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Extracting Local Quantitative Atomic-resolution Strain Information from High-precision STEM Data of Supported Nanocatalysts

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Since the advent of aberration-correction around two decades ago, scanning transmission electron microscopy (STEM) has been providing structural and compositional materials information that was previously unattainable. However, for many applications the quality of the STEM data is limited by environmental and experimental factors, such as microscope instabilities and signal to noise ratio, rather than sophisticated instrument capabilities, such as aberration correction. New data science techniques offer the possibility to overcome some environmental and experimental limitations and produce data that contain higher spatial precision and signal to noise ratio, making it richer in materials information. We acquire high-precision STEM data by using non-rigid registration (NRR) and averaging of a high angle annular dark field (HAADF) STEM image series [1,2]. NRR corrects STEM image distortions and enables image averaging and SNR enhancement without the negative effects of the image distortions. The usefulness of this techniques has been demonstrated in a number of applications, such as achieving sub-pm precision in locating atom positions 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], measuring point defect structures, and improving atomic-scale composition information [5].

We have further developed these techniques to allow for local quantitative atomic-resolution strain measurements and apply this toward understanding the intrinsic and extrinsic strain behavior of supported NPs that may help explain their catalytic activity. High-precision side-view STEM experiments (Figure 1a) of various Pt NPs supported on alumina and ceria reveal pm-scale crystallographic deformations at the free surfaces, NP-support interfaces, and defects such as twin boundaries. Atomic column displacement maps (Figure 1b) show the displacement of atom columns from their unstrained position. This representation of lattice deformation is sufficient for understanding the global NP behavior, but it does not directly reveal the local lattice deformations that are more useful for deducing materials properties such as catalytic activity. Atomic-resolution projected strain maps (Figure 1c-e) and angle maps (Figure 1f-h) better show the local lattice deformations in various crystallographic directions. In addition, the full 2D strain tensor can be calculated for each projected unit cell from this data.

These 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. {111} twin boundaries show ~1% lattice expansion perpendicular but not parallel to the boundaries, while {311} twin boundaries show much larger lattice deformations. All NP-support interfaces for the alumina and ceria supports show strong and localized strain near the interface. However, the strain at the alumina support appears to originate primarily from surface corrugation and steps, while for the ceria support it appears to originate from lattice mismatch. To assesses 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].

Minimizing the electron dose used to achieve high-precision STEM data is crucial for characterizing beam sensitive materials such as small metallic NPs. Our first sub-pm STEM results on single crystal materials utilized a large dose of ~10^7-10^8 e/Å^2, while our first measurements of atom displacements of NP surface atoms utilized a smaller dose of ~3x10^6 e/Å^2 [2]. Then efforts to reduce the dose, maintain high precision, and capture a whole NP in the same image resulted in a dose of ~5x10^5 e/Å^2 [3]. Our recent high-precision data of side-view supported NPs were acquired with a further reduced dose of ~10^4-10^5 e/Å^2. This is possible by increasing pixel size, decreasing dwell times, and reducing the STEM beam current. These doses could easily be reduced by a factor of four by minimizing the number of STEM images in the series with only a minor effect on image precision [7][8].

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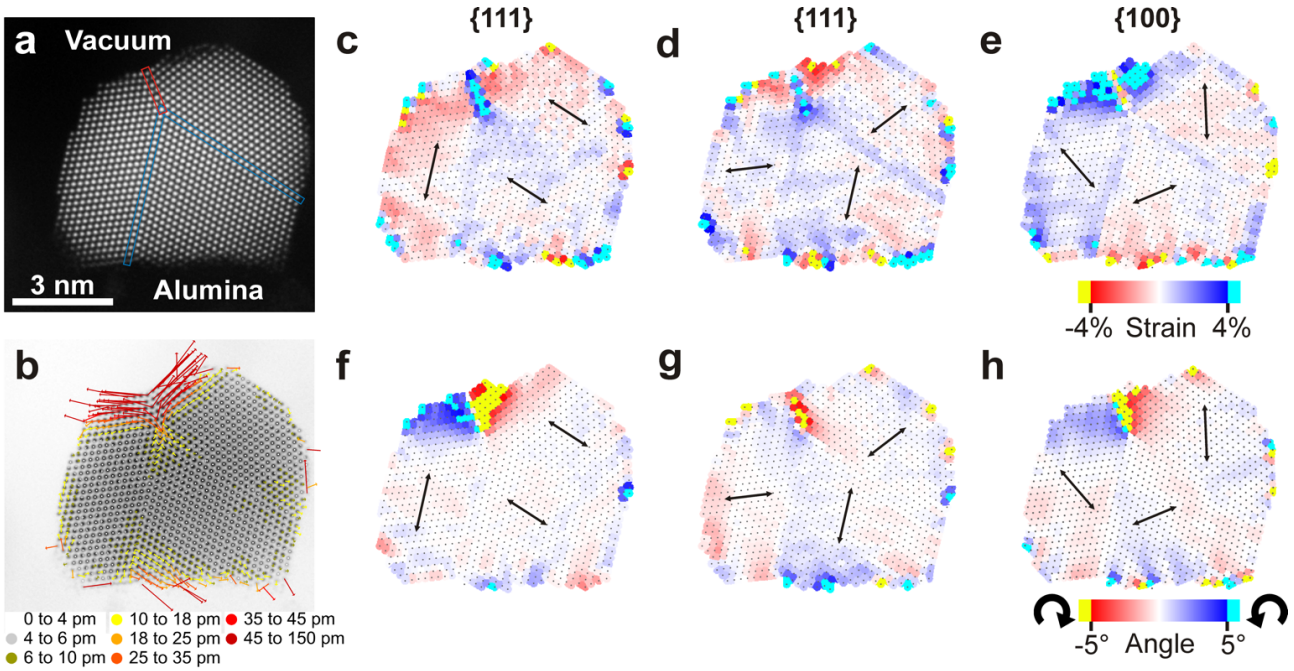

Figure 1. (a) High-precision side-view HAADF STEM image of an alumina-supported Pt NP. Blue and red rectangle mark {111} and {311} twin boundaries respectively. (b) Atomic column displacement map showing the direction and magnitude of deformations. Local strain maps (c-e) and angle maps (f-h) for the labeled crystallographic planes marked by black arrows. Red signifies compressive strain and CW angle rotation. Blue signifies expansive strain and CCW angle rotation. Bright yellow and light blue signify large values off the figure color scale as indicated by the legends.

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