Using High-precision STEM Imaging to Measure Local Quantitative Atomic-resolution Strain in Supported Nanocatalysts

Yankovich, A.[1], Nilsson Pingel, T.[1], Jørgensen, M.[1], Grönbeck, H.[1] and Olsson, E.[1]

[1] Chalmers University of Technology, Sweden

Scanning transmission electron microscopy (STEM) is providing new information about the structure and composition of materials, especially since the inception of aberration-correction. For many atomic resolution STEM applications, the data is no longer limited by the image resolution, but by environmental and experimental factors, such as microscope and environmental instabilities, that reduce the caliber of quantitative information. New data science techniques offer solutions to some limitations and allow for higher precision and enhanced signal to noise ratio(SNR) data that is richer in materials information. We use non-rigid registration (NRR) and averaging of STEM image series to improve STEM data quality[1,2]. We have previously demonstrated this techniques usefulness in a number of applications, such as achieving sub-pm precision in single crystals[2], measuring pm-scale atomic column displacements at nanocatalyst surfaces[2,3], enhancing 3D atomic structural information in STEM data of nanoparticles (NPs)[2,4], and improving atomic-scale composition information[5]. In this work, we have extended these techniques to quantitatively extract local strain with atomic resolution[6]. In addition, we have reduced the electron dose needed for high precision from 10^7-10^8 e/Å^2[2] down to 10^4-10^5 e/Å^2 in order to minimize electron beam damage and allow for experiments on more beam sensitive materials. This dose can easily be reduced by a factor of four by truncating the image series with a minor effect on image precision.

We have used these capabilities to study the intrinsic and extrinsic strain behavior of Pt NPs supported on alumina and ceria. High-precision side-view STEM experiments were performed on various NPs and reveal pm-scale crystallographic deformations at the free surfaces, NP-support interfaces, and defects. Figure 1a shows one high-precision image of a decahedral Pt NP with five {111} twin boundaries and the ceria support on zone axis. The interface (Figure 1b) contains periodic dislocations and is composed of a Pt {711} and a ceria {111} facet. The atomic column displacement map (Figure 1c) reveals the major global lattice deformations are along the twin boundaries and the interface. Displacement maps are sufficient for understanding the global NP behavior, but are insufficient for interpreting local lattice deformations that are useful for deducing local materials properties. Atomic-resolution projected strain maps (Figure 2a-c) and angle maps (Figure 2d) better show the local lattice deformations in various crystallographic directions, and can be used to calculate the full 2D strain tensor for each projected unit cell. These strain analysis tools reveal moderate strain of atoms at the free surfaces that can be either expansive or compressive and of varying magnitude depending on whether the site is at an edge, corner, or facet. All of the observed NPs show strong and localized strain at the interface, but the strain appears to primarily originate from surface corrugation for the alumina support and lattice mismatch for the ceria support. To assess the influence of the various types of local lattice strain on the catalytic activity of Pt NPs, we have used the quantitative strain measurements as inputs for a theoretical DFT-based scaling relation kinetic Monte Carlo method[6,7].

References:

[1] B Berkels *et al*, Ultramicroscopy **138** (2014) p. 46.

[2] A Yankovich *et al*, Nature Communications **5** (2014) p. 4155.

[3] A Yankovich *et al*, Advanced Structural and Chemical Imaging **1**(1) (2015), p. 2.

[4] M Yu *et al*, ACS Nano **10**(4) (2016), p. 4031.

[5] A Yankovich *et al*, Nanotechnology **27** (2016) 364001.

[6] T Nilsson Pingel *et al*, Manuscript in preparation (2018).

[7] M. Jørgensen *et al.* ACS Catalysis., **7** (2017) 5054.

Acknowledgements:

The authors acknowledge funding from the Competence Centre for Catalysis hosted by Chalmers University of Technology, the Knut and Alice Wallenberg Foundation, the Swedish Research Council, and the European Network for Electron Microscopy (ESTEEM2).

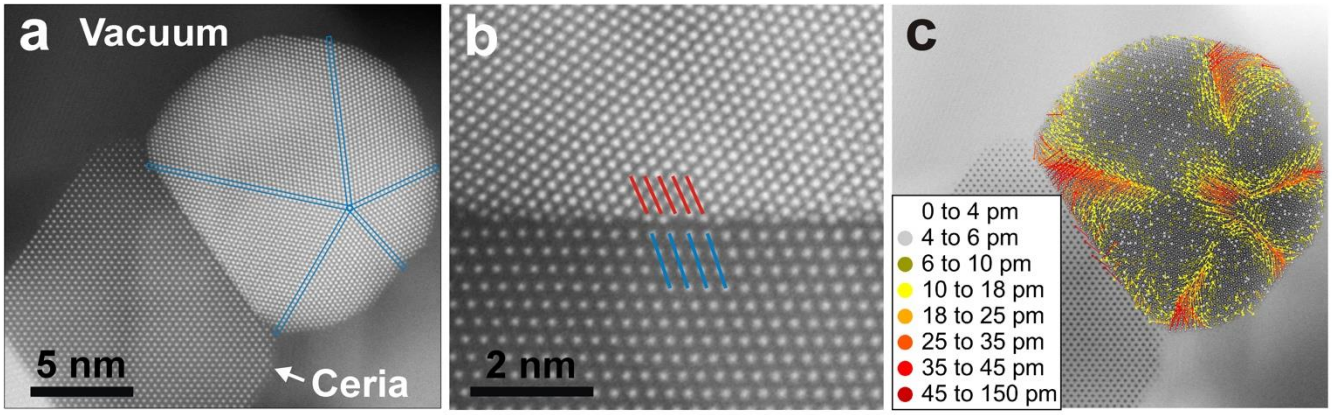

Figure 1. (a) High-precision side-view HAADF STEM image of a ceria-supported Pt NP in the [110] zone axis. Blue rectangles mark the five {111} twin boundaries separating the grains of the decahedron NP structure. (b) Enlarged image of the NP-support interface region in (a) with {111} planes marked on either side of the interface to reveal the presence of an interface dislocation. (c) Atomic column displacement map showing the direction and magnitude of lattice deformations.

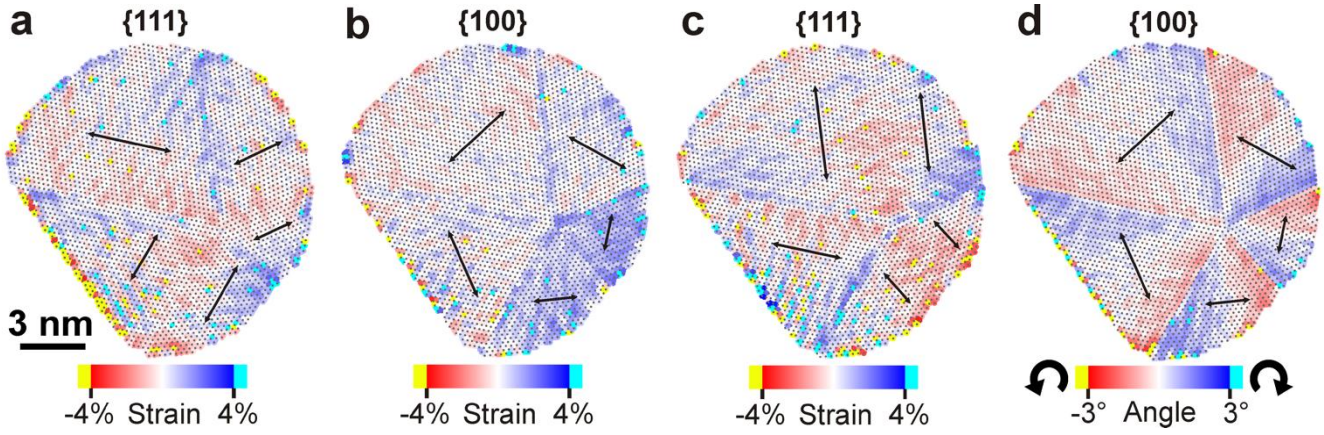

Figure 2. (a-c) Local strain maps and (d) angle map for the labeled crystallographic planes that are marked by black arrows. Red signifies compressive strain and CCW angle rotation. Blue signifies expansive strain and CW angle rotation. Bright yellow and light blue signify large values off the figure color scale.