Does the solvent matter? - Influence of the solvent in hybrid halide perovskites precursor solution

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Hybrid halide perovskites (HHPs) are highly promising photovoltaic absorbers not only for using low-cost solution-based processing methods but also for the outstanding increase in power conversion efficiency of solar cells up to 25.5\% in 2021 \cite{1}.

Despite the popularity of HHPs, the growth mechanism of HHP crystals in solution is still unknown. With this study, we aim to bring more clarity about the precursor arrangement in solution prior to crystallization and how the solvent affects the atomic arrangement in this early state. For this purpose, we applied small angle synchrotron X-ray scattering (SAXS) to investigate precursor solutions of different HHPs (MAPbI\textsubscript{3}, MAPbBr\textsubscript{3}, MAPbCl\textsubscript{3}, MAPbI\textsubscript{3}(I,Br) and FAPbI\textsubscript{3}) in different common solvents used to synthesize HHPs layers, such as γ-butyrolactone (GBL), dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and mixtures thereof. We systematically investigated the influence of the A-cation in the precursor solution using full inorganic formulations based on varying alkaline metal cations as well as the pure precursors in their pristine solutions.

SAXS is a non-destructive characterization technique based on the difference between elastic scattering objects in a solution. With SAXS, it is possible to investigate the size and shape of scattering objects ranging between 1 – 100 nm, determining also the distance between adjacent scattering objects and their interaction with each other \cite{2,3}. We performed SAXS experiments at the HZB synchrotron radiation source BESSYII, at the four-crystal monochromator beamline of the Physikalisch-Technische Bundesanstalt \cite{4} using the ASAXS endstation \cite{5}. Samples have been prepared by dissolving binary precursors (e. g. MAI and PbI\textsubscript{2} to synthesize MAPbI\textsubscript{3}) in a solvent. The solutions with a concentration of 0.8 M were measured by SAXS 60 minutes after their preparation.

Our measurements show a clear maximum in the scattered intensity at q-values of \approx 3 nm\textsuperscript{-1}, except for MAPbCl\textsubscript{3} precursor solution in DMF:DMSO 1:1, which did not show any peak. The maximum holds two essential pieces of information: it demonstrates the agglomeration of scattering objects and the peak position corresponds to the most abundant distance of scattering objects in a range of 2-3 nm. While all solutions show agglomerations, we were able to demonstrate that the size of those agglomerates changes with the composition of HHP precursors, but also with the solvent. Based on this information, we have developed a core-shell model with [PbX\textsubscript{6}] octahedra (X = Cl, Br, I) in the core surrounded by solvent molecules to describe the scattering objects. The size of the solvent molecules as well as the radii of Pb and halides forming [PbX\textsubscript{6}] octahedra were derived from a combination of experimental values from diffraction and computationally obtained electron density distributions. We can explain the solvent dependent variation of the experimentally determined distance between the scattering objects by a core size variation realized by a combination of isolated octahedra or corner-sharing octahedra as core, respectively. Since the solvent molecules can be described as an ellipsoid, their orientation must be taken into account. We can explain the variations of the minimal possible distance between the scattering objects (R_{\text{min}}), evaluated from the structure factor determined by analysing the SAXS data (using SASfit) by a preferred orientation of the solvent molecules in the solvent shell of the scattering objects. Therefore, the choice of the solvent may not only depend on the precursor solubility but also on their chemical and physical behaviour.

We will discuss the influences of precursor composition and solvent on the core as well as the solvent shell of the scattering objects, since they have the potential to influence the crystallization process of the HHP and therefore the performance of a device produced from solution processing.

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