

Enhancing Performance of SnO₂-Based Perovskite Solar Cells by Introducing Hydroxyethylpiperazine Ethane Sulfonic Acid for Interfacial Adjustment

*Putao Zhang, Yiming Chen, Shenghan Wu, Xiaohui Li, Meiyue Liu, Shengjun Li**

Key Laboratory of Photovoltaic Materials, Henan University, Kaifeng, Henan, 475004, China

* Corresponding author E-mail: lishengjun@henu.edu.cn

Experimental Section

Materials.

SnO₂-colloid precursor (Tin (IV) oxide, 15% in H₂O colloidal dispersion) and HEPES were purchased from Alfa Aesar. Dimethyl sulfoxide (DMSO, 99%), lithium bis (trifluoromethanesulfonyl) imide (Li-TFSI, 99%), 4-tert-butylpyridine (TBP, 96%), and 2, 20, 7, 70-tetrakis (N, N-di-p-methoxy-pheny-lamine)-9, 90-spirobifluorene (Spiro-MeOTAD) were purchased from Xi'an Polymer Light Technology Corp. N, N-dimethylformamide (DMF, 99.5%) and chlorobenzene (CB, 99.5%) were obtained from Sigma-Aldrich. Lead iodide (PbI₂), methylammonium iodide (MAI) were purchased from Preferred technology. All of the other salts and solvents were used without further purification if no special statement was presented.

Device Fabrication.

ITO conductive glass was ultrasonically cleaned in detergent, alcohol, acetone, IPA and deionized water for 10 minutes respectively, and blow dry with air. Before use, the washed conductive glass were treated with plasma for 10 minutes. Afterwards, A mixture of SnO₂ and deionized water with a volume ratio of 2:1 was spin-coated onto the ITO substrates at 6500 rpm for 10 s, and annealing at 150 °C for 30 min. And then soaked it in an aqueous solution of 0.1 M HEPES. The perovskite layer was prepared in a glove box, and the perovskite precursor solution was prepared by mixing PbI₂ (1 M) and CH₃NH₃I (1 M) in DMF/DMSO (volume ratio 7:3). The MAPbI₃ films were deposited onto the SnO₂ substrates via a two-step spin-coating procedure, prespun for 10 s at 500 rpm and spun for 30 s at 4000 rpm. During which 500 μL chlorobenzene was quickly added onto the spinning substrate at 10 s before the end of this process. Next, the as-prepared films annealed at 60 °C for 5 min and continued to anneal at 100 °C for 10 min. The hole-transport layer (HTL) was prepared by spin-coating a Spiro-OMeTAD solution on top of MAPbI₃ films (72.3 mg Spiro-OMeTAD, 18.5 μL bis (trifluoromethane) sulfonimide lithium (Li-TFSI, 520 mg mL⁻¹ in acetonitrile), 29 μL 4-tert-butylpyridine (TBP) in 1 mL of chlorobenzene). Finally, 100 nm thick Ag layer was thermally evaporated at a rate of about 0.5 Å s⁻¹ to complete the device fabrication.

Characterization.

The photovoltaic device performances were tested by using 1.5 G illuminations (100 mW cm⁻²) with a solar simulator (Newport, 94043A-S, The United States)

equipped with a 300 W xenon lamp and a Keithley 2400 source meter. Monochromatic incident photon-to-electron conversion efficiency were evaluated by using Crown Technology IPCE measurement system (500ADX, The United States). The optical absorption spectra of the perovskite films and transmission spectra of the SnO₂ ETL films were measured by using a ultraviolet-visible spectrophotometer ((UV-vis) Cary 5000, The United States). The surface morphology of perovskite films were characterized by using Scanning ElectronMicroscopy (SEM, JSM-7001F, Japan). Moreover, for SCLC mobility, device structure of ITO/ETL/Perovskite/PCBM/Ag was used to evaluate the electron mobility of ETLs. The XRD patterns of the samples were obtained by using X-ray diffraction (XRD, DX-2700, China), which to characterize crystal structure of the perovskite. For TPV and TPC measurements, the samples were serially connected to a digital oscilloscope, respectively, to form the open- and short-circuit conditions, respectively, for monitoring the charge density decay and charge extraction time. The FTIR spectra were recorded with a VERTEX 70 Infrared Fourier transform microscope (Bruker Co., Germany). Steady-state PL and Time resolved PL were measured by Fluorescence Spectrophotometer (FLS980E, Unite Kingdom) with the excitation provided by a 470 nm diode laser.

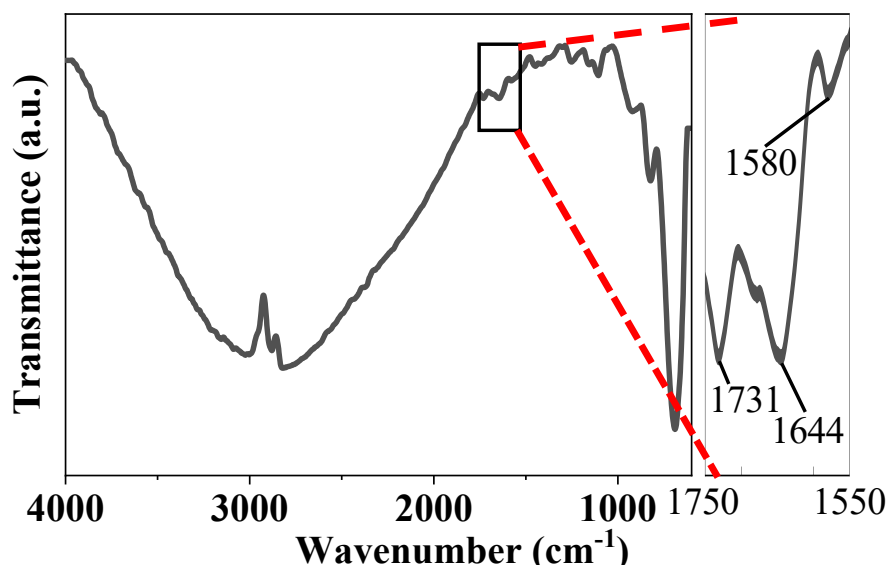


Figure S1. Fourier transform infrared spectra of fresh SnO₂ film treated by plasma.

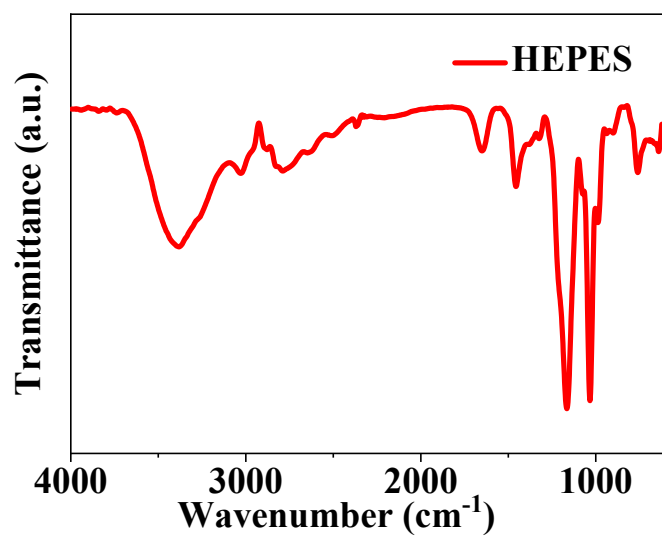


Figure S2. Fourier transform infrared spectra of HEPES.

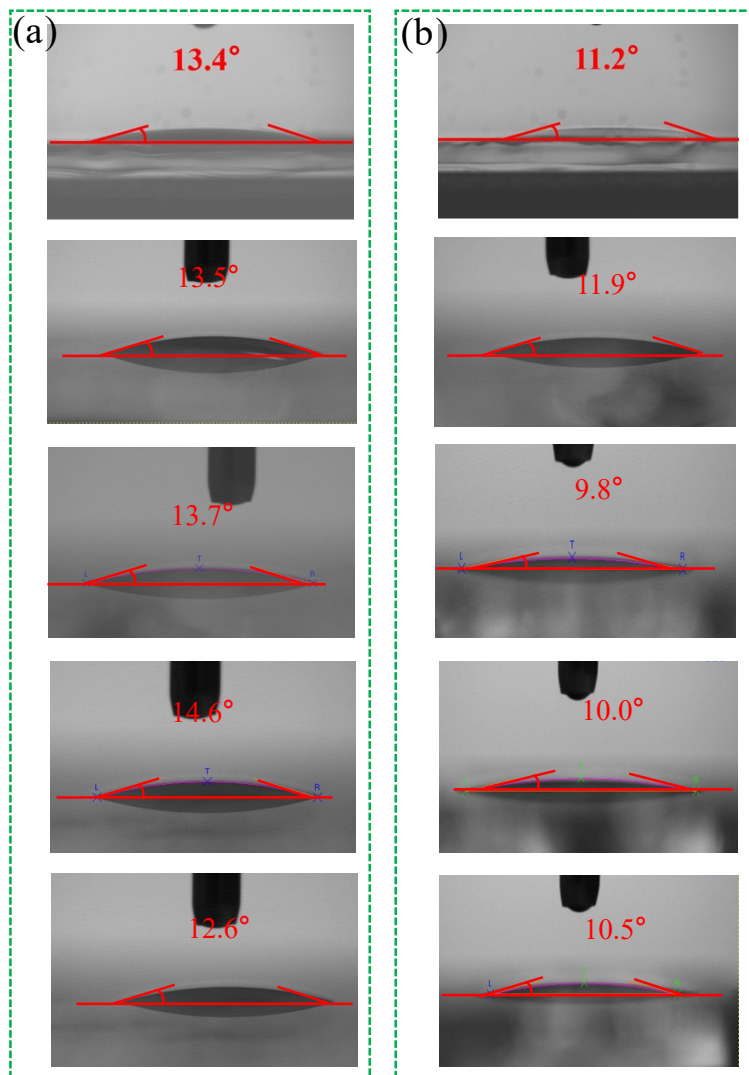


Figure S3. Water contact angles of SnO₂ (a) and SnO₂/HEPES (b) substrates.

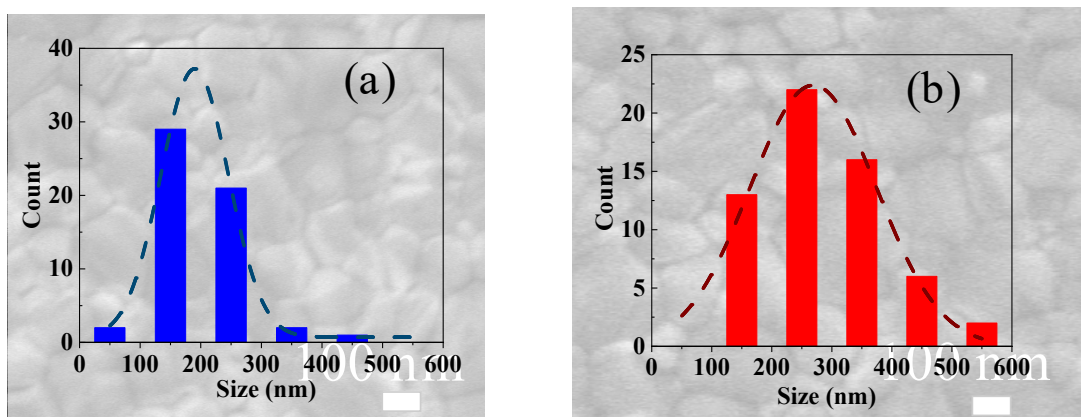


Figure S4. Statistical distribution of perovskite grain size. Perovskite film deposited on SnO₂ (a) and SnO₂/HEPES (b) substrate.

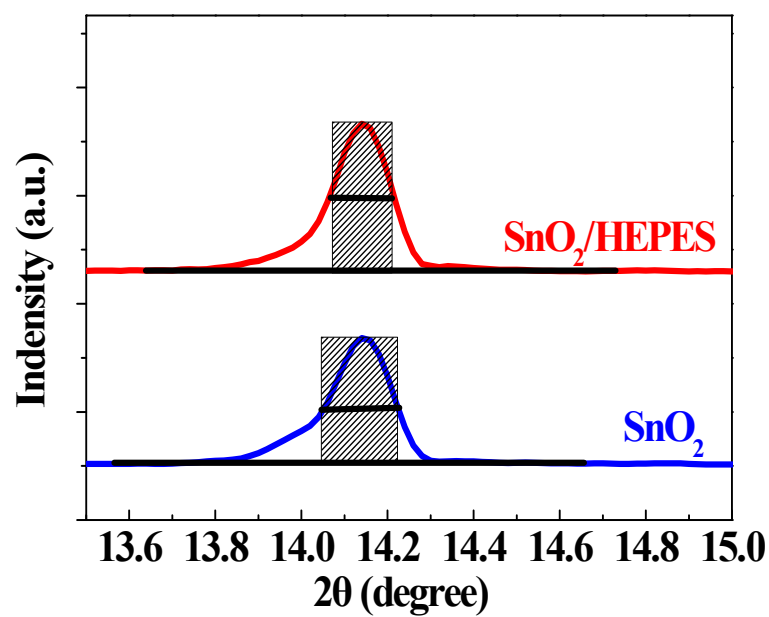


Figure S5. The full width at half maximum (FWHM) of the peak at 14.1° .

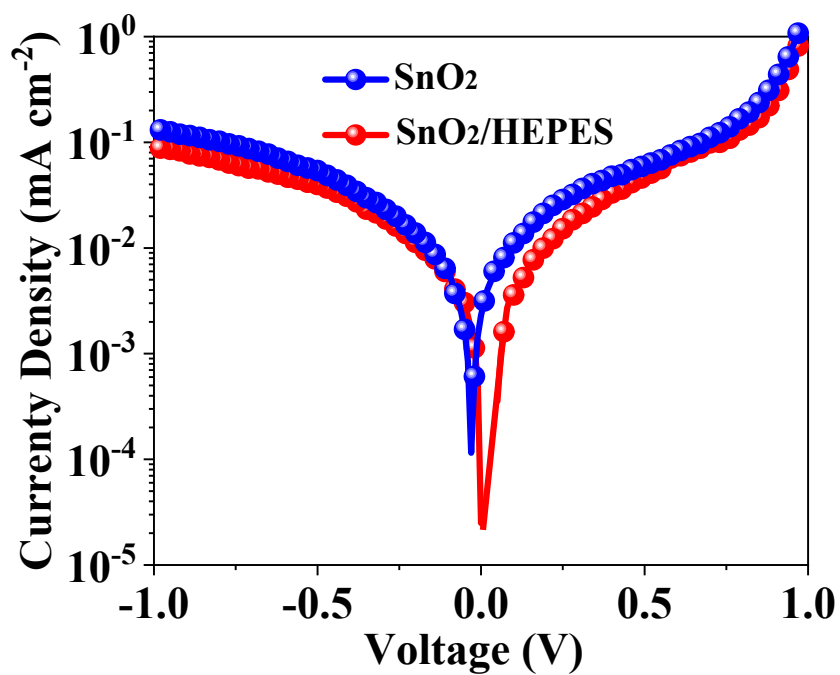


Figure S6. Dark J-V curves of champion PSCs under forward scan.

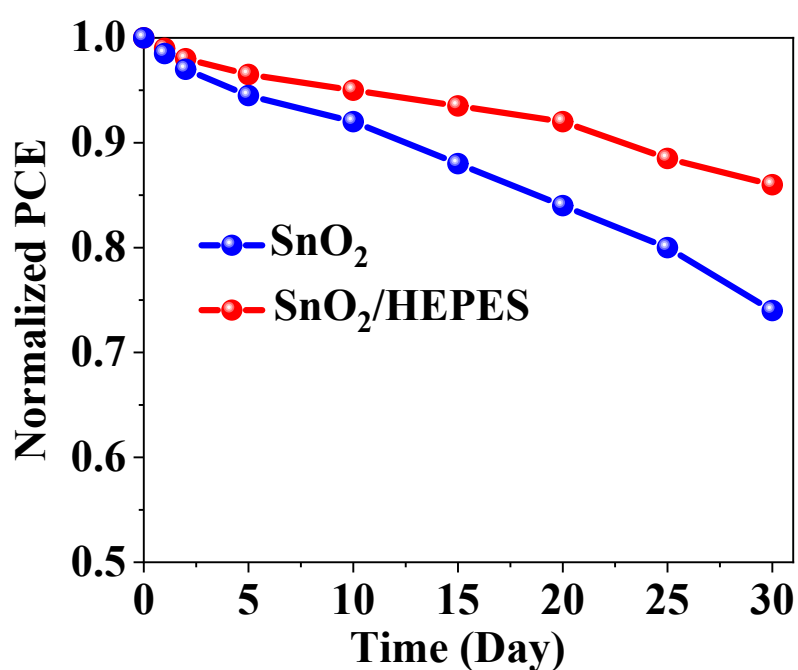


Figure S7. PCE of SnO₂ and SnO₂/HEPES based devices normalized to the initial efficiencies as a function of storage time in ambient environment. (T≈25 °C, RH≈50 %)

Table S1. Fitting parameters extracted from the PL decay traces.

films	τ_1 (ns)	τ_2 (ns)
SnO ₂ /MAPbI ₃	11.93	38.63
SnO ₂ /HEPES/MAPbI ₃	7.86	46.12

Table S2. Summary of the photovoltaic parameters of the PSCs without and with HEPES layer.

ETL	Voc	Jsc	FF	PCE
SnO ₂ R	1.063	22.57	76.79	18.43
SnO ₂ F	1.059	22.53	75.41	17.99
SnO ₂ /HEPES R	1.072	23.59	79.86	20.22
SnO ₂ /HEPES F	1.068	23.52	79.12	19.88

Table S3. Fitting parameters used in the equivalent circuit modeling of impedance

spectra of SnO₂ and SnO₂/HEPES based solar cells under dark condition (bias at 0.8 V).

ETL	R _s (Ω)	R _{rec} (Ω)
SnO ₂	43	733
SnO ₂ /HEPES	32	1053