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Evolution of $CsPbBr_3$ Nanocrystals Upon Post-Synthesis Annealing Under Inert Atmosphere

F. Palazon, F. Di Stasio, S. Lauciello, R. Krahne, M. Prato and L. Manna

Methods:

Materials. Lead(II) bromide ($PbBr_2$, 99.999% trace metals basis), cesium carbonate (Cs_2CO_3, reagentPlus, 99%), 1-octadecene (ODE, technical grade, 90%), oleylamine (OLAM, 70%) and oleic acid (OA, 90%) were purchased from Sigma-Aldrich. Toluene (TOL, anhydrous, 99.8%) was 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. $CsPbBr_3$ NCs were synthesized as described in our previous work.[1] In a typical synthesis, 69 mg of $PbBr_2$ (0.188 mmol), 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 Cs_2CO_3 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. Thin films were deposited on 5 x 5 mm silicon substrates by drop-casting 10 µL of concentrated CsPbBr3 NCs in TOL.

Annealing. Samples were annealed on a hot-plate under nitrogen (glove box). Annealing at different temperatures (50 °C, 100 °C, 150 °C, and 200 °C) was performed for one hour in a cumulative way: 4 samples were annealed one hour at 50 °C, one was taken out, then temperature was risen to 100°C where the remaining 3 samples were annealed for an extra hour, another sample was taken out; temperature was risen again to 150 °C to anneal the remaining two samples for an extra hour after which only one sample was kept for a final hour at 200 °C.

Electrical characterization. Samples were prepared by drop-cast deposition of the NC solutions on glass substrates with arrays of interdigitated Cr/Au electrodes. Channel length and width in the interdigitated array were 100 µm and 4 µm, respectively. Electrical measurements were performed in air with a Suss Microtec PM5 probe station connected to a Keithley 2612 sourcemeter. For illumination a white LED (OSRAM, Oslon square, output power 2W) connected to a programmable 2200-60-2 Keithley power supply was used.

Photoluminescence characterization. Steady-state PL spectra, PLQY and time-resolved PL lifetime measurements of the annealed CsPbBr3 NCs films were carried out with an Edinburgh Instruments fluorescence spectrometer (FLS920). The system is equipped with a Xenon lamp and monochromator for steady-state PL, and a time-correlated single photon counting unit coupled with a pulsed laser diode (λ = 405 nm, pulse width = 50 ps) for time-resolved PL. PLQY values of the annealed CsPbBr3 NCs films were obtained using excitation wavelength (λ = 450 nm) and a calibrated integrating sphere.

HRSEM characterization. High-resolution SEM imaging was carried out using a JEOL JSM 7500FA (Jeol, Tokyo, Japan) equipped with a cold field emission gun (FEG), operating at 5 kV acceleration voltage. The electrons used for imaging are backscattered electrons.

X-ray diffraction. XRD analysis was performed on a PANalytical Empyrean X-ray diffractometer equipped with a 1.8 kW Cu Kα ceramic X-ray tube and PIXcel3D 2 × 2 area detector, and operating at 45 kV and 40mA. The diffraction patterns were collected in air at room temperature using parallel-beam (PB) geometry and symmetric reflection mode. XRD data analysis was carried out using HighScore 4.1 software from PANalytical.

Nanochemistry Department, Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy. E-mail: mirko.prato@iit.it; liberato.manna@iit.it

Table S1. Fitting parameters used in the PL time decays. All PL decays we measured at PL peak and fitted with an multi-exponential decay: $I = A_1 e^{(-t/\tau_1)} + A_2 e^{(-t/\tau_2)} + A_3 e^{(-t/\tau_3)} + y_0$. <□> is the calculated weighted average PL lifetime. The time-resolved PL measurement was carried out using a time-correlated single photon counting unit and a pulsed laser diode as excitation source (λ = 405 nm, pulse width = 50 ps)

	A_1	τ_1	A_2	τ_2	A_3	τ_3	<τ>
reference	0.08	1.34	0.75	6.05	0.17	23.1	8.57
50C	0.46	4.13	0.47	11.09	0.07	85	13.1
100C	0.11	2.94	0.64	4.18	0.25	14.4	6.6
150C	0.65	2.48	0.3	6.84	0.05	22.5	4.78
200C	0.4	2.05	0.51	3.61	0.09	15.1	4

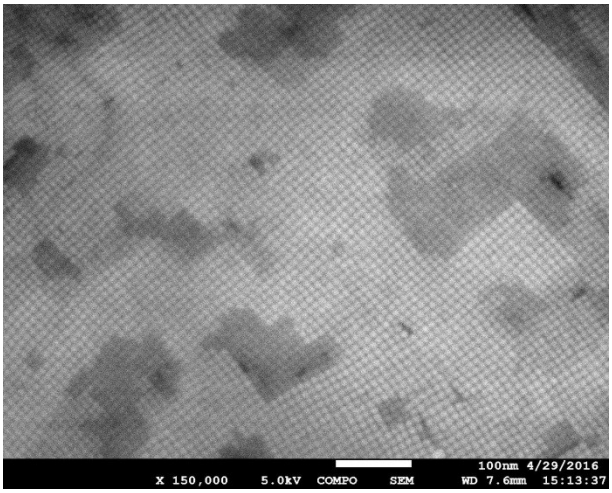

Figure S1: HRSEM image of reference sample

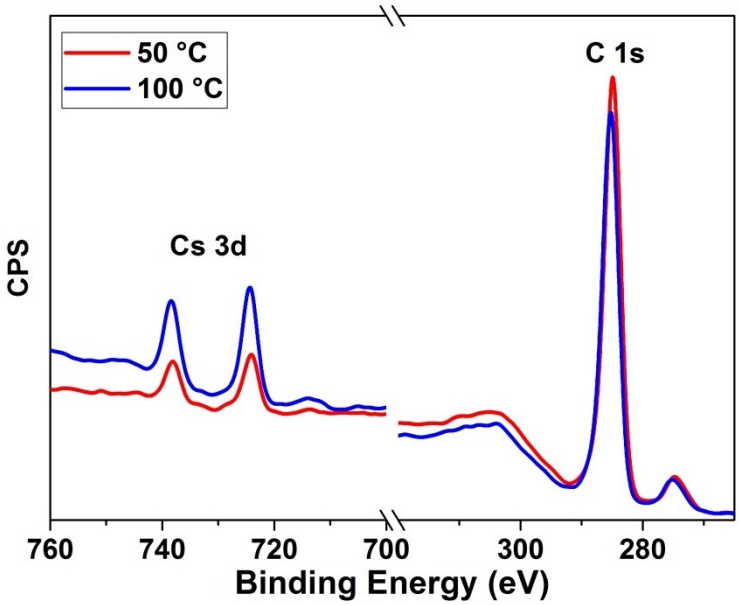

Figure S2: XPS spectra of samples annealed at 50°C and 100°C. The relative amount (atomic percentage) of carbon-to-cesium decreases by ca. 50% at 100°C, owing to the removal of organic residues and ligands.

References

1. Q. A. Akkerman, V. D'Innocenzo, S. Accornero, A. Scarpellini, A. Petrozza, M. Prato and L. Manna, *J. Am. Chem. Soc.*, 2015, **137**, 10276-10281.