Supplementary Information

Room temperature synthesis of blue and green emitting CsPbBr$_3$ perovskite nanocrystals confined in mesoporous alumina film

Daimiota Takhellambam, [‡a] Tinku Ram Meena [‡a] and Debrina Jana*[a]

[a] Department of Chemical Sciences
Indian Institute of Science Education and Research Mohali
SAS Nagar, Mohali 140306, India
*E-mail: debrina@iisermohali.ac.in

Table of Contents

Experimental details

Materials

Aluminum-tri-sec-butoxide (ASB), Pluronic F127, $PbBr_2$ (98%) were supplied by Sigma-Aldrich; while 1-propanol ($CH_3CH_2CH_2OH$), hydrochloric acid (HCl) and methanol were obtained from s. d. fine-chem limited and Ranbuxy fine chemicals. CsBr (99.9%) and N,N-Dimethylformamide (DMF, 98%) were purchased from Alfa-Aesar and SRL Pvt. Ltd. respectively. Coumarin 540A was obtained from Exciton. Mili-Q (Millipore) water (18 MΩ) was used throughout the study.

Methods

For preparation of boehmite sol, Yoldas method was followed which involves hot hydrolysis (>80 °C) of ASB and subsequent peptization of boehmite precipitates using HCl.[1] The molar ratios of water/ASB and HCl/ASB were 100 and 0.10, respectively. Post peptization, the sol was stirred vigorously in refluxing condition for 5 h and then kept another 48 h under refluxing condition without stirring. The resultant sol was concentrated to about 7.5 wt % of $AlO_{1.5}$ content by distilling off the butan-2-ol and some portion of water. Required amount of methanol was added to bring the $AlO_{1.5}$ content to 5.3 wt%. In the next step, mesoporous alumina films were prepared from boehmite sol using F127 as structure directing agent. A calculated amount of F127 (0.001 mol per mol of $AlO_{1.5}$) was dissolved in 1-propanol and boehmite sol was added to it. $AlO_{1.5}$ content at this stage was maintained at 4 wt% and micellar arrangement forms inside the sol. This sol was used for preparation of the films on glass slides using dip-coating method by single dipping technique. The as-prepared films were dried initially at 60 °C in a hot-air oven. Surfactant from the films were removed by calcination at 500 °C (ramp of 2 °C min^{-1} with a holding time of 60 min) in case of glass substrates whereas ethanol extraction method was used for flexible polypropylene and polyethylene terephthalate sheets. Thus, mesoporous alumina film was formed on the glass slide/polypropylene sheet. For generation of PNCs inside the mesoporous film matrix, two-step dipping procedure was undertaken. First, the mesoporous alumina film was dipped into 0.025-0.5 M $PbBr_2$ solution in DMF with a holding time of 2 min and withdrawal speed was maintained at 140 mm/s. This film was kept in air for about 45 s before washing it in DMF solvent, followed by oven drying

for 15 min at 60 °C. 0.025-0.5 M solution of CsBr was prepared in water: ethanol mixture (1.5/6.5 v/v), and stirred for 30 min. The oven dried film was kept in open air for some time to come back at room temperature and then it was dipped in CsBr solution with a holding time of 45 s. Withdrawal speed was maintained as above and finally the slide was washed with ethanol and put inside desiccator. Vacuum pump attached to the desiccator was kept switched on for 10 mins initially and then it was removed. The slide was kept inside desiccator overnight in this condition and all the characterizations were done after that.

Characterization

UV-visible spectra of the films deposited on silica/quartz glass substrates were measured using Cary 5000 UV-Vis NIR (Agilent Technologies) spectrophotometer at the scan rate of 1 nm/s. Photoluminescence (PL) spectra were recorded using Horiba Fluromax-4 with slit widths of 1 nm x 1.5 nm and a scan integration time of 0.5 s at an excitation wavelength $\lambda_{ex} = 400$ nm. The PL lifetime measurements were carried out using Horiba Fluorohub-B at an excitation wavelength of 375 nm using a pico second diode laser at a repetition rate of 1 Mhz. The instrument response function (IRF) was recorded using 1% ludox (colloidal silica) solution. For relative PL quantum yield (PL QY), same alumina film was soaked in 10^{-4} M Coumarin 540A dye solution (standard QY of 53%) in ethanol and was used as reference.[2] Grazing incidence X ray diffraction (GIXRD) pattern of the thin films were recorded by Rigaku Smartlab GIXRD machine using Cu Kα ($\lambda \approx 1.54059$ Å) radiation operating at 9 kW (tube current 200 mA and tube voltage 45 kV) equipped with a rotating anode. X-ray intensity was enhanced using cross-beam optics. Grazing incidence angle was maintained at 0.3 °. Transmission electron microscopic (TEM) measurements were carried out with Tecnai G^2 30ST (FEI) and Tecnai G^2 20 STWIN (FEI) equipped with energy dispersive X-ray scattering (EDS) facility. For TEM sample preparation, scratched off coatings were dispersed in acetone and drop casted onto the carbon-coated grid. The thickness of the coatings was measured by a Surfcorder SE-2300 profilometer (Kosaka Laboratory Ltd., Japan). Nitrogen adsorption-desorption isotherms of the scratched off film samples were performed at -196 °C using BELSORP Max instrument. BET and BJH models were used to evaluate the surface area and porosity of the films, respectively. The pore size distributions of the films were determined from the adsorption bench of the isotherms. Prior to analysis, heat-treated (500 °C) alumina film samples were degassed at 125 °C under vacuum (1.99 x 10^{-4} Pa) for 5 h.
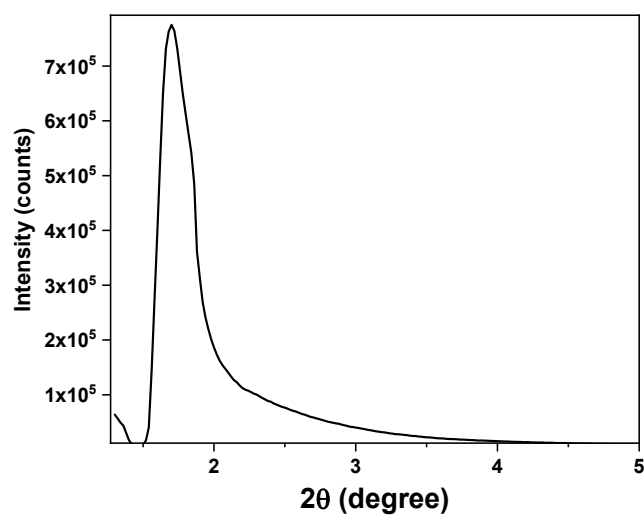
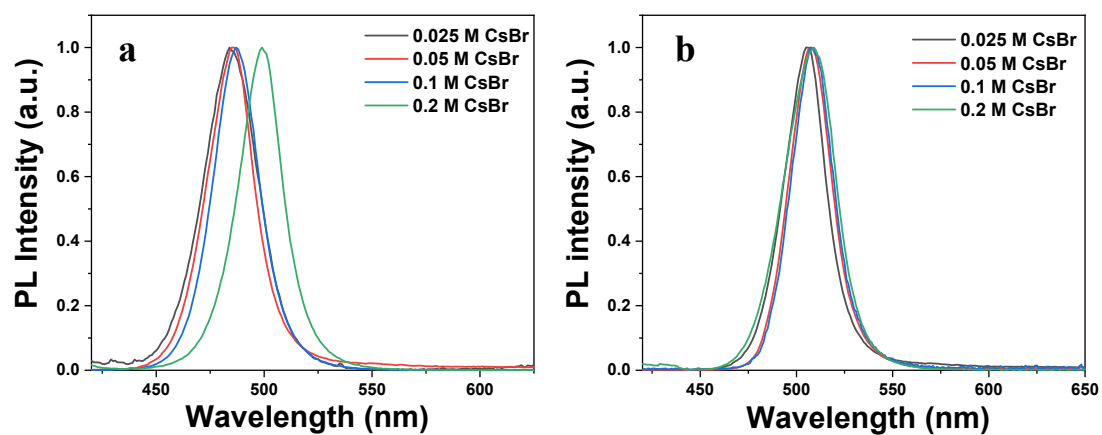**Figure S1.** Low angle XRD of γ-Al₂O₃ film shows broad peak indicating the existence of disordered mesopores.

Figure S2. Photoluminescence spectra of $CsPbBr_3$ NCs-Al_2O_3 composite films prepared using variable concentrations of CsBr keeping $PbBr_2$ concentration fixed at (a) 0.025 M and (b) 0.1 M.
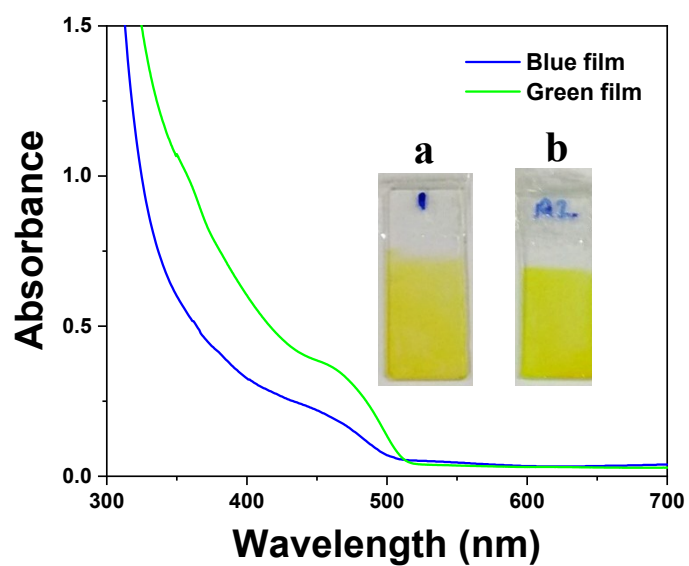
Figure S3. UV-visible spectra of the $CsPbBr_3$ NCs-Al_2O_3 composite films. Inset shows the digital image of a) blue and b) green film at day light.
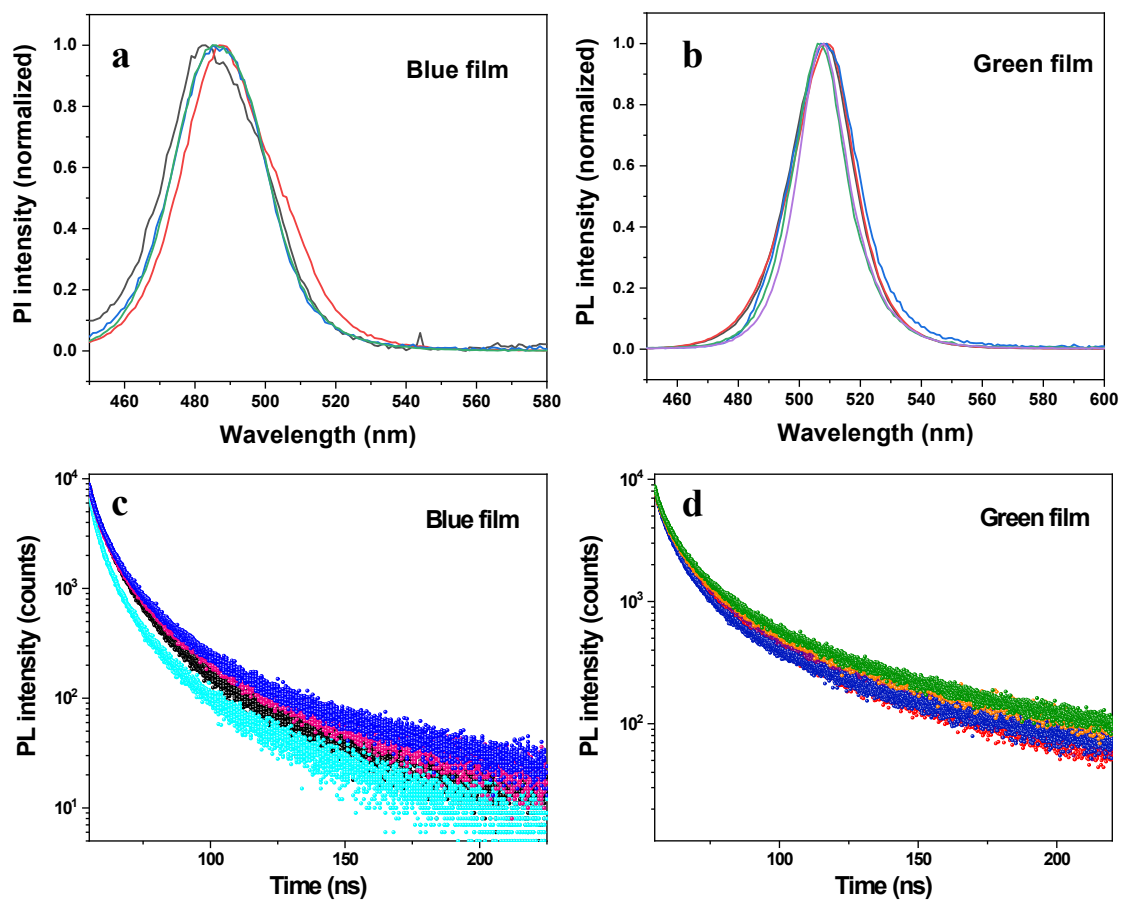
Figure S4. (a,b) Photoluminescence spectra and (c,d) decay curves of few blue and green films respectively on glass substrates. PL maxima of blue films range from 482-487 nm, whereas for green film 505-509 nm. Lifetimes range from 9-12 ns and 17-24 ns for blue and green films respectively.
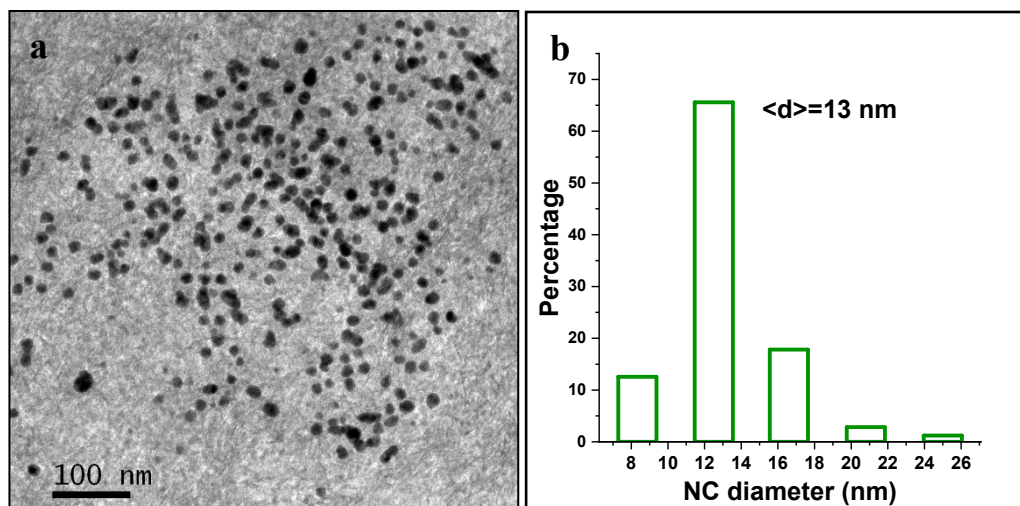
Figure S5. (a) TEM image showing the formation of larger $CsPbBr_3$ NCs (mean particle size is 13 nm, as evident from (b) particle size distribution) inside γ-Al_2O_3 film while concentrations of precursors $PbBr_2$ and CsBr solutions were kept at 0.5 M and 0.1 M respectively.
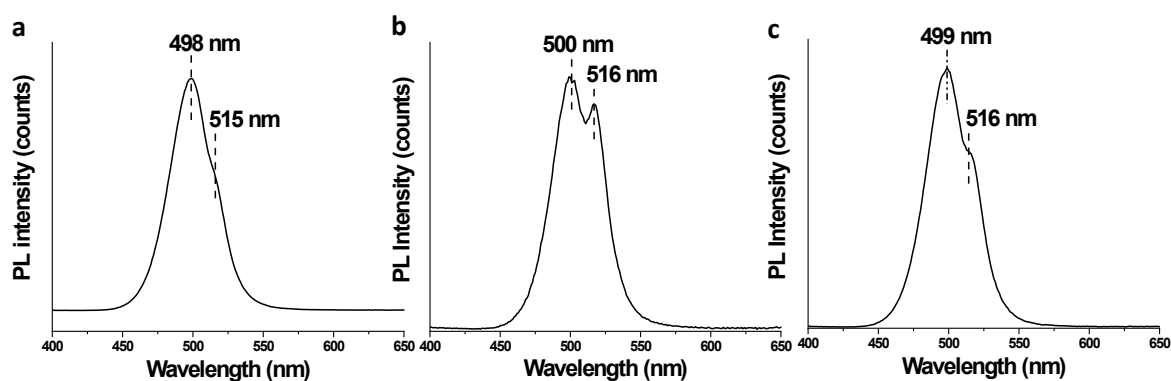

Figure S6. Photoluminescence spectra of few films (a-c) where higher concentrations of precursor solutions were used ($PbBr_2 > 0.1$ M, CsBr ≥ 0.1 M) for dipping. TEM image of one such combination has been shown in Figure S5.
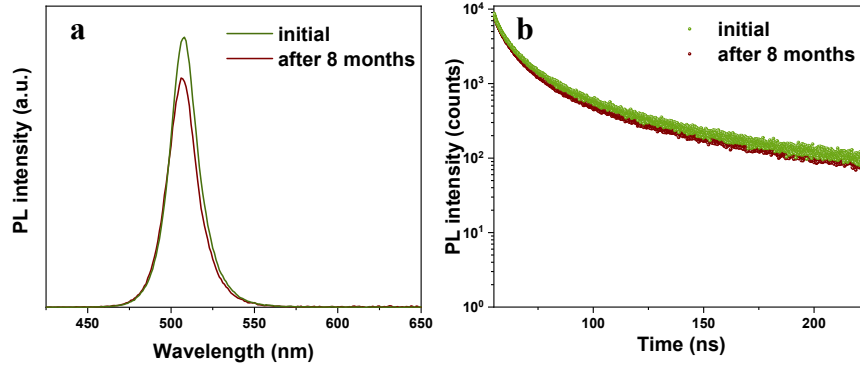
Figure S7. (a) PL spectra and (b) decay curves of $CsPbBr_3$ NCs-Al_2O_3 composite films: as prepared and after 8 months.

Table S1. Fitting parameters for the tri-exponential PL decay graphs in Figure 2b (T_1, T_2, T_3: component lifetimes; A_1, A_2, A_3: relative amplitudes; $<T_L>$: average luminescent lifetime), measured photoluminescence quantum yield (PL QY) and calculated radiative and non-radiative lifetimes (T_r and T_{nr}, respectively).

PL decay graphs were fitted using the tri-exponential function of the following form

$$A(t) = A_1 e^{-t/T1} + A_2 e^{-t/T2} + A_3 e^{-t/T3}$$

Average lifetime $<T_L>$ is calculated as

$$<TL> \ = \frac{A1T1^2 + \ A2T2^2 + \ A3T3^2}{A1T1 + \ A2T2 + \ A3T3}$$

Radiative and non-radiative lifetimes were calculated according to the following equation

Film type	T_1 (ns)	T_2 (ns)	T_3 (ns)	A_1 (%)	A_2 (%)	A_3 (%)	X^2	$<T_L>$ (ns)	PL QY (%)	T_r (ns)	T_{nr} (ns)
Blue film	4.49	15.43	1.033	50	22	28	1.13	10.59	41.32	25.63	18.05
Green film	6.35	25.34	1.34	48	23	29	1.20	18.08	42.00	43.06	31.18

$$PL \ QY = \ \frac{<TL>}{Tr} \ = \frac{Tnr}{Tr \ + \ Tnr}$$

References

1   B.E. Yoldas, *Am. Ceram. Bull.*, 1975, **54**, 289–290.

2   M. Grabolle, M. Spieles, V. Lesnyak, N. Gaponik, A. Eychmüller, U. Resch-Genger, *Anal. Chem.* 2009, **81**, 6285–6294.