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High Performance Perovskite Solar Cells based on a PCBM:polystyrene blend electron transport layer

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Experimental Section

NiO precursor solution: Nickel (II) acetylacetonate ($Ni(C_5H_7O_2)_2$, 95%, Sigma-Aldrich) was dissolved in ethanol with diethanolamine ($NH(CH_2CH_2OH)_2$, ≥98.0%, Sigma-Aldrich) (0.4 mol·L^{-1}).[1] The mole ratio of Ni^{2+}: DEA was maintained at 1:1 in solution. The solution was stirred in a sealed glass vial in air at 70 ^oC overnight. To fabricate the solar cells, the patterned FTO-coated glass substrates were UV ozone treated for 15 min before spin-coating NiO precursor soltion. The NiO precursor was heated to 150 ^oC and annealed for 45 min to form a sol suspension, which was spin-coated onto an FTO-coated glass substrate at 3000 r.p.m for 30 s. Then, the substrate was heated to 500 ^oC for 1 h in air.

CH_3NH_3I was synthesized under an ice bath for 2 hrs by reacting methylamine (CH_3NH_2, 33 wt% in ethanol from Sigma-Aldrich) with hydroiodic acid (HI, 57 wt% in water from Sigma-Aldrich). The white powders were precipitated by drying at 60 °C and washed for 3 times with diethyl ether (Sigma-Aldrich) before further dried out to be stored in nitrogen-filled glove-box. $CH_3NH_3PbI_{3-x}Cl_x$ precursor solution was prepared by dissolving 0.88M lead chloride (99.999%, Sigma-Aldrich) and 2.64 M CH_3NH_3I in anhydrous *N,N*-Dimethylformamide (DMF, 99.8%, Sigma-Aldrich).

PCBM solution was prepared by dissolving Phenyl-C61-butyric acid methyl ester (PCBM, 6 g, Nano-C) into chlorobenzene with a concentration of 20 mg mL^{-1}, and stirred in glove box under 50 ^oC overnight. Then, the solution was purified by the 200 nm filter to get the pure PCBM solution. The polystyrene (Polystyrene, Mw=12,650,000, American Polymer Standards Corp.) precursor was prepared by dissolving polystyrene into chlorobenzene to obtain a solution with 6 mg mL^{-1}, and was stirring under 60 ^{o}C overnight before using. The PS/PCBM solution was prepared by mixing the pure PCBM solution with the PS precursor at a certain ratio.

Device fabrication and characterization: The perovskite precursor solution was spin-coated at 3000 r.p.m. for 60 s. After drying for more than 10 mins, the as spun films were annealed over 50 mins at 100 °C in the case of $CH_3NH_3PbI_{3-x}Cl_{x.}$ Then, the PCBM electron transport layer was deposited by spin coating at 1500 r.p.m for 60 s and 2000 r.p.m for 5 s. Finally, a 100-nm-thick aluminum layer was deposited by thermal evaporation at a base pressure of 1x10^{-7} mbar. All the process are carried out inside glove box.

The morphologies of the device sample were characterized by a field emission scanning electron microscope (FE-SEM; JEOL 6700F) operated at 5 kV. The surface of device sample were characterized by an atomic force microscope (Veeco diInnova) with a Si tip. Fabricated photovoltaic cells were characterized by open circuit voltage decay measurement, current-voltage (J-V) characteristics and incident photon-to-current conversion efficiency (IPCE). Photocurrent and voltage were measured by a solar simulator (Oriel, 450 W Xe lamp, AM 1.5 global filter) equipped with an electrochemical workstation (Zanher, Zennium). The light source was calibrated to 1 sun (100 mW/cm^2) using an opticalpower meter (Newport, model 1916-C) equipped with a Newport818P thermopile detector. The IPCE measurements were carried out with a Zahner Zennium CIMPS-PCS system established with the tunable light source (TLS). Cyclic voltammetry was carried out on a CH Instruments

Electrochemical Analyzer at a scan rate 100 mV s-^{1}. The oxidation potential of the sensitizers was measured in DMF with TBAPF6 (0.1 M) as electrolyte. The film thickness was determined by a Tencor Alpha-Step 200 surface profiler system. Charge-carrier mobilities (μ) were calculated from the J–V characteristics using the space-charge-limited current (SCLC) method with the Mott-Gurney equation for the current density J_{SCLC} expressed as $J = \frac{9\varepsilon_r\varepsilon_0\mu V^2}{8L^3}$ □, where ε0 is the vacuum permittivity, εr is the dielectric constant of the film (εr = 3 was assumed), and L is the thickness of the active layer.

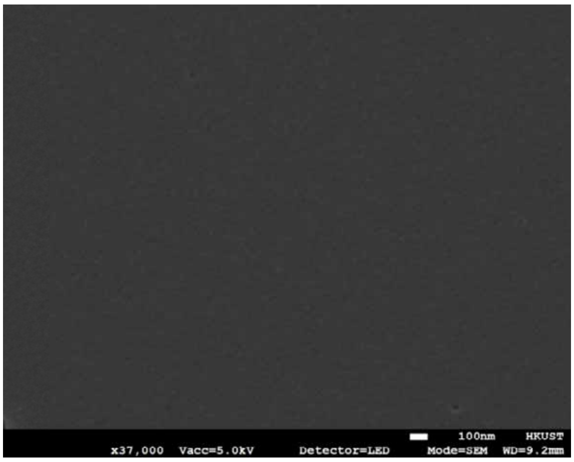

Figure S1 Top-sectional SEM image of NiO NCs/ $CH_3NH_3PbI_{3-x}Cl_x$/PCBM：1.5 wt% PS perovskite solar cell.

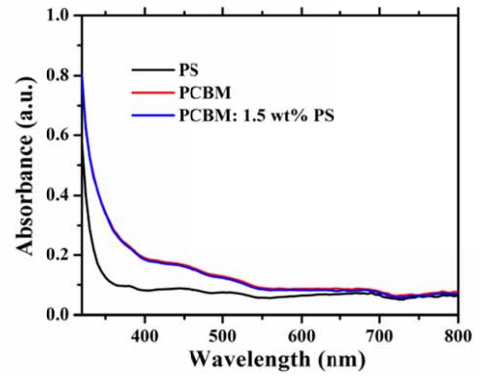

Figure S2 Absorption spectra of PS, PCBM and PCBM: 1.5wt% PS films.

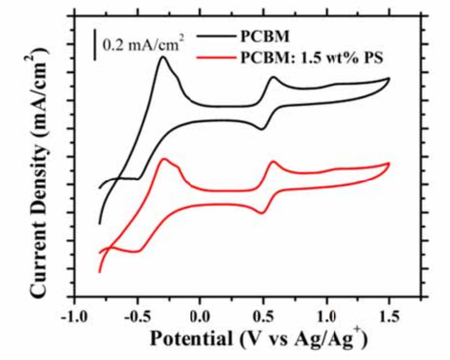

Figure S3 Cyclic voltammograms of PCBM and PCBM: 1.5wt% PS films in acetonitrile with 0.1 mol L^{-1} TBAPF6 at 100 mV s^{-1}.

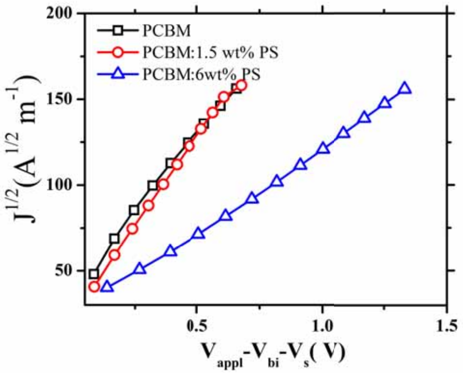

Figure S4 The injection characteristics of the electron-only devices based on the structure of ITO/ZnO/electron transport layer/Ca/Al.

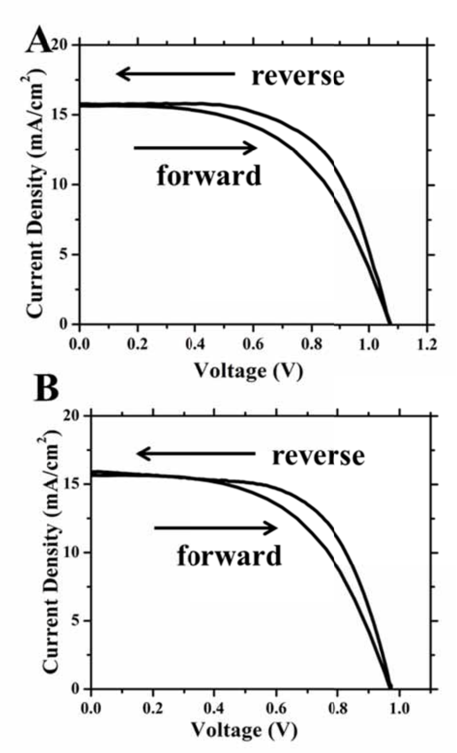

Figure S5 Photocurrent density-voltage (*J-V*) characteristics of PCBM: 1.5wt% PS (A) and pure PCBM (B) perovskite devices, measured with 50 mV/s voltage steps.

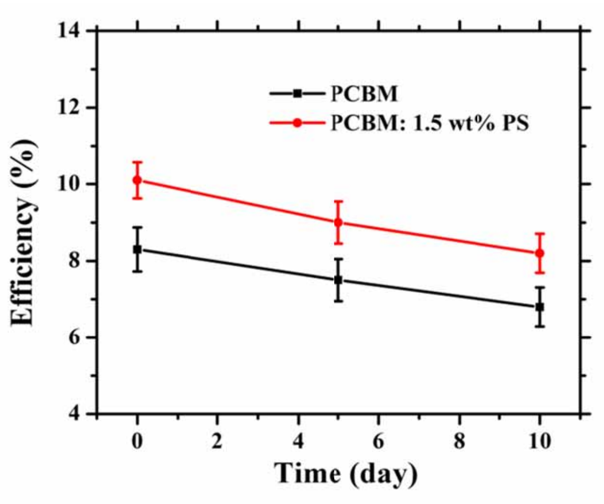

Figure S6 Stability of photovoltaic performance was measured every 5 day under illumination at 100 mW cm^{-2}. The cell was packed with UV glue and tested at room temperature in ambient air with 70% air humidity.

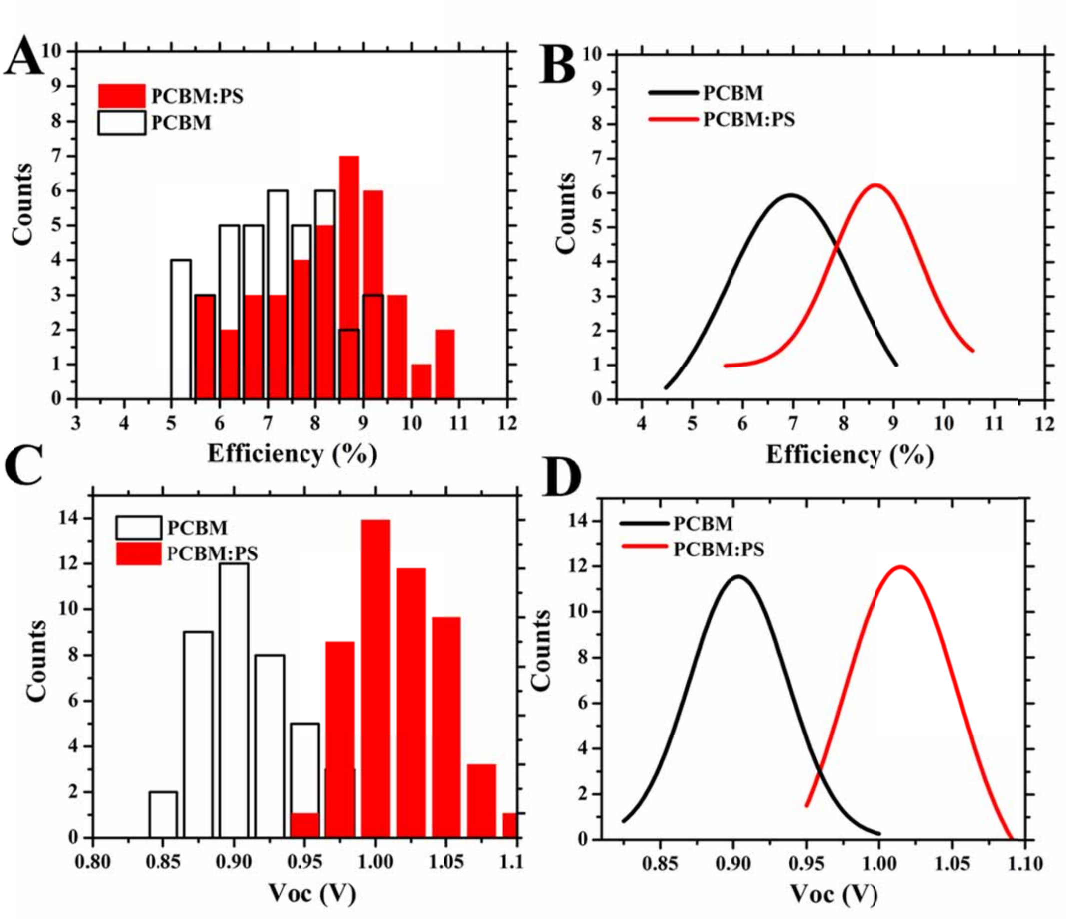

Figure S7 Comparison statistics of the cell performance between PCBM and PCBM:1.5 wt% PS : histograms and the fitted Gaussian distributions of cell efficiency (A, B) and V_{OC} (C, D).

Table S1: The electron mobility of the PCBM, PCBM:1.5wt% and PCBM: 6wt% PS films. The electron only devices for the measurements have a structure of ITO/ZnO/PCBM or composite films/LiF/Al.

	PCBM	PCBM:1.5 wt% PS	PCBM: 6wt% PS
mobility/×10-4 cm2 V-1s-1	12	11	4.6
Thickness (nm)	49	45	53

Table S2 Average and best device performance parameters of solar cells based on different PCBM composite electron transport layers.

HTMs used in devices		V_{OC} (V)	J_{SC} (mA/cm^2)	*FF*	PCE (%)
Pure PCBM	Average	0.90±0.05	14.11±1.46	0.58±0.03	7.26±1.60
	highest	0.99	16.13	0.64	NA
PCBM:1.5 wt%PS	Average	1.01±0.06	13.95±1.97	0.60±0.03	8.39±1.73
	highest	1.08	15.86	0.65	NA
PCBM:6.0 wt% PS	Average	0.79±0.07	9.21±1.70	0.58±0.03	4.22±1.50
	highest	0.90	10.90	0.63	NA

Table S3 Parameters of the best performing solar cells based on different PCBM composite electron transport layers

HTMs used in devices	Scan Direction	V_{OC} (V)	J_{SC} (mA/cm^2)	*FF*	PCE (%)
Pure PCBM	Reverse	0.97	15.91	0.62	9.56
	Forward	0.97	15.89	0.57	8.78
PCBM: 1.5 wt%PS	Reverse	1.07	15.62	0.64	10.68
	Forward	1.07	15.60	0.59	9.84

Reference

1. Zhu, Z., Bai, Y., Lee, H. K. H., Mu, C., Zhang, T., Zhang, L., Wang, J., Yan, H., So, S. K. and Yang, S. (2014), Polyfluorene Derivatives are High-Performance Organic Hole-Transporting Materials for Inorganic−Organic Hybrid Perovskite Solar Cells. Adv. Funct. Mater.. doi: 10.1002/adfm.201401557.