Electronic Supplementary Information

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Implications of Gas-Barrier Properties in Realizing the Self-Recovery of Photodegraded $CsPbBr_3$ Perovskite Nanocrystals

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Experimental section

Materials

Cs_2CO_3 (99.99%, Mitsuwa Pure Chemical), $PbBr_2$ (99%, Mitsuwa Pure Chemical), granular EVA polymer (Evaflex EV150, Du Pont-Mitsui Polychemicals), and 15-μm-thick EVOH film (EVAL EF-XL, Kuraray) were used as received without further purification. 1-Octadecene (>90.0%, Tokyo Chemical Industry), oleic acid (>85.0%, Tokyo Chemical Industry), oleylamine (80%–90%, Acros Organics), tert-butanol (>99.0%, Tokyo Chemical Industry), and toluene (>99.5%, Kanto Chemical) were dehydrated over molecular sieves (3A 1/8, FUJIFILM Wako Pure Chemical) prior to use.

Preparation of Cs-oleate precursor

Cs_2CO_3 (2.50 mmol) was added into a mixture of 1-octadecene (40.0 mL) and oleic acid (2.5 mL). The mixture was dried for 1 h at 120 °C and then heated under Ar gas to 150 °C until the Cs_2CO_3 completely dissolved. The Cs-oleate precursor was preheated to 100 °C before injection.

Synthesis of $CsPbBr_3$ NCs

A mixture of 1-octadecene (5.0 mL) and $PbBr_2$ (0.376 mmol) was vacuum dried for 1 h at 120 °C and then purged with Ar gas. Oleylamine (1.0 mL) and oleic acid (1.0 mL) were added to the mixture, followed by heating to 180 °C. Once the $PbBr_2$ was completely dissolved, the preheated Cs-oleate precursor was rapidly injected, and 10 s later, the resulting crude $CsPbBr_3$ NC solution was cooled in an ice-water bath and were aggregated by adding tert-butanol (25.0 mL). Then, the NCs were collected by centrifugation at ~19,000 ×*g* (13,000 rpm using a rotor with a diameter of 10 cm) for 5 min. After vacuum drying for 1 d, a paste-like NC material was obtained.

Preparation of EVA film

Granular EVA (200 mg) was completely dissolved in toluene (20 mL) under vigorous stirring. Then, 4 mL of the obtained solution was dropped onto a Petri dish with a diameter of 5.8 cm and dried for half a day in an electric desiccator to fabricate an EVA film. The resulting film with a thickness of ~14 μm was cut into a square (25 mm × 25 mm).

Preparation of $CsPbBr_3$ NCs films

Silicone rubber film (25 mm × 25 mm × 0.5 mm) with a square hole (5 mm × 5 mm) was placed on a soda-lime glass plate (25 mm × 25 mm × 1 mm) to prepare a film mold (see Fig. S1), which was filled with the paste-like $CsPbBr_3$ NCs and sealed with a soda-lime glass plate, EVA film, or EVOH film to shut out ambient air. As a reference, an NC film exposed to ambient air was also prepared.

Blue LED irradiation of NC films

The NC films were irradiated using a flat panel blue LED (TE-4556, Nissin Electronics) equipped with a power supply (LPR-10W, Nissin Electronics) for 72 h. The luminescence wavelength and irradiance were 468 nm and 48.5 W m^{-2}, respectively. The irradiated sample was stored in the dark. A series of these experiments was performed with thermo-hygrostat (IG401, Yamato Scientific) which was set at 25 °C and 60% relative humidity. Herein, sample temperature was evaluated by a thermography camera (TG167, FLIR). Only a slight increase in temperature was observed after LED irradiation for 24 h, as shown in Fig. S2; therefore, heating by LED irradiation in this research is negligible.

Characterization

XRD profiles were obtained with an X-ray diffractometer (Rint-2200, Rigaku) equipped with a Cu Kα radiation source and a monochromator. UV–Vis absorption spectra of dispersion and film samples were measured using UV/visible/near-infrared optical absorption spectrometers (V-750 and V-570, JASCO). The Tauc plot was prepared according to Eq. S1 to determine the E_g of the NCs [S1].

$$(\alpha h\nu)^{\frac{1}{n}} = A\left(h\nu - E_{\mathrm{g}}\right) \tag{S1}$$

where α is absorbance, h is the Planck constant, v is frequency, and A is a constant. The value of n was 0.5 because $CsPbBr_3$ is a direct transition-type semiconductor [S2].

PL spectra were measured using a fluorescence spectrometer (FP-8500, JASCO). The obtained spectra were calibrated using a calibrated detector (SID-844, JASCO). PL decay curves were recorded with a fluorescence lifetime spectrometer (Quantaurus-Tau C11367, Hamamatsu Photonics) equipped with 405-nm LEDs as the light source. The PL decay curves were fitted with the following triexponential equation:

$$f(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) + A_3 \exp\left(-\frac{t}{\tau_3}\right) \tag{S2}$$

where A_1, A_2, and A_3 are the amplitudes, and τ_1, τ_2, and τ_3 are the PL lifetimes. The average PL lifetime <τ> was calculated using Eq. S3.

$$\langle\tau\rangle = \frac{A_1{\tau_1}^2 + A_2{\tau_2}^2 + A_3{\tau_3}^2}{A_1\tau_1 + A_2\tau_2 + A_3\tau_3} \tag{S3}$$

The particle morphologies were observed using a field-emission transmission electron microscope (Tecnai G^2, FEI). TEM samples were prepared by vacuum drying a drop of NC dispersion on carbon-reinforced collodion-coated copper grids (COL-C10, Oken Shoji) overnight. XPS spectra were measured on an XPS instrument (JPS-9010TR, JEOL) equipped with an Al Kα radiation source. The peak of C 1s at 285.0 eV was used for the charge-up correction.

References

S1) J. Tauc and A. Menth, *J. Non-Cryst. Solids*, 1972, **8−10**, 569–585.

S2) L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X. Yang, A. Walsh and M. V. Kovalenko, *Nano Lett.*, 2015, **15**, 3692–3696.

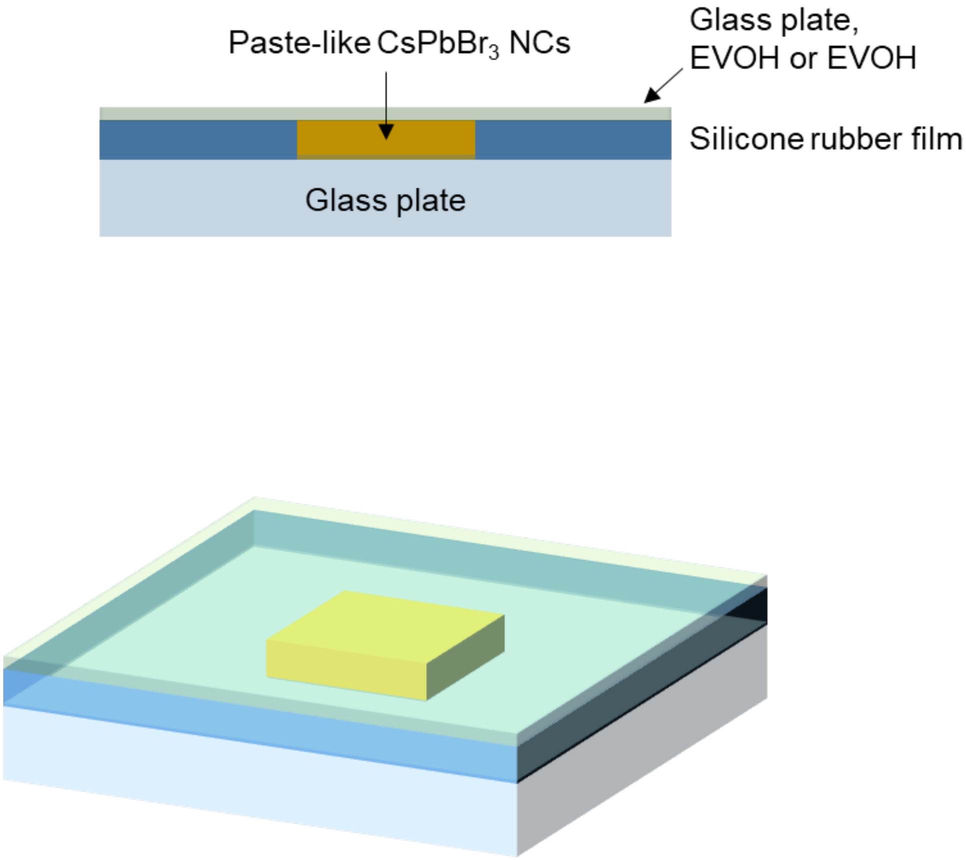

Fig. S1 Schematic structure of a CsPbBr$_3$ film.

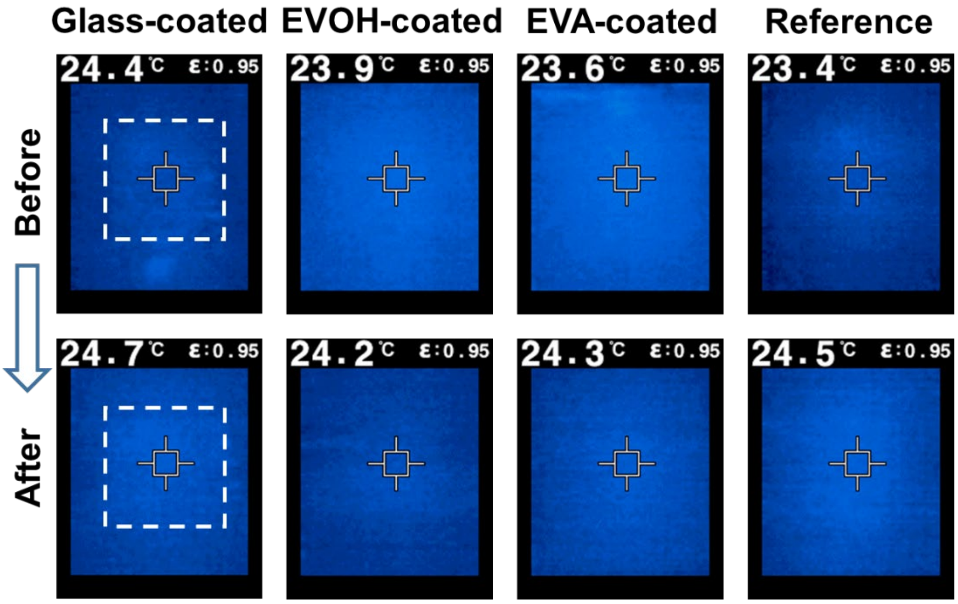

Fig. S2 Thermography images of the prepared $CsPbBr_3$ NCs films before and after LED irradiation for 24 h. $CsPbBr_3$ NCs are centered in the dotted area of a glass plate (25 mm × 25 mm).

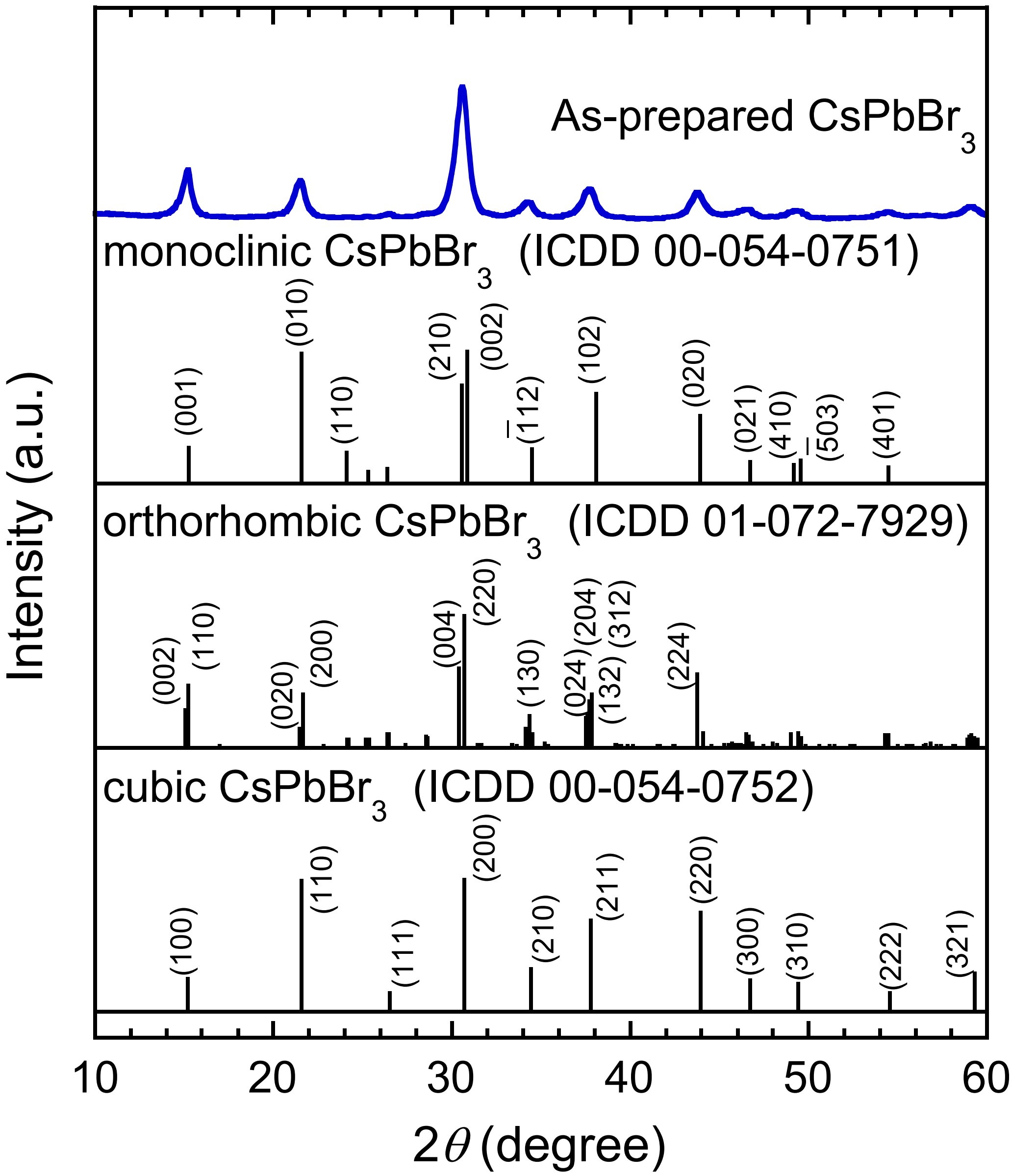

Fig. S3 XRD profile of as-prepared CsPbBr$_3$ NCs. ICDD card data of representative phases of CsPbBr$_3$ are also shown.

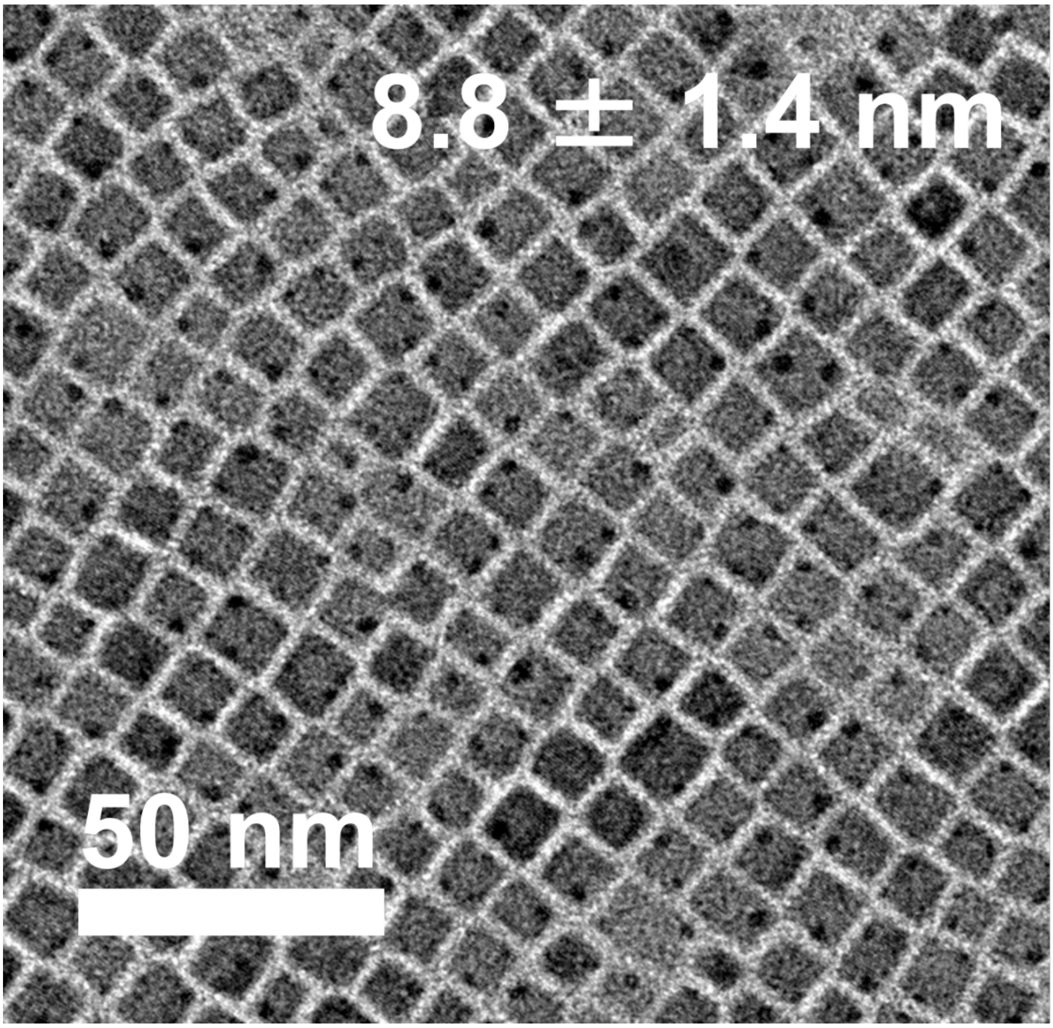

Fig. S4 TEM image of as-prepared $CsPbBr_3$ NCs.

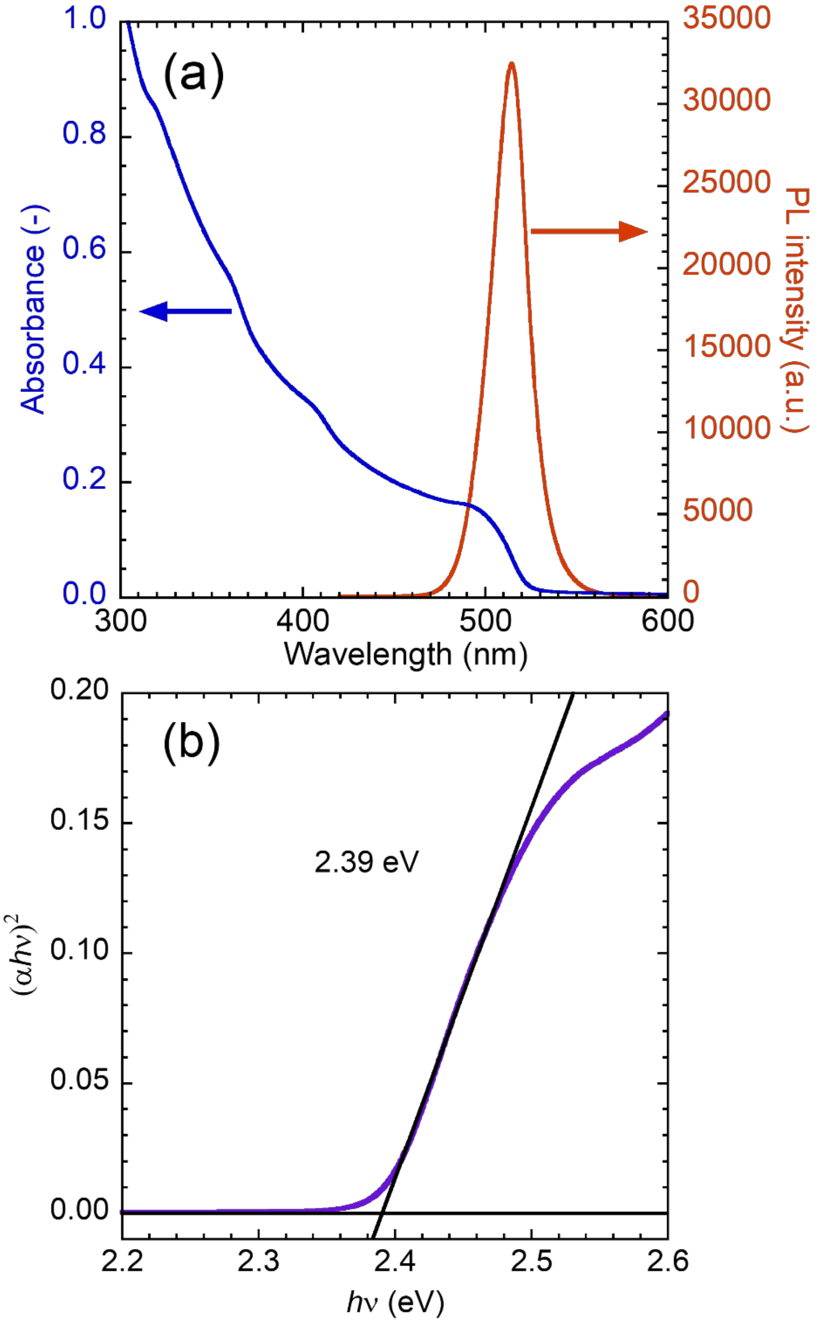

Fig. S5 (a) UV–vis absorption and PL spectra of $CsPbBr_3$ NCs in toluene. $\lambda_{ex} = 400$ nm. (b) Tauc plot derived from the UV–vis spectrum.

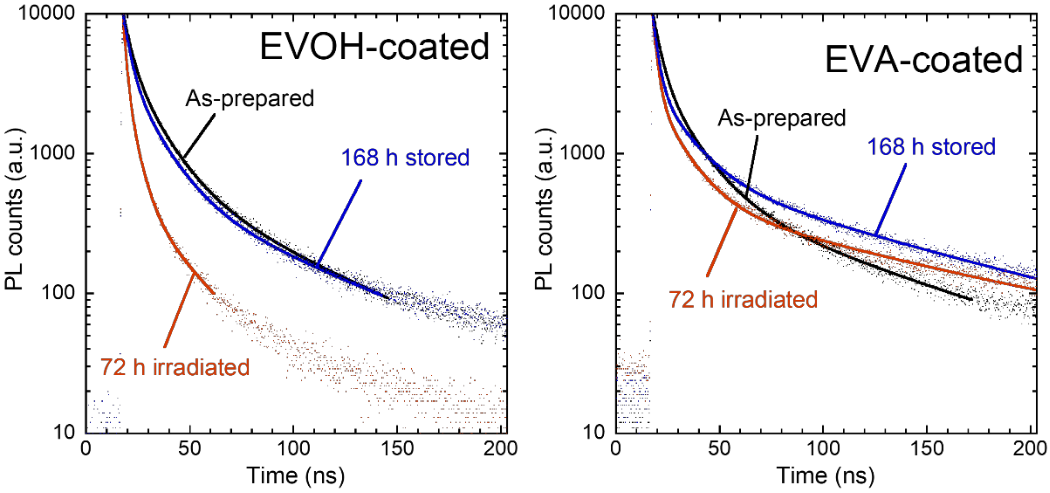

Fig. S6 PL decay curves for the EVOH- and EVA-coated $CsPbBr_3$ NCs films before and after 72 h irradiation and after 168 h dark storage. λ_{ex} = 405 nm.

Table S1 Summary of PL lifetimes estimated from Fig. S6.

		Average	PL lifetime (ns)			Amplitude (%)			χ^2
		$<\tau>$	τ_1	τ_2	τ_3	A_1	A_2	A_3	
EVOH-coated	As-prepared	27.8	3.7	13.0	57.2	53.5	39.3	7.3	1.05
	72 h irradiated	11.1	1.5	5.1	26.7	68.4	27.3	4.3	1.24
	168 h stored	29.9	3.1	12.9	63.6	60.8	33.4	5.8	1.23
EVA-coated	As-prepared	35.3	3.7	14.6	76.7	63.4	31.3	5.3	1.11
	72 h irradiated	57.0	2.1	12.7	103.3	74.0	21.7	4.3	1.35
	168 h stored	58.3	2.5	14.6	96.4	70.2	23.1	6.7	1.26

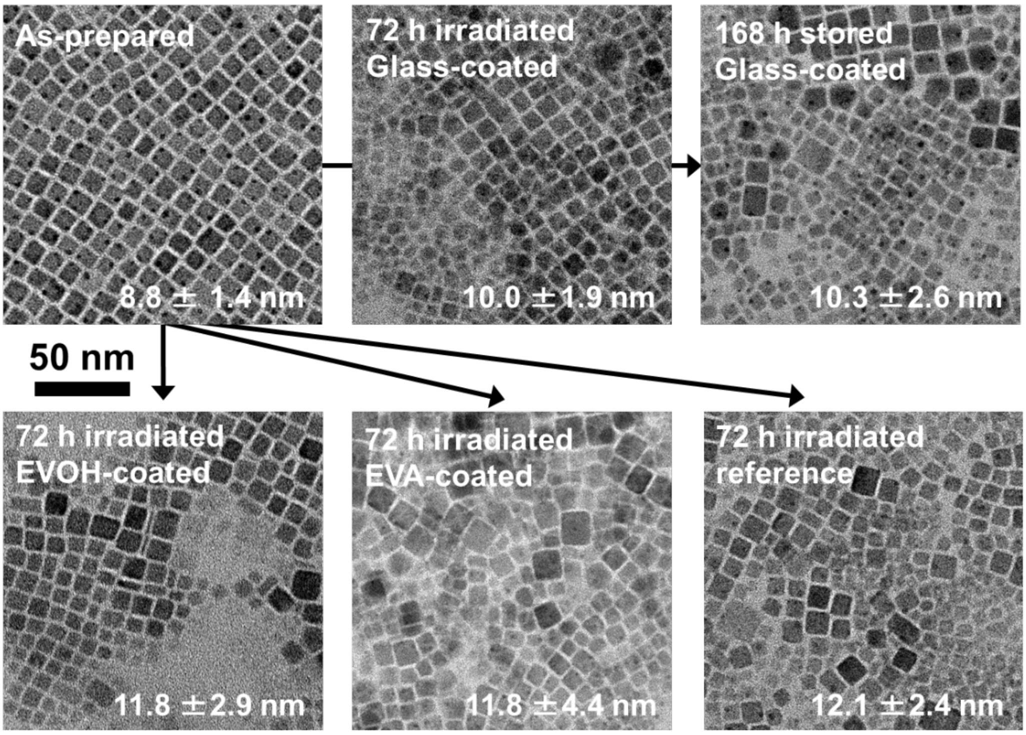

Fig. S7 TEM images of the prepared $CsPbBr_3$ NCs films before and after 72 h irradiation. The glass-coated NCs film upon subsequent 168 h dark storage is also shown.

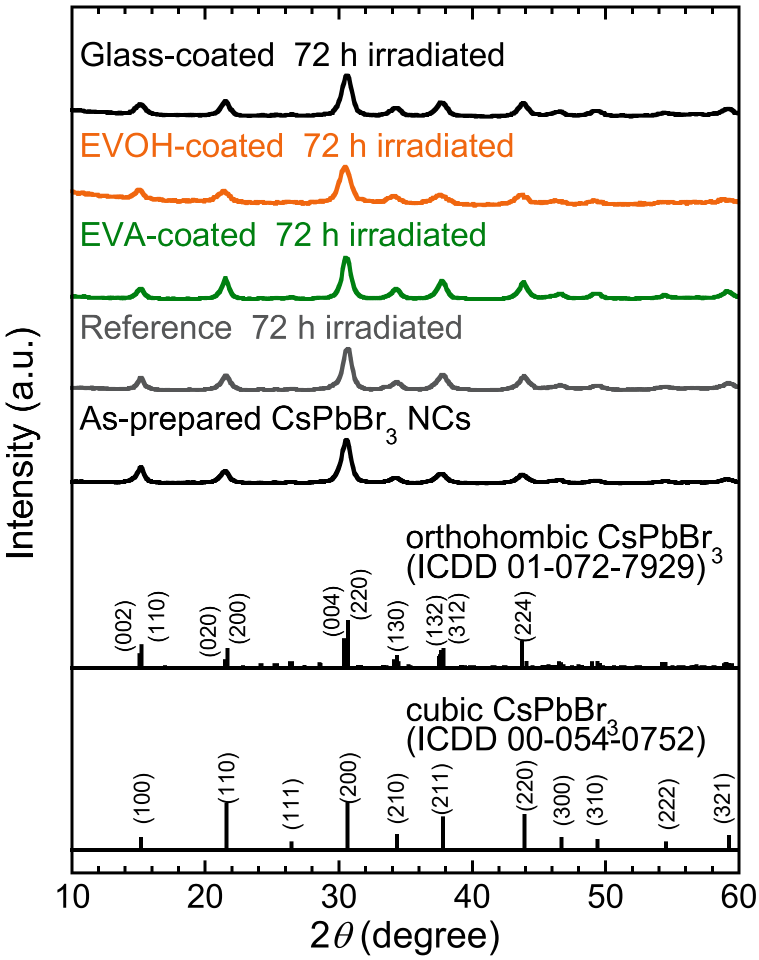

Fig. S8 XRD profiles of the prepared $CsPbBr_3$ NCs films before and after 72 h irradiation. ICDD card data of representative phases of $CsPbBr_3$ are also shown.

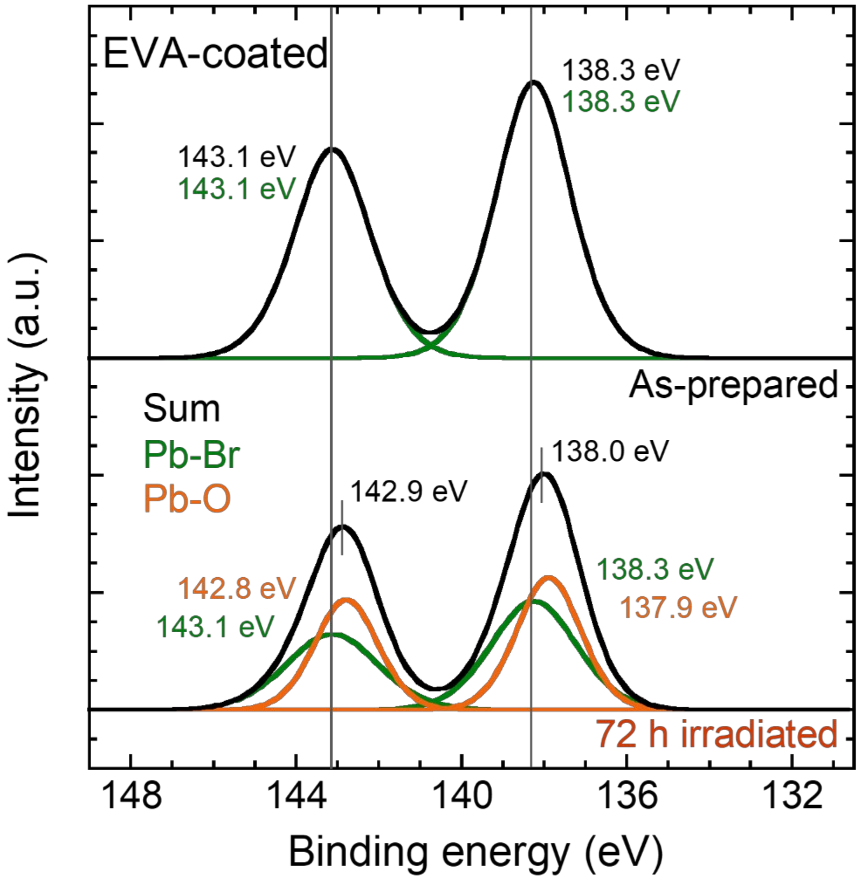

Fig. S9 Deconvolution of the Pb 4f XPS peaks for an EVA-coated NC film irradiated for 72 h. Peak fitting for the as-prepared $CsPbBr_3$ NCs is also shown.