

Supporting Information

High-efficiency carbon-electrode CsPbI₂Br solar cells prepared by double ion regulation of Cadmium Acetate additive

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Experimental section

Materials

Cesium iodide (CsI, ≥99.99%), lead iodide (PbI₂, ≥99.99%), lead bromide (PbBr₂ ≥99.99%), and Fluorine-doped tin oxide (FTO, 1.5 × 1.5 cm²) substrates with a surface resistance of 14 Ω cm⁻² were purchased from Advanced Election Technology Co., Ltd. Cadmium acetate (CdAc₂, ≥99.99%) were purchased from Macklin. Dimethyl sulfoxide (DMSO, ≥99.9%) were purchased from Sigma-Aldrich. Dimethyl sulfoxide (DMSO, ≥99.9%) were purchased from Sigma-Aldrich. SnO₂ colloidal dispersion (tin (IV)oxide, 15% in H₂O) were purchased from Alfa Aesar. Conductive carbon paste was supplied by Shanghai MaterWin New Materials Co., Ltd.

Device Fabrication

Pretreatment of FTO conductive glass

First, the FTO conductive glass is etched according to a pre-set pattern by a laser etcher, and multiple independent small-area battery devices can be prepared in a piece of FTO conductive glass. Subsequently, the etched FTO conductive glass was ultrasonic cleaned with distilled water, ethanol and isopropyl alcohol respectively for 20 minutes each time. After ultrasonic cleaning, it is collected in a glass dish and then placed in the oven for drying.

Preparation of SnO₂ electron transport layer

FTO conductive glass is treated with ozone for 20 mins to remove impurities from its surface. At the same time, SnO₂ was mixed with ultra-pure water at a ratio of 1:4 and placed in an ice water bath for ultrasonic treatment for 15 min. The prepared SnO₂ aqueous solution was deposited on the surface of FTO conductive glass by spinning coating method, rotated at 3500rpm for 25s, then annealed on a 150 °C heating table for 30 min, and then cooled to room temperature to prepare SnO₂ETL.

Deposition of CsPbI₂Br perovskite absorbent layer

A 1.2M CsPbI₂Br perovskite precursor solution was obtained by mixing 0.3118g CsI, 0.2766g PbI₂ and 0.2202g PbBr₂ in 1ml DMSO in a nitrogen glove box and then stirring on a 65 °C heating table until it became clear. In a nitrogen glove box, DMSO solution of 14mg mL⁻¹ CdAc₂ was prepared first, and a certain amount of CdAc₂-DMSO solution was added to 3 parts of undissolved CsPbI₂Br precursor solution with a concentration of 1.2 M. CdAc₂-CsPbI₂Br solution with cadmium acetate content of 0.25%(50 μL CdAc₂-DMSO), 0.5%(100 μL CdAc₂-DMSO, CsPb_{0.995}Cd_{0.005}I₂Br) and 0.75%(150 μL CdAc₂-DMSO) (molar ratio of Cd to Pb) was prepared, and then stirred on a heating table at 65 °C until the perovskite precursor liquid became clear. A solution of CdAc₂-CsPbI₂Br perovskite precursor with a concentration of 1.2 M was prepared and filtered with an organic filter with a pore size of 0.22 microns before use. FTO containing SnO₂ ETL was treated with ozone for 15min and preheated in a nitrogen glove box at 60 °C for 10 mins. Then, dark brown CsPbI₂Br films were obtained by rotating coating 50 μl precursor solution at 4000 rpm for 35s and annealing at 38 °C and 180 °C for 80 s and 10 mins, respectively.

Preparation of carbon electrode

In this work, carbon electrode was prepared by screen printing method, and the aperture of the screen was 250 mesh. Before the carbon brush begins, the surrounding humidity is controlled below 20 % to avoid the erosion of perovskite by

moisture in the air during the screen-printing process. Carbon paste should be checked before use to see if it has the right fluidity, too thick carbon paste is not conducive to printing a uniform carbon electrode. We apply a sufficient amount of carbon paste to one side of the wire mesh, and then, immediately use a scraper to scrape the carbon paste onto the CsPbI_2Br perovskite film, after that, place it on a heating table at 120°C , and anneal it in the air for 15 mins to form a uniform carbon electrode. The remaining carbon paste on the screen is recovered to reduce the manufacturing cost of the device.

Device Characterization

KPFM (Multimode-8J) provided the contact potential difference of the perovskite surface. AFM (Multimode-8, America) was used to measure the roughness of the CsPbI_2Br and CdAc_2 - CsPbI_2Br films in an intelligent mode with a scan rate of 0.977 Hz. UV-vis absorption spectra were measured by the UV-vis-NIR spectrometer, Lambda 950 (UV-VIS-NIR spectrometer). A SEM (Hitachi S-8010) and an energy dispersive spectrometer (Oxford X-Max) were used to observe the morphology and elements of the samples. XRD measurements of the perovskite films were performed using an X-ray diffractometer with a scan rate of $10^\circ \text{ min}^{-1}$ in the continuous scanning mode (Cu $K\alpha$ radiation, SmartLab, Rigaku, Japan). An X-ray photoelectron spectrometer (Thermo Scientific K-Alpha+) was used to measure the UPS and XPS of the CsPbI_2Br films. Device performance and electrochemical characterization were applied under ambient condition with a controlled humidity of about 30%RH at 25°C . AM 1.5G illumination was Keithley 2400 source-meter was used to measure J-V curves of PSCs under ambient conditions and the standard one sun illumination (AM 1.5G, 100 mW cm^{-2}) with a scan rate of 0.15 V s^{-1} . Device active area was defined by a mask with an aperture area of 0.0525 cm^2 . Enli Tech's QE-R666 EQE system was used to measure the EQE curves in the DC mode without bias voltage. An electrochemical workstation (Zahner, Germany) was used for impedance spectroscopy with a bias voltage of 0 V under dark conditions. Time-resolved photoluminescence (TRPL) spectra were characterized by Zolix time correlated single photon counting on Omin- λ Monochromator/Spectrograph. Steady-state PL spectra were performed using a fluorescence spectrophotometer (LF-1303003, Thermo Scientific Lumina) with an excitation wavelength of 468 nm.

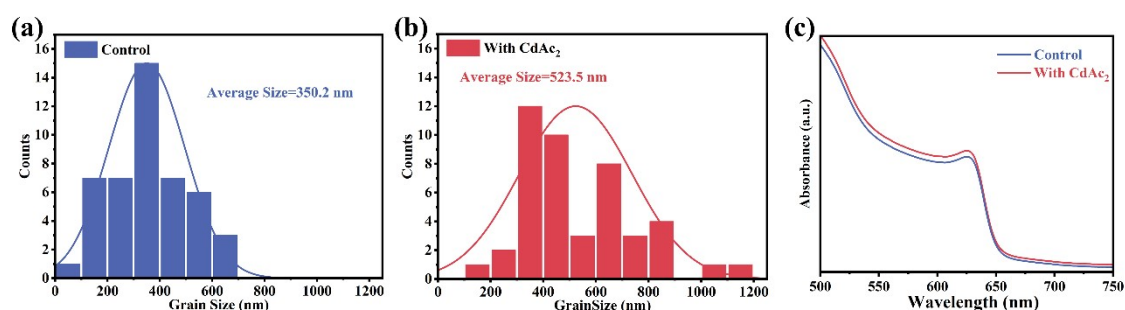


Figure S1. Average particle size of (a) control and (b) CdAc_2 -doped CsPbI_2Br films. (h) UV-vis absorption curves of control and CdAc_2 -doped CsPbI_2Br films.

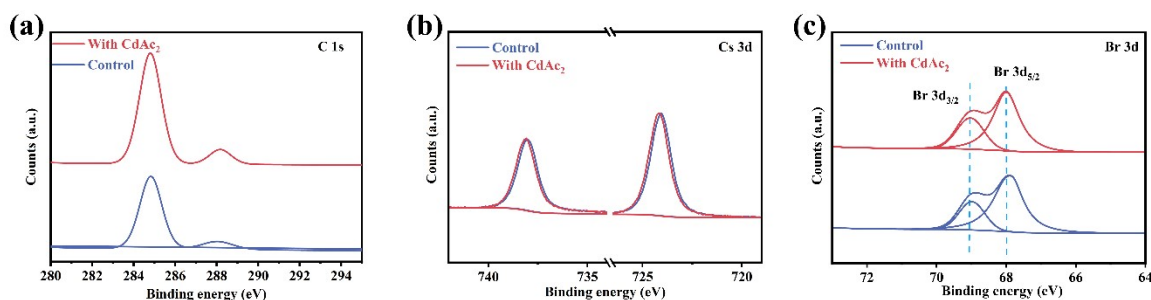


Figure S2. XPS profiles for the control and CdAc_2 -doped CsPbI_2Br films: (a) C 1s, (b) Cs 3d, (c) Br 3d.

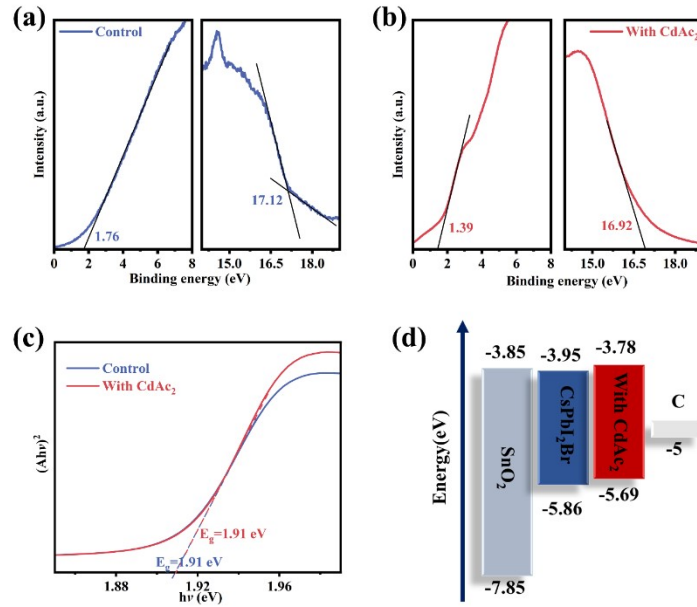


Figure S3. UPS spectra of a) control and b) with CdAc₂ CsPbI₂Br films. c) Tauc plots of control and with CdAc₂ CsPbI₂Br films. d) Schematic energy level diagram of the control and with CdAc₂ CsPbI₂Br films.

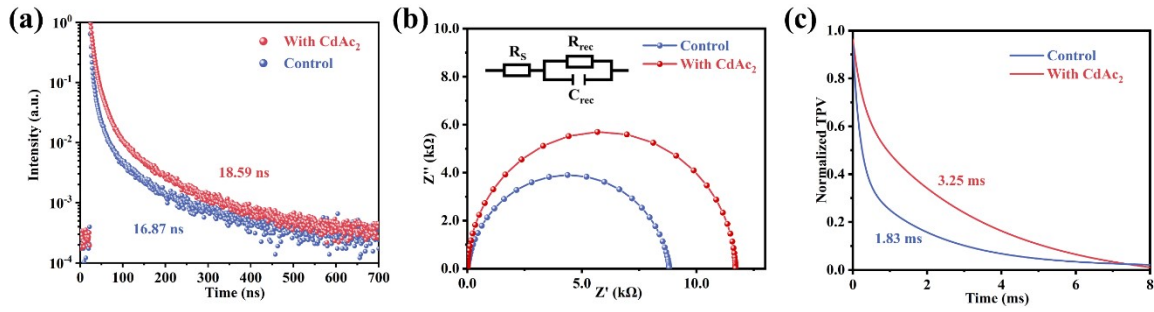


Figure S4. TRPL spectra of control and CdAc₂-doped CsPbI₂Br films. (g) Nyquist plots, (i) TPV curves.

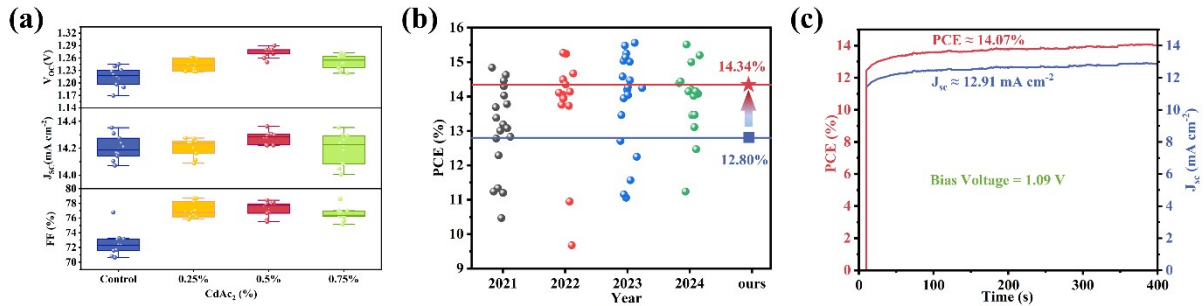


Figure S5. (a) box diagram of FF、J_{sc}、V_{oc} of control and CdAc₂-doped CsPbI₂Br PSCs. (b) Statistical PCE of reported C-CsPbI₂Br PSCs. (c) the SPO curves.

Table S1. The energy level parameters of CsPbI₂Br and CdAc₂- CsPbI₂Br films calculated by UPS analysis. (Band gap (E_g), Fermi level (E_F), valence band (E_{VB}) and conduction band (E_{CB}) of functional layers in the device.)

Sample	$E_{cutff,1}(eV)$	$E_F (eV)$	$E_{cutff,2}(eV)$	$E_{VB} (eV)$	$E_g (eV)$	$E_{CB} (eV)$
CsPbI ₂ Br	17.12	-4.1	1.76	-5.86	1.91	-3.95
CdAc ₂ - CsPbI ₂ Br	16.92	-4.3	1.39	-5.69	1.91	-3.78

Table S2. photovoltaic parameters corresponding to different concentrations of CdAc₂ PSCs.

CdAc ₂		V _{oc} (V)	J _{sc} (mA cm ⁻²)	FF (%)	PCE (%)
0 %	Champion	1.22	14.20	73.89	12.80
	Average	1.21±0.007	14.20±0.029	72.56±0.552	12.55±0.069
0.25 %	Champion	1.26	14.23	76.77	13.76
	Average	1.24±0.004	14.21±0.021	77.07±0.339	13.62±0.039
0.5 %	Champion	1.29	14.23	78.14	14.34
	Average	1.27±0.003	14.28±0.014	77.26±0.32	14.08±0.063
0.75 %	Champion	1.27	14.22	76.24	13.77
	Average	1.25±0.006	14.20±0.037	76.55±0.289	13.60±0.04

Formula S1 ^[1]:

$$CPD = (WF_{tip} - WF_{sample}) / e$$

Where e represents the elementary charge, and WF_{tip} and WF_{sample} denote the work functions (WF) of the tip and the sample, respectively. A smaller contact potential difference (CPD) correlates with a higher WF of the sample.

Formula S2 ^[2,3]:

$$N_{trap} = \frac{2\varepsilon_0\varepsilon V_{TFL}}{qL^2}$$

The parameter q represents the base charge, ε₀ is the vacuum dielectric constant, ε denotes the dielectric constant of the CsPbI₂Br perovskite film, and L is the thickness of the CsPbI₂Br perovskite film. The trap state density, N_{trap} can be derived by substituting the relevant values, offering a quantitative analysis of the defect state density within the film.

Notes and references

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