ESRF	**Experiment title:** In situ SXRD on graphene supported Pt and Ir nanocatalysts	**Experiment number**: SI2292
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Names and affiliations of applicants (* indicates experimentalists):

Andreas Stierle, Uta Hejral, Dirk Franz, Surface / Interface Group University of Siegen, Germany, Timm Gerber, University of Cologne, Germany, Nils Blanc, ESRF, France, Johann Coraux, Institut Néel, France

Report:

Metallic nanoparticles play an important role in heterogeneous catalysis. The catalytic activity is strongly connected to shape, atomic structure and size of the particles. Often particles within the 1-2 nm size regime show extended activity and a fundamental knowledge of particle structure may lead to improved future catalyst materials. The aim of the present experiment was to study shape, structure and structure changes of graphene supported Pt nanoparticles for different Pt coverages under different environmental conditions as UHV, CO and O_2.

Sample preparation and measurements were carried out with the UHV chamber for in-situ surface preparation and growth, which is mounted onto the horizontal geometry z-axis diffractometer in experimental hutch 2 of beamline ID03. For sample preparation the UHV chamber was equipped with a sputter gun and an e-beam evaporator. Auxiliary CO, oxygen and ethylene inlets were installed to the chamber and have been used for graphene growth. Apart from the FreLoN 2D camera used for grazing incidence small angle x-ray scattering (GISAXS) the MAXIPIX photon-counting detector was employed for surface x-ray diffraction (SXRD) and x-ray reflectivity (XRR) measurements.

At least 4 shifts of beamtime were lost due to insulation problems of the sample which precludes the use of e-beam heating making a time consuming in and out transferring of the sample necessary. Throughout the entire beamtime an internal leak kept the base pressure of the UHV chamber above $1 \cdot 10^{-9}$ mbar and gave rise to some adsorption induced structural changes of the clusters during measurements, which complicates the analysis and questions to a large extent the reliability of the data. Due to the time losses the experimental program was restricted to Pt nanoparticles only (Ir particles, included in the proposal could not be studied).

Each time preceding cluster growth the Ir(111) sample surface was sputtered with argon and heated in oxygen environment. A high quality graphene layer was grown on the ordered crystal surface by well established procedures [1, 2] using ethylene as a carbon source. After characterization of the graphene covered surface we grew in two attempts clusters by deposition of 0.4 respectively 0.2 ML of Pt. During cluster growth we performed selected linescans and GISAXS measurements. Afterwards reflectivity and a complete SXRD dataset was taken. In the following the clusters were exposed to O_2 (10^{-8} mbar up to 10^{-6} mbar) and CO (10^{-8} mbar up to 10^{-7} mbar) at room temperature. Also cycles of O_2 and CO exposition were performed. To increase the chance of oxidizing adsorbed CO we annealed the sample in O_2 environment up to 570 K as well. During gas exposition certain linescans were performed. In case of changing diffraction signal we took a complete SXRD dataset after the surface system achieved a stable state.

The GISAXS images provide information about cluster size, shape and superstructure periodicity. After Pt deposition the first two orders of superstructure peaks are observable in the GISAXS image (Fig. 1 (right)).

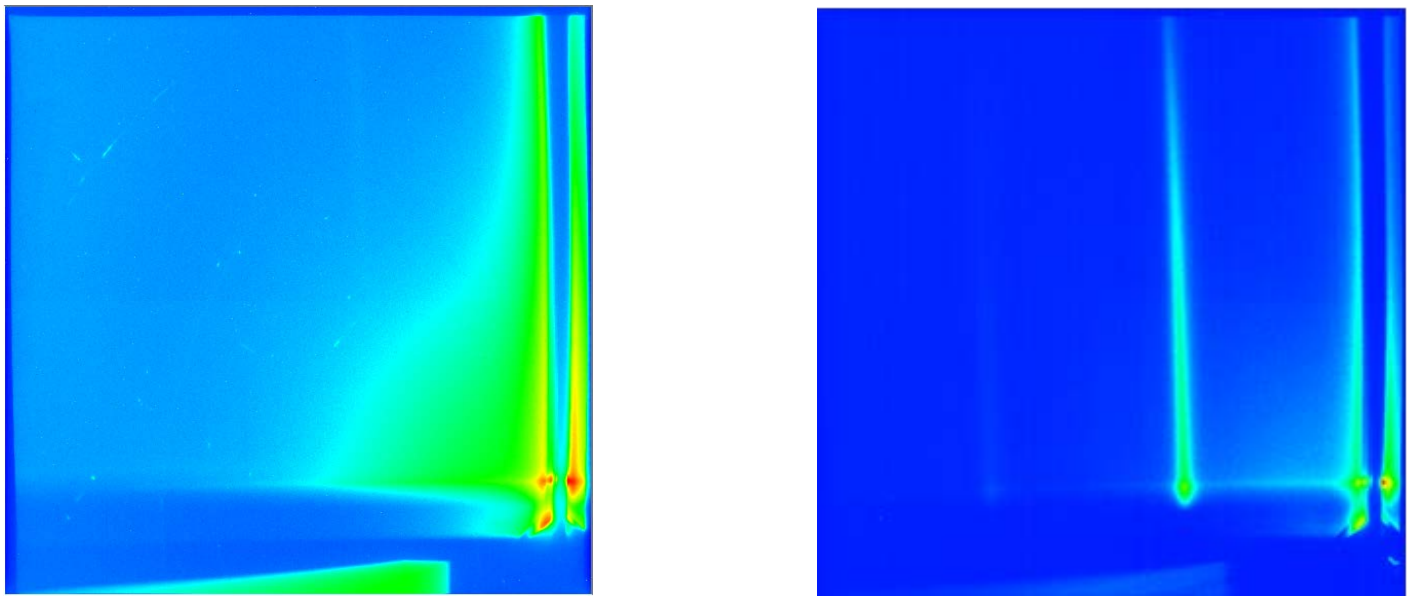

Fig. 1: (left) GISAXS image of graphene on Ir(111) – 35 sec. counting time. The weak first order graphene superstructure peak is observable. (right) GISAXS image of 0.4 ML Pt on graphene/Ir(111) – 1 sec. counting time. Due to the scattering contribution of Pt two orders of superstructure peaks are observable.

Specular rod measurements (reflectivity) reveal Pt coverage and the height distribution of cluster atoms and graphene (Fig. 2). In-plane linescans provide information on the crystallographic structure and arrangement of the clusters (Fig. 3). The linescan signal is modulated by the cluster shape function and contains therefore strain and size information.

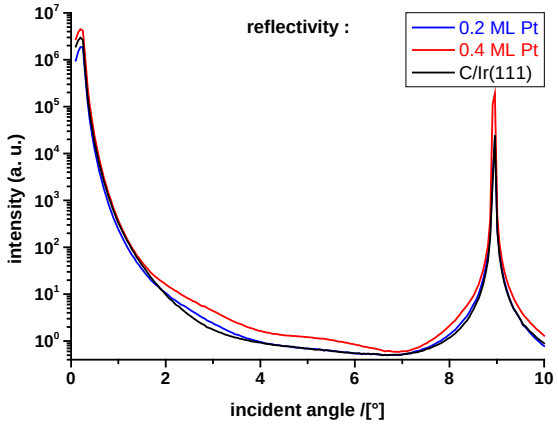

Fig. 2: specular rod for different Pt coverages – the distance of the oscillations reveals the layer thickness.

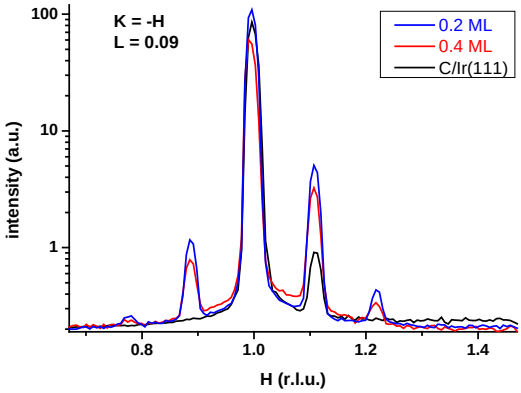

Fig. 3: in-plane linescans disclose superstructure periodicity particle strain and shape (envelop function).

A detailed analysis of the integrated SXRD data is on its way and it will shed light on the average cluster shape and structure depending on gas environment. Starting from that point a detailed investigation of shape, structure and size induced enhanced catalytic activity will be feasible in future research.

[1] J. Coraux, A. T. N'Diaye, M. Engler, C. Busse, D. Wall, N. Buckanie, F. J. Meyer zu Heringdorf, R. van Gastel, B. Poelsema, T. Michely, NJP 11 (2009), 023006
[2] A. T. N'Diaye, S. Bleikamp, P. J. Feibelman, T. Michely, Phys. Rev. Lett. 97 (2006), 215501