Supporting Information

Decreasing Energy Loss and Optimizing Band Alignment for High Performance $CsPbI_3$ Solar Cells through Guanidine Hydrobromide Post-Treatment

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Experimental

Materials preparation: We used 2.2 mm FTO-coated glass as the substrate. The CsI and $TiCl_4$ were gained from Alfa Aesar. The DMF and DMSO were obtained from Sigma-Aldrich. The $DMAPbI_3$ and PTAA were acquired from Xi'an Polymer Light Company, the GABr was purchased from Tokyo Chemical Industry Company. We did no further purification to all the experimental materials before we used.

Precursor solution preparation: We produced the $CsPbI_3$ precursor solution using $DMAPbI_3$ and CsI with a molar ratio 1:1 and concentration of 1.2 M, dissolved in DMF/DMSO (v/v 9:1) and stirred for more than 2 hours until the solute completely dissolved. GABr solutions were prepared by dissolving GABr into isopropanol with different concentration. HTL solution was prepared by dissolving PTAA (36 mg), a sulfonyl imide (Li-TFSI, 22 μL, 520 mg Li-TFSI in 1 mL acetonitrile), and tert-butylpyridine (TBP, 36 μL) in 1 mL of chlorobenzene solution.

Device fabrication preparation: The TiO_2-blocking layer was prepared with a classical chemical bath deposition method as reported.[1] Then, $CsPbI_3$ film was fabricated using one-step spin-coating the solution at 1000 rpm for 10 s, and accelerated to 3500 rpm holding for 40 s after the substrate was disposed by O_2-plasma. After the substrates annealed at 210 °C for 10 min to form the $CsPbI_3$ films, and cooled down to the room temperature, the GABr solution (150 μL) was applied to the surface and the spin coater was accelerated to 5000 rpm for 30 s immediately to wipe off the superfluous solution. After that, the films were annealed at 120 °C for 2 min to embellish the $CsPbI_3$ film. The HTL layer was spin-coated the PTAA solution onto the $CsPbI_3$ film at 5000 rpm for 30 s and annealed at 75 °C for 6 min. Finally, a gold electrode was thermally evaporated to accomplish the whole device.

Characterization Section: Absorbance spectra were collected using a Shimadzu UV-3600. The PL spectra were measured using a PicoQuant FluoTime 300. XRD patterns of the samples were obtained using a Bruker D8 GADDS Diffractometer with the Cu Kα line. FTIR spectra were measured with a Bruker Vertex 70. The XPS measurements were performed in a VG ESCALAB MK2 system with monochromatized Al Kα radiation under a pressure of 5.0×10^{-7} Pa. The UPS measurements were analyzed using a Thermo Scientific ESCA Lab 250Xi system with helium gas admitted employing the HeI (21.22 eV) emission line. The cross-section of device and film morphology were characterized by a FE-SEM (SU-8020, Hitachi). The AFM images were acquired using a Veeco NanoScope IV with a silicon cantilever. TAS was measured with TA100 (Time-Tech Spectra). The device active area was varied with a mask used to prevent any scattered light or light piping to contribute to the photocurrent. The J-V measurement was performed via the solar simulator (SS-F5-3A, Enlitech) along with AM 1.5G spectra calibrated by the certified standard silicon solar cell (SRC-2020, Enlitech) at $100mW/cm^2$. This used reverse scan mode (from V_{OC} to I_{SC}) and forward scan mode (from I_{SC} to V_{OC}) with a scan rate of 30 mV/s. The EQE data were obtained by using the solar-cell spectral-response measurement system (QE-R3011, Enlitech).

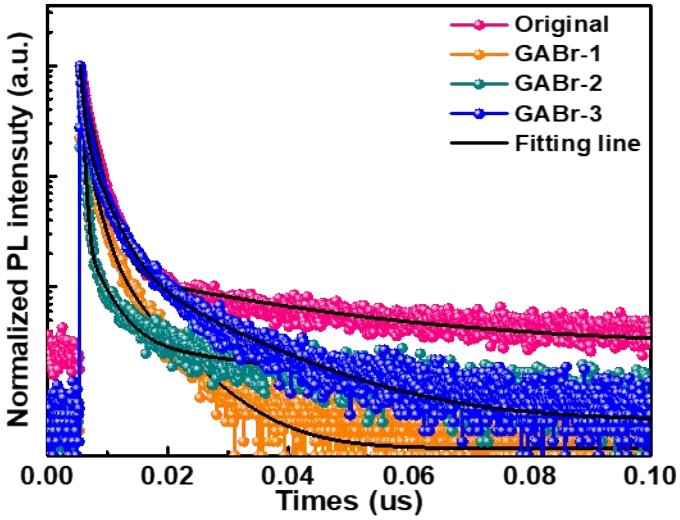

Figure S1. TRPL curves of the FTO/TiO_2/perovskite films with different concentration gradient GABr treated.

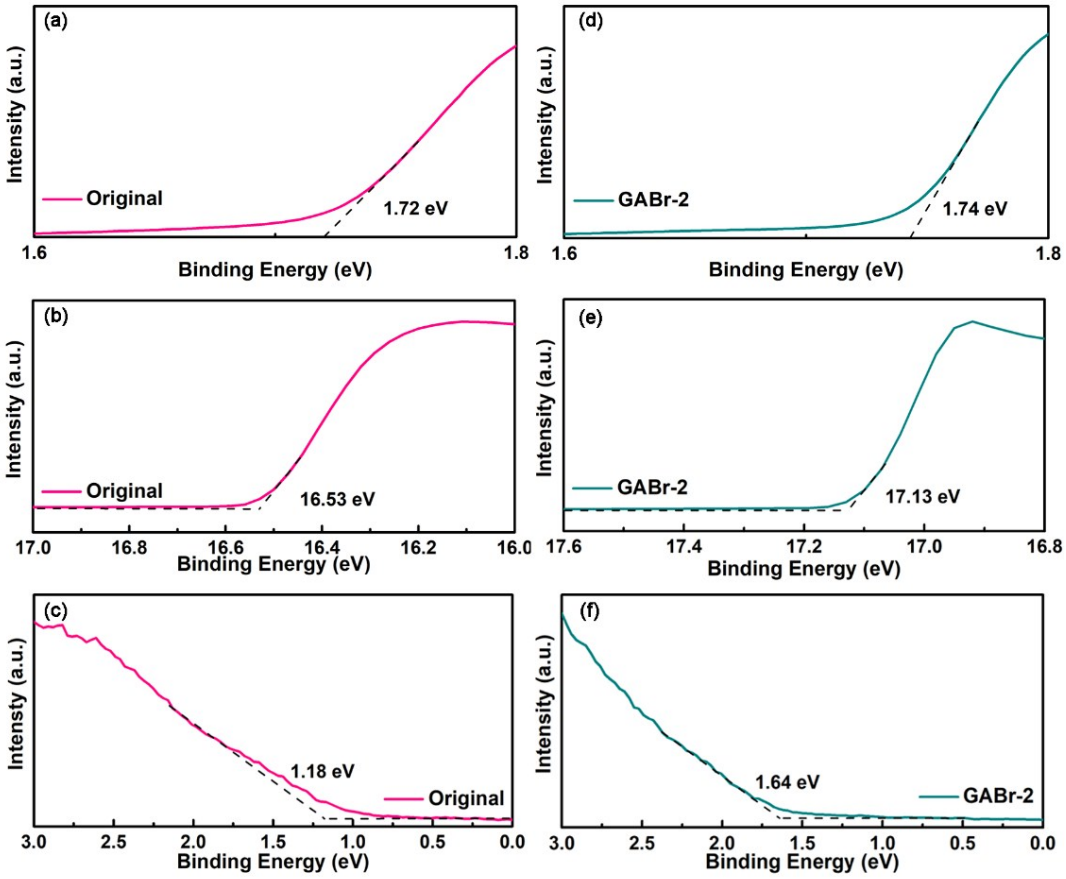

Figure S2. Optical and UPS spectra for the original and the optimized films: (a, d) Magnification of the band edge; (b, e) Secondary-electron cutoffs for work function determination; (c, f) Narrow binding energy range valence spectra.

Table S1. Key band parameters of the original and the optimized films extracted from **Figure S2**.

Sample	E_V-E_F (eV)	E_F (eV)	E_V (eV)	E_C (eV)
Original	1.18	4.69	5.87	4.15
Optimized	1.64	4.09	5.73	3.99

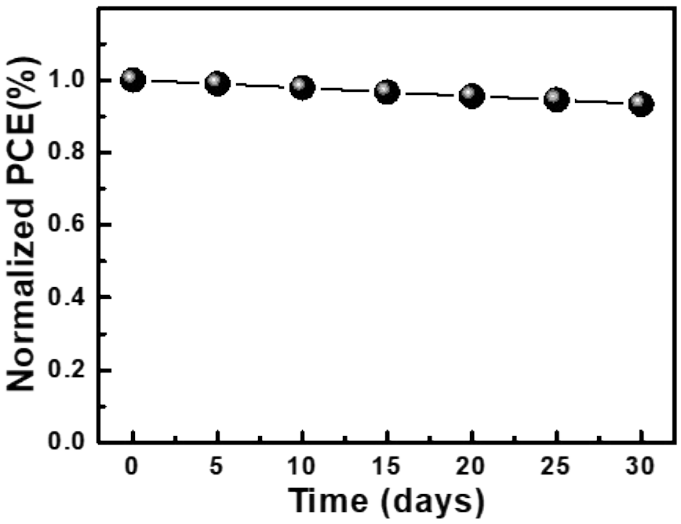

Figure S3. Long-term stability of normalized PCEs of fabricated PSCs stored in ambient condition (20%-30% relative humidity).

Reference:

1. K. Wang, Z. Jin, L. Liang, H. Bian, D. Bai, H. Wang, J. Zhang, Q. Wang & S. Liu. *Nat. Commun.* 2018, **9**, 4544.