Time-resolved study of a silver nanoparticle self-assembly into a 3D nanocrystal

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Self-assembly of monodisperse colloidal nanoparticles during the solvent evaporation is an attractive and simple way for fabrication of highly-ordered nanocrystals. To date, colloidal nanoparticles were found to form three-dimensional (3D) ordered structures with hexagonal-close packed (HCP), face-centered cubic (FCC) or body-centered cubic (BCC) symmetry. However, control of the self-assembly process that affects the nanocrystal perfection or interparticle distance is still a big issue. Here we report on a time-resolved study of the self-assembly of silver nanoparticle self-assembly performed at the micro- and nanofocus X-ray scattering beamline (P03) at PETRA III. High photon flux with the spot size of 40×20 μm² and fast PILATUS 300K detector P03 allow in-situ investigation of the nanocrystal formation after the drop casting. The final GISAXS pattern of the dried nanoparticle droplet is shown in Fig. 1a. The pattern reveals the face-centered cubic lattice of nanoparticles with the [111] preferred orientation, i.e. the ABC type of stacking close-packed nanoparticle monolayers with hexagonal symmetry. The lattice constant of the nanocrystal was determined as \( a=11.9 \) nm that gives the interparticle distance in the hexagonal layers \( a/\sqrt{2}=8.4 \) nm and the interlayer distance between the adjacent layers \( a/\sqrt{3}=6.9 \) nm. The temporal series of GISAXS patterns was analyzed following the paracrystal model that get a time-resolved picture of the nanocrystal formation. The paracrystal model considers correlation between the positions of neighboring nanoparticles that results in a cumulative type of disorder. Consequently, the Bragg peak width grows linearly with the square of the diffraction order. Therefore we performed a linear fit of such a dependence for the 111, 222, 333 Bragg peaks in each GISAXS pattern of the series. The slope of the linear fit was recalculated into a distortion parameter in the [111] direction (surface normal) that provides information on the stacking quality. A vertically and laterally ordered nanoparticle structure is observed in GISAXS patterns already from the early stages of the solvent (toluene) evaporation. Obviously, well diluted silver nanoparticles with hydrophobic organic surfactant shell (oleic acid and oleylamine) have high mobility to re-arrange as documented in Fig. 1b by initial oscillations of the paracrystal distortion parameter. After some 100 s we observe a sudden temporary improvement of the nanoparticle order (black arrow in Fig. 1b). Here, majority of the organic solvent is already evaporated and the volume for the nanoparticle re-arrangement is strongly reduced but still large enough to allow the nanoparticles to keep their full hydrodynamic size and to organize themselves into a well ordered 3D structure. Finally, the rest of the solvent giving mobility to the nanoparticles via their surfactant shell is evaporated and the conditions for the 3D nanocrystal formation are worsened (180-400 s). Here we observe a partial increase of the disorder parameter that levels off at a saturated value of 4 %.

![Figure 1](image.png)

Figure 1 a) Final GISAXS map of nanoparticle crystal. b) Temporal evolution of crystal disorder.