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 Au25, Au24, Au32. The shape of these clusters varies from Tetrahedral (Au25) 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 Au25 followed by tubular structures at Au24 and Au26, and a highly stable Au32 cage [6] cluster with the icosahedral \((I_0)\) symmetry same as \( C_{60} \). 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 \((n = 1–31)\) 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\( _x \), (\( M = \text{Si, Ge, Sn}; \ x = 5–8\)) 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 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 3s\(^2\)3p\(^2\). 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 0.01eV/Å.

We have verified the computational procedure by calculating the ionization potential (IP) for a gold atom and performing test calculations on Au2 and Si2 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 Au2 are found to be 2.55 Å respectively which is in agreement with experimental values 2.47 Å [15]. For Si2, the bond length is 2.28 Å which agree with the experimental values of 2.25 Å [16]. The ionization potential of Si2 is 7.97 eV which agrees with the experimental reported values, 7.87eV [17].

III. RESULTS AND DISCUSSIONS

A: Structure and Energetic

Au20@Si12: The structure of the hollow golden fullerene Au32 can be regarded as Ih symmetry 12-atom icosahedron combined with Ih symmetry Au20 dodecahedron. We have replaced Au atom at the center of each pentagon of Au32 with Si atom to construct Si12@Au20 clusters. The optimized structures of Au32 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 Au32 cage. The Si atoms have preferred exohedral arrangement. The final optimized structure was found to be similar to Meng et al [19].

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Symmetry</th>
<th>$E_b$ (eV/atom)</th>
<th>$E_g$ (eV)</th>
</tr>
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<tbody>
<tr>
<td>Au32</td>
<td>Ih</td>
<td>3.16</td>
<td>1.59</td>
</tr>
<tr>
<td>Si12@Au20</td>
<td>Ih</td>
<td>4.02</td>
<td>0.57</td>
</tr>
<tr>
<td>Au24</td>
<td>D3h</td>
<td>2.437</td>
<td>0.97</td>
</tr>
<tr>
<td>Si3Au24</td>
<td>D3h (slightly distorted)</td>
<td>2.679</td>
<td>0.27</td>
</tr>
</tbody>
</table>

Au19 @Si: Au20 is a highly stable and chemically inert cluster possessing a tetrahedral pyramidal structure.

The tetrahedral structure of the Au20 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 Au20, 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 Au20 [21].

To obtain the optimized geometry the silicon atom is placed at different positions namely at the center and on the edge of Au20. The optimized geometries are shown in Fig. 2. It is found when the Si atom is doped inside the Au20 cage, after minimization the Si atom has come out and prefers an exohedral position.

The binding energy of the low lying isomer of SiAu19 is found to be 3.08eV/atom, higher than that of pure Au20 which is 3.03eV/atom. Si atom doping in Au20 cage has enhanced its stability.
Fig. 2. Lowest energy geometries of Si@Au_{19}. The Si atom is represented by blue sphere.

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

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Symmetry</th>
<th>E_b (eV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si_{19}@Au</td>
<td>C_{3v}</td>
<td>3.08</td>
</tr>
</tbody>
</table>

**Au_{24}@Si_{3}:** Another structure we have considered is Au_{24}, 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 Au_{24} tube, Si prefer the exohedral position i.e., on the surface of Au_{24} cluster just like the case of Au_{20} and Au_{32} cluster. The binding energy per atom of SiAu_{24} cluster was found to be 2.549 eV/atom with Si atom on the surface and 2.527 eV/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 Au_{24} 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 Au_{24} and Si_{3}@Au_{24} is as shown in Fig. 3.

IV. CONCLUSION

In summary, we have made relativistic DFT studies on the difference in behaviour of gold clusters of different size i.e., Au_{24} and Au_{32} 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 Au_{32} and endohedral position in Au_{24}. 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 Au_{24} and Au_{32} and also retain the original geometry with slight distortion.

REFERENCES


