

Supporting Information for

Potassium-Regulated for Enhanced Scintillation Properties of Lead-Free Cesium Copper Iodide Cs₃Cu₂I₅ Perovskite and Their Applications for High-Resolution X-Ray Imaging

Tong Wu¹, Yun Shi^{2,3*}, Haodi Wu⁴, Mingyue Chen¹, Hongbing, Ran¹, Jiaqian
Zheng², Xiang Li², Junfeng Chen^{2,3}, Yiwen Tang^{1*}

1. *College of Physical Science and Technology, Central China Normal University,
Wuhan 430079, China;*

2. *Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 201899,
China;*

3. *Center of Materials Science and Optoelectronics Engineering, University of Chinese
Academy of Science, Beijing 100049, China;*

4. *Wuhan National Laboratory for Optoelectronics (WNLO) and School of Optical and
Electronic Information, Huazhong University of Science and Technology (HUST),
Wuhan 430074, P. R. China.*

**Corresponding Author: E-mail: ywtang@ccnu.edu.cn; shiyun@mail.sic.ac.cn*

Experimental process

Materials. Cesium iodide (CsI, 99.999%), Copper(I) iodide (CuI, $\geq 99.95\%$), and Poly (methyl methacrylate) (PMMA) were purchased from Aladdin. Potassium iodide (KI, 99.95%) was purchased from 3A. Dimethyl sulfoxide (DMSO, 99.9%) of reagent grade was purchased from Sigma—Aladdin. N, N-dimethylformamide (DMF, $\geq 99.8\%$, anhydrous) was purchased from ACROS Organics. Isopropanol was purchased from Sinopharm Chemical Reagent. The powders and solvent were stored in a nitrogen-filled glovebox and used without further purification.

Cs₃Cu₂I₅:K⁺ films deposition by a spin coating method. Using quartz /FTO glass as the substrates, it was ultrasonic cleaned with glass water cleaner, deionized water, and alcohol in turn, blown dry and cut to 1*1cm size, and treated with ozone for 15 minutes before use. CsI, CuI, and KI commercial powders were mixed into powders at different K⁺ concentrations according to the molecular formula (Cs_{1-x}K_x)₃Cu₂I₅ (denoted as Cs₃Cu₂I₅:K⁺), where x = 0, 0.5 at. %, 1 at. %, 2 at. %, 4 at. % and 8 at. %, respectively. Then the mixed powders were dissolved into DMSO (1 mL) and stirred for 12 h at 60 °C to form a 1 M concentration Cs₃Cu₂I₅:K⁺ precursor solution. Subsequently, thin films were formed by one-step spin coating of the fully dissolved precursor solution (50 μL) at a speed of 3000 rpm for 60 s on a quartz/FTO substrate. Finally, it was annealed at 100°C on a hot table for 1h.

Cs₃Cu₂I₅:K⁺@PMMA composite films deposition by a spin coating method.

Firstly, 15 wt.% PMMA/DMF was mixed with 1 M concentration Cs₃Cu₂I₅:K⁺ precursor solution at a volume ratio of 3:1 and ultrasonically dispersed. Then,

$\text{Cs}_3\text{Cu}_2\text{I}_5:\text{K}^+$ @PMMA flexible films were obtained by spin-coating with the 200 μL mixture adhesive on a size of $2.5 \times 2.5 \text{ cm}^2$ glass substrate at 200 rpm for 60 s, followed by annealing at 70 °C for 120 min on a hot plate and peeling it from the glass substrate by using a blade.

The single crystals $\text{Cs}_3\text{Cu}_2\text{I}_5$ and $\text{Cs}_3\text{Cu}_2\text{I}_5:\text{K}^+$ were grown by VSA. A 1M solution of $\text{Cs}_3\text{Cu}_2\text{I}_5$ precursor was titrated with methanol. A white precipitate will appear at the beginning of the titration process and quickly disappear at dissolution. Titrate several times until the precipitate is no longer dissolved, at which point the solution is saturated. Then, the solution was filtered using a polytetrafluoroethylene (PTFE) filter head with a pore size of 0.45 μm . The clarified yellow precursor solution was injected into a 10 ml glass bottle and sealed with layers of paraffin films with several holes designed to control the amount of methanol evaporation. The reaction device was placed in a polytetrafluoroethylene liner containing an appropriate amount of methanol and sealed with a high-pressure reaction kettle. High-quality $\text{Cs}_3\text{Cu}_2\text{I}_5$ single crystals with a size of about $9 \times 6 \times 3 \text{ mm}^3$ were obtained after 48 h growth in an oven at 60°C. Single crystal $\text{Cs}_3\text{Cu}_2\text{I}_5:1\%\text{K}^+$ was grown by the same synthesis method.

Synthesis of $\text{Cs}_3\text{Cu}_2\text{I}_5:1\%\text{K}^+$ Polycrystalline Powders. The synthesized 1 ml $\text{Cs}_3\text{Cu}_2\text{I}_5:1\%\text{K}^+$ precursor solution was extracted into 10 mL isopropanol and ultrasound oscillation was performed for 5 min. Subsequently, a significant white precipitate can be observed in the mixed solution. Then, the precipitation was obtained by centrifugation at 9,500 rpm for 5 min two times and the supernatant was discarded. Finally, the wet $\text{Cs}_3\text{Cu}_2\text{I}_5:1\%\text{K}^+$ polycrystalline powders need to be dried at 70 °C under

vacuum for 12h before further use.

Characterization Methods.

The X-ray diffraction (XRD) patterns of the $\text{Cs}_3\text{Cu}_2\text{I}_5$ thin films were obtained using a Rigaku Ultima IV diffractometer with a Cu K α source (40 kV, 40 mA, Rigaku Ultima IV, Japan) at a scanning speed is $5^\circ/\text{min}^{-1}$ in the 2θ range of $10 - 90^\circ$. X-ray photoelectron spectroscopy (XPS) (Thermo Scientific ESCALAB Xi+) was used to analyze the valence states of Cs, Cu and I. The morphology and elemental analysis were performed on a JSM-7900F scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS). High-resolution inductively coupled plasma atomic emission spectrometry (ICP-AES) (Agilent 720ES (OES)) was measured to characterize the actual doping concentration of K^+ . Software Nano Measurer was used to calculate the grain size. The absorption spectra were collected using a UV-vis-NIR photometer (Varian Cary 5000). Photoluminescence (PL) and excitation (PLE) spectra were recorded on a Hitachi F-4600 fluorescence spectrophotometer. The absolute PL quantum yield (PLQY) was measured on an MCPD-7000 multichannel spectrometer (Otsuka Electronics Company, Osaka, Japan) equipped with an integrating sphere with an excitation wavelength of 299 nm. The time-resolved PL (TRPL) decay spectra of $\text{Cs}_3\text{Cu}_2\text{I}_5$ powder measurements were obtained by using an Edinburgh Instruments FLS1000. The single crystal data and structure were examined by X-ray diffraction (XRD) with Cu K α radiation (Bruker, Venture, Germany). Stead-state radioluminescence spectra of the single crystals were collected by a 928P photomultiplier tube (PMT) and analyzed by an Edinburgh FLS920

fluorescence spectrometer. (Amptek Mini-X-OEM X-ray tube: 40 V, 80 μ A). The light output of the single crystals under γ -ray excitation (Cs-137 source , 662KeV) was measured by using a PMTR2059 with a shaping time of 0.5 μ s. The scintillation decay was measured on-site by an oscilloscope (TELEDYNE Lecroy 8104). Imaging was performed using Newton Scientific X-ray tube, Au target, bulb tube voltage 50 kV, and dose of about 20 mGy_{air} s⁻¹.

Table S1. Composition of K⁺- doped Cs₃Cu₂I₅ powders measured by ICP-OES instrument.

K / (Cs + K) precursors ratio (%)	ICP-OES analysis	
	Composition	K / (Cs + K) (%)
0	Cs₃Cu₂I₅	/
1	Cs₃Cu₂I₅:1%	0.2
4	Cs₃Cu₂I₅:4%	0.4
8	Cs₃Cu₂I₅:8%	0.9

Table S2. Crystal data and structure refinement for Cs₃Cu₂I₅.

Empirical formula	Cs ₃ Cu ₂ I ₅
Formula weight	1160.31
Temperature/K	200.0
Crystal system	orthorhombic
Space group	Pnma
a/Å	10.1262(7)
b/Å	11.6141(9)
c/Å	14.3142(11)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	1683.4(2)
Z	4
ρ _{calc} /cm ³	4.578
μ/mm ⁻¹	97.406
F(000)	1952.0
Crystal size/mm ³	0.06 × 0.04 × 0.03
Radiation	Synchrotron (λ = 1.34139)
2θ range for data collection/°	8.53 to 104.86
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -16 ≤ l ≤ 16
Reflections collected	10823
Independent reflections	1530 [R _{int} = 0.1778, R _{sigma} = 0.1104]
Data/restraints/parameters	1530/0/56
Goodness-of-fit on F ²	1.006
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0671, wR ₂ = 0.1472
Final R indexes [all data]	R ₁ = 0.0928, wR ₂ = 0.1592
Largest diff. peak/hole / e.Å ⁻³	2.79/-2.35

Table S3. Crystal data and structure refinement for Cs₃Cu₂I₅:1%K⁺.

Empirical formula	(KCs) ₃ Cu ₂ I ₅
Formula weight	1160.31
Temperature/K	200.0
Crystal system	orthorhombic
Space group	Pnma
a/Å	10.129(4)
b/Å	11.614(4)
c/Å	14.308(5)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	1683.2(10)
Z	4
ρ _{calc} /cm ³	4.579
μ/mm ⁻¹	97.418
F(000)	1952.0
Crystal size/mm ³	0.04 × 0.03 × 0.02
Radiation	Synchrotron (λ = 1.34139)
2θ range for data collection/°	8.53 to 115.894
Index ranges	-11 ≤ h ≤ 11, -4 ≤ k ≤ 9, -7 ≤ l ≤ 17
Reflections collected	2461
Independent reflections	1209 [R _{int} = 0.2516, R _{sigma} = 0.1704]
Data/restraints/parameters	1209/0/56
Goodness-of-fit on F ²	1.179
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.1201, wR ₂ = 0.3114
Final R indexes [all data]	R ₁ = 0.1344, wR ₂ = 0.3295
Largest diff. peak/hole / e.Å ⁻³	3.12/-4.98

Table S4. Bond Angles for I-Cu-I of Cs₃Cu₂I₅.

Atom	Atom	Atom	Angle/°
I(3)	Cu(1)	I(1)	102.50(11)
I(3)	Cu(1)	I(1) ¹⁰	102.50(11)
I(1) ¹⁰	Cu(1)	I(1)	104.28(15)
I(2)	Cu(1)	I(3)	121.63(17)
I(2)	Cu(1)	I(1) ¹⁰	112.05(11)
I(2)	Cu(1)	I(1)	112.05(11)
I(4)	Cu(2)	I(1) ¹⁰	120.10(11)
I(4)	Cu(2)	I(1) ¹⁰	120.10(11)
I(4)	Cu(2)	I(1)	120.10(11)

Table S5. Bond Angles for I-Cu-I of Cs₃Cu₂I₅:1%K⁺.

Atom	Atom	Atom	Angle/°
I(2)	Cu(1)	I(3)	121.63(17)
I(1)	Cu(1)	I(3)	102.73(17)
I(1)	Cu(1)	I(3) ¹²	102.73(17)
I(2)	Cu(1)	I(1)	121.2(3)
I(2)	Cu(1)	I(3) ¹²	111.89(16)
I(2)	Cu(1)	I(3)	111.89(16)
I(3)	Cu(1)	I(3) ¹²	104.7(2)
I(3)	Cu(2)	I(3) ¹²	117.4(3)
I(4)	Cu(2)	Cu(1)	156.7(6)
I(4)	Cu(2)	I(3)	120.17(16)
I(4)	Cu(2)	I(3) ¹²	120.17(16)

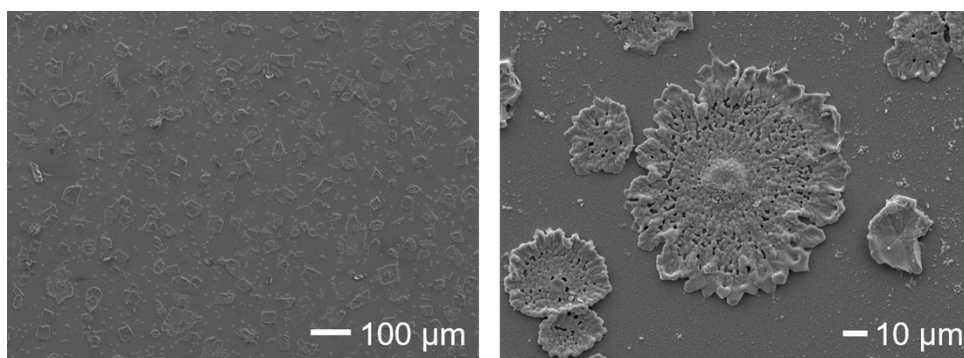


Figure S1. SEM image of as-prepared $\text{Cs}_3\text{Cu}_2\text{I}_5:1\%\text{K}^+$ film

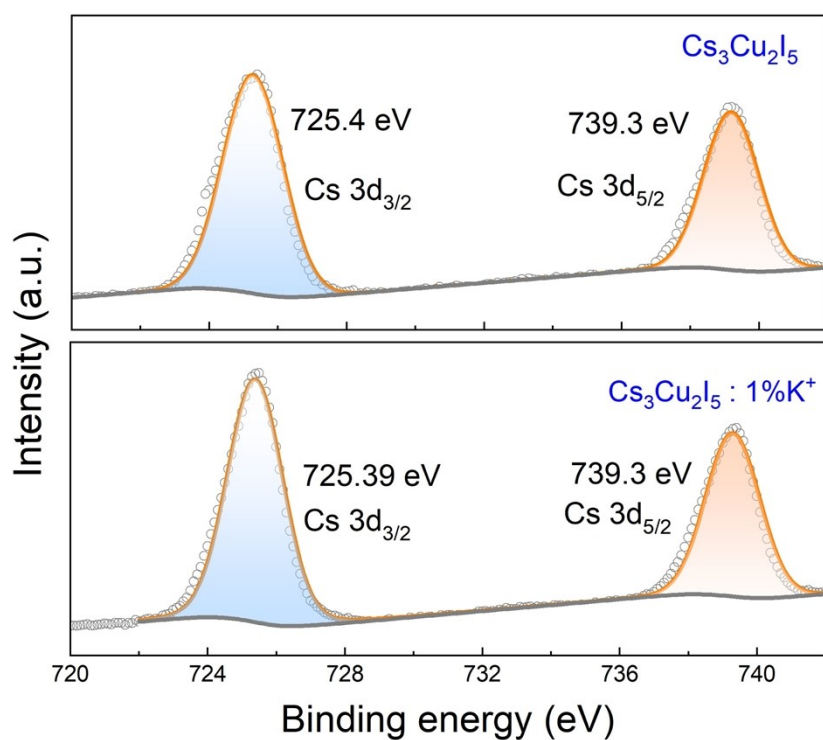


Figure S2. High-resolution XPS spectrum of Cs ($3d_{5/2}$ and $3d_{3/2}$) of $\text{Cs}_3\text{Cu}_2\text{I}_5:x\%K^+$ powder synthesized with and without K, respectively.

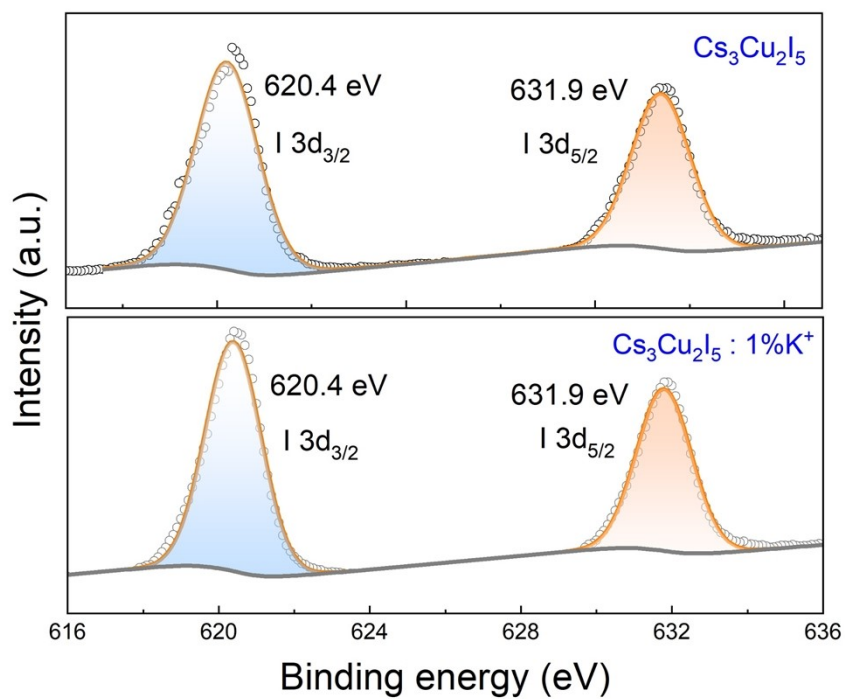


Figure S3. High-resolution XPS spectrum of I (3d_{3/2} and 3d_{5/2}) of $\text{Cs}_3\text{Cu}_2\text{I}_5 : x\% \text{K}^+$ powder synthesized with and without K, respectively.

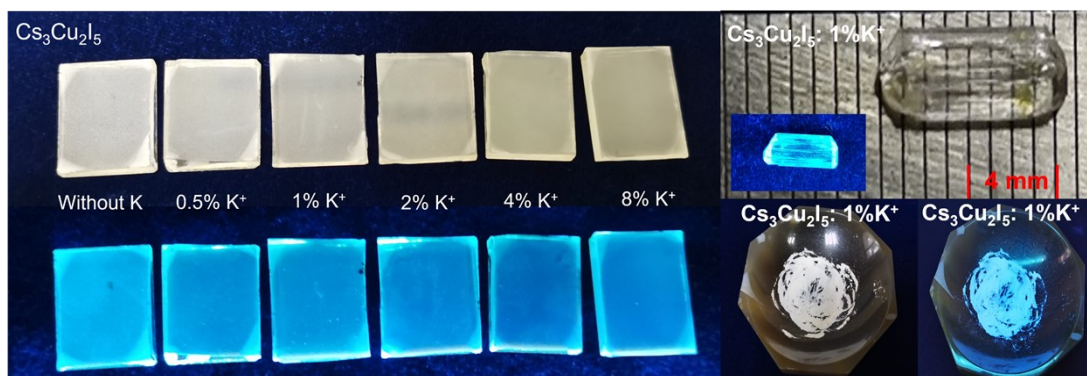


Figure S4. Photographs of the $\text{Cs}_3\text{Cu}_2\text{I}_5$:x%K⁺ films, powders, and single crystal under daylight and ultraviolet light ($\lambda = 254 \text{ nm}$)

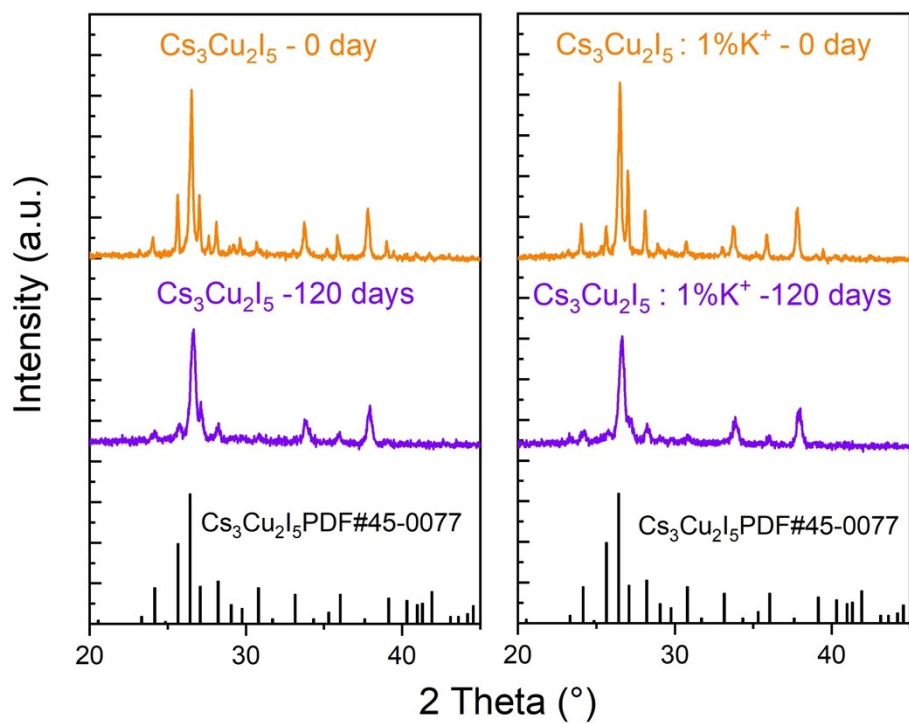


Figure S5. XRD stability of the as-prepared $\text{Cs}_3\text{Cu}_2\text{I}_5$ and $\text{Cs}_3\text{Cu}_2\text{I}_5:1\% \text{K}^+$ films.

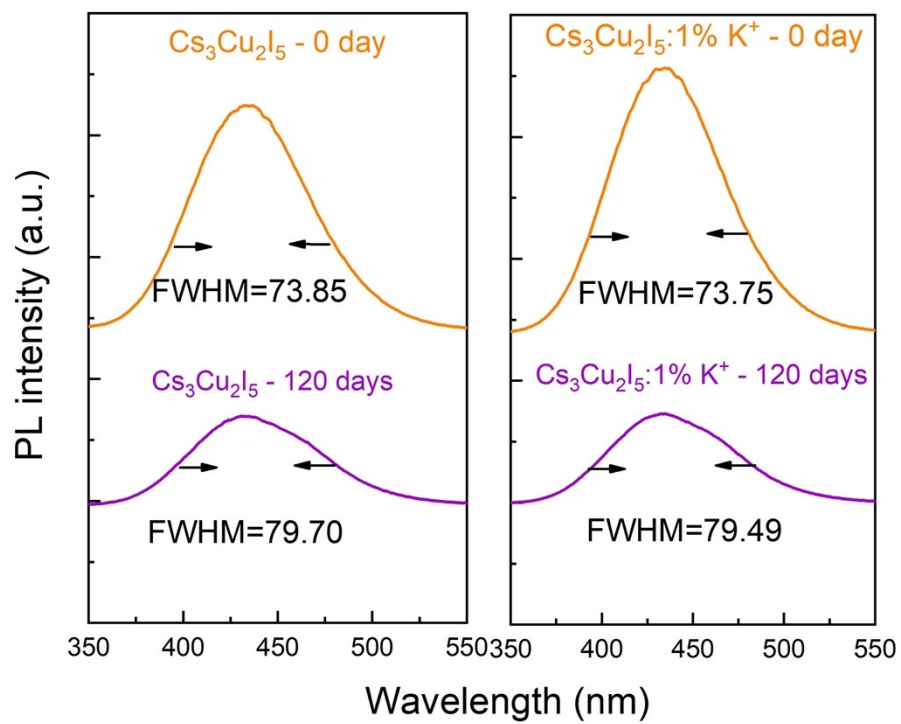


Figure S6. PL stability of the as-prepared $\text{Cs}_3\text{Cu}_2\text{I}_5$ and $\text{Cs}_3\text{Cu}_2\text{I}_5:1\% \text{K}^+$ films.

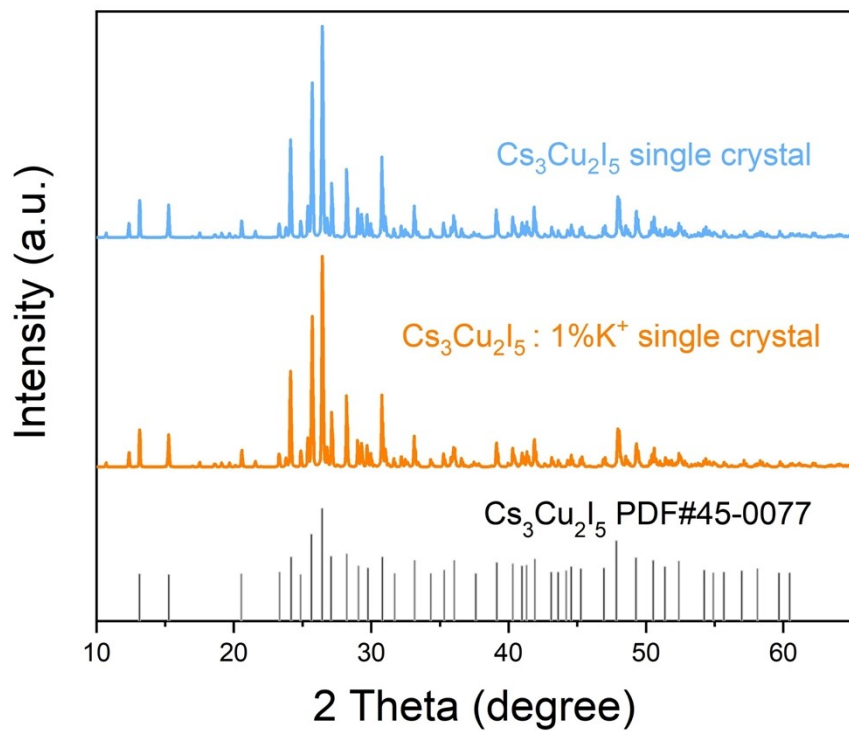


Figure S7. XRD patterns of the as-grown Cs₃Cu₂I₅ and Cs₃Cu₂I₅:1% K⁺ single crystals.

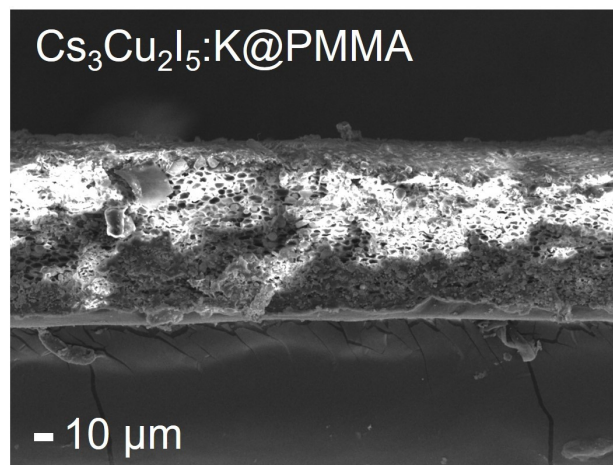


Figure S8. The cross-sectional SEM image of the Cs₃Cu₂I₅:K⁺@PMMA flexible film.