Supporting Information

Revisiting Effects of Ligand-Capped Nanocrystals in Perovskite Solar Cells

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Experimental details

Materials for the synthesis of nanocrystals (NCs)

Cesium carbonate (Cs₂CO₃, 99.9%, Sigma-Aldrich), lead iodide (PbI₂, 99.9985%, Alfa Aesar), lead bromide (PbBr₂, \geq 98%, Sigma-Aldrich), zinc bromide (ZnBr₂, 99.999%, Sigma-Aldrich), zinc iodide (ZnI_2 , \geq 98%, Sigma-Aldrich), indium(III) chloride (InCl₃, 98%, Sigma-Aldrich), tris(dimethylamino)phosphine (DMA₃P, 97%, Sigma-Aldrich),1-octadecene (ODE, technical grade, Sigma-Aldrich), oleylamine (OLA, technical grade, Sigma-Aldrich), oleic acid (OA, technical grade, Sigma-Aldrich), anhydrous toluene (99.8%, Sigma-Aldrich), anhydrous hexane (95%, Sigma-Aldrich), and methyl acetate (CH₃COOCH₃, 99.5 %, Sigma-Aldrich) were purchased. Degassed OA was prepared by heating the OA at 110 °C under vacuum overnight, which was stored in a glovebox. Distilled OLA was prepared by vacuum distillation at 150 °C under 0.2 Torr.

Materials for the fabrication of perovskite solar cells (PSCs)

Fluorine-doped tin oxide glass substrates (FTO, TEC 8, Pilkington), titanium chloride (TiCl₄, 99%, JUNSEI), formamidinium iodide (FAI, 99.9%, GreatCell Solar), methylammonium bromide (MABr, 99.9%, GreatCell Solar), cesium iodide (CsI, 99.9%, Sigma-Aldrich), methylamine hydrochloride (MACl, 98%, Sigma-Aldrich), lead iodide (PbI₂, 99.99%, TCI), lead bromide (PbBr₂, 99.99%, TCI), Spiro-OMeTAD (> 99.5%, Lumtec), 4-tert-butyl pyridine (tBP, 98%, Sigma-Aldrich), lithium bis (trifluoromethylsulfonyl)imide (Li-TFSI, 99.95%, Sigma-Aldrich), N,N-dimethylformamide (DMF, 99.8%, Sigma-Aldrich), dimethyl sulfoxide (DMSO, 99.9%, Sigma-Aldrich), chlorobenzene (CB, 99.8%, Sigma-Aldrich), and acetonitrile (ACN, 99.8%, Sigma-Aldrich) were purchased.

Methods

Synthesis of NCs

Preparation of Cs-oleate solution

For the preparation of Cs-oleate solution, 0.326 g of CsCO₃ powder was loaded into a 100 ml 3neck flask with 1.0 ml of degassed OA and 16 ml of ODE. The solution was degassed at 105 °C under 0.29 Torr for 1 h. After degassing, the solution was heated at 150 °C under N₂ condition.

Preparation of CsPbBr₃

The synthesis method of CsPbX₃ was slightly modified from the synthetic method suggested by Protesescu et al. and Woo et al. for scale-up purposes.^{1,2} A mixture of 0.69 g of PbBr₂ and 0.475 g of ZnBr₂ were loaded into a 100 ml 3-neck flask with 5.0 ml of degassed OA, 5.0 ml of distilled OLA, and 50 ml of ODE. The solution was then degassed at 105 °C under 0.6 Torr for 2 h. After degassing, the solution was heated at 170 °C under N₂ condition. After waiting for 10 min for temperature stabilization, 4.0 ml of the prepared Cs-oleate solution was injected into the resulting solution. The reaction was quenched using an ice bath soon after the injection process. **Preparation of CsPbI**₃

The synthesis method of CsPBI₃ was the same as that of CsPbBr₃ NCs, except that 0.69 g of the PbBr₂ and 0.475 g of ZnBr₂ were replaced with 0.865 g of PbI₂ and 0.67 g of ZnI₂ respectively. **Precipitation of CsPbBr₃**

The precipitation of CsPbBr₃ was conducted in the glove box. The crude solution of CsPbBr₃ NCs was transferred from the 3-neck flask into three conical tubes (22.5 ml of solution in each tube). The tubes were then centrifuged at 13,000 rpm and 18 °C for 32 min. The supernatants in the tubes were discarded, and the tubes were turned upside down for 10 min to remove the residual organic solution. Afterwards, 4 ml of anhydrous toluene was added to these tubes. The

precipitated samples were re-dispersed in anhydrous toluene and re-centrifuged at 6000 rpm for 5 min. The precipitates were disposed, and the supernatants were gathered and stored in the glove box.

Precipitation of CsPbI₃

The precipitation of CsPbI₃ was conducted in the glove box. The crude solution of CsPbI₃ nanocrystals (NCs) was transferred from the 3-neck flask to six conical tubes (11 ml of solution in each tube). The tubes were centrifuged at 13,000 rpm and 18 °C for 32 min. The precipitates were disposed, and the supernatants were transferred into new 50 ml conical tubes. Then 30 ml of anhydrous methyl acetate was added into these tubes, and the tubes were centrifuged at 6,000 rpm for 5 min. The supernatants in the tubes were discarded and the tubes were turned upside down for 10 min to remove the residual organic solution. Then 4 ml of anhydrous toluene was added to these tubes. The precipitated samples were re-dispersed in anhydrous toluene, which were then gathered and stored in the glove box.

Preparation of tetrahedral-shaped InP

We adopted the synthesis method of tetrahedral InP NCs reported by K. Kim et al.³ A mixture of 0.24 g of InCl₃ and 5 ml of OLA were loaded into a 100 ml 3-neck flask. The solution was degassed at 110 °C under 1.0 Torr for 1 h. After degassing, the solution was heated at 250 °C under N₂ condition. A mixture of 0.18 ml of DMA₃P and 0.5 ml of distilled OLA solution was injected into this solution. The reaction was stopped after 1 h. Then 5 ml of this solution was transferred into a 50 ml conical tube. 25 ml of butanol was added, and the tube was centrifuged at 6,000 rpm for 5 min. The precipitate was re-dispersed in hexane and stored in the glove box.

Device fabrication

The etched FTO glass substrates were sequentially washed with 2% Hellmanex water solution, DI water, acetone, and ethanol for 10 min in ultrasonic bath. The 2 M aqueous TiCl₄ solution was prepared by gradually dropping TiCl₄ in ice water, which was then stored in a freezer at -5 °C. The compact-TiO₂ layer was deposited by chemical bath deposition on the cleaned FTO glass. The substrate was soaked in 0.16 M TiCl₄ solution at 70 °C for 45 min after treatment with UV-Ozone (UV-O) for 30 min. The substrate was immediately cleaned several times with DI-water and annealed at 150 °C for 60 min. Then 229.8 mg of FAI, 653.2 mg of PbI₂, 20.9 mg of CsI, 21.6 mg of MABr, 70.9 mg of PbBr₂, and 35 mg of MACl were dissolved in 1 mL anhydrous DMF:DMSO (7:3 v/v) to prepare the 1.61 M of FA_{0.83}MA_{0.12}Cs_{0.05}PbI_{2.64}Br_{0.36} perovskite precursor solution in the glove box. All processes henceforth were conducted in low humidity ambient air conditions (21 °C, under 5% relative humidity). The perovskite precursor solution was stirred in this air condition for 1 h. The TiO₂-deposited FTO substrate was treated with UV-O for 15 min before conducting the spin-coating process of perovskite. The perovskite precursor solution was spread on the substrate and spin-coated at 5000 rpm for 25 s. Then 0.5 mL of anisole was dropped into the spinning substrate at 18 s. The perovskite film was treated by heating on a hot plate at 150 °C for 10 min. Each NC solution diluted to 20 mg/ml in toluene was spin-coated on the perovskite film at 2000 rpm for 30 s (in OLA case, 15 mg/ml in toluene). Without any treatment, the Spiro-OMeTAD solution comprising 72 mg of Spiro-OMeTAD, 28.8 µL of tBP, and 17.6 µL of lithium bis(trifluoromethylsulfonyl)imide (Li-TFSI) solution (720 mg Li-TSFI in 1 mL acetonitrile) in 1 mL of chlorobenzene was spin-coated onto the perovskite film with or without an additional layer at 3000 rpm for 30 s. Finally, the Au electrode was deposited using a thermal evaporator in high vacuum.

Characterization

The absorption spectra of NCs were obtained through a ultraviolet-visible (UV-Vis) spectrophotometer provided by Thermo Scientific (Evolution 201), and that of perovskite films w/wo additional layer were obtained through UV-Vis spectroscopy as well (PerkinElmer, Lambda 35). The photoluminescence (PL) spectra of NCs and the perovskite films w/wo additional layer were recorded using PL spectrometers purchased from Hamamatsu Photonics (Quantaurus). The external quantum efficiency (EQE) and the integrated current density were measured by the EQE system (PV Measurement Inc.) with a 75 W xenon source lamp (USHIO, Japan). The transmission electron microscopy (TEM) images of NCs were obtained using a Tecnai F20 field emission transmission electron microscope (200 kV, FEI). The cross-sectional TEM images of the device were captured using a Cs-corrected high resolution transmission electron microscope (JEM ARM 200F). The surface images of the perovskite film and each additional layer on top of the perovskite film were captured through field emission scanning electron microscopy (JSM-7600F, JEOL). The photovoltaic parameters were measured using a potentiostat (CHI660D, CH Instruments) for all devices. These parameters of general and HTLfree devices were measured using a solar simulator (Newport Oriel Solar 3A Class AAA, 64023A) with a 450 W xenon lamp under AM 1.5 G sun (100 mA/cm²) illumination. The devices were covered using a thin metal mask with an active area of 0.14 cm^2 . The 1 sun illumination condition was corrected using a standard Si solar cell (Oriel, VLSI standard). The dark current-voltage characteristic of the device was obtained with the light completely blocked.



Figure S1. Scanning electron microscopy surface images of each additional layer on top of the perovskite film. (scale bars, 500 nm)

Sample		J_{sc} (mA/cm ²)	V _{oc} (V)	FF -	PCE (%)
Control	average	22.00	1.15	0.77	19.48
	deviation	0.14	0.012	0.011	0.44
with NC-CPB	average	22.13	1.18	0.80	20.89
	deviation	0.14	0.011	0.009	0.36
with NC-CPI	average	22.10	1.18	0.80	20.86
	deviation	0.14	0.010	0.007	0.35
with NC-InP	average	22.11	1.18	0.79	20.61
	deviation	0.13	0.010	0.008	0.35
with OLA	average	22.15	1.20	0.81	21.53
	deviation	0.14	0.010	0.007	0.34

Table S1. Photovoltaic parameters of optimized devices with each additional layer (20 cells per each case).



Figure S2. Ultraviolet-visible light absorbance and photoluminescence spectra of perovskite films with each additional layer.



Figure S3. Schematic energy band diagram of device with nanocrystals layer.³⁻⁵



Figure S4. *J-V* curves and photovoltaic parameters of hole transport layer-free devices with each additional layer.



Figure S5. Space charge limited current measurement of each device and its respective trap density.



Figure S6. The stability test of perovskite film w/wo an additional layer (a) XRD patterns of perovskite film at an ambient and relative humidity of 50% for 85 days. (b) Color changes of perovskite film after dropping a water droplet for 25 min.

REFERENCES

Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Krieg, F.; Caputo, R.; Hendon,
 C. H.; Yang, R. X.; Walsh, A.; Kovalenko, M. V., Nanocrystals of Cesium Lead Halide
 Perovskites (CsPbX(3), X = Cl, Br, and I): Novel Optoelectronic Materials Showing Bright
 Emission with Wide Color Gamut. *Nano Lett* 2015, *15* (6), 3692-6.

2. Woo, J. Y.; Kim, Y.; Bae, J.; Kim, T. G.; Kim, J. W.; Lee, D. C.; Jeong, S., Highly Stable Cesium Lead Halide Perovskite Nanocrystals through in Situ Lead Halide Inorganic Passivation. *Chemistry of Materials* **2017**, *29* (17), 7088-7092.

3. Kim, K.; Yoo, D.; Choi, H.; Tamang, S.; Ko, J. H.; Kim, S.; Kim, Y. H.; Jeong, S., Halide-Amine Co-Passivated Indium Phosphide Colloidal Quantum Dots in Tetrahedral Shape. *Angew Chem Int Ed Engl* **2016**, *55* (11), 3714-8.

4. Ravi, V. K.; Markad, G. B.; Nag, A., Band Edge Energies and Excitonic Transition Probabilities of Colloidal CsPbX3 (X = Cl, Br, I) Perovskite Nanocrystals. *ACS Energy Letters* **2016**, *1* (4), 665-671.

5. Chueh, C.-C.; Li, C.-Z.; Jen, A. K. Y., Recent progress and perspective in solutionprocessed Interfacial materials for efficient and stable polymer and organometal perovskite solar cells. *Energy & Environmental Science* **2015**, *8* (4), 1160-1189.