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Materials Today: Proceedings 3 (2016) 1563–1568

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Recent Advances In Nano Science And Technology 2015 (RAINSAT2015)

Theoretical analysis: Electronic and optical properties of gold-silicon nanoalloy clusters

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Abstract

Due to diverse applications in the field of science and engineering, the clusters formed between Gold and Silicon are attractive building blocks for future nano-scale and optical devices. It has remarkable catalytic, electronic, optical and magnetic properties. A number of experimental as well as theoretical researchers are actively involved into this research domain. Theoretical approach is very popular in terms of Density Functional Theory (DFT) to compute the electronic structure of matter. Conceptual DFT based descriptors have been invoked to correlate the experimental properties of nano compounds and composites. In this report, we have studied Au_nSi (n=1-8) nano alloy clusters. Generalized Gradient Approximation (GGA) with basis set LanL2DZ have been used in this analysis. The experimental properties of the Au_nSi (n=1-8) nanoalloy clusters are correlated in terms of DFT based descriptors viz. HOMO-LUMO gap (eV), Electronegativity (χ), Global Hardness (η), Global Softness (S) and Electrophilicity Index (ω). The calculated HOMO-LUMO gap exhibits interesting odd-even oscillation behaviour, indicating that even numbered clusters possess higher stability in comparison with odd numbered clusters.

Selection and Peer-review under responsibility of [Conference Committee Members of Recent Advances In Nano Science and Technology 2015.].

*Keywords:*Nanoalloy, Conceptual Density Functional Theory, Descriptors, Hardness, Odd-even oscillation;

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1. Introduction

In the recent decades, nanomaterials have deeply integrated into human life. Since last few years, nanomaterials and nanotechnology have emerged as important research domains of science and technology [1]. The classification of nanoparticles is done in terms of size range of 1-100 nm. That particular size range exists between the levels of atomic/ molecular and bulk material [1-5]. Due to existence of a large number of quantum mechanical and electronic effects, nanoparticles possess various unique physico-chemical properties [2-4]. But, there are still some instances of nonlinear transition of certain physical properties, which may vary depending on their size, shape and composition [6, 7]. A large number of scientific reports are available for describing the effects of size and structure to change the optical, electronic, magnetic, chemical and other physical properties of nanoparticles [1, 3, 4].A deep insight into the research of nanoparticles with well –defined size and structure may lead to some other alternatives for better performance [8]. The nanoparticles, due to its variousapplications in the areas of biological labeling, photochemistry, catalysis, information storage, magnetic device, optics, sensors, photonics, optoelectronics, nanoelectronics etc. have got immense importance [1, 3, 9-11].

Gold nanoclusters due to its unique electronic, optical and magnetic properties are very much popular and a potential candidate for medical applications [12-28]. These nanoclusters have applications in radiotherapy, photothermal therapy, imaging of cancer cells [15-28]. A number of reports are available for describing that impurity atoms can enhance the above mentioned properties of doped gold clusters that are sensitive towards the nature of dopant atom [28-30]. Nowadays, different compositions of nanoalloysare being utilized for advancement of methodologies and characterization techniques [29-31]. A deep study of core-shell structure of nano compounds is very much popular as because its properties can be tuned through the proper control of other structural and chemical parameters. Silicon doped metal nanoclusters have been focus of extensive theoretical and experimental investigation due to its high importance in the field of microelectronics industry [28, 32]. A large number of theoretical studies have been reported to the determination of equilibrium geometry, electronic and structural properties of Si doped Au nanoclusters. Pal et al.[33] reported doped gold anion clusters of $Au_{16}M^{-}$(M=Si, Ge, Sn) and found that $SiAu_5^{-}$ have a tetrahedral based 3D structure and MAu_x^{-}(x=6,7) (M=Si, Ge, Sn) have quasi-planar structures. From this study it reflects that Au-Au interactions and Au-M interactions in the in MAu_x^{-} clusters have a dangling unit of Au-Si, resembling that of larger Si-doped gold cluster $SiAu_{16}^{-}$. Majumder et al [34]reported that Au_5M, (M= Na, Mg, Al, Si, P and S) and found that impurities with p electrons (Al,Si,P) exhibits nonplanar geometries while with s electrons (Na, Mg) shows planar geometries, the exception occurs for Au_5S.Sun et al [35] reported the cage structure of $Au_{16}Si$, and observed that endohedral configuration is metastable and the silicon atom prefers to bind on the exterior surface of the cage, which is also the lowest energy structure. In the nanostructures of Au-Si, the covalent bond between Au-Si and Au-Au is examined as a dominant feature of the stability [35].Though, a number of experimental and theoretical studies have been done on this particular type of compounds, a theoretical analysis invoking Density Functional Theory (DFT) is still unexplored.

DFT is one of the most successful techniques of quantum mechanics to explore the electronic properties of materials in terms of quantitative descriptors. As for the larger systems electron density is more manageable as compared to wave function, DFT is very much popular to study the many- body systems [8]. Super conductivity of metal based alloys [36], magnetic properties of nano alloy clusters [37, 38] quantum fluid dynamics [39], molecular dynamics [40], nuclear physics [41, 42] can be extensively studied by DFT methodology. Recently we have established the importance of DFT based descriptors in the domain of drug designing and nano-engineering materials [43-47]. The study of density functional theory is broadly classified into three sub categories viz. theoretical, conceptual, and computational [48-51]. The conceptual density functional theory is highlighted following Parr's dictum "Accurate calculation is not synonymous with useful interpretation. To calculate a molecule is not to understand it" [52].

In this venture, we have studied Au-Si nano-clusters in terms of DFT based conceptual descriptors. An attempt has been made to correlate the computed descriptors of the compounds with their experimental counterparts.