ESRF	**Experiment title:** Operando coherent X-ray diffraction imaging of surface oxides of a single catalyst PtRh nanoparticle	**Experiment number**: HC-3802
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Report:

In this experiment we aimed to track the formation and disappearance of facet-dependent surface oxides on a single PtRh nanoparticle (PtRh NP) as function of the catalytic gas environment, i.e., oxidizing or reducing conditions using Bragg coherent X-ray diffraction (BCDI) and surface X-ray diffraction. In particular, we aimed to address the following questions: What are the facet-dependent oxidation mechanisms and the role of the Rh segregation? How is the strain state in the nanoparticle related to the surface oxide formation?

We investigated several single PtRh NPs on a (100)-oriented $SrTiO_3$ single crystal surface using coherent Bragg diffraction in an X-ray beam of 9 keV photon energy focused with KB mirrors to a nominal beam size of 400 nm (H) x 100 (V) nm. Several PtRh NPs were pre-selected in the SEM at DESY NanoLab and subsequently marked by ion- and e-beam induced deposition of Pt markers. These hierarchical markers along with the "Advanced Nano-Object Transfer and Positioning" protocol developed within the framework of the EU funded program Nanoscience Foundries and Fine Analysis (NFFA) and implemented at beamline ID01 enabled us to re-localize the pre-selected single PtRh NPs. The re-localization was simplified by a Python script converting our existing Matlab script to be compatible with the ID01 operation software providing a SPEC-compatible handover (input/output) of position coordinates. The gas flow and the pressure in our mini-reactor were kept at 50 ml/min and 0.1 bar, respectively throughout the whole experiment. We collected the signal of the gases during the experiment by a mass spectrometer located in the exhaust gas line.

We were able to re-localize several single PtRh NPs and to collect for each a BCDI data set, which could be reconstructed to create the real space shapes (see, e.g., Fig. 1).

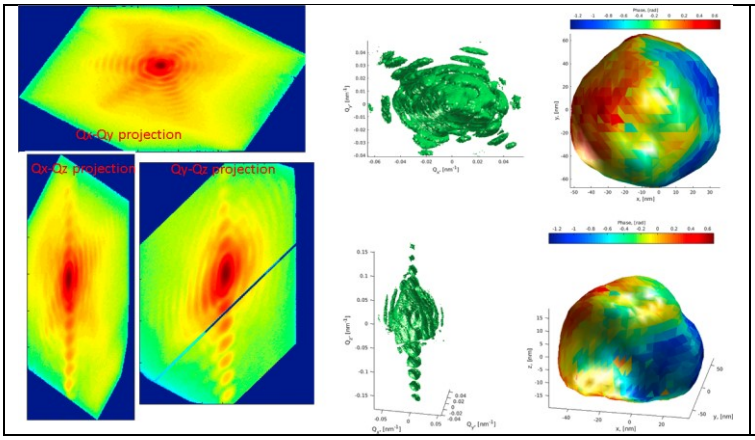

Fig. 1: Projections of the reconstructed BCDI signals (left) 3D reciprocal space plot of the scattering intensity distribution (centre) and reconstructions of the real space nanoparticle (right) of one of the investigated PtRh nanoparticles.

Due to several technical issues related to sample temperature stability (nanoparticles were partially drifting), the X-ray probe including KB mirrors and alignment of the OSA (see, e.g. Fig. 2) and vacuum leaks in our gas dosing system, we did not manage in several attempts to succeed in i) finding a suitable nanoparticle, ii) taking a BCDI scan to reconstruct the particle in real space, and finally iii) track the particle while moving from a specular Pt 111 geometry to an asymmetric Pt [220] Bragg peak in order to search the surface oxide signal in close vicinity to the latter.

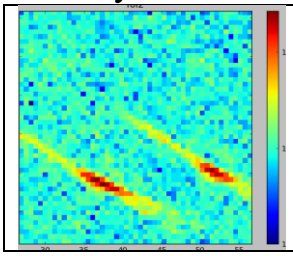

Fig. 2: Intensity distribution in a continuous KMAP scan of our sample arising from twice the same nanoparticle, presumably, due to a non- Gaussian shaped X-ray beam with two maxima.

From the experiment HC-3802 at ID01 we conclude:

- We obtained one-to-one structure information from exactly the same single PtRh NP at ID01 beamline and DESY NanoLab.
- We are able to repeatedly re-localize pre-selected single NPs at different lab-based nanoscience instruments and at the ID01 nano-focus X-ray beamline.
- However, we did not succeed in this demanding experiment to locate a single PtRh NP and subsequently analyse the appearance of the surface oxide as function of the gas environment.
- We gained significant experience, and based on this insight, we are now able to more reliably locate, detect, and track the appearance of the facet-dependent surface oxide signal as function of the catalytic conditions in a follow-up experiment.

In particular, a future experiment on the tracking of surface oxides on single nanoparticles will be improved by the

a) Known / pre-determined nanoparticle crystal orientation as available from electron back-scatter diffraction (EBSD).
b) An optimized tracking of the nanoparticle tracking by X-ray diffraction or X-ray fluorescence.
c) The EBS upgrade with increased coherent photon flux.