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Harnessing Solar Energy with NH_4Cl-doped Hole Transport Layer in Inverted Perovskite Solar Cells

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Experimental Section

Methods and Materials

The aqueous solution of PEDOT: PSS (Clevios PVP Al 4083) with a concentration of 1.3-1.7 by weight ratio of 6 from PSS to PEDOT is purchased from Heraeus (Germany). FTO glass (15Ω/sq) was purchased from Nippon Glass. 2,9 Dimethyl-4,7 Diphenyl-1,10-phenanthroline (BCP) with a purity of 99.8% was obtained from Aladdin, and PCBM (>99%) was obtained from Xi'an polymer Light Technology Corp. NH_4Cl was purchased from Tianjin Dingshengxin chemical industry co., Ltd. The rest of all reagents were obtained from Sigma Aldrich.

Preparation of Perovskite Precursor Solution

Lead acetate (Pb $(Ac)_2$. $3H_2O$ Sigma Aldrich) was converted into Pb $(Ac)_2$ powder by dehydration at 80°C by nitrogen flow. The stock solutions were then prepared by mixing 0.02 mol of Pb $(Ac)_2$ and 0.01 mole of MAI (Lumtech) dissolved in 1 mole of anhydrous DMF. The as-prepared precursor solution was stirred overnight.

Device Fabrication. The devices were fabricated with the construction of FTO/NH_4Cl-PEDOT: PSS/Perovskite/PCBM//BCP/Ag. The Fluorine-doped tin oxide (FTO) coated glass was patterned and etched with Zn powder under the influence of diluted HCl in distilled water. The etched FTO glass was cleaned ultrasonically with detergent (KOH saturated solution in isopropanol), acetone, water, deionized water and isopropanol and then dried with clean, dry N_2. The pre-clean FTO glass was further treated with ozone ultraviolet (UVO) for 15 min and then cooled at room temperature. Ammonium chloride was directly mixed into PEDOT: PSS solution with a desirable concentration of (2mg, 5mg, 10mg, 20, and 50 mg, respectively). The as-prepared solution was sonicated for 45 minutes and then spun coat on the patterned FTO glass at 4000 rpm for 40 seconds. After spin coating, the substrate was heated for 15 mint at 135°C in air, and the sample was then transferred into N_2 filled glovebox under optimized conditions

(<1.0 ppm of O_2 and H_2O). The perovskite solution was spin coat on the surface of NH_4Cl-PEDOT: PSS film at 2000 rpm and annealed for 5 min at 100^oC. After that, PCBM with a concentration of (20 mg/ml in chlorobenzene) was spin-coated on the top of the perovskite layer by spin coating at 2500 rpm for 30 s. To improve the Ohmic contact of the BCP layer (0.5 mg/ml in ethyl alcohols) was pasted on the surface of PCBM at 3500 rpm for 30 sec. Finally, a shadow mask was finished by evaporation of Ag deposition in a thermal evaporator chamber at approximately 1 x 10-6 torr. The active area of the device was defined as about 0.1 cm^2.

Device Characterization. A computer-controlled Keithley 2612A was used under simulated AM 1.5G irradiation (100mW/cm^2) with a combined solar simulator unit (SAN-Ei, 3A, 1150 W) to measure the current density vs. voltage (J-V) curves of both forward and reverse scan. The lamp was turned on 15 min before measurement, and silicon reference cell NREL traceable KG5 filtered was used to calibrate precise light intensity. External quantum efficiency (EQE) was measured using a QEX10 photo response system (PV Measurement Inc.). To investigate the structure and morphology of the devices were characterized by using X-ray diffraction (XRD, D8-Advance, Bruker Germany) using Cu Kα radiation (λ = 1.5406 Å) and Quanta FEG250 field emission scanning electron microscope, respectively. The film morphology was characterized by scanning electron microscope (SEM, QUANTA FEG250). The surface roughness of NH_4Cl: PEDOT-PSS film was measured using atomic force microscopy (AFM, MFP-3D-Stand Alone, Asylum Research). Absorption and transmission spectra were measured with a Shimadzu UV-3600 spectrometer. The photoluminescence was measured by using an FLS920 fluorescence spectrometer (Edinburgh instrument. The conductivity of HTL film was measured by using four points probes method.

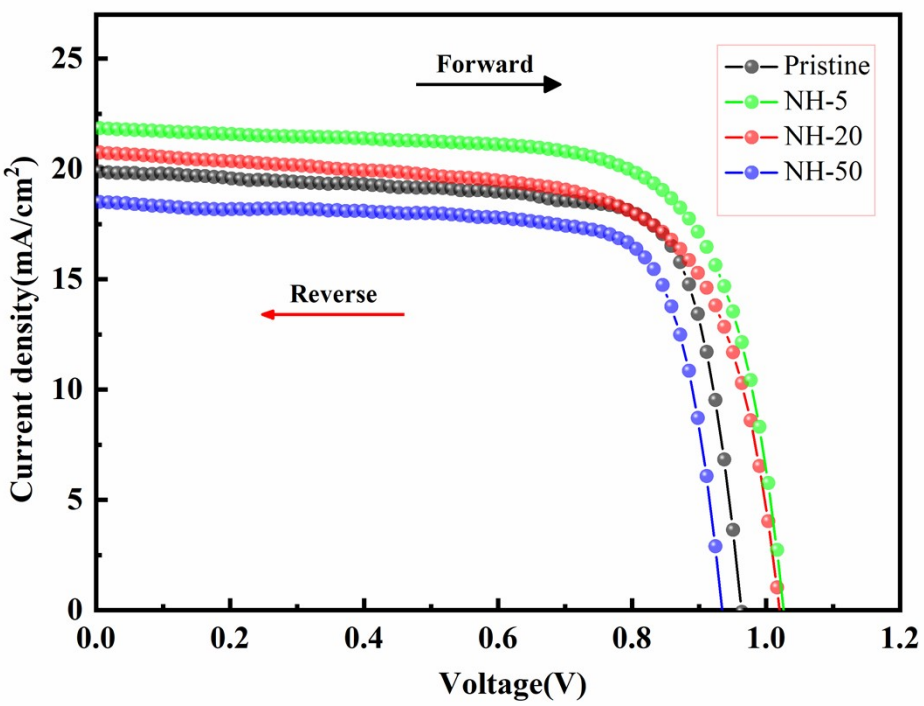

Figure S1. Typical J-V curves of the PSCs based pristine and various concentration of NH_4Cl-doped PEDOT: PSS.

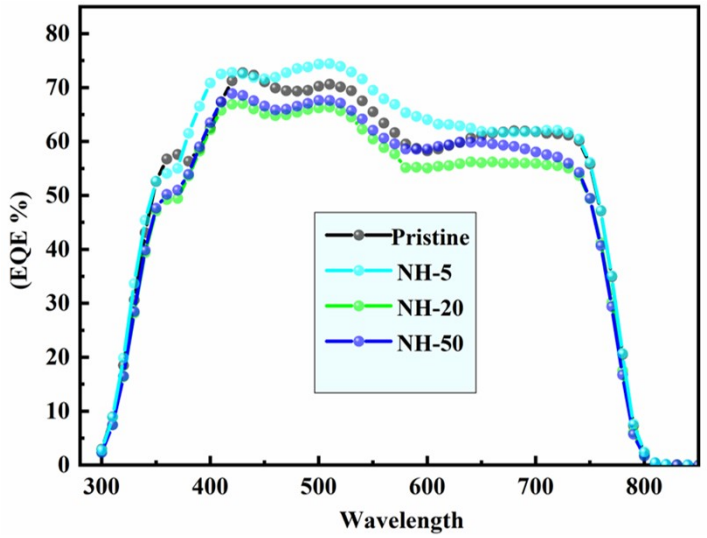

Figure S2. EQE spectra of the pristine and various concentration of NH_4Cl-doped PEDOT: PSS.

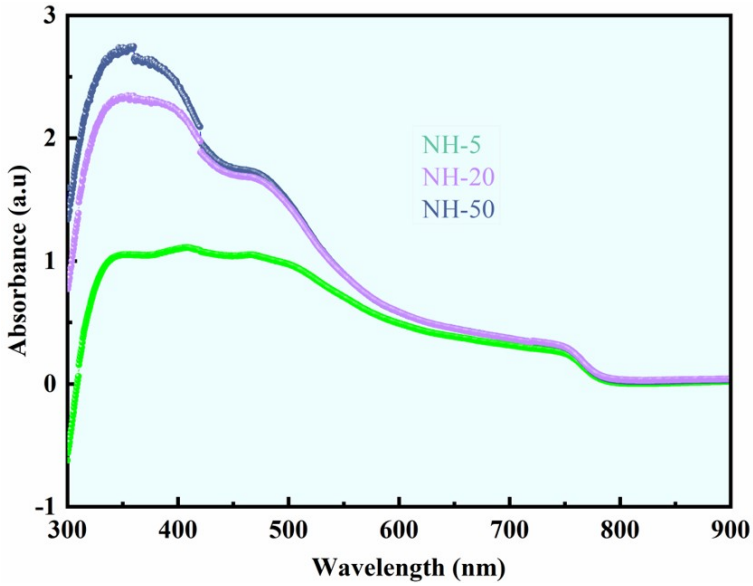

Figure S3. UV-visible absorbance spectra of the pristine and various concentration of NH_4Cl-doped PEDOT: PSS.

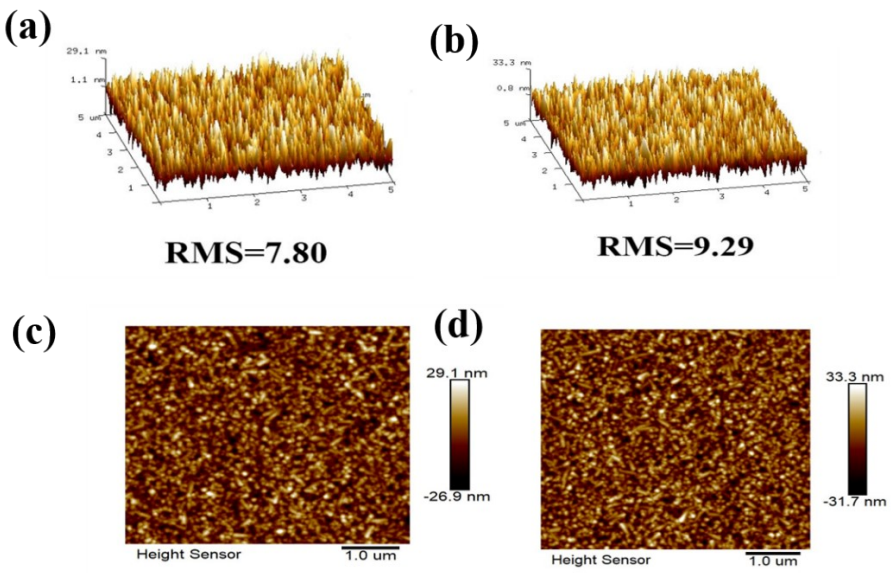

Figure S4: AFM topography of (a, c) Pristine, and b, d) NH_4Cl-5 doped PEDOT

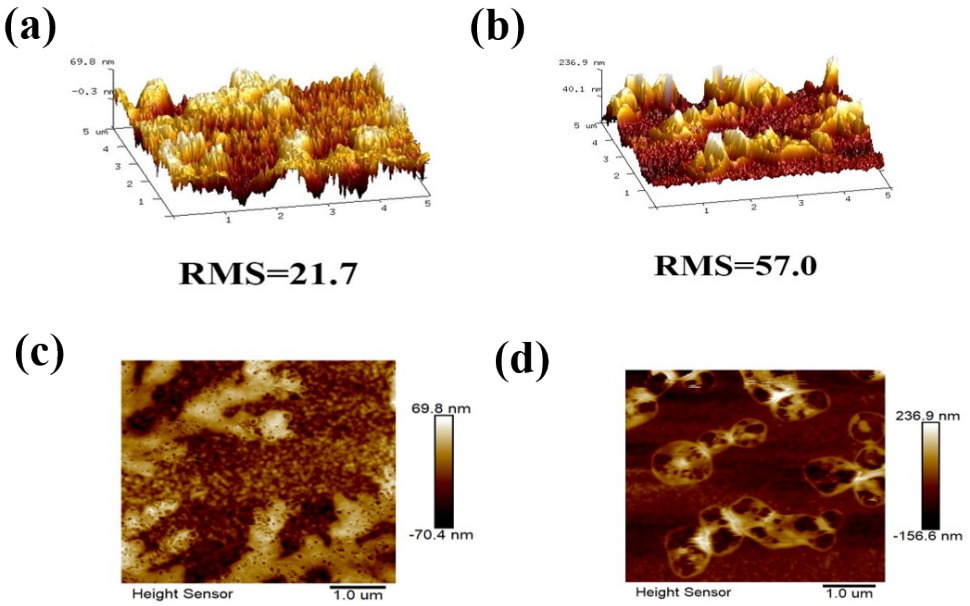

Figure S5: AFM topography of (a, c) NH_4Cl-20, and b, d) NH_4Cl-50 doped PEDOT: PSS

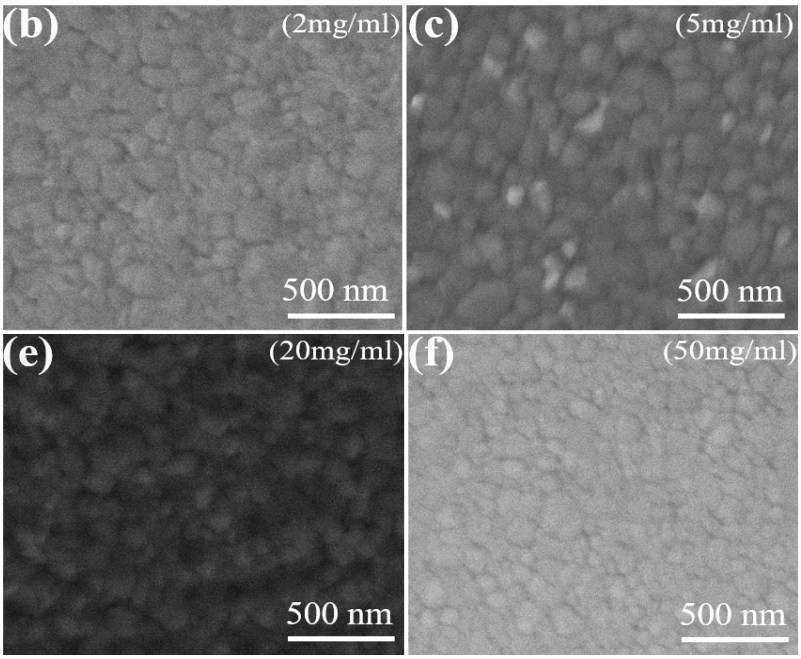

Figure S6: SEM images of perovskite films deposited on, (a) NH_4Cl-2, b) NH_4Cl-5, c) NH_4Cl-20, and d) NH_4Cl-50 PEDOT: PSS

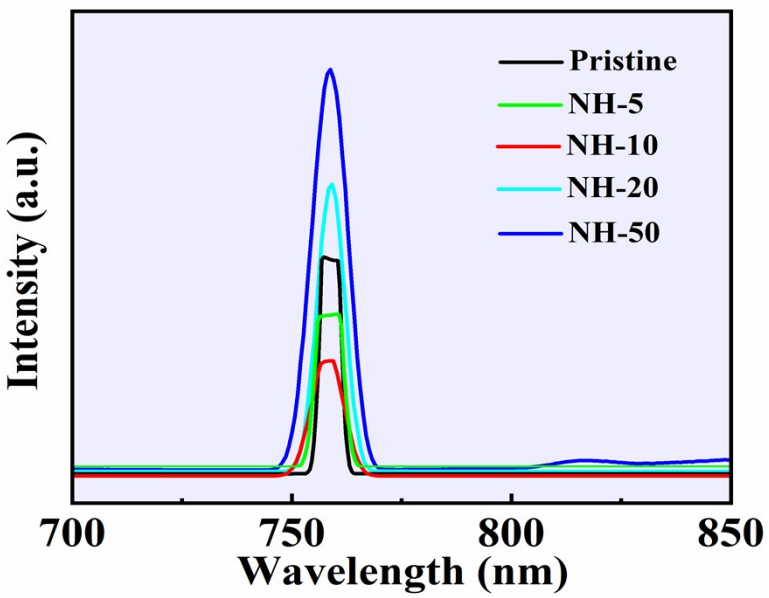

Figure S7: PL spectra of different NH_4Cl doped concentrations.

Table 1. Details of RMS roughness, sheet resistance and conductivity of the various NH_4Cl-doped PEDOT: PSS

NH_4Cl doped PEDOT: PSS	**Roughness (nm)**	**Sheet resistance (ohm/cm)**	**Conductivity (S/cm)**
Pristine	7.98	7.803	$5.3*10^{-4}$
NH-2 (2mg/ml)	8.59	8.503	$6.25*10^{-4}$
NH-5 (5mg/ml)	9.29	9.209	$2.11*10^{-3}$
NH-10 (10mg/ml)	15.0	15.035	$1.39*10^{-3}$
NH-20 (20mg/ml)	21.7	21.073	$7.20*10^{-4}$
NH-50 (50mg/ml)	57.0	57.031	$9.25*10^{-4}$

Table 2. The overall photovoltaic parameters of the inverted PSCs doped with various concentrations of NH_4Cl PEDOT: PSS.

PSCs	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
Control	0.96/0.96	19.5/19.2	75.7/78.4	14.3/14.2
NH-2	0.98/0.97	19.9/20.01	76.5/7316	15.0/15.4
NH-5	0.99/0.98	21.3/21.4	77.3/71.14	16.3/16.1
NH-10	1.02/1.01	26.4/26.9	79.7/70.5	17.5/17.1
NH-20	0.95/0.94	17.3/16.7	71.3/74.20	12.3/11.9
NH-50	0.94/0.93	17.1/17.09	69.4/65.5	11.1/ 10.2