

## Disorder-order transition and segregation effect in PtAg nanoalloys

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Pt-based alloys are especially known to be efficient catalysts and electrocatalysts for different reactions [1]. Most of studies try to combine the Pt to another metal in order to increase the stability of single-metal catalysts as well as to improve the catalytic selectivity and/or activity. In this prospect, PtAg alloyed nanoparticles (NPs) are particularly interesting for carbon monoxide oxidation: Pt sites can chemisorb CO and Ag sites activate O<sub>2</sub> [2]. Therefore, a quite uniform distribution of Pt and Ag surface sites is essential, the reaction efficiency being more efficient if Ag and Pt sites are close to each other.

At the macroscopic scale, PtAg alloy shows an interesting but complex phase diagram at low temperature [3] (under 800 °C). Indeed, an ordered alloy is formed within the miscibility gap which extends from 15 % to 97 % of Ag. This ordered alloy, which is a L<sub>1</sub> phase (alternative planes of Ag and Pt in the [111] direction of the fcc lattice), is formed only at the equicomposition of PtAg [4]. At the nanoscale, the size reduction and the segregation effect can modify the stability of the ordered alloy. Indeed, due to its low surface energy and its large atomic radius, the Ag has a high tendency to go to the surface of the nanoparticles in order to form a core/shell segregation depending on the Ag concentration [5], [6].

Our objective is to determine, through high resolution structural investigation technique combined with DFT calculations, the equilibrium phase for the PtAg alloy at different compositions. PtAg nanoalloys was prepared by atomic evaporation using two separate sources operating simultaneously under ultra-high vacuum (UHV) conditions. The obtained nanoparticles show an ordered L<sub>1</sub> core with a monolayer-thick Ag shell depending on the composition. These experimental results are in agreement with our DFT calculations.

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