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Core/shell formation and surface segregation of multi shell icosahedral silver-palladium bimetallic nanostructures: A dynamic and thermodynamic study

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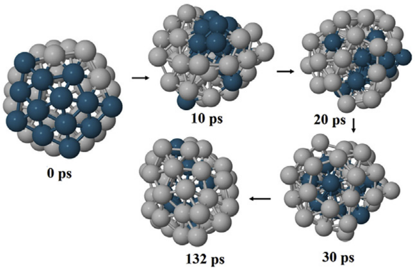
HIGHLIGHTS

- Nanostructures of Pd_mAg_n clusters for $m + n = 55$ and 147 have been studied.
- Structures favor the formation of palladium-core surrounded by silver shell.
- Calculated thermodynamic parameters confirm the energetic results.
- Core/shell formation is favored at concentration of silver.
- Silver segregation on surface while palladium penetration to core is observed.

GRAPHICAL ABSTRACT



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ABSTRACT

Core/shell formation and surface segregation of multi shell icosahedral bimetallic silver-palladium nanostructures with the size of 55 and 147 atoms were studied by using the Molecular Dynamics simulations, and calculating Helmholtz free energy changes in the penetration of palladium atoms from shell to core, core to shell transition of silver and melting temperatures by using statistical mechanical densities of states. In 55 atoms icosahedra, two core–shell motifs, $Ag_{13}Pd_{42}$ and $Pd_{13}Ag_{42}$ with their isomers $Pd_{13}(Pd_{29}Ag_{13})$ and $Ag_{13}(Ag_{29}Pd_{13})$ were considered. Similarly in 147 atoms icosahedra, all mutations corresponding to the occupations of either silver atoms or palladium atoms in the core, inner shell or outer shell and their isomers generated by interchanging thirteen core atoms with thirteen atoms of the other type in the inner and outer shells were considered. It is found that the palladium-core clusters are more stable than the silver-core clusters and cohesive energy increases with the palladium composition. Phase transition of each cluster was studied by means of constant volume heat capacity. The trend in variation of melting temperature is accordance with the energy trend. Helmholtz free energy changes in palladium penetration, core to shell transition of silver and in surface mixing and segregation revealed the thermodynamic stability of the formation of $Pd_{core}Ag_{shell}$ structures especially at silver rich environment and the surface segregation of silver.

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1. Introduction

Recent attention on bimetallic nanostructures especially made of Ag and Pd is due to the wide range of their applications in

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technology, catalysis, medicine, and hydrogen separation and storage [1–8]. Amandusson et al. [9] has revealed a considerable permeation rate in Ag–Pd hydrogen separation membranes. These alloys have also been used as selective hydrogenation catalysts [10–12] and electrocatalysts for both the anode and cathode of direct fuel cells because of their better catalytic properties and lower cost than Pt-based catalysts [13,14].

In experimental studies, it is extremely difficult to vary the size and the spatial distributions of the components freely whereas in computer simulation, we can model various structures and check for properties especially dynamics and thermodynamics of phase transition. Several computational methods such as electronic structure calculations [15–18], generic algorithms [19–21], Monte Carlo [22,23] and molecular dynamics [1,24–26] methods have been used to investigate the most stable structures of bimetallic clusters. In comparison on these methods, electronic structure calculation is a challenging task for transition metal system due to the complexity of their potential energy landscape and the complexity increases further in bimetallic alloys [27]. As a result, in optimization process, system may optimize to local minima instead of desired global minimum. On the other hand, the genetic algorithm is suitable for producing the final global minimum cluster morphology, but bimetallic clusters which are experimentally synthesized as the solid solution cannot be explained [28,29]. Similarly, considering the Monte Carlo method, it fails to account the dynamics properties and also calculation involves in the constant temperature despite the fact that an isolated cluster evolves at constant energy. Instead, molecular dynamics technique is more capable of locating and passing local minima to locate the global structure and the same time it allows drawing the thermodynamics parameters.

Temperature effects cause significant changes in the stability, structure and physical properties of finite system compared to the bulk. Both experimental and theoretical studies have shown the decrease of the melting temperature with the reduction of the cluster diameter [30–33]. Therefore understanding the temperature effect is essential for any technological application. Apart from the electronic properties and structural properties obtained from electronic structure calculations and generic algorithms technique, thermodynamic properties of clusters are mainly investigated by applying either the Monte Carlo or Molecular dynamics techniques. Recently Nieves-Torres et al. [22] and Cheng et al. [23] used the Monte Carlo simulated annealing (MCSA) technique to investigate the phase transitions of two-dimensional seven atoms and three-dimensional thirteen atoms Ni/Pd clusters and the composition effect on the melting processes of the 55-atom icosahedral Ag/Pd bimetallic clusters, respectively. Hewage [34,35] investigated the dynamic and thermodynamic properties of icosahedral nickel-palladium clusters by using the molecular dynamics and histogram methods.

In recent past, we reported a serious of our work on transition metal heterogeneous systems to understand the structural and thermodynamics properties especially of the systems consists of nickel, silver and palladium. In our systematic approach, we first focused on small thirteen particle motifs of binary systems, Ag/Ni, Ni/Pd and Ag/Pd, which are suitable precursors for large core–shell entities. Our results of $Ag_nNi_{(13-n)}$ for $n \leq 13$ show that nickel centered clusters are more stable than those of silver centered and in general, nickel-centered clusters show ordered structures closer to the regular icosahedrons while silver centered clusters lose the symmetry indicating the favorable nickel core cell structures [36]. In case of $Ni_nPd_{(13-n)}$ for $n \leq 13$, it is found that the nickel-centered clusters are more stable than the palladium-centered clusters and cohesive energy increases along the palladium end to nickel end. Notable difference we observed compared to the Ag/Ni system is that the trend in variation of melting temperature from one end-species to the other end-species is opposite to the energy trend [34]. In $Ag_nPd_{(13-n)}$ bimetallic system, similar to the Ag/Ni clusters, trend in variation of melting temperature is accordance with the energy trend and the palladium-centered clusters are more stable than the silver-centered clusters [37]. Moving into the larger clusters which are more applicable in nanoscience, we first extended our studies on Ni/Pd beyond the size of thirteen atoms [35]. Our structural, energetic and thermodynamic approach to Ni/Pd larger system revealed the formation of nickel core-palladium shell particles and palladium segregation on the surface of nickel. The trend in melting temperature and energies are similar to the trend observed in the thirteen particle system.

In this paper, core–shell formation and surface segregation of silver on multi shell icosahedral Pd_mAg_n ($n + m = 55$ and 147) clusters will be discussed. In addition to the methodologies we used in previous work, dynamic behavior in surface segregation, mixing and penetration of unstable entities on surface to core will be used. We explicitly selected the icoshahedral geometry based on previous reports that the icosahedra and polyicosahedra are more favorable for nanoalloys especially because small atoms can be accommodated inside the cluster to reduce the compressive strain [38].

2. Interaction potential and calculation methods

In this study, metal–metal interactions were modeled using the Sutten-Chen potential [39] which is the extended version of the original Finnis-Sinclair pair potential [40] to represent all pair wise interactions: Pd–Pd, Ag–Ag, and Pd–Ag. Complete description on pair potential can be found elsewhere [34,35]. Table 1 shows the parameters used in this calculation for neat palladium and silver atoms given by the Sutton and Chen [39]. Parameters corresponding to interactions between different atoms (Ag and Pd) were predicted by using the combination rules. The geometric mean was used to obtain the energy scaling parameter and an arithmetic mean was used for n, m, and a.

Molecular dynamics simulations of a variety of multi shell clusters (Pd_mAg_n for $n + m = 55$ and 147) were performed by solving the classical equations of motion using the predictor corrector algorithm due to Gear [41,42]. The fifth order scheme was used to treat translational motions. Initial positions of mixed clusters were taken from positions of atoms in a quenched icosahedral structure. The linear velocities of atoms were then chosen randomly from the Boltzmann distribution. All motions were reset with respect to the center-of mass of the cluster. The typical time step of 10^{-15} s yielded energy conservation about a part in 10^4 over about 10^6 steps (typical simulation time of 1 ns). As in all straightforward MD calculations, a trajectory at a given energy yields equilibrium information using standard averaging techniques [43,44]. Stable structures (global minima) for a given cluster are found by extracting the positions of atoms of the trajectory at regular time intervals, and using these data as the staring points for a conjugate gradient minimization procedure [45–47].

The fundamental quantity for studying the thermodynamics of a finite system is the classical density of states, $\Omega(E)$. The

Table 1
Parameters corresponding to the dimers of palladium and silver atoms used in the Sutton–Chen interaction potential model [39].

	N	m	ε/eV	C	a/Å
Ag	12	6	2.5415×10^{-3}	144.42	4.09
Pd	12	7	4.1790×10^{-3}	108.27	3.89

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