity [1-3]. In doped gold clusters the chemical activity can be tuned because the introduction of a dopant atom induces changes in electronic charge distribution and leads to geometric reorganization [4, 5]. Gold is known for its remarkable different geometrical structures. They favor the two-dimensional planar structures up to $n = 13$ and a perfect tetrahedron at Au₂₀ followed by tubular structures at Au₂₄ and Au₂₆, and a highly stable Au₃₂ cage [6] cluster with the icosahedral (I_h) symmetry same as C₆₀. These structures have been widely studied as a suitable candidate for doping with different atoms [7]. Deng et al have studied DFT optimization of structures of Au₃₂Ag_n ($n = 1-31$) clusters and found hollow cage-like Au₃₁Ag is the most stable in all the studied Au-Ag mixed clusters, and is even more stable than Au₃₂ [8]. There is

lot of studies on doping of gold clusters with Ag and Cu atoms but they limited to smaller size range. Another important dopant can be Silicon. Si clusters have been investigated both experimentally [9] and theoretically [10] for their potential applications as building blocks to build up well controlled nanostructures. A joint experimental and theoretical study on the structures of gold clusters doped with a group-14 atom: MAu_x (M = Si, Ge, Sn; $x = 5-8$) have shown that these doped clusters have a strong tendency of forming stable planar structures [11]. As Si doped gold clusters can form a stable geometry. Hence it is of interest to study the interaction of Si atoms with Au_n clusters of various dimensionalities.

In our present work we will perform the DFT study on the effect of doping single Si atom in different structure of Gold i.e, Au₃₂ and Au₂₄. With Si and Ge atoms doping we can have early onset of 3D geometries in small planar gold clusters. We have calculated the binding energies, bond lengths, HOMO-LUMO gaps of these clusters.

The organization of the paper is as follows. The computational details are given in Section 2, results and discussions are presented in Section 3

II. METHODOLOGY

We have used the SIESTA code, based on Density Functional theory method. The electron density functional is treated by the generalized gradient approximation (GGA) with exchange correlation functional parameterized by Perdew, Zunger and Ernzerhof (PBE) scheme [12, 13]. The pseudo potentials for Silicon atom is generated with atomic valence electron 3s²3p². For Silicon, cut off radii are: s (1.77), p (1.96), d (2.11) and f (2.11). The valence states were described using DZP (double-zeta + polarization) basis sets. The reciprocal space integrations are carried out at the gamma point. The clusters are optimized inside simulation cell of 15 Å and energy cutoff of 200 Ry.

The symmetry unrestricted geometry optimization is carried using conjugate gradient and quasi Newtonian methods until all the forces are less than $0.01\text{eV}/\text{\AA}$.

We have verified the computational procedure by calculating the ionization potential (IP) for a gold atom and performing test calculations on Au_2 and Si_2 dimer. The IP of the gold atom is found to be 8.90 eV which is in fair agreement with the experimental value of 9.22eV [14]. The structural parameters such as bond length for Au_2 are found to be 2.55 \AA respectively which is in agreement with experimental values 2.47 \AA [15]. For Si_2 , the bond length is 2.28 \AA which agree with the experimental values of 2.25 \AA [16]. The ionization potential of Si_2 is 7.97 eV which agrees with the experimental reported values, 7.87eV [17].

III. RESULTS AND DISCUSSIONS

A: Structure and Energetic

$\text{Au}_{20}@\text{Si}_{12}$:The structure of the hollow golden fullerene Au_{32} can be regarded as I_h symmetry 12-atom icosahedron combined with I_h symmetry Au_{20} dodecahedron. We have replaced Au atom at the center of each pentagon of Au_{32} with Si atom to construct $\text{Si}_{12}@\text{Au}_{20}$ clusters. The optimized structures of Au_{32} after doping are given in Figure 1 and various computed values are given in Table 1.

In our preliminary studies we have doped the small gold clusters with Si atoms and found that silicon prefers exohedral site [18]. The similar behavior is observed when doped in the Au_{32} cage. The Si atoms have preferred exohedral arrangement. The final optimized structure was found to be similar to Meng et al [19].

TABLE I: Symmetry, Average Binding Energy per Atom (E_b) and HOMO-LUMO gap (E_g)

Cluster	Symmetry	E_b (eV/atom)	E_g (eV)
Au_{32}	I_h	3.16	1.59
$\text{Si}_{12}@\text{Au}_{20}$	I_h	4.02	0.57
Au_{24}	D_{3h}	2.437	0.97
$\text{Si}_3\text{Au}_{24}$	D_{3h} (slightly distorted)	2.679	0.27

$\text{Au}_{19}@\text{Si}$: Au_{20} is a highly stable and chemically inert cluster possessing a tetrahedral pyramidal structure.

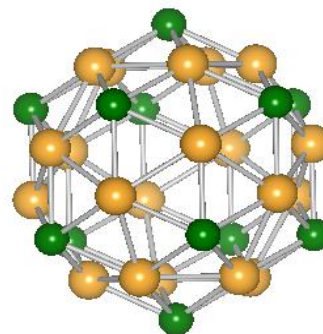
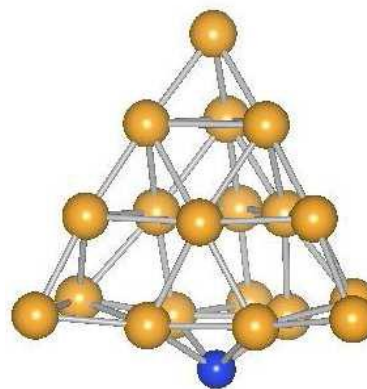


Fig. 1. The low lying geometries of the $\text{Si}_{12}@\text{Au}_{20}$ clusters obtained from symmetry unrestricted optimization using density functional theory. The Si atom is represented by green spheres

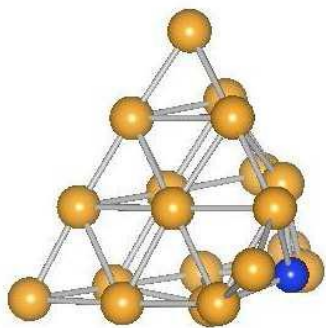
The tetrahedral structure of the Au_{20} cluster can be viewed as a relaxed small piece of bulk gold with a face-centered cubic (fcc) lattice. Along with high stability and symmetry, it has also been found that as compared to the neutral cluster Au_{20} , its anion is extremely active due to the presence of a weakly bound unpaired electron in it [20]. As shown in literature that Si can act as electron donor in gold cluster, affects the chemical reactivity of Au_{20} [21].

To obtain the optimized geometry the silicon atom is placed at different positions namely at the center and on the edge of Au_{20} . The optimized geometries are shown in Fig. 2. It is found when the Si atom is doped inside the Au_{20} cage, after minimization the Si atom has come out and prefers an exohedral position.

The binding energy of the low lying isomer of SiAu_{19} is found to be 3.08eV/atom , higher than that of pure Au_{20} which is 3.03eV/atom . Si atom doping in Au_{20} cage has enhanced its stability.



(a) Si atom is placed at the centre



(b) Si atom is placed at the edge

Fig. 2. Lowest energy geometries of Si@Au₁₉. The Si atom is represented by blue sphere

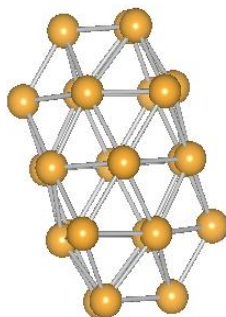
TABLE II: Symmetry, Average Binding Energy per Atom (E_b)

Cluster	Symmetry	E_b (eV/atom)
Si ₁ @Au ₁₉	C _{3v}	3.08

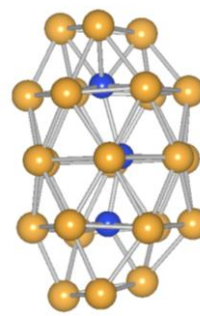
Au₂₄@Si₃: Another structure we have considered is Au₂₄, a tubular cage like structure of gold with hexagonal cross-section. The hollow-tubular structures dominate at larger size range in the low-lying isomers for gold [22, 23]. It is found when we place Si atom at two different positions namely on the surface and at the centre of Au₂₄ tube, Si prefer the exohedral position i.e., on the surface of Au₂₄ cluster just like the case of Au₂₀ and Au₃₂ cluster. The binding energy per atom of SiAu₂₄ cluster was found to be 2.549 eV/atom with Si atom on the surface and 2.527eV/atom with Si atom at the centre; the difference in energy of two low lying configurations is being only 0.022 eV.

But on placing three Si atoms at the center axis of the Au₂₄ tube it is found that the binding energy per atom has increased to 2.679 eV/atom.

Here the Si atoms are preferring endohedral position to exohedral position. The optimized geometry of Au₂₄ and Si₃@Au₂₄ is as shown in Fig. 3.



(a)



(b)

Fig. 3. Lowest energy geometries of a) Au₂₄, (b) Si₃Au₂₄

IV. CONCLUSION

In summary, we have made relativistic DFT studies on the difference in behaviour of gold clusters of different size i.e., Au₂₄ and Au₃₂ towards the same dopant (Si atom). It is found that

- In both cases the HUMO-LUMO gap is reduced indicating increased reactivity.
- Though the number of Si atoms is different in both cases it is seen that the Si atoms prefer exohedral site in Au₃₂ and endohedral position in Au₂₄. Thus it is suggested that different structure of gold behaves differently for same dopant atleast in case of Si atom.
- In both cases Si atoms increase the stability of the gold clusters Au₂₄ and Au₃₂ and also retain the original geometry with slight distortion.

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