

Growth of Three-Shell Onionlike Bimetallic Nanoparticles

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We show by molecular dynamics simulations on three systems ($B/A = \text{Pd/Ag}$, Cu/Ag , and Ni/Ag) that three-shell metallic nanoparticles made by a core of a metal A , an intermediate shell of metal B and an external shell of metal A (A - B - A nanoparticles) can be grown by deposition of B atoms onto an A core. The growth of the intermediate B shell is triggered by the fact that the most favorable positions for isolated B impurities inside A clusters are located just one layer below the cluster surface.

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The possibility of controlling the structure and the chemical composition of particles at the nanoscale level has an enormous importance for both basic science and technological applications. Very recently, bimetallic nanoparticles have attracted noticeable experimental and theoretical interest because of their optical and catalytic properties [1–3]. In many systems these particles can be formed with a core-shell (CS) structure, where a core of metal A is surrounded by a thin shell of metal B . The B overlayer is usually strained, and thus can present peculiar catalytic properties [4]. Core-shell B - A nanoparticles have been produced by different experimental methods [1] (laser vaporization sources, synthesis from organometallic compounds) for several systems (Au-Ag , Ni-Ag , Pd-Ag , and Pt-Au). In recent molecular dynamics (MD) simulations it has been shown that almost perfect external shells can be easily grown by direct deposition of Ag atoms above a Cu or Pd core (a three-dimensional nanocluster) [3]. Having a lower surface energy and a larger size, silver has a strong tendency to remain on the surface when deposited above Cu , Pd , and Ni clusters [3,5]. On the contrary, Cu , Ni , and Pd atoms incorporate when deposited on Ag substrates. Ni has the strongest tendency to incorporation [5] followed by Cu and Pd . In this Letter, we show that a novel kind of structures, namely, the A - B - A onionlike nanoparticles, can be grown by *inverse deposition*, i.e., by depositing, above a core of element A , adatoms of an element B having a tendency to incorporate inside A . In our simulations the role of A is played by Ag , while we consider three different B metals: Pd , Cu , and Ni . Depending on the temperature and on the *morphology of the initial core*, B atoms can either accumulate in the layer just below the surface, thus forming an intermediate shell (A - B - A structure), or diffuse fast towards the cluster center to form a CS B - A structure. We show that A - B - A structures are easily obtained by deposition above initial fcc clusters, such as truncated octahedra (TO), while they are not formed by deposition above icosahedra (Ih). Finally, we show that the formation of A - B - A structures is triggered by the fact that, for an isolated impurity

inside an fcc cluster, the most favorable sites are placed *just one layer below the surface*, namely, in the subsurface layer, *especially below edges and vertices*. On the contrary, an isolated impurity is better placed at the center of an icosahedron (except for Pd in Ag).

Our growth simulations are performed by the method developed in [6] to model cluster growth in a condensing vapor. B atoms are deposited one by one above the growing cluster by placing them on a large sphere centered around the cluster, with an initial velocity v_i (directed towards the cluster) which is chosen from a Maxwell distribution at typical metal vapor temperatures (1000–2000 K); v_i corresponds to a small fraction of the cohesive energy of the atoms in the bulk solid, and therefore has very little influence on the growth morphologies [6]. Incoming atoms do not incorporate at the moment of the deposition, but later on by diffusive moves of the exchange type [3]. A time interval τ is elapsed between two subsequent depositions; τ is chosen as 7 ns, a value which is close to the experimental deposition times in gas aggregation experiments (see [6] for a discussion). The cluster temperature T is kept constant by an Andersen thermostat. The interaction among the cluster atoms are modeled by semiempirical many-body potentials derived within the second-moment approximation to the tight-binding model; the total energy E_{tot} of the system is written as $E_{\text{tot}} = \sum_i E_i$, where E_i is the energy of atom i , which contains a repulsive two-body part and an attractive many-body term. For each bimetallic system, the interaction potential depends on three sets of four parameters (A , ξ , p , q) each. The explicit form of E_i and the parameters can be found in [3], except the ones for the Ni-Ni and Ag-Ni interactions, which are given in [7]. As starting cores of the growth simulations, we choose two different Ag clusters: a TO of 201 atoms (TO_{201}) and an Ih of 147 atoms (Ih_{147}). These initial structures are shown in Figs. 1 and 2.

Let us first show the results of the growth simulations. Representative snapshots from a simulation of inverse deposition of Cu above a TO_{201} of Ag at 500 K are given in Fig. 1. Cu atoms are incorporated quite fast below the

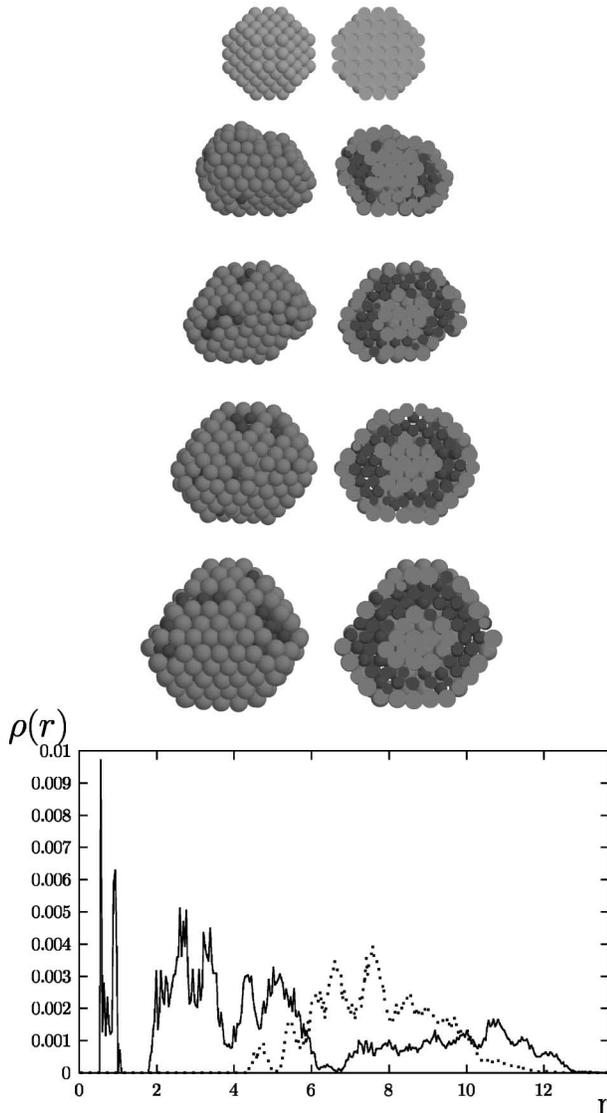


FIG. 1. Growth sequence for the deposition of Cu above a TO_{201} of Ag at $T = 500$ K and $\tau = 7$ ns. Snapshots are taken (from top to bottom) at the beginning of the simulation and after the deposition of 67, 108, 122, and 201 atoms. In the left column we show the cluster surface, in the right column a cross section of the cluster to show its internal arrangement. Ag and Cu atoms are represented in light and dark gray, respectively. Below the growth sequences we plot the radial distribution functions (in arbitrary units) at the end of the simulation: ρ_{Ag} (full line) and ρ_{Cu} (dotted line) versus the distance r (in Å) from the geometrical center of the cluster.

substrate, and begin to accumulate one layer below the surface to form an intermediate shell which increases in thickness but remaining always almost completely covered by a single layer of Ag atoms. On the other hand, a well-defined Ag core occupies the center of the cluster. The separation of the structure in concentric shells can be well understood by looking at the radial distribution functions $\rho_{A,B}(r)$ of the two different species, which show (see Fig. 1) that Ag is practically absent at inter-

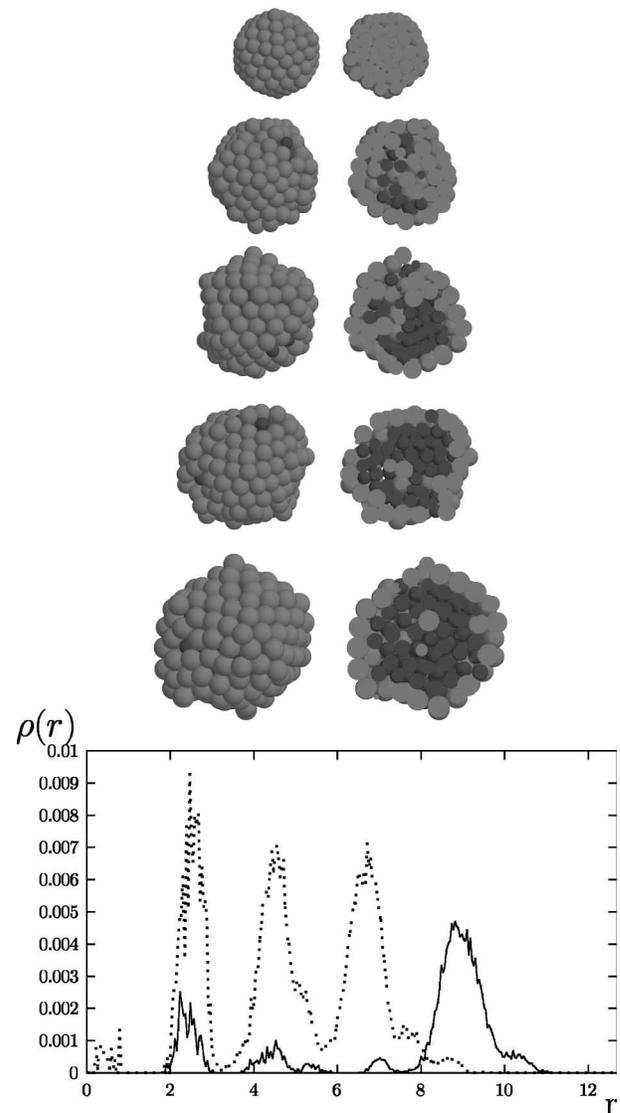


FIG. 2. The same as in Fig. 1, but for deposition above an Ih_{147} . Snapshots are taken (from top to bottom) at the beginning of the simulation and after the deposition of 54, 92, 121, and 162 atoms.

mediate r , while few Cu atoms are in the surface layer. On the contrary, if we deposit Cu atoms above an Ih_{147} of Ag at the same T of 500 K, the A - B - A structure is not obtained, but Cu atoms accumulate fast at the cluster center, as shown in Fig. 2. At 400 K with the same τ , results are qualitatively of the same kind, with A - B - A structures after deposition on the TO_{201} , and CS structures after deposition on the Ih_{147} . On the contrary, if T is raised to 600 K, CS structures are obtained *both* after deposition on the TO_{201} and on the Ih_{147} , indicating that the A - B - A structures could be metastable. This point is under investigation. When Pd is deposited above a TO_{201} of Ag, A - B - A structures can be obtained around 600 K (see Fig. 3), but they are not as sharp as in Cu/Ag, because Pd has a weaker tendency to incorporate inside Ag, and

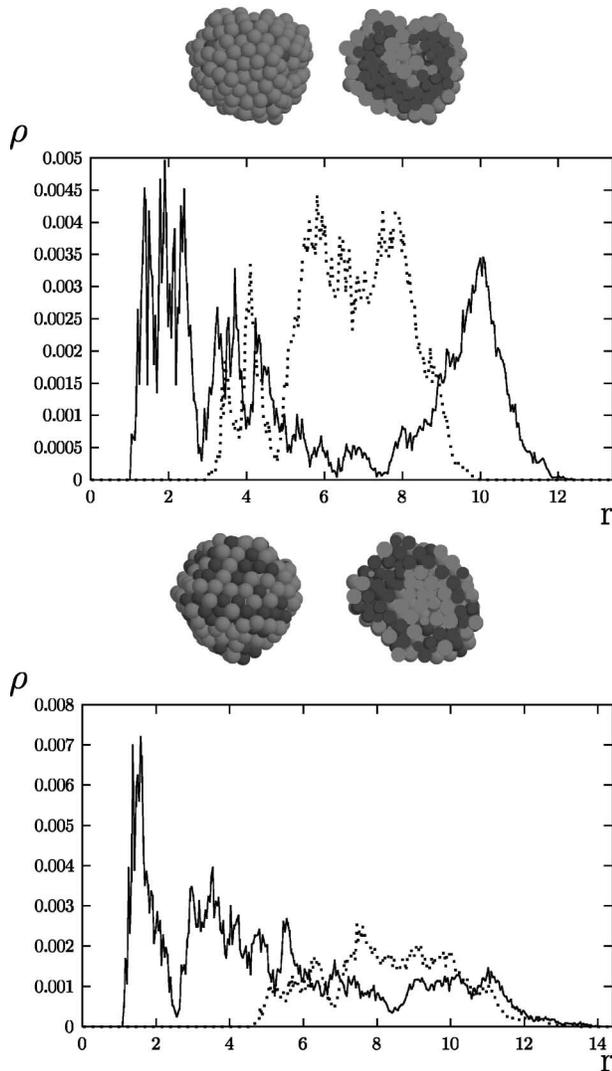


FIG. 3. Final structures after the deposition of 200 atoms of Ni at 300 K (top row) and of 200 atoms of Pd at 600 K (third row) above a TO₂₀₁ of Ag. Ag atoms are represented in light gray, Pd and Ni atoms in dark gray. The radial distribution functions are plotted with the full line corresponding to Ag and the dotted line to Pd (second row) or Ni (fourth row).

several Pd atoms remain in the surface layer. The deposition of Pd on an Ih₁₄₇ of Ag causes a structural transformation of the cluster into a decahedron (see Ref. [6] for examples of such transformation in pure Ag clusters), which then grows with the same qualitative behavior as the TO₂₀₁. After the deposition of Ni above the TO₂₀₁ of Ag, *A-B-A* structures are found around 300 K (as in Fig. 3), but their quality is never as good as in Cu/Ag because Ni has a very strong tendency to separate and to form compact aggregates inside the cluster [5]. This tendency becomes more and more evident at increasing T . The deposition of Ni above an Ih₁₄₇ of Ag gives the same qualitative behavior as in Cu/Ag, with fast incorporation and formation of a CS structure.

In summary, our simulations show that it is possible to grow *A-B-A* structures by the deposition on fcc clusters such as the TO₂₀₁. At a given deposition rate, these structures are obtained in an intermediate T range which depends on the system: around 300, 500, and 600 K for Ni, Cu, and Pd, respectively. On the contrary, when depositing on an Ih₁₄₇, CS clusters structures are obtained when depositing Cu and Ni, the case of Pd being different because of the possible transformation of the cluster into a decahedron after the deposition of a few tens of atoms. Now two questions arise: Why are the *A-B-A* structures formed? Why can they be obtained by depositing above fcc clusters and *not* above icosahedra?

The answer to both questions can be inferred from the analysis of the total energy of Ag clusters with single Ni, Cu, and Pd impurities. For completeness, we consider, besides the TO₂₀₁ and the Ih₁₄₇, also two larger clusters, the TO₅₈₆ and the Ih₃₀₉. Inside each cluster we single out all the energetically inequivalent sites where the impurity can be placed in, which are 12 for the TO₂₀₁, 7 for the Ih₁₄₇, 24 for the TO₅₈₆, and 11 for the Ih₃₀₉. Then we calculate the total energy E_{tot} of the cluster of N atoms after relaxation (by quenched MD [8]), with the impurity placed in one of the inequivalent sites. The results are shown in Fig. 4, where we report the quantity ΔE^* related to the excess energy ΔE defined by

$$\Delta E = E_{\text{tot}} - (N - 1)\varepsilon_{\text{coh}}^{\text{Ag}} - \varepsilon_{\text{coh}}^{\text{imp}}, \quad (1)$$

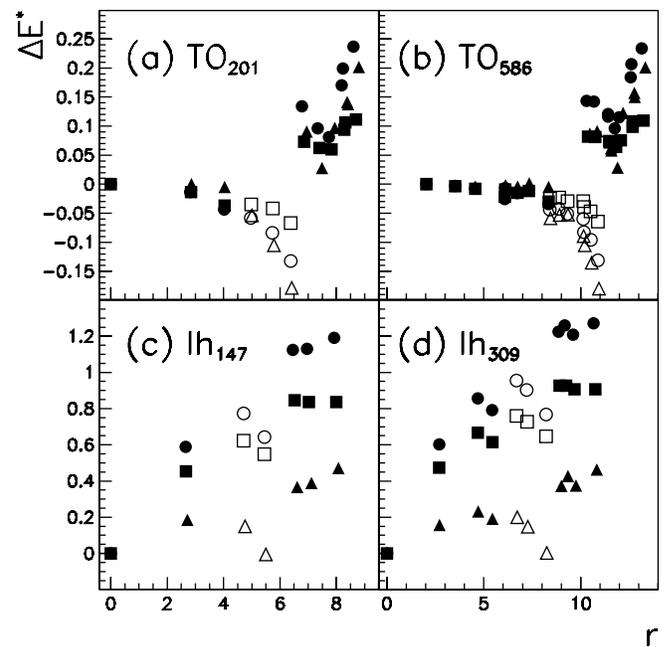


FIG. 4. Energies ΔE^* (in eV) for impurities in inequivalent sites in four different clusters. r is the distance (in Å) of the impurity is placed from the geometrical center of the clusters. In all panels, circles, squares and triangles refer to Ni, Cu, and Pd impurities, respectively. Open symbols refer to subsurface sites, full symbols for all other sites.

where $\varepsilon_{\text{coh}}^{\text{Ag}}$, $\varepsilon_{\text{coh}}^{\text{imp}}$ are the cohesive energies per atom of Ag and impurity atoms, respectively. ΔE^* is simply obtained by shifting ΔE by its value for an impurity placed in the cluster site which is closest to the geometrical center, so that central impurities have $\Delta E^* = 0$. The results about TO structures are qualitatively similar for all kinds of impurities [see Figs. 4(a) and 4(b)]. Not surprisingly, since Ni, Cu, and Pd prefer to incorporate in the inner of Ag clusters, the sites in the surface layer are not favorable, being much higher in energy than interior sites. What is much more interesting is that not all interior sites are equivalent: an isolated impurity is better located in the subsurface layer than in the central part of the cluster. Let us now take a Pd impurity to fix the ideas; the behavior of Ni and Cu impurities is analogous. We calculate the atomic energies E_i depending on the position of the impurity comparing two different situations: impurity in a subsurface site k_{ss} and impurity in a central site k_c . The energy of the impurity E_{Pd} is practically the same in sites k_{ss} and k_c ; the significant differences comes from the Ag atoms in the nearest-neighbor sites of k_{ss} and k_c . If the Pd impurity is in k_c , its 12 Ag nearest neighbors are in the inner of the cluster and decrease their energy by about 0.06 eV each with respect to the situation where in k_c there was an Ag atom. If the impurity is in k_{ss} , some of its nearest neighbors are in the surface layer. For these atoms, the decrease in energy with respect to the situation where in k_{ss} there is an Ag atom can be of 0.08–0.12 eV, because the surface atoms are more free to relax in order to accommodate the size mismatch with the impurity, especially when they are at edges or vertices. For Ih cores, with Ni and Cu impurities, completely different results are obtained. In fact, if the impurity is much smaller than core atoms, as for Ni and Cu in Ag, the central Ih site becomes by far the most favorable one [see Figs. 4(c) and 4(d)]. This happens because the central atom in Ih is highly compressed, and if it is substituted by a smaller one [2,9], a noticeable strain relief is obtained. For Pd impurities the size mismatch with Ag is smaller, so that the central Ih site becomes as favorable as some subsurface sites.

These results explain the formation of *A-B-A* structures by deposition on TO clusters: the first deposited atoms incorporate fast, and stay preferentially in subsurface sites. Then further impurity atoms meet the subsurface impurities thus nucleating the intermediate *B* shell which can be quite stable. On the contrary, impurities are attracted towards the center of an Ih, where they nucleate a CS structure.

In summary, we have demonstrated that a novel kind of nanoparticles, the three-shell *A-B-A* structures, can be obtained by inverse deposition of *B* atoms above *A* cores. The *A-B-A* structures can be grown depending on the structure of the initial *A* core and on temperature. When

the starting *A* core is an fcc cluster, *A-B-A* structures are obtained in all systems (Ni/Ag, Cu/Ag, and Pd/Ag) in different *T* ranges. On the contrary, *A-B-A* structures are not obtained by deposition on Ih cores, where core-shell structures are grown. The explanation of these results follows from the energetics of isolated *B* impurities inside *A* cores. When the core has a TO symmetry, subsurface sites, especially below edges and vertices, are the most favorable for a single impurity, because the surface atoms surrounding the impurity are more free to relax efficiently. For the strained Ih cores, the central site better accommodates huge size mismatches, thus being the most favorable for Ni and Cu impurities in Ag. Therefore, *B* intermediate shells nucleate in TO clusters, while inner *B* cores nucleate inside Ih clusters. In conclusion, our results indicate a novel possibility for controlling the chemical ordering in structures at the nanoscale level. For example, subsurface layers could be obtained also by inverse deposition above mounds on crystal surfaces.

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