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doi:10.1017/S1431927619011346
Microsc. Microanal. 25 (Suppl 2), 2019

Lattice Tetragonality and Local Strain Depending on Shape of Gold Nanoparticles

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Metal nanoparticles have attracted many research interests and are applied to various functional materials, such as optical devices, catalysts and so on. It is well known that lattice strain in nanoparticles affects the functional properties through local variation in the electron state [1]. It is quite important to understand basic mechanisms to cause the local strain in nanoparticles. The present study was aimed to analyse systematically the local lattice strains in gold nanorods as a function of the aspect ratio by HAADF-STEM atomic resolution observations.

Atomic resolution HAADF-STEM observations of gold nanorods were carried out using a JEM-ARM200CF at an acceleration voltage of 120 kV. Plural HAADF-STEM images of a nanorod were obtained under fast probe scanning (1.0 μsec/pixel) to suppress the image distortion due to specimen drift and they were superimposed to improve the S/N ratios of the images. Figure 1 shows atomic resolution HAADF images of single-crystalline gold nanoparticles observed along $[\bar{1}10]$ crystal direction. The [001] and [110] directions of the nanoparticles are set to the lateral direction x and the longitudinal direction y of the images, respectively. We observed three nanoparticles which were the almost same in width as ~9.0 nm but were different in length, or in the aspect ratio (AR) such as 1.0 (Fig. 1a), 2.1 (Fig. 1b) and 3.6. Hereinafter they are referred to as NP1, NP2 and NP3, respectively.

The coordinates of atom columns were determined from 2D Gaussian functions fitted to the image intensity profiles. The inter-columnar distances d_{110} and d_{001} measured from the coordinates were distributed around the mean values of $\bar{d}_{001}$ and $\bar{d}_{110}$ with the standard deviations less than 4 pm. The ratio $c/a = \bar{d}_{001}/\sqrt{2}\bar{d}_{110}$ decreases from one with the aspect ratio, as shown in Fig. 2. It indicates the crystal lattice is distorted to be tetragonal in the rod-like nanoparticles. To confirm the tetragonal distortion, molecular dynamics (MD) simulations were conducted for the corresponding shapes of gold nanoparticles using LAMMPS with an Embed Atom Method (EAM) potential [2,3]. The projected positions of $[\bar{1}10]$ atom columns in the models relaxed in the MD simulations also show the tetragonal deformation of crystal lattice corresponding well to the experimental results, as shown in Fig. 2. It is suggested that the tetragonality comes from the anisotropic shape of the rod-like nanoparticles.

Local displacements of atom columns were evaluated on the basis of the averaged periodicity in the inner area of the particles, and were smoothed into the displacement functions via Gaussian Process Regression based on Bayesian statistics. Then the local strains $e_{xx}(x,y)$ and $e_{yy}(x,y)$ were evaluated. The surface lattice contraction was recognized in the three nanoparticles. It is explained in terms of surface tension due to less number of coordinating atoms at the surface [4]. It should be noticed in Fig. 3 that positive $e_{xx}(x,y)$ about ~0.7 %, or dilatation strain along x-direction, occurs localized in the tip parts in the nanorods of NP2 and NP3 [5]. The MD simulations were also confirmed to reproduce well the localized dilatation strain along the long axis in the rod shape models [6].

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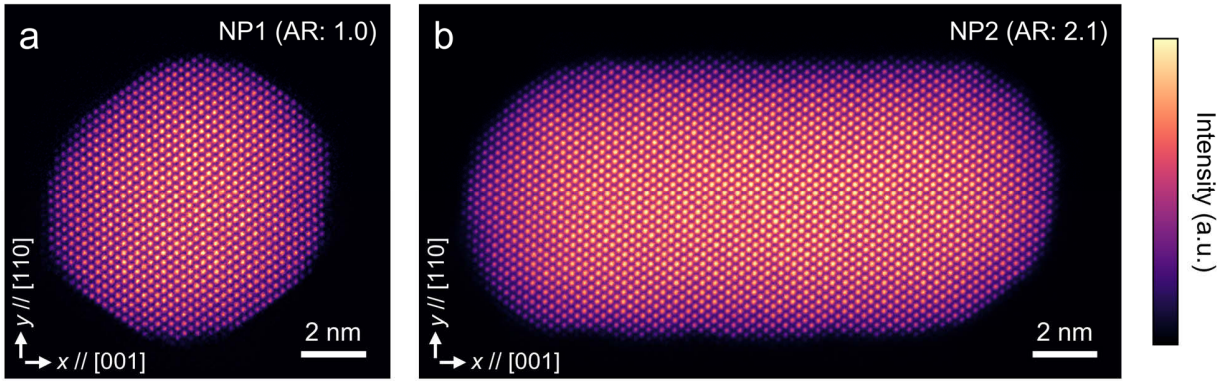

Figure 1. Atomic resolution HAADF images of gold nanoparticles with the similar width of ~9 nm, but different ARs of 1.0 (a) and 2.1 (b), which are referred as NP1 and NP2, respectively [6].

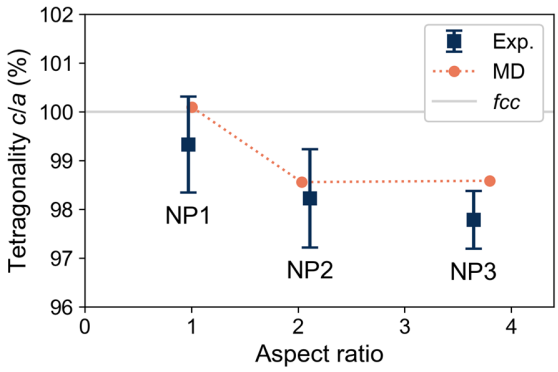

Figure 2. Tetragonality *c*/*a* as a function of the aspect ratio of the nanoparticles [6].

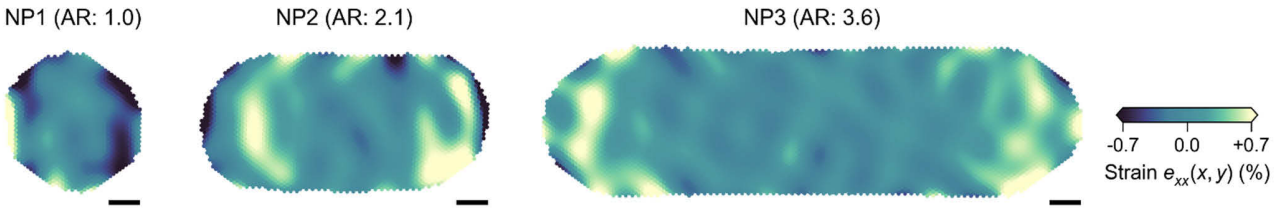

Figure 3. Strain $e_{xx}(x, y)$ 2D maps of the gold nanoparticles. The scale bars correspond to 2 nm [6].

https://doi.org/10.1017/S1431927619011346 Published online by Cambridge University Press