Direct conversion of Pb or Sn to halide perovskite

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The most common method of preparing halide perovskite (HaP) films is by spin-coating a solution of the HaP or precursor (most common general formula ABX_3, where A is a monovalent cation, e.g. methylammonium (MA) or Cs), B is usually Pb and sometimes Sn, and X is a halide) from an organic solution. There are two main variations of this method: either a one-step deposition from a solution of all the constituents or a 2-stage process involving deposition of the metal halide followed by treatment with an AX solution or vapour.

Here we describe a method based on conversion of Pb or Sn *metal* (see refs. 1-3 for recent similar or related methods) from an alcoholic solution of AX, which does not require toxic organic solutions. In our study, the metal layer is deposited by evaporation, although other methods can be envisioned. For Pb-HaPs, it is enough to immerse the Pb film in an alcoholic (isopropanol is commonly used, although the optimal alcohol depends on the HaP composition) solution of AX, while for Sn-HaPs, the alcoholic solution needs to be acidified (e.g. with HI). The HI can accelerate the oxidation of the metal to Pb^{2+} or Sn^{2+} at the surface, thus accelerating the overall conversion reaction. We found that reaction of Sn with MAI + HI resulted in $MASnI_3$ while reaction with CsI + HI gave the Sn(IV) compound, Cs_2SnI_6.

The main variables in the film preparation are composition of the alcohol, solution pH, concentration of AX, presence of elemental halogen (as polyhalide) and temperature. Fig. 1 gives some idea of how MAI concentration and addition of elemental I_2 can affect the film morphology in terms of grain size and coverage.

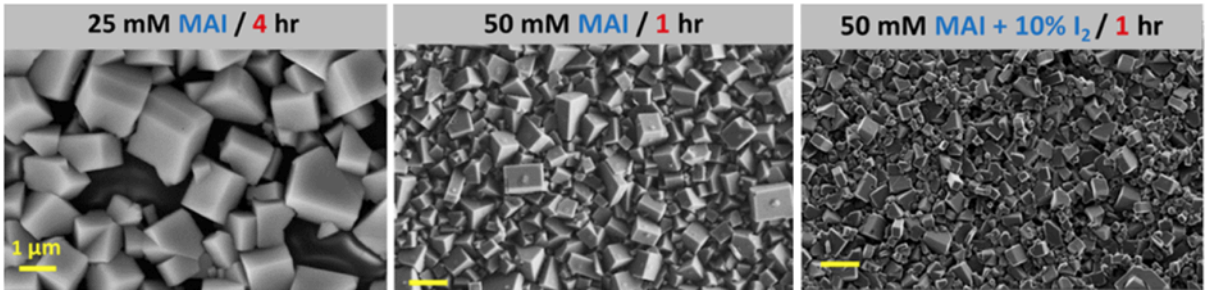

Figure 1. Variation of MAPI film morphology on MAI (in isopropanol) concentration and on addition of I_2. All films deposited at room temperature. Substrates: left image – glass; centre and right image – FTO. All scale bars are 1 μm.

The method can be extended to solid solutions of the HaPs. Thus, by using a mixture of MAI and MABr in isopropanol, we were able to form films of $MAPb(I,Br)_3$, with optical absorption onsets between the pure iodide and bromide.

By using a positive bias on the metal films, we can accelerate metal oxidation and thus the rate of the conversion reaction, providing further control over the HaP film properties. In fact, a negative bias applied to the HaP can reduce it back to the metal. This electrochemically-assisted conversion might be particularly useful for the Sn HaPs since the bias can be used to control oxidation of Sn(II) to Sn(IV). Another variant would be to use

pulsed potential control that would reduce Sn(IV) back to Sn(II) during the more negative pulses.

Finally, time resolved photoluminescence of both MAPI and MAPBr showed charge lifetimes (>200 ns) comparable to other high-quality films and preliminary photovoltaic cells made using these films showed conversion efficiencies >2%.

References

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