

Supporting information

Forming a composite electron blocking layer to enhance the performance of carbon-based CsPbI₃ perovskite solar cells

Yongfa Song^a, Weiping Li^{a*}, Hailiang Wang^a, Huicong Liu^a, Yue Deng^a, Qixian Zhang^a, Han Rao^a, Xiaoyu Jiang^b
, Haining Chen^{a}

^a School of Materials Science and Engineering, Beihang University, No. 37 Xueyuan Road, Haidian District, Beijing 100191, People's Republic of China.

^b Department of Information Communication, Army Academy of Armored Forces, Beijing 100072, People's Republic of China.

*E-mail: liweiping@buaa.edu.cn (Weiping Li), jiangxiaoyu2007@gmail.com (Xiaoyu Jiang), chenhaining@buaa.edu.cn (Haining Chen)

Methods

Materials:

Cesium carbonate (Cs_2CO_3 , 99.9%), lead(II) chloride (PbCl_2 , 99.99%), OLAM (OLAM, 80–90%), oleic acid (OA, 90%), 1-octadecene (ODE, 90%), ethyl acetate (99.8%) and cyclohexane (99.9%, with molecular sieves, water ≤ 50 ppm) were purchased from Shanghai Macklin Biochemical Co., Ltd. Dimethylamine Hydroiodide (DMAI, 99.9%), Cesium iodide (CsI, 99.99%) and lead(II) iodide (PbI_2 , 99.999%) were purchased from Xi'an Polymer Light Technology Corp. N,N-dimethylformamide (DMF) was purchased from Shanghai Aladdin Biochemical Technology Co. Ltd.

1. Preparation of Cs-oleate precursor

0.815 g CsCO_3 , 2.5 ml oleic acid and 20 ml 1-octadecene were added into a 100 ml three-neck flask with magnetic stirring for 60 min at 120 °C under nitrogen protection. Then heated to 150 °C until the solution turned clear. The Cs-oleate solution was stored at room temperature and pre-heated to 100 °C before used for preparation of CsPbCl_3 QDs.

2. Synthesis of CsPbCl_3 QDs

Typically, 0.278 g PbCl_2 and 24 ml 1-octadecene were added into a 100 ml three-neck flask with magnetic stirring for 30 min at 120 °C under nitrogen atmosphere. 2.5 ml oleic acid and 2.5 ml oleylamine were injected into the PbCl_2 1-octadecene solution until the solution turned clear. And the temperature was raised to 180 °C and then 2 ml hot Cs-oleate precursor solution was swiftly injected into the flask. The reaction was quenched by ice-water bath after 5 s. The crude solution was centrifugated at 10000 rpm at room temperature for 5 min.

The precipitate CsPbCl_3 QDs were dispersed in a mixed solution of cyclohexane and ethyl acetate (1:1), sonicated and centrifuged at 10,000 rpm for 5 minutes, and thus centrifuged 3-5 times. The precipitate CsPbCl_3 QDs were dispersed in cyclohexane solution.

3. Device fabrication

Deposition of TiO_2 films:

FTO glass was cleaned with successive sonication in deionized water, ethyl alcohol and isopropanol. TiO_2 blocking layer was then spin coated onto FTO glass at 2000 rpm for 20 s, using a titanium diisopropoxide bis(acetylacetonate) solution in 1-butanol (0.15 M), and then heated at 120 °C for 5 min. TiO_2 mesoporous scaffolds were deposited by spin coating at 5000 rpm for 30 s using a commercial TiO_2 paste (Dyesol 30 NRD, Dyesol) dispersed in ethanol, followed by sintering at 100 °C for 5 min and then at 550 °C for 30 min.

Deposition of perovskite films:

Precursor solutions were prepared by mixing DMAI, PbI_2 and CsI in DMF. The ratio of DMAI: PbI_2 :CsI was 1.5:1.5:1 and the concentration of CsI in the solution set at 1 M. Perovskite layers were deposited by spin coating the precursor solution on substrate at 2000 rpm for 20 s, followed by annealing at 220 °C for 5 min.

QDs/CsCl film:

After the substrate was cooled to room temperature, the CsPbCl_3 QDs (5 mg/ml) dispersed in cyclohexane were spin coated onto the above CsPbI_3 perovskite layer at 2000 rpm for 20 s followed by annealing at 100 °C for 5 min. Then, CsCl ethanol solution (1 mg/ml) was spin coated with above films at 4000 rpm for 30 s followed by annealing at 100 °C for 3 min.

QDs film:

The CsPbCl_3 QDs (5 mg/ml) dispersed in cyclohexane were spin coated onto the above CsPbI_3 perovskite layer at 2000 rpm for 20 s followed by annealing at 100 °C for 5 min.

CsCl film:

The CsCl ethanol solution (1 mg/ml) was spin coated with above films at 4000 rpm for 30 s followed by annealing at 100 °C for 3 min.

Deposition of carbon electrodes:

For fabricating C-PSCs, carbon electrode was directly deposited on the perovskite films. The carbon paste was purchased from Guangzhou Seaside Technology Co. Ltd and used without any treatment. Carbon paste was painted on the perovskite films at room temperature, followed by annealing at 100 °C for 20 min. The whole procedure was conducted in dry air atmosphere.

4. Characterization

X-ray diffraction (XRD) patterns for perovskite films were obtained on a Rigaku D/MAX-2500 diffractometer with an X-ray tube Cu K α radiation. ($\lambda = 1.5406 \text{ \AA}$). Chemical states of film surface were evaluated by an X-ray photoemission spectroscopy (XPS, ESCALab250Xi). Ultraviolet-visible-infrared spectrophotometer (UV-vis) absorption spectra were measured using a Shimadzu UV-3600 ultraviolet-visible (UV-vis) spectrometer. Scanning electron microscopy (SEM) images and EDS were obtained on a SUPRA55 SEM at an accelerating voltage of 5 kV. Surface roughness of these films were characterized by a Bruker Dimension ICON atomic force microscopy (AFM). The transmission electron microscopic (TEM) images was obtained using an JEM2100F at an accelerating voltage of 200 kV.

Time-resolved PL (TRPL) spectra taken on an ultrafast lifetime Spectrofluorometer (Delta flex) and a 475 nm ultrafast laser was used as the excitation light source. Confocal photoluminescence (PL) maps were recorded on a laser scanning confocal microscope (A1R-si).

The photovoltaic performance was tested under a solar light simulator (Newport Oriel Sol 3A, model number 94063A, AM 1.5 global filter) in ambient air. The light intensity was calibrated to 1 Sun (100 mW/cm²) using an Oriel reference solar cell (monocrystalline silicon) and meter. The active area of cells was masked at around 6.25 mm². Current density-voltage (J - V) curves, dependence of J_{sc} and V_{oc} on light intensity, Dark J - V measurement of the electron-only device and Mott-Schottky curves were measured on ZENNIUM pro electrochemical workstation (ZAHNER-Elektrik GmbH & Co., KG, Germany).

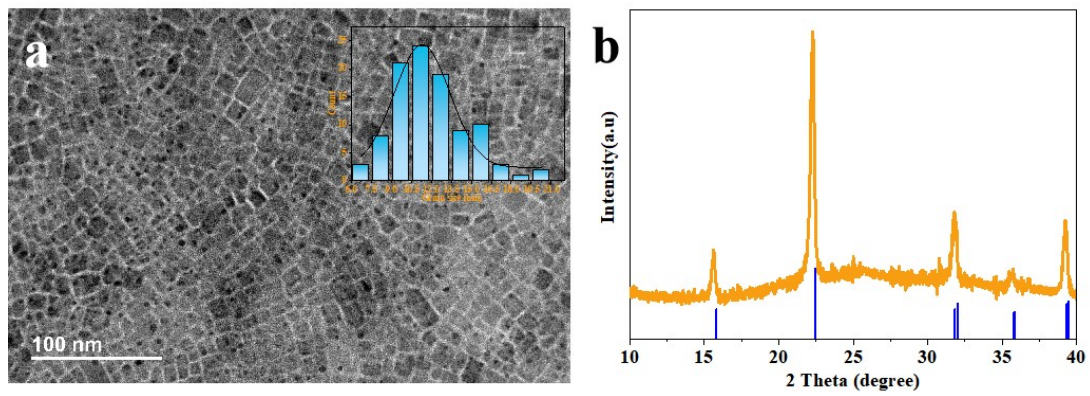


Figure S1. (a) TEM image and (b) XRD pattern of CsPbCl₃ QDs, inset: CsPbCl₃ QDs particle size distribution.

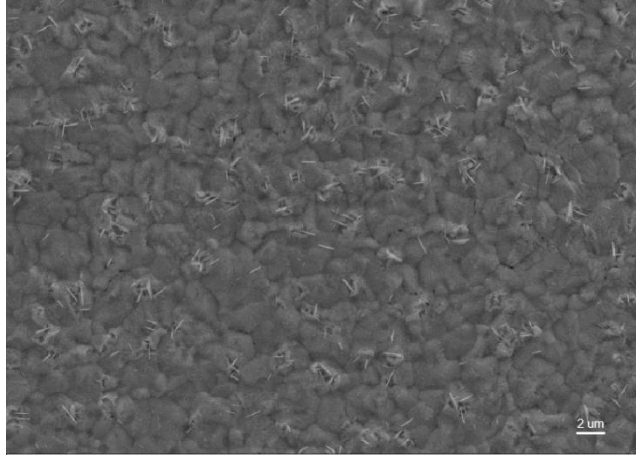


Figure S2. Surface SEM image of CsPbI₃-CsCl film

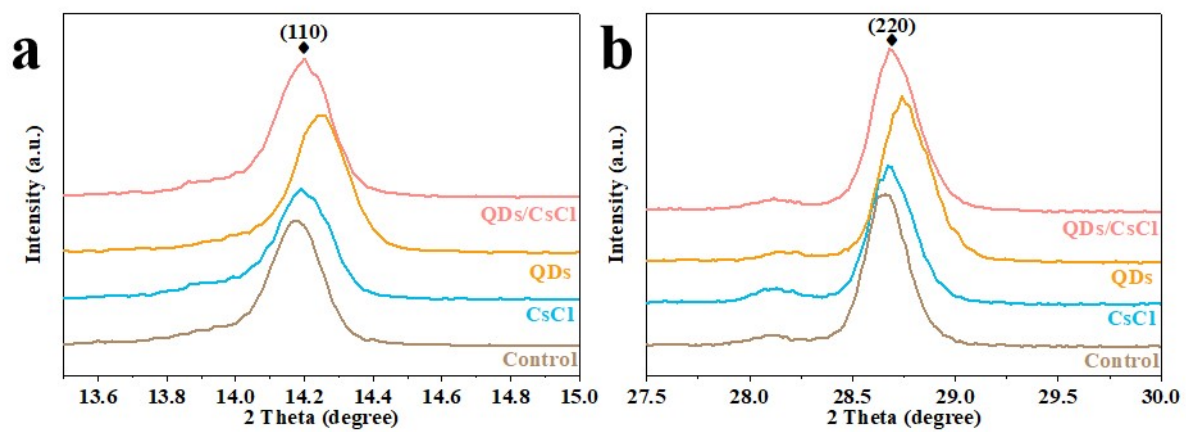


Figure S3. Magnified XRD patterns of (a) (110) and (b) (220) peaks of the perovskite films

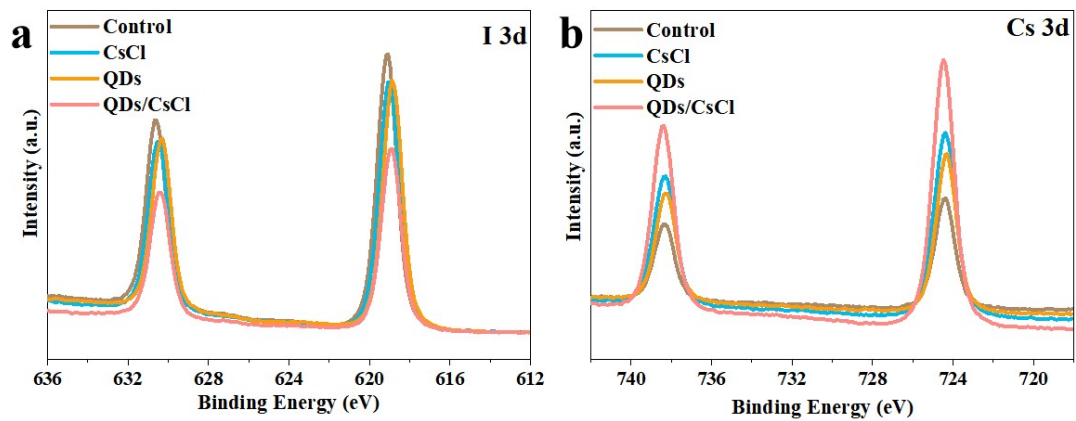


Figure S4. XPS spectra of CsPbI₃, CsPbI₃-CsCl, CsPbI₃-QDs and CsPbI₃-QDs/CsCl films: (a) I 3d, (b) Cs 3d

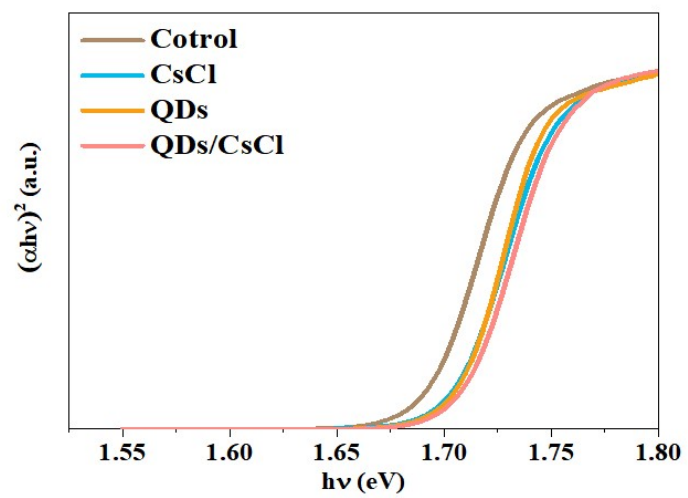


Figure S5. Tauc plots of CsPbI₃, CsPbI₃-CsCl, CsPbI₃-QDs and CsPbI₃-QDs/CsCl films

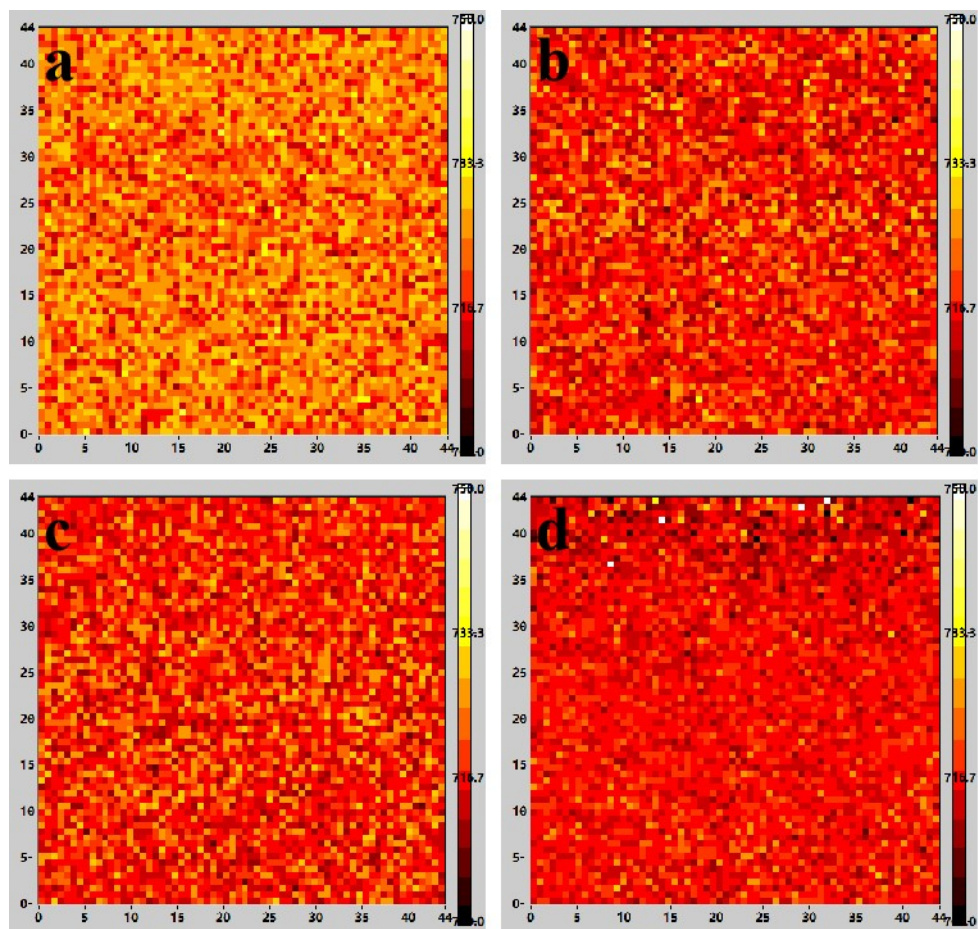


Figure S6. Confocal PL mapping of (a) CsPbI₃, (b) CsPbI₃-CsCl, (c) CsPbI₃-QDs and (d) CsPbI₃-QDs/CsCl films

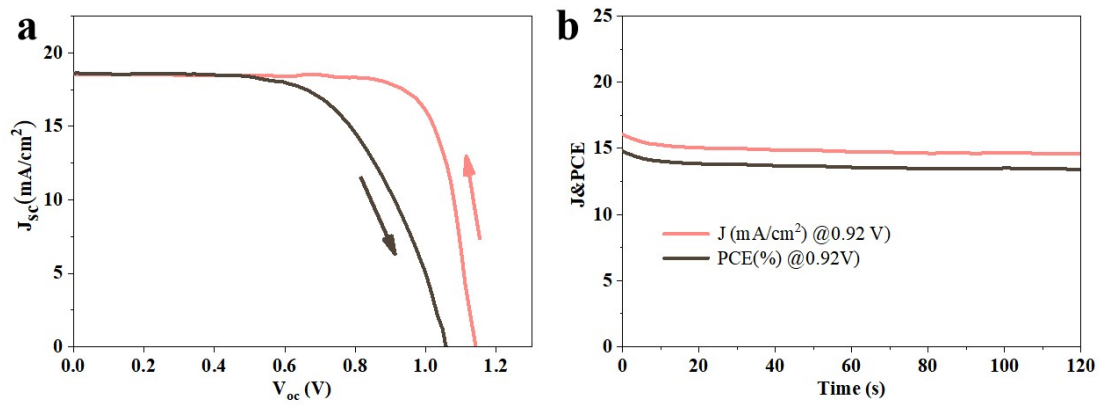


Figure S7. Other photovoltaic performance of CsPbI₃-QDs/CsCl C-PSCs: (a) J - V curves under forward and reverse scans, (b) steady-state power output

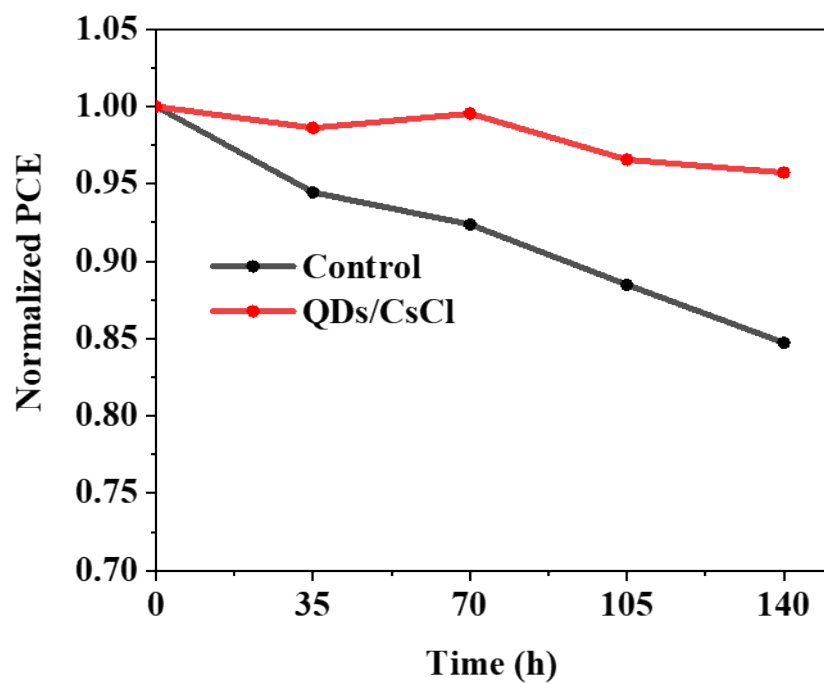


Figure S8. Normalized PCE of the control and QDs/CsCl devices at 85°C in N₂ condition

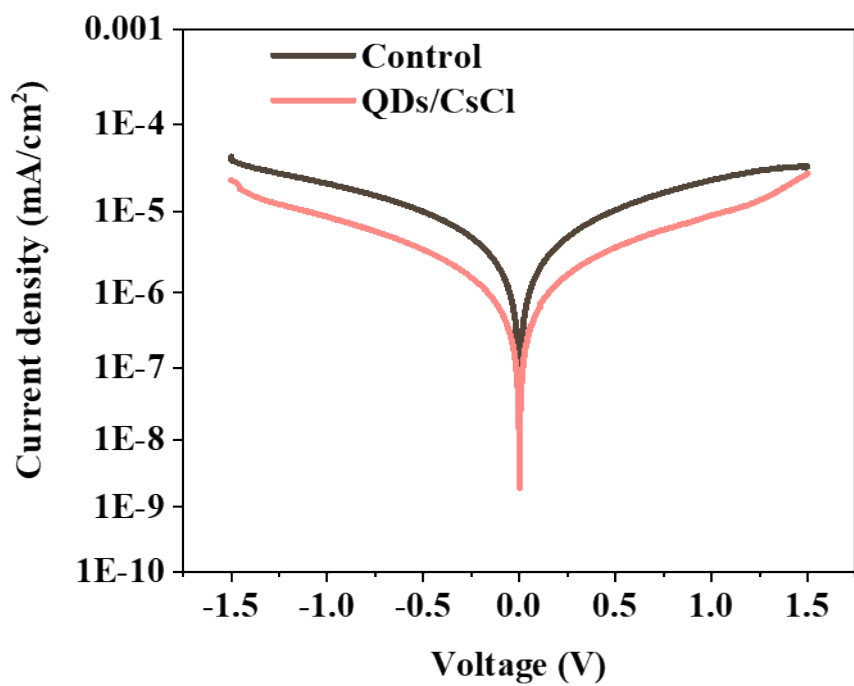


Figure S9. Dark J - V curves of the control and QDs/CsCl devices

Table S1. The fitting results of carrier lifetimes (τ) of different perovskite films

Devices	τ_1 (ns)	A ₁ (%)	τ_2 (ns)	A ₂ (%)	τ_{ave} (ns)
CsPbI ₃	2.561	63.5	19.872	36.5	8.87
CsPbI ₃ -CsCl	3.222	15.8	47.606	84.2	40.60
CsPbI ₃ -QDs	2.995	43.0	66.140	57.0	38.94
CsPbI ₃ -QDs/CsCl	4.362	45.6	70.583	84.4	60.24

Table S2. Comparison of photovoltaic parameters obtained from different C-PSCs.

Devices	V_{oc} (V)	J_{sc} (Mw/cm ²)	FF (%)	PCE (%)
CsPbI ₃	1.081	16.46	0.703	12.51
CsPbI ₃ -CsCl	1.099	17.67	0.703	13.65
CsPbI ₃ -QDs	1.105	18.14	0.708	14.18
CsPbI ₃ -QDs/CsCl	1.137	18.74	0.755	16.10