

Supporting Information

The 0D Cs₂TeI₆ Perovskite: Solution Processed Thick Films with High X-Ray Sensitivity

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Synthesis of TeI_4

Elemental Te (99.999% wt.) and I_2 (99.999% wt.) with the ratio of 1:2 were loaded into a fused silica ampoule with an inner diameter of 10 mm and sealed under a vacuum of 5×10^{-2} Pa. The sealed samples were heated to 170 °C over 10 h and held at the maximum temperature (300 °C) for 48 h before cooling to room temperature. Then the resulting dark gray (TeI_4) products, as confirmed by powder X-ray diffraction, were ground and stored in a nitrogen-filled glovebox for further use.

Characterization

Powder X-ray diffraction data (XRD) were collected on a Rigaku MiniFlex600 X-ray diffractometer ($\text{Cu K}\alpha$, 1.5406 Å) operating at 40 kV and 20 mA. Both Hitachi 4800 and 8030 SEM instrument was used for surface morphology observation. Simultaneously, the chemical compositions of local areas in Cs_2TeI_6 films were characterized using energy dispersive spectrometer (EDS) analysis. Transmittance of the perovskite films was obtained from 300 to 1200 nm at room temperature using a Shimadzu UV-3600 PC double-beam, double-monochromator spectrophotometer. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an Omicron ESCA Probe XPS spectrometer (Thermo Scientific ESCALAB 250Xi) using 150 eV pass energy and 1 eV step size for survey scan and 50 eV pass energy and 0.05 eV step size for band edge scan. Surface etching was performed by Ar-ion sputtering with 3 keV accelerating for 10 seconds.

Current-voltage (I-V) curves were measured at room temperature using a Keithley 6517b picoammeter/voltage supply under both low and high bias. The photosensitivity was conducted using a custom-made setup. The multilayer device was put inside a guarded dark box. Then the device was exposed to either ambient visible light or 473 nm laser source ($30 \text{ mW}\cdot\text{cm}^{-2}$, 1.2 mm laser spot diameter) with an ON-OFF state. The current- time (I-t) was obtained by Keithley 6517b. In addition, current density-voltage (J - V) characteristics of the devices were measured in air under 1 sun illumination (AM1.5G, $100 \text{ mW}\cdot\text{cm}^{-2}$) using a certified solar simulator (Abet Technologies) and Keithley 2400 source meter. For X-ray response measurements, Cs_2TeI_6 detectors were exposed to an X-ray source (Amptek Mini-X X-ray tube system with a silver target) with the low dose rate of $0.2\text{-}2 \text{ R}\cdot\text{min}^{-1}$. X-rays from the source were collimated using a brass cylinder with a 2-mm-diameter circular central bore. The source-to-detector distance was 5 cm. The X-ray intensity was modulated by adjusting the tube bias and current. The induced photocurrent signal of the detector was recorded as a function of time using a Keithley 6517b.

Synthesis and growth of Cs_2TeI_6 bulk crystal

The Cs_2TeI_6 crystals were synthesized from TeI_4 (mentioned above) and CsI (Sigma-Aldrich, 99.9%). The carbon coating silica ampoules were used for synthesis and crystal growth. The starting materials were sealed under a vacuum of $\sim 10^{-4}$ torr and heated at 610 °C for 24 h. The polycrystalline samples were directly subjected to crystal growth in a modified vertical two-zone Bridgman furnace equipped with a computer controlled linear stage. The temperature of the hot zone was 630 °C, while the cold zone was 450°C. The crystal growth was carried out with a lowering rate of 0.5 mm per hour. After the crystal growth, black Cs_2TeI_6 ingots 10 mm in diameter and 60 mm in length were obtained.

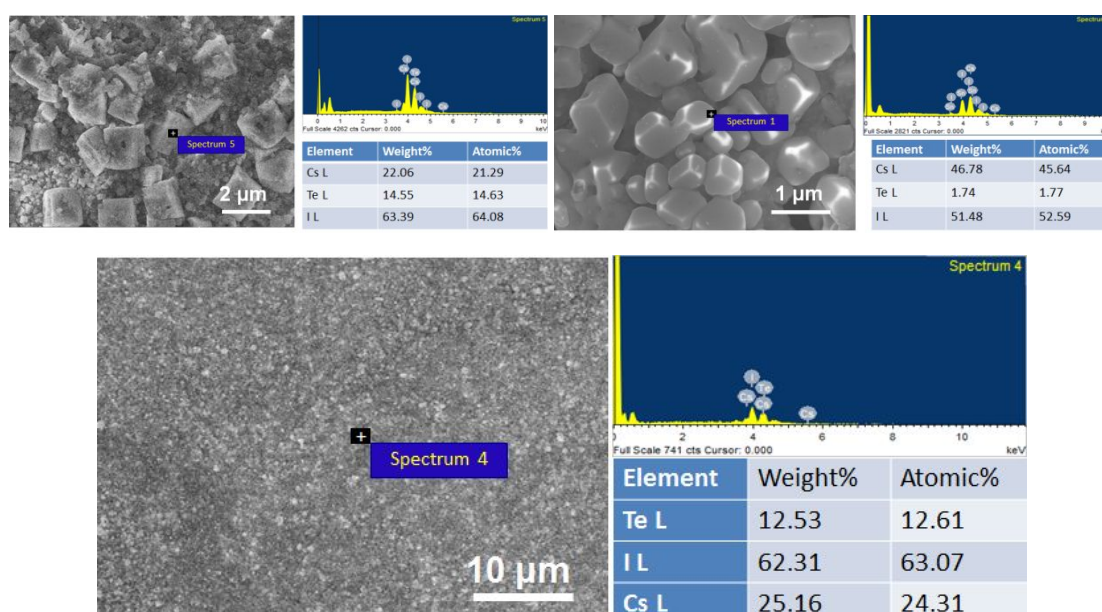


Figure S1. Composition measurements for Cs_2TeI_6 films using SEM-EDS.

Table 1. E-spray parameters for Cs_2TeI_6 thick film.

Organic solvents	Substrate temperature / $^{\circ}\text{C}$	DC bias /KV	Substrate-nozzle distance D_{sn} /cm	Spray rate / $\text{mL}\cdot\text{h}^{-1}$
DMF: Ethanol	160	15	7.5	1.2

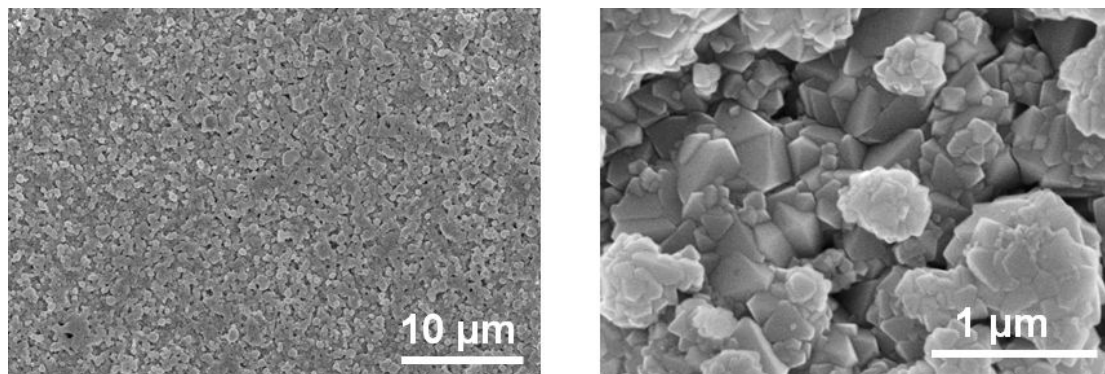


Figure S2. SEM images of Cs_2TeI_6 films when the solvent evaporated rapidly, nano size clusters are formed.

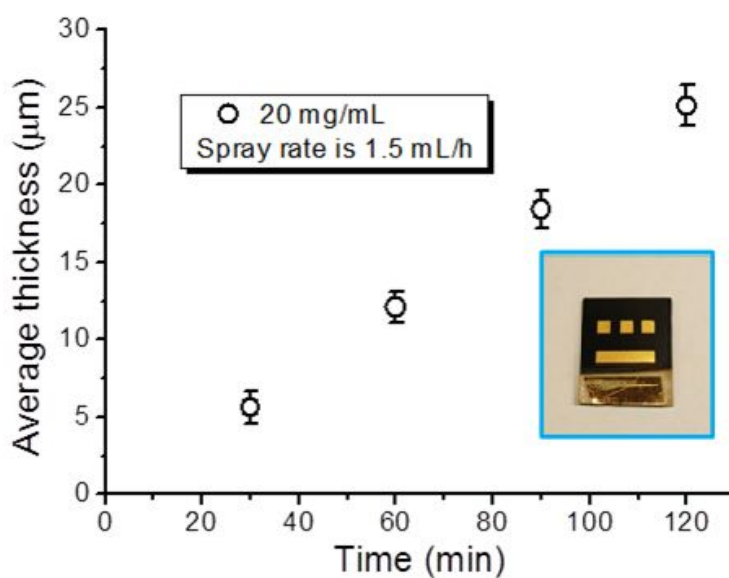


Figure S3. Average thickness of Cs_2TeI_6 films as a function of spray time. Inset is a completed multilayer Cs_2TeI_6 device.

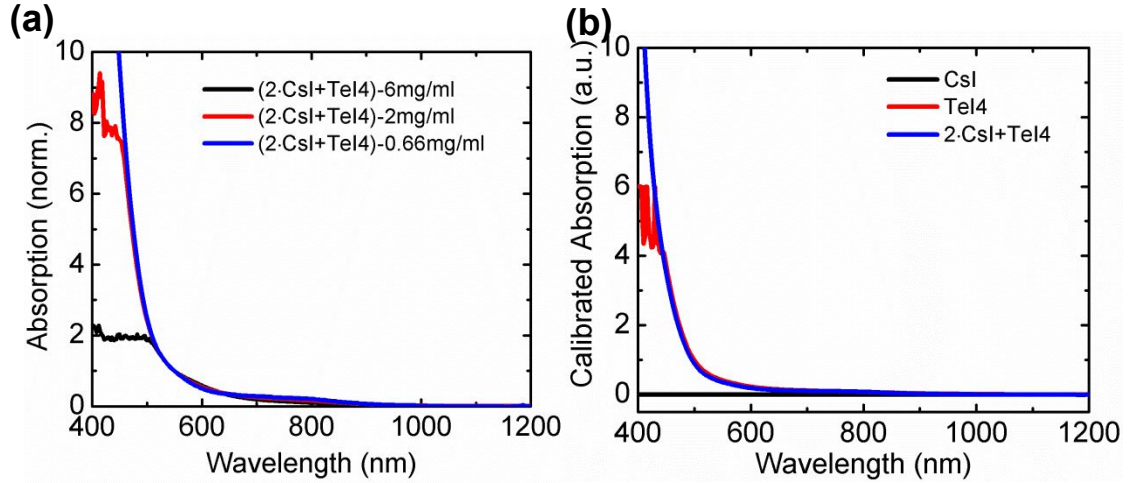


Figure S4. Absorption spectra of the Cs_2TeI_6 precursor solution. (a) Absorption spectra of Cs_2TeI_6 precursor solution at different concentrations (normalized at 550 nm), showing significant blue shift of the absorption with respect to Cs_2TeI_6 absorption. (b) Absorption spectra of Cs_2TeI_6 precursor solution, and each precursor absorption. The Cs_2TeI_6 precursor absorption is comparable with the TeI_4 absorption, indicating nano size Cs_2TeI_6 precipitates were not formed in the solution. The CsI solution shows no absorption at the visible range and it is also transparent by eye (also at high concentrations).

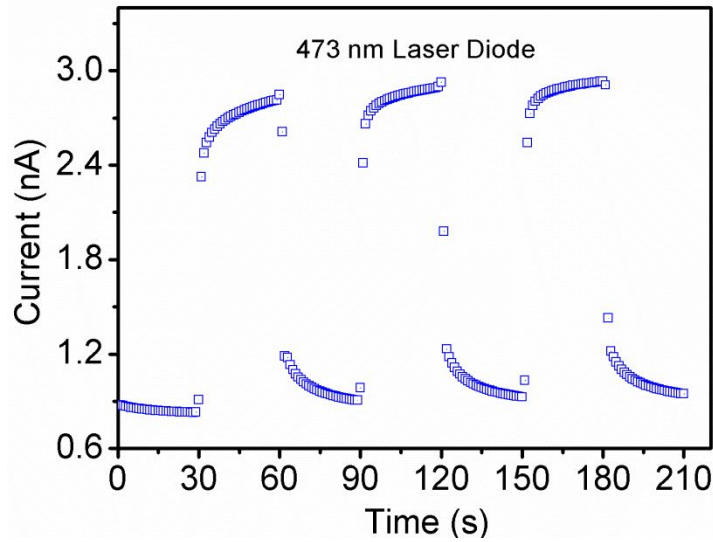


Figure S5. Steady-state I-V measurements under applied electric field of $400 \text{ V} \cdot \text{cm}^{-1}$, illuminated by a 473 nm laser diode, with bias applied to the FTO contact.

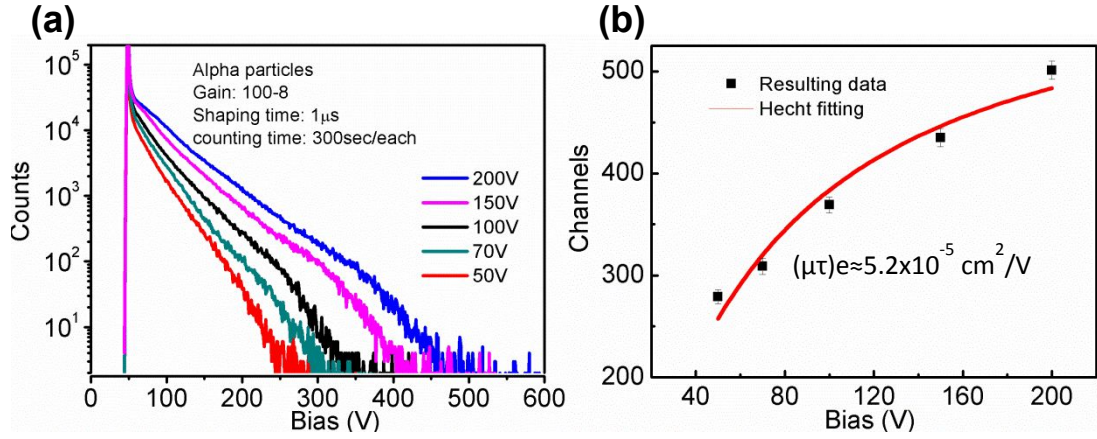


Figure S6. Alpha response of Cs_2TeI_6 bulk crystals obtained by vertical Bridgman method. (a) After wafer processing and device fabrication, α particle induced pulse height spectra was measured using an un-collimated ^{241}Am (5.48 MeV) radioactive source at room temperature. The electron mobility lifetime products $(\mu\tau)_e$ of the Cs_2TeI_6 crystals were expected by fitting the plots of photo-peak position vs electrical field strength using the single carrier Hecht equation.

$$CCE \approx \frac{\mu\tau V}{d^2} \left[1 - \exp\left(-\frac{d^2}{\mu\tau V}\right) \right] \quad (1)$$

where CCE is the charge collection efficiency, μ and τ are the carrier mobility and lifetime, respectively. D is the sample thickness. V is the applied electrical bias. (b) A $(\mu\tau)_e$ value of $5.2 \times 10^{-5} \text{ cm}^2 \text{V}^{-1}$ was obtained for the as-grown Cs_2TeI_6 crystals.

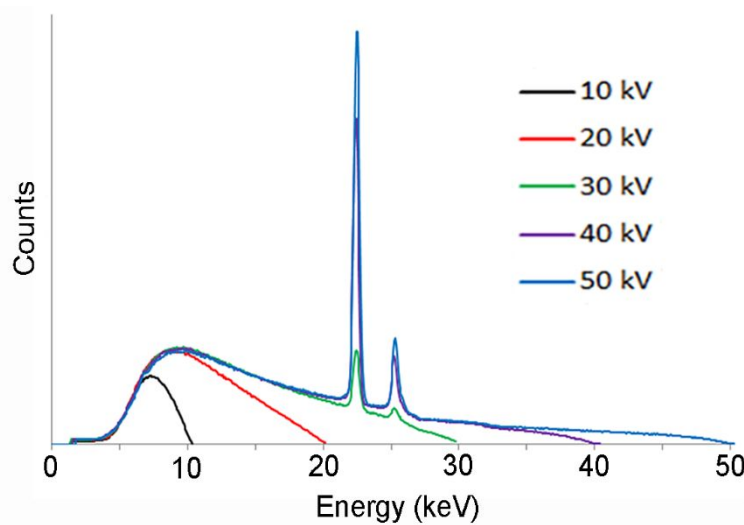


Figure S7. Mini-X silver (Ag) output spectrum at 10, 20, 30, 40 and 50 kVp, from Amptek, Inc. <http://amptek.com/products/mini-x-ray-tube/>

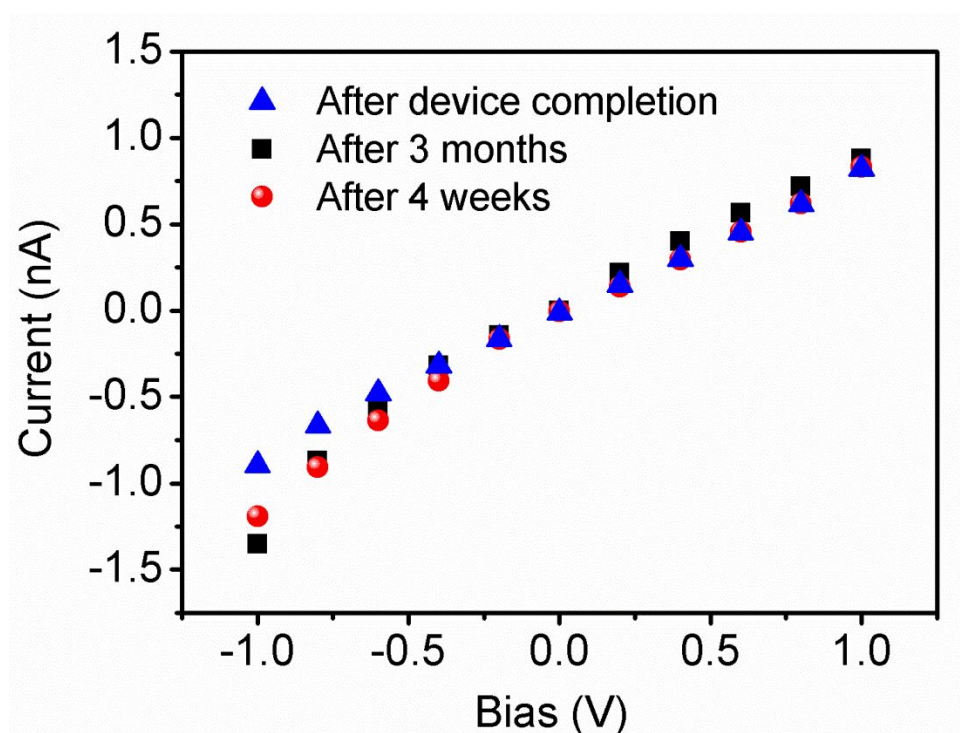


Figure S8. Room-temperature I-V characteristics over a period of 3 months for a 25- μm -thick planar Cs_2TeI_6 device under applied electric field of $400 \text{ V}\cdot\text{cm}^{-1}$.