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Supporting Information

Efficient Chromium Ion Passivated $CsPbCl_3$:Mn Perovskite Quantum Dots for Photon Energy Conversion in Perovskite Solar Cells

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EXPERIMENTAL SECTION

Materials. Cs_2CO_3 (99.9%), $PbCl_2$ (99.9%), octadecene (ODE, technical grade, 90%), oleic acid (technical grade, 90%), and oleylamine (OLA, technical grade, 90%) were purchased from Aldrich. $MnCl_2$ (99.9%) and $CrCl_3$ (99.9%) were purchased from Aladdin Industrial Corporation, China. Hexane and ethyl acetate were purchased from Beijing Chemical Reagent Ltd., China, and used as received without further purification.

Preparation of Cesium−Oleate Solution. 0.8 g of Cs_2CO_3 was loaded into a mixture of 30 mL of octadecene and 2.5 mL of oleic acid and then heated to 200 °C until the white powder was completely dissolved. Then, the mixture was kept at 130 °C for 1 h under vacuum. Note that, during the synthesis of perovskite QDs, the temperature of Cs−oleate mixture should be kept at least at 130 °C to avoid precipitation.

Synthesis of $CsPbCl_3$: Cr^{3+}, Mn^{2+} perovskite quantum dots.

Firstly, rare earth chloride $MnCl_2$ (0.25 mmol), $CrCl_3$ (0.25 mmol), $PbCl_2$ (0.5 mmol), OAm (1 mL), OA (1 mL), and ODE (10 mL) were adequately dissolved at 160℃ for 1h under purging N_2 gas. After complete dissolution, the temperature was raised to 200℃ under purging N_2 gas. The as-prepared Cs-oleate (1 mL) was then injected into the contents promptly, after 10s, which was immediately transferred to an ice-water bath. Lastly, ethyl acetate was added into the crude solution with a volume ratio of 3:1, the precipitate was collected separately after centrifugation and dispersed in 2 mL 1-octane or hexane. 6 mL ethyl acetate was added into the 2 mL hexane dispersion with a volume ratio of 3:1, the precipitate was collected and redispersed in 1-octane or hexane. The process was repeated once more, and the final product was dispersed in hexane.

The synthesis of $CsPbCl_3$: Mn^{2+} perovskite quantum dots were according to ref 26.

Fabrication of perovskite solar cells.

SnO_2 Electron Transport Layer

The solution for SnO_2 layers was prepared by dissolving 0.05 M $SnCl_2$•$2H_2O$ (Sigma Aldrich) in anhydrous ethanol, and then 10 mL of 0.1M $InCl_3$ stock solution in ethanol was added to 1 mL of $SnCl_2$ solution to get a 2% (molar ratio) doped $SnCl_2$•$2H_2O$ solution. SnO_2 layer was prepared by using a two steps spin-coating program (1,500 rpm for 10 s and 5,000 rpm for 10 s).

Perovskite Layer

The perovskite precursor solution were prepared by mixing MABr (42.0 mg), $PbBr_2$ (151.44 mg), FAI (322.5 mg), PbI_2 (950.82 mg) and CsI (78.9 uL) in 1.2 mL DMF and 0.3 mL DMSO solution. The perovskite layer was prepared by using a two steps spin-coating program (1,500 rpm for 10 s and 5,000 rpm for 10 s).

Hole Transport Layer and Electrode

The Spiro-OMeTAD solution was prepared by dissolving 72.3 mg of Spiro-oMeTAD powder (Lumtec) in 1 mL of chlorobenzene and stirring it until it is uniform. Thereafter, 28.5 mL of TBP solution and 17.5 mL of bis(trifluoromethane)sulfonamide lithium salt solution (520 mg/mL Li-TFSI in ACN) were added and stirred for 10 min. The Spiro-oMeTAD layer was deposited by spin coating at 3,000 rpm. A100-nm gold electrode was deposited onto the Spiro-OMeTAD layer by using thermal evaporation.

Long-term stability

The $CsPbCl_3:Cr^{3+},Mn^{2+}$ PQD film and the coated solar cells were stored in the air with 25% humidity and 15~20 ^{o}C temperature. The luminescence intensities and PCEs were recorded every 10 days, which was tracked for 150 days.

Characterizations

UV/vis−NIR absorption spectra were measured with a Shimadzu UV-3600PC UV/vis−NIR scanning spectrophotometer in the range from 300 to 2000 nm. Patterns were recorded in thin film mode on a Bruker AXS D8 diffractmeter using Cu Kα radiation (λ = 1.54178 Å). The morphology of the products was recorded with a Hitachi H-8100IV transmission electron microscope (TEM) under an acceleration voltage of 200 kV. The samples were imaged in EFTEM mode with a 20 eV energy slit inserted around the zero energy loss of electrons to acquire high-resolution TEM (HRTEM) micrographs. The solar cell devices were tested under a Class A solar simulator (ABET Sun 2000) at AM1.5 and 100 mW/cm^2 illumination conditions calibrated with a reference Silicon cell (RERA Solutions RR-1002), using a Keithley 2400 as a source-meter in ambient condition without sealing for *J-V* measurements from + 1.5 V to -1.5 V. IPCE was measured at AC mode under bias light using a IPCE system (PV measurement Inc.) with a computerized setup consisting of Solar Cell Quantum Efficiency — Solar-Cell Scan100. PL spectra and dynamics were measured using the spectrofluorometer (FLS980, Edinburgh Instruments).

Photoluminescence quantum yields (PLQY). The PLQYs of the samples were acquired using an integrating sphere incorporated into a spectrofluorometer (FLS980, Edinburgh Instruments). Absolute photoluminescence quantum yield measurements were performed on colloidal PQD samples dispersed in hexane placed in a sealed 1 cm path length quartz cuvette and positioned in a teflon-based integrating sphere using a custom cuvette holder. The samples were directly excited with a 365 nm Xe lamp and attenuated with neutral density filters, as necessary. Excitation power was measured through a power meter to calculate excitation power.

Quantum yield was then calculated by using the Edinburgh L980 software package, which was calculated based on the following equation:

$$PLQY = \frac{N_{em}}{N_{abs}} = \frac{\int I_{sample}(\lambda) - I_{ref}(\lambda) d\lambda}{\int E_{ref}(\lambda) - E_{sample}(\lambda) d\lambda},$$

where "I" indicates the spectrally corrected intensity of the emitted light, "E" indicates the spectrally corrected intensity of the excitation light, "sample" indicates measurements of PQD samples, and "ref" indicates measurements of a reference cuvette containing neat hexane.

Our PLQY equipment was calibrated using the recognized dye emission standards, which was in good agreement with literature values: Rhodamine 6G – Measured (91.1%), Literature (90-92%).

Dynamics

Dynamics in Figure 2c and 3b were fitted with biexponential curves (Eq. 1).

$$I = I_1 \exp\left(-t/\tau_1\right) + I_2 \exp\left(-t/\tau_2\right) \tag{1}$$

In the perovskite QDs the emission process frequently involves not just a single-exciton state but a set of closely spaced fine-structure states due to the size-dependent splitting of fine-structure states. Therefore, the dynamics displayed a biexponential feature.

Calculation of ΔJ_{sc}

We define that *q* is the electron charge and *F(λ)* is the incident photon flux density (AM 1.5, ASTM G173) at wavelength *λ*, *IPCE (610 nm)* is the IPCE response around 610 nm. As the emission of Mn^{2+} ions is a broadband, the IPCE response at this region floats around 93 to 96%. *A(λ)* is the absorption coefficient of QDs. *T(film)* is the transmittance of $CsPbCl_3$: Cr^{3+}, Mn^{2+} film after considering the absorption of PQDs and the sub band gap scattering, which varied from 95% to 98%.

$\Delta Jsc =$

$$\int qA(\lambda)F(\lambda)PLQY_{ex}IPCE(404nm)T(film)d\lambda + \int qA(\lambda)F(\lambda)PLQY_{Mn}IPCE(610nm)T(film)d\lambda \quad (1)$$

$$= [IPCE\ (404nm)PLQY_{ex} + IPCE\ (610nm)PLQY_{Mn}]T(film)\int qA(\lambda)F(\lambda)d\lambda \quad (2)$$

In this equation, the range of λ is 300-400 nm. $\int qA(\lambda)F(\lambda)d\lambda$ is the maximal integrated photocurrent we can get from the absorbed sunlight ranging 300-400 nm by perovskite QDs on the assumption that the IPCE is 100%. Then, the absorbed light was converted to emissions at 404 and 610 nm. $\boldsymbol{\int qA(\lambda)F(\lambda)PLQY_{ex}\,IPCE(404nm)T(film)d\lambda}$ means the integrated photocurrent of excitonic emission light at 404 nm converted from absorbed sunlight at 300-400 nm. Because the perovskite film is not totally transparent, we need to consider the transparency of the perovskite film (*T(film)*). Correspondingly, this part $\boldsymbol{\int qA(\lambda)F(\lambda)PLQY_{Mn}IPCE(610nm)T(film)d\lambda}$ means the integrated photocurrent of Mn^{2+} emission light at 610 nm converted from absorbed sunlight at 300-400 nm. For a given perovskite QDs and PSC, the *IPCE(404nm), IPCE(610nm),* $PLQY_{ex}$, $PLQY_{Mn}$ are all constants. Then, we can get equation 2.

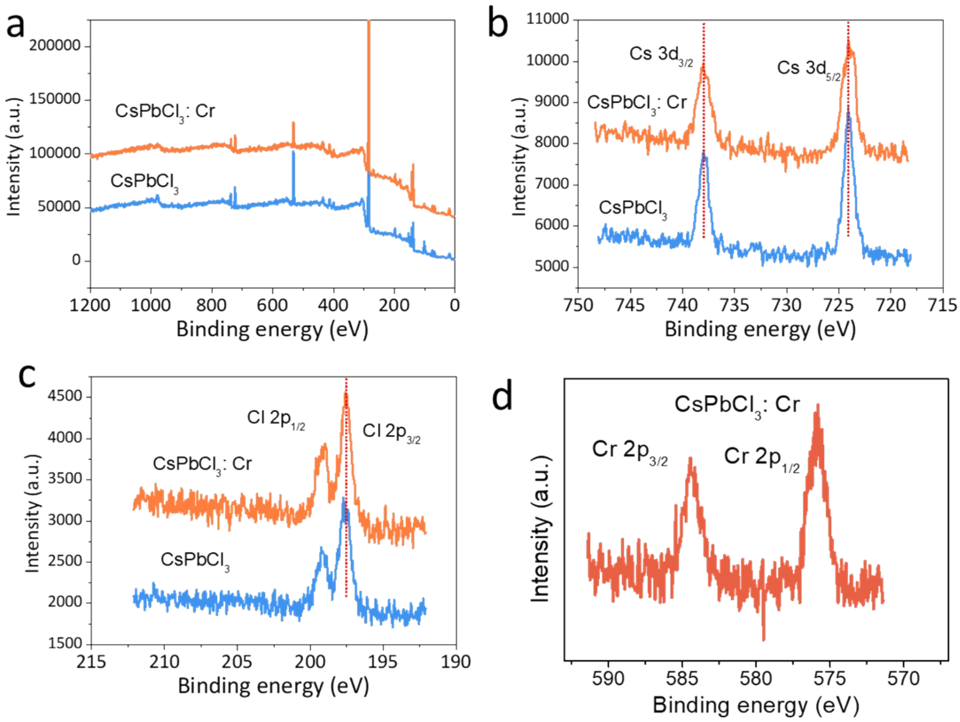

Figure S1 (a) XPS spectra of $CsPbCl_3$ and $CsPbCl_3$: Cr QDs. (b-d) High-resolution XPS analysis corresponding to Cs^+3d (b), Cl^- 2p (c), and Cr 2p (d) respectively.