

Engineering of Ti_N ($N = 1 - 15$) nanoclusters by doping osmium impurity

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Abstract. Bimetallic transition metal nanoclusters have attracted significant attention in recent years due to their wide range of applications such as heterogeneous catalysts, electrochemistry and alloy design. However many studies were reported on pure transition metal nanoclusters and bimetallic of late transition metal nanoclusters. In this study the density functional theory (DFT) with PBEsol exchange correlation functional was employed to investigate the structural and electronic properties of $Ti_{N-1}Os$ ($N = 2-16$) nanoclusters. The calculations showed that osmium impurity mostly prefers to be encapsulated by titanium nanoclusters. The binding energies gradually decrease with the cluster size N . The Os dopant was found to enhance the binding energy of titanium nanoclusters. The relative stability or second order energies showed that Ti_6Os and $Ti_{12}Os$ clusters are the most stable. Interestingly, osmium dopant converted the nanocluster with 13 atoms to be the most stable. Furthermore, the dissociation energy or first order energies showed an excellent correlation with the relative stability trend. The HOMO-LUMO revealed the lowest energy gap at $Ti_{12}Os$ ($N = 13$) which correlates well with the predicted binding energy, relative stability and dissociation energy.

1. Introduction

Metal nanoparticles display properties which mainly differ from their bulk materials. This is attributed to their smaller size and larger specific surface area in comparison with the bulk. These nanoclusters are extensively studied because of various potential applications [1, 2]. The atomic nanoclusters of transition metal elements have been found to be suitable to undertake catalytic reactions [3, 4]. There is a notable interest in the structure and electronic properties of clusters for their use in heterogeneous catalysis and electrochemistry. Particularly, doped nanoclusters offer the chances of engineering their activity and selectivity [5]. However, the scientific community has concentrated much work on the smaller clusters of late transition metals, for instance, noble and platinum metals, while less work has been done for early transition metals, such as titanium, vanadium, etc [6]. The inconsiderable interest in the structures and properties of early transition metals might be due to their almost empty d orbital that provides unique bonding properties [5]. Hence, there is need to fully understand the reactivity of titanium nanoclusters. The electronic configuration of titanium is $[Ar] 3d^23s^2$ and it has an open-shell d orbital with only two electrons. The formation of its stable nanoclusters is a matter of discussion among theoreticians and experimentalists. Ascencio *et al.* [6] identified three magic number clusters, Ti_7 , Ti_{13} , and Ti_{15} , corresponding

to closed-packed structures using molecular dynamics simulations based on density functional theory (DFT) with a local density approximation.

Sakurai *et al* [7] employed time-of-flight (TOF) mass spectra to experimentally study titanium clusters and found $N = 7, 13, 15, 19,$ and 25 as the magic numbers. The kinetic energy dependence of the collision-induced dissociation (CID) of Ti_N ($N = 2-22$) was studied by Li *et al* [8] and found that the dissociation energy changes significantly as a function of cluster size N , with local maxima at $N = 7, 13$ and 19 . Recent studies [9] showed that the chemical and electronic properties of titanium clusters could be tuned by doping. In particular, doped titanium clusters with formula $Ti_{12}M$ have shown higher stability when the metal dopant turns out to be placed at the centre of the cage, which can be understood from the pseudospherical icosahedral structure, which has been observed with high stability for other metallic clusters.

Rodríguez-Kessler and Rodríguez-Domínguez [5] investigated the effect of vanadium on Ti_N ($N = 1 - 16$) nanoclusters using DFT with the generalized gradient approximation (GGA) and found that $Ti_{12}V, Ti_{14}V, Ti_6V,$ and Ti_4V are magic clusters. Phaahla *et al.*[10] investigated the effect of doping with Pt impurity on Ti nanoclusters and found that the stability at $N = 7, 9, 11, 13$ and 15 nanoclusters was enhanced more as compared to pure Ti nanoclusters. Additionally, the magic number of Ti nanoclusters was tuned from $N = 7$ to $N = 13$. In this study, we investigate the effect of osmium dopant on titanium nanoclusters to probe the geometrical and stability of the $Ti_N M$ ($N = 1 - 15, M = Os$).

2. Computational methodology

Calculations were carried out using the Knowledge-Led Master Code (KLMC) software suite [12, 13] and its recently improved genetic algorithm (GA) module, [14] which has proved to locate efficiently local (LM) and global (GM) minima on potential energy surface (PES). The PES of Ti_N nanoclusters is evaluated using a many-body embedded atom method (EAM), which includes a combination of a many-body attractive term, E_a , and a repulsive two-body Born–Mayer IP, E_r ,

$$E_a = -\sum_i \left(A \sum_j e^{-\beta \left(\frac{r_{ij}}{r_0 - 1} \right)} \right)^{\frac{1}{2}}, \quad (1)$$

$$E_r = \sum_{i>j} B e^{-\rho r_{ij}} \quad (2)$$

where B and A are empirical parameters; r_0 is the equilibrium first neighbour distance in hcp solid; r_{ij} represents the distance between atom i and atom j . After completing the search on the IP PES, we have selected for refinement a subset of the lowest energy LM within approximately 1.0 eV energy range above the corresponding tentative GM. The selected clusters were re-optimised at the quantum mechanical, DFT level using the all-electron, full potential electronic structure code FHI-aims [11]. Additionally, FHI-aims was further used to evaluate the effect of substituting one Ti atom with Os impurity.

3. Results and discussion

3.1 Structure analysis

The most preferred position for Os dopant on the Ti clusters ($N = 2-16$) obtained using FHI-aims software [11] are presented in figure 1. The $N = 3$ cluster is an isosceles configuration that preferred to occupy the Os impurity on the atom that is capped on Ti_2 isomer. At $N = 4$, which is the tetrahedral isomer, the Os impurity prefers to occupy the atom that is capped on the face and the surface of the isosceles isomer. The $N = 5$ is a triangular bi-pyramidal

configuration that was found to occupy the Os dopant on the face of the surface of the tetrahedral isomer. The Os dopant preferred the position of the atom that is capped on the two face and surfaces of the triangular bi-pyramidal for the octahedral isomer ($N = 6$). The $N = 7$ is the pentagonal bi-pyramid configuration which is observed to occupy Os impurity on the atom that is capped on the face of the octahedral isomer ($N = 6$). The bi-capped octahedron isomer ($N = 8$) preferred to place the Os impurity on one of the two atoms that are capped on the octahedral configuration. At $N = 9$ which is a bi-capped pentagonal bi-pyramid, the Os impurity was placed on one of the two atoms that are capped on the pentagonal bi-pyramid isomer. For $N = 10$ which is the tri-capped pentagonal bi-pyramid, the Os atom preferred to occupy one of the position of the three atoms that are capped on the pentagonal bi-pyramid isomer. $N = 11$ is a tetra-capped pentagonal bi-pyramid isomer which was observed to encapsulate the Os impurity. Rodríguez-Kessler and Rodríguez-Domínguez reported the same observation [5]. The $N = 12$ and 13 preferred the encapsulation of the Os impurity. For $N = 14$ which is the Z13-Frank Casper polyhedra preferred to occupy the Os impurity on the face of the pentagonal bi-pyramid.

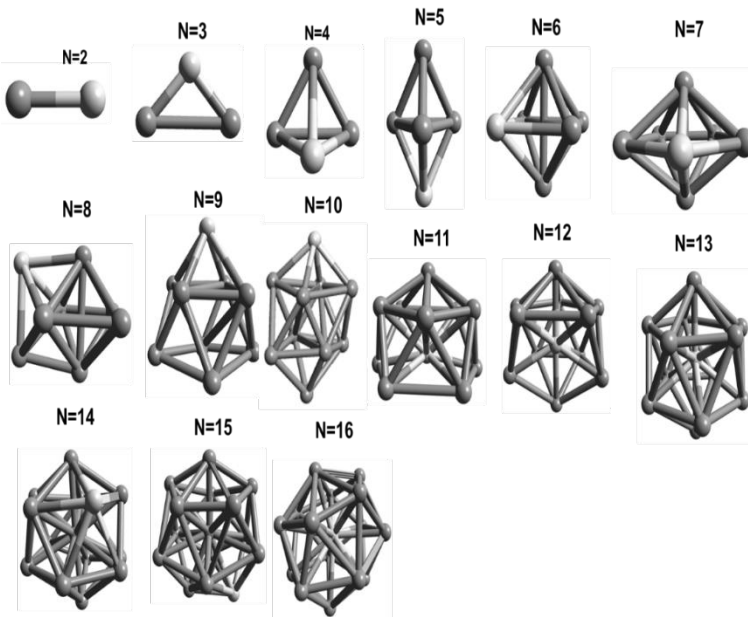


Fig.1. Ground-state structures and low-Lying isomers of Ti_N and $Ti_{N-1}Os$ ($N=2-16$)

The Os impurity was observed to be placed on one of the two atoms that are capped on the hexagonal ring of a Z14-Frank Casper polyhedral configuration. At $N = 16$ the Os impurity was observed to be encapsulated on the Z15-Frank Casper polyhedral.

3.2 Structural stability

The stability of pure Ti_N nanocluster can be investigated on the basis of the binding energy per atom (E_b), relative stability or second order energy difference (D_2E) and dissociation energy (E_d). These quantities can be calculated using the following formulas:

$$E_b(Ti_N) = (NE_T(Ti) - E_T(Ti_N))/N \quad (N = 2, 3, 4, \dots, 16) \dots\dots\dots (3)$$

$$D_2E(Ti_N) = E_T(Ti_{N+1}) + E_T(Ti_{N-1}) - 2E_T(Ti_N) \dots\dots\dots (4)$$

$$E_d(Ti_N) = E_T(Ti_{N+1}) + E_T(Ti) - E_T(Ti_N) \dots \dots \dots (5)$$

where $E_T(Ti)$ is the total energy of pure Ti atom, $E_T(Ti_N)$ is the total energy of Ti nanoclusters and N is the number of atoms.

and the stability for M doped Ti_N nanoclusters were investigated using the following formulas:

$$E_b(Ti_N M) = \frac{NE_T(Ti) + E_T(M) - E_T(Ti_N M)}{N+1}, \dots \dots \dots (6)$$

$$D_2E(Ti_N M) = E_T(Ti_{N+1} M) + E_T(Ti_{N-1} M) - 2E_T(Ti_N M) \dots \dots \dots (7)$$

$$E_d(Ti_N M) = E_T(Ti_{N-1} M) + E_T(Ti) - E_T(Ti_N M) \dots \dots \dots (8)$$

where $E_T(Ti)$ is the total energy of the pure Ti atom, $E_T(M)$ is the total energy for Os atom, $E_T(Ti_N M)$ is the total energy for Os doped Ti nanoclusters, M representing Os atom and N represents the number of atoms per nanocluster.

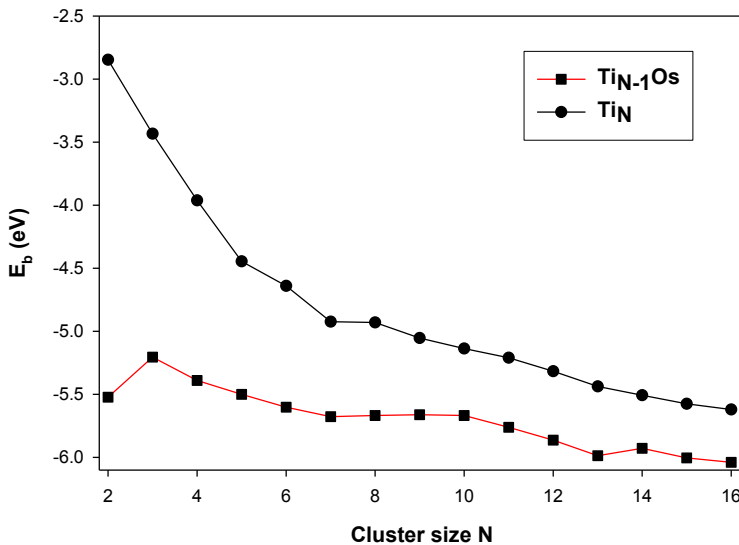


Fig.2. Comparison of the binding energies of Ti_N and $Ti_{N-1}Os$ clusters.

Figure 2 shows the binding energy of pure Ti and $Ti_{N-1}Os$ clusters for $N = 2 - 16$. For the pure Ti_N clusters, binding energy gradually decreases rapidly with the cluster size N down to $N \leq 7$; then the size dependence becomes smooth at $N > 7$. The lowering of the binding energy for pure titanium clusters at $N = 7$ illustrates that this cluster is a magic cluster or most stable. In case of Os doped titanium clusters, the binding energy is observed to be more enhanced for all cluster sizes, which implies that Os dopant improves the binding energy for pure Ti clusters. However, for $N = 8 - 10$ the binding energies of $Ti_N Os$ and Ti_N are observed to decrease towards each other. Interestingly, the Os impurity is observed to enhance the binding energy at $N = 13$. The lowering of the binding energy at $N = 13$ converted the cluster from a non-magic configuration into a magic cluster.

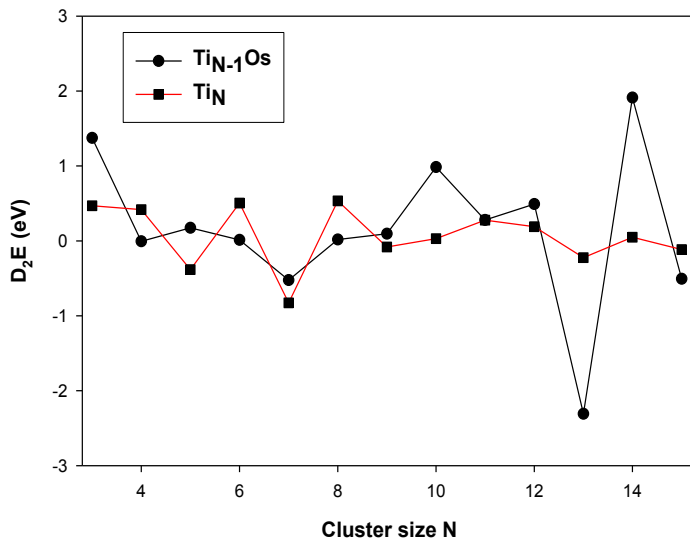


Fig.3. Comparison of the relative stability of Ti_N and Ti_{N-1}Os clusters.

Phaahla *et al.* [10] also reported the shifting of clusters from N = 7 to N = 13. At N = 14, the binding energy is slightly higher, while for N = 15 onwards the Ti_{N-1}Os energy becomes stable. Figure 3 shows the relative stability plot with respect to cluster size N. The relative stability for tetrahedral isomer (N = 4) revealed that Os impurity enhances the stability of the cluster. For N = 5 the magic like features of the cluster were converted into non-magic like features. This implies that the Os impurity destabilized the N = 5 cluster. At N = 6 the Os impurity was found to stabilize the cluster, whereas, for N = 7 the relative stability was found to be less stable as compared to pure titanium clusters.

The relative stability for N = 8 was as well found to be less stable as compared to the pure Ti. For N = 9 the stability energies are observed to be relatively similar, however at N = 10 the stability energy was observed to be highly destabilized. At N = 11 and 12 the relative stability was found to be relatively similar. Furthermore, for the icosahedral (N = 13) the relative stability was found to be more enhanced as compared to pure Ti clusters and Ti doped clusters. The same observations were reported by Rodríguez-Kessler and Rodríguez-Domínguez [5] and Phaahla *et al.* [10]. These results displayed the shifting of stability of titanium metal clusters from N = 7 to N = 13. For N = 14 and 15 the stability is observed to be highly reduced and enhanced respectively.

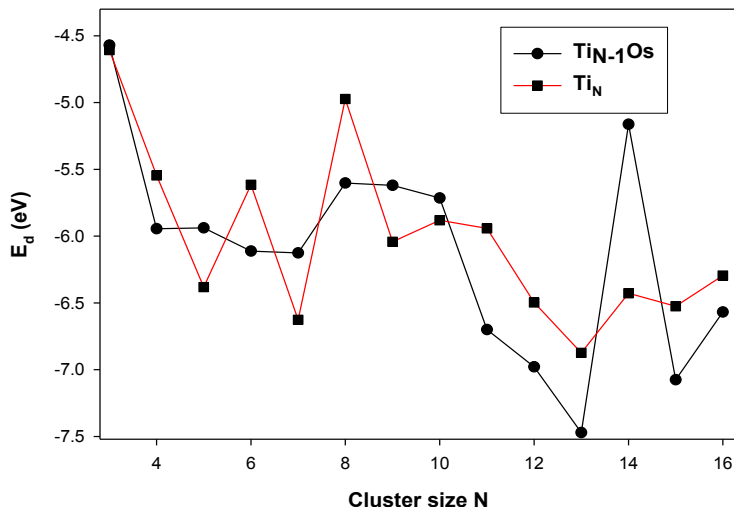


Fig.4. Comparison of the dissociation energies of Ti_N and $Ti_{N-1}Os$ clusters.

The dissociation energy plot with the increase in cluster size N is shown in figure 4. It is observed that at $N = 4$ the Os impurity was found to stabilise the tetrahedral cluster. For $N = 5$ the Os impurity destabilized the triangular bipyramidal cluster, whereas, the dissociation for the octahedral isomer ($N = 6$) revealed that the Os impurity enhances the stability of the cluster. For pentagonal bipyramidal configuration ($N = 7$), the magic-like features of the cluster were converted into non-stable features.

This implies that the Os impurity converted the $N = 7$ cluster into a less-stable cluster. At $N = 8$ the dissociation energy revealed a more stable energy for Os doped Ti clusters. For $N = 9$ and 10 the dissociation energy for the Os impurity revealed that the clusters are less stable. At $N = 11, 12$ and 13 the Os impurity enhances stability and at $N = 13$ it was found to be more stable as compared to pure Ti cluster and other doped clusters. For $N = 14$ the Os doped Ti nanocluster was found to be less stable, while at $N = 15$ and 16 the Os dopant was found to be energetically enhanced. The dissociation energy is observed to have a similar trend as the relative stability.

Figure 5 shows the average energy gap for Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO). The average HOMO-LUMO gap is observed to decrease with increasing cluster size N . At $N > 6$ the HOMO-LUMO gap is observed to rapidly decrease. This may be attributed to the consequence of the lowering of the LUMO energy as the cluster size increases, where the quantum confinement effect on the more diffuse conduction-band-like states decreases and HOMO-LUMO becomes more stable. Furthermore, the HOMO-LUMO gap is observed to be lowered at $N = 13$ which correlates well with the relative and dissociation energies, indicating greater stability. The energy gaps at $N = 2, 4, 12$ and 15 indicate that electrons in the HOMO would not easily move to the LUMO.

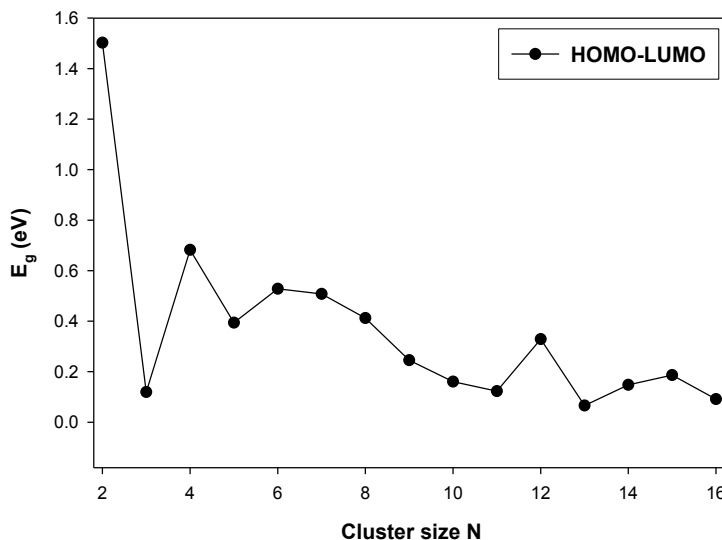


Fig.5. Electronic properties of $Ti_{N-1}Os$ clusters.

4. Conclusion

In this work, the electronic and geometric structures of Ti_N and $Ti_{N-1}Os$ ($N = 1-16$) have been investigated using DFT calculations with PBEsol exchange correlation functional. The lowest-energy structures of $Ti_{N-1}Os$ cluster have been determined by extensive searches for each cluster size. The ground-state structures of the $Ti_{N-1}Os$ clusters mostly favours the encapsulation of the Os impurity. The doping of Os enhanced the binding energy of the titanium cluster. The relative stability revealed higher stabilities at $N = 7$ and $N = 13$ with $N = 13$ as the most stable clusters. Osmium impurity shifted $N = 7$ to $N = 13$ as magic cluster. The dissociation energy depicts a similar trend with the relative stability. The HOMO-LUMO revealed the lowest energy gap at $N = 13$, which correlates well with the predicted relative stabilities and dissociation energies.

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