ESRF	**Experiment title:** **Growth of high-index faceted (HIF) Pt electrocatalyst particles and their response to electrochemical stimuli: an in-situ Bragg Coherent X-ray Diffraction Imaging study**	**Experiment number**: MA2846
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Shifts: 18	**Local contact(s)**: Dr. Gilbert Chahine	

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Report

Our goal was to study the structural and catalytic properties of single Platinum (Pt) nanocrystals (NCs) using coherent X-ray diffraction imaging (CDI) in Bragg condition under *in situ* electrochemical reaction conditions. The 3D intensity distribution in reciprocal space in the vicinity of a selected Bragg reflection contains information about the shape and strain states of the nanostructure; it provides crucial insight into the nature of nanoscale deformation following chemical stimuli, such as change of electrochemical potential and pH. For this purpose, a special electrochemical thin layer cell has been designed to fit on the goniometer of ID01. The cell allows control of liquid phase composition and electrochemical potential via a three electrode configuration (working, reference, and counter electrodes) connected to a GPIB controlled PAR263 potentiostat. To minimize beam attenuation, the cell was constructed in a thin layer design. Using 6 µm PEEK membranes to close the cell on the top together with an adjustable sample height allows for electrolyte layers below 100 µm thus minimizing beam attenuation.

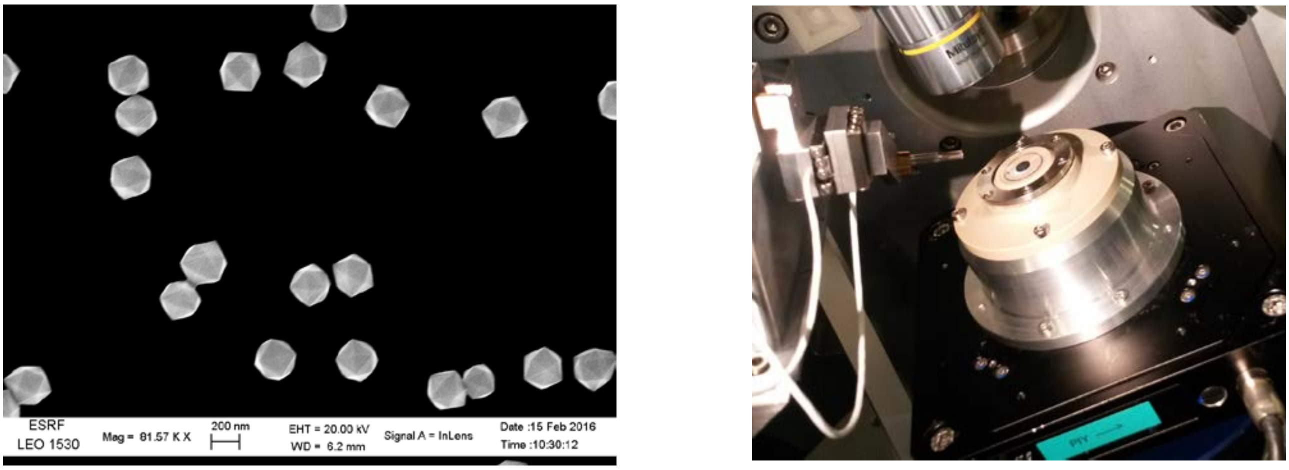

***Fig. 1** Left: Representative scanning electron microscopy (SEM) image of THH Pt nanocrystals. Right: Photograph of the newly developed thin layer electrochemistry cell at ID01.*

High-index tetrahexaedral (THH) Pt nanocrystals were electrochemically synthesized in the electrochemical laboratory of ESRF (see **Fig. 1**). The THH NCs supported (fixed) on a glassy carbon substrate were investigated by coherent X-ray diffraction in Bragg condition using the nano-focused X-ray beam at the ID01 beamline. The diameter of the Pt NCs varied from 50 to 500 nm as determined by SEM. The required spatial resolution was obtained with a circular Fresnel Zone plate, giving a measured focal size of ≈ 100 × 400 nm^2 (vertical × horizontal) with coherent illumination. We have defocused the beam to increase its vertical size to 500 nm to entirely illuminate *single* nanostructures.

The nano-diffraction experiment was carried out at beam energy of 8 keV, so that the **002** Pt Bragg peak was accessible at a scattering angle of 23.269°. Isolated THH Pt particles have been located using the quicK-Mapping technique developed at beamline ID01 [1].

We succeeded to measure *single* Pt NCs using nano-focused coherent X-ray diffraction under electrochemical conditions. Reciprocal space maps (RSMs) were collected around the **002** Bragg reflection for different *single* THH Pt NCs employing a two-dimensional (2D) Maxipix detector. We have carried out 3D coherent imaging of several *single* NCs as a function of pH value and electrochemical potential. Measurements were taken at pH values of 0, 7, and 14 (in 0.5 M H_2SO_4, 0.1 M Na_2SO_4, and 1 M KOH, respectively).

Potential scans (cyclic voltammetry) were carried out on each sample before starting the CDI experiments. In a typical experiment, a set of rocking curves was recorded per potential to be able to assess the evolution of the average strain of an individual particle as well as possibly do 3D reconstruction of real-space morphology and strain field. Potentials were varied between the onset of the hydrogen evolution reaction (HER) and the adsorption of hydroxyl. The oxygen evolution (OER) range was not reached since at these high positive potentials the particles became unstable. The maximum potential range scanned was 1100 mV vs. Ag/AgCl.

We succeeded in following the average strain variation along potential stepping. A first analysis of the data is presented in **Fig. 2a** for a sample in 1 mol/l KOH (pH = 14). At lower and higher potentials, expansion of lattice is observed, corresponding to the proton and hydroxide ions adsorption, respectively.

A detector image of the same particle at potential of −500 mV is shown in **Fig. 2b**. From this data we expect to extract the behavior of strain of a single Pt NC under different potentials related to surface processes. We aim for full reconstruction of the CDI pattern to obtain 3D real space information on the particle shape and localize strain to certain facets or regions of the particle and relate these information with known electrochemical behavior of Pt single crystalline electrodes.

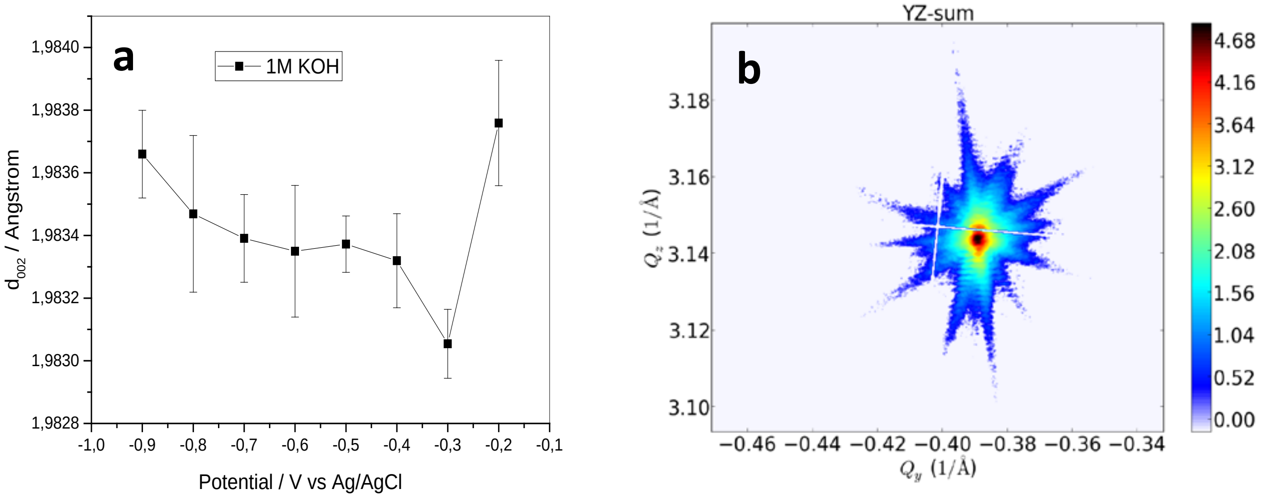

Fig. 2 a) *Evolution of average strain of an individual particle under different potentials in 1 mol/l KOH.* ***b)*** *Detector image at the maximum of the rocking-curve for the same THH Pt particle at potential of −500mV.*

References

[1] G. A. Chahine, M.-I. Richard, R. A. Homs-Regojo, T. N. Tran-Caliste, D. Carbone, V. L. R. Jacques, R. Grifone, P. Boesecke, J. Katzer, I. Costina, H. Djazouli, T. Schroeder, and T. U. Schülli, J. Appl. Crystallogr. **47**, 762 (2014).