

Supplementary Information

Tin(II) Precursor is an Active Site to determine the Crystal Framework in CsSnI₃ Perovskite

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ADDITIONAL EXPERIMENTS

Additional Materials

Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS, Clevios™ P VP AI 4083) was purchased from Heraeus. Phenyl-C61-butyric acid methyl ester (PC₆₁BM) was purchased from Organic Semiconductor Materials (OSM Co., Ltd.). Bathocuproine (BCP, 98 %) was obtained from Alfa Aesar. Chlorobenzene (anhydrous, ≥ 99.8 %) and Isopropanol (anhydrous, ≥ 99.5 %) were obtained from Sigma-Aldrich and used for PC₆₁BM and BCP solution, respectively.

Preparation of Perovskite Precursor Solutions

A CsSnI₃ perovskite precursor solution including each precursor such as CsI, SnI₂, or SnF₂ was prepared as dissolving the materials in DMF, DMSO, or DMF:DMSO (1:4 v/v) mixed solvent. The precursor solutions were stirred on the hot plate under the 50 °C heating condition in the N₂-filled glove box.

Crystal Growth of Sn²⁺ Precursor-based Crystals or CsSnI₃ perovskites with ATMS

SnI₂ (0.298 g - 0.8 M concentration) + SnF₂ (0.026 g - 0.16 M concentration) precursor solutions with various ATMS amount (0.1, 0.5, 1, 2, 4, and 8 % v/v) were prepared under the 50 °C heating temperature in the N₂-filled glove-box for 2 h. The precursor solutions were spin-cast onto the indium tin oxide (ITO)/PEDOT:PSS substrate with a spinning speed of 1000 rpm (10 s) and 5000 rpm (45 s). The deposited tin precursor layer was aged at room temperature for 30 min and annealed at 70 °C for 10 min. With a similar method, the CsSnI₃ crystal film including ATMS anion was generated from a CsSnI₃ + ATMS precursor solution. The crystal was grown on the ITO/PEDOT:PSS substrate by spin-coating and annealing process.

Fabrication of CsSnI₃ Perovskite Solar Cells

An ITO-coated glass substrate was sequentially cleaned under ultra-sonication with acetone

and isopropyl alcohol for 30 min, respectively. The cleaned-ITO substrate was treated with UV ozone for 20 min to remove additional alien materials on the surface of the substrate. A PEDOT:PSS that have storage in the refrigerator at ca. 5 °C was spin-cast onto the pretreated ITO substrate with a ~ 40 nm thickness in the air. The ITO/PEDOT:PSS substrate was transferred to the N₂-filled glove box. A perovskite precursor solution (SnI₂ + SnF₂ or CsSnI₃) was prepared with proper concentration and/or stoichiometric ratio under 50 °C temperature. The solution was deposited onto the ITO/PEDOT:PSS substrate with a 0.2 μm filtration by spin-coating, the perovskite-coated substrate was subsequently annealed on the hot plate. A PC₆₁BM layer (20 mg ml⁻¹ concentration in chlorobenzene) was deposited above the perovskite crystal film with a spinning rate of 1500 rpm and annealed at 70 °C for 10 min. Finally, a ca. 120 nm of silver (Ag) was deposited as a top electrode by thermal evaporation under 1.2×10^{-5} Torr.

General Characterization

UV-vis absorption spectra with a baseline correction were recorded using a UV-2700 spectrometer (Shimadzu, Japan). The measurement system was two-detector absorbance mode and the slit width was 5 nm. Scan speed and data intervals were 100 nm/min (medium) and 0.05 nm, respectively. For the solution samples, perovskite precursor solutions were filled in a quartz cuvette with a path length of 10 nm and measured. Perovskite film was coated onto the ITO/PEDOT:PSS substrate and scanned as a solid state. A DMF or DMSO solution and ITO/PEDOT:PSS substrate were used as a reference sample for the solution and solid system, respectively.

Transmission electron microscopy (TEM) was conducted to obtain lattice phases of perovskite crystals at a solution or solid state. JEOL-2100F or JEM-F200 instrument equipped with a high-angle annular dark-field (HAADF) was operated at an acceleration voltage of 200 kV. The high-resolution (HR) TEM images were recorded at various focus and magnification

(1.0, 1.2, or 1.5 M) conditions. For the solution samples, perovskite precursor dispersions were diluted 1/6 in DMF:DMSO (1:4) mixed solution, and they were dropped onto the carbon support film grids (300 mesh, Cu). For the film samples, perovskite crystals that were grown on the ITO/PEDOT:PSS substrate were scratched and dropped onto the same grids as the solution sample. A droplet of anti-solvent was dropped onto the grid to fix the scratched powders. Samples were dried in vacuum condition for over 70 h before loading into the TEM instrument. All the TEM sample preparation processes were conducted in the N₂-filled glovebox.

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were recorded on a TENSOR 27 (Bruker, Germany) with a platinum ATR accessory at room temperature. A DLATGS detector that provides a resolution of 4 cm⁻¹ was used and scan time was 32. The liquid samples were filled into the ATR accessory with ca. 300 μl, and then measured.

¹H NMR and ¹¹⁹Sn NMR spectra of the perovskite precursor samples were recorded by using an AvanceIII 500 MHz spectrometer (Bruker, Germany) with a 5 mm HR-MAS probe. The samples were dispersed in DMSO-d₆ solvent (concentration = 0.75 mL) and filled into the NMR tube to measure. Tetramethyltin was used as a reference for the ¹¹⁹Sn NMR measurements.

A New D8-Advance X-ray diffractometer (Cu Kα radiation, 8.04 keV) equipped with a diffracted beam monochromator was employed to measure the crystal diffraction patterns of perovskite films. All XRD data were recorded with a coupled two theta (2θ)/theta mode in the 2θ range from 10° to 50° at room temperature. The scanning rate was 2° min⁻¹ and the X-ray exposure time per point was 0.5 s.

The surface morphologies of perovskite films were investigated by field emission scanning electron microscopy (FE-SEM) using a JSM-7100F (JEOL, Ltd.) instrument. An acceleration voltage was 20 kV and the focused images were obtained at various magnifications.

Transmission small-angle X-ray scattering (SAXS) measurements were conducted at the 4C SAXS-II beamline of the PLS-II synchrotron facility, Pohang Accelerator Laboratory (Pohang, Korea). The X-ray beam with an energy of 16.09 keV was used, and scattering data were collected with a two-dimensional charged-coupled detector (CCD: model Rayonix 2D SX 165). The beam was exposed to solution samples in 1.5 mm quartz capillaries and the exposure time was set to 10 s for each sample. The capillary cell (a thickness of 0.01 mm and an external diameter of 1.5 mm, Charles Supper Company) was placed in a metal holder with a lateral direction to eliminate the thickness effect of the capillary cell. When the solution was changed, the cell was washed to di-water and acetone 3 times. Sample-to-detector distance (SDD) was 1.0 m with a confidence interval, $0.032 \text{ \AA}^{-1} < q < 0.700 \text{ \AA}^{-1}$. The scattering angles were calibrated by using a pre-calibrated Ti-SBA-15 (Sigma-Aldrich) and silver behenate (Tokyo Chemical Industry) as standards. Buffer solutions (DMF, DMSO, or DMF:DMSO) were separately measured and subtracted from perovskite solutions in SAXS data treatment.

Device Characterization

All device measurements were carried out in ambient conditions (room temperature and relative humidity (RH) of 30 - 35 %). Current-voltage (J - V) characteristics of solar cell devices were measured using a solar simulator (PEC-L01, Peccell Technologies) under standard AM1.5 illumination (100 mW cm^{-2}). The light source was calibrated with a silicon photodiode detector (BS-500BK, BUNKOUKEIKI CO., LTD.). Each device was measured with a scan rate of 100 mV s^{-1} using a Keithley 2400 source meter. The external quantum efficiency (EQE) spectra were characterized using a CompactStat instrument (Ivium Technologies; Eindhoven, Netherlands) with a power source (Abet Technologies 150 W xenon lamp, 13014) and a monochromator (DongWoo Opteron, MonoRa500i). The system was calibrated with the same photodiode detector for the solar simulator.

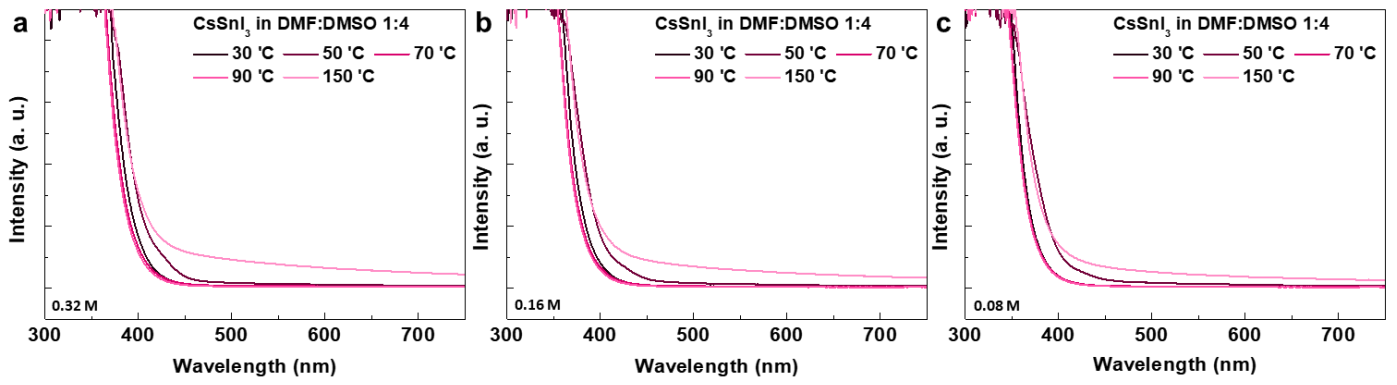


Fig. S1 UV-vis absorption spectra of CsSnI₃ precursor solution dissolved in DMF:DMSO mixed solvent with 1:4 volume ratio at various measurement conditions that control the solution concentration: (a) 0.32 mM, (b) 0.16 mM, and (c) 0.08 mM.

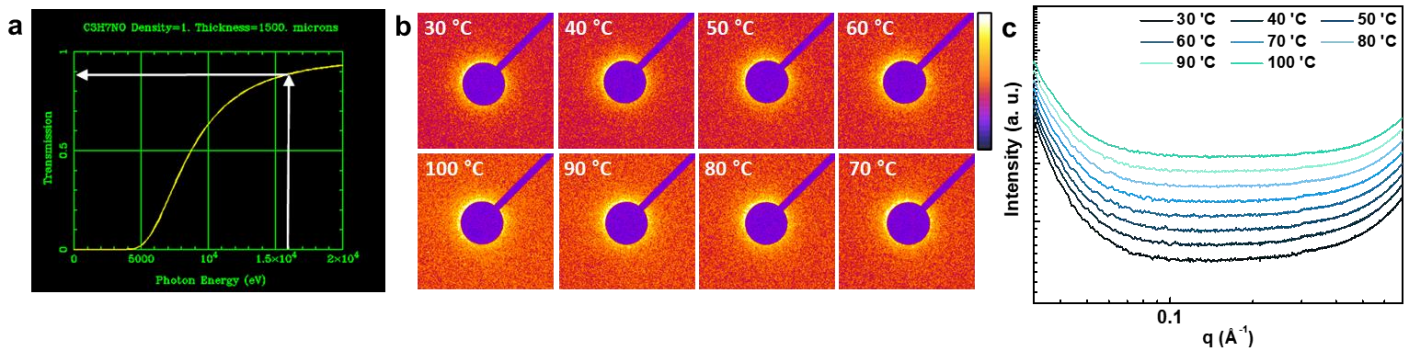


Fig. S2 Transmission SAXS results with the theoretical X-ray transmission factor for DMF solvent: (a) X-ray photon energy versus transmission curve, (b) two-dimensional diffraction patterns, and (c) corresponding average radial integrations.

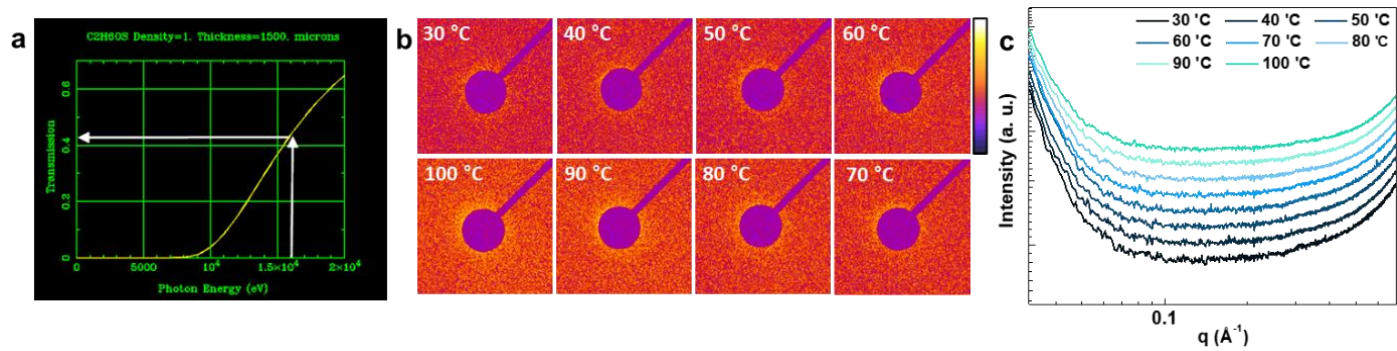


Fig. S3 Transmission SAXS results with the theoretical X-ray transmission factor for DMSO solvent: (a) X-ray photon energy versus transmission curve, (b) 2D diffraction patterns, and (c) corresponding average 1D profiles.

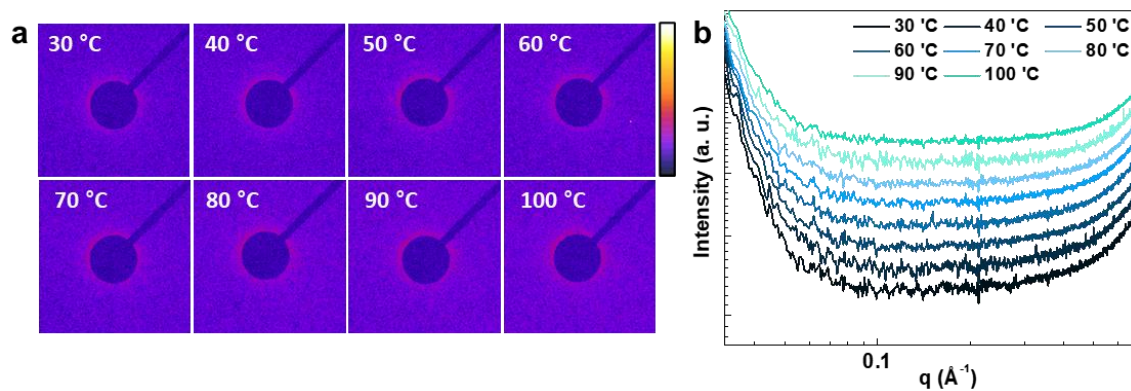


Fig. S4 Transmission SAXS results for DMF:DMSO mixed solvent: (a) two-dimensional diffraction patterns, and (c) corresponding average 1D integrated plots.

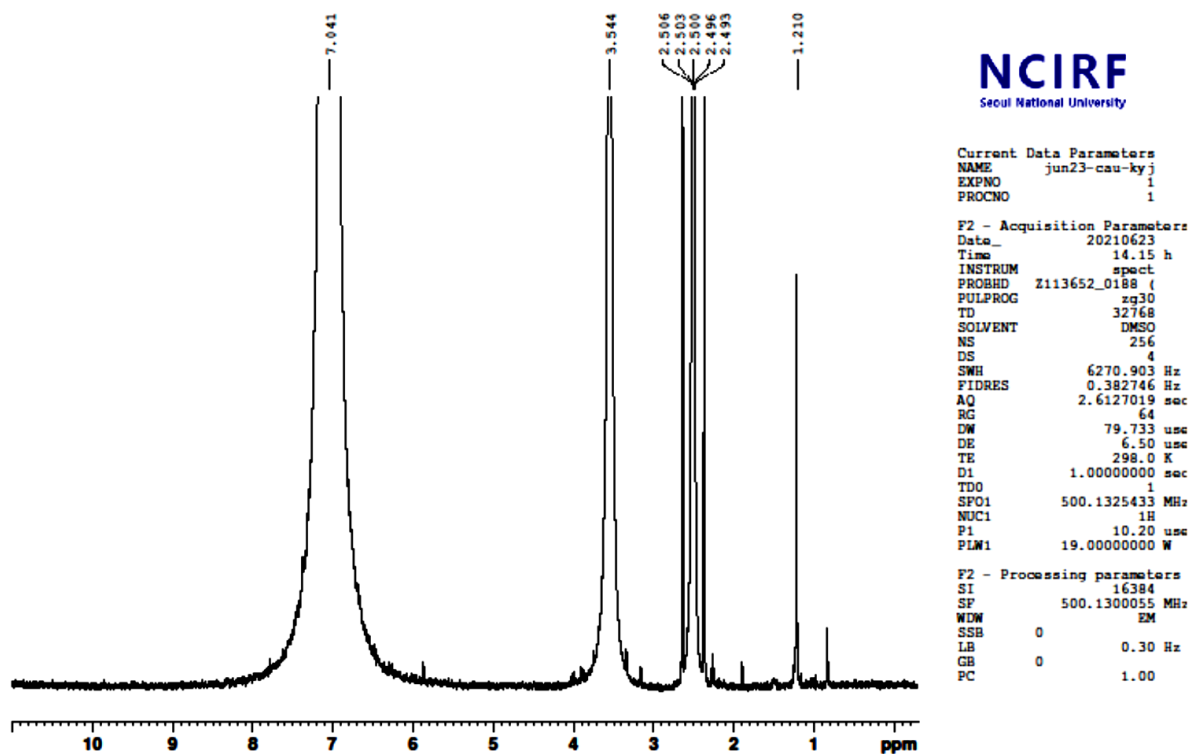


Fig. S5 ^1H NMR spectrum of ATMS sample in deuterated DMSO- d_6 solution.

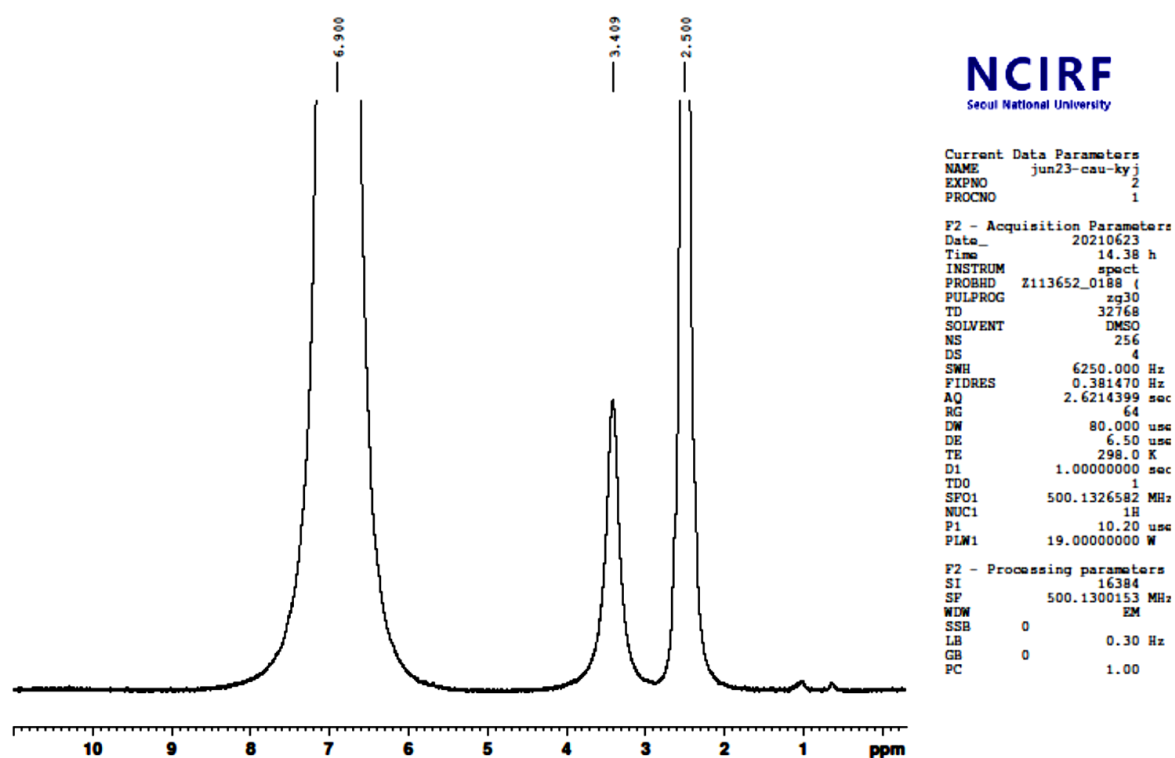
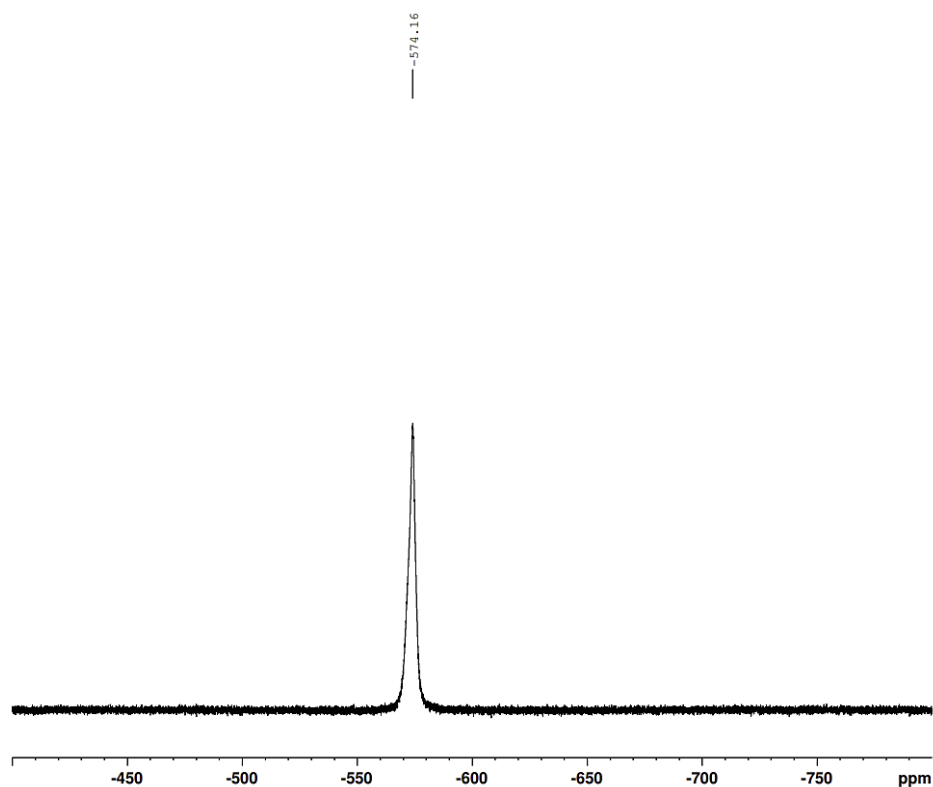


Fig. S6 ^1H NMR spectrum of CsSnI_3 - ATMS sample in deuterated DMSO-d_6 solution.



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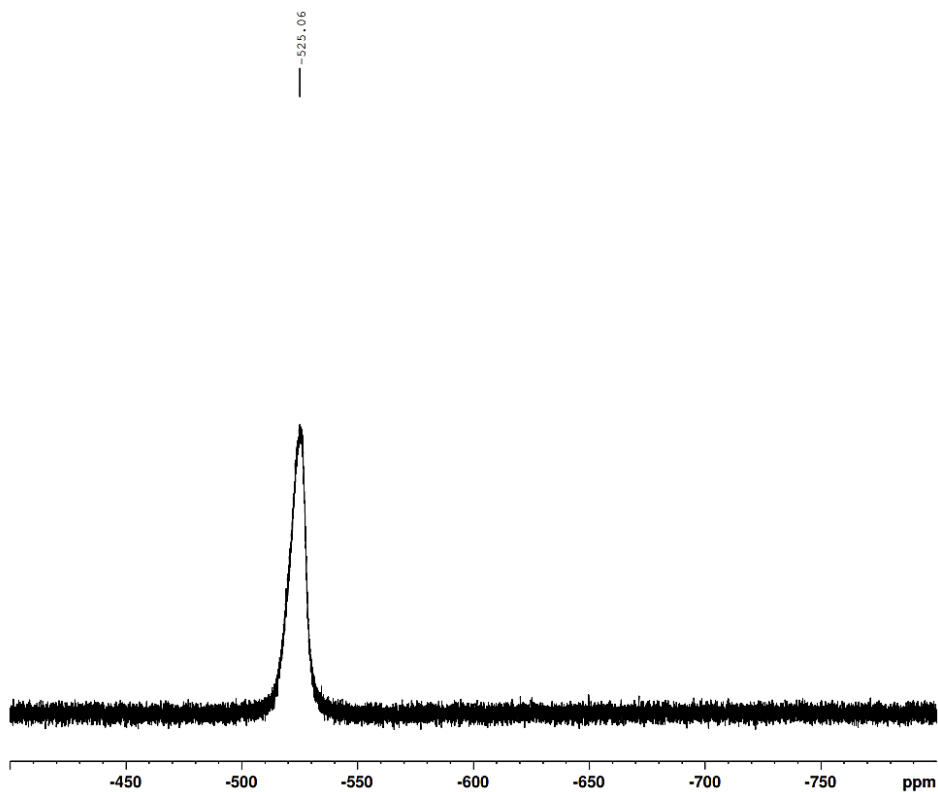
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Fig. S7 ^{119}Sn NMR spectrum of CsSnI_3 perovskite in deuterated DMSO-d_6 solution.



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Fig. S8 ^{119}Sn NMR spectrum of CsSnI_3 perovskite precursor with ATMS anion in deuterated DMSO-d_6 solution.

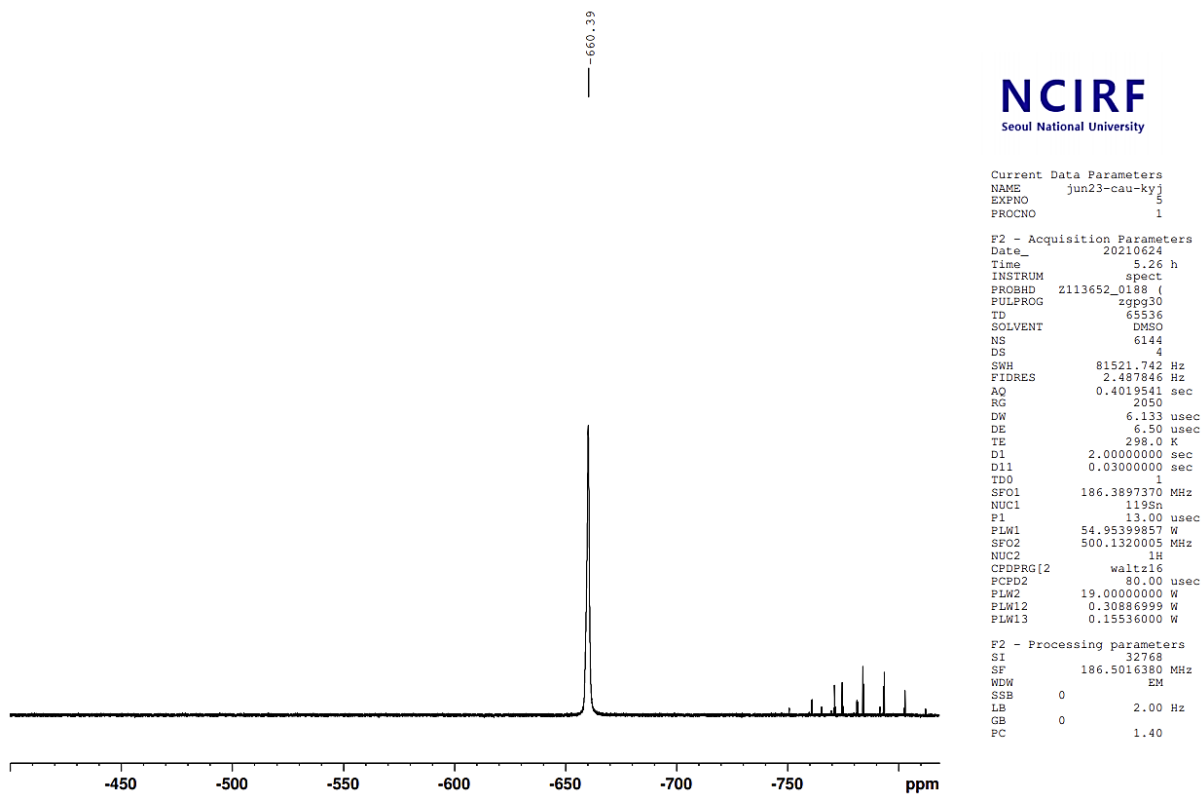


Fig. S9 ^{119}Sn NMR spectrum of SnI_2 precursor with SnF_2 in deuterated DMSO-d_6 solution.

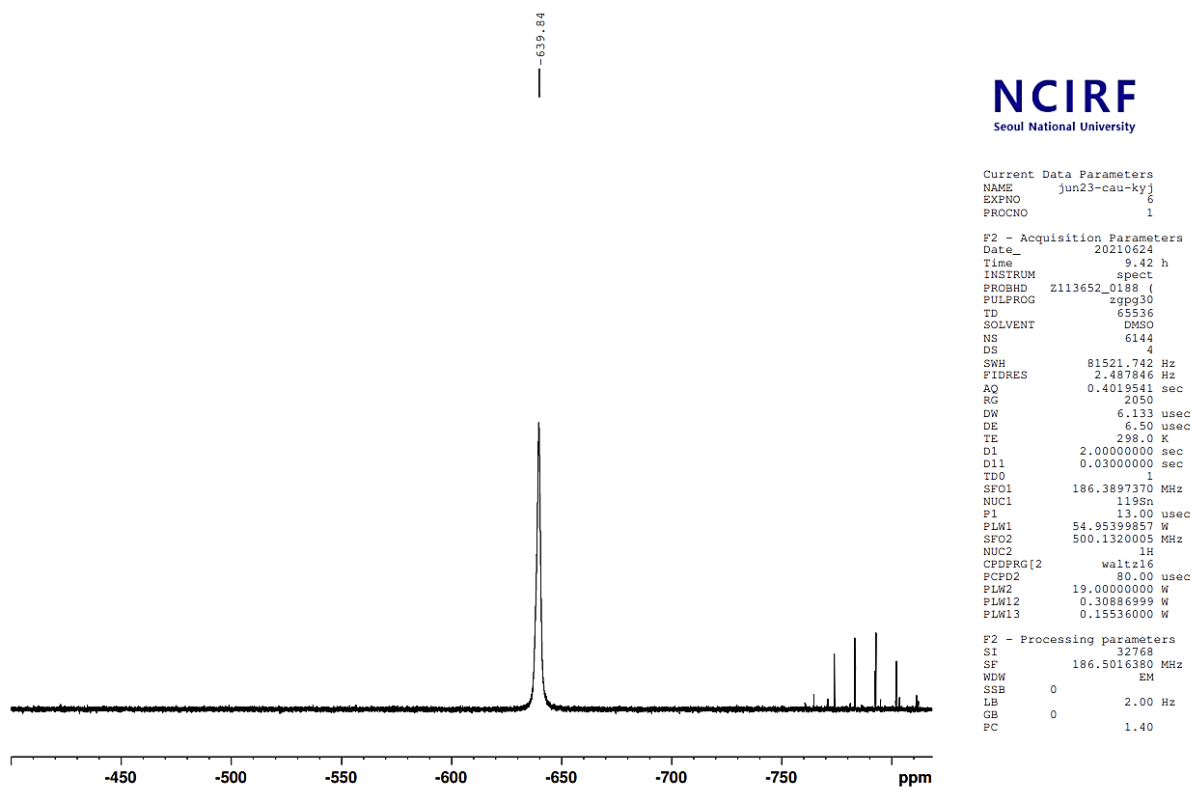


Fig. S10 ^{119}Sn NMR spectrum of $\text{SnI}_2 + \text{SnF}_2$ sample with ATMS anion in deuterated DMSO-d_6 solution.

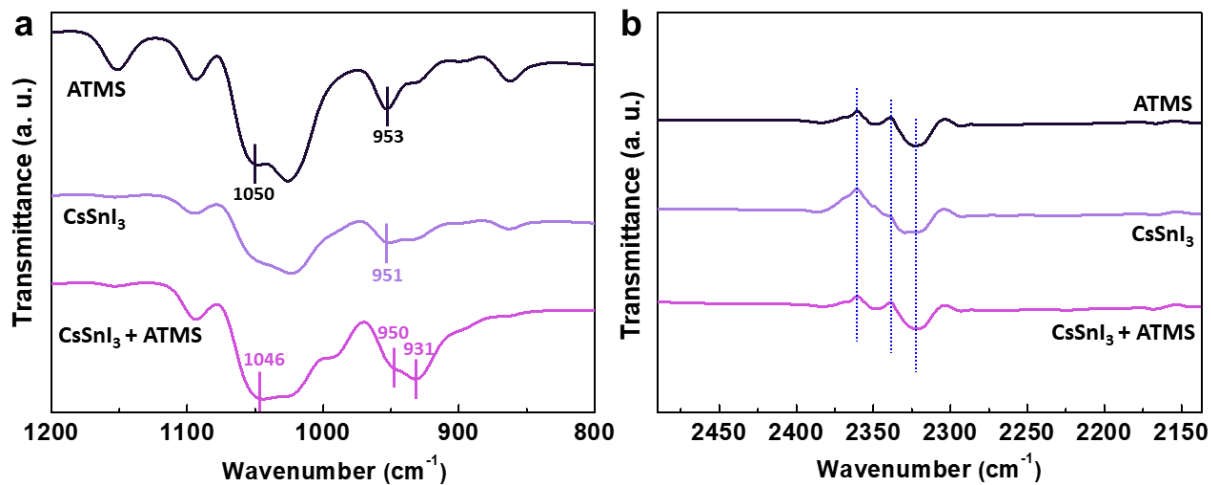


Fig. S11 Partial magnification spectra from Figure 3d with a range of (a) 1200 – 800 cm⁻¹ and (b) 2490 – 2140 cm⁻¹.

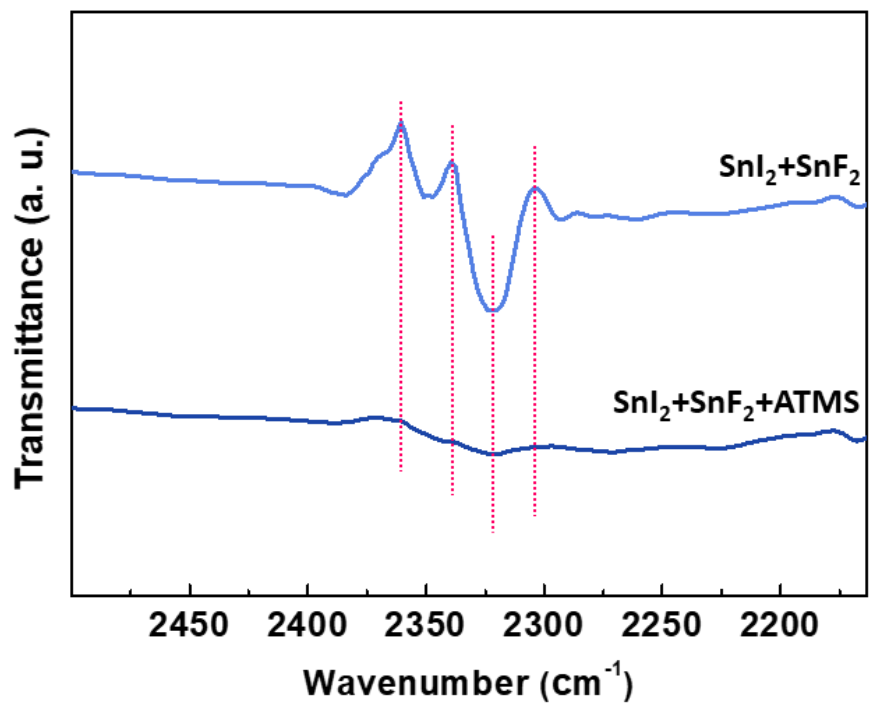


Fig. S12 Magnification of FTIR spectra from Figure 3e with a range from 2160 to 2500 cm⁻¹.

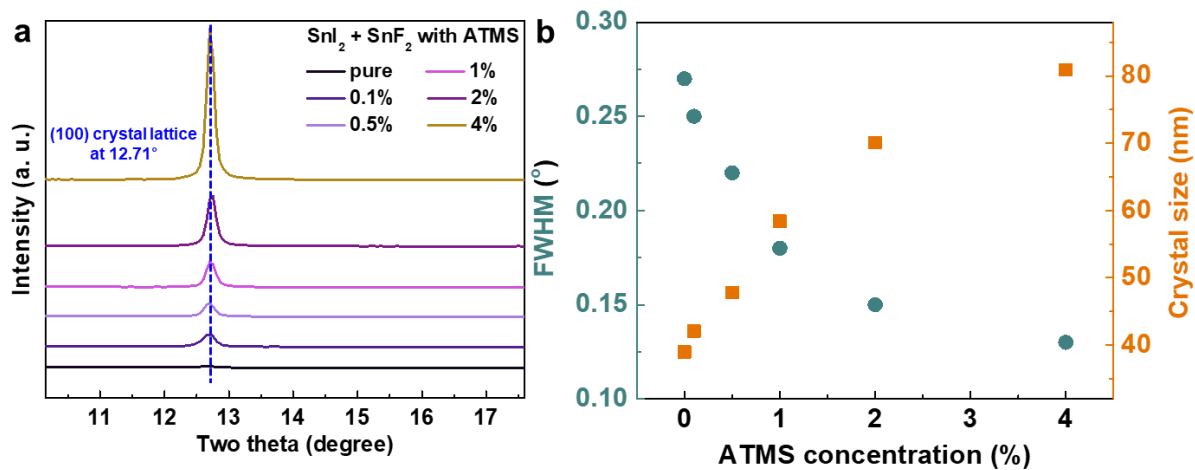


Fig. S13 (a) Magnified XRD results from Fig. 4c to highlight the (100) crystal lattice peak. (b) The trends of FWHM and corresponding calculated crystal size of $\text{SnI}_2 + \text{SnF}_2$ precursor as a function of ATMS concentration.

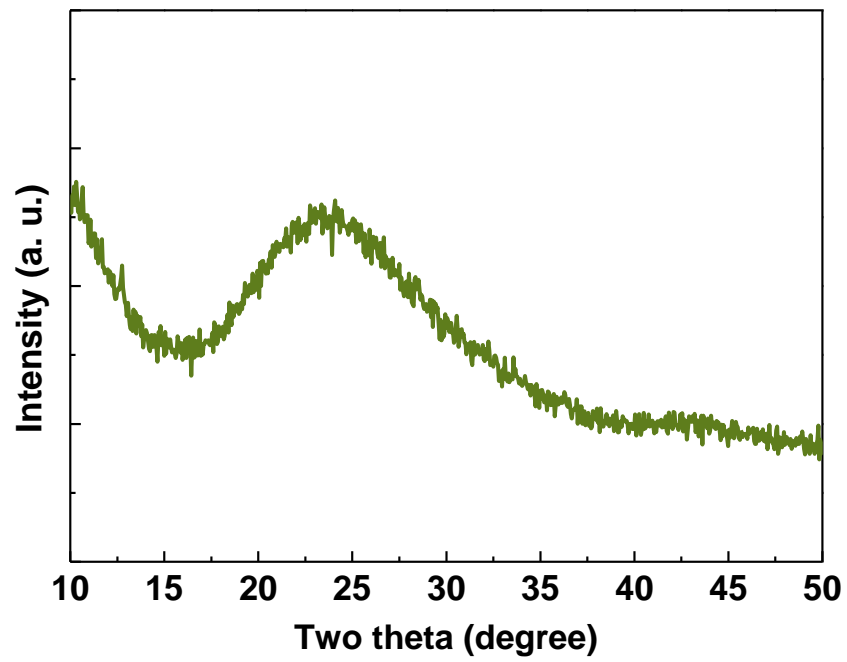


Fig. S14 A XRD pattern of $\text{SnI}_2 + \text{SnF}_2$ precursor film with ATMS of 8% concentration.

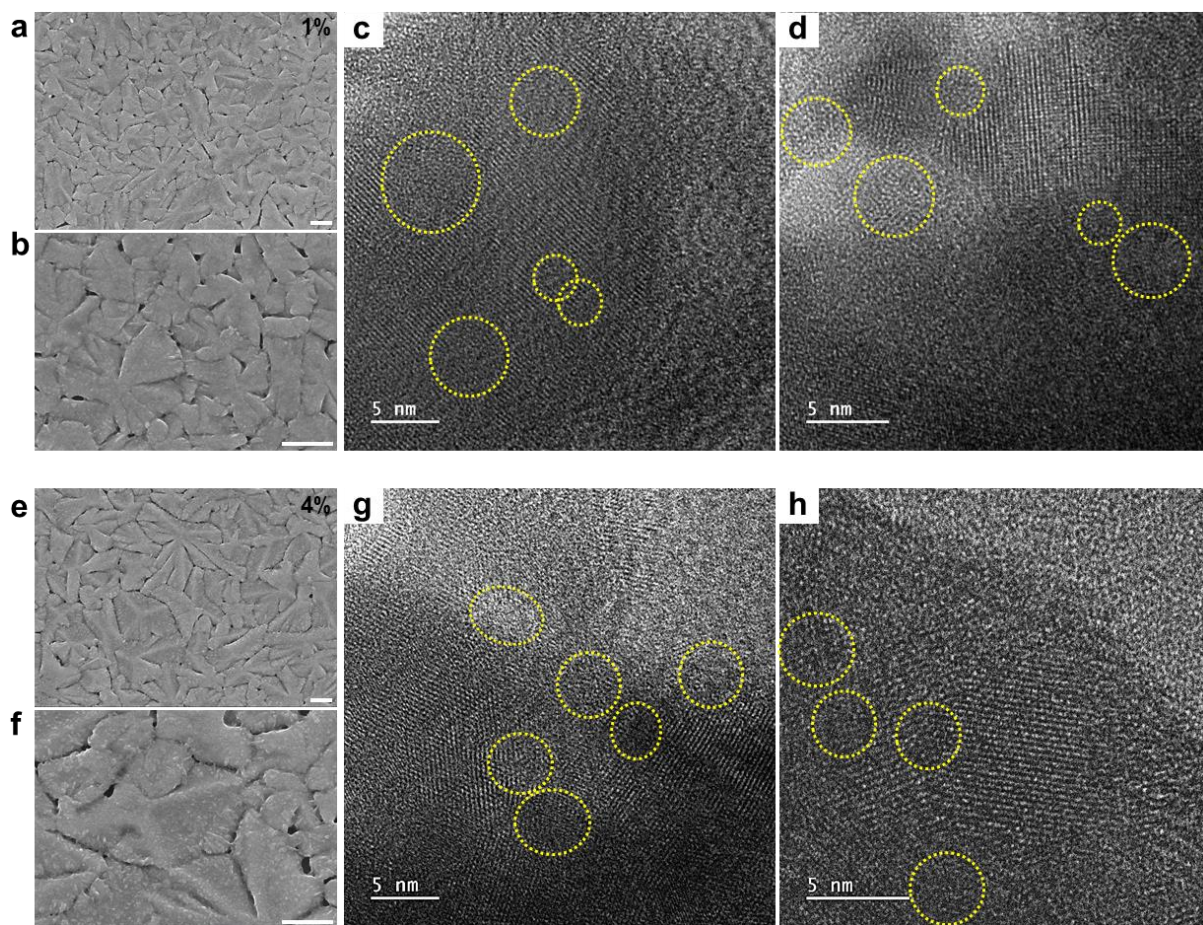


Fig. S15 CsSnI₃ crystal structures with ATMS anion of 1% (a-d) and 4% (e-h) concentrations. They were created from a conventional (mixed single – CsSnI₃ + ATMS) solution: (a-b and e-f) SEM images. Two images for each condition have different magnifications. The scale bar is 1 μm. (c-d and g-h) TEM images. Two images for each condition were measured by 1.0 M (left) and 1.2 M (right) magnification. Yellow circle dash lines show the collapsed crystal lattices in the CsSnI₃ phase.

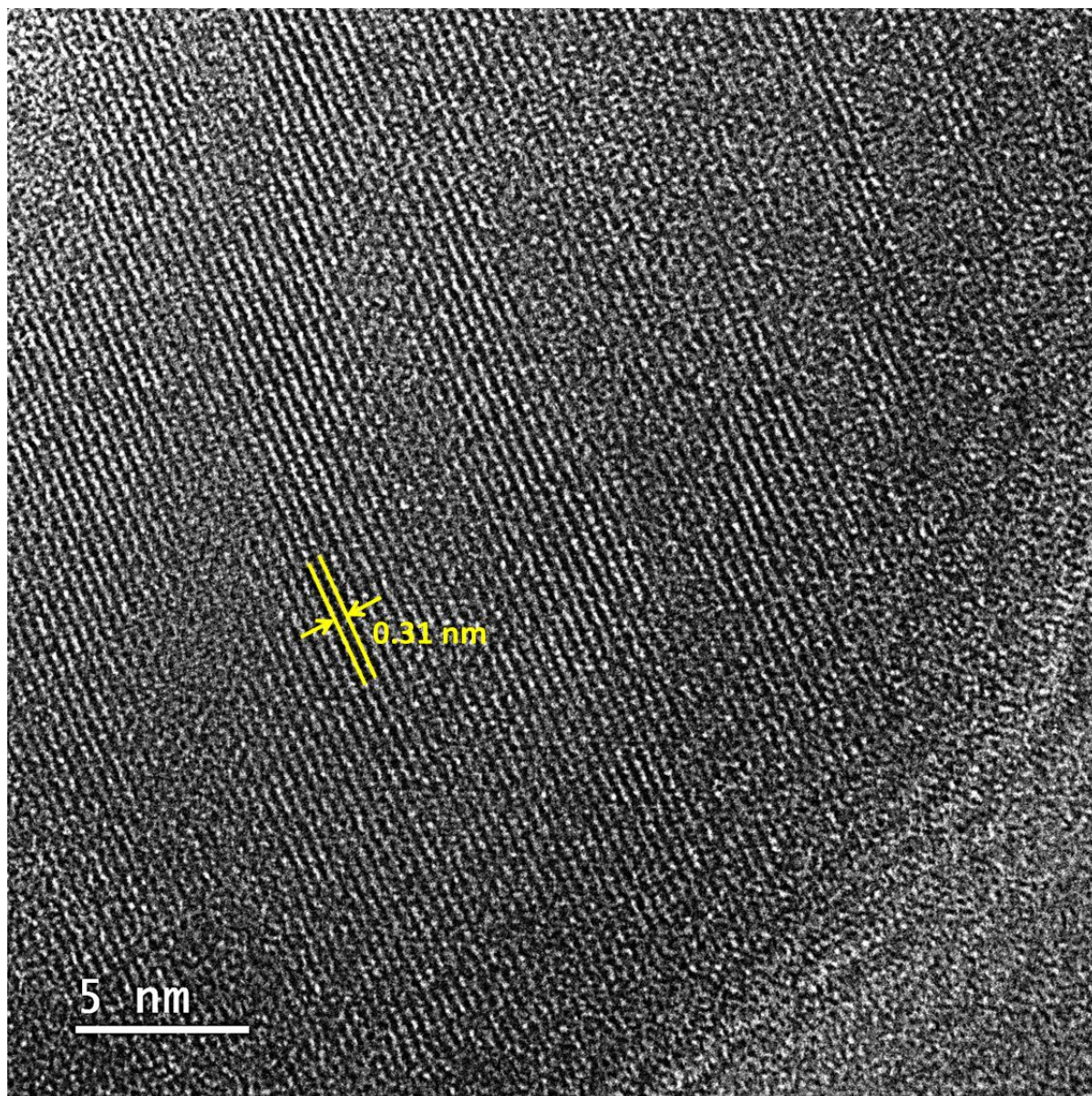


Fig. S16 Large-sized TEM image (raw data) of the synthesized CsSnI₃ perovskite crystal with the conventional method.

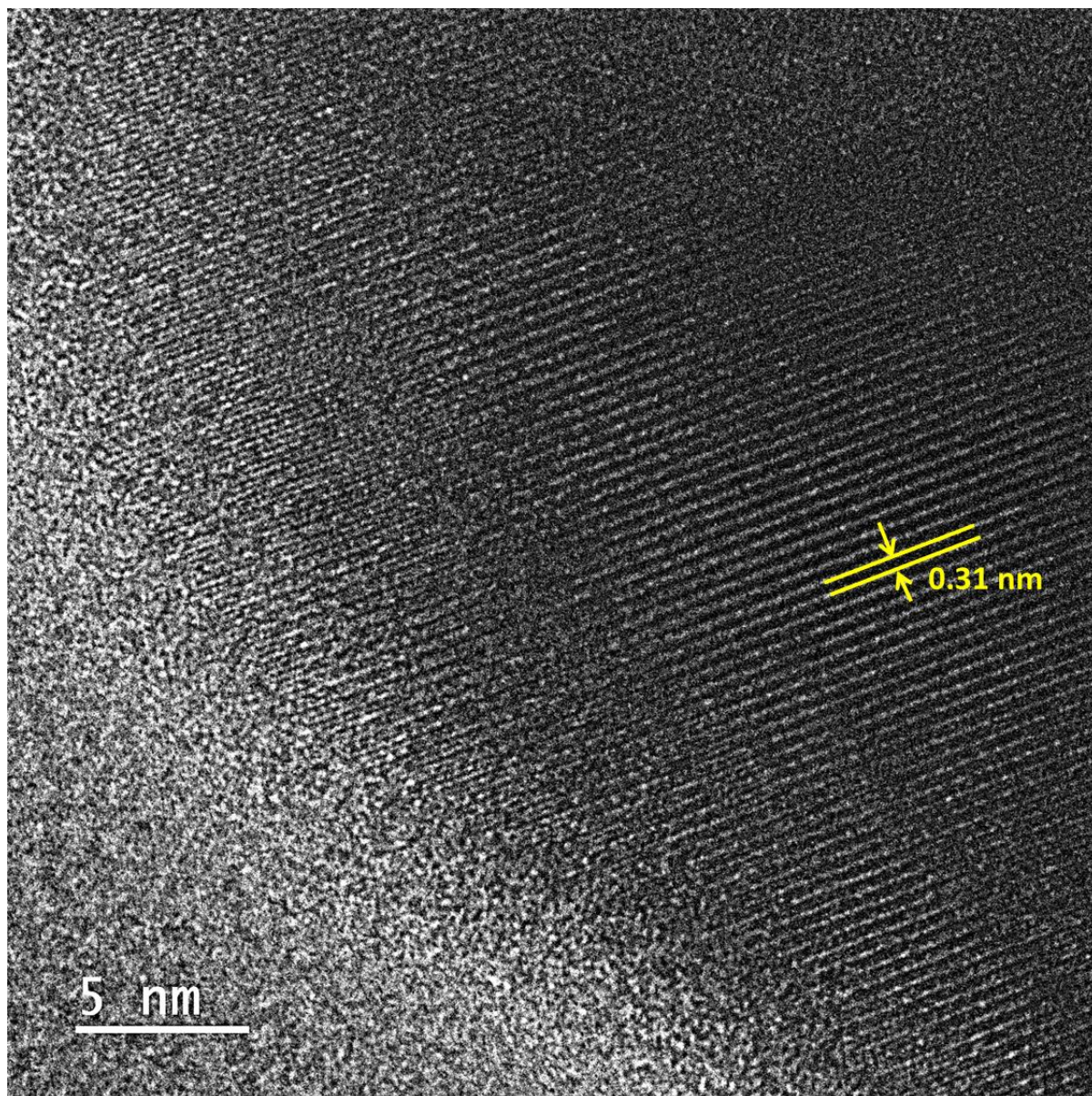


Fig. S17 Large-sized TEM image (raw data) of the synthesized CsSnI₃ perovskite crystal with the two-step process.