Local lattice strain in gold nanoparticles depending on their outer shapes

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Metal nanoparticles are known to involve lattice strain due to the large specific surface area. It is predicted that the strain depends on the outer shape, or the local curvature of the surface. However, the details of local strain have not been fully understood. Systematic studies of the local strain in nanoparticles and the dependence on the shape is required for optimization of the specific functions, for example, catalytic activity governed by the surface structure [1].

In this study, the local strain in gold nanoparticles with various aspect ratios were characterized experimentally by using atomic-resolution high-angle annular dark field (HAADF) imaging with a scanning transmission electron microscope JEOL JEM-ARM200CF operated at an acceleration voltage of 120 kV.

Figure 1 shows HAADF images of gold nanoparticles with different aspect ratios, such as approximately 1.0(a), 2.1(b) and 3.6(c). The atomic displacement fields were extracted as deviation from the averaged regular periodicities of atomic column configuration [2]. The axial strain e_{xx} toward the X direction of the major axis along [001] is plotted as a function of X positions in Fig. 2. Here e_{xx} (X) was evaluated from an average of 16 planes of (110) at the center of the particle. The spherical particle shows negative e_{xx} (X) in both sides near the surface in Fig. 2(a). It indicates that inward contraction takes place in the spherical particle. The experimental e_{xx} (X) curve is not symmetrical in contrast to the result of molecular dynamics (MD) simulation for an ideal sphere, since the shape is slightly deformed from the ideal. It is therefore suggested that the local strain in a nanoparticle sensitively depends on the local curvature of the surface. In contrast, positive e_{xx} (X) fields appear in tip portions of both sides in nanorods, as shown in Fig. 2(b) and (c). The positive e_{xx} (X) characterizes tensile strain toward outer direction along the longer axis. However, the both tip ends involve negative e_{xx} (X), as noticed in the MD simulations in (b) and (c) as well as the experimental result in (b), similarly to the sphere case seen in (a). An MD simulation on a simple cylindrical rod without semi-spherical tips, or with flat ends, indicates outward displacements at surfaces of ends. It would be resulted from the inward contraction along the radial direction due to the cylindrical curvature. Therefore, the positive e_{xx} (X) fields in tip portions in the nanorods shown in Fig. 2(b) and (c) are also considered to appear owing to the inward contraction along the radial

direction in the cylindrical main body part. At the end portions, the spherical curvature of the tip surface results in the opposite inward contraction.

[1] P. Strasser et al., Nat. Chem., vol. 2 (2010), p. 454.

[2] K. Aso, et al., Microscopy, vol. 65 (2016), p. 391.

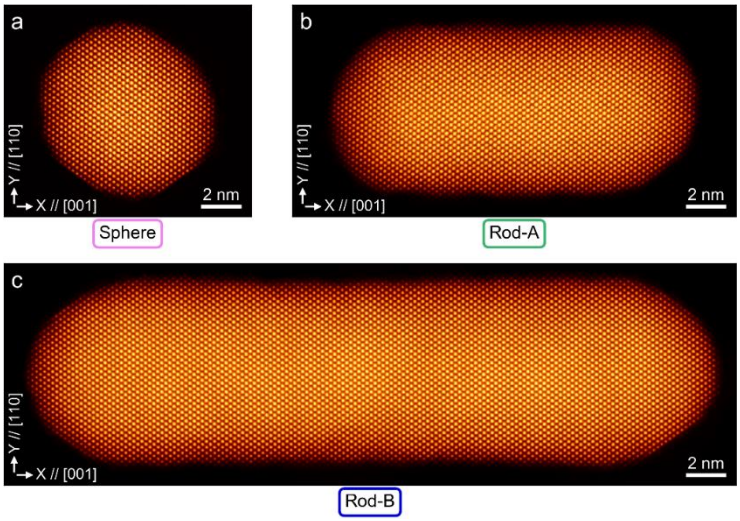

Fig. 1: HAADF images of gold nanoparticles. (a) Sphere with aspect ratio of 1.0. (b) Rod with aspect ratio of 2.1 (rod-A). (c) Longer rod with aspect ratio of 3.6 (rod-B). The diameters of the three are almost same to be 9 nm.

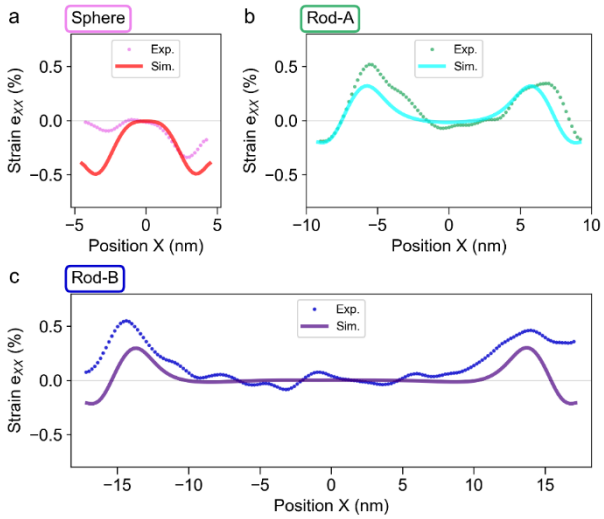

Fig. 2: Plots of 1D strain e_{xx}, which show lattice expansion or contraction along X // [001]. The plot (a), (b) and (c) corresponds to the particles in the Fig. 1(a), (b) and (c), respectively.