Supporting Information

Effect of Solvent Vapour Annealing on Bismuth Triiodide Film for Photovoltaic Applications and its Optoelectronic Properties

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Figure S1. Schematic of the fabrication approach of the BiI$_3$ thin film. (a) Precursor solution of BiI$_3$, (b) precursor deposition on the ITO/HTL substrate. The crystallization of BiI$_3$ thin film by (c) thermal annealing (TA), (d) annealing the antisolvent (chlorobenzene (CB)) dripped film (AS), and (e) annealing under ambient solvent (CB or dimethylformamide (DMF)) vapor (CB or DMF-SVA).
**Figure S2.** Cross-sectional SEM images of the BiI₃ thin films crystallized via (a) TA, (b) CB-AS, (c) CB-SVA, (d) DMF-SVA.

**Figure S3.** XRD pattern of BiI₃ (tetragonal) (ICSD-56570) as references (Inorganic Crystal Structure Database) and calculated XRD pattern from the VESTA using BiI₃ crystal CIF file.

**Figure S4.** The PL spectra of BiI₃ thin films crystallized under different ambient conditions (a) and (b) bandgap energy ($E_g$) estimated from the differentiation of EQE spectra (Fig. 3d and Fig. S6b).
Figure S5. Photoelectron spectra of (a) BiI$_3$ film and (b) plasma-treated PTAA HTL layer.

Figure S6. (a) Schematics of the device structure, (b) $EQE$ spectra of corresponding devices. (c) Steady-state $J_{SC}$ and PCE of the BiI$_3$ device prepared by CB-SVA approach at maximum power point tracking (MPPT) under AM 1.5G 100 mW cm$^{-2}$ illumination and (d) stability of the device stored in ambient air conditions.
Figure S7. Statistics of device parameters for the BiI₃ based solar cells with BiI₃ thin film fabricated by various methods; TA, CB-AS, CB, or DMF-SVA. Histogram of device parameters: (a) $V_{OC}$, (b) $J_{SC}$, and (c) $PCE$ ($\eta$) of 12 devices fabricated four different batches.

Figure S8. XPS spectra of BiI₃ films prepared under different conditions. (a) Survey spectra, (b) The core-level peak for I-3d, and (c) Bi-4f. The two steric symbols in the plot (c) at ~162 eV and 157 eV assigned for metallic Bi. Note that the spectra (b) and (c) are normalized.
Figure S9. The density (carrier + defect) profile of the BiI$_3$ device prepared by the CB-SVA approach extracted from capacitance-voltage (C-V) curves at different modulated frequencies bias.

Fig. S10. The XRD patterns of fresh and aged (kept under ambient air for 30 days) BiI$_3$ (TA (a) and CB-SVA) (b) films.