ESRF	**Experiment title:** **Temperature-induced alloying in multi-twinned Co/Pt and Ag/Co core-shell clusters**	**Experiment number**: 32. **23971**
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CRG Report:

In order to understand mechanisms leading to these morphological and structural changes, we have performed in situ and real time x-ray scattering measurements during the growth at room temperature (to follow the core/shell formation) and the annealing (to follow the alloying and ordering) of CoPt nanoparticles NPs at the UHV setup of BM32 beamline. Grazing Incidence Small Angle X-ray Scattering (GISAXS) gives the size, dispersion and mobility of NPs, from an analysis in the framework of the DWBA theory. The necessity to record a large reciprocal space range induces to use a high energy (at 20KeV). In addition, Monte Carlo simulations of relaxed cluster structures (ordered, disordered fcc, multi-twinned decahedra and icosahedra) was performed using a semi-empirical tight-binding potential, to compare with Grazing Incidence X-ray Diffraction (GIXD) experimental results obtained simultaneously with GISAXS measurements. The small size and random orientation of the particles (weak interaction with the substrate, quasi-spherical shape) allow the use of the Debye framework for the diffraction data analysis. The real-time aspect of the experiment is of particular interest to study dynamical processes during each stage of the experiment (core formation, shell deposition and annealing).

The aim of this project was to investigate the structure and morphology evolution of core@shell particles obtain by sequential deposition of Co and Pt.

The Co and Pt atoms was deposited in-situ by condensation on weakly-interacting a-C/SiO2 substrate, from two EFM Omicron evaporation sources with very low atom flux (0.5ML/h). At room temperature, 2.5nm-size particles on a-C substrate correspond to about 4ML of metals (Co and Pt). While the atoms flux will be calibrated preliminarily, it will be necessary to control the core size, i.e. atom number, about 2nm (~400 atoms/particle) and the shell size, about 0.5nm (~400 atoms/particle = one monolayer around the particle) through the real time GISAXS measurement. We have already demonstrated that the sequential deposition lead to the formation of core-shell particles. In the first stage, the A metal is deposited in a Volmer-Weber growth regime, yielding pure NPs monodispersion. In the second stage, as the particles occupy all nucleation sites of the amorphous carbon layer, the second metal deposition on the as-grown core will lead to the metallic shell formation. Then, the annealing will be follow for temperature up to 700°C.

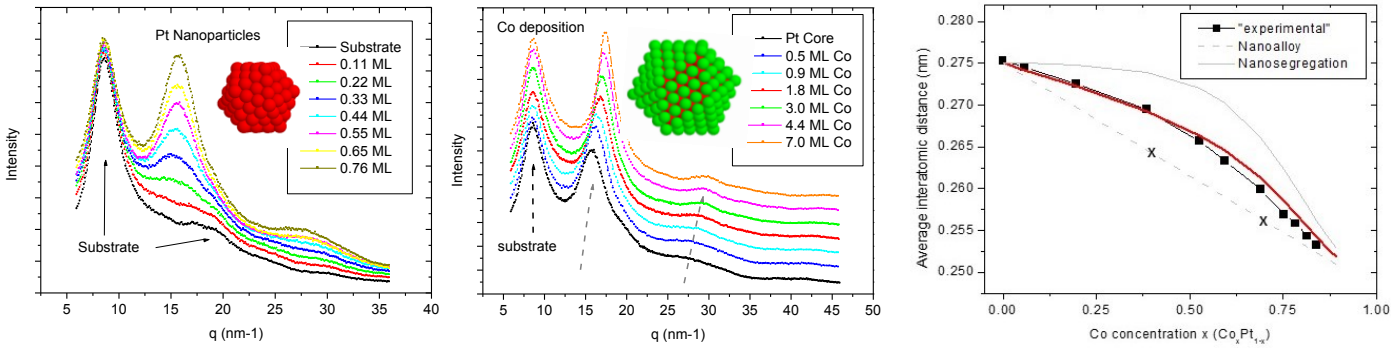

Figure 1 : GIWAXS patterns in the initial core Pt deposition and the Co deposition on the Pt cores and average interatomic distance evolution from the Pt core to the final Co deposition, the red line corresponds to a surface shell of Co with a relaxation of distances, while the grey dashed line and plain line correspond to a nanoalloy and a segregation between Co an dPt respectively.

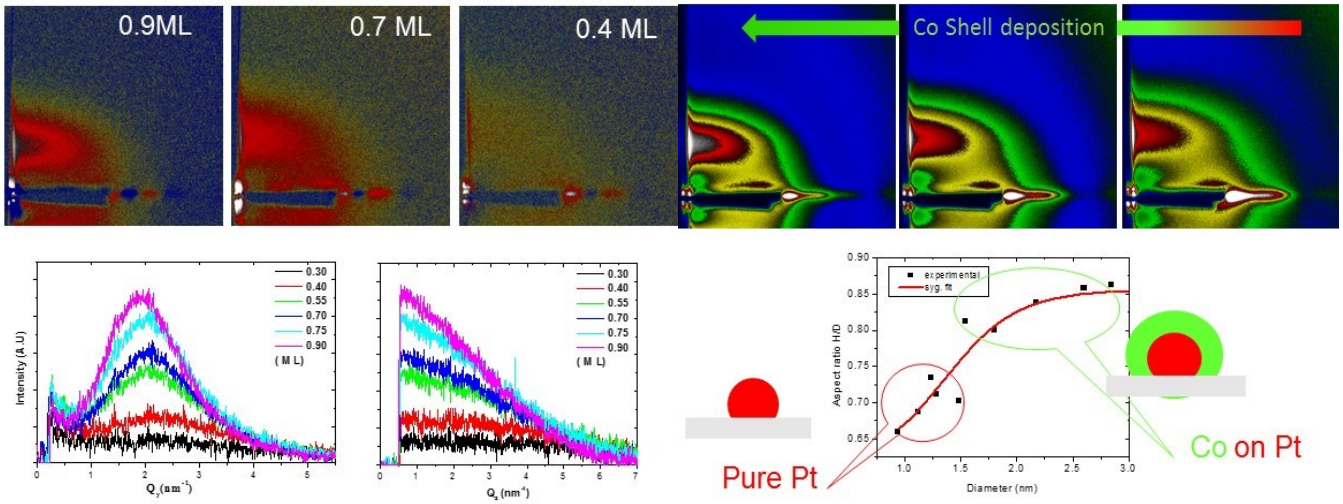

Figure 2 : GISAXS 2D and 1D patterns in the initial core Pt deposition and the Co deposition on the Pt cores and aspect ratio versus size evolution from the Pt core to the final Co deposition.

We have performed Pt-Co sequential deposition and compared with Co-Pt codeposition in the same size range. The supported clusters were observed post-mortem by TEM technique after annealing.

The initial Pt core of 1.4nm are in an icosahedral structure with an aspect ratio in agreement with adhesion energy calculation of Pt on amorphous carbon. After Co deposition, the density of particles are equal which confirm the Co deposition on the Pt core particles. The average interatomic distance evolution is in agreement with a preservation of the initial core and a Co deposition in a shell configuration without alloying. These results are consistent with Molecular dynamic calculation of a Pt-Co core shell structure in a metastable state but with a small variation of energy with respect to an alloyed equilibrium structure at this size. The relaxation of Co-Co interatomic distance is limited and the Co atoms appear as a partial pseudomorphy with the Pt core. By codeposition, the particles are clearly chemically mixed and not segregated, whatever the particle size.

At increasing annealing temperature, the particles go to a mixed configuration. While from room temperature to 600K, only multitwinned icosahedral (Ih) structure are detected, annealing above 700K yields the decahedral (Dh) structure (fig.1b) from the coalescence of Ih morphology. Meanwhile, the particle size (fig. 2) increases which stabilises the Dh structure, more stable at intermediate size. This mechanism is favoured by the temperature activation and the planar defects induce by the coalescence. Above 820K, the atom rearrangement leads to fcc structure transition predicted by MC calculations. At this stage, the transition from fcc chemically disordered structure to ordered L10 structure (fig 1d) is more favourable than that stemming from multi-twinned (Ih or Dh) structures. At 900K, the resulting structure of the nanoparticles assembly is size-dependent with two clusters population (fcc disordered and L10 ordered) on each side of a critical size (around 3.7nm).

These results evidence a metastable state of as grwn supported cluster due to a lack of atom mobility a RT.