Supporting Information

Enhanced Crystallization by Polystyrene towards High Performance Perovskite Solar Cells

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Experimental Section

Materials

Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) and [6.6]-phenyl-C\textsubscript{60}-butyric acid methyl ester (PC\textsubscript{60}BM) was purchased from HC Stark Clevious and Nano-C.

Perovskite solution preparation

Methyl-ammonium Iodide (CH\textsubscript{3}NH\textsubscript{3}I) was purchased from Lumtec and Lead Iodide (II) (PbI\textsubscript{2}), Dimethyl Sulfoxide (DMSO), \(\gamma\)-butyrolactone (GBL) was purchased from Sigma-Aldrich. For fabricating 45 wt% CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} solutions, solute mixed CH\textsubscript{3}NH\textsubscript{3}I and PbI\textsubscript{2} (1:1 ratio by weight) was dissolved in DMSO and GBL (3:7 molar ratio) mixed solvents. The solutions were stirred at 70 °C temperatures at least 6 hours. And then, the solution was filtered through a 0.45μm filter before use.

HTL preparation

For deposition of HTL, the PEDOT:PSS was filtered through a 0.45μm PVDF filter.

ETL preparation
For ETL, the PCBM (>99.5%, Sigma Aldrich) was prepared with a 2 wt% PC₆₀BM in chlorobenzene (Anhydrous, Sigma Aldrich) and filtered through a 0.45 μm PTFE filter.

**Devices fabrication**

Indium tin oxide (ITO) glass (9 Ω/sq.) substrates were patterned in our laboratory (25 mm × 25 mm, length × width). The substrates were cleaned with a sonicator in acetone, methanol and isopropyl-alcohol (IPA) for 20 mins each before rinsed with deionized water (DI-water) and N₂ blowing. Cleaned ITO substrates were and later treated by a UV-ozone (Model:42, Jetlight, USA) for 15 mins. The PEDOT:PSS as HTL was spin coated at 4000 rpm for 30 sec on the ITO substrate, and annealed at 135 °C for 20 mins on a hot plate inside the N₂ glove box. Next, the CH₃NH₃PbI₃ solution was spin coated at 4000 rpm for 60s on the PEDOT:PSS/ITO substrate. We dropped toluene after 25 sec to eliminate residue solvent, DMSO and to promote good perovskite grain growth. Later, the films were annealed at 100 °C for 2 hrs on a hot plate in air condition. PC₆₀BM as ETL was spin coated at 2000 rpm for 40 sec on the CH₃NH₃PbI₃/PEDOT:PSS/ITO. To complete the fabrication procedure, a 100-nm-thick Al layer was deposited by thermal evaporation at a base pressure of 1 × 10⁻⁷ Torr through a shadow mask. All our fabricated devices had 0.04 cm² active area. All devices were encapsulated prior to any electrical measurements.
Figure 1. Device structure, energy level diagrams of complete perovskite solar cell, and materials properties. (a) Schematic design of complete perovskite solar cell (ITO/PEDOT:PSS/CH$_3$NH$_3$PbI$_3$(with or without polystyrene(PS))/PC$_{60}$BM/Al), (b) diagram of energy levels of each layers in the device.

**Time-Resolved Photoluminescence**

The time-resolved PL experiments were performed with a spectrophotometer (Gilden Photonics) using a pulsed source at 460 nm (Ps diode lasers BDS-SM, pulse with < 100 ps, from Photonic Solutions, approx. 1mW power, 20MHz repetition rate, approx. 500 um spot radius) and the signal was recorded at 770 nm by the Time Correlated Single Photon Counting detection technique with a time resolution of 1 ns. A monoexponential and bi-exponential fitting were used to analyse the background-corrected PL decay signal.

**Current-Density Characteristics**

The performance of the perovskite solar cells was obtained from J-V characteristics measured using a Keithley 2400 LV source meter. Solar cell performance was measured using a solar simulator, with an Air Mass 1.5 Global (AM 1.5 G) and had an irradiation intensity of 100 mW cm$^{-2}$. All measurements were carried out at room temperature, under a relative humidity of 40%.
**External Quantum Efficiency**

The EQE measurements were performed using the EQE system (Model 74000) obtained from Newport Oriel Instruments USA and HAMAMATSU calibrated silicon cell photodiodes as a reference diode. The wavelength was controlled with a monochromator of 200-1600 nm.

**Stability**

Stability measurements were carried out with a periodically exposure to AM1.5G conditions, 100 mW m\(^{-2}\) and the J-V characteristics were recorded every day up to 10 days according to the ISOS-L-1 procedure.\(^{26}\)

**Atomic Force Microscope**

The surface morphology of the thin films was obtained by tapping mode using an atomic force microscope (AFM, Digital Instrument Multimode equipped with a nanoscope IIIa controller).

**X-ray Diffraction**

The X-ray diffraction (XRD) analysis was performed using a XRD Diffractometer X’Pert PRO with Cu K\(\alpha\) targets (\(\lambda=0.154\) nm) at a scanning rate of 2°/min and an operating voltage of 40 kV with a current of 100 mA.

**Scanning Electron Microscope**

For SEM, the scanning was conducted using a SEM, Hitachi S-4700. The film thickness was measured using a Dektak AlphaStep Profiler.

**Absorption**
The ultraviolet visible (UV-vis) spectroscopy data at ambient temperature was recorded using a UVS-2100 SCINCO spectrophotometer.

**Dewetting**

The measurements were conducted using Owens–Wendt–Rabel–Kaelbe (OWRK) microscope.

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Fig. S1. Leakage current of perovskite solar cells with and without polystyrene.
Fig. S2. $J_{SC}$ as a function of PS composition for four solar cells.
**Fig. S3.** Performance parameters of CH$_3$NH$_3$PbI$_3$ perovskite solar cells with different PS concentrations (a-d) Histograms of the perovskite solar cells parameters obtained from 48 tested devices of the different concentrations of PS: (a) $J_{SC}$, (b) $V_{OC}$, (c) FF, and (d) PCE.
Fig. S4. Stacked XRD patterns of CH$_3$NH$_3$PbI$_3$ with different concentrations of polystyrene.