Supplementary information for:

Polymer-free films of inorganic halide perovskite nanocrystals as UV-to-white color-conversion layers in LEDs

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EXPERIMENTAL DETAILS

Materials.

Lead(II) bromide (PbBr₂, 99.999% trace metals basis), lead(II) iodide (PbI₂, 99.999% trace metals basis), cesium carbonate (Cs₂CO₃, reagentPlus, 99%), iodine (I₂, 99.99%), hydrochloric acid (HCl, ACS reagent, ≥ 37%), hydriodic acid (HI, 57wt.% in H₂O), hydrobromic acid (HBr, 48 wt % in H₂O, ≥ 99.99%), indium(III) acetate (In(Ac)₃, 99.99%), copper(I) iodide (CuI, purum, ≥99.5%), 1-dodecanethiol (DDT, ≥98%), zinc(II) stearate (Zn(StA)₂, technical grade), 1-octadecene (ODE, technical grade, 90%), oleylamine (OLAM, 70%) and oleic acid (OA, 90%), and chloroform (CHCl₃, >99%) were purchased from Sigma-Aldrich. Cadmium(II) oxide (CdO, >99%), selenium powder (Se, >99%) and sulfur powder (S, 99%), trioctylphosphine (TOP, 90%) and trioctylphosphine oxide (TOPO, 99%) were purchased from STREM Chemicals. Octadecylphosphonic acid (ODPA, >99%) was purchased from PCI Synthesis. Toluene (TOL, anhydrous, 99.8%), methanol (MeOH, >99%), ethanol (EtOH, >99%), and isopropanol (IPrOH, >99%) were bought from Carlo Erba reagents. All chemicals were used without any further purification, except for OLAM, OA, and ODE, which were degassed at 100 °C for 2 h in vacuum.

Synthesis and film deposition.

CsPbBr₃ NPLs and CsPbI₃ NSs were synthesized as described by Protesescu et al., but at 150 °C and with a pure OA Cs-precursor. In a typical synthesis, 69 mg of PbBr₂ or 87 mg of PbI₂, 5 mL of ODE, 0.5 mL of OA and 0.5 mL of OLAM were loaded in a 25 mL 3-neck flask and dried under a vacuum for 1 h at 100 °C (in case of CsPbI₃, 15 mg of I₂ was added). After degassing, the temperature was raised to 150 °C and a 0.5 mL of Cs-oleate (0.4 g of Cs₂CO₃ degassed 20 mL of OA at 150 °C) was swiftly injected. Immediately after the injection, the nanocrystal solution was quickly cooled down to room temperature with an ice bath, and the nanocrystals were transferred to a glovebox. The nanocrystals as delivered from the synthesis (the “crude” nanocrystals) could be purified via high speed centrifugation (at 12 000 rpm for 30 min), followed by redispersion in TOL.

CsPbBr₃ and CsPbI₃ NCs were synthesized as described in our previous work. In a typical synthesis, 69 mg of PbBr₂ (0.188 mmol) or 87 mg of PbI₂, 5 mL ODE, 0.5 mL OA and 0.5 mL OLAM were loaded in a 25 mL 3-neck flask and dried under vacuum for 1 h at 120 °C. After degassing, the temperature was raised to 165 °C and a 0.6 mL ODE with 0.4 mL of previously synthesized Cs-oleate (0.4 g Cs₂CO₃ degassed in 15 mL ODE and 1.75 mL OA at 150 °C) mixture was swiftly injected. Immediately after the injection, the NC solution was quickly cooled down to room temperature with an ice bath, and the NCs were transferred to a glovebox.

CIZS nanocrystals were synthesized according to the procedure described by De Trizio et al. In a typical synthesis, a solution of CuI (0.2 mmol), In(Ac)₃ (0.4 mmol), and 5 mL of DDT was loaded into a three-neck flask and was then degassed.
under vacuum at 80 °C for 1 h until a clear solution was obtained. The temperature was then raised to 230 °C for 11 min to let the particles grow. The reaction was quenched by cooling the solution to room temperature and reheated to 120 °C (still under inert atmosphere) followed by the dropwise addition (in about 1 min) of Zn(StA)₂ (0.4 mmol) dissolved in 5 mL of ODE and 0.5 mL of TOP. The temperature was then raised to 210 °C for 60 min, after which the flask was cooled to room temperature and the NCs were then separated by addition of ethanol followed by centrifugation. The nanocrystals were washed three times by repeated dissolution in toluene and reprecipitation in ethanol.

**Giant-shell CdSe/CdS nanocrystals** were synthesized as described by Christodoulou *et al.* CdSe seeds were synthesized at 380 °C, according to the procedure described by Carbone *et al.* After synthesis, the nanocrystal suspensions were purified by precipitating them with MeOH, followed by centrifugation and resuspension in toluene (procedure repeated 3 times). For the shell growth, Cd and S-precursors were prepared separately as a 0.5 M solution of TOP-S, and Cd-OA dissolved in ODE, respectively. Next, 2 × 10⁻⁷ mol of CdSe nanocrystals were added to 10 mL of ODE and heated up to 300 °C. The shell precursor solution is then added dropwise over the course of 4 hours. After synthesis, the samples were purified by precipitation with isopropanol, followed by centrifugation and resuspension in toluene. A second purification step was performed with methanol as nonsolvent and samples were finally suspended in toluene.

**Thin films** were deposited on previously-cleaned fused silica substrates (3x3 mm) by depositing a 4 µL drop of concentrated nanocrystals in toluene and spin-coating at 1500 rpm for 1 min.

**X-ray stabilization.** Nanocrystal films were irradiated in vacuum (10⁻⁶ mbar) with the AlKα monochromatic source of the X-ray Photoelectron Spectrometer (photon energy = 1486.6 eV) with an emission current of 20 mA, corresponding to a photon flux of 2.4 × 10¹¹ photons/mm²·s for 3 h.

**TEM characterization.** Conventional TEM observations were carried out using a JEOL JEM 1011 microscope equipped with a thermionic gun operating at 100 kV of accelerating voltage. Samples were prepared by dropping washed and diluted (in TOL) nanocrystal solutions onto carbon-coated 200 mesh copper grids with subsequent solvent evaporation.

**Photoluminescence measurements in solution.** Photoluminescence spectra of different nanocrystal solutions in toluene were acquired with a Varian Cary Eclipse UV-Visible spectrophotometer. Excitation wavelength was set to 400 nm. Spectra were acquired between 420 nm and 780 nm.

**LED setup and measurements.** As excitation source for the color converting layer we used a 365 nm LED (max power = 1150 mW) from Thorlabs. Films were placed on fused-silica substrates and placed on top of the LED. Spectra were collected using an Ocean Optics HR4000+ spectrometer coupled with an optical fiber and a long-pass filter (λ₅₀% = 450 nm) to remove the excitation UV light. The excitation power VS emitted power curves were obtained controlling the LED through a Labview interface and a Keithley 2612 Source Measure Unit (SMU), while the emitted power was measured using a calibrated Si-photodiode and the previously mentioned optical filter.

**Colorimetry.**

The International Commission for Illumination (Commission Internationale de l’Eclairage, CIE) has standardized the measurement of color through the use of color-matching functions representing the eye sensitivity and the chromaticity diagram. Chromaticity coordinates (x and y) reported in the manuscript were calculated using the CIE 1931 color-matching functions \(x(\lambda), y(\lambda), z(\lambda)\) (available online) to obtain the tristimulus values X, Y and Z:

\[
X = \int_{380}^{780} \bar{x}(\lambda)P(\lambda)\,d\lambda \\
Y = \int_{380}^{780} \bar{y}(\lambda)P(\lambda)\,d\lambda \\
Z = \int_{380}^{780} \bar{z}(\lambda)P(\lambda)\,d\lambda
\]

In equations (1), (2) and (3) \(P(\lambda)\) is the spectral power distribution of the emitter. From the tristimulus values the chromaticity coordinates can be calculated using the following equations:

\[
x = \frac{x}{x+y+z}
\]
The obtained chromaticity coordinates (x and y) were used to calculate the color temperatures (CCT) reported in the manuscript using the following equation:

$$\text{CCT} = 446n^3 + 3525n^2 + 6823.3n + 5520.3$$

(6)

Where \( n = (x - 0.0332)/(0.1858 - y) \). Finally, the color rendering index (CRI) was obtained directly from the OceanView software controlling the Ocean Optics HR4000+ spectrometer used to collect all spectra.

Figure S1. Non-irradiated CsPbBr\(_3\) NPLs on CsPbI\(_3\) nanocrystal films and vice-versa lead to anion-exchange and single-peak emission films.

Figure S2. CIE diagram of Br-NC, Br-NPL and I-NS mixed in solution at different ratios. Circled dots correspond to spectra presented in the main manuscript.
Figure S3. CIE coordinates of thin films of mixed CsPbBr$_3$ NPLs, CsPbBr$_3$ NCs and CIZS nanocrystals used as color conversion layer on top of a commercial UV LED. Square markers present the pristine emission at low excitation power while red dots present the response after degradation of CIZS by high UV illumination power.

Figure S4. PL spectra of a film of mixed CsPbBr$_3$ and giant-shell CdSe/CdS nanocrystals before and after illumination at high power.

Additional references
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