Surface Composition during Sintering of Silver-Gold Alloyed Nanoparticles

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Keywords: alloys, silver, gold, molecular dynamics.
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Bimetallic nanoparticles have gained significant commercial interest because of their superior electronic, chemical, optical, magnetic and even plasmonic properties (Sotiriou et al., 2014) compared to the monometallic counterparts (Sinfelt, 1983) making them excellent candidates for catalytic and biomedical applications. Core-monolayer shell bimetallics exhibit often unique properties that are not an interpolation between those of their parent metals. This behavior is attributed to the lattice mismatch (strain effect) and charge transfer between layers (ligand effect) resulting in different electronic properties. Such synergetic effects of multicomponent surface compositions allow to control the morphology of self-assembling organic molecules or oligomers that find potential use in biomedicine.

Here, the sintering rate and surface composition of free-standing, coalescing Ag-Au nano-alloys are investigated for different particle sizes and temperatures by atomistic molecular dynamics (MD; Goudeli and Pratsinis, 2016). The MD method is validated by the attainment of the melting point of Ag-Au core-shell nanoparticles that increases with increasing particle size and follows closely the size-dependent melting temperature of pure Ag and Au nanoparticles. The characteristic sintering time of Ag-Au nanoparticles is determined by tracking the evolution of the surface area during sintering or coalescence. Upon sintering, Ag molecules exhibit increased mobility that is quantified by the mean square displacement. The Ag occupies gradually the alloyed particle surface in agreement with experimental data.

Figure 1 shows the evolution of surface Ag fraction during sintering of two free-standing Ag and Au nanoparticles (inset) with particle diameter of 3 nm at 600 (squares), 700 (circles) and 800 K (triangles). Initially ($t < 10^{-3}$ ns), the Ag surface fraction is ~0.5 but when sintering starts taking place it increases as Ag diffuses on the surface of the Au nanoparticle. Increasing the sintering temperature results in higher Ag surface fraction for any given time. For example, Ag atoms occupy about 65% of the final particle surface for $t > 30$ ns during their sintering at 800 K.

Figure 2 shows cross-sections of unequally-sized Ag (blue) and Au (orange) nanoparticles with diameters 2 and 4 nm, respectively (left), and 4 and 2 nm, respectively (right), coalescing at 800 K at $t = 0$, 0.1, 1 and 10 ns. Initially ($t \leq 0.1$ ns), adhesion takes place and practically the same particle morphology is obtained, regardless of the Ag and Au particle size ratio. At sufficiently long times ($t > 0.1$ ns), however, when the small Ag nanoparticle coalesces with a bigger Au nanoparticle, Ag atoms diffuse on the Au surface

forming a thin layer ($t = 10$ ns: patched nanoparticle). In contrast, this is not the case when Au is the smallest particle.
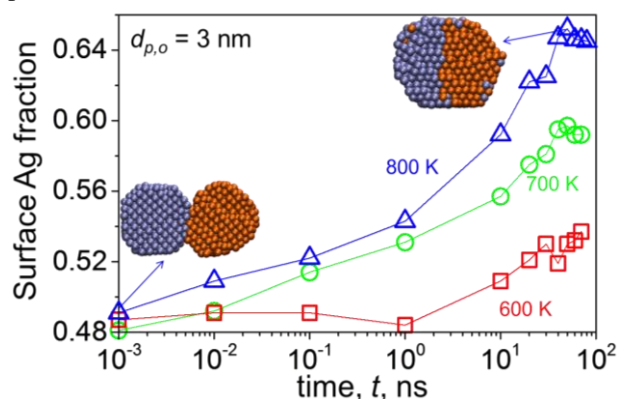

Figure 1: Evolution of the surface Ag fraction of Ag-Au nano-alloys with $d_{p,o} = 3$ nm during sintering at 600 (red line), 700 (green line) and 800 K (blue line).
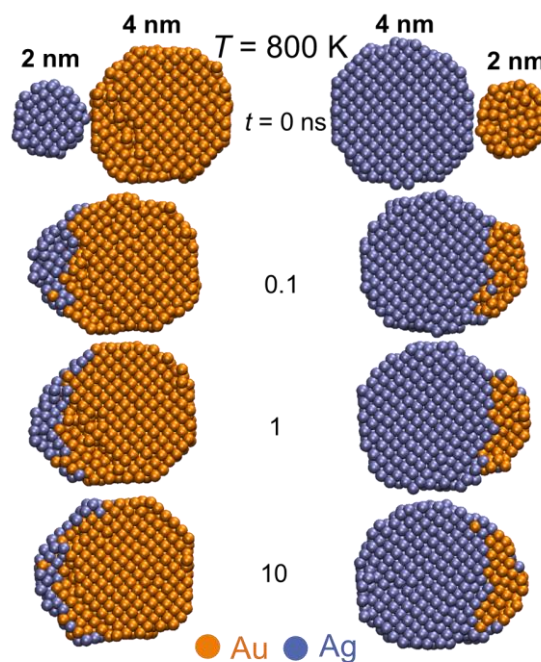

Figure 2: Cross-sections of Ag-Au nanoparticles coalescing at 800 K for $t = 0$, 0.1, 1 and 10 ns.

Goudeli, E., Pratsinis, S. E. *AIChE J.* **2016**, 62, 589-598.

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