Quantitative High-Resolution TEM/STEM and Diffraction

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Surface-near lattice relaxation in single crystalline Au nanoparticles

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Whereas bulk gold is one of the most noble metals, nanoparticles of Au show high catalytic activities and are presently of large interest for applications in fields such as biomedicine, heterogeneous catalysis, and plasmonics, to name a few. These modified properties of Au at small sizes originate from both an enhanced surface-to-volume ratio and the fact that its physico-chemical properties critically depend on the different local atomic environments of Au atoms on different facets. Consequently, the properties of Au particles depend strongly on the type of faceting and thus on the nanoparticles' shape.

In this report we used aberration-corrected transmission electron microscopy to study directly the lattice structure of single crystalline Au nanoparticles. Due to the delocalization-free imaging a direct measurement of atom position and lattice constants even at the surface layers is possible. It was recently reported that decahedral Au particles exhibit an expansion of the lattice along the (111) direction close to the particle surface [1]. In nanoparticles of binary metallic alloys similar surface-near lattice expansions were attributed to segregation phenomena [2, 3, 4].

Au nanoparticles with a mean diameter of 6.9 nm and a narrow size distribution are prepared by inert gas condensation. The particles nucleate and growth from a supersaturated vapour provided by DC magnetron sputtering from an Au target at a continuous flow of Argon at a pressure of 1.5 mbar. The particles are subsequently ejected into high vacuum through differential pumping and deposited on carbon-coated copper grids in the deposition chamber. Ar with a purity of 99.999% Ar is further purified by means of an oxygen getter prior to feeding it to the sputter gun. Whereas this process produces predominantly icosahedral particles, single crystalline Au nanoparticles were obtained upon modifying the surface (free) energies of Au by adding 5 vol.% oxygen to the process gas [5].

The atomic structure of the likewise prepared Au nanoparticles is investigated by means of aberration-corrected HRTEM using a FEI Titan^3 80-300 microscope. Fig 1a. shows an exemplary HRTEM image of a single crystalline Au nanoparticle as seen along the [011] zone axis. In Fig 1b, the resulting profile of the lattice parameter along the <100> direction is shown after averaging over 52 surfaces, pointing to a significant decrease of the lattice spacing upon approaching the surface. This surface-near lattice compression on (100) facets is due to the so-called smoothing effect at surfaces [6]. In order to properly account for artefacts in the measured lattice relaxation due to lens aberrations, HRTEM contrast simulations of model particles are performed. The simulations show that the effect of aberrations is small compared to errors imposed by the amorphous carbon support. In addition to the experimental investigations, molecular dynamic (MD) simulations are conducted to investigate the lattice relaxation in Au model nanoparticles (s. Fig. 2b).

Since the elastic constants of Au are well known, the effective surface stress can be estimated from the experimentally determined lattice relaxation using a simple thin film model which is also applicable to nanoparticles [7]. The resulting surface stress of the (100) and (111) surfaces will be presented and discussed in comparison with results from MD-simulations.

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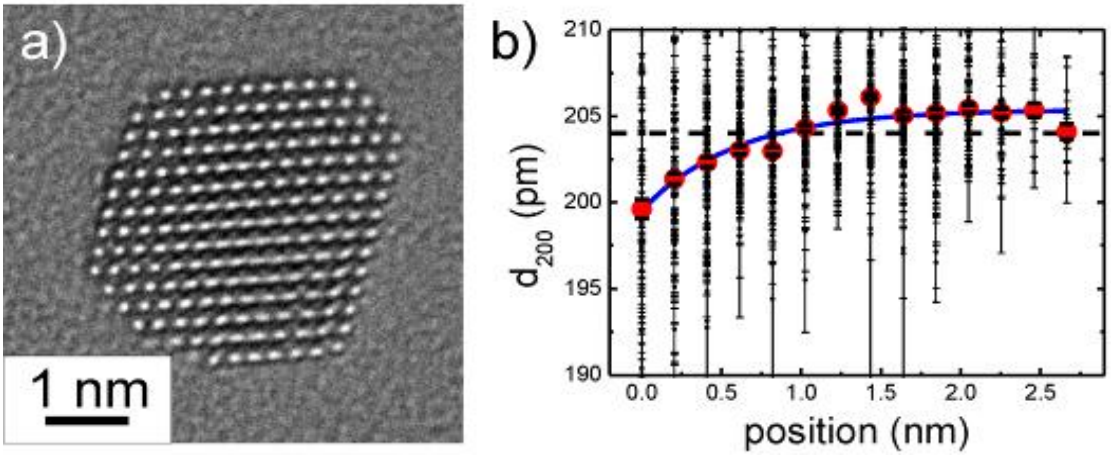

Figure 1. a) Exemplary HRTEM image of a single crystalline Au nanoparticle as seen along a [011] zone axis. b) Measured lattice relaxation along the <100> direction after averaging over 52 surfaces.

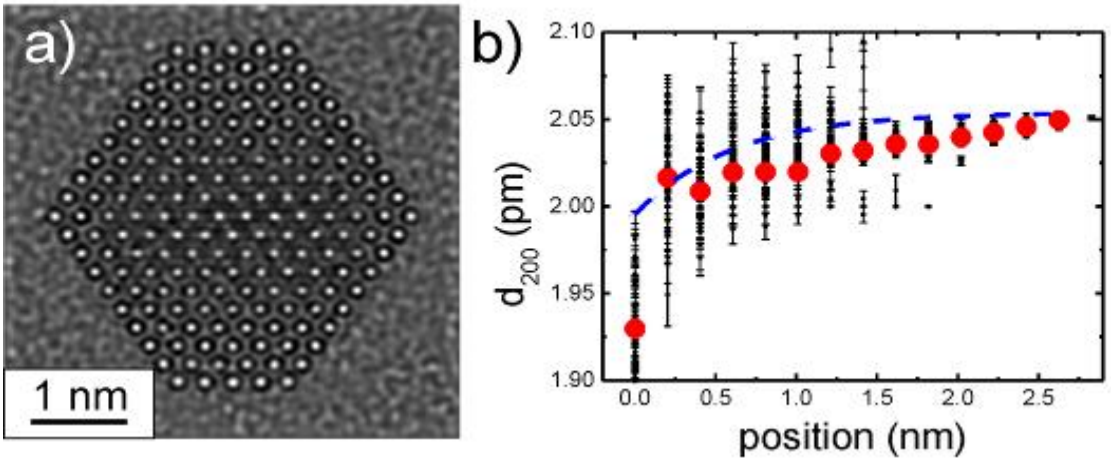

Figure 2. a) Simulated HRTEM image of a single crystalline Au nanoparticle as seen along a [011] zone axis. b) Measured lattice relaxation for model Au particles after structural relaxation by means of MD simulations. The blue line represents experimental lattice relaxation shown in Fig. 1b.