STRUCTURAL CHANGES OF (AgX-Pd1-X)256  BIMETALLIC NANOCLUSTERS SUPPORTED ON SWCNT: A MOLECULAR DYNAMICS SIMULATION

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Abstract - The molecular dynamics simulations were used to examine the structural changes of (Ag_x-Pd_1-x)_{256} bimetallic nanoclusters supported on single walled carbon nanotube (SWCNT) with different concentrations (x = 0, 0.25, 0.5, 0.75, 1). Structural changes, atoms segregation and dynamics properties were monitored during heating and cooling processes as a function of temperature and nanocluster concentration. Nanoclusters structural changes and segregation of Ag and Pd atoms during the melting and freezing processes were considered. For this aim several useful methods such as deformation parameters, radial deformation parameters, radial distribution function, density profile, mean square displacement and self-diffusion coefficient were employed. Atoms segregation and surface enrichment with Ag atoms and core enrichment with Pd atoms in nanoclusters were observed during the processes. In addition, it was found that this structural changes were strongly irreversible.

1. Introduction
The composition and size of bimetallic nanoclusters affect their physical and chemical properties. Because, bimetallic nanoclusters have different properties from pure metal nanoclusters of their constituent elements. Therefore, designing and controlling of composition and particle size produce the different bimetallic nanoclusters. Palladium has attractive applications in heterogeneous catalysis such as microelectronic and optoelectronic device and in industry. Silver nanoclusters can be applied in various basis such as optical sensors, biosensor materials and etc. The Silver-Palladium alloys are more interesting for their applications in domains such as dentistry, LCD screens, hydrogen separation and storage and hydrogenation reactions with enhanced selectivity. Carbon nanotubes (CNTs) are of great interest in materials science and technology because of their interesting structures and mechanical, thermal and electrical properties. Carbon nanotubes are appropriate substrate in field of substrate supporting materials such as catalysts and sensors [1, 2].

In this paper, we investigated different concentrations of Ag-Pd nanoclusters with 256 atoms supported on single walled carbon nanotube (SWCNT) at wide temperature range. The structural changes, atoms segregation and dynamics properties were monitored with temperature. Nanoclusters surface and segregation of Ag and Pd atoms during the melting and freezing processes were taken into account and several useful methods were employed to get these aims. Structural evolution of nanoclusters with temperature can be used to determine the catalytic properties.

2. Computational methods
The Sutton-Chen (SC) potential [3] is used to predict the metal-metal interactions. For the metal-C interactions the Lennard-Jones (LJ) 12-6 potential was used. The classical molecular dynamics (MD) simulations were used in canonical ensemble (NVT). Equations of motion were integrated by Verlet leapfrog algorithm. Temperature was kept in constant value by Berendsen thermostat.

All systems were simulated in heating and cooling processes at temperature range of 200 to 1600K with steps of 100K. The final system configuration in each step was employed for initial configuration of the next step. In simulations the systems achieve the equilibration at 400 ps and then nanocluster properties were calculated for 600 ps.

3. Results and discussion
Several methods were used to investigate the structural changes and atoms segregation during the heating and cooling, such as deformation parameters and , radial distribution function (RDF), density profile and snapshots of nanoclusters.

To investigate the atoms segregation in nanoclusters during the processes, we calculated deformation parameters for Ag atoms and Pd atoms. Figure 1(a) and 1(b) shows separated deformation parameters of (Ag_{0.75-Pd_{0.25})_{256} nanocluster supported on SWCNT. By comparing figures 1(a) and 1(b) it can be concluded that after phase transition and when the diffusivity of atoms in liquid state is considerable, Ag atoms come to nanocluster surface and Pd atoms lie.

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interior because the Ag atoms have less surface energy than Pd atoms.

In figure 2, the density profile \((Ag_{0.75}Pd_{0.25})_{256}\) and \((Ag_{0.5}Pd_{0.5})_{256}\) nanoclusters supported on SWCNT and snapshots of them at 300K in heating and cooling were plotted. It can be observed that Ag and Pd peaks have equal values and monotonic distributions in z direction in heating approximately. However, when the nanocluster melts and atoms segregation occur, in density profiles Ag has peaks in total range of z direction of nanocluster while Pd has higher peaks only in middle of z direction of nanocluster in cooling. This shows core-shell structure in nanocluster.

4. Conclusion

Structural changes of \((Ag_{x}Pd_{1-x})_{256}\) bimetallic nanoclusters supported on single walled carbon nanotube (SWCNT) were monitored by several applied methods. Deformation parameters, radial deformation parameters, density profile in z direction and radial distribution function (RDF) are main methods for investigation the structural evolution during the processes. We observed nanocluster surface was enriched with Ag atoms and core was enriched by Pd atoms during the processes. Results show the atoms segregation begins near the melting points when atoms have the enough mobility for separation. This separation completes in phase transition point and in cooling process below the melting point the nanoclusters have a core-shell structure that are comparable with nanoclusters structure in heating process bellow the melting point when nanoclusters have a monotonic distribution of different atoms.

5. References