

Supporting Information

Monolayer CVD Graphene Barrier Enhances Stability of Planar p-i-n Organic-Inorganic Metal Halide Perovskite Solar Cells

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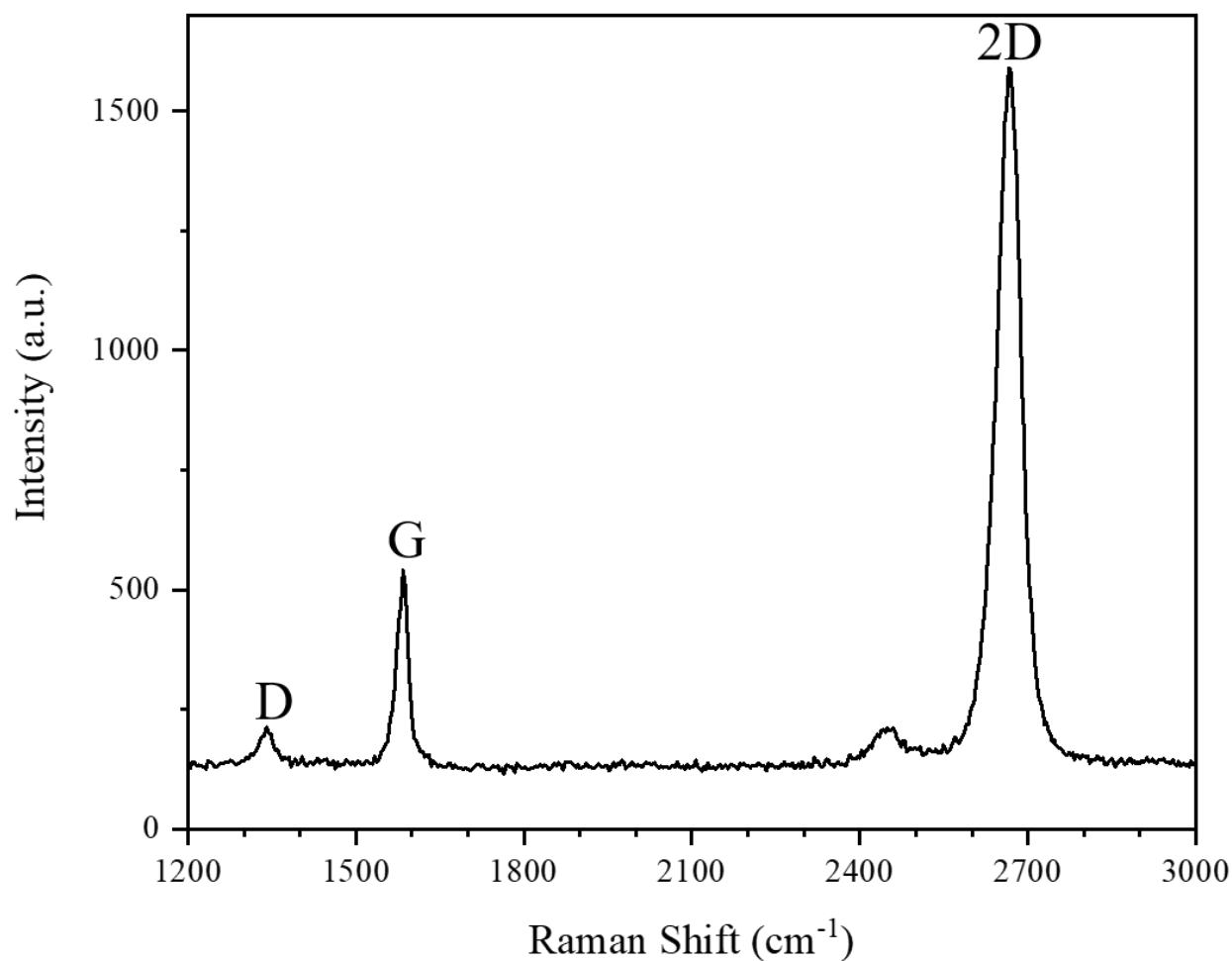


Figure S1: Raman spectrum of monolayer graphene transferred onto an SiO₂/Si substrate.

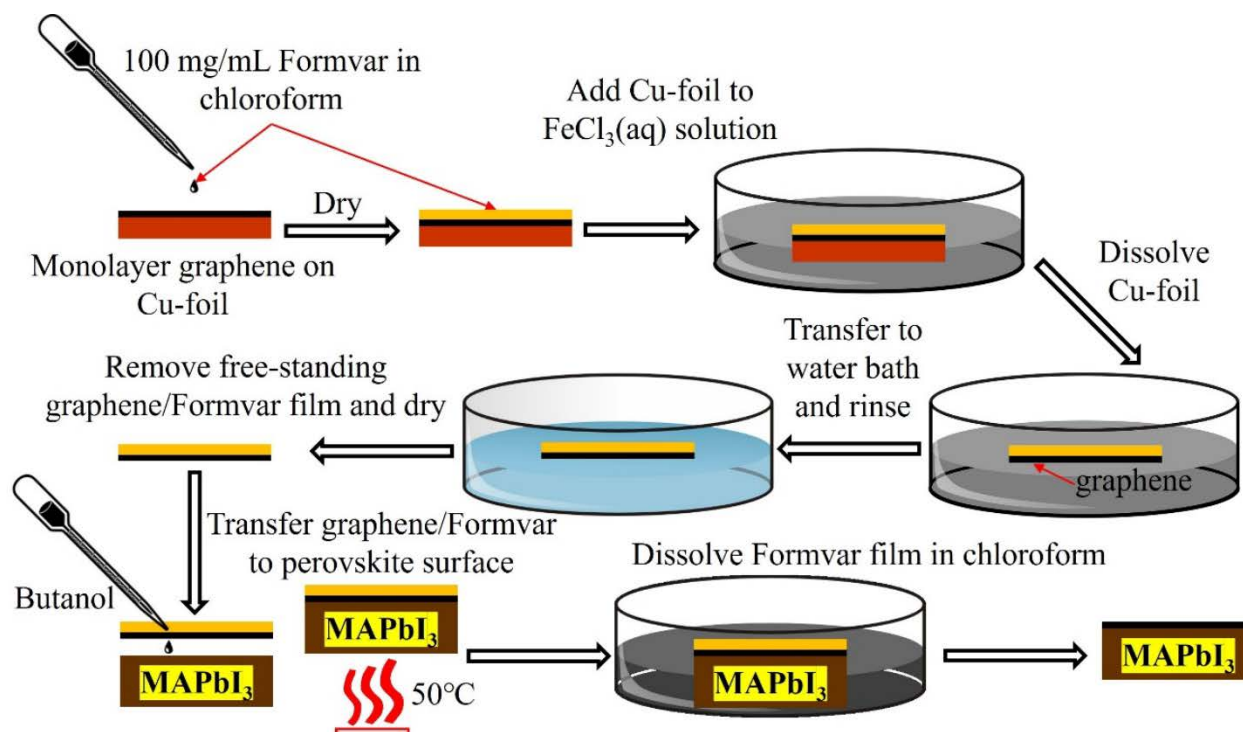


Figure S2: Schematic representation of the pseudo dry graphene transfer process.

Experimental.

Preparation of Solutions. A polyvinyl formal (Formvar) graphene transfer medium was prepared by dissolving Formvar resin in chloroform (Fisher) at room temperature at a ratio of 100 mg Formvar per 1 mL chloroform. A copper iodide (CuI) solution was prepared by dissolving 15 mg CuI (Alfa Aesar) in 1 mL acetonitrile (anhydrous, Acros) for 2 h at room temperature, and then filtering with a 0.45 μm PTFE filter. To prepare the $\text{PbI}_2(\text{DMSO})$ complex solution, a 1:1 molar ratio of lead iodide (PbI_2) (Alfa Aesar) and dimethyl sulfoxide (DMSO) (anhydrous, Acros) was dissolved fully at room temperature in N,N-dimethylmethanamide (DMF) (anhydrous, Acros), and then filtered with a 0.45 μm PTFE filter. Specifically, 461 mg PbI_2 /944 mg DMF and 78 mg DMSO/944 mg DMF were used for a 1.0 M $\text{PbI}_2(\text{DMSO})$ complex solution. A methylammonium iodide (MAI) solution was prepared by fully dissolving 60 mg MAI (Greatcell Solar) in 1 mL 2-propanol (anhydrous, Acros), and then filtering with a 0.45 μm PTFE filter. A phenyl-C61-butyric acid methyl ester (PCBM) solution was prepared by dissolving 10 mg of PCBM (nano-C) in 1 mL chlorobenzene (anhydrous, Sigma-Aldrich) at 55 $^{\circ}\text{C}$ overnight, cooling to room temperature while stirring, and then filtering with a 0.45 μm PTFE filter. A C_{60} -N cathode interlayer solution was prepared by dissolving 3 mg C_{60} -N (1-Material) in 1 mL 2,2,2-trifluoroethanol (TFE) (Acros) overnight, and then filtering with a 0.45 μm PTFE filter.

Graphene Synthesis. Continuous, monolayer graphene was synthesized on 3 in² sheets of 35 μm copper (Cu) foil (Graphene Platform) by chemical vapor deposition in a quartz tube furnace (Planar Tech). Prior to growth, the Cu foil was pre-cleaned with DI water and ethanol (Fisher), and then dried with N_2 . The Cu foil was annealed under low pressure (2 torr) and 1020 $^{\circ}\text{C}$ with a gas flow of 20 SCCM of H_2 for 2 h. To begin the graphene growth, 10 SCCM of CH_4 was

introduced to the chamber (still at 1020 °C and 2 torr) for 20 min, followed by a rapid cooling to room temperature under a gas flow of 20 SCCM of H₂ and 20 SCCM of Ar. Following the growth, the graphene/Cu foil sheets were adhered to thermal release tape (TRT) (Graphene Supermarket) and cut into smaller 15 cm² squares for the transfer process.

Graphene Transfer. A 15 cm² graphene/Cu foil/TRT square was placed in a glass dish against the wall at a 60° incline with the graphene side facing upwards. A pipet was used to evenly coat the graphene surface with the Formvar solution. The Formvar/graphene/Cu foil/TRT was dried for 15 min, baked at 100 °C to remove the TRT, and then floated (graphene side up) atop a 1:1 volume ratio DI water and ferric chloride copper etchant solution (MG Chemicals). After 3 min, the Formvar/graphene/Cu foil was removed, and the bottom (non-graphene side) of the substrate was washed with DI water to remove any backside graphene. The Formvar/graphene/Cu foil was then placed atop a 3:1 volume ratio DI water and ferric chloride copper etchant solution with the graphene side up. After 45 min, the Cu foil was dissolved, leaving only graphene adhered to the Formvar. The free-standing Formvar/graphene was washed thoroughly by floating in several baths of DI water to remove any remaining copper etchant solution, and then placed gently between two cleanroom wipe squares to dry. The free-standing Formvar/graphene was moved to an N₂-glovebox (N₂ and O₂ < 5.0 ppm) for the remainder of the transfer. In the glovebox, 100 µL of n-butanol (Fisher) was used to cover the surface of a MAPbI₃ perovskite film. The free-standing Formvar/graphene was gently placed (graphene side down) atop the MAPbI₃/n-butanol such that it covered the entire surface of the perovskite. A Teflon rod was rolled over the system to enhance the contact between the graphene and the perovskite before transferring the device to a hot plate set to 50 °C. The device was baked for 15 min to further promote the graphene

adhesion and to remove any remaining butanol. Once cooled to room temperature, the device was placed in a chloroform (Fisher) bath for 2 min, removed, and washed with additional chloroform to fully remove the Formvar layer, leaving only the graphene adhered to the perovskite film.

Device Fabrication. Patterned indium-doped tin oxide (ITO) substrates ($20 \text{ } \Omega/\text{sq}$, 14.7 cm^2 , Thin Film Devices) were cleaned with a 2% MucosolTM (Sigma-Aldrich) soap solution, deionized water, acetone (Fisher), and 2-propanol (Fisher) (in that order) with 10 min of ultra-sonication at each step, followed by drying in an oven at $140 \text{ } ^\circ\text{C}$ overnight. Prior to use, the cleaned ITO substrates were exposed to UV/Ozone treatment for 20 min. Following the cleaning and surface polarization, the ITO substrates were transferred to an N_2 -glovebox (N_2 and $\text{O}_2 < 5.0 \text{ ppm}$) for the remainder of the procedure. $50 \text{ } \mu\text{L}$ of the CuI solution were spun onto the bare ITO at 3000 rpm for 60 s, and then annealed at $100 \text{ } ^\circ\text{C}$ for 10 minutes. Once cooled to room temperature, $50 \text{ } \mu\text{L}$ of the $\text{PbI}_2(\text{DMSO})$ complex solution was spun onto the CuI-coated substrates at 1500 rpm for 15 s, immediately followed by a spin-coating of $100 \text{ } \mu\text{L}$ of the MAI solution at 2500 rpm for 30 s. The resulting perovskite film was annealed at $100 \text{ } ^\circ\text{C}$ for 1 hr in the dark. After the MAPbI_3 perovskite was formed and the substrate cooled to room temperature, $50 \text{ } \mu\text{L}$ of the PCBM solution was spun onto the perovskite film at 1000 rpm for 30 s. Following a previous report,¹ the films were covered with a petri dish and allowed to solvent anneal in the dark for 24 hours. The perovskite devices were completed by spin-coating $80 \text{ } \mu\text{L}$ of the $\text{C}_{60}\text{-N}$ solution at 4000 rpm for 60 s, followed by thermal evaporation of a 100 nm thick Ag electrode at a base pressure of $3 \times 10^{-6} \text{ mbar}$ through a shadow mask. An overlap of the Ag electrode and patterned ITO substrate

defined a device area of 0.06 cm². For the devices with the graphene layer, monolayer graphene was transferred onto the MAPbI₃ perovskite prior to the deposition of the PCBM.

Inductively Coupled Plasma Mass Spectroscopy. After the complete PSCs with or without the graphene barrier layer were subjected to the thermal annealing treatment for 12 hours at 85 °C, scotch tape was used to remove the Ag electrodes from the tops of the devices. This process was repeated two additional times to ensure the Ag electrodes had been thoroughly removed. The PCBM layers were removed by submerging the samples in a chlorobenzene bath for 5 min. The samples, now with the perovskite layer with or without graphene as the top layer, were then rinsed with additional chlorobenzene, dried with a nitrogen gun, and then placed in separate vials each containing 5 mL of 4:1 HCl (37%)/HNO₃ (67%) aqua regia for 12 hours to dissolve. The aqua regia solutions were transferred to 15 mL Falcon tubes and diluted in a 5:7 v/v ratio with water. ICP-MS analysis was performed with a Perkin-Elmer NexION 350D ICP-MS on the aqua regia solutions. The detection limit for Ag was ~0.1 ng in 1 mL of the solution.

Characterization. Current–voltage (*J-V*) curves were tested inside a N₂-glovebox using a Keithly 2400 source-meter under simulated AM 1.5G solar irradiation at 100 mV/cm² light intensity. The light source was a 300 W Xe lamp (Newport 91160) that was adjusted with an NREL-calibrated Si reference solar cell and KG-5 filter. No photomask was used for the *J-V* measurements. X-ray diffraction (XRD) measurements were made with a PANalytical X'Pert³ X-ray diffractometer having a Ni filter, 1/2 in. diverging slit, vertical goniometer, and X'Celerator detector. Measurements were made under Cu K α (λ = 1.542 Å).

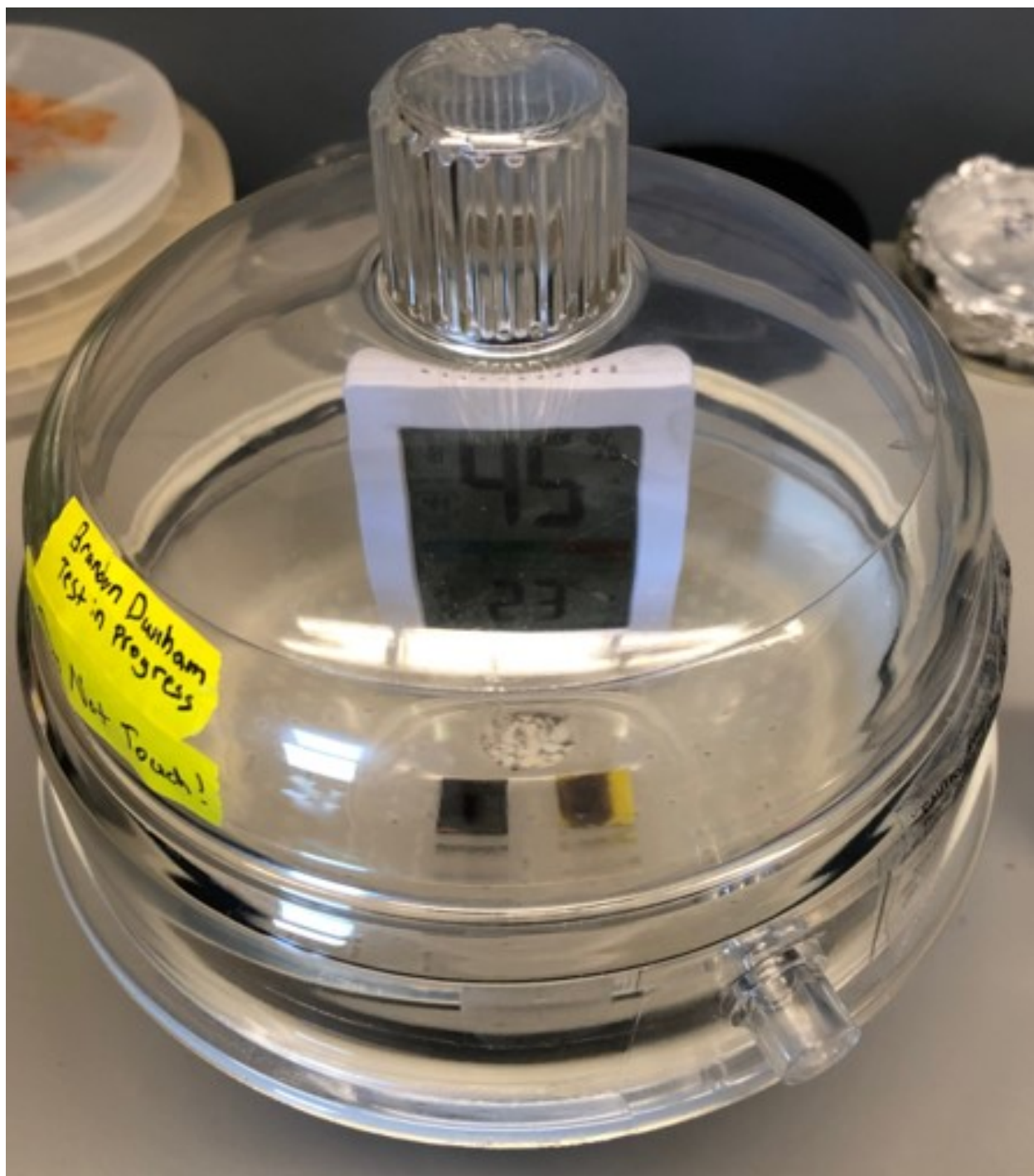


Figure S3: Apparatus used to maintain a controlled humidity environment in air during moisture stability studies. The relative humidity inside the container was kept between 30-50%.

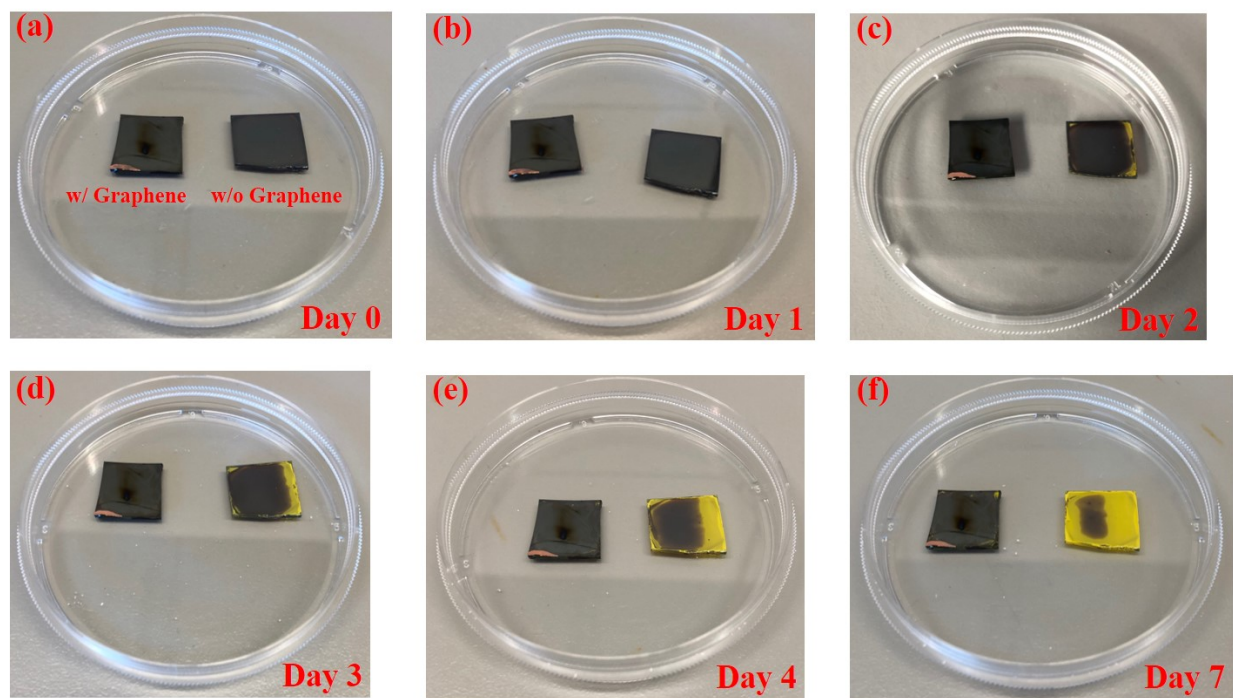


Figure S4: MAPbI₃ films on glass substrates with or without a graphene barrier layer during storage in air at 30-50% relative humidity for 7 days.

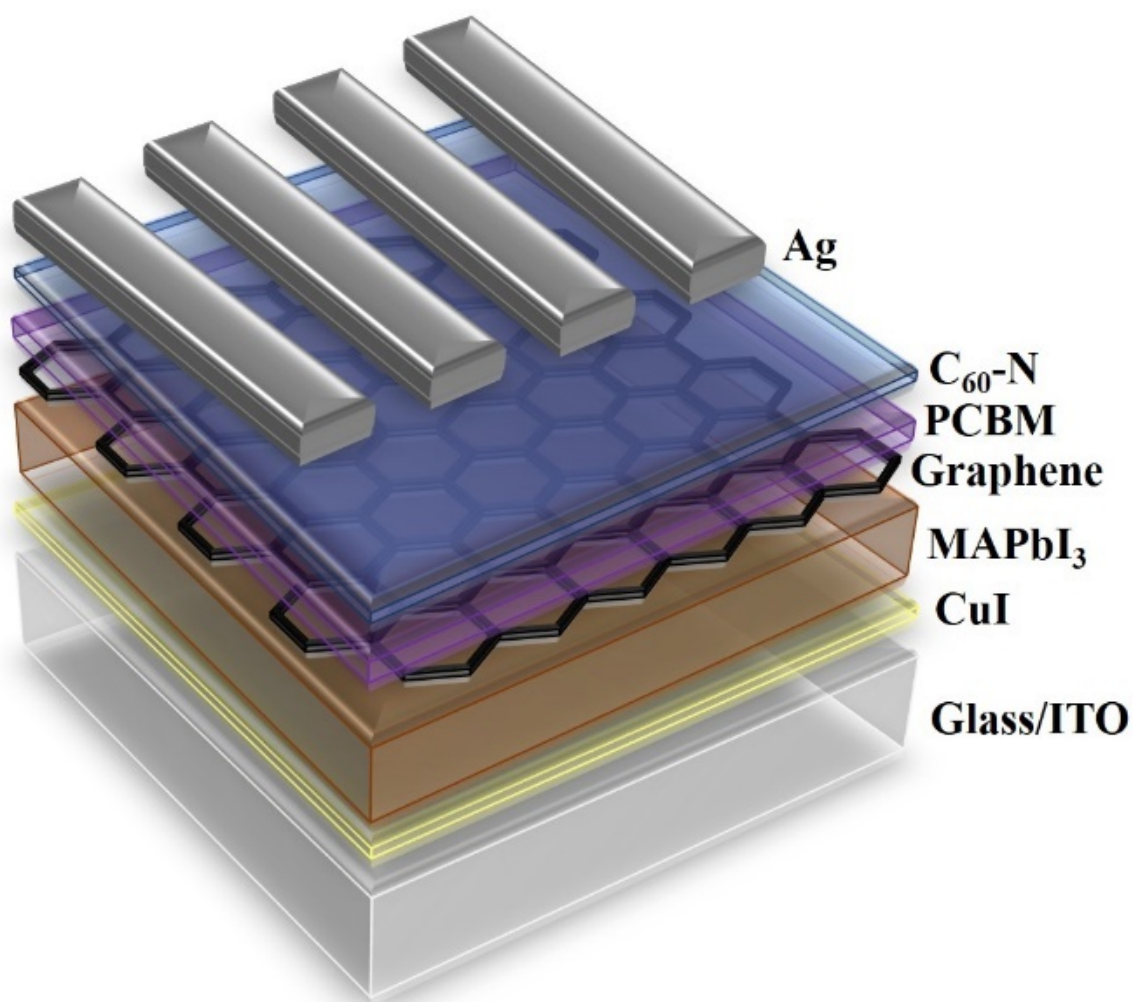


Figure S5. Schematic of the inverted, planar p-i-n PSC used in this study. Note that the graphene layer may or may not be included in the final device architecture.

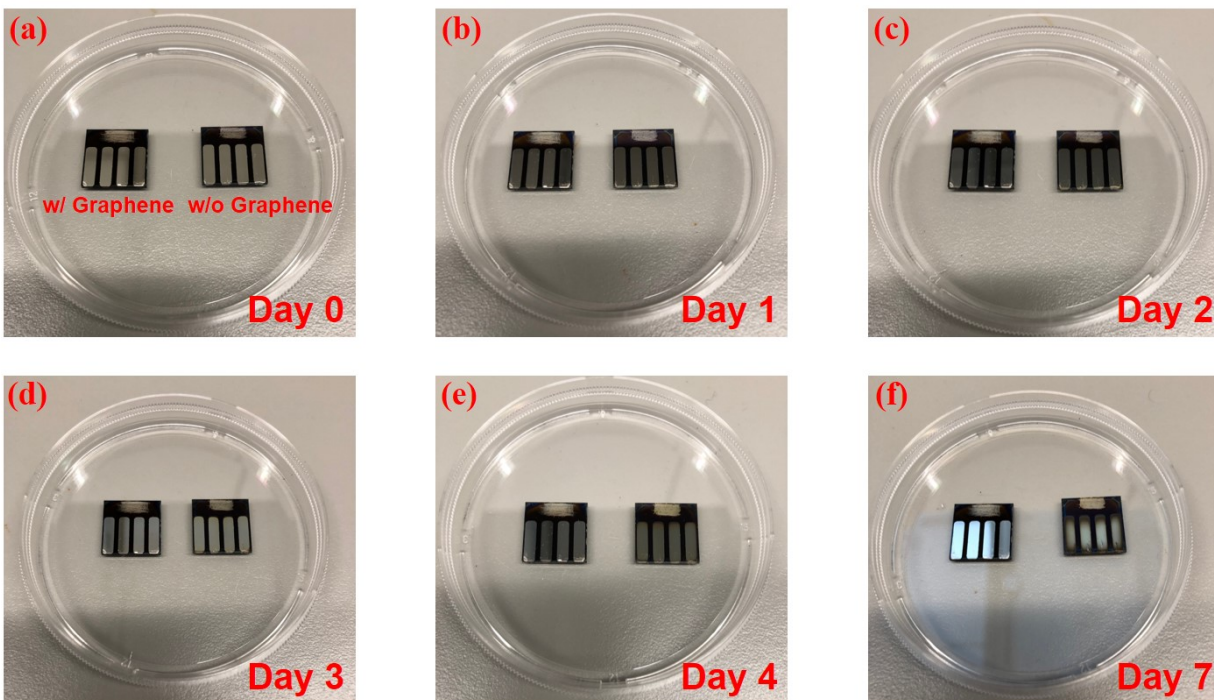


Figure S6: Glass/ITO/CuI/MAPbI₃/PCBM/C₆₀-N/Ag full devices with or without a graphene barrier layer during storage in air at 30-50% relative humidity for 7 days.

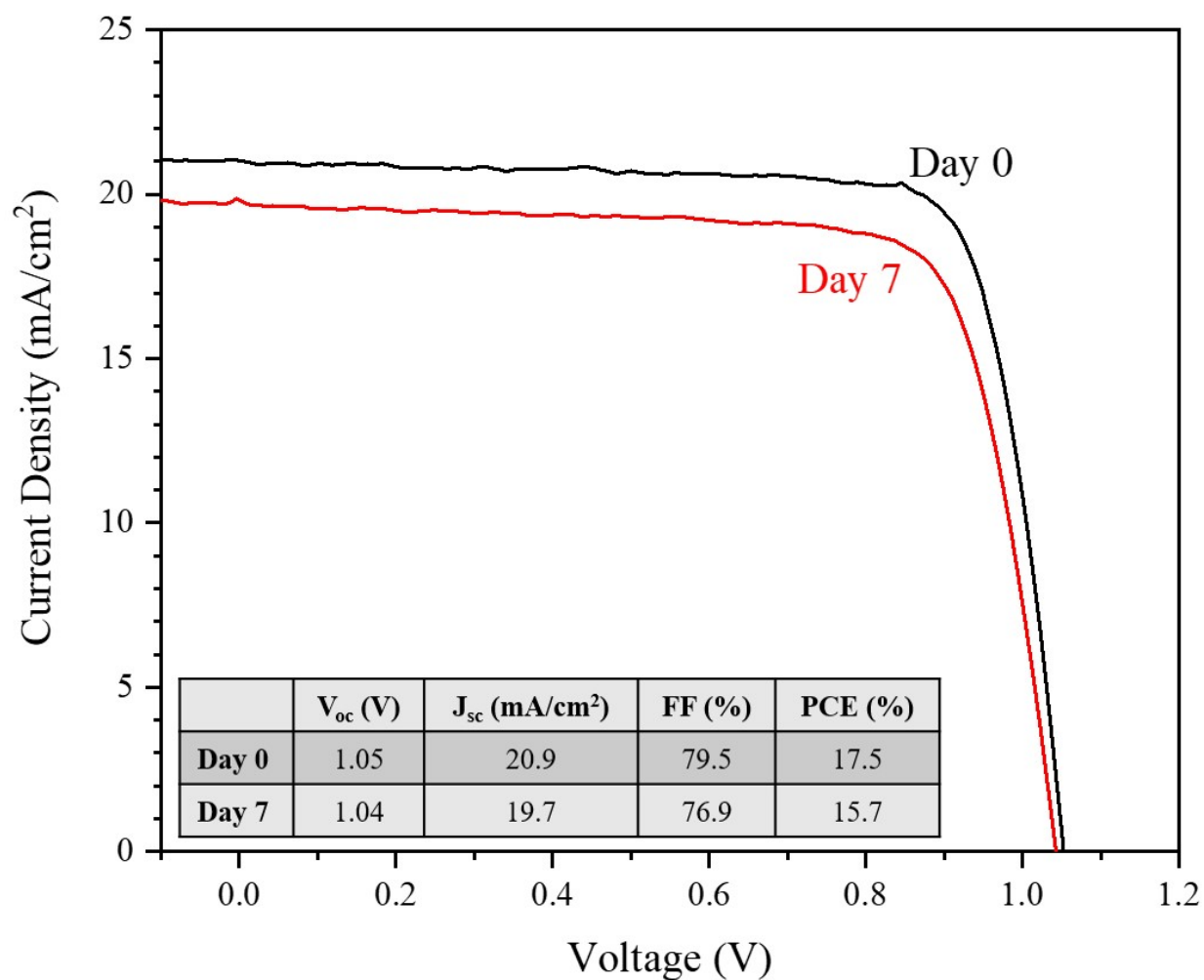


Figure S7: Forward bias scan J - V curves with corresponding performance parameters (inset) for the highest performing PSC with a graphene barrier layer after 0 days and 7 days in air at 30-50% relative humidity.

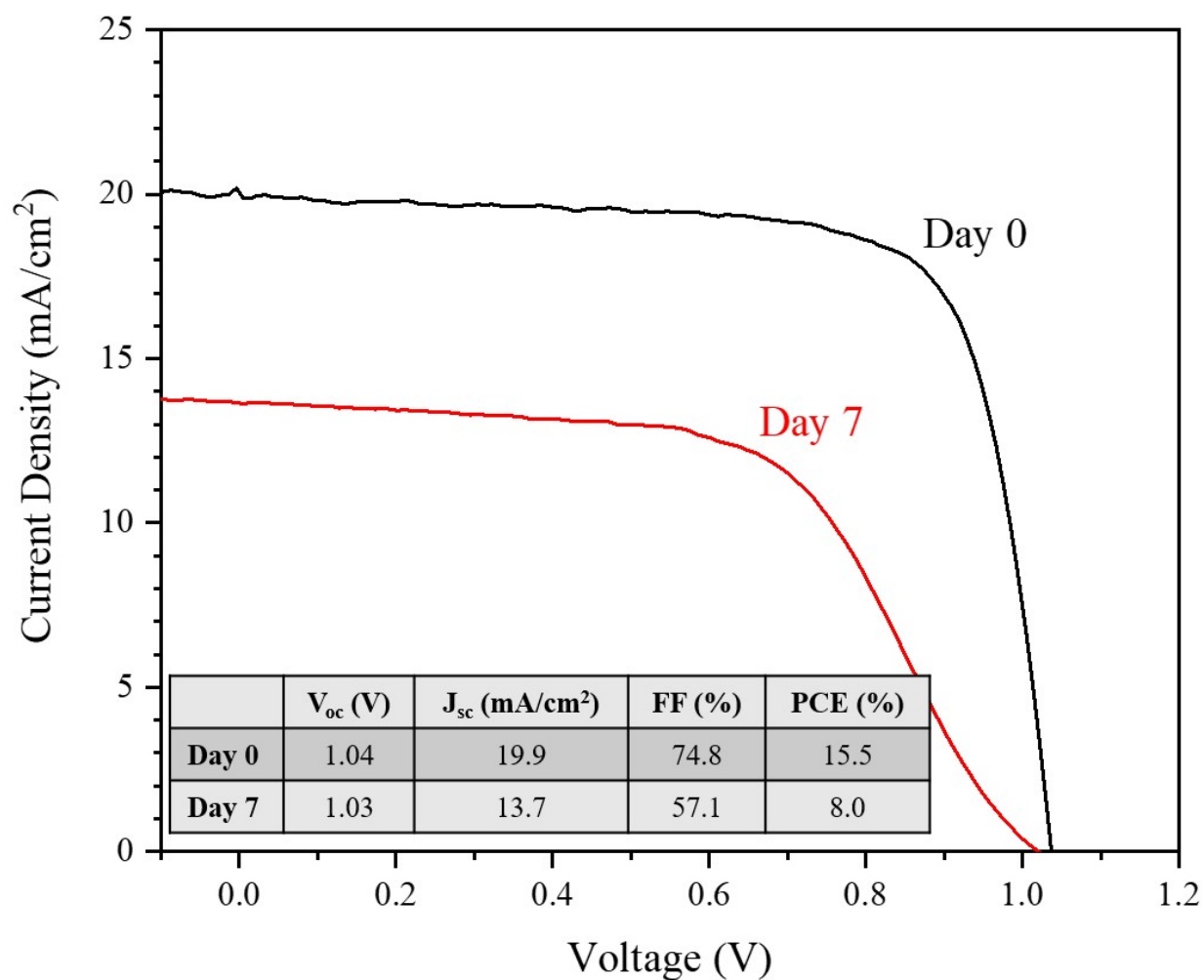


Figure S8: Forward bias scan J - V curves with corresponding performance parameters (inset) for the highest performing PSC without a graphene barrier layer after 0 days and 7 days in air at 30-50% relative humidity.

Edge of graphene film on SiO₂/Si wafer.

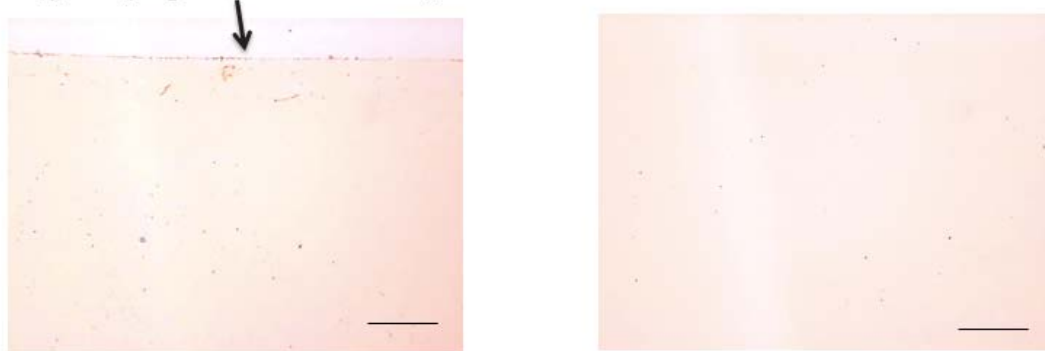


Figure S9: Optical microscope images of large area monolayer graphene transferred on a silicon wafer with a 200 nm-thick SiO₂ layer. Scale bar: 30 mm. From reference 1.

References:

- 1) Bi, E.; Chen, H.; Xie, F.; Wu, Y.; Chen, W.; Su, Y.; Islam, A.; Grätzel, M.; Yang, X.; Han, L. Diffusion Engineering of Ions and Charge Carriers for Stable Efficient Perovskite Solar Cells. *Nature Communications* **2017**, 8 (1), 1–7. <https://doi.org/10.1038/ncomms15330>.
- 2) Wang, Y. "Graphene Growth and Transfer and Beyond: Engineering Twist-Angle Layered Graphene and Interlayer Bond Formation Between Graphene Layers" (2019). *Doctoral Dissertations*. 1574. <https://doi.org/10.7275/14104313>.