

# The effects of solution processing methods on halide perovskite nanostructure

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## Background:

Over the last decade, hybrid lead halide perovskite (LHP) materials have emerged as auspicious candidates for next-generation thin-film photovoltaics. This is largely due to both impressive optoelectronic properties and photovoltaic power conversion efficiencies, making them ideal for next-generation solar applications. Within this class of materials, formamidinium lead triiodide (FAPbI<sub>3</sub>)-based perovskites are of particular interest due to their near-ideal bandgaps and improved thermal stability [1]. However, the photoactive ( $\alpha$ -) phase of FAPbI<sub>3</sub> is only meta-stable at room temperature, and a variety of compositional tuning and additive-based approaches have therefore been employed to stabilise this phase.

While a range of methods can be used to fabricate LHP thin films, the most common of these is one-step spin coating. Precursor salts may be dissolved in a range of solvents to form a precursor ink, into which additives that improve film properties and stability may be incorporated. However, little is known about the effect of both solvent choice and additives on film nanostructure. This ultimately limits the practical application of LHPs in devices, as higher performance materials tend to be less stable. Understanding how precursor ink chemistry affects thin film crystallisation can thus inform improvements in long-term stability of films and devices, and is pivotal to improving this technology moving forward.

## Methods:

In this work, we examine 'neat' FAPbI<sub>3</sub> films prepared via different solution processed routes including films prepared from the conventional precursor salts formamidinium iodide and PbI<sub>2</sub> and single-crystal precursors in solutions of 4:1 DMF/DMSO and 4:1 DMF/NMP, both with and without the addition of a 40% MACI additive.

High-resolution transmission electron microscopy (HRTEM) is used to elucidate the nanoscale structure of these films at the atomic scale. However, FAPbI<sub>3</sub> is highly susceptible to electron beam-induced damage; doses in excess of 100e-/Å<sup>2</sup> induce degradation into PbI<sub>2</sub> indistinguishable from that natively present in the film [2]. Here, all HRTEM is performed at doses below this critical threshold to ensure beam-induced effects are minimised.

## Results:

While bulk characterisation data suggests that these varied approaches to FAPbI<sub>3</sub> film formation result in structurally the same material (albeit with varying levels of electronic defects and morphological film changes) [3], HRTEM shows at the nanoscale these films exhibit significant structural and compositional differences. Figure 1(a) shows a typical low-dose HRTEM image of a FAPbI<sub>3</sub> film prepared from conventional precursor salts in DMF/DMSO. The FFT of this image (Figure 1(b)) shows poor agreement with spacings expected for  $\alpha$ -FAPbI<sub>3</sub> (red rings) and the 2H-polytype of PbI<sub>2</sub> (blue rings). In comparison, the HRTEM image of a single-crystal precursor sample in the same solvent system and the corresponding FFT (Figure 1c,d) shows good agreement with the spacings expected for the photoactive perovskite phase. We attribute these differences to the presence of unreacted precursor material and the presence of non-photoactive FAPbI<sub>3</sub> polytypes.

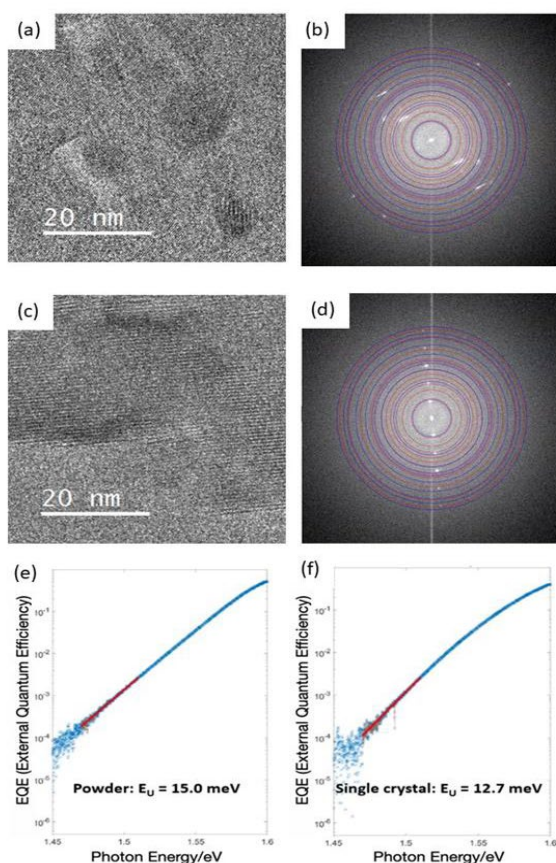
It has been previously suggested that in some more structurally stable compositions, degradation in these materials occurs as a result of the inclusion of various unwanted FAPbI<sub>3</sub>

polytypes during crystallisation [4]. Our HRTEM images show direct evidence of these phases, and in combination with other characterisation techniques support the suggestion that the inclusion of these undesirable phases can be controlled and ultimately eliminated through careful modulation of the precursor ink chemistry. By using a single crystal precursor we have been able to achieve better precursor ink purity, which results in films with significantly reduced structural disorder (evidenced by lower Urbach energies, as shown in Figure 1e,f). In this work, we link these observations directly to nanostructural changes visible in the HRTEM data.

**Conclusions:**

Precursor ink chemistry undoubtedly affects LHP thin-film composition and structure. We show a direct link between these properties and laboratory-based results through the use of low-dose HRTEM. These links provide an important stepping stone on the path to truly understanding precursor ink chemistry, which ultimately may be the key to perfecting the crystallisation of LHPs.

**Graphic:**



**Keywords:**

perovskites, photovoltaics, low-dose, HRTEM, STEM

**Reference:**

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