Influence of the palladium amount on the ordering, final size, and composition of Pd-Au nanoparticle arrays

Aude Bailly[1], Georges Sitja[2], Marie-Claire Saint-Lager[1], Séverine Le Moal[3], Frédéric Leroy[2], Maurizio De Santis[1], Claude R. Henry[2] and Odile Robach[4]

[1] *Univ. Grenoble Alpes, CNRS, Grenoble INP, Institut Néel, 38000 Grenoble, France*
[2] *Aix-Marseille Université, CNRS, CINaM, 13000 Marseille, France*
[3] *Institut des Sciences Moléculaires d'Orsay, CNRS Université Paris-Sud, 91000 Orsay, France*
[4] *CEA, INAC-MEM, 38000 Grenoble, France*

aude.bailly@neel.cnrs.fr

The design of metallic nanoparticles (NPs) with well-controlled features is very important for fields such as catalysis, molecular electronics and magnetism. Several routes towards tailored NP systems have been explored. Among them, nanostructured substrates exhibiting a regular two-dimensional network of defects appeared to be good candidates for growing long-range ordered NP arrays with a narrow size distribution and a similar local environment around each NP [1, 2].

In this frame, we have examined the growth of Pd-Au NP arrays on an ultrathin Al_2O_3 film obtained by oxidation of a $Ni_3Al(111)$ single crystal surface [3]. The NP composition ranges from pure palladium to almost pure gold with a mean diameter of 2 nm. Small-angle X-ray scattering and X-ray diffraction in grazing incidence (GISAXS and GIXRD) were performed *in situ* during the sequential deposition of Pd and Au. Combining these complementary techniques allowed us (i) to determine how the long-range order is affected by the NP size progressive increase and by the relative Au/Pd amount and (ii) to assess structural parameters, such as interatomic distances within the NPs and their epitaxial relationship to the substrate.
Interestingly, GISAXS highlighted a diffuse scattering contribution whose appearance is linked to the progressive disordering of the NP arrays. It is correlated to the size of the initial Pd clusters and to the Au/Pd final ratio: the lower the ratio is, the better the organization of the NP array. More specifically, we evidenced that the arrays start to disorder as soon as one atomic-thick Au layer is deposited on the Pd seeds. The mean morphological parameters of the ordered nanoparticles were obtained from GISAXS and complemented by structural information derived from GIXRD. This study provides new insights into the link between the size and the composition of these bimetallic nanoparticles for synthesizing ordered arrays. Such tailored samples might then be used as model systems for making the connection between macroscopic (catalytic, magnetic, and so on) properties and atomic-scale parameters.

References:

[1] Stefan Degen, Conrad Becker, Klaus Wandelt, Faraday Discussions **125**, 343 (2004).
[2] Maxence Marsault, Georges Sitja, Claude R. Henry, Phys. Chem. Chem. Phys. **16**, 26458 (2014).
[3] Aude Bailly, Georges Sitja, Marie-Claire Saint-Lager, Séverine Le Moal, Frédéric Leroy, Maurizio De Santis, Claude R. Henry, Odile Robach, J. Phys. Chem. C **121**, 25864 (2017).