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Solvent-free deposition of hybrid halide perovskites onto thin films of copper iodide p-type conductor

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Chemicals and reagents

Iodine (99% purity, Rushim), PbI_2 (99.99%, TCI), CH_3NH_3I (99.9%, Dyesol) were used as starting reagents. CuI was produced by sonication of metal copper (99.9%) in the solution containing I_2 in ethanol.

Deposition of CuI and $CH_3NH_3PbI_3$ films

CuI films were spin-coated from the 20 mg/ml solution in acetonitrile in a dynamic regime with 100 μl of the solution being dripped on the rotating at 4000 rpm glass substrate.

A mixture of PbI_2 (461 mg, 1 mmol) and MAI (159.0 mg, 1 mmol) were mixed in a vial and DMF/DMSO mixture was added to obtain 1.3M solution. The mixture was stirred under moderate heating (60˚C) for at least one hour prior to deposition. The precursor solution was spin-coated on glass substrates using the two-step program – 1000→6000 rpm. The antisolvent (chlorobenzene, 80 μL) was dripped on the substrate 5-15 seconds after reaching the steady speed on the second step.

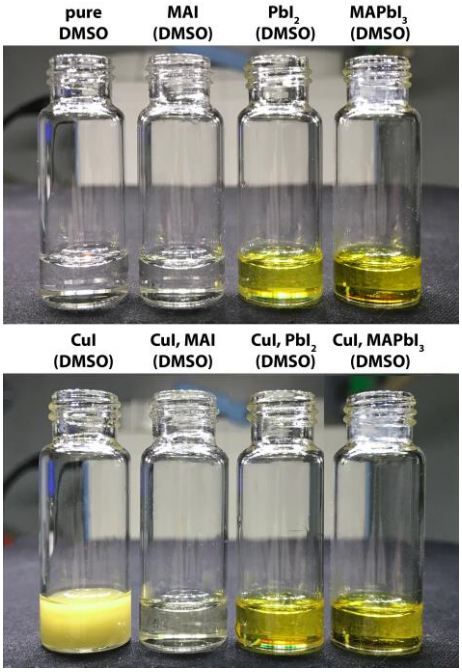

Figure S1 Demonstration of CuI-solubility enhancement induced by the components of a typical halide perovskite solution; the top row represents solutions without CuI, bottom row represents solutions with CuI (0.3M dispersion/solution); we note that yellow color of CuI (DMSO) dispersion appeared within several minutes upon exposure to air and suggest that this is due to iodine being released upon oxidation.

Solid-state synthesis of $MAPbI_3$-CuI powder samples

For the solid-state synthesis of $MAPbI_3$-xCuI samples powders of $MAPbI_3$ and CuI were grinded in a mortar, pressed into pellets, placed into ampules sealed under vacuum and sintered at 200˚C for 24h. MAI pellets were added to ampoules.

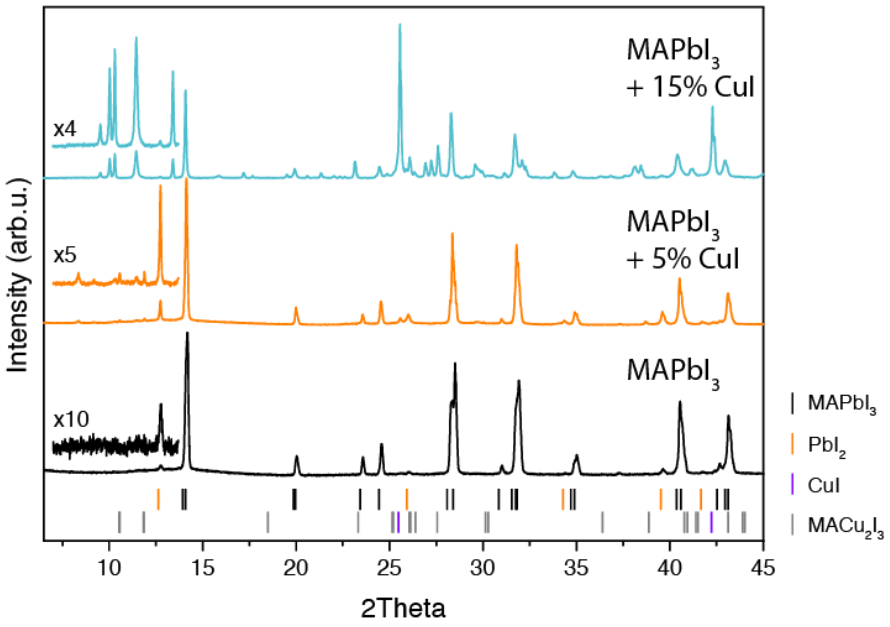

Figure S2 XRD patterns of $MAPbI_3$-xCuI samples obtained using solid-state synthesis in sealed ampoules; note that multiple reflections are present at small angles in samples with CuI.

RP-MAGIC (reactive polyiodide melt-assisted growth under isothermal conditions)

a) Deposition of metallic lead

Thin films of Pb were deposited by thermal evaporation of metallic Pb (99.99%) in vacuum from a molybdenum boat under 10^{-5} Torr vacuum. The deposition rate and target thickness were controlled by means of quartz crystal microbalance (QCM). The target thickness was set to 62 nm and deposition rate was adjusted to 0.1 nm/s. During the deposition the temperature of the substrates and the QCM sensor was maintained at 10 °C using the chiller. After the deposition, the samples were transferred into an Ar-filled glovebox.

b) Conversion of metallic lead into perovskite

MAI_2 precursor solution was prepared by dissolving of MAI and I_2 powders mixtures in anhydrous isopropyl alcohol (Sigma Aldrich). Perovskite films were fabricated by spin-coating of precursors solution (3000 rpm/s for 20 s, slope 3 s) onto Pb layer with a subsequent I_2 vapor treatment for complete Pb conversion. For the iodination, samples were put into a Petri dish with a lid, fully covered with Iodine crystals, thus a continuous source of I_2 vapor was located in ~1 cm above the samples. Finally, the converted samples were transferred onto a hot plate and annealed at 100˚C for 10 minutes.

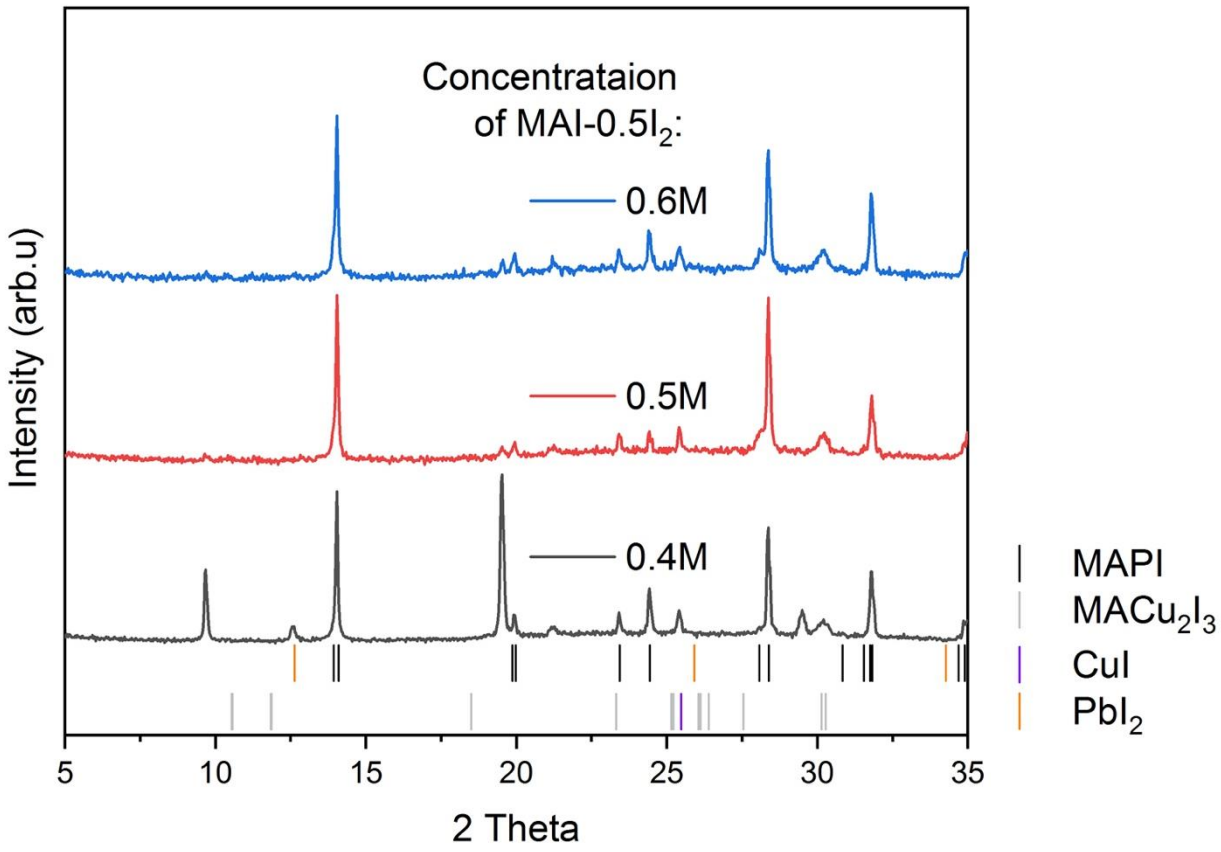

Figure S3 XRD patterns of glass/CuI/$CH_3NH_3PbI_3$ stacks obtained by the conversion of glass/CuI/Pb using RP-MAGIC approach with different concentrations of RPM.