3D-printed continuous flow reactor for high yield synthesis of $CH_3NH_3PbX_3$ (X = Br, I) nanocrystals

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Experimental

Synthesis of CH_3NH_3X: First, an equal molecular ratio of HX (X = Br, I) was added to a solution of methylamine in absolute ethanol, and the mixture was cooled to 0 °C, and then the reaction solution was stirred for 2 hours. The solvent was evaporated by rotary evaporation at 40 °C. Finally, the obtained solid was washed three times with diethyl ether and dried in a vacuum oven at a temperature of 50 °C for 6 hours to give the corresponding CH_3NH_3X (X = Br, I).

Preparation and use of $CH_3NH_3PbX_3$ precursors:

Precursor with DMF as the solvent:

17.8 mg CH_3NH_3Br and 73.5 mg $PbBr_2$ was added to 5 mL of DMF which contained 20 μL of n-octylamine and 0.5 mL of oleic acid. The resulting mixture was sonicated for 10 min to form a precursor solution. The precursor solutions using DMF as the solvent were mainly used to explore the performance of the microreactor and the factors affecting the crystallization of perovskite nanocrystals.

Precursor with THF as the solvent:

(1) 2.2 mg CH_3NH_3Br and 9.1 mg $PbBr_2$ was added to 10 mL of THF which contained 75 μL of n-octylamine and 1 mL of oleic acid. The resulting mixture was sonicated for

3 min to obtain a precursor solution.

(2) 25.4 mg CH_3NH_3I and 18.8 mg PbI_2 was added to 4 mL of THF which contained 30 μL of n-octylamine and 0.4 mL of oleic acid. The resulting mixture was sonicated for 12 min to obtain a precursor solution.

Two precursor solutions using THF as the solvent were used to prepare perovskite nanocrystals of different emission wavelengths. Also, $CH_3NH_3PbI_3$ nanocrystals prepared from precursors with THF as the solvent were involved in the assembly of WLED devices.

Precursor with ACN as the solvent: 25.4 mg CH_3NH_3I and 18.8 mg PbI_2 was added to 4 mL of acetonitrile which contained 30 μL of n-octylamine and 0.4 mL of oleic acid. The resulting mixture was sonicated for 12 min and centrifuged for 5 min at 9000 r min^{-1}. Finally, the supernatant was taken as the precursor solution. The precursor solutions using acetonitrile as the solvent was used to prepare stable $CH_3NH_3PbI_3$ nanocrystals.

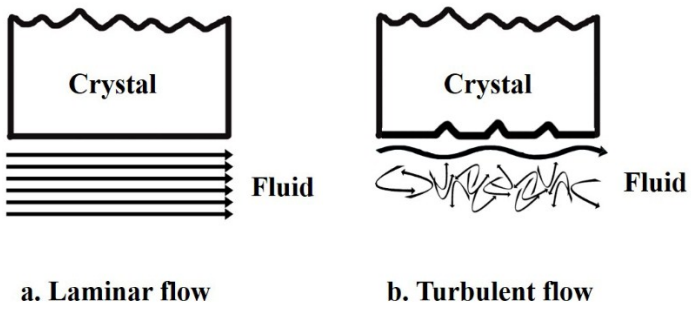

Figure S1. Flow state at the solid-liquid interface.

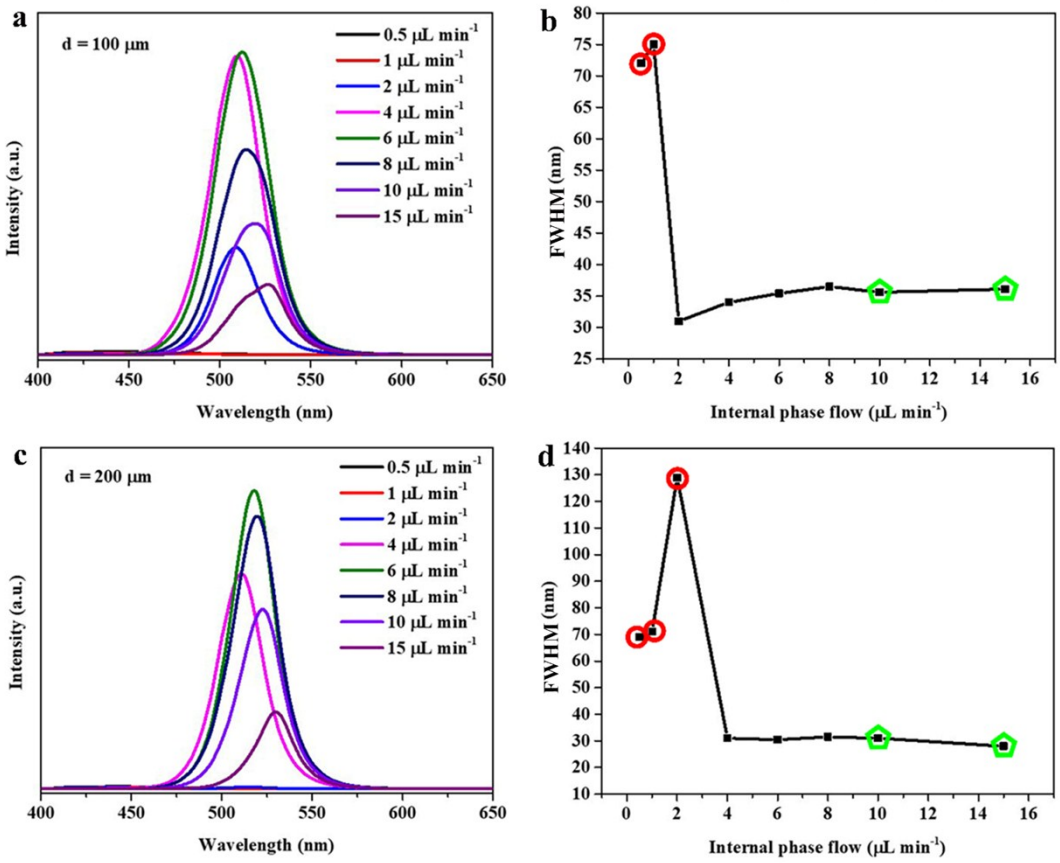

Figure S2. PL emission spectra and the FWHM values of the $CH_3NH_3PbBr_3$ nanocrystals prepared by microreactors with (a) (b) 100 μm and (c) (d) 200 μm nozzle diameter and various internal flow rate. In the (b) (d), the red circles represent the products of large FWHM; the green pentagons represent the products of large particles.

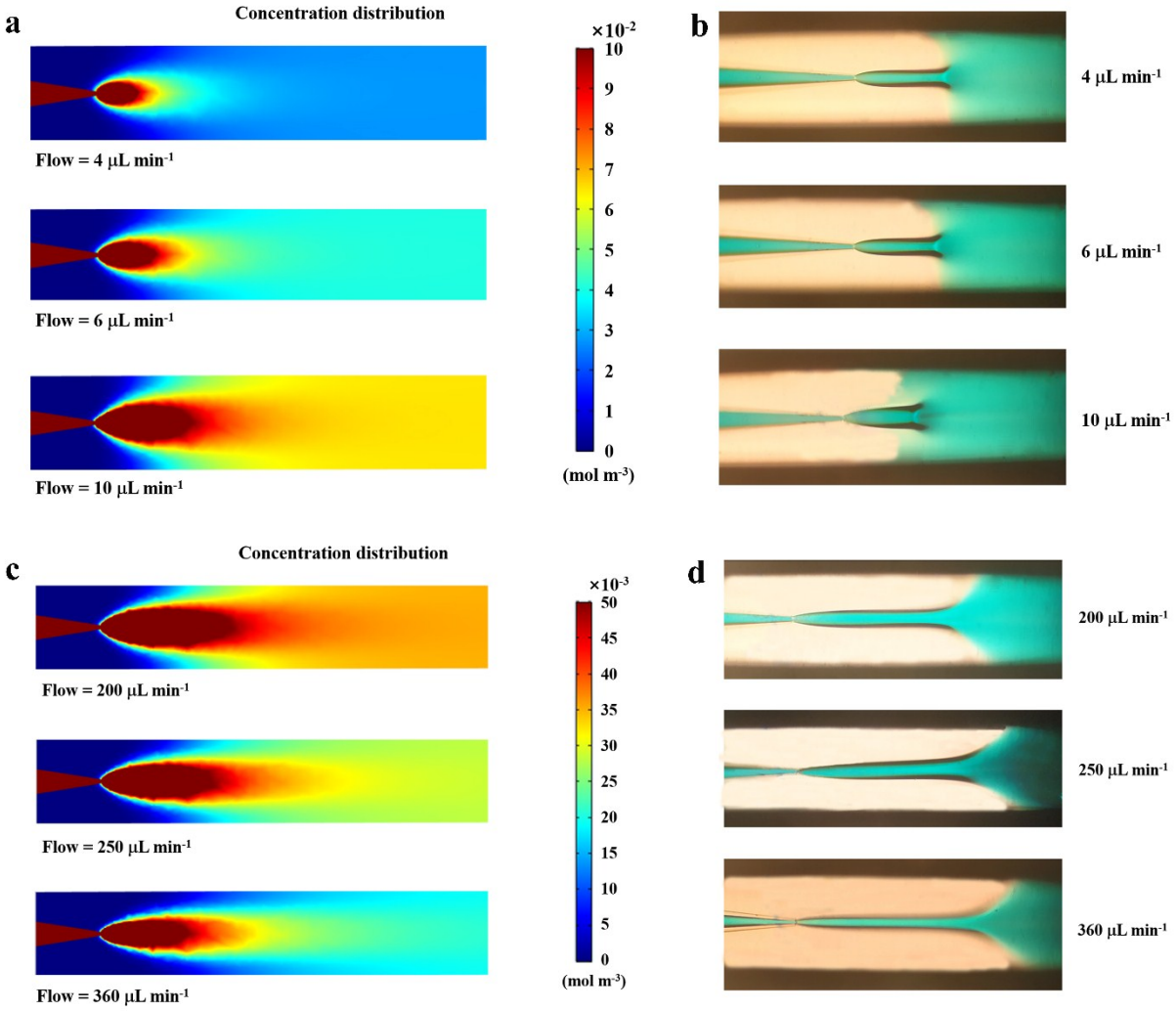

Figure S3. (a) Simulation results and (b) optical images of different internal phase flows when the external phase flow rate is 130 μL min^{-1}. (c) Simulation results and (d) optical images of different external phase flows when the internal phase flow rate is 8 μL min^{-1}.

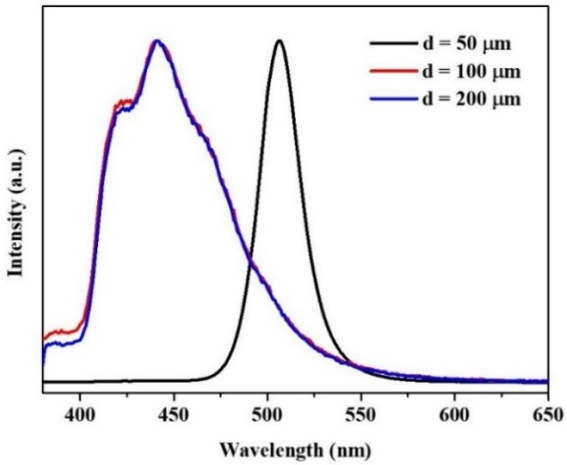

Figure S4. PL emission spectra of $CH_3NH_3PbBr_3$ nanocrystals prepared from reactors with different nozzle diameters at a internal phase flow rate of 1 μL min^{-1}.

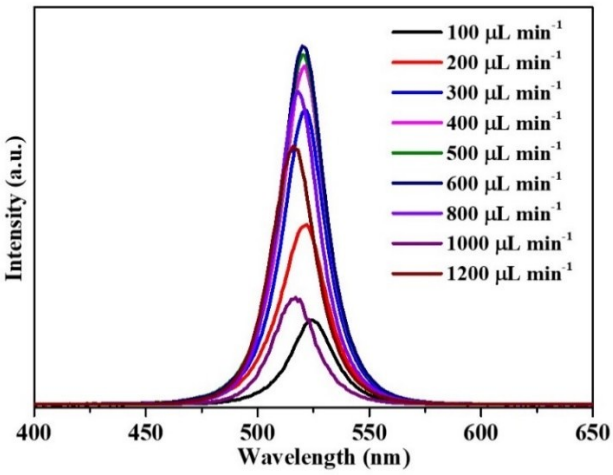

Figure S5. PL emission spectra of $CH_3NH_3PbBr_3$ nanocrystal prepared with different flows rates of the external phase.

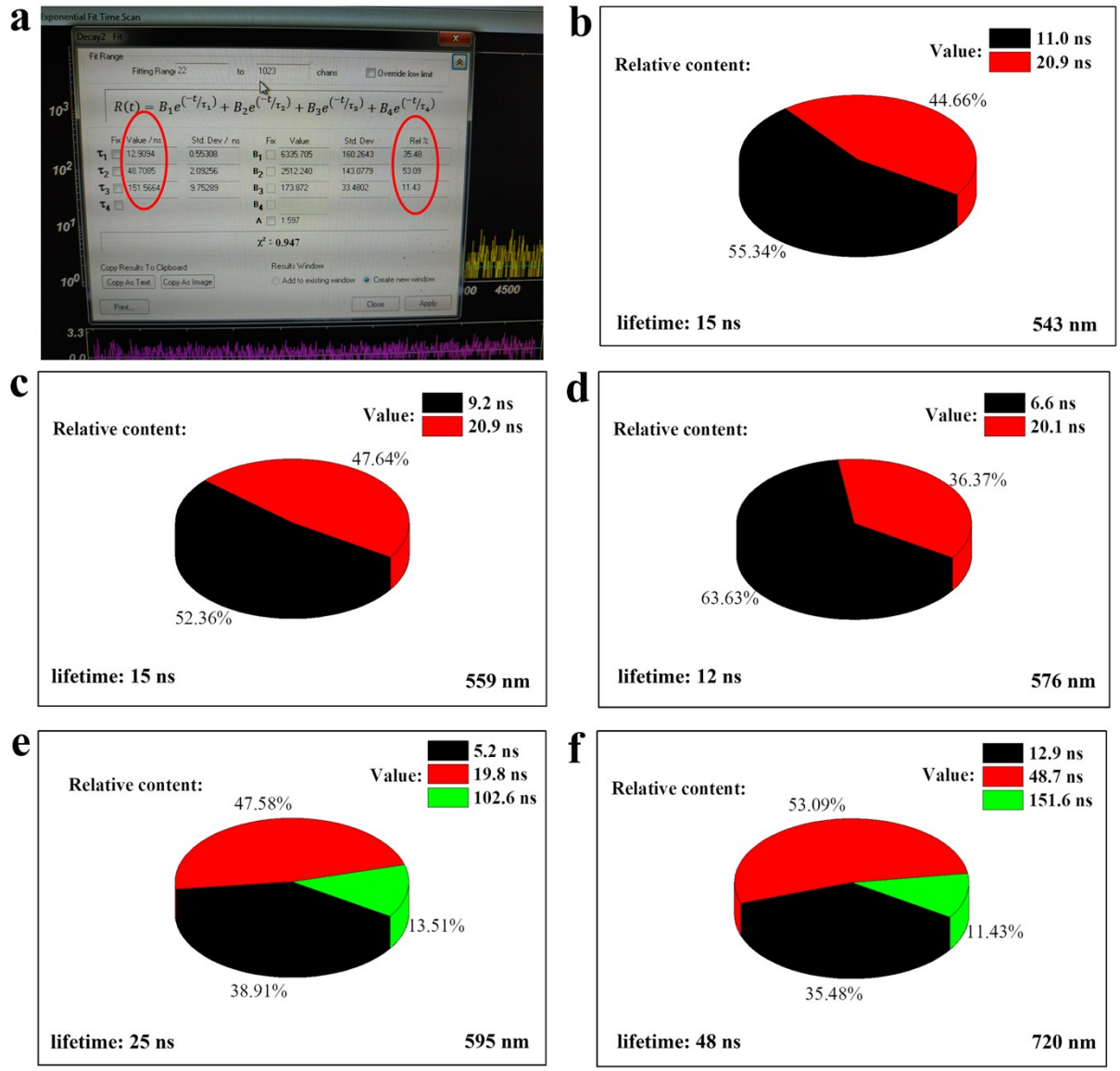

Figure S6. (a) An example of a software fitting result. The data "Value" and "Rel" required for the calculation are marked with an ellipse. (b) (c) (d) (e) and (f) are data plots required to calculate the fluorescence lifetime of five different emission wavelength perovskite nanocrystals.

Calculation of fluorescence lifetime:

$$R(t) = Value1 * Del1 + Value2 * Del2 + Value3 * Del3 \qquad (3)$$

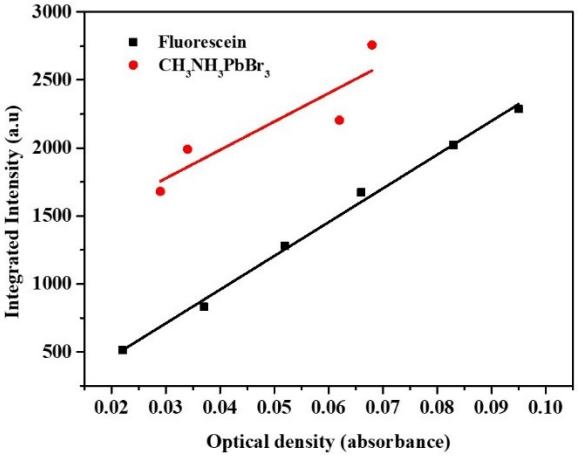

Figure S7. Quantum yield of $CH_3NH_3PbBr_3$ nanocrystals.

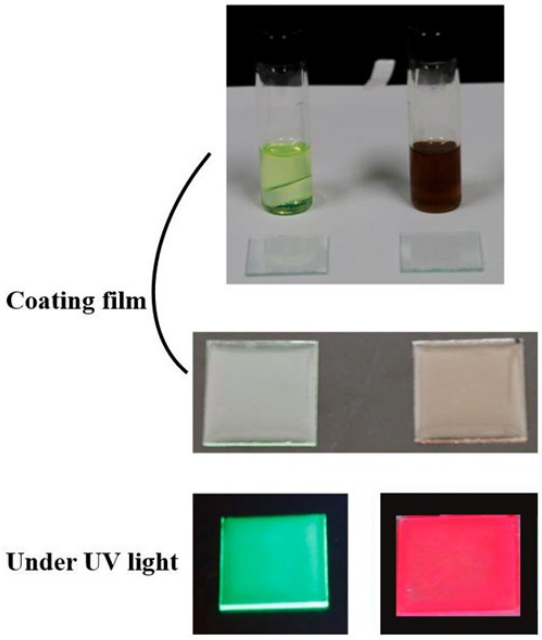

Figure S8. Schematic diagram of the mixing of the $CH_3NH_3PbBr_3$ and $CH_3NH_3PbI_3$ perovskite nanocrystal solutions with the polystyrene solution and the coating process.

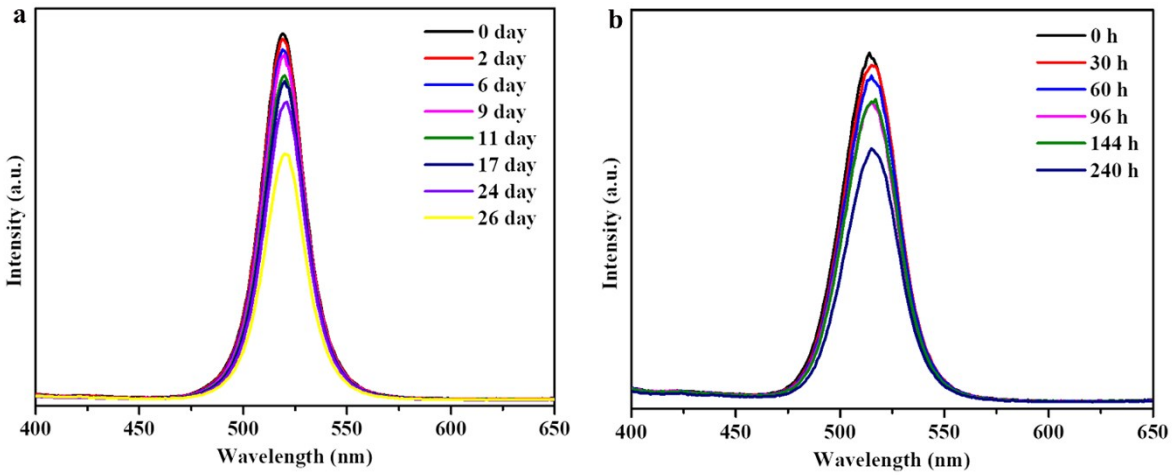

Figure S9. PL emission spectra of nanocrystal-polystyrene films in (a) air and (b) 1 ppm Hg^{2+} at different residence time.

Table S1. Detailed information of different emission wavelength samples.V_1 is the volume of the precursor liquid of $CH_3NH_3PbBr_3$. V_2 is the volume of the precursor liquid of $CH_3NH_3PbI_3$. (x, y) are CIE coordinates.

Sample	V_1/ V_2	Emission peak (nm)	FWHM (nm)	(x, y)
1	1:0	433	18	(0.16, 0.04)
2	13:1	474	36	(0.12, 0.13)
3	10:1	543	35	(0.35, 0.64)
4	7:1	559	33	(0.43, 0.57)
5	4:1	576	31	(0.52, 0.48)
6	3:2	583	31	(0.55, 0.45)
7	2:3	595	33	(0.61, 0.39)
8	0:1	720	55	(0.73, 0.27)