Supporting Information

**Electrochemical Synthesis of Annealing-free and Highly Stable Black-Phase CsPbI\textsubscript{3} Perovskite**

Chuyun Ding,\textsuperscript{a} Xi Chen,\textsuperscript{a} Tianju Zhang,\textsuperscript{b,c} Chaocheng Zhou,\textsuperscript{a,d} Xiaolin Liu,\textsuperscript{a,*} Jun Wang,\textsuperscript{b,c,e} Jia Lin,\textsuperscript{a,*} and Xianfeng Chen\textsuperscript{d,f}

\textsuperscript{a} Department of Physics, Shanghai Key Laboratory of Materials Protection and Advanced Materials in Electric Power, Shanghai University of Electric Power, Shanghai 200090, China.

\textsuperscript{b} Laboratory of Micro-Nano Optoelectronic Materials and Devices, Key Laboratory of Materials for High-Power Laser, Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800, China.

\textsuperscript{c} Center of Materials Science and Optoelectronic Engineering, University of Chinese Academy of Sciences, Beijing 100049, China.

\textsuperscript{d} State Key Laboratory of Advanced Optical Communication Systems and Networks, School of Physics and Astronomy, Shanghai Jiao Tong University, Shanghai 200240, China

\textsuperscript{e} CAS Center for Excellence in Ultra-intense Laser Science, Shanghai 201800, China

\textsuperscript{f} Collaborative Innovation Center of Light Manipulation and Applications, Shandong Normal University, Jinan 250358, China

\*E-mail: jlin@shiep.edu.cn; jwang@siom.ac.cn; xlliu@shiep.edu.cn

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Experimental and Methods

Materials: Ti foil (thickness 0.127 mm, 99.7%), ammonium fluoride (NH\(_4\)F, ≥98.0%), cesium iodide (CsI, 99.9%), lead iodide (PbI\(_2\), ≥98.0%), ethylene glycol (EG, ≥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\(_4\)F, 0.01 M PbI\(_2\) and 3 vol% deionized (DI) water was prepared\(^1\). A Ti sheet with a size of 1 × 5 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 ℃). It was then immersed in 4, 8, and 16 mg/ml CsI/methanol solution at room temperature or heating conditions (25–50 ℃).

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 ℃. 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 size\textsuperscript{2-24}.
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℃, (d) the red emission of black phase CsPbI$_3$ under UV light.
**Fig. S7** Photographs of a CsPbI$_3$ nanocomposite film on Ti sheet under normal light (left) and UV light (right) obtained by anodizing for 12 h in NH$_4$F/EG, soaking in NH$_4$F/PbI$_2$/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.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$A_1$</th>
<th>$\tau_1$ (ps)</th>
<th>$A_2$</th>
<th>$\tau_2$ (ps)</th>
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<tr>
<td>24 h-16 mg/ml</td>
<td>0.34472</td>
<td>112.2</td>
<td>0.02124</td>
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<tr>
<td>Structures, crystal size</td>
<td>Temperature (℃)</td>
<td>Treatment</td>
<td>Humidity</td>
<td>Stability</td>
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<td>---------------------------------------</td>
<td>-----------------</td>
<td>-----------------</td>
<td>----------</td>
<td>-----------</td>
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<tr>
<td>CsPbI$_3$ thin films</td>
<td>330</td>
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<td>35%</td>
<td>several min</td>
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<tr>
<td>AAO template, 40 nm</td>
<td>100</td>
<td>PMMA coating</td>
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<td>3 months</td>
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<tr>
<td>Additive, 15 nm</td>
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<td>SiO$_2$ coating</td>
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<td>90</td>
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<td>30-40%</td>
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<tr>
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<td>35%</td>
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<td>1 month</td>
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<td>Additive, 18 nm</td>
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<td></td>
<td></td>
<td>&gt; 2 h in water</td>
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<td></td>
<td>20%</td>
<td>15 days</td>
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<tr>
<td>Additive, 100 nm</td>
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<td>Solvent-controlled</td>
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<td>In situ electrochemistry</td>
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<td>70%</td>
<td>&gt; 11 days</td>
</tr>
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</table>

Table S2 Comparison of the stability of CsPbI$_3$ black phase under different humid environments.
References

27. Y. Hu, Q. Xu and W. Ruan, Solar RRL, 2019, 3, 1900287.