Hole-conductor-free planar perovskite solar cells with 16.0 % efficiency

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Experimental Section

Materials: Methylammonium iodide (CH₃NH₃I) was synthesized by the reaction of methylamine with hydroiodic acid as previously reported.3 ITO coated glass substrates was obtained from Huayulianhe Co., Ltd. Its sheet resistance and ITO thickness are 8 Ω /sq and 180 nm, respectively. PbI₂ (99.9985%), C₆₀ (99.9%) and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) (99.9%) were purchased from H. C. Stark Company, Alfa Aesar, Puyang Yongxin Fullerene Technology Co., Ltd and Xi'an Polymer Light Technology Corp. (PLT), respectively. All materials were used without any further purification.

Device Fabrication: The ITO coated glass substrate was cleaned sequentially in detergent, deionized water, acetone and isopropyl alcohol in an ultrasonic bath for 20 min, respectively. A 10 min ultraviolet-ozone treatment was further carried out for the ITO to improve its work function. A 10 nm hole conductor of NiO_x was deposited by spin-coating at 3000 rpm for 60 s using a nickel acetate precursor solution31 which was filtered through a 0.22 μ m filter before use. The CH₃NH₃I solution (40 wt %) was prepared by mixing the synthesized CH₃NH₃I and PbI₂ (1:1 molar ratio) in anhydrous N,N-dimethylformamide (DMF) by stirring at 70 °C for 1 hour to produce a clear precursor solution. After cooling to room temperature, the perovskite precursor solution was dropped onto the corresponding substrate. After the substrate was spun at 6000 rpm for 4.5 s, a 200 μ L anhydrous chlorobenzene was quickly dropped onto the center of the substrate. Then the substrate continues to spin at 4000 rpm for 60 s without pause. After CH₃NH₃PbI₃ films were annealed at 100 °C for 10 min, C₆₀ (40 nm), BCP (8 nm) and Ag (100 nm) layers were sequentially deposited on the CH₃NH₃PbI₃ film by thermal evaporation under vacuum (10⁻⁶ mbar). The active area of all devices was 0.100 cm².

Characterization: All measurements of photovoltaic performance were performed in glove box. The current-voltage curves of perovskite solar cells were measured with a Keithley 4200 Semiconductor Characterization System (scan speed 300 mV/s). The solar cells were illuminated using an Oriel 300 W solar simulator (Thermo Oriel 91160-1000) as an excitation source (100 mW/cm2 white light illumination under AM 1.5G conditions). The incident-phototo-current conversion efficiency was recorded on a Keithley 2400 source meter under an irradiation of a 150 W tungsten lamp with a 1/4 m monochromator (Spectral Product DK 240). Scanning electron microscope (SEM) and atomic force microscope (AFM) images of ITO, NiO_x film and CH3NH3PbI3 film were collected on a Hitachi S-4800 and SPI3800/SPA400 SPM (Seiko Instrument Inc), respectively. The thickness of the thin films was measured with a KLA-Tencor Alpha-Step Surface Profiler. Steady-state PL measurements were taken using a steady state spectrometer (FLS920, Edinburgh Instruments Ltd.). The femtosecond timeresolved fluorescence spectra were recorded by a high resolution streak camera system (Hamamatsu C10910). Work functions were determined by photoelectron spectroscopy (Rikken Keiki AC-2).





Fig. S1. Photoelectron spectra. (a) ITO without UVO treatment. (b) ITO with 10 min UVO

treatment. (c) NiO_x. (d) MAPbI_{3.}



Fig. S2. The current density-voltage (*J-V*) curves of the planar heterojunction hole-conductorfree perovskite solar cells based on the treated-ITO (black) and untreated-ITO (red) under a simulated AM 1.5G solar irradiation at 100 mW cm⁻².



Fig. S3. Scan rate effects and steady output. (a) J-V curves obtained at different scanning rates from 100 mV/s to 500 mV/s. (b) The steady photocurrent output measured under different bias potentials and continuous light illumination.



Fig. S4. Stability study of the hole-conductor-free perovskite solar cell stored in a glove box $(H_2O < 0.01 \text{ ppm}, O_2 < 50.00 \text{ ppm}).$



Fig. S5. The stability comparison of the unpackaged devices without a hole conductor (green) and with NiO_x (red) hole conductor in ambient air, respectively.