

## Electron microscopy and X-ray techniques correlative in situ studies in microfluidic conditions on hybrid perovskites

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Hybrid organic-inorganic perovskites (HOIP), a class of materials with a cubic unit cell (ABX<sub>3</sub>) possess remarkable physical and chemical properties and have aroused growing interest in the scientific community in the last decade. The A-cation, at eight corners of the cube, is surrounded by twelve X-anions (mainly halides, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>), while the B-cation (typically divalent metal ions such as Pb<sup>2+</sup>, Sn<sup>2+</sup> or Cu<sup>2+</sup>) is located at the body center surrounded by six X-anions in an octahedral [BX<sub>6</sub>]<sup>4-</sup> cluster. When the A cation is replaced by methylammonium cations (MA=CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>), three-dimensional hybrid organic-inorganic structures are obtained, known as 3D hybrid perovskites, with potential applications in solar cell technologies. Their high power conversion efficiency (PCE), together with their low-cost and scalable, solution-based fabrication processes lead to intense research efforts towards their industrialization. Despite these advantages, 3D perovskite solar cells also face significant challenges. The long-term stability of these materials remains a major concern, as they can be sensitive to moisture and other environmental factors, leading to a premature degradation. In this context, there has been growing interest in 2D HOIPs. These materials include larger organic cations as hydrophobic spacers, isolating the inorganic metal halide octahedra and leading to improved stability compared to their 3D counterparts. A wide variety of structures can be obtained for these materials, depending on the organic or inorganic cations and the synthesis conditions. Indeed, their synthesis in solution implies complex chemistry, with pre-organization, nucleation, reorganization and precipitation. Controlling the properties of these materials need a precise control over their structure, hence over their synthesis pathways.

For a better understanding of the synthesis of HOIPs by ligand assisted re precipitation (LARP) and to control their structures and properties, we developed a new approach for observing the structural evolution of 3D/2D lead halide hybrid perovskites based on a time-resolved acquisition protocol of the structural data. By combining in situ liquid transmission electron microscopy (TEM) and X-ray absorption techniques, we can monitor in real time the birth and the structural and chemical evolution of the different phases in well-controlled and realistic conditions and have a better understanding of the associated mechanisms. Specific microfluidic devices were developed for this work, which were used to perform in situ X-ray

absorption studies and can be applied to other X-ray techniques as well. This new device reproduces the precipitation of 3D/2D lead halide hybrid perovskites under X-ray in particular for X-ray absorption near edge structure (XANES), for Extended X-ray Absorption Fine Structure (EXAFS) and for Small-angle X-ray scattering (SAXS) analyses. This micro fluidic chip has been designed to be versatile and adaptable to the specific needs of synthesis. The internal microfluidic pathway can be easily changed in design, from a T to observe the interface between two fluids, or a mixer to reproduce the conditions required for precipitation. By combining this information with those obtained from in situ liquid TEM with the Protochips technologies Poseidon AX and X-ray diffraction, we propose mechanisms for the formation and structural transition of different phases of this family of perovskites. This method highlighted the importance of studying the precursor solution to the LARP method, at which stage an atomic arrangement was found. This indicates that the synthesis of HOIPs begins before precipitation with the formation of a forerunner atomic structure of the intermediate phase. We will also show how the method presented could be applied to the study of a variety of nanomaterials under in situ liquid conditions.

**Keywords:**

perovskite, insitu TEM, microfluidic device

**Reference:**

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