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Cu-based quaternary chalcogenide Cu_2BaSnS_4 thin films acting as hole-transport layers in inverted perovskite $CH_3NH_3PbI_3$ solar cells

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Experimental Section

Materials synthesis and device fabrication:

Cu_2BaSnS_4 (CBTS): CBTS precursor films were deposited on commercial fluorine–doped SnO_2 (FTO) glass (TEC 15, NSG) substrates by co−sputtering Cu, SnS and BaS targets (3 in., Plasma Materials Co.) using the LAB Line SPUTTER 5 system (Kurt J Lesker Co.). The substrate temperature was kept at 150 °C during the co−sputtering. The Cu poor composition of film precursors was controlled by varying the radio−frequency powers for each target, Cu: 45W; SnS: 45 W; BaS: 110 W. The co−sputtered precursor films were then annealed in sulfur vapor at 540 °C for 30 min to yield the CBTS with the desirable *p*−type conductivity. The film thickness was adjusted by varying the cosputtering deposition time: 100 nm for 5 min; 150 nm for 8 min; 500 nm for 30 nm. The sulfurized CBTS films were dipped in a 1 M KCN aqueous solution for 30 s, followed by deionized water and methanol rinsing for 2 min and drying with nitrogen.

$CH_3NH_3PbI_3$ ($MaPbI_3$): The perovskite precursors were prepared by spin-coating the precursor solution consisting of 461 mg of PbI_2 and 159 mg of CH_3NH_3I dissolved in 723 μL of N,N-dimethylformamide and 81 μL of dimethyl sulfoxide. The molar ratio between PbI_2 and CH_3NH_3I is 1:1. All the perovskite precursors were annealed at 60 °C for 2 min and then 120 °C for 15 min in a glovebox.

Phenyl-C_{61}-butyric acid methyl ester (PCBM): PCBM films were spin-coated using 10 mg mL^{-1} PCBM dichlorobenzene solutions with a spin rate of 2000 rpm for 30 s and then annealed on a hotplate at 100 °C for 10 min in a glove box.

2,20,7,70-tetrakis-(N,Ndi-pmethoxyphenylamine) 9,90-spirobifluorene (Spiro): The Spiro solution consisted of 26 mM Li-bis(trifluoromethanesulfonyl) imide (LiTFSI) (Sigma, 99.95%), 55 mM 4-tert-butylpyridine (TBP), and 68 mM Spiro, which were dissolved in a mixed solvent of acetonitrile and chlorobenzene with a volume ratio of 1:10. The Spiro solution was spin-coated on the perovskite films at 500 rpm for 1 s and subsequently 2000 rpm for 60 s in a dry box.

Poly (3,4-ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT:PSS): PEDOT:PSS (Baytron 4083) was then spin-cast onto clean FTO substrates, followed by annealed at 150 °C for 10 min in air.

TiO_2: a compact TiO_2 blocking layer was spin-coated with 0.3 M titanium diisopropoxide bis(acetylacetonate) in 1-butanol solution by the spin-coating method, which was heated at 200 °C for 15 min. On the prepared compact TiO_2 blocking layer, the nanocrystalline TiO_2 paste (Dyesol) diluted with ethanol was spin-coated and the deposited film was annealed at 550 °C for 1 h to produce mesoporous TiO_2 thin layer.

Metal electrode: 60 nm thick Au and Ag electrodes were thermally evaporated on top of Spiro and PCBM, respectively. The total area of the solar cells was 0.08 cm^2.

Film characterization:

X–ray diffraction (XRD) data were collected using a Rigaku Ultima III diffractometer with Cu Kα lines (0.15418 nm) in Bragg−Brentano Theta–2Theta scans, with the Cu source

operated at 40 kV and 44 mA electron excitation current. Theta calibration was done using a standard Si sample prior to the measurements. The phase identification and the refinement of lattice constants were done using the software of MDI Jade 2010 equipped with a monthly synchronized ICDD database (International Centre for Diffraction Data). Confocal Raman spectroscopy was carried out using a 632.8 nm laser (HORIBA Scientific), with the Raman shift calibrated by a Si sample at 520.4 cm^{-1}. The optical transmittance of a CBTS thin film deposited on a FTO substrate was measured by an ultraviolet–visible spectrophotometer (PerkinElmer Lambda 1050). The composition of our CBTS thin films were characterized by energy dispersive X–ray spectroscopy (EDS) equipped in a field–emission scanning electron microscope (FE–SEM) (Hitachi S4800 FE–SEM).

To determine the band positions of CBTS, we performed the dark capacitance-voltage (C-V) measurement in a neutral electrolyte (pH=6.4) containing sodium sulfite (0.5 M) and potassium phosphate (0.5 M) based on 3-electrode configuration, where FTO/CBTS serves as the working electrode, a Ag/AgCl (1 M KCl) electrode serves as the reference electrode, and a Pt wire serves as the counter electrode. A photoelectrochemistry workstation equipped with a frequency analyzer (ModuLab, Solartron Analytical) was used for this measurement. Potentials versus the Ag/AgCl (1 M KCl) electrode ($E_{Ag/AgCl}$) were converted to potential versus reversible hydrogen electrode (RHE, V_{RHE}) using the Nernst equation, namely, $V_{RHE}=V_{Ag/AgCl}+0.059\times pH+0.222$.

Device Testing:

The $J-V$ curves of the perovskite solar devices measured under a simulated AM1.5G irradiation with a standard solar simulator (PV Measurements Inc.). The EQE data were measured using a commercial EQE system (PV Measurements Inc.). EQE derived photocurrent/short circuit current densities (J) can be integrated from the expression $J=\frac{e}{hc}\int \lambda(EQE*AM1.5G)d\lambda$.

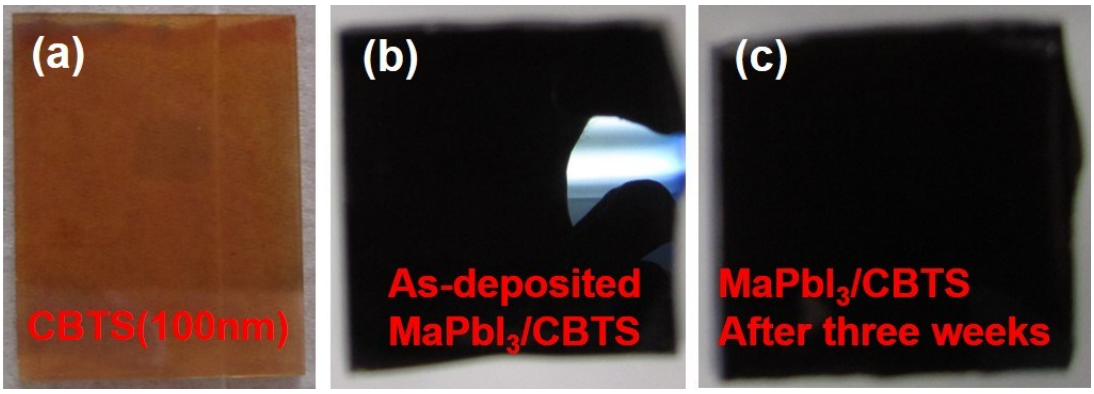

Figure S1 Digital photos of a 100 nm thick CBTS film (a), a just-made $MaPbI_3$ film on CBTS (b), and a $MaPbI_3$/CBTS sample which was stored in a N_2 filled desiccator for three weeks.

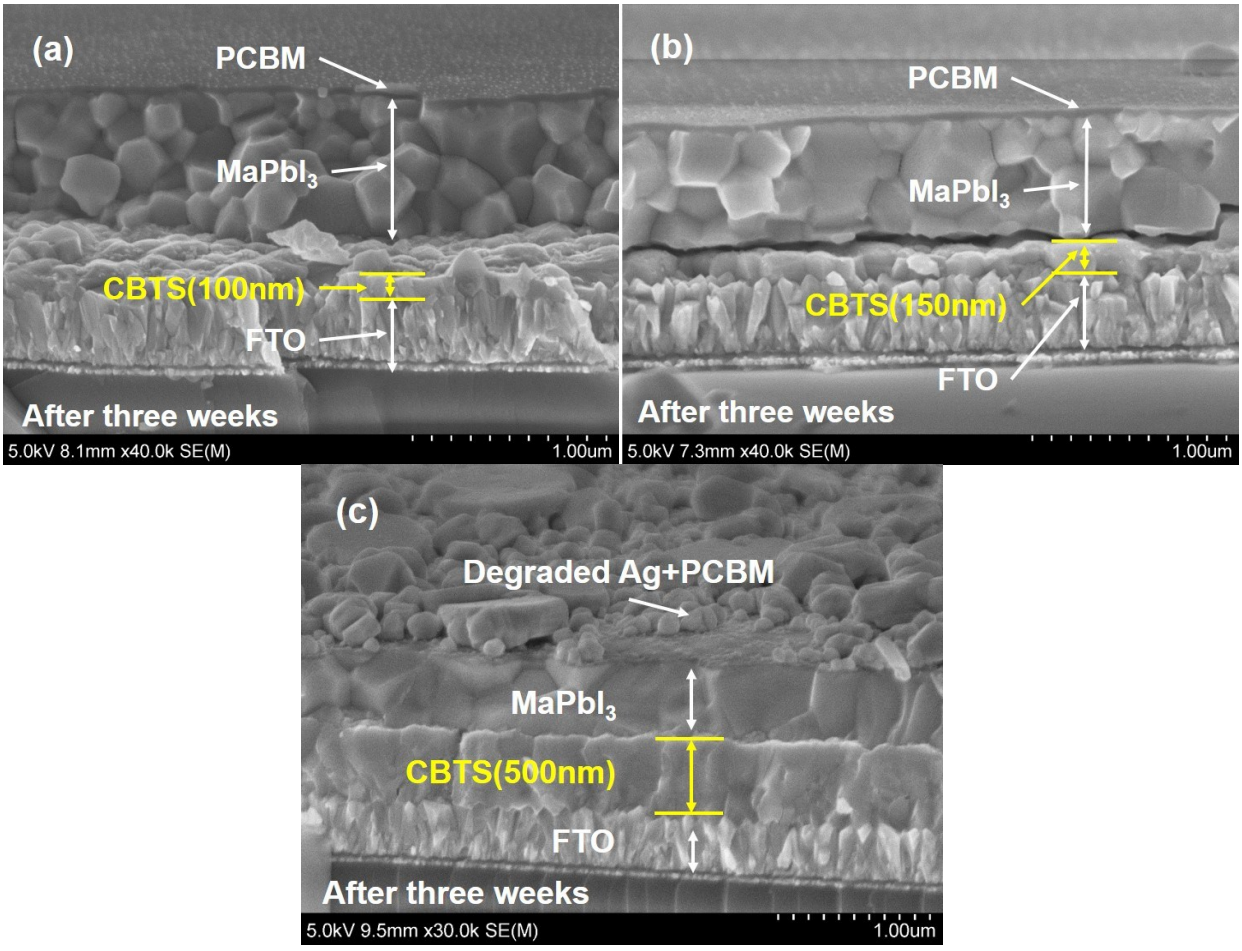

Figure S2 Cross-sectional SEM images of inverted $MaPbI_3$ solar cells based on 100 nm (a), 150 nm (b), and 500 nm (c) thick CBTS HTLs. Solar cells were stored in N_2 filled desiccator for three weeks.

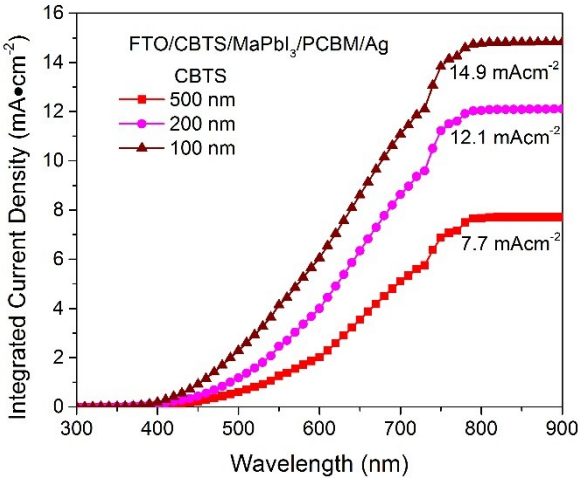

Figure S3 Integrated current densities from the EQE data of CBTS based inverted $MaPbI_3$ solar cells in Figure 5b.

Table S1 Device parameters under reverse ($V_{OC} \rightarrow J_{SC}$) and forward ($J_{SC} \rightarrow V_{OC}$) voltage scans of our best perovskite $MaPbI_3$ solar cells with various device structures.[a]

Device Structure	Scan	PCE (%)	V_{OC} (V)	FF (%)	J_{SC} (mA cm^{-2})
FTO/PEDOT:PSS/	$V_{OC} \rightarrow J_{SC}$	8.5	0.927	66.69	13.75
$MaPbI_3$/PCBM/Ag	$J_{SC} \rightarrow V_{OC}$	8.1	0.924	65.52	13.38
FTO/$MaPbI_3$/	$V_{OC} \rightarrow J_{SC}$	3.5	0.684	50.05	10.15
PCBM/Ag	$J_{SC} \rightarrow V_{OC}$	2.5	0.673	45.85	8.22
FTO/TiO_2/$MaPbI_3$	$V_{OC} \rightarrow J_{SC}$	14.2	1.04	74.12	18.42
/Spiro/Au	$J_{SC} \rightarrow V_{OC}$	13.5	1.04	68.51	18.80

[a] These device parameters come from the light J-V curves given in Figure S3a.

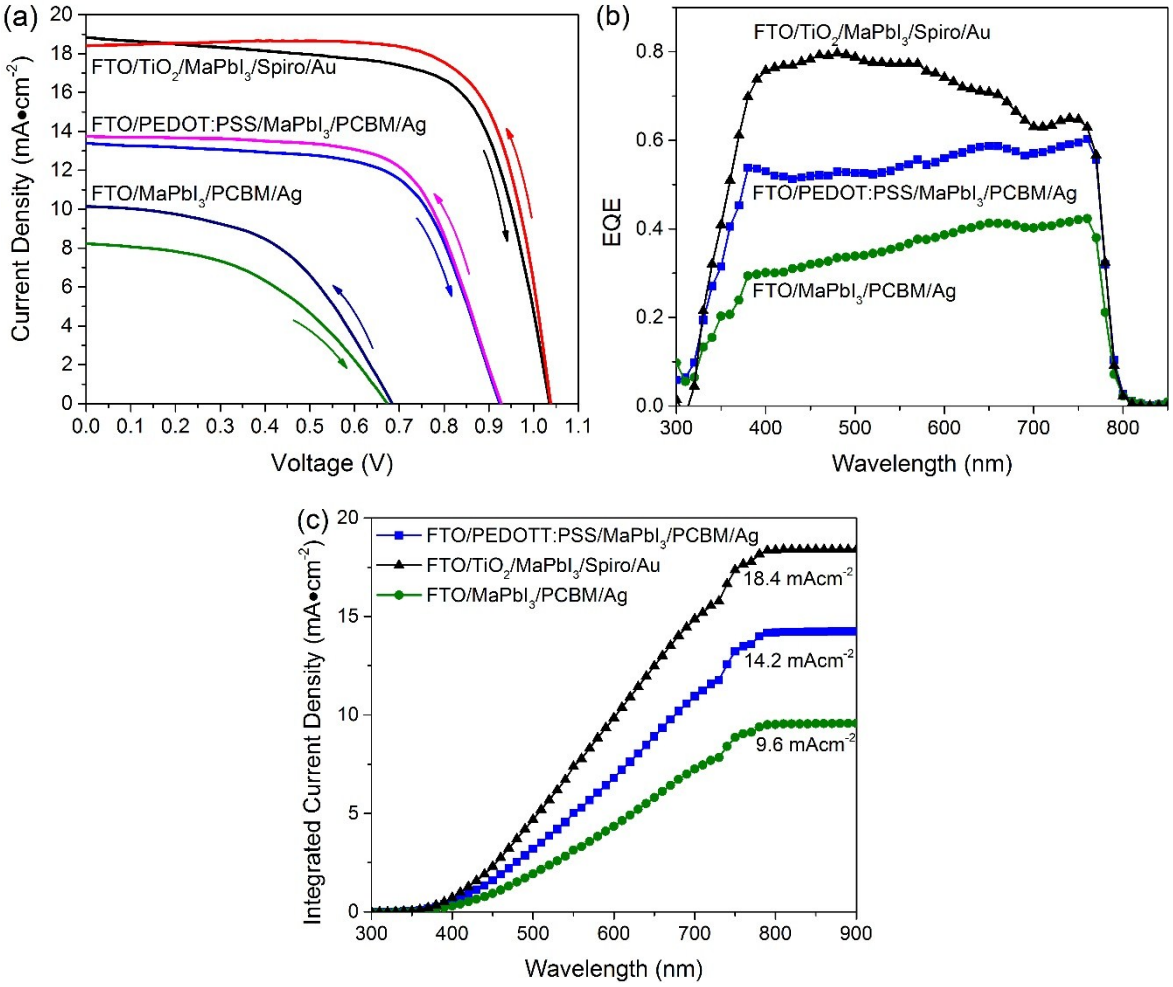

Figure S4 AM 1.5G illuminated J–V characteristics under reverse ($V_{OC} \rightarrow J_{SC}$) and forward ($J_{SC} \rightarrow V_{OC}$) voltage scans (a), corresponding EQE curves (b) and EQE integrated current densities (c) of our best $MaPbI_3$ solar cells with various device structures: FTO/PEDOTT:PSS/$MaPbI_3$/PCBM/Ag, FTO/$MaPbI_3$/PCBM/Ag, and FTO/TiO_2/$MaPbI_3$/Spiro/Ag. Note: these devices were measured immediately as obtained under the ambient air condition (relative humidity: 70%).

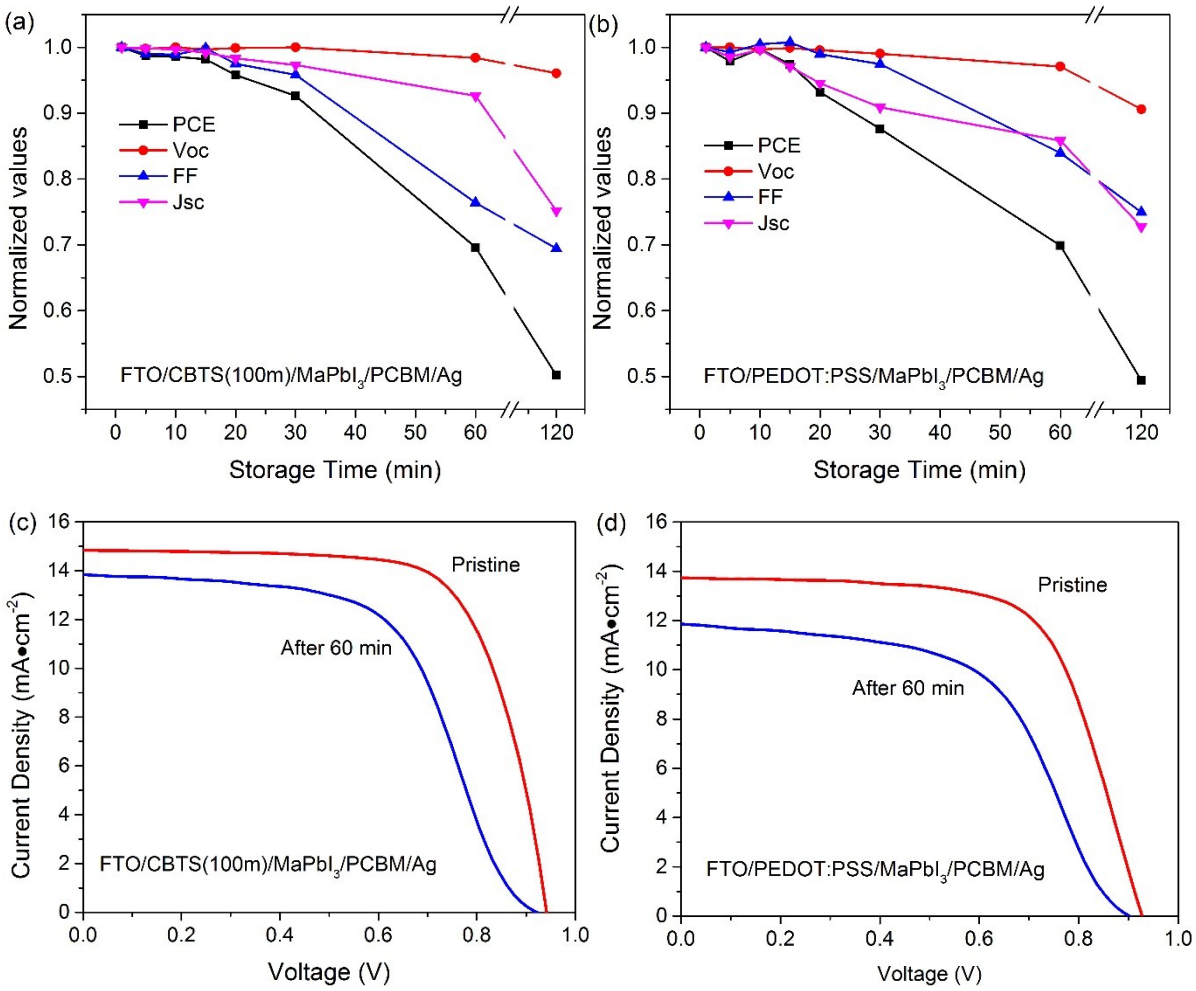

Figure S5 Device stability tests in the air for our best inverted $MaPbI_3$ solar cells based on a 100 nm CBTS (a) HTL and a PEDOTT:PSS HTL (b); light J-V curves of these two inverted $MaPbI_3$ solar cells based on CBTS (c) and PEDOTT:PSS (d), respectively. Note: device stability tests were measured under the ambient air condition (relative humidity: 70%).