Electronic Supplementary Material

In-situ Synergistic Halogen Passivation in the Direct Synthesis of PbS Quantum Dot Semi-conductive Inks for High-Efficiency Photovoltaics

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Chemicals

Lead iodide (PbI_2, 99+ %), Lead bromide ($PbBr_2$, 98 %), lead chloride ($PbCl_2$, 98 %), Lead acetate trihydrate ($PbAc_2 \cdot 3H_2O$, 99 %), hexamethyldisilathiane (TMS-S, 98 %), Diphenyl thiourea (DPhTA, 99 %), Zinc acetate dihydrate ($ZnAc_2 \cdot 2H_2O$, 99.0 %), Potassium hydroxide (KOH, 99.98 %), Methanol (MeOH, 99.9 %), Chloroform (CF, 95 %), Ethanol (95 %), Oleic acid (OA, 90 %), 1-Octadecene (ODE, 90 %), Hexane (95 %), Isopropanol (IPA, 95 %), Acetone (95 %), Toluene (95 %), N,N′-dimethylformamide (DMF, 99.8 % anhydrous), Butyl amine (BA, >99 %), Acetonitrile (ACN, 99 %), Ethanedithiol (EDT, 99 %).

Synthesis of PbS-OA CQDs

Oleate-capped PbS CQDs were synthesized using a hot injection method with some modifications.[1-2] The synthesis is the same as in previous work. Briefly, 10 mmol of lead acetate trihydrate and 7 g of OA were dissolved in 60 g of ODE in a three-neck flask by heating the mixture to 100 °C under vacuum for 2 h. The sulfide precursor was mixed with 1 mL of hexamethyldisilathiane and 9 mL of 1-octadecene. The reaction was initiated by rapid injection of the sulfide precursor into the lead precursor solution. After synthesis, the solution was transferred into a nitrogen-filled glovebox. CQDs were purified by adding isopropanol, followed by centrifugation. The extracted CQDs were redispersed in hexane and acetone was added to precipitate CQDs, followed by centrifugation. Then the CQDs were stored in the glovebox.

Synthesis of ZnO Nanoparticles

ZnO nanoparticles were synthesized according to the literature with some modifications. [3] 2.95 g of zinc acetate dihydrate ($ZnAc_2 \cdot H_2O$) was added to 125 mL methanol (MeOH) in a three-necked flask. 1.48 g potassium hydroxide (KOH) was dissolved in 60 mL MeOH and dropwise added to the zinc acetate solution under vigorous stirring at 63.5 °C for 3 h. After cooling down, ZnO nanocrystals were extracted via centrifugation and washed twice with methanol. Finally, 10 mL of chloroform (CF) and 10 mL MeOH were added to the precipitates and the solution was filtered with a 0.45 μm filter.

SCLC measurements

Electron-only devices were fabricated (Glass/ITO/ZnO/PbS-CQD/ZnO/Ag) The I-V curves were scanned from 0 V to +5.0 V at 0.01 V interval steps. The trap-filling region can be identified by a significant increase in the current injection at a voltage ($>V_{TFL}$) where all the traps are filled. From this region, the trap density was estimated using the following equation:

$$N_t = \frac{2V_{TFL}\varepsilon\varepsilon_0}{eL^2} \qquad \text{Eq. (1)}$$

where V_{TFL} is the trap-filled limit voltage, ε is the relative dielectric constant (18 for PbS CQDs), ε_0 is the vacuum permittivity, e is the electron charge, and L is the thickness of the CQD films. The thickness was determined using a thickness profilometer.

The electron mobilities (μ_e) can also be extracted from the SCLC measurements, as calculated from the logarithm of the *J-V* curve obtained in the dark condition according to the mobility formula:

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu_{h,e}\frac{V^2}{d^3}$$

where ε is the relative dielectric constant (18 for PbS CQDs), ε_0 is the vacuum permittivity, and d is the thickness of the CQD films. The thickness was determined using a thickness profilometer.

TRPL Fitting

The TRPL decay curves were fitted with a bi-exponential decay function of I(t) =$A_1 \times \exp[-t/\tau_1] + A_2 \times \exp[-t/\tau_2]$. Here, A_1 and A_2 correspond to the decay amplitudes of the curve. τ_1 and τ_2 correspond to the decay time constants of fast and slow components, respectively. The average lifetime τ_{avg} was calculated by $\tau_{avg} = (A_1\tau_1 + A_2\tau_2)/(A_1 + A_2)$.

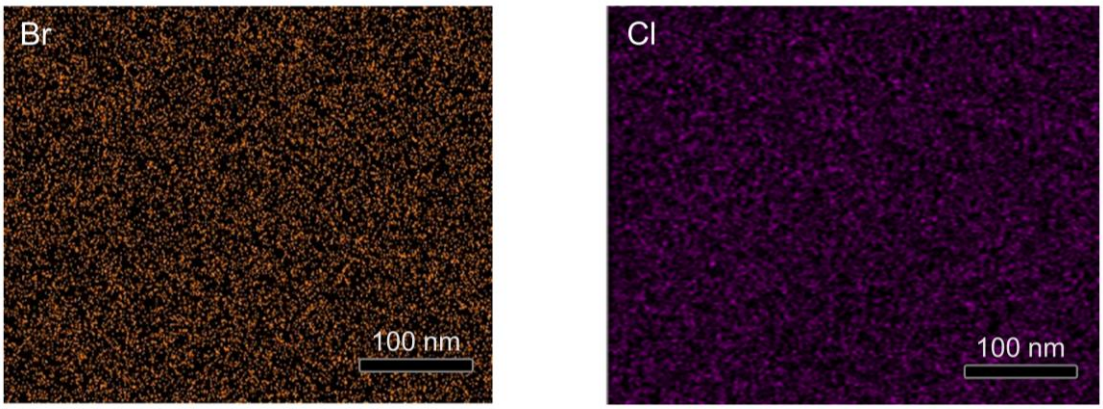

Figure S1. Energy dispersive spectroscopy (EDS) mappings of the MHP CQD films.

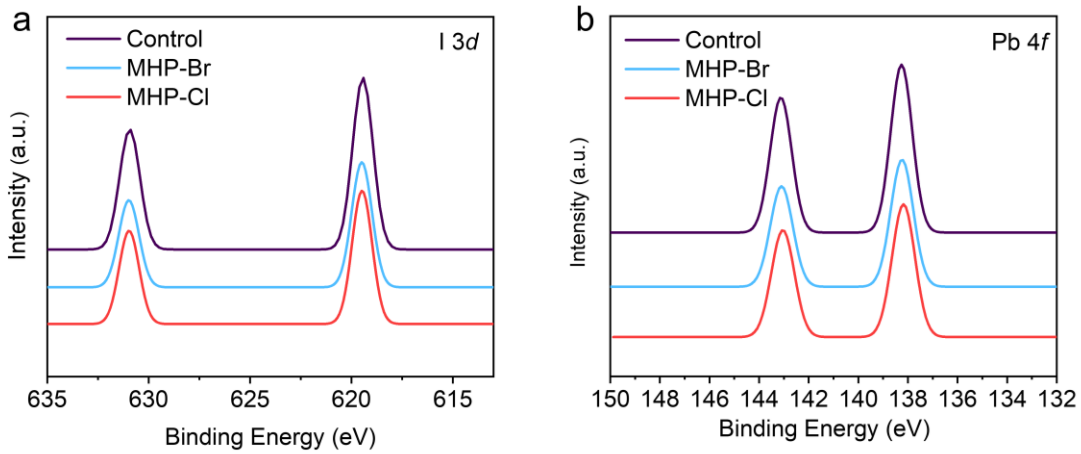

Figure S2. XPS spectra of the CQD films in the I 3d and Pb 4f regions.

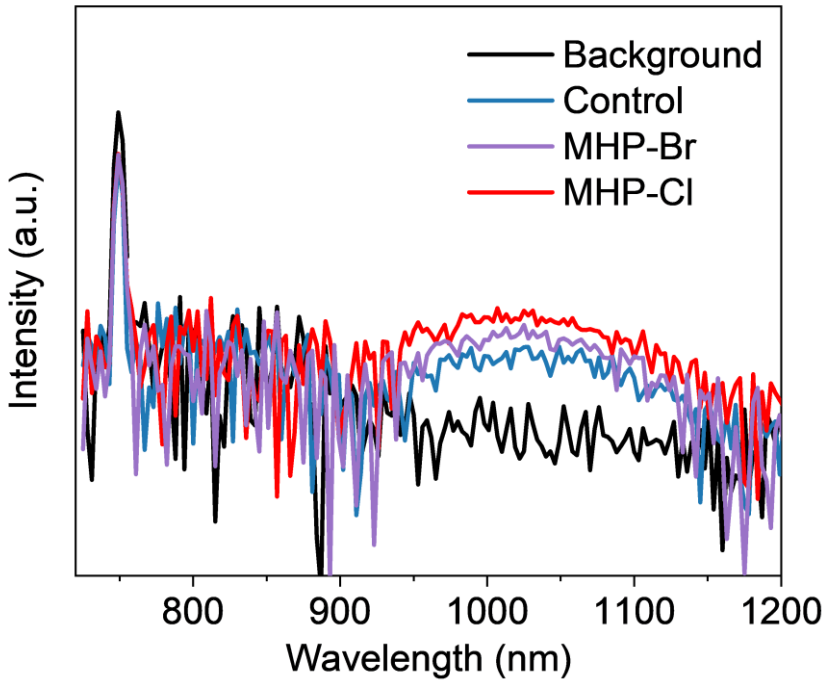

Figure S3. PLQY measurements of the CQD inks.

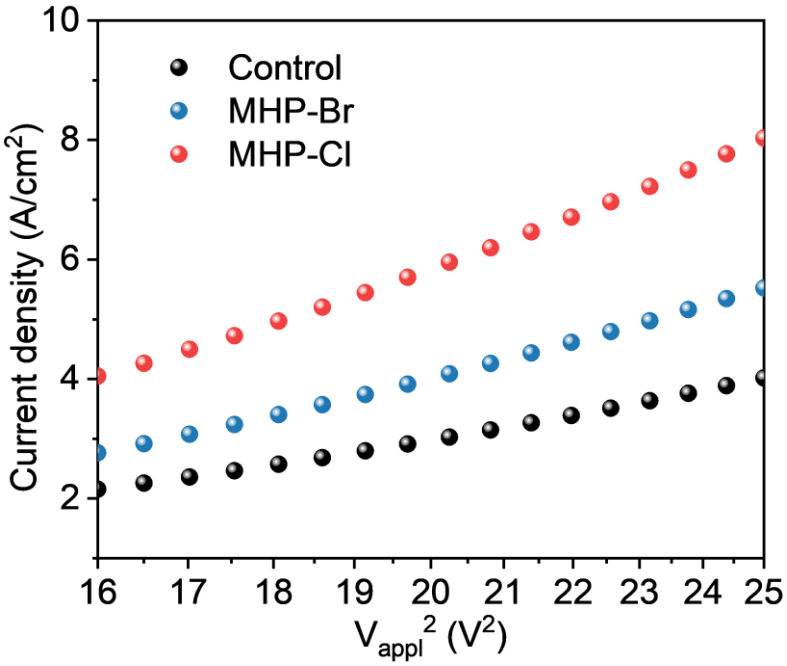

Figure S4. *J-V* ^{2} curve of SCLC devices for the CQD films.

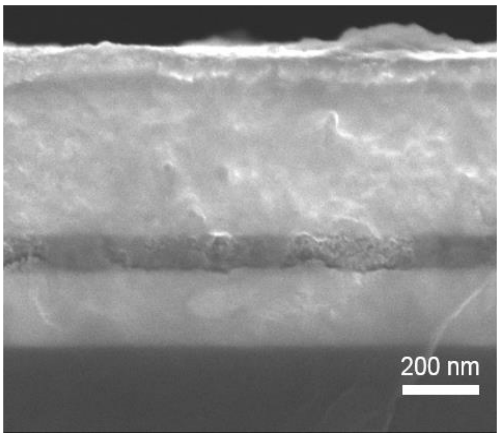

Figure S5. Cross-section SEM image of control device.

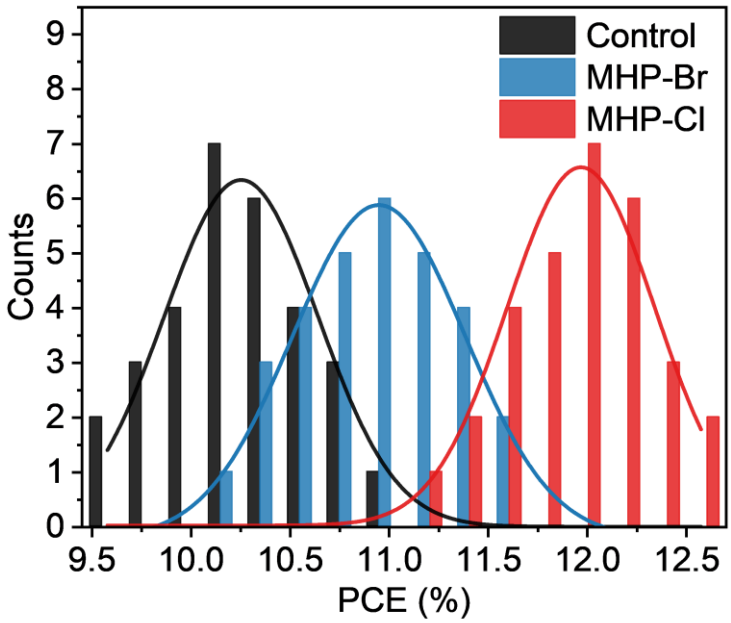

Figure S6. Efficiency histogram of the CQD devices.

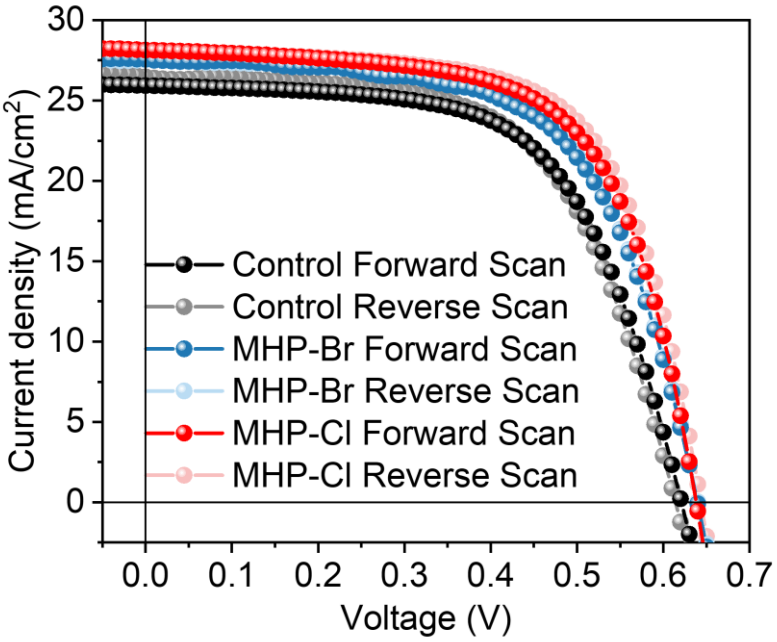

Figure S7. *J-V* curve of the CQD devices (forward scan and reverse scan).

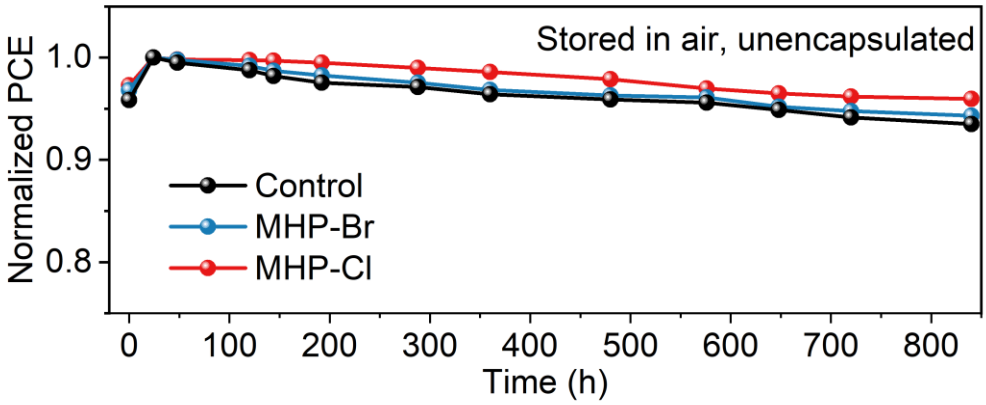

Figure S8. Stability test of unencapsulated devices stored in the air.

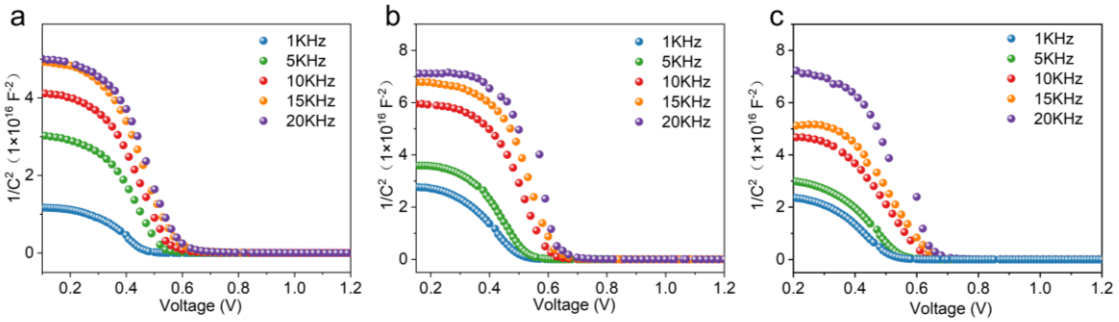

Figure S9. C-V measurement of control (a), MHP-Br (b) and MHP-Cl (c) devices at different frequencies.

Table S1. TRPL measurement of the CQD inks.

Condition	A_1	τ_1 (μs)	A_2	τ_1 (μs)	τ_{avg} (μs)
Control	0.21	0.20	0.20	2.06	1.10
MHP-Br	0.23	0.32	0.24	2.7	1.54
MHP-Cl	0.19	1.29	0.17	3.24	2.21

Table S2. TRPL measurement of the CQD films.

Condition	A_1	τ_1 (ns)	A_2	τ_1 (ns)	τ_{avg} (ns)
Control	0.53	0.74	0.47	28.35	13.72
MHP-Br	0.57	0.72	0.43	19.55	8.81
MHP-Cl	0.59	0.69	0.41	18.76	8.09

Table S3. Photovoltaic parameters of PbS CQD devices synthesized with different amounts of $PbBr_2$ in the precursor.

Condition	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
Control	0.64	26.63	62.45	10.64
$PbBr_2$ 5 %	0.65	27.56	64.86	11.61
$PbBr_2$ 10 %	0.65	26.78	64.32	11.19
$PbBr_2$ 20 %	0.63	26.13	63.69	10.48

Table S4. Photovoltaic parameters of PbS CQD devices synthesized with different amounts of $PbCl_2$ in the precursor.

Condition	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	PCE (%)
Control	0.64	26.63	62.45	10.64
$PbCl_2$ 5 %	0.65	25.18	67.07	10.98
$PbCl_2$ 10 %	0.66	27.73	68.78	12.58
$PbCl_2$ 20 %	0.64	28.05	65.49	11.76

Table S5. EIS parameters of the CQD photovoltaic devices.

Condition	Rs (Ω)	Rp (Ω	CPE (F)
Control	61.72	6894	2.91×10^{-8}
MHP-Br	29.08	4321	6.26×10^{-9}
MHP-Cl	15.25	1957	3.24×10^{-9}

1. M. A. Hines, G. D. Scholes, Colloidal PbS Nanocrystals with Size-Tunable Near-Infrared Emission: Observation of Post-Synthesis Self-Narrowing of the Particle Size Distribution, *Adv. Mater.,*2003, **15**, 1844-1849.
2. Y. Wang, K. Lu, L. Han, Z. Liu, G. Shi, H. Fang, S. Chen, T. Wu, F. Yang, M. Gu, S. Zhou, X. Ling, X. Tang, J. Zheng, M. A. Loi, W. Ma, In Situ Passivation for Efficient PbS Quantum Dot Solar Cells by Precursor Engineering, *Adv. Mater.,*2018, **30**, 1704871.
3. W. J. Beek, M. M. Wienk, M. Kemerink, X. Yang, R. A. Janssen, Hybrid zinc oxide conjugated polymer bulk heterojunction solar cells, *J. Phys. Chem. B,*2005, **109**, 9505-9516.