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ABSTRACT. The compositional stability of bimetallic nanoparticles (NPs) is crucial for many applications. We have studied the coarsening of amorphous carbon supported Au-Pd NPs during annealing at 873K. Using scanning transmission electron microscopy and energy dispersive spectroscopy measurements, we show that in spite of a complete miscibility of the two metals, the particle assembly undergoes a phase separation during annealing, which leads to two distinct populations: Au-rich NPs of mean radius 3.5 nm and large Pd-rich NPs of mean radius 25 nm. Thermodynamic calculations and kinetic Monte-Carlo simulations explain this behavior which is driven by the competition between surface and mixing energy, and by the different mobilities of the two atomic species.

Bimetallic nanoparticles (NPs) are widely used for optical, magnetic or catalytic applications. In this last case, NPs are usually used at relatively high temperatures and/or in gas conditions and their structural stability is a key point to maintain their catalytic activity.[1] In particular, coarsening that directly leads to a decrease of the surface/volume ratio of the catalyst is undesirable. Many efforts have been undertaken to understand the mechanisms leading to coarsening, such as Smoluchowski ripening[2] or Ostwald ripening.[3] Ostwald ripening is a general kinetic and thermodynamic mechanism which drives the coarsening of an assembly of particles in a bulk medium or on a surface, with conserved mass. Larger particles grow at the expense of smaller ones through mass exchange of monomers, the driving force of coarsening being the difference of chemical potential between large and small particles, due to a decrease of the surface to volume ratio as particle size increases. The seminal works of Lifshitz, Slyosov and Wagner[4,5] for three-dimensional clusters in a bulk medium (3D/3D) have highlighted two different regimes: a diffusion-limited regime in which the chemical potential of the diffusing species is continuous at the interface between the clusters and the medium, and an attachment-limited regime in which the chemical potential is constant in the medium. Since then, various studies have been devoted to Ostwald ripening of particles, including also monolayer islands on a surface (2D/2D)[6] and three-dimensional particles on a surface (3D/2D).[7] 3D/2D coarsening has been intensively studied for its impact on ageing of catalysts and a large number of theoretical works have been devoted to the scaling behaviour of NPs supported on surfaces.[7–11] Analytical models predict that the asymptotic particle-size distribution has a self-similar behaviour with a

mean radius that follows a power law growth rate. For the diffusion-limited coarsening, the rate exponent is equal to 1/4, and for the attachment-limited coarsening, it is equal to 1/3. More sophisticated descriptions have been developed in order to take into account the effects of faceting,[12] non uniform interfacial energy,[13] quantum size effects,[14] interfacial stress[15] or the heterogeneity of the support.[16]

More recently, Ostwald ripening of supported alloyed metal NPs has also been investigated. Several experiments have shown that coarsening can modify the composition of the particles, and lead to a size-dependent composition distribution.[17–20] High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) experiments have shown that hydrogenation of Pd-Au bimetallic NPs results in hydrogen-induced Ostwald ripening by which the distributions of size and composition of the NPs change. After hydrogenation, the small NPs are gold-rich while the large NPs become palladium-rich.[17] Similar observations have been performed by TEM after thermal annealing of Co-Pt NPs deposited on carbon: small particles are Pt-rich, whereas large particles are Co rich.[18] High resolution TEM imaging of single atom dynamics brought the experimental evidence that this composition gradient was due to a faster detachment rate for Co than for Pt. Contrary to Pt, Co can thus reach thermodynamic equilibrium, leading to a relation between size and composition.[18,21] A good agreement was found between experiments and theory. Such thermodynamic model has been further invoked to interpret the evolution of Pd-Ir catalysts during thermal activation treatments,[19] or the composition dependence of ternary Au-Pd-Pt NPs.[20] The kinetics of Ostwald ripening of bimetallic NPs has also been studied theoretically,[22] but with a questionable derivation of the chemical potential. The exploration of the changes induced in particle size-composition distributions during Ostwald ripening of nanoalloys still has to be done.

In this paper, we demonstrate an Ostwald-driven phase separation in a population of alloyed metal NPs. We have recently observed that annealing under vacuum of Au-Pd NPs supported on amorphous carbon also led to an enrichment of large particles with Pd.[23] In this paper, we present further TEM experiments showing that despite the complete miscibility of Au and Pd in the bulk phase diagram, Ostwald ripening can lead to a phase separation between small nearly pure Au particles and large nearly pure Pd particles. Kinetic Monte-Carlo simulations and thermodynamic calculations explain this instability.

RESULTS AND DISCUSSION

Figure 1a shows a typical STEM-HAADF of the Au-Pd NPs after growth. In agreement with previous ultra-high resolution TEM (UHRTEM) observations[23], Au-Pd NPs are mostly FCC single crystals with a truncated octahedron shape (see Figure 1c). The average projected area radius, i.e. the radius of a perfect circle enclosing an area equivalent to the projection area of the NP, follows a narrow unimodal distribution with a mean radius of 3.4 nm ± 1.0 nm, shown in Figure 1b. According to STEM-energy dispersive X-ray spectroscopy (EDS) measurements, the mean composition of the NPs is also narrow, namely 40±5 at.% Pd.

Figure 1. (a) STEM-HAADF image of as-grown $Au_{60}Pd_{40}$ embedded in amorphous carbon. (b) Corresponding histogram of particle radius generated by analyzing 360 NPs. (c) UHRTEM

image of an as-grown $Au_{60}Pd_{40}$ particle. (d) STEM-HAADF image of $Au_{60}Pd_{40}$ NPs after annealing in vacuum at 873 K for 10 hours. (e) Corresponding distribution of particle radii after annealing. (f) UHRTEM image of a Au-Pd particle after annealing.

Figure 1d shows a typical STEM-HAADF image of the Au-Pd NPs after annealing in vacuum at 873 K for 10 hours. Whereas size distribution of the as-grown NPs was unimodal, it is clearly bimodal after annealing (see Figure 1e). Two populations of NPs can be identified. Small NPs having a mean radius of 4 nm coexist with larger NPs having a mean radius of 25 nm. Small particles, as the one shown in Figure 1f, have a more or less rounded shape that should correspond to a sphere most likely truncated at the interface with the substrate. Large particles are facetted. HAADF intensity profiles show that they have a 3D shape although their precise morphology cannot be determined by this technique. Moreover, STEM-EDS measurements show that small NPs are depleted in Pd, with a mean Pd content of 20 at.%, whereas larger particles are enriched in Pd, with a mean Pd content of 60 at.%. This Pd concentration can reach up to 78% in the largest particles.

Thus, TEM experiments evidence a phase separation between two populations, despite the miscibility of the two metals in the whole compositional range. This coarsening may have different origins. The most common are Smoluchowski ripening (diffusion-coalescence) and Ostwald ripening. Whereas coalescence of NPs does not lead to variation of composition with size, Ostwald ripening has been shown to induce, for nanoalloys, a dependence of composition with size.[18] This is clearly what we observe here for Au-Pd NPs. In the following, we derive an optimized thermodynamic model to provide a deeper understanding of the atomic-scale mechanisms leading to such drastic changes in nanoalloys composition, and to the phase separation observed.

Ostwald ripening of supported monometallic NPs has been intensively described in the past.[7,8,24] In the absence of chemical reaction for monomer attachment, it is usually admitted that the attachment barrier is relatively small and that coarsening is diffusion-limited.[8] For example, this has been experimentally evidenced for Sn/Si(111) and Sn/Si(100) islands.[25] In this regime, the particles are assumed to be in thermodynamic equilibrium with their vapor pressure (the adatom gas at the substrate surface). At the interface between the particles and the substrate, there is thus no discontinuity of the chemical potential for atoms in the particles or adsorbed on the surface. Atomic fluxes between particles are driven by the gradient of chemical potential on the substrate surface.

The concentration of adatoms in the vicinity of a particle is given by the rate of atom detachment/attachment. It depends on the difference of cohesive energy for an atom in the particle and on the substrate. Due to surface energy, the cohesive energy in the particle is size-dependent. At each time, there exists a critical size for which a particle is in equilibrium with the mean concentration of diffusing atoms at the surface of the substrate. Larger particles have a lower chemical potential and grow while smaller particles shrink.

In the case of bimetallic NPs, the rate of detachment of atoms depends not only on the size of the particle, but also on the chemical nature of the atom since cohesive, surface and adsorption energies may be different for the two species. Two asymptotic regimes are possible. Either the rates of detachment are roughly the same for both species, or they are very different. In the latter case, it has been shown that the chemical potential of the highly diffusing species reaches thermodynamic equilibrium.[18] For non-wetting spherical Co-Pt NPs, an equation relating size and composition has been previously derived using a themodynamic approach.[18]

In this paper, we extend this thermodynamic approach to the general case of a supported bimetallic AB NP having a truncated spherical shape. We assume that the detachment rate for atoms of type A is much smaller than the one of atoms of type B. Details are given in the Supporting Information.

For an alloyed particles of $N = N_A + N_B$ atoms, the chemical potential of the B element is given by $\mu_B = \dfrac{\partial G}{\partial N_B}\bigg|_{T,P,N_A}$ where the Gibbs free enthalpy, $G = G_{\text{bulk}} + G_{\text{surf}}$, is given by the sum of a bulk contribution and a surface term.

The bulk term of the Gibbs free enthalpy is given by $G_{\text{bulk}} = N_A g_0^A + N_B g_0^B + N(g_{\text{mix}}^{\text{id}} + g_{\text{mix}}^{\text{e}})$ where $g_{\text{mix}}^{\text{id}}$ is the free enthalpy of mixing of an ideal solution and $g_{\text{mix}}^{\text{e}}$ is the excess free enthalpy of mixing. $g_{\text{mix}}^{\text{e}}$ can well be approximated with $g_{\text{mix}}^{\text{e}} = x(1-x)\big(g_0 + g_1(1-2x) + g_2 x(1-x)\big)$,[26] where $x = N_B/N$. Neglecting the energy of particle edges, the surface term G_{surf} is given by $G_{\text{surf}} = 3\gamma\alpha(N\Omega)^{2/3}$ where Ω is the mean atomic volume, γ the free surface energy, and $\alpha = \dfrac{\pi}{3}\big(2 - 3\cos(\theta) + \cos^3(\theta)\big)$ a geometrical coefficient depending on the contact angle θ between the particle and the substrate.

In the following, we define $\Delta\mu_B(T,N,x) = \mu_B(T,N,x) - \mu_B^0(T)$ as the difference of chemical potential of element B between a bimetallic NP and the pure bulk material. $\Delta\mu_B(T,N,x)$ can also be decomposed into a mixing and a surface contribution:

$$\Delta\mu_B(T,N,x) = \mu_{B,\text{mix}}(T,x) + \mu_{B,\text{surf}}(T,N,x) \tag{1}$$

with

$$\mu_{B,\text{mix}}(T,x) = (1-x)^2(g_0 + g_1(1-4x) + g_2 x(2-3x)) + kT\ln(x) \tag{2}$$

and

$$\mu_{B,surf}(T,N,x) = 2\frac{\gamma\Omega}{r} + 3(1-x)\frac{\partial}{\partial x}\frac{\gamma\Omega}{r}\bigg|_N = \frac{\tilde{\gamma}(x)}{N^{1/3}} \qquad (3)$$

with $\tilde{\gamma}(x) = 2\gamma\alpha^{1/3}\Omega^{2/3} + 3(1-x)\frac{\partial}{\partial x}\left(\gamma\alpha^{1/3}\Omega^{2/3}\right)\bigg|_N \qquad (4)$

At the thermodynamic equilibrium, $\Delta\mu_B$ is the same for all NPs. The particle radius and composition are thus related:

$$r = \left(\frac{\Omega}{\alpha}\right)^{1/3}\frac{\tilde{\gamma}(x)}{\Delta\mu_B - \mu_{B,mix}(T,x)} \qquad (5)$$

It is of course difficult to know the exact compositional dependence of $\tilde{\gamma}$. The variation of Ω can be easily derived from the composition dependence of the lattice constant, which, for Au-Pd follows the Vegard's law.[27] We have assumed a similar linear variation for γ and $\cos(\theta)$.

In the hypothesis of thermal equilibrium for Pd in the Au-Pd NPs, we have fitted the experimental results with Eq (5). We have first assumed that γ, Ω, h_0, h_1 and h_2 are the same for a particle as for a bulk alloy. In particular, we have taken the following values: h_0 = -0.308 eV.at^{-1}, h_1 = -0.175 eV.at^{-1}, h_2 = 0 for the mixing enthalpy,[27] and s_0 = -0.13 meV.K^{-1}.at^{-1}, s_1 = 0 and s_2 = 0 for the excess entropy.[27] The values of the surface free energies have been set to γ_{Au} = 9.4 eV.nm^{-2} and γ_{Pd} = 12.7 eV.nm^{-2}.[28] The values of the contact angle for Au NPs on amorphous carbon has been taken from the literature, namely θ_{Au}=122°.[29] We did not found similar measurements for Pd. We have assume that, due to a stronger interaction between Pd and C atoms, the contact angle was lower for Pd and we have taken, for simplicity, θ_{Pd}=90°. In that case, the only free parameter is $\Delta\mu_B$.

The comparison between experiments and theory is presented in Figure 2, for different values of $\Delta\mu_{\text{B}}$, the Pd chemical potential.

Figure 2. Composition of the $Au_{1-x}Pd_x$ NPs after annealing 10h at 873K. Comparison between experiments (orange dots) and equation (5) with $\gamma_{Au} = 9.4$ eV.nm^{-2}, $\gamma_{Pd} = 12.7$ eV.nm^{-2} and $\Delta\mu_{\text{B}} = -8$ meV (blue dotted line), -80 meV (green dotted line) or -280 meV (red dotted line), or with $\gamma_{Au} = 9.4$ eV.nm^{-2}, $\gamma_{Pd} = 28$ eV.nm^{-2} and $\Delta\mu_{\text{B}} = +1$ meV (continuous black line).

As shown by the dotted lines, it is not possible to fit the whole distribution with the same chemical potential and the previous set of parameters. In particular, the chemical potential of the large particles is higher than the one of smaller particles. It could be explained by the fact that the Pd chemical potential is not constant, or by the fact that the parameters used for Eq. 5 are not correct. In particular, the surface energy term could be modified by taking into account that particles, and especially large particles that are Pd rich, have not their equilibrium shape. The mixing enthalpy and entropy could also be different for small particles as compared to the bulk limit, which is roughly similar to add higher order terms in the composition dependence of the surface energy. The validity of the Vegard's law for surface energies and contact angle is also questionable.

For simplicity, we have chosen to fit the experimental data by varying the value of the Pd surface energy. For this purpose, we have performed a minimization of the normalized sum of squared deviations (χ^2) between experimental and theoretical values, by letting free the Pd surface energy and the Pd chemical potential. The best fit is shown in Figure 2 (continuous black line). A good agreement is obtained for $\Delta\mu_{\text{B}} = +1$ meV and $\gamma_{Pd} = 28$ eV.nm^{-2}. This shows that,

for the Au-Pd NPs studied, the surface energy plays a larger role as expected, relatively to the mixing enthalpy. This larger contribution of the surface energy could be related to the fact that large particles have not their equilibrium shape, which necessarily results in an increase of the surface contribution to the chemical potential. Shape effects on the chemical potential have been recently observed for Ag NPs in solution: it was found that, for a given size, the chemical potential was driven by the surface/volume ratio but that a few other factors also contribute to total chemical potential energy of the NP, such as structural defects and the difference in the surface energies of atoms on different crystalline facets.[30]

In order to understand the phase separation observed, we have undertaken kinetic Monte-Carlo (kMC) simulations of the ripening. Figure 3 shows the size and composition evolution of NPs with initial $Au_{60}Pd_{40}$ composition annealed at 873K for 10h as predicted by kMC simulations.

Before annealing, the concentration is nearly the same for all NPs (see Figure 3a), and the size distribution shown in Figure 3d is maximum around 3 nm. Two sets of parameters have been tested. First, we have used the experimentally-known values of the Au and Pd surface energies. The result after annealing is presented in Figure 3b. A small coarsening of the island distribution is observed, larger particles become Pd-rich whereas smaller particles become Au-rich, as can be seen in the histogram distribution shown in Figure 3e. However, no phase separation is observed, contrary to experiments. In a second simulation, we have used, as in the thermodynamic calculations, $\gamma_{Pd} = 28$ eV.nm^{-2} for the Pd surface energy. For these parameters, a much larger coarsening is obtained, due to the larger contributions of surface energy terms in the chemical potential. Moreover, as experimentally observed, a phase separation occurs between two populations: small Au-rich particles and large Pd-rich ones (see Figures. 3c and 3f). Figure S1 of the Supporting Information shows the size dependence of the chemical potential for Au and Pd

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atoms in the particles after 10h annealing at 873K, for $\gamma_{Au} = 9.4$ eV.nm^{-2} and $\gamma_{Pd} = 28$ eV.nm^{-2}. Whereas the Au chemical potential strongly varies with size, the Pd chemical potential is nearly constant, with a small size-dependant variation for the large particles. Due to these variations of chemical potential, the situation shown after 10h annealing does not correspond to an equilibrium state since the population of the population of small particles continue to coarsen due to Au diffusion and large particles continue to coarsen due to Pd diffusion.

Experiments and kMC simulations show thus that starting from a relatively narrow size and composition distribution, a phase separation between two populations of NPs can be obtained: Au-rich small particles and Pd-rich large particles. Each population then coarsens with a different kinetics. This is surprising since Au and Pd form alloys in all proportion in the bulk state. This confirms also that a higher Pd surface energy is needed to model the experimental behavior observed. In the following, we demonstrate that this behavior is related to an instability of the size-composition relation.

Figure 3. Top view of Au$_{60}$Pd$_{40}$ islands on carbon before (a) and after annealing 10h at 873K (b-c). Size: 300x300 nm^2. (b) For $\gamma_{Pd} = 12.7$ eV.nm^{-2}. (c) For $\gamma_{Pd} = 28$ eV.nm^{-2}. The colorscale range from red for pure Au ($x = 0$) to blue for pure Pd ($x = 1$). (d-f) Corresponding size distributions, with the same colorscale for the mean composition at each size.

Eq. 5 gives the relation between size and composition for a given chemical potential of Pd $\Delta\mu_B$. If one considers a single particle, its chemical potential is given by Eqs. 1-3. Assuming

that, due to their low mobility, the number N_A of Au atoms in the particle is fixed, Eq. 1 can be written as a function of N_B, the number of highly mobile Pd atoms. The result is presented in Figure 4 for $N_A = 1000$ and for $\gamma_{Pd} = 28$ eV.nm^{-2}.

Figure 4. Evolution of the Pd chemical potential for Au-Pd particles as a function of the number of Pd atoms N_{Pd}, and for $N_{Au} = 1000$ and $\gamma_{Pd} = 28$ eV.nm^{-2}.

The stability of the particle is obtained if $\left.\dfrac{\partial \Delta \mu_B}{\partial N_B}\right|_{T,P,N_A} > 0$. This relation is satisfied in the left part of the curve, for $x_{Pd} < 0.4$, i.e. $N_{Pd} < 700$. For this condition, if the particle size increases due to a capture of a Pd atom, the Pd chemical potential increases. This favors detachment of a Pd atom from this particle and the system return in its initial state. This is not the case in the right part of the curve, where the chemical potential of Pd atoms in the particle decreases upon growth. Note that this last case corresponds to the classical one for Ostwald ripening of elements. The transition between these two behaviors is obtained for $\left.\dfrac{\partial \Delta \mu_B}{\partial N_B}\right|_{T,P,N_A} = 0$. Using Eq. (5), the transition corresponds to:

$$N = \left(\frac{\dfrac{\tilde{\gamma}(x)}{3(1-x)} - \dfrac{\partial}{\partial x}\tilde{\gamma}(x)}{\dfrac{\partial}{\partial x}\mu_{B,mix}(x)} \right)^3 \tag{6}$$

The onset of instability is shown in Figure 5 for two sets of surface energies. Below the curve, particles are stable relatively to Pd exchange. Above the curve, i.e. if they are small or Pd-rich, they are unstable. The instability region is larger for higher surface energies. In the experimental case considered here, the NPs have a mean composition of $Au_{60}Pd_{40}$ after synthesis and are thus all stable. During coarsening, the size-composition relation is modified and the Pd concentration increases for larger particles. The size and composition of Au-Pd particles after 10h annealing at 873 K is also shown in Figure 5 for the two sets of parameters. Using $\gamma_{Pd} = 12.7$ eV.nm^{-2}, all NPs are in the stable region after coarsening (Figure 5a). For $\gamma_{Pd} = 28$ eV.nm^{-2}, the larger coarsening observed leads to NPs having a composition larger than $x = 0.6$ with sizes larger than 6 nm. This corresponds to the onset of instability drawn in Figure 5b. Below the curve, the Pd chemical potential is nearly constant ($\Delta\mu_{Pd}$=0.065±0.010 eV). Above the curve, $\Delta\mu_{Pd}$ is not constant in the particles. Some of them have a value $\Delta\mu_{Pd} > 0.065$eV and will decay, the larger ones have a value $\Delta\mu_{Pd} < 0.065$eV and they will continue to grow. This corresponds to the set of large Pd particles drawn in blue in the detailed view (Figure 3c).

Figure 5. Size-composition relation for Au_{1-x}-Pd_x NPs. Black dots: kMC simulation results after 10h annealing at 873 K, blue continuous line, onset of instability given by Eq. (6). (a) For $\gamma_{Pd} = 12.7$ eV.nm^{-2} and (b) for $\gamma_{Pd} = 28$ eV.nm^{-2}. Note that the two graphs have different horizontal radius scales.

CONCLUSIONS

Using STEM-EDS measurements, we have shown that in spite of a complete miscibility of the two metals, Au-Pd supported NPs can undergo, after annealing, a phase separation leading to two distinct populations: Au-rich NPs of mean radius 3.5 nm and large Pd-rich NPs of mean radius 25 nm. Thermodynamic calculations and kMC simulations explain this behavior. As they have a higher mobility, Pd atoms can reach thermodynamic equilibrium during the coarsening process. Since there is a competition between mixing enthalpy which favors alloying and surface energy which favors larger particles, this leads to a size-dependant concentration where larger particles contains more Pd than smaller ones. Below a critical size, NPs are stable relatively to change of Pd concentration: the increase of the number of Pd atoms in the NP corresponds to an increase of the Pd chemical potential which favors the subsequent loss of Pd atoms. Above a critical size, the situation is reversed and the classical Ostwald ripening behavior is observed: larger islands grow at the expense of smaller ones. If, during coarsening, some NPs reach this critical size, a phase separation is observed between two populations, a population of small Au-rich NPs for which ripening is governed by Au exchange, and a population of large Pd-rich NPs for which ripening is governed by Pd exchange. The size dependence of the critical concentration depends on the mixing free enthalpy, on the surface energy and on the contact angle of the NPs. Knowing these parameters, it is thus directly possible to evaluate the risk that a population of bimetallic NPs undergoes a phase separation during annealing.

METHODS

NP synthesis

Gold-palladium bimetallic NPs were prepared by a two-steps procedure. They were firstly grown by alternate pulsed laser deposition (PLD) in a high vacuum chamber under a pressure of about 10^{-5} Pa and deposited on a sodium chloride (001) single crystal surface heated at 300°C. This ensures good shape and size control.[23] For high-temperature annealing, the as-grown Au-Pd NPs were subsequently transferred to standard TEM grids (holey carbon on 200 mesh grid in copper, Agar Scientific) by carbon replica. After transfer, the sample consists of finely dispersed NPs in amorphous carbon matrix that were suitable for electron microscopy studies without further sample preparation. Further details about both the synthesis conditions used to achieve high control in particle structure (size, shape and composition) and the carbon replica process can be found in ref. [23]. The high-temperature annealing were undertaken under vacuum in the same chamber used for particle deposition.

TEM measurements

Size and composition changes induced by high-temperature annealing were studied by aberration-corrected transmission electron microscopy (TEM) in a JEOL ARM 200F microscope equipped with cold-field emission gun (operated at 200 kV) and an objective lens aberration corrector.[31] To study the evolution of particle size and shape, high-angular annular dark field images were acquired in scanning mode (STEM-HAADF images) with spot 1C and a camera length of 6 cm. In parallel, energy dispersive X-ray spectroscopy in scanning mode (STEM-EDS) was conducted at single particle level to uniquely correlate particle size and composition. STEM-EDS spectra were acquired for either 50 or 100 s depending on X-ray counting statistics. Particle composition was determined by analyzing the intensities under the Au-$M_{\alpha,\beta}$ (between

2.00 and 2.24 keV) and Pd-L$_{\alpha,\beta}$ (between 2.70 and 2.94 keV) edges using the Cliff–Lorimer method[32] with an experimentally-determined K factor.

Monte-Carlo simulations

A multi-scale kMC algorithm[11] has been used to simulate the thermal evolution of truncated spherical particles on an atomically flat homogeneous surface. Atomic detachment and diffusion events have been assumed to be thermally driven with attempt frequencies $v_d = 10^{16}$ Hz. The energy barriers for detachment from the particles where given by the difference of cohesive energy for an atom in the particle and on the surface, with corresponding adsorption energy $E_a(\text{Pd}) = -1.081\text{eV}$, $E_a(\text{Au}) = -0.096\text{eV}$, and diffusion barriers, set to $E_d(\text{Pd}) = 0.037\text{eV}$ and $E_d(\text{Au}) = 0.007\text{eV}$.[33] Simulations have been performed on a surface cell of size 1.5x1.5 μm^2. The initial NP assembly has been generated using a classical on-site kMC algorithm,[34] leading to $1.4\ 10^8$ atoms in $2.3\ 10^4$ Au$_{60}$Pd$_{40}$ islands with a mean radius of 3 nm. Details are available in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information.

Details of thermodynamic calculations and kinetic Monte-Carlo (kMC) simulations. This material is available free of charge *via* the Internet at http://pubs.acs.org."

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Table of Contents Graphic and Synopsis

Scanning transmission electron microscopy and energy dispersive spectroscopy measurements show that amorphous carbon supported Au-Pd nanoparticles undergo a phase separation during annealing at 873K, which leads to the coexistence of small Au-rich nanoparticles and large Pd-rich particles. Thermodynamic calculations and kinetic Monte-Carlo simulations explain this behavior.