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Supporting Information

Performance Enhancement of Inverted Perovskite Solar Cells by GlyHCl Additive

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Contents:

Experimental Section

Materials: Formamidinium iodide (99.99%) (FAI), methylammonium iodide (99.99%) (MAI) and Phenethylammonium iodide (99.99%) (PEAI) were purchased from Greatcell solar materials. Methylammonium bromide (99.99%) (MABr), Cesium (99.99%) (CsI) and Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (Mn=15000-25000) (PTAA) were purchased from Xi'an Polymer Light Technology Corp. (China). Iodide Lead iodide (99.99%) (PbI_2) and dimethylmethanamide (99.8%) (DMF) were obtained from Alfa Aesar Inc. N,N-, dimethyl-sulfoxide (99.9%) (DMSO), chlorobenzene (99.9%) (CB) and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (96%) (BCP) were purchased from Sigma-Aldrich, Inc. Phenyl-C_{71}-butyric acid methyl ester (99%) (PCBM) was purchased from Nano-C, Inc. GlyHCl (99%) was purchased from BLD pharm, Inc. All chemicals were used as received without further purification.

Preparation of triple cation mixed Perovskite solution: the triple cation perovskite solution was prepared by mixing two 1.2 M $FAPbI_3$ and $MAPbBr_3$ perovskite solutions in DMF: DMSO (4:1 volume ratio, v: v) in a particular ratio (e.g. 95:5). The 1.2 M $FAPbI_3$ solution was thereby prepared by dissolving FAI (722 mg) and PbI_2 (2130 mg) in 2.8 mL DMF and 0.7 mL DMSO which contains a 10 molar % excess of PbI_2. The 1.2 M $MAPbBr_3$ solution was made by dissolving MABr (470 mg) and $PbBr_2$ (1696 mg) in 2.8 mL DMF and 0.7 mL DMSO which contains a 10 molar % excess of $PbBr_2$. Lastly, 40 μL of a 1.5 CsI solution in DMSO (389 mg CsI in 1 mL DMSO) was mixed with 960 μL of the above-described mixture of $FAPbI_3$ and $MAPbBr_3$ resulting in a nominal perovskite stoichiometry of $Cs_{0.05}(FA_{0.95}MA_{0.05})_{0.95}Pb(I_{0.95}Br_{0.05})_3$, respectively.

Device fabrication: To fabricate a device structure of glass/ ITO/ PTAA/ Perovskite/ PCBM/ BCP/ Ag, ITO glass substrates were ultrasonically cleaned by deionized (DI) water, acetone and isopropanol for 15 min, respectively. Then, the cleaned ITO substrates were dealt with air plasma for 8 mins before use. Then the substrates were transferred to N_2 glovebox. After the substrates were transferred into glovebox, poly(triaryl amine) (PTAA) solution (2 mg mL^{-1}) was spin-coated at 5000 rpm for 30 s and annealed at 100 °C for 10 min. The substrates were cool down to room temperature before use. 1.2 M perovskite precursor solutions were constructed by mixing FAI, PbI_2, MABr, $PbBr_2$ and CsI in DMF: DMSO mixed solvent with a chemical formula of $Cs_{0.05}(FA_{0.95}MA_{0.05})_{0.95}Pb(I_{0.95}Br_{0.05})_3$. 50 μL of the prepared precursor solution was spin-coated at 1000 rpm for 10 s and 5000 rpm for 30 s onto the PTAA-coated ITO substrate, 50 μL CB as anti-solvent was dripped on the film at 10 s before the end of the last procedure and then annealed at 100°C for 30 min. Afterward, PCBM (20 mg mL^{-1}) and BCP (0.5 mg mL^{-1}) were spin-coated on the films at 1500 rpm for 60 s and 4500 rpm for 30 s, respectively. For solution with PEA_2PbI_4 and GlyHCl, different molar ratio of PEA_2PbI_4 and GlyHCl was added to the original 1.2 M $FAPbI_3$ solution. Finally, 200 nm silver electrodes were thermally evaporated onto the films at a chamber pressure of 10^{-7} Torr with a deposition rate of 0.5 Å s^{-1}.

Characterization: J-V curves were measured by a Keithley 2400 source meter with a solar simulator under AM 1.5 G one sun illumination (Newport 66902). An antireflecting layer was adopted while testing the devices. The scanning rate was 100 mV s^{-1} with a voltage step of 10 mV. The EQE of the PSCs was obtained from an EQE system under DC mode. To reduce the optical reflection loss, an antireflection (AR) layer was added on the glass side during the test of the champion 5 °C antisolvent treated devices. SEM images were measured by a field-emission SEM (Tescan MAIA3). The TEM images of perovskite films were conducted using JEOL JEM-2100F TEM/STEM operated at 200 kV, using Gatan Enfina electron spectrometer (CA, USA). XRD patterns were measured using Cu K_α radiation (Rigaku, Smartlab) to analyze the crystallization of perovskite. PL was measured by the FLS 920 (Edinburgh Instruments, Ltd) with excitation at 645 nm. TOF-SIMS (ION-TOF GmbH) was used for depth profiling of the elements distribution in the perovskite films. The Bi^{3+} primary ion beam (25 keV, 0.3 pA) was used for analysis and scanned at an area of 50×50μm^2. The sputtering was accomplished with the Cs^+ ion beam (1 keV, 5 nA) over an area of200×200μm^2

Statistical Analysis: The data, figure and statistical graph (*J-V* curves, XRD figures, XPS figures, Williamson−Hall plots, PL, UV-vis, SCLC, EQE, stability tests) in the article is pre-processed and drawn by Origin Pro (ver. 2019). The SEM figure is processed by Digital Micrograph (ver. 3.4). The TEM image is processed with GMS3. The AFM figure is processed by NanoScope Analysis (ver. 1.7).

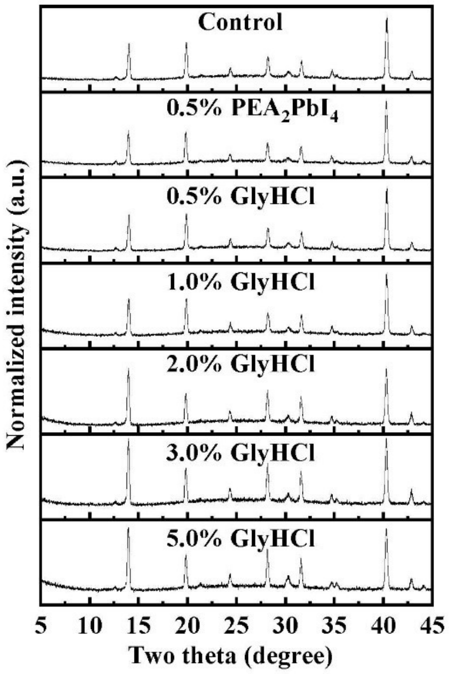

Figure S1. The XRD patterns of perovskites with and without different ratio of GlyHCl.

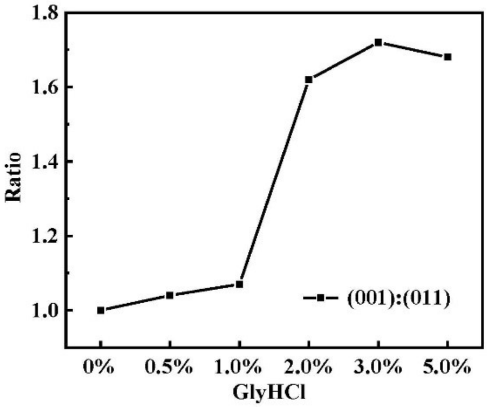

Figure S2. The change in ratio of peak intensity of (001): (011) in XRD patterns.

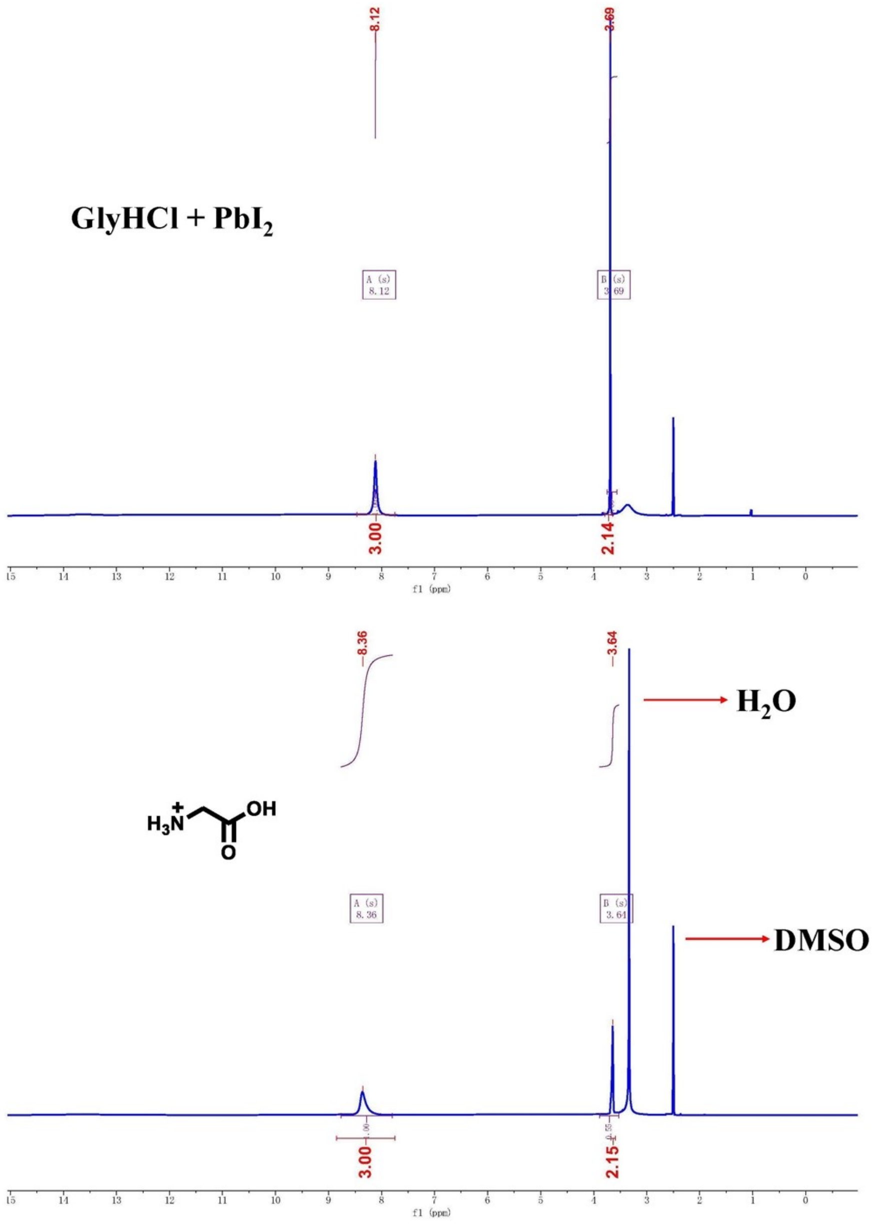

Figure S3. The full ^{1}H NMR spectra of pure GlyHCl and PbI_2 with GlyHCl.

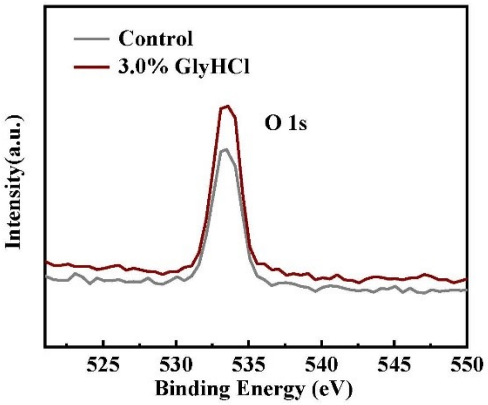

Figure S4. The characteristic peaks in XPS spectra of O.

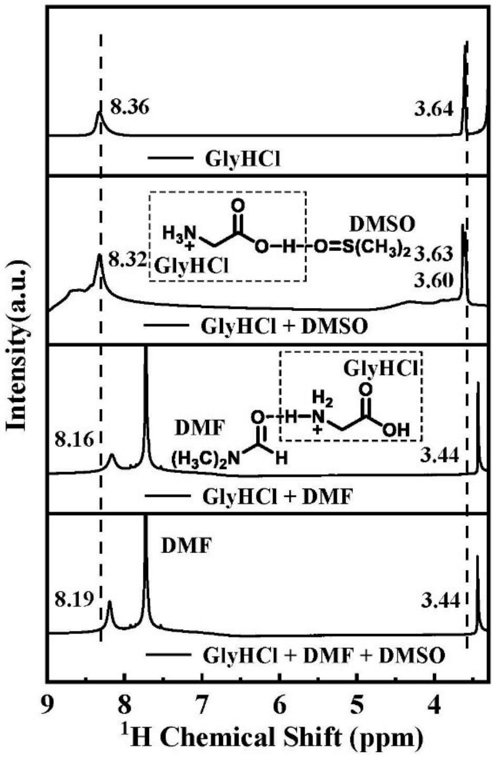

Figure S5. The ^{1}H NMR spectra of GlyHCLin DMF, DMSO and mixture of DMF/DMSO.

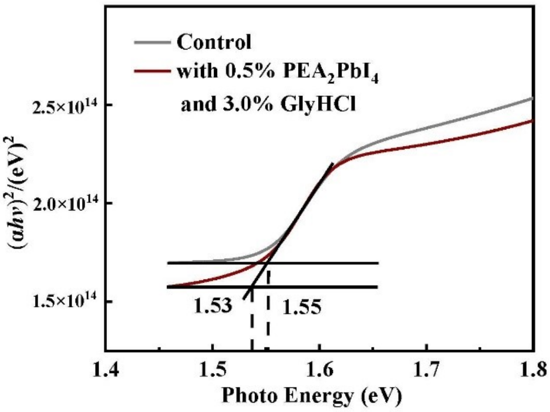

Figure S6. The tauc plot (($\alpha h\upsilon)^2$- $h\upsilon$) of control sample and sample with GlyHCl and PEA$_2$PbI$_4$.

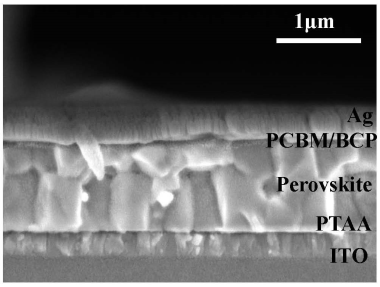

Figure S7. The cross-section SEM imgae of the PSC.

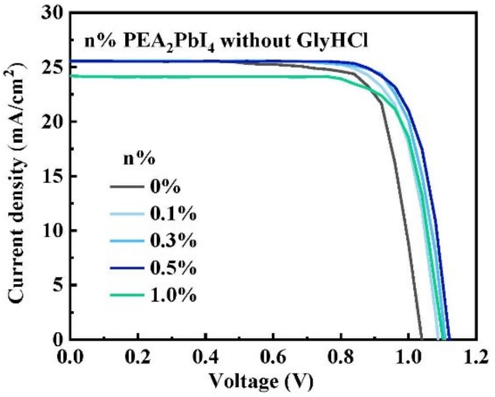

Figure S8. The *J–V* curves of control devices and champion devices with different molar ratio of PEA_2PbI_4 and GlyHCl, respectively.

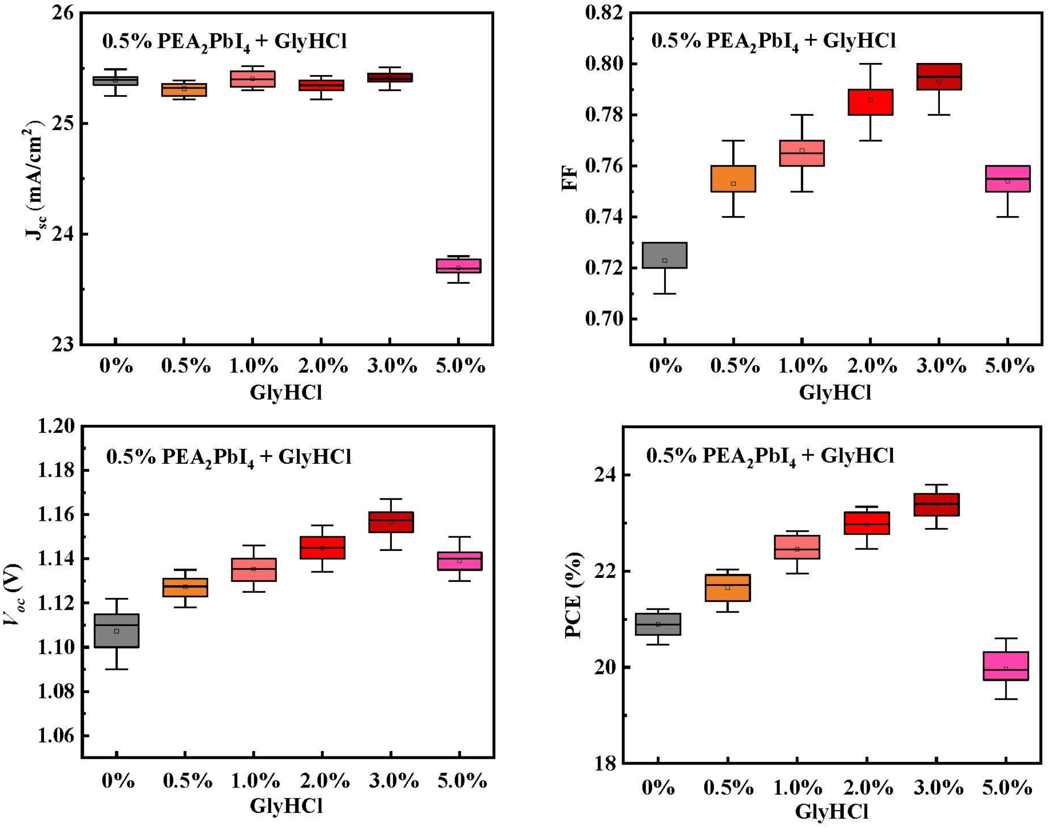

Figure S9. Comparisons of photovoltaic performance parameters between control devices and devices with different ratio of GlyHCl.

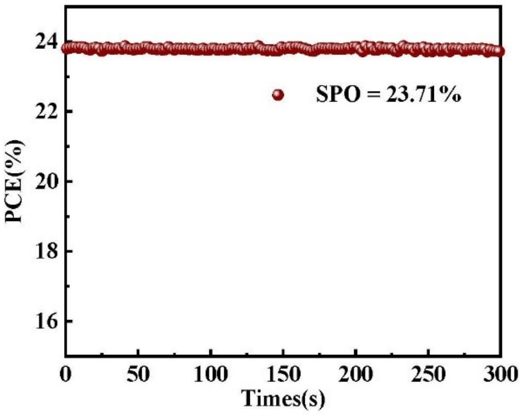

Figure S10. The stable power output of a champion PSC with the PEA_2PbI_4 and GlyHCl.