

Supporting Information

Electrochemical Synthesis of Annealing-free and Highly Stable Black-Phase CsPbI₃ Perovskite

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Experimental and Methods

Materials: Ti foil (thickness 0.127 mm, 99.7%), ammonium fluoride (NH_4F , $\geq 98.0\%$), cesium iodide (CsI , 99.9%), lead iodide (PbI_2 , $\geq 98.0\%$), ethylene glycol (EG, $\geq 99.5\%$), and methanol (99.8%) were all purchased from Sigma Aldrich without further purification.

Methods: Pb^{2+} ions were incorporated in TiO_2 by electrochemical reaction. First, an EG electrolyte consisting of 0.5 wt% NH_4F , 0.01 M PbI_2 and 3 vol% deionized (DI) water was prepared¹. A Ti sheet with a size of $1 \times 5 \text{ cm}^2$ was ultrasonically cleaned with acetone, ethanol, and DI water in sequence for 10 min each and dried in an argon stream. The well-cleaned Ti sheet was served as an anode and a Pt foil was used as a cathode. The distance between the anode and cathode is 2 cm. The Ti sheet was anodized at 30 V for 12, 24, and 36 h at room temperature (about 25 °C). It was then immersed in 4, 8, and 16 mg/ml CsI /methanol solution at room temperature or heating conditions (25–50 °C).

Characterizations: The surface morphology of the CsPbI_3 nanocomposite was observed by scanning electron microscopy (SEM, FEI Nova Nano 450). The elemental analysis was conducted using energy-dispersive X-ray (EDX) spectroscopy and X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi). The steady-state photoluminescence (PL) was excited by a CW laser with a central wavelength of 473 nm, which is separated by the 150 gr/mm grating in the Monochromator SP2500 of the Princeton Instruments. Then, the spectral information was collected by the PIXIS-100BX CCD at $-75 \text{ }^\circ\text{C}$. The time-resolved PL (TRPL) kinetics was detected by HORIBA DeltaFlex ultrafast time-resolved fluorescence spectrometer, where the excitation wavelength is 405 nm and the detection time scale is 10 ns. The variation of the PL intensity was tracked under highly humid conditions (RH = 70%).

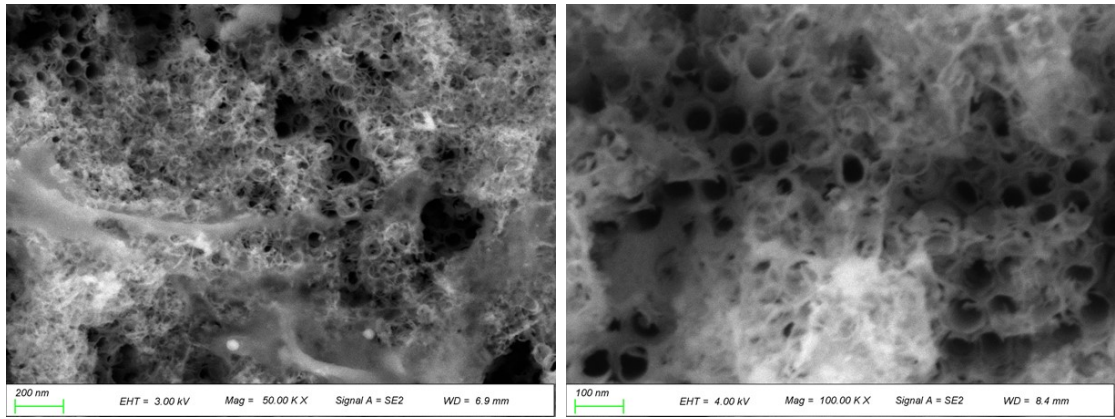


Fig. S1 SEM images of the nanostructure obtained by electrochemical anodization.

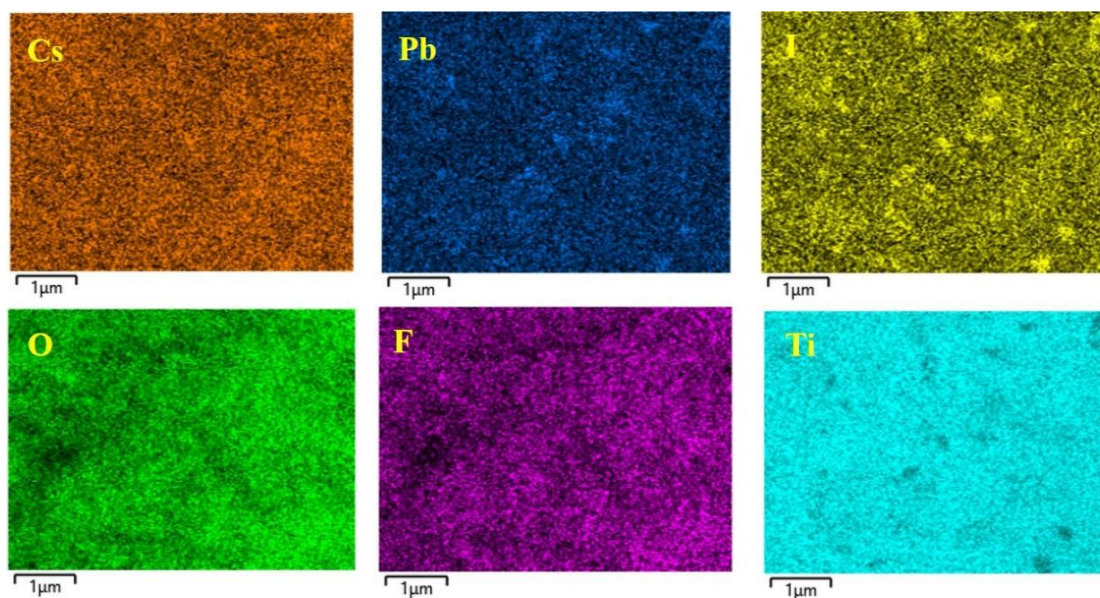


Fig. S2 SEM element mapping of Cs, Pb, I, O, F and Ti on the surface of the nanocomposites.

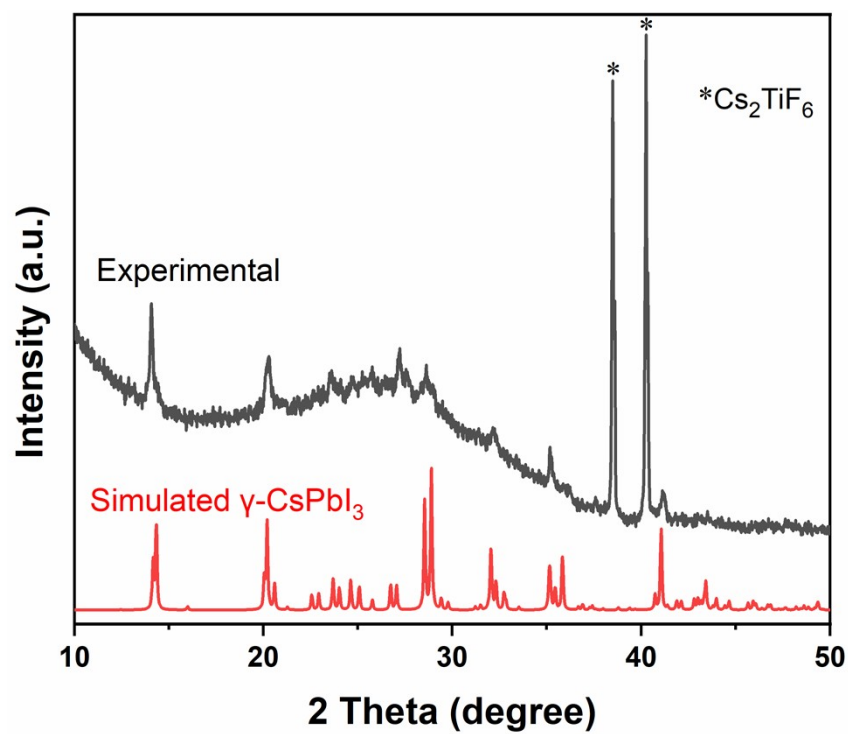


Fig. S3 PXRd pattern of the nanocomposites.

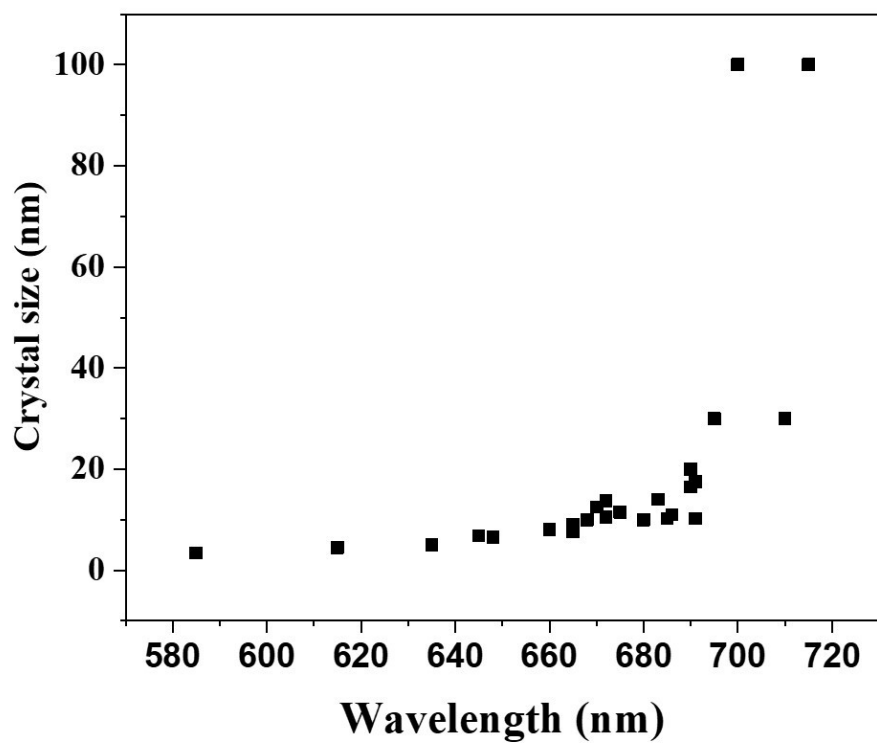


Fig. S4 Variation of the emission wavelength with the crystal size²⁻²⁴.

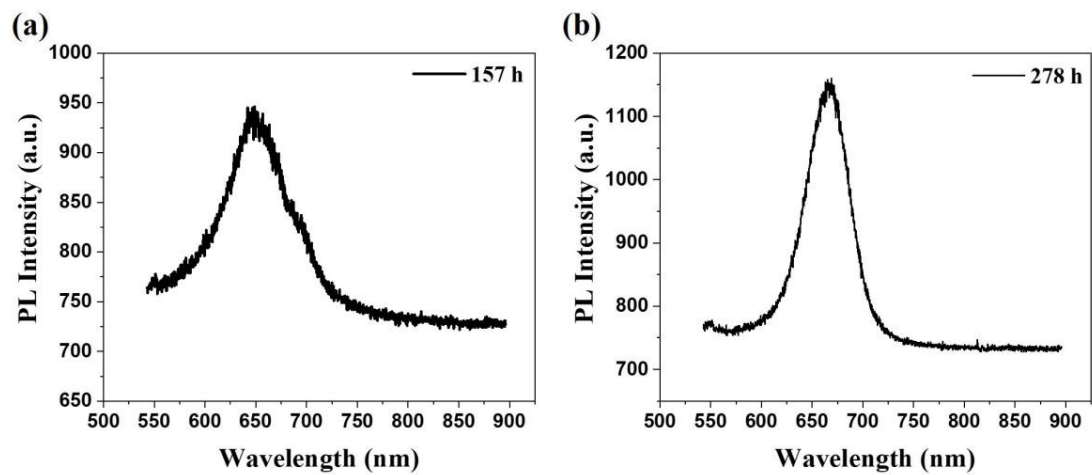


Fig. S5 Room-temperature PL spectra in highly humid air (RH = 70%) of (a) 12 h-8 mg/ml sample at 157 h, and (b) 24 h-16 mg/ml at 278 h.

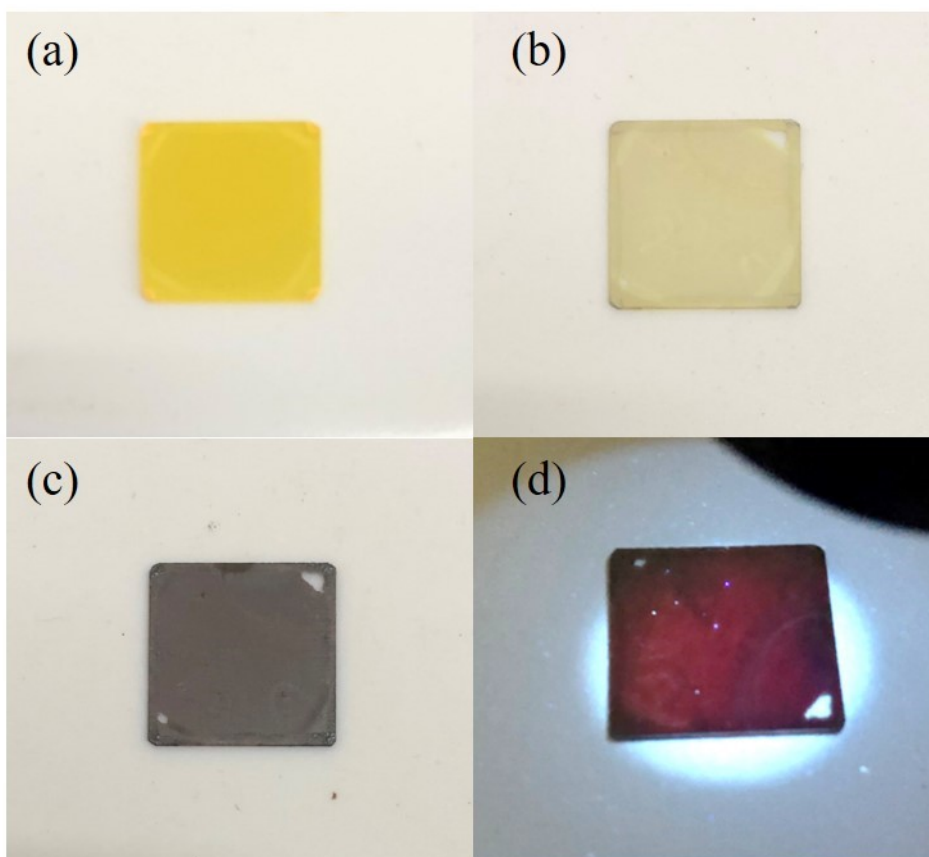


Fig. S6 Photographs of (a) spin-coated PbI_2 thin film on FTO glass substrate, (b) yellow-phase CsPbI_3 thin film after soaking the film in (a) in 8 mg/ml CsI /methanol solution, (c) black-phase CsPbI_3 obtained by heating the film in (b) above the phase transition temperature of 320°C , (d) the red emission of black phase CsPbI_3 under UV light.



Fig. S7 Photographs of a CsPbI₃ nanocomposite film on Ti sheet under normal light (left) and UV light (right) obtained by anodizing for 12 h in NH₄F/EG, soaking in NH₄F/PbI₂/EG for 12 h, and then soaking in 8 mg/ml CsI/methanol solution at 50°C for 20 min.

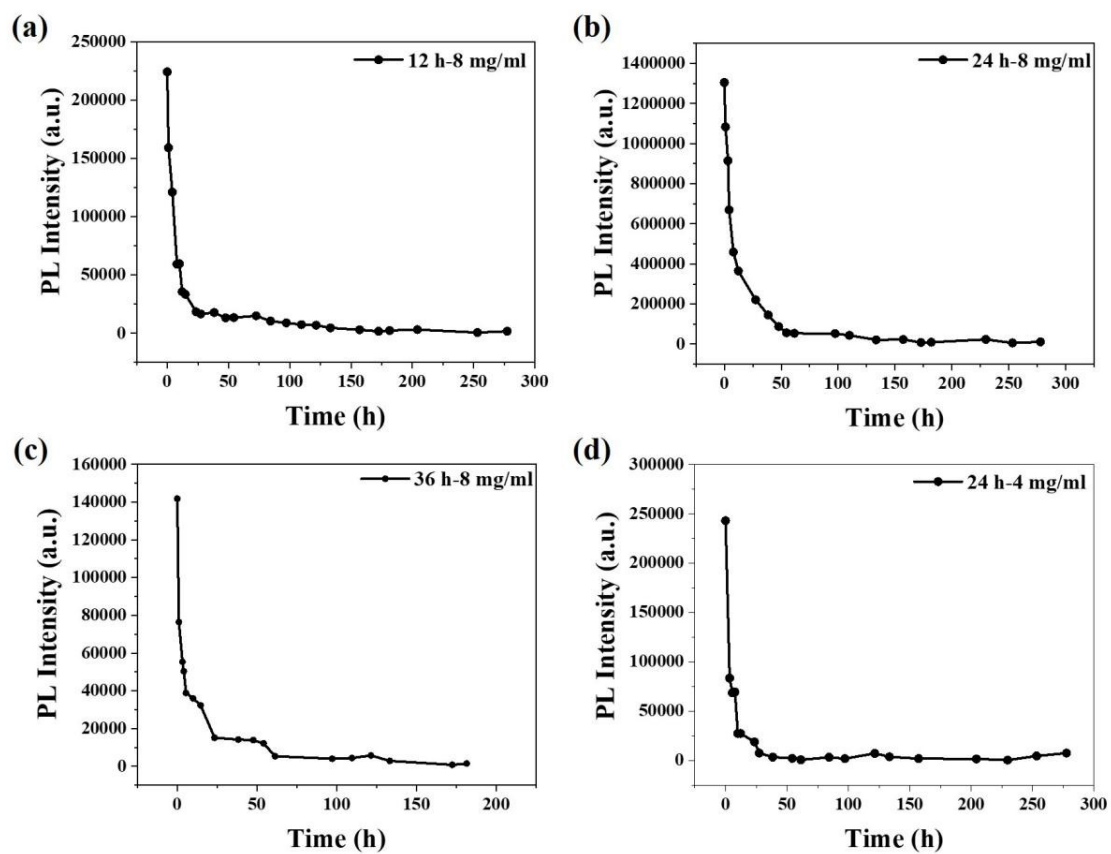


Fig. S8 Variation of the PL intensity with time under highly humid condition (RH = 70%). (a) 12 h-8 mg/ml, (b) 24 h-8 mg/ml, (c) 36 h-8 mg/ml, and (d) 24 h-4 mg/ml.

Table S1 Fitting results of time-resolved PL decay of the 24 h-16mg/ml sample.

Samples	A_1	τ_1 (ps)	A_2	τ_2 (ps)
24 h-16 mg/ml	0.34472	112.2	0.02124	880.9

Table S2 Comparison of the stability of CsPbI₃ black phase under different humid environments.

Structures, crystal size	Temperature (°C)	Treatment	Humidity	Stability	Ref.
CsPbI ₃ thin films	330		35%	several min	16
AAO template, 40 nm	100	PMMA coating	-	3 months	8
Additive, 15 nm	160	SiO ₂ coating	boiling water	above 2 days	15
Additive, 30 nm	90		30-40%	2 months	25
Additive, 100 nm	80		35%	24 h	16
Additive, 35 nm	150		dry box	1 month	26
Additive, 18 nm	140		-	> 2 h in water	4
Additive, 70 nm	100		20%	15 days	27
Additive, 100 nm	100		10%	1 month	28
Solvent-controlled synthesis, 5 nm	350		dry N ₂ box	2 months	29
Solvent-controlled synthesis, 13 nm	130	capping DDAB	-	> 2 months	6
In situ electrochemistry	room temperature		70%	> 11 days	Our work

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