Shape-dependent chemical-induced strains in gold nanocrystals

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The especially strong bond that forms between sulphur and gold is the basis for numerous self-assembled metal-organic devices. Gold is a noble metal towards almost all environmental species with the exception of sulphydryl-containing species, such as thiols, which readily form monolayer coatings of high stability. The structure of the sulphur-gold interface is remarkably complex. A recent crystallographic study of a monodispersed $Au_{101}RS_{44}$ gold nanoparticle-thiol complex revealed a crystalline core particle coated with a shell of 1nm thickness with enlarged Au-Au spacings and interpenetration of the thiol ligand species. Far from having a well-defined boundary between the metal and the organic sides of the interface, this unusual complex was found to contain a mixed compound layer as its lowest energy configuration [1]. We report the structure of facetted gold nanocrystals before and after coating with propane thiol, C_3H_7SH, one of the simplest SAM-forming organic molecules. As formed by dewetting a film from a silicon wafer substrate, the shape of our nanocrystals is found to be spherical with {111} facets, as expected from the theory of Equilibrium Crystal Shapes (ECS). The structure of a single 300nm-diameter particle was measured using the powerful technique of Coherent X-ray Diffraction (CXD), which is highly sensitive to the pattern of internal strains within the nanocrystal [2]. Our results show that the strain is profoundly modified by the thiol adsorption. We are able to establish the magnitude of this stress difference using finite element calculations and suggest a model involving preferential reaction on the curved regions of the crystal surface.

[1] "Structure of a thiol monolayer-protected gold nanoparticle at 1.1 angstrom resolution" P. D. Jadzinsky, G. Calero, C. J. Ackerson, D. A. Bushnell and R. D. Kornberg, Science 318 430-3 (2007)
[2] "Coherent Diffraction Imaging of Strains on the Nanoscale", I. K. Robinson and R. Harder, Nature Materials 8 291-298 (2009)

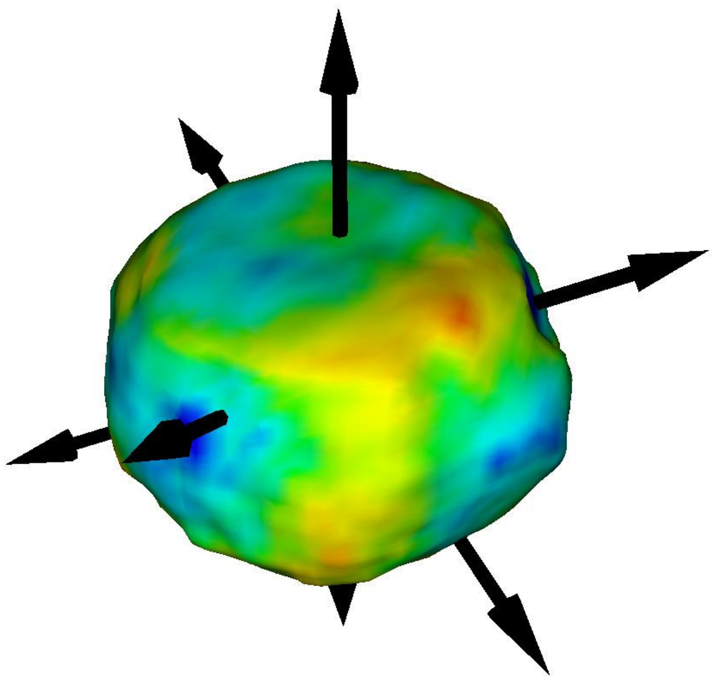

Figure showing the shape of the crystal and the phase found on the surface of the particle before dosing on a colour scale from -1 (blue) to +1 radian (red). The arrows indicate the {111} directions; the substrate surface normal direction is parallel to the large facet at the top of the figure. The (111) Q-vector used for imaging is on the right hand side. The phase is the projection of the crystal's displacement field onto this direction [2].