

SUPPORT INFORMATION

All-green Cs₄CuSb₂Cl₁₂ perovskite films deposited in situ by AACVD and their doping with F⁻ ions for photodetectors and memdiodes.

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Diffuse reflectance measurement details and optical bandgap calculation

Diffuse reflectance spectra of the CCSC and CCSCF films deposited on top of glass substrates were measured using an integrating sphere under synchronous scan, i.e., both, excitation and emission monochromators are set to the same wavelength. To eliminate any optical signals originating from the glass substrate, the sample was enclosed within a Teflon mask that featured an open window. This design allowed only the surface of the perovskite films to be exposed while concealing the glass substrate from the excitation light. For optical bandgap determination from reflectance spectra, the procedure reported elsewhere was employed as follows:¹

The CCSC and CCSCF reflectance spectra acquired were transformed into pseudo-absorbance spectra using the Kubelka-Munk equation:

$$\alpha = (1 - R) / (2R),$$

where R represents the reflectance, and α stands for the pseudo-absorbance. Subsequently, a modified Kubelka-Munk function was determined by multiplying α by the photon energy $h\nu$, incorporating the relevant coefficient n associated with an electronic transition:

$$\alpha * h\nu,$$

with n equaling 2 for direct transitions. To determine the band gaps, a linear portion of the plot ($\alpha * h\nu$)² against E (photon energy) was fitted, and the x-intercept was used for extraction.

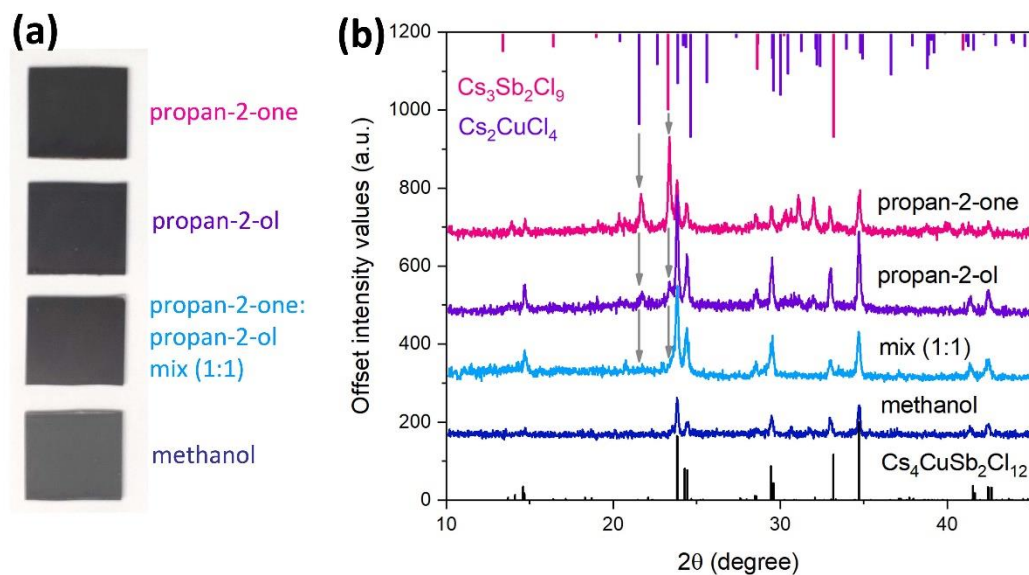


Figure S1. Digital photographs taken under ambient light illumination of four $\text{Cs}_4\text{CuSb}_2\text{Cl}_{12}$ films deposited by AACVD using different solvent conditions for the $\text{CuCl}_2 - \text{SbCl}_3$ precursor solution (a), and their respective X-ray diffractograms (b). The diffraction patterns for the $\text{Cs}_4\text{CuSb}_2\text{Cl}_{12}$ (black lines), $\text{Cs}_3\text{Sb}_2\text{Cl}_9$ (pink lines), and Cs_2CuCl_4 (purple lines) were simulated from CIF data.

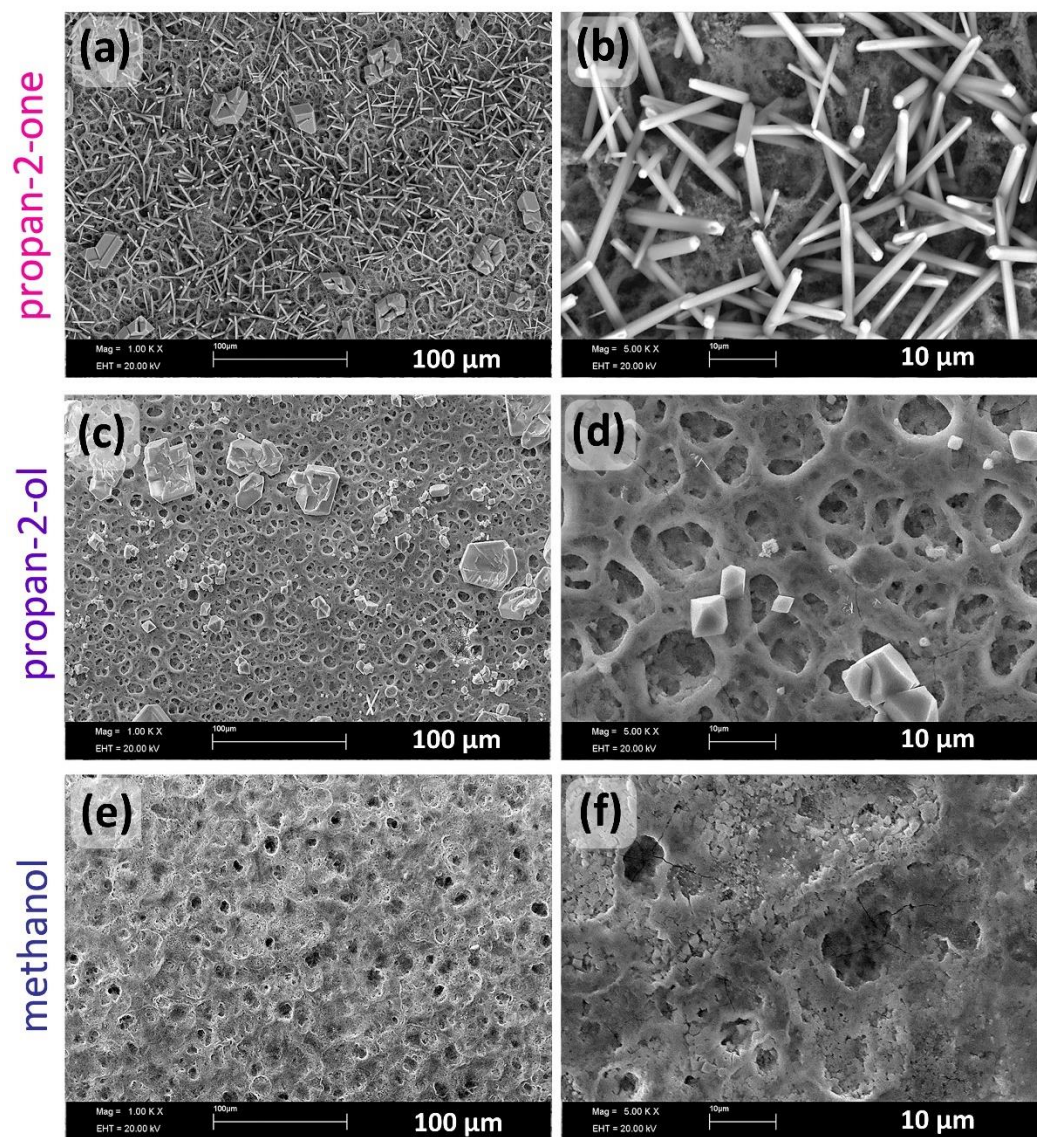


Figure S2. SEM images at different magnifications of the films using propan-2-one (a-b), propan-2-ol (c-d), and methanol (e-f), as solvents for the $\text{CuCl}_2 - \text{SbCl}_3$ precursor solution.

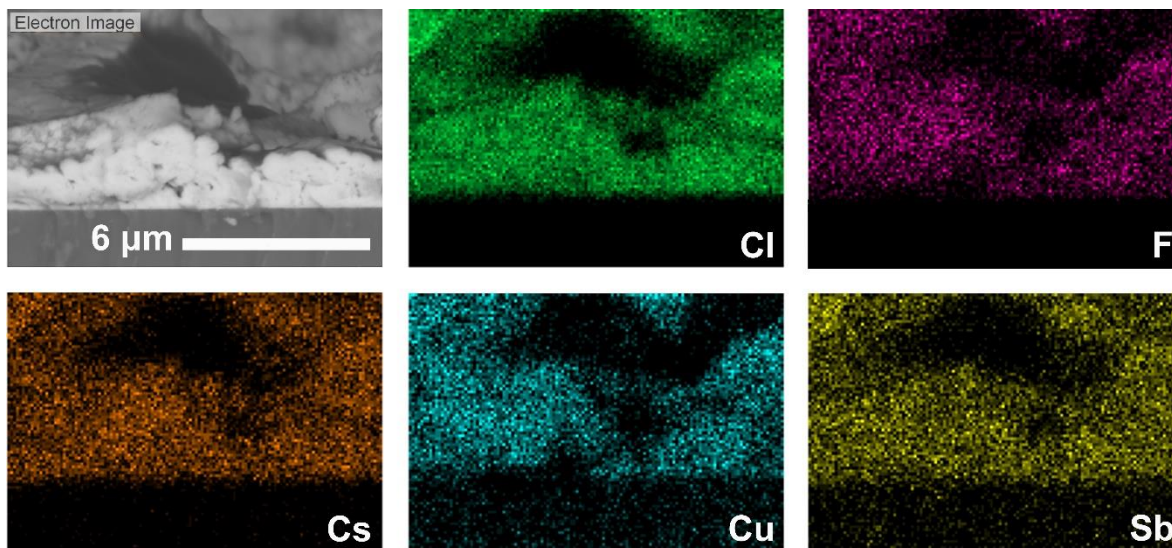


Figure S3. Cross-sectional SEM image of the CCSCF film mapped area and the elemental mapping of the Cl, F, Cs, Cu, and Sb elements.

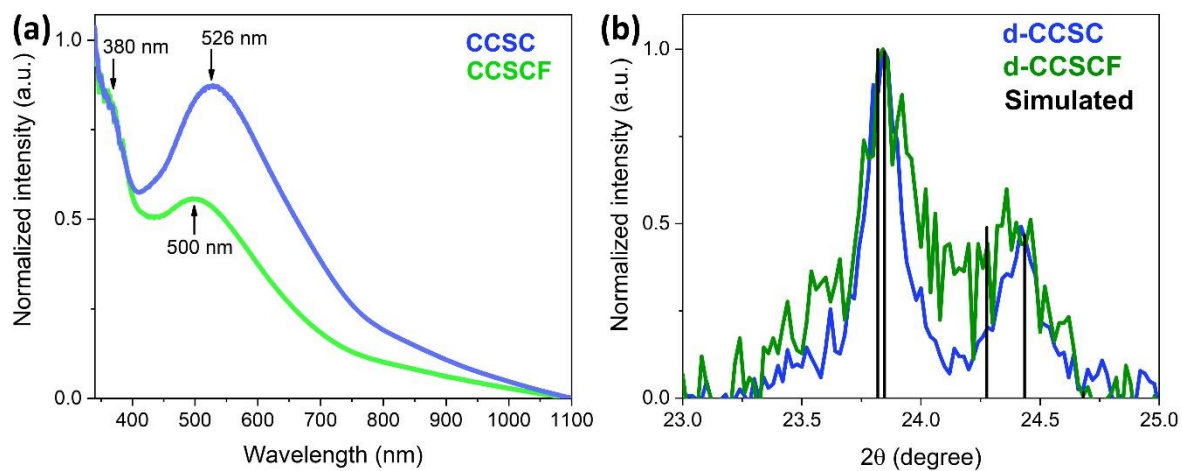


Figure S4. Normalized UV-Vis-NIR absorbance spectra of the CCSC and CCSCF films (a). Normalized diffraction patterns of the d-CCSC and d-CCSCF films, along with the simulated diffraction pattern from CIF data (b).

Table S1. Solubilities (g/100 g solvent) of the precursor salts in the respective solvents used in this study.

	water	methanol	propan-2-one	propan-2-ol
CsCl	186.5 (20 °C) ²	3.39 (18 °C) ³		
CuCl₂			2.97 (18 °C) ⁴	19 (40 °C) ⁵
SbCl₃			537.6 (18 °C) ⁶	Soluble ⁷
SbF₃			70 (25°C) ⁵	42.7 (25°C) ⁵

Table S2. Undoped Cs₄CuSb₂Cl₁₂ bandgap values reported for different crystal presentations.

Presentation	E_g (eV)	Ref
Microcrystals	1.02	1
Microcrystals	1.14	8
Nanocrystals	1.6	9
Nanocrystals	1.79	10
Microcrystals	1.16	11
Nanocrystals	1.56	12
Nanocrystals	1.92	13
Nanocrystals	1.96	14
Nanocrystals	1.67	15
Microcrystals	1.4	15
Microcrystals	1.32	16
Nanocrystals	2.2	16
Single crystal	1.13	17
Microcrystals	1.66	18
Film	1.65	This work

Table S3. Electrical characteristics of metal halide perovskite materials

Sample	Mobility (cm ² /Vs)	Carrier density (cm ⁻³)	Conductivity (S/cm)	Method	Ref.
Cs ₄ CuSb ₂ Cl ₁₂ nanocrystals	2.5 (electrons) 2.5 (holes)	-	.	Input parameter in device modelling and simulation	19, 20
FA _{0.83} CS _{0.17} Pb(I _{0.9} Br _{0.1}) ₃ polycrystalline films	0.04 – 1.4 (sum of electrons and holes)	-	-	Time resolved microwave conductivity (TRMC)	21
(FA _{0.83} MA _{0.17}) _{0.95} CS _{0.05} Pb(I _{0.9} Br _{0.1}) ₃	0.3 – 6.7 (electrons and holes)	1.1x10 ¹⁴	1 x 10 ⁻⁵	TRMC	21
(C ₆ H ₅ C ₂ H ₄ NH ₃) ₂ SnI ₄ film (2D)	0.6 (holes)	-	-	Field effect transistor (FET)	2223
PEASnI ₄ film (2D)	15 (holes)	-	-	(FET)	2324
MA _{n-1} PEA ₂ Pb _n I _{3n+1} film (2D)	6-11 (electrons and holes)			Optical pump probe spectroscopy	23
MAPbI ₃ thin films	8 – 35 (electrons and holes)		-	Space Charge Limited current (SCLC), Transiet absorption spectroscopy, Hall Effet, FET	252627
α-phase FAPbI ₃ thin film	1.1	1.3x10 ¹⁶	1.1x10 ⁻⁷		28
δ-phase FAPbI ₃ single crystals	0.179	3.1x10 ¹¹	8.9x10 ⁻⁹		28
MAPbI _{3-x} Cl _x	11.6	10 ¹⁵ -10 ¹⁷	-		26
MAPbBr ₃	13	1x10 ¹³		SCLC	29
MAPbI ₃	8	9x10 ¹⁴	-	Hall and solid state photoconductivity	30
MAPbBr ₃	60	1x10 ¹²	-	Hall and solid state photoconductivity	30
MAPbBr ₃	8	2x10 ¹²		Hall	31
Cs ₄ CuSb ₂ Cl ₁₂ :F film	0.4	1.65x10 ¹⁵	1.94 x 10 ⁻⁵	Hall	[This work]

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