

In-situ SAXS / WAXS coupled with UV-Vis spectroscopy for the time-resolved investigation of nucleation and growth of lead halide perovskite nanocrystals

N Dengo^{1,2}, F Bertolotti¹, D N Dirin^{3,4}, S C Boehme^{3,4}, M Kotyrba^{3,4}, P Rikard^{3,4}, M V Kovalenko^{3,4}, A Cervellino⁵, N Masciocchi¹, and A Guagliardi⁶

¹Dip. di Scienza e Alta Tecnologia and To.Sca.Lab, Università dell'Insubria, Como, Italy. ²Dip. di Scienze Chimiche, Università di Padova, Padova, Italy ³Dept. of Chemistry and Applied Biosciences, ETH Zürich, Zürich, Switzerland. ⁴Empa-Swiss Federal Lab.s for Mat. Science and Technology, Dübendorf, Switzerland. ⁵SLS, Laboratory for Sync. Radiation-Condensed Matter, Paul Scherrer Institut, Villigen, Switzerland. ⁶Istituto di Cristallografia and To.Sca.Lab, CNR, Via Valleggio 11, I-22100 Como, Italy.

nicola.dengo@uninsubria.it

Colloidal lead halide perovskite (LHP) nanocrystals (NCs) are currently considered the next-generation quantum dot (QD) materials due to their exceptional optical properties and straightforward preparation methods. Traditional synthesis methods have primarily produced larger cuboidal NCs (10 nm or above), leaving a gap in our understanding and capabilities regarding ultrasmall (3-4 nm) NCs and those of different shapes. For these systems, in-situ X-ray scattering techniques are promising methods to characterize their structure and morphology, and their evolution over time. However, the typical sub-second reaction times have posed an insurmountable obstacle. This study builds upon a recent breakthrough by Kovalenko's group¹, which developed a room-temperature synthesis that improved the separation between nucleation and growth steps, thereby extending reaction times to minutes. Leveraging the extended timescale of this new synthetic approach, we performed in-situ time-resolved coupled small (SAXS) and wide-angle (WAXS) total scattering experiments to monitor reaction stages from nucleation to final sizes, reconciling atomic and nanometer-scale information. The use of total scattering is pivotal for NCs to take advantage of both diffuse scattering and Bragg peaks. Crucially, the entire Q-range for both SAXS and WAXS measurements was collected with the same detector in a single exposure, allowing ideal coupling of patterns in both Q-range and time. We also integrated scattering measurements with simultaneous UV-Vis spectroscopy. For the first time, this enabled accurate reconstruction of the sample's structural features in terms of size, distribution, morphology, and crystal structure, while directly correlating these to the NCs' optical properties. Performing simultaneous measurements also avoids reproducibility issues often encountered when comparing results from different techniques, thereby making the obtained information more reliable and robust.

The experiments were performed at the X04SA-MS beamline of the Swiss Light Source (SLS) synchrotron facility, using the single-photon counting Mythen III detector. The detector's linear strip design allows for the simultaneous acquisition of patterns over a wide angular range, minimizing instrumental broadening and aberrations and making data reduction and solvent subtraction procedures highly reliable. The X-ray beam energy was set at 12.4 keV to enable the simultaneous acquisition of both SAXS and WAXS patterns. Syntheses were performed in a specially designed reactor situated close to the X-ray measurement spot. This setup allowed for complete remote control of the necessary reagent injections concurrent with X-ray measurements, necessary for capturing the earliest reaction steps. The reaction mixture was continuously drawn from the reactor through the spectroscopy and scattering measuring capillaries. The entire system was designed to ensure reaction concentrations and capillary thickness optimized for both spectroscopy and scattering measurements with minimal instrumental broadening. The SAXS/WAXS analysis was conducted using the Debye scattering equation (DSE)-based modelling approach implemented in the Debussy software package.²

[1] Q. A. Akkerman et al, *Science*, **2022**, 377, 1406-1412.

[2] A. Cervellino et al, *J. Appl. Crystallogr.*, **2015**, 48, 2026-2032.

Acknowledgements: Financial support by the project "Novel SUSTAINABLE double PERovskites: multiscale characterization from the atomic structure to functional properties (SU-PER)" funded by the MIUR Progetti di Ricerca di Rilevante Interesse Nazionale (PRIN) Bando 2022 – and by the project AMOCAT (Advanced Molybdenum Oxide Catalyst Analysis with Total scattering) funded by the National Recovery and Resilience Plan (PNRR - M4C2 - Investment 1.2 "Funding of projects submitted by young researchers") as part of the EU programme NextGenerationEU.