

Revealing 3D Colloidal Supercrystal Growth Conditions by combining *in-situ* Synchrotron SAXS and MC-simulations

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Colloidal supercrystals using designed nanocrystals (NCs) as artificial atoms offer the opportunity for realising solids with tailored properties [1]. The brilliant beams of modern synchrotron sources allow to study *in-situ* many wet chemical processes used e.g. for the synthesis of colloidal nanocrystals NCs [1], but allow also to follow *in-operando* the electrochemistry within nanostructures of working devices [2,3].

In this work we studied by *in-situ* small angle x-ray scattering (SAXS) the colloidal crystallization by diffusion of a non-solvent into the colloidal dispersion of faceted Bi NCs with around 22 nm size [4]. The SAXS patterns of the NC ensembles were recorded below the NC-solvent/non-solvent interface at the SAXS beamline at the synchrotron ELETTRA. Hence, we could follow the crystallization process as a function of time and thus the non-solvent concentration (see Fig. 1a). Furthermore, by measuring at different positions below the interface the solvent/non-solvent *gradient* could be varied and thus its influence on the crystallisation process studied.

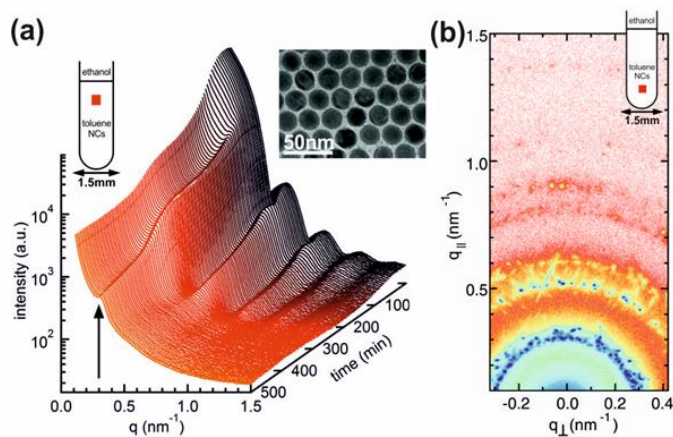


Fig. 1 (a) *In-situ* 1D SAXS patterns plotted over the scattering vector q and time of the self-assembly of colloidal supercrystals using Bi-NCs (see inset TEM) as building blocks. The beam was positioned only few millimetres below the non-solvent/sovent interface. (b) 2D reciprocal space map showing the powder diffraction pattern of many micrometer sized individual supercrystals. The 2D SAXS patterns we recorded several millimetres away from the interface. The *in-situ* studies have been performed at the synchrotron ELETTRA at the Austro-SAXS beamline

Many sharp Bragg peaks in the 2D reciprocal space map proved the formation of well-ordered superlattice structures at the capillary wall. The 2D peak patterns can be indexed using a single fcc crystal structure with a lattice constant of around 24 nm. The crystallite size and the orientation of these supercrystals with respect to the capillary wall, however, differ for different growth conditions: Close to the interface smaller crystallites with hcp stacking faults and a fixed orientation to the glass wall are found, whereas far away from the interface random orientated 3D supercrystals with micrometer size are detected.

To test, if this experimentally obtained supercrystals structure is related to the equilibrium superstructure of our densely packed faceted Bi-NCs we theoretically model the crystallization using Monte Carlo (MC) simulations [5, 6]. As an input we need the exact 3D shape of the individual Bi NCs. For obtaining this shape we developed a new method to retrieve the mean particle shape of slightly polydisperse nanoparticles by advanced SAXS analysis methods [7]. The resulting shape deviates significantly from a sphere and can be described by a strongly faceted ellipsoid related to the rhombohedral crystal structure of Bi. This resultant mean shape was used for the theoretical modelling of the crystallisation. We found that the simulated and experimental derived structure factors match very well.

Furthermore, combining SAXS data and MC simulations revealed that besides a long range positional ordering also an *orientational ordering* of the Bi-NCs exists, i.e., an global parallel alignment of the large NC surface facets [6]. Thus we are able to link the supercrystal structure of 3D free standing nanocrystal solids via the NC-shape to the atomic Bi NC structure.

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