

Growth of GNTs with backbone $X_n@Au_{6n}(n=1,3,5,7,9)$ ($X = Ag, Cu, Au$)

Sumali Bansal^{1*}, Priyanka², Rajiv Bhandari³, Keya Dharamvir⁴

¹DAV College, Sector 10, Chandigarh, India

²Guru Gobind Singh College for Women, Sector 26, Chandigarh, India

³Post Graduate Government College Sector 11, Chandigarh, India

⁴Department of Physics, Punjab University, Chandigarh, India

*Corresponding author

DOI: 10.5185/amp.2018/014

www.vbripress.com/amp

Abstract

Gold clusters are known to have size dependent geometries. The study of golden cages of different sizes and dimensions has gained momentum in recent years as they can accommodate guest atoms to form a new kind of endohedral structure. We will be studying the doping of gold tubular cages with transition metal (TM=Ag, Cu and Au). Their geometrical structures, relative stabilities, binding energies and bond lengths are studied using Model Potential approach- Gupta Potential (GP). AuAg and AuCu have been chosen because they may be expected to show different behaviors. As far as our knowledge no such work has been reported earlier. It is observed that doping of Ag and Cu atom at the centre of planar Au_6 results in a three dimensional geometry. The atom-atom interaction potential predicts the dominance of the finite size effect as the number of Cu and Ag atoms increases along with the size of gold tubular cage. Copyright © 2018 VBRI Press.

Keywords: Gold clusters, Gupta potential (GP), endohedral doping.

Introduction

The possibility of a hollow tubular Au_n cage at $n=24$ has opened the possibilities of new stable bigger tubular structures in competition with other possible structures, such as the amorphous, the bulk fragment, and the cage-like ones.

The tubular structure of Au_{24} has been verified both theoretically and experimentally [1]. The study of growth of tubular gold cages pure as well as doped can have applications in the field of nanotechnology. There has been intense research activity on gold nanostructures motivated by their potential applications in the areas of nanostructured materials, electronics and catalysis [1-3]. Due to relativistic effects gold clusters favours two-dimensional planar structures up to $n = 13$ and three-dimensional structures occur for $n > 13$, hollow cages for $n = 16$ and 17, followed by the appearance of a tetrahedral structure at $n = 20$ [4], and the emergence of a highly symmetric tube like structure at $n = 24$. Along with pure gold clusters, bimetallic doped gold clusters have also been considered for the catalytic applications. With a suitable choice of metallic impurity atoms doped in a pure gold cluster, it is possible to tune the geometric and electronic structures and consequently the chemical reactivity of these clusters in desirable fashion. A lot of theoretical and experimental work on doped Au clusters focuses mainly on transition metal atoms as dopant [5-10]. Zhao et al. have studied structural and electronic properties of M_2 -doped Au_n ($M = Ag, Cu; n = 1-10$) clusters [11]. Recently Baletto et al. have studied the

effect of doping of golden cages of 32. It is shown that Ag and Cu doping affects the geometrical stability of the icosahedral fullerene Au_{32} cage [12]. The study of golden cages of different sizes and dimensions has gained momentum in recent years as they can accommodate guest atoms to form a new kind of endohedral structure.

A detailed study of the effect on structural properties of gold tubular cages encapsulating transition metal atoms have been done using -model potential – Gupta Potential (GP). It is observed that doping of Ag and Cu atom at the centre of planar Au_6 results in a three dimensional geometry. The current work agrees well with other similar studies which predict that the isoelectronic substitution induces an earlier onset of 3D structures in gold clusters. The atom-atom interaction potential predicts the dominance of the finite size effect as the number of Cu and Ag atoms increases along with the size of gold tubular cage. The study of binding energy predicts that the $Cu_n@Au_{6n}$ (B.E. of Cu_9Au_{54} is 1.58) clusters are more stable than the $Ag_n@Au_{6n}$ (B.E. of Ag_9Au_{54} is 15.054 - 1.51) clusters.

The organization of the paper is as follows. The computational details are given in Section II, results and discussions are presented in Section III followed by conclusion in Section IV.

Computational details

Gupta potential (GP) [13] was adopted to describe the interatomic interactions which is a many body potential developed on the basis of second moment approximation

of the tight binding or linear combination of atomic orbitals (LCAO) scheme. This is a very ‘chemical’ point of view as it is related in a natural way to yield the metallic character of cohesive energy. The total energy of the system is calculated using eqn.1

$$V = \frac{1}{2} \left\{ \sum_{i=1}^N \left[\sum_{j=1}^N A \exp \left(-p \left[\frac{r_{ij}}{r_0} - 1 \right] \right) - \sqrt{\sum_{j=1}^N \xi^2 \exp \left(-2q \left[\frac{r_{ij}}{r_0} - 1 \right] \right)} \right] \right\} \quad (1)$$

where r_{ij} is the distance between atoms i and j . r_0 is the bulk first neighbor distance. A , p , q and ξ are parameters fitted to experimental values of the cohesive energy, lattice parameters, and independent elastic constants for the crystal structure at 0K. For GP the parameters for Au-Au, Au-Cu and Au-Ag clusters are taken from the literature [14-16]. The appropriateness of this potential to describe transition and noble metal structures is well recognized [16].

Results and discussion

We have encapsulated transition metal and their monatomic chains within tubular $Au_{6n}X_{n=1,3,5,7,9}$ ($X = Ag, Cu, Au$) cages of various lengths. The initial structure considered is only one Au hexagonal cross sectional layer and one TM atom. Then the number of dopants are increased along with number of Au hexagonal cross sectional layers. This can be considered as a short segment of the SWGNT (single – wall gold nanotube) without capping at both ends, yielding a highly symmetric open tube like cage. The TM (Ag, Cu and Au) atoms are placed at the central axis of the tubular Au structure and geometry optimizations were performed. Initial structures (not optimized) and optimized geometries of the pure as well as doped gold cages are shown in the Fig. 1 to Fig. 3.

On optimisation, the pure tubular gold structures are found to form different three dimensional cages or have deformed tubular geometry.

In case of doped Cages, on observing $Ag@Au_6$ and $Cu@Au_6$ optimized geometries it can be concluded that they prefer three dimensional structures. As the size of the gold clusters increases along with the number of dopant atoms, it is found that silver and copper atoms forms a linear chain within the golden cage. Also, both Ag and Cu atoms have longer bond length than the interlayer distance of gold cage so these atoms come out of the cage. As size of the monatomic chains of Ag and Cu atoms increases, it breaks the golden cage. It is found that the after optimization the structure Ag_1Au_6 and Cu_1Au_6 become highly distorted and do not retain their original ring form. However, as soon as there is stacking in the structure, the form tends to be retained. We find (see Fig. 2 and 3) that Ag and Cu spines are nicely accommodated inside these long gold cages except in a few cases. The splitting up of the longer cages into shorter units is due to size mismatch - the interatomic distance between the Ag atoms and Cu atoms is larger than the interlayer separation between the gold hexagons. We predict that very long Au cages with

spinal support can be made with careful size matching - select a metal with interatomic distance in the chain exactly equal to that between the gold hexagons, or, there be a missing atom in the spine at regular intervals to accommodate the size mismatch. The Au_{6n} cages with spinal support i.e., $Au_n@Au_{6n(n=1,3,5,7,9)}$ ($X = Ag, Cu, Au$) cage, start preferring tubular arrangement except for $n = 6$.

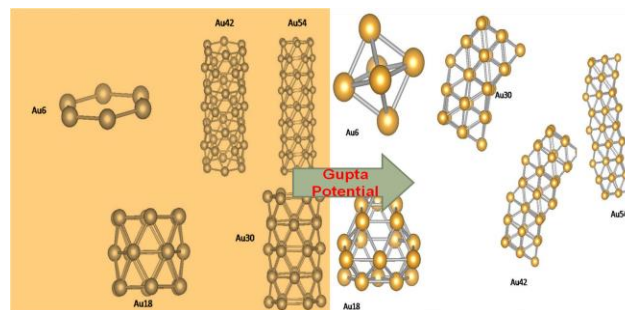


Fig. 1. Initial and Optimized geometries of Hollow Au_{6n} ($n = 1, 3, 5, 7, 9$) tubular structure.

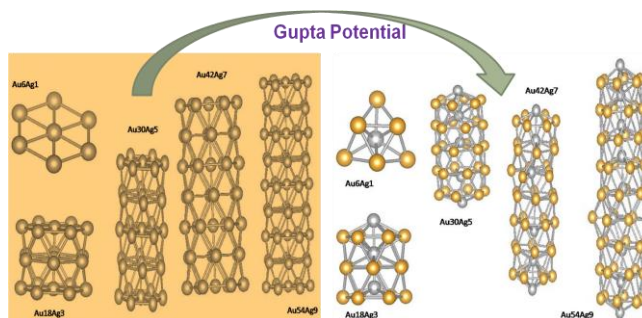


Fig. 2. Initial and Optimized geometries of Doped $Ag_n@Au_{6n}$ ($n=1,3,5,7,9$) tubular structure.

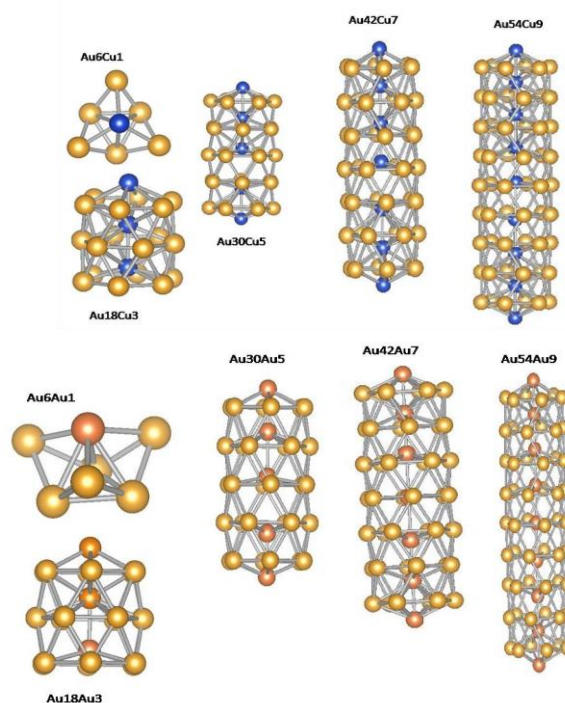


Fig. 3. Optimized geometries of Doped $Cu_n@Au_{6n}$ ($n=1,3,5,7,9$) and $Au_n@Au_{6n}$ ($n=1,3,5,7,9$) tubular structure respectively.

Table 1. Average Binding Energy per Atom (E_b), Average Distances of Dopants from the bonded Au atoms in the shell (R).

Cluster	E_b (e V)	R (Å)	
		Au - Au	M- M
Au@6	-1.5491	2.631	
Au@18	-1.624	2.662	
Au@30	-1.649	2.657	
Au@42	-1.660	2.657	
Au@54	-1.666	2.657	
Au6@ag1	-1.308	2.63 – 2.71	
Au18@ag3	-1.461	2.62 – 2.71	2.60 – 2.68
Au30@ag5	-1.489	2.62 - 2.72	2.63 – 2.68
Au42@ag7	-1.505	2.61 – 2.71	2.59 – 2.70
Au54@ag9	-1.514	2.57 – 2.71	2.59 – 2.71
Au6@cu1	-1.306	2.43 – 2.48	
Au18@cu3	-1.511	2.39 – 2.53	2.37 – 2.43
Au30@cu5	-1.548	2.40 – 2.52	2.39 – 2.53
Au42@cu7	-1.571	2.37 – 2.54	2.36 – 2.52
Au54@cu9	-1.584	2.36 – 2.79	2.32 – 2.49
Au6@au1	-1.545	2.59 – 2.76	
Au18@au3	-1.675	2.59 – 2.77	2.59 – 2.70
Au30@au5	-1.699	2.60 – 2.76	2.62 – 2.67
Au42@au7	-1.713	2.60 – 2.76	2.61- 2.75
Au54@au9	-1.720	2.57 – 2.77	2.57 – 2.72

Amongst the dopant, the gold prefers Au atoms over Cu and Ag atoms as backbone to their tubular arrangement. This trend is clearly visible in our binding energy calculations. Though the DFT calculations prefer Cu atoms over Au and Ag atoms for doping [11]. This can be explained as Gupta potential favours Au-Au bonding over its bonding with the others elements. The binding energy values for $X_n@Au_{6n(n=1,3,5,7,9)}$ ($X = Ag, Cu, Au$) cage are given in **Table 1**.

Conclusion

We have presented a study using model potential – Gupta Potential (GP) of the structural properties of gold tubular cages $X_n@Au_{6n}$ ($n=1, 3, 5, 7, 9$) ($X = Ag, Cu, Au$) cage encapsulating transition metal atoms. The optimized geometries of pure gold clusters were found to be deformed or distorted. We can summarize the results by concluding that on addition of suitable impurity as a backbone to the Au_n cages we can form long stable tubular structure which can be further investigated for application in the field of nano- electronics.

Acknowledgements

We express our gratitude to the Computational HPCC facility provided by Department of Physics, P.U., Chandigarh. We also gratefully acknowledge the financial support from UGC for providing us BSR Research Fellowship for Meritorious Students (RFMS) scheme via UGC Grant Reference No. F. 5-89/2007(BSR).

References

1. A.C. Templeton, W.P. Wuelfing, R. W. Murray, *Acc. Chem. Res.*, 33, 27 (2000).
2. N. Lopez, J. K Norskov, *J. Am. Chem. Soc.*, 124, 38, 11262-11263(2002).
3. H. Hakkinen, M. Moseler, U. Landman, *Phys. Rev. Lett.*, 89, 033401(2002).
4. J. Li, X. Li, H. J. Zhai, L. S. Wang, *Science*, 299, 864-867 (2003).
5. H. Hakkinen, S. Abbet, A. Sanchez, U. Heiz, U. Landman, *Angew Chem. Int. Ed.*, 2, 1297(2003).
6. E. Janssens, H. Tanaka, S. Neukermans, R. E. Silverans, P. Lievens, *New J. Phys.*, 46(2003).
7. E. Janssens, H. Tanaka, S. Neukermans, R. E Silverans, P. Lievens, *Phys. Rev. B*, 69, 085402 (2004).
8. H. Tanaka, S. Neukermans, E. Janssens, R.E. Silverans, P. Lievens, *J. Am. Chem. Soc.*, 125, 2862 (2003).
9. D.W. Yuan, Y. Wang, Z. Zeng, *J. Chem. Phys.*, 122, 114310 (2005); B. R. Sahu, G. Maofa, and L. Kleinman, *Phys. Rev. B*, 67, 115420 (2003).
10. M. B. Torres, E. M. Fernandez, L.C. Balbas, *Phys. Rev. B*, 71, 155412 (2005).
11. Ya-Ru Zhao, Xiao-Yu Kuang, Bao-Bing Zheng, Yan- Fang Li, Su-Juan Wang, *J. Phys. Chem. A*, 115, 569–576 (2011).
12. R. Ferrando, R. L. Johnston, C. Louis, *Phys. Chem. Chem. Phys.*, 17, 27920 27921(2015).
13. R.P. Gupta, *Phys. Rev. B*, 1981, 23, 6265.
14. F.Cleri, V. Rosato, *Phys. Rev. B*, 1993, 48, 22.
15. T. W. Nicholas, R. L. Johnston, *J. Mater.Chem.*, 2002, 12, 2913–2922.
16. L.O. Paz-Borbón, R. L. Johnston, G. Barcaro, and A. Fortunell, *J. Chem. Phys.* 2008, 128, 134517.