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Crystal Structure and Defect Analysis of Colloidal Supraparticles by Lab-Based X-ray Microscopy

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In this study, we present a systematic analysis routine for deciphering the crystallographic and defect structure of self-assembled colloidal clusters by nano X-ray microscopy (nano-XRM). The routine uses a multi-axis tilting stage for precise orientation and imaging of colloidal clusters along low-index crystallographic projections. This enables a unique identification of the crystal structure and symmetry of colloidal clusters as well as comprehensive analysis of crystallographic defects, including stacking faults, twin boundaries and lattice dislocations. The nano-XRM investigation of the inner structure of colloidal clusters is correlated with scanning electron microscopy (SEM) of the cluster surface and optical microscopy (OM) of structural color effects. Finally, the formation mechanism of colloidal clusters and their defects is discussed with the help of event-driven molecular dynamics (MD) simulations.

Self-assembled colloidal clusters are formed from spherical polystyrene primary particles (PP) (230 nm – 500 nm in diameter) in water droplets via a slow evaporation process. The final structure is determined by the total number of PP, the droplet drying speed, and random nucleation events. Corresponding "magic number" structures exist when the clusters form a closed shell with a size-specific crystalline arrangement [1]. While the clusters are spherical and PP are in face-centered cubic (FCC) lattice, three types of global symmetry, multi-twinned icosahedral, decahedral, or single-crystalline octahedral clusters are formed (Figure 1 and 2). The clusters often contain entropy-driven structural defects such as incorporated amorphous regions [1], stacking faults, twin boundaries and dislocations (Figure 1a) similar to those found in atomic crystals and nanoparticles.

The closed-packed periodic structure in the colloidal clusters acts as a Bragg-diffracting photonic crystal that can be investigated under reflective OM and UV/Vis spectroscopy (Figure 2a). Their faceted surface can be investigated by SEM (Figure 2c). To characterize especially the inner structure in more detail and in three dimensions (3D), in previous studies, we utilized transmission electron microscopy (TEM) combined with electron tomography (ET) and X-ray nanotomography (Nano-CT) [1-2]. To identify and investigate the colloidal clusters consisting of PP with few hundred nanometer diameters, lab-based nano-XRM (ZEISS Xradia 810 Ultra) is ideally suited, as it provides a spatial resolution down to $(50\ \text{nm})^3$ to resolve the PP and a field of view up to $(64\ \mu\text{m})^2$ to image large clusters. Zernike phase contrast is the chosen imaging mode to reveal the arrangement of the low-absorbing polystyrene PP for precise crystal structure analysis. Using full 3D tomography, every single particle position can be accurately registered in Nano-CT reconstructions after segmentation (see Figure 1c or ET examples in

[3]), which is a very robust and comprehensive approach and also works for amorphous non-periodic particle arrangements. For clusters with high internal crystallinity, a faster and more versatile strategy is to take individual transmission nano-XRM 2D images along specific low-index zone axes of the cluster, where the PP are aligned along columns and can clearly be distinguished already in single projections, as demonstrated in Figures 1a, b and 2e.

In this study, we mainly focus on the latter approach, applying direct transmission imaging for the structural analysis of decahedral and octahedral clusters. Both cluster types contain at least one specific symmetry axis (low-index crystallographic zone axis) with characteristically-aligned stacks of particles. The developed multi-axis tilting approach (cf. Figure 1e), which integrates additional tilt stages into the standard XRM setup, enables the analysis of defects, such as stacking faults, twin boundaries and dislocations if oriented edge-on in the nano-XRM images (Figure 1a).
After a precise orientation of a decahedral colloidal cluster, our analysis clearly reveals the unique 5-fold twinned symmetry (Fig. 1a). Although, the projected structure looks astonishingly similar to that of decahedral nanoparticles imaged with high resolution TEM [4] concerning symmetry, twinning at grain boundaries, stacking fault and dislocations. However, in a much larger length scale than atoms, the colloidal PP are subjected to different driving forces and hence formation mechanism, resulting in vacancies in the cluster's 5-fold center that are rarely observed in nanoparticles.
Another application of the multi-axis tilting approach is the detailed investigation of single-crystalline octahedral clusters. Figure 2 illustrates the multimodal and correlative OM-SEM-XRM approach for the identification and structural investigation of such supraparticles. An ensemble of polydisperse supraparticles is first screened in OM and SEM for octahedral (as well decahedral) clusters. The crystal structure as well as the approximate orientation of the cluster (on the SiN window) can be deduced already from the structural color appearance in OM (Figure 2a, c) and further verified from the surface facets of the PP in SEM (Figure 2b, d). The selected supraparticle with known approximate orientation can then be retrieved in nano-XRM and precisely oriented using the multi-axis tilting method (Figure 2e), which completes the multimodal and correlative microscopy approach. By orienting the supraparticles into different low-index zone axes like, e.g., <111> (Figure 2e), <110> and <100> we are able to verify the FCC structure and uncover crystal defects. In return, surface facets and symmetries can be compared to the SEM and OM images, respectively, from the acquired nano-XRM tilt series.

In conclusion, we report on a correlative microscopy study focusing on X-ray transmission imaging of colloidal supraparticles to investigate crystal structure and defect formation complemented by event-driven MD simulations (cf. Figure 1d) [6].

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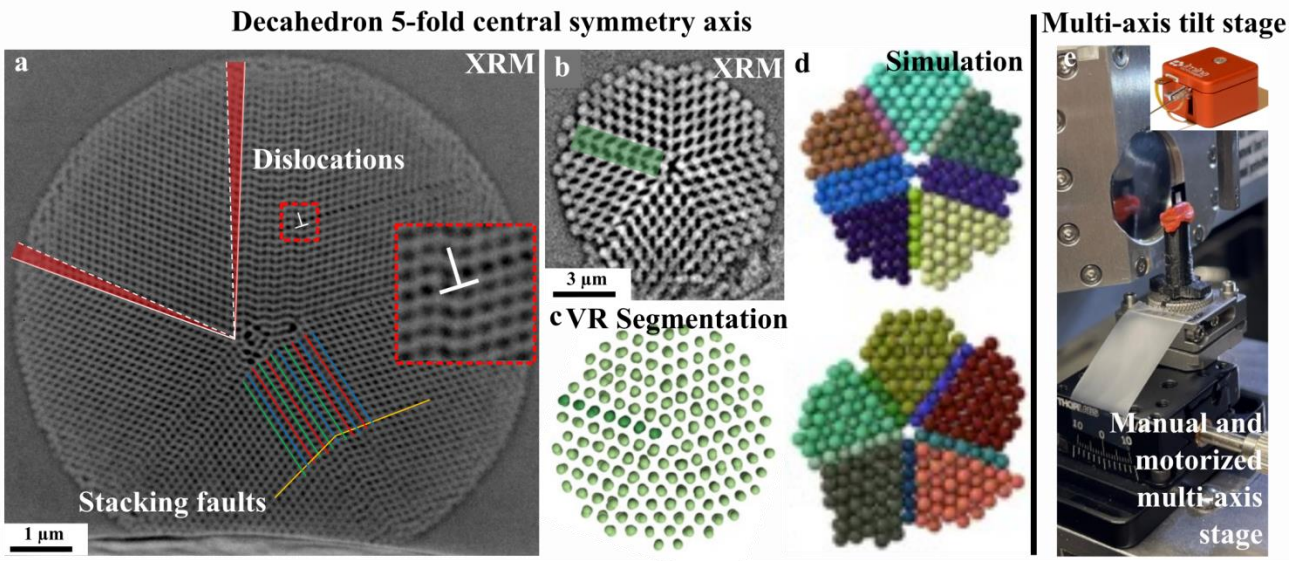

Figure 1. (a) Inverted bright-field XRM image of a decahedral colloidal cluster viewed along the 5-fold twinned symmetry axis aligned using our multi-axis tilting approach to reveal the inner defect structure. Apart from the twin boundaries stacking faults (colored stripes) and individual dislocations (inset) are imaged edge-on in this projection enabling their detailed characterization. These defects partly relax mechanical strain associated with the well-known closure error [5] of the five-fold twinned structure (red triangular regions). (b-d) Smaller decahedron with single stacking fault: (b) Single XRM image in projection along <110> axis and (c) Nano-CT 3D reconstruction segmented by virtual reality (VR) procedure. The stacking fault at one twin boundary is already revealed in (b) and highlighted in (c) as dark green spheres. (d) MD simulations of a supraparticle arrangement with an equal number of primary particles are employed to understand the evolution of a stacking fault upon a relaxing structure. (e) Development of a tilting approach for precise orientation and positioning of supraparticles using a manual or motorized multi-axis stage in the lab-based XRM instrument ZEISS Xradia 810 Ultra.

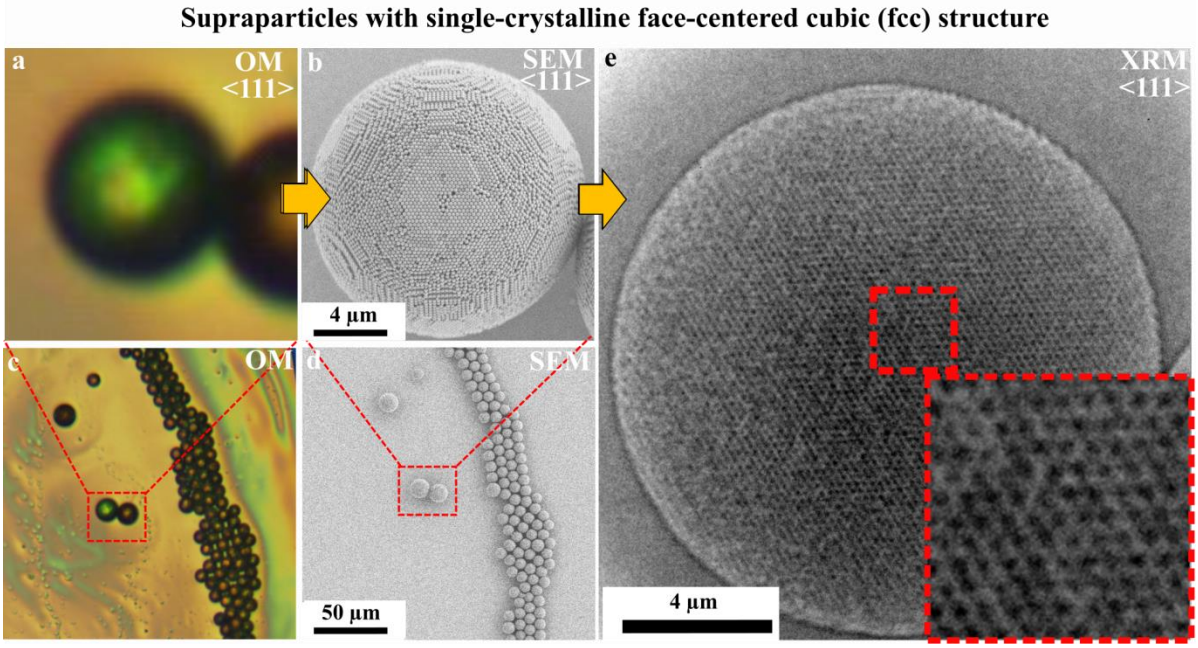

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Figure 2. Correlative OM, SEM and XRM of octahedral supraparticle with single-crystalline FCC structure viewed along <111> zone axis. (a-d) Firstly, the most prominent and characteristic structural details of the supraparticles like color, size, ordering and surface facets are determined by OM and SEM and, subsequently, (e) a detailed crystallinity and defect analysis is pursued using nano-XRM imaging. The inverted bright-field phase-contrast XRM image (magnified in inset) reveals the aligned primary particle columns viewed along <111> zone axis fitting FCC crystal structure (bright contrast: primary particle columns).

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