Electronic Supplementary Information

High-Performance Hole-Transporting Layer-Free Conventional Perovskite/Fullerene Heterojunction Thin-Film Solar Cells

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Experimental Section

Materials and Sample Preparation:

Methylammonium iodide (MAI) was synthesized by reacting 24 mL of 0.20 mol methylamine (33 wt% in absolute ethanol, Aldrich), 10 mL of 0.04 mol hydroiodic acid (57 wt% in water with 1.5% hypophosphorous acid, Alfa Aesar), and 100 mL ethanol in a 250 mL round bottom flask under nitrogen at 0 °C for 2 h with stirring. After reaction, the white precipitate of MAI was recovered by rotary evaporation at 40 °C and then dissolved in ethanol followed by sedimentation in diethyl ether by stirring the solution for 30 min. This step was repeated three times and the MAI powders were finally collected and dried at 50 °C in a vacuum oven for 24 h. To prepare the perovskite precursor solution, MAI and lead iodide (PbI_2, Alfa Aesar) powders were dissolved in mixed gamma-butyrolactone and dimethyl sulfoxide solution with 7:3 volume ratios. The solutions (1M) were stirred overnight at 80 °C and filtered with 0.45 μm polyvinylidene fluoride filters before device fabrication.

Fabrication of thin-film perovskite solar cells:

Indium tin oxide (ITO) glass substrates (Colorado Concept Coating LLC) were cleaned via ultra-sonicated in the sequential detergent, DI water, Acetone, and isopropanol for each 10 min immersion. For the conventional HTL-Free PVSCs, the ITO substrates were transferred into the glove box immediately after the UV-Ozone cleaning with 5 min treatments. For the regular conventional devices, poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS, AI 4083) was spun-cast onto UV-ozone treated ITO via 5000 rpm with 30 sec, followed by annealing in the 140°C for 10 min in air. Solvent-washing technique was chosen in this study for creating high dense and homogeneous perovskite thin film. $MAPbI_3$ was spun-cast with three steps, 500 rpm for 5 s, 1000 rpm for 10s, and 3500 rpm for 35 s.

Anhydrous toluene was *in-situ* dropped at the third stage of spinning. Deposited perovskite thin films were then annealed at 100°C for 10 min in glove box. 15 mg/mL of [6,6]-phenyl-C61-butyric acid methyl ester (P_{61}CBM) chloroform solution and 2 mg/mL of bis-C_{60} surfactant dissolved in isopropanol were sequentially spun-cast with spin rate of 1000 rpm and 3000 rpm for 1 min, respectively. 120 nm thickness of Ag electrode with the size of 3.14 mm^2 was thermal deposited under $1*10^{-6}$ torr vacuum environment.

***Characterization of thin-film perovskite solar cells*:**

For the measurement of J-V curves, the light intensity had been calibrated via the standard Si photodiode detector equipped with a KG-5 filter, which can be traced back to the standard cell of the National Renewable Energy Laboratory. The J-V curves of devices were measured by source-meter Keithley 2400 under AM 1.5 G of simulated solar light with the intensity of 100 mW/cm^2 .The monochromatic incident photon-to-electron conversion efficiency setup equipping with a 450 W Xenon lamp (Oriel) as the incident light, a monochromator, a chopper with a frequency of 100Hz, a lock-in amplifier (SR830, Stanford Research Corp), and a Si-based diode (J115711-1-Si detector) for calibration to obtain external quantum efficiency spectra. XPS spectra and secondary electron cutoff were generated using a PHI Versaprobe system with an Al Kα X-ray source and a 100 μm beam size. Measurements were taken while the sample was under ultrahigh vacuum (10^{-10} Torr). The surface work function can be determined from the energetic separation of the secondary cutoff (E_{cutoff}) and the Fermi level. Since the total incident energy of X-Ray is conserved, the smaller E_{cutoff} is attributed to the higher work function. Hence, the work function is calculated via the incident photon energy minus E_{cutoff}. All the samples were measured at least three different potions for calculating the work function.

Table S1. The average device performance for the studied HTL-free PVSCs and the devices using a PEDOT: PSS HTL

	Voc (V)	*Jsc* (mA/cm^2)	FF	PCE (%)
ITO	0.99 ± 0.036 (1.01)	14.70 ± 0.61 (15.69)	0.67 ± 0.01 (0.70)	9.69 ± 0.67 (11.02)
ITO/ PEDOT:PSS	0.88 ± 0.015 (0.89)	17.44±1.16 (18.91)	0.77 ± 0.02 (0.80)	11.76 ± 1.16 (13.46)

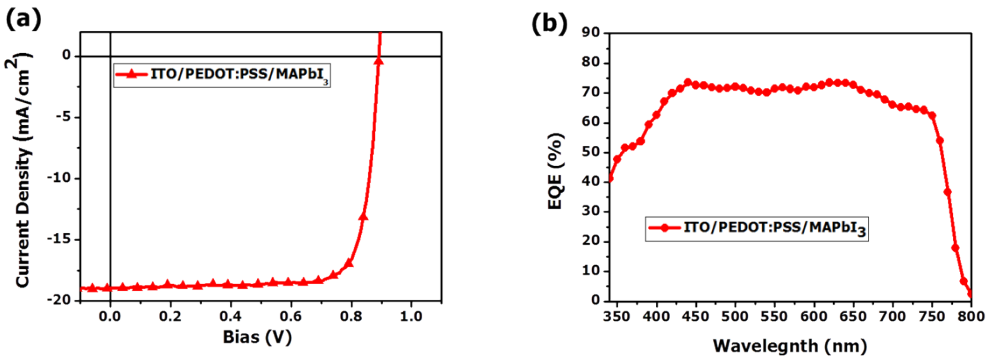

Fig. S1 (a) *J-V* curve and (b) EQE of the devices using a PEDOT: PSS HTL.

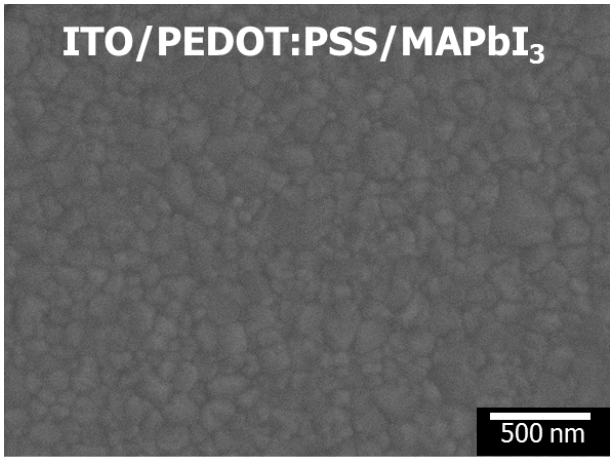

Fig. S2 SEM images of ITO/PEDOT: PSS/MAPbI$_3$

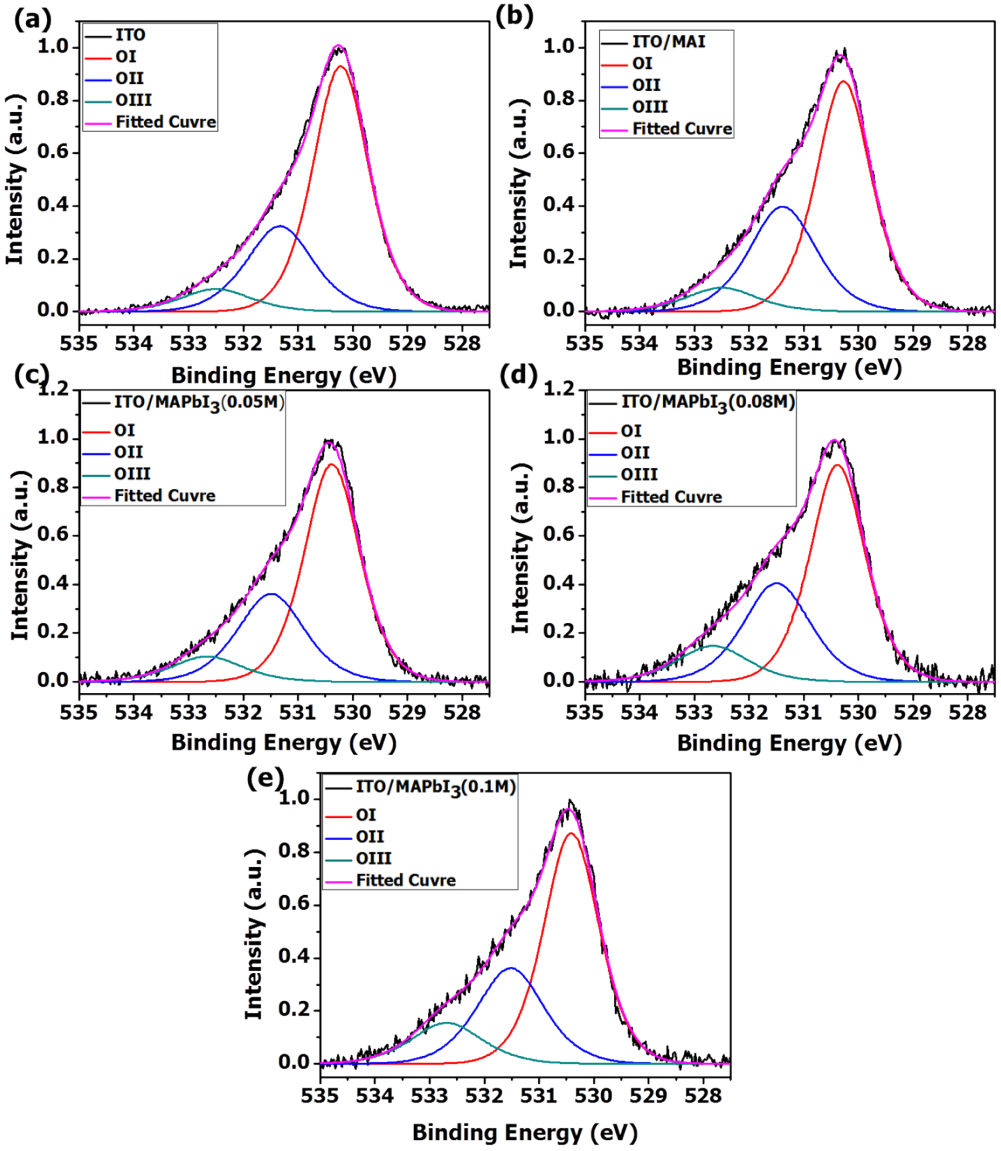

Fig. S3 Deconvolution of XPS O 1s spectra: (a) ITO, (b) ITO/MAI, (c) ITO/$MAPbI_3$ (0.05 M), (d) ITO/$MAPbI_3$ (0.08 M), & (e) ITO/$MAPbI_3$ (0.1 M). (FWHM for OI, OII, and OIII are 1.24, 1.5, 1.59 eV, respectively.)

Table S2. The fitting parameters for deconvolution of XPS O 1s spectra

	Deviation from ITO for OI (eV)	***Deviation from ITO for OII (eV)***	***Deviation from ITO for OIII (eV)***	***Integrated area of (OII + OIII) / OI***
ITO	0 (530.22)	0 (531.33)	0 (532.5)	0.35
ITO/MAI	+ 0.05	+ 0.05	0	0.4
ITO/MAPbI$_3$ (0.05 M)	+ 0.15	+ 0.15	+ 0.15	0.39
ITO/MAPbI$_3$ (0.08 M)	+ 0.16	+ 0.16	+ 0.16	0.43
ITO/MAPbI$_3$ (0.1 M)	+ 0.19	+ 0.19	+ 0.19	0.43