In Situ Nanofocused Microsecond XPCS Enables Spatiotemporal Mapping of 8 nm-diameter Nanoparticle Diffusion During Mesocrystal Assembly

Leonardo Oliveira[1], Maik Kahnt[2], Jesper Wallentin[3], Klara Suchan[3], Matheus Ferreira[3], Simon Liedtke[3], Iason Andronis[4], Jake Hardy[3], Martin Trulsson[3], Petter Persson[3], Foivos Perakis[4], Dmitry Baranov[3]

[1] *Lund University & Max IV Laboratory, Sweden*
[2] *MAX IV Laboratory, Lund University, Sweden*
[3] *Lund University, Sweden*
[4] *Stockholm University, Sweden*

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Nanoparticles (NPs) can self-assemble into highly ordered mesocrystals, in which long-range interparticle correlations give rise to collective phenomena such as superfluorescence. The degree of ordering critically determines the extent of these collective effects. NP diffusivity is decisive for whether ordered assembly or kinetic disordered arrest occurs but has remained challenging to study experimentally. X-ray photon correlation spectroscopy (XPCS) correlates coherent speckles between rapidly acquired frames to quantify particle diffusion. However, applying XPCS to studies of small NPs, in our case 8 nm CsPbBr , has been out of reach due to the fast dynamics and weak scattering.

We address this with in situ XPCS combining three recent advances: a fourth-generation synchrotron (MAX IV) providing ~100× higher coherent flux than third-generation sources, a nanofocused beam (70 nm) enabling spatially resolved measurements and enhanced contrast, and a prototype detector operating at 120 kHz frame rate giving access to microsecond dynamics. Together, these enable direct, spatiotemporally resolved quantification of NP diffusivity simultaneously with the evolving SAXS signal and local volume fraction throughout evaporation.

We observe a 30-fold slowdown of collective dynamics from 3 µs to 80 µs at volume fractions ~8%, far below geometric close-packing, driven primarily by hydrodynamic suppression rather than thermodynamic clustering. Spatial mapping reveals two distinct pathways. Regions up to 100 µm below the evaporation front maintain sufficient diffusive mobility for ordered mesocrystal formation, while regions further down undergo premature agglomeration and kinetic arrest. Our results establish hydrodynamic interactions as the decisive factor governing pathway selection in evaporative self-assembly and provide direct design criteria for improving mesocrystal yield through tailored solvent and ligand choice. More broadly, they demonstrate nanofocused XPCS as a powerful spatially resolved probe of sub-10 nm NP dynamics in complex, evolving colloidal environments.