

IN-SITU CHARACTERIZATION OF SELF-ASSEMBLED NANOPARTICLES FILMS UNDER HARSH CONDITIONS

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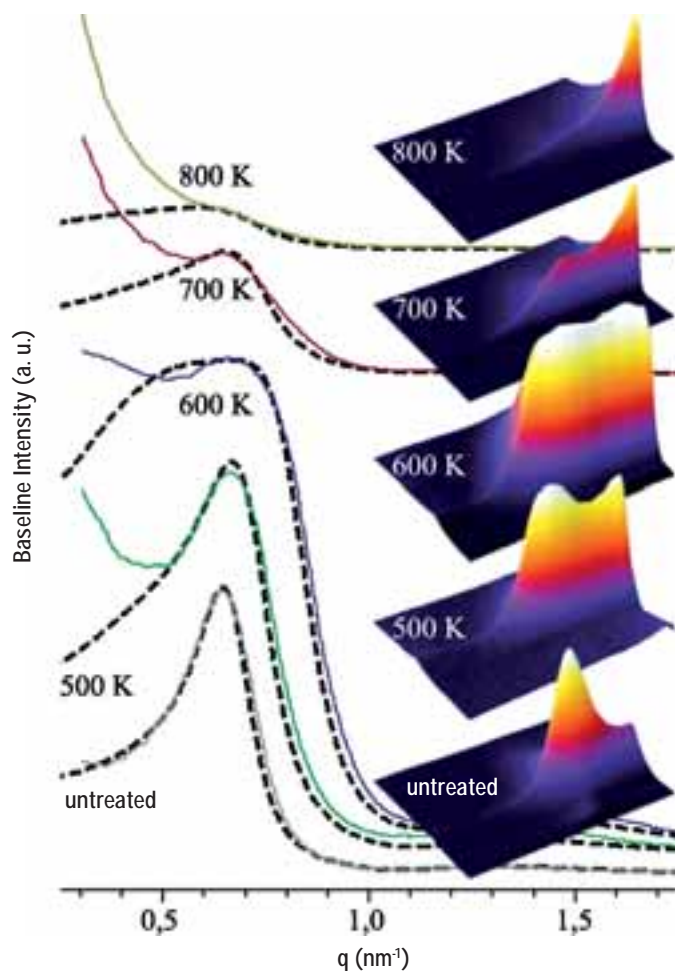
Sincrotrone Trieste S.C.p.A., S.S. 14 km 163,5 in AREA Science Park - 34012 Basovizza, Trieste, ITALY

Figure 1. Left: GISAXS baseline intensity measured from nanoparticle arrays annealed at different temperatures for 120 minutes. Right: 3D representation of the respective spectra.

Arrays of metal nanoparticles on oxidic surfaces have become a widely-researched type of materials systems in various disciplines of chemistry and physics. In contrast to techniques in which particles are grown directly on the substrate, the approach of self-assembling layers of colloidal metal particles offers increased flexibility in terms of materials combinations and particle size and structure.

Prior to deposition on a substrate surface, such particles are generally prepared by wet chemistry and thus are surrounded by a shell of stabilizing and coordinating ligands. To access the properties of the metal particle surface without an interfering organic shell, e.g. for applications in the field of catalysis, the ligands have to be removed. Among the requirements to be met by any method for ligand shell removal is the conservation of particle and layer structure. In this article, the effects of two different techniques, thermal annealing and reactive sputtering treatment on bimetallic cobalt-platinum particle films [1] are examined by grazing-incidence small-angle x-ray scattering (GISAXS), with a particular focus on ordering and size distribution.

The impact of thermal annealing was studied based on a series of samples heated under ultra-high vacuum (UHV) conditions, whereas a second series of samples was exposed to oxygen plasmas in order to strip off the ligand shells, and subsequently to hydrogen plasmas in order to reduce them back to the metallic state. The plasma treatment was carried out in a custom-built RF plasma source [2], with treatment time, plasma power, and the partial pressure of argon in the gas feed as variable parameters. The GISAXS experiments were performed *ex situ* at the SAXS beamline at Elettra. Due to the exposure of the bare metal particles after the treatment to an oxygen-containing and contaminating atmosphere, the oxidation of their cobalt content could not be precluded. However, this affects both types of samples to a similar extent and, therefore, does hardly distort the results of the comparison.



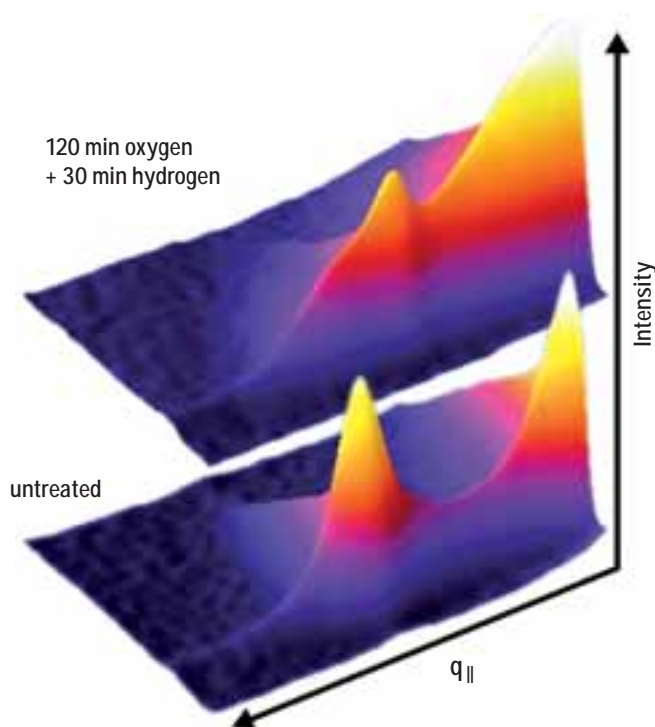


Figure 2. 3D representation of GISAXS spectra measured from nanoparticle arrays before and after exposure to an oxygen plasma at 20 W for 120 min and then to a hydrogen plasma at 20 W for 30 min.

For the samples heated in UHV it was found that they had undergone a thermally induced melting process at elevated temperatures. The GISAXS measurements showed an increasing loss of order with rising temperatures and a loss of structural definition above 700 K (see Figure 1). These findings were complemented by scanning electron micrographs which show sintering and agglomeration of distinct particles into larger structures upon heating.

In-situ x-ray photoemission spectroscopy showed that the thermal annealing procedure removed only about 70% of the initial carbon species, whereas after plasma treatment, carbon could not be detected. Hence, the organic ligand molecules can completely be removed. From the GISAXS spectra recorded after plasma treatment (see Figure 2), a slight reduction of the mean interparticle distance in the order of 3% can be deduced. However, the main result obtained by GISAXS is that, compared to thermal annealing, plasma treatment under appropriate conditions has almost negligible impact on layer order and particle definition.

References

- [1] J. I. Flege, T. Schmidt, V. Aleksandrovic, G. Alexe, T. Clausen, B. Gehl, A. Kornowski, S. Bernstorff, H. Weller, J. Falta, *Nucl. Instr. Meth. B* **246** (2006) 25.
- [2] B. Gehl, U. Leist, V. Aleksandrovic, P. Nickut, V. Zielasek, H. Weller, K. Al-Shamery, M. Bäumer, *Review of Scientific Instruments* **77** (2006) 083902.