Precise measurement of lattice strain in gold nanoparticles

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Metal nanoparticles have been extensively studied as catalysts, such as fuel cell electrodes and exhaust gas purification. Because of the presence of the surface, the nanoparticles involve a spatial change in atomic distance, lattice strain. It has been reported that the lattice strain affects the catalytic performance [1], so the clarification of lattice strain distribution plays an important role to elucidate the improvement of catalytic performance. Whereas lattice strain has been macroscopically measured as an average value of plural particles by X-ray diffraction in previous works, it is necessary to measure them microscopically to gain deeper insights. In this study, we have measured lattice strain at the atomic level with high precision. In addition, to investigate the factor that determines lattice strain, we have carried out systematic experiments focusing on the relationship between the lattice strain and the aspect ratio (AR) of gold nanoparticles.

Atomic-resolution images of gold nanoparticles were acquired by using high-angle annular dark field (HAADF) imaging with a scanning transmission electron microscope (STEM). The atomic displacements were extracted as deviation from the averaged regular periodicities of atomic column configuration [2]. Lattice strain field corresponds to partially differentiating of continuous atomic displacement field, which requires a continuous function fitted to smoothed atomic displacements. For this mathematical processing, Gaussian process regression based on Bayesian statistics was applied.

Gold nanoparticles with different ARs of approximately 1.0 (NP1), 2.1 (NP2) and 3.6 (NP3) were used in the present study. Figure 1 shows a HAADF image of the NP1, where the incident electrons were illuminated along the crystal orientation of [01-1]. The NP2 and the NP3 have anisotropic rod-shape with its longer axis oriented along [001] (Fig. 2b, c). Statistical fluctuations from the ideal periodic structures of the atomic column positions were less than 4 pm (10^{-12} m) at the central parts of the particles. This value corresponds to ~20% of the pixel size and ~1% of the nearest neighbor atomic distance of gold (~300 pm). Figure 2a-c are lattice strain e_{XX} maps in the direction of the X of NP1-3, where the contraction and expansion strain are represented by negative values (black dots) and positive values (white dots). Figure 2d-f show strain profiles averaged over the central band (4.5 nm width, shown as bracket in Fig. 2d-f). While isotropic NP1 shows ~0.2-0.5% shrinkage strain at both ends, anisotropic NP2 and 3 shows a contraction strain of ~0.2-0.6% at the rod ends and expansion strain of ~0.6% at the rod-hemisphere connected region. Since molecular dynamics (MD) structural relaxation calculations (dashed lines in Fig. 2d-f) showed the same tendency as experiments, it can be concluded that the local strains in nanoparticles depend on the particle shape.

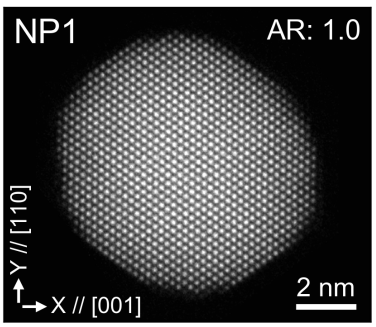

Figure 1. An atomic-resolution HAADF image of a gold nanoparticle with AR=1.0.

[1] *e.g.*, P. Strasser et al., Nat. Chem., vol. 2 (2010), p. 454.
[2] K. Aso, et al., Microscopy, vol. 65 (2016), p. 391.

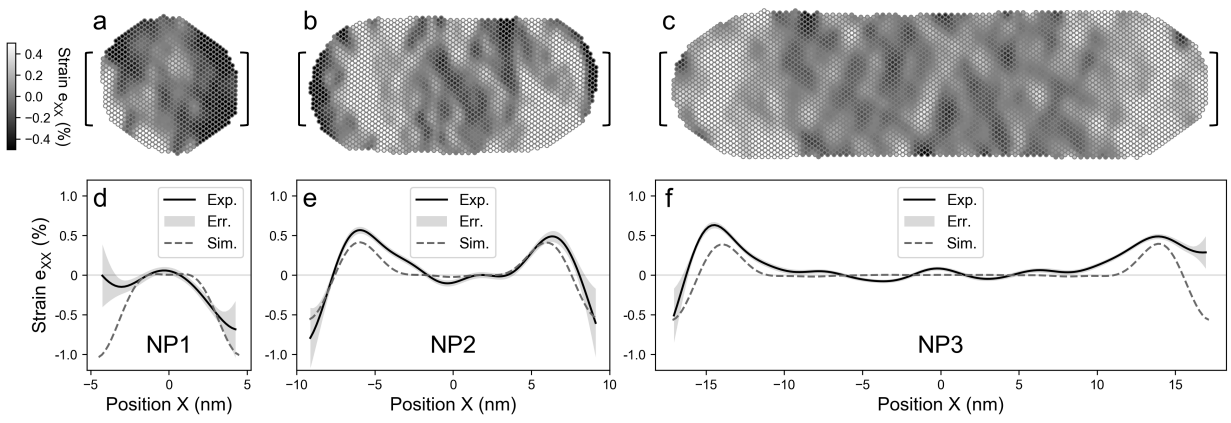

Figure 2. **(a-c)** Lattice strain along X direction map of NP1-3. **(d-f)** Lattice strain profile averaged in the central band indicated by brackets. The label Exp., Err. and Sim. correspond to the experiments, the fit error to the experimental value (95% confidence region) and the MD calculation.