

Supporting Information

Surface treatment via Li-bis-(trifluoromethanesulfonyl) imide to Eliminate the Hysteresis and Enhance the Efficiency of Inverted Perovskite Solar Cells

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Experimental Section

Materials

All the chemicals were purchased and used without further purification. CH₃NH₃I and PbI₂ were purchased from TCI. [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) was obtained from NANO-C, chlorobenzene, Dimethyl sulfoxide (DMSO) and N,N-dimethylformamide (DMF) were supplied from Aldrich. Others are from Sinopharm Group.

NiO_x film fabrication

FTO glass with sheet resistance of 15 Ω/□ was washed with detergent, followed sequentially by ultrasonication with deionized water, isopropyl alcohol and acetone for 10 min, respectively. The preparation of the NiO_x films were prepared according to the previous report.¹ The precursor solution was prepared by dissolving 25.6 mg nickle acetylacetonate in 1 mL ethyl alcohol with 10 uL hydrochloric acid. The solution was stirred for 3 h at 40 °C in a sealed vial before deposition. The precursor solution was deposited on the clean FTO substrates by spin coating at 3000 rpm for 30 s and then the substrates were annealed at 400 °C for 1h in air. For surface treatment, the as-prepared NiO_x films were treated with the Li-TFSI/acetonitrile (20 mg/1 mL) at 3000 rpm for 30 s, followed by annealing at 300 °C for 1h in air.

Perovskite precursor preparation

A 40 wt% $\text{CH}_3\text{NH}_3\text{PbI}_3$ precursor solution was prepared by mixing PbI_2 , $\text{CH}_3\text{NH}_3\text{I}$ and DMSO in DMF with a 1:1:1 molar ratio. The as-prepared precursor solutions were stirred at 60 °C overnight before spin-coating.

Device fabrication

The perovskite precursor solution was spin-coated on the Li-treated NiO_x/FTO and the pristine NiO_x/FTO substrates at 4000 rpm for 30s via a fast deposition crystallization method or heterojunction engineering in a Ar-filled glove box. At the 10th second of the spinning, 300 μL chlorobenzene or 300 μL chlorobenzene dissolving moderate PCBM (1 mg/mL) was dropped. After the perovskite film was annealed at 100 °C for 10 min, a mixture solution of PCBM and chlorobenzene (20 mg mL^{-1}) was spin-coated on the perovskite film at 2000 rpm for 30 s and then the substrate was baked at 80 °C for 10 min. Next, a thin layer of BCP (0.5 mg in 1 mL alcohol) was deposited on the top of PCBM layer. Finally, a 70 nm of silver was deposited by thermal evaporation under a vacuum of $\sim 1 \times 10^{-6}$ Torr. The active area of the device is 0.09 cm^2 .

Perovskite device characterization

Hall effect measurements was conducted with a hall measurement system (LakeShore 7704A) at room temperature in dark using van der Pauw geometry. The topographic images of NiO_x/FTO and Li-treated NiO_x/FTO were characterized by atomic force microscopy (AFM) (SPM-9500J3, Shimadzu, Japan). The cross-sectional image of the PSC with Li-

TFSI treatment and the top morphologies of perovskite layer on different substrates were observed by a field emission scanning electron microscope (FESEM) (JSM 6700F, Japan). The current density-voltage (J-V) curves of the PSCs were measured on a CHI 660D electrochemical workstation (Shanghai Chenhua Instruments, China) with a standard ABET Sun 2000 Solar Simulator. A standard silicon solar cell was used to calibrate the light intensity. The external quantum efficiency (EQE) was conducted by a QE/IPCE system (Enli Technology Co. Ltd. China) in the range of 300~800 nm wavelength. Ultraviolet-visible transmittance and absorbance spectra were measured by an ultraviolet-visible (UV-vis) spectrophotometer (CARY5000, Varian, Australia). Steady-state photoluminescence (PL) spectra were measured by a FLS980 Spectrometer-Edinburgh Instruments. The excitation wavelength was 488 nm. The electrochemical impedance spectra (EIS) were conducted on a CHI 660D electrochemical workstation (Shanghai Chenhua Instruments, China) over a frequency range of 1 MHz ~ 1 Hz applied at 0 bias in the dark. The obtained spectra were fitted with ZView software. The kinetic energy spectra of the NiO_x films with and without Li-TFSI treatment were characterized by an ultraviolet photoelectron spectroscopy (UPS) system (Thermo Scientific, Escalate 250Xi). The crystallinity of perovskite films was examined by an X-ray diffraction (XRD) (D8 Advance, Bruker AXS, Germany).

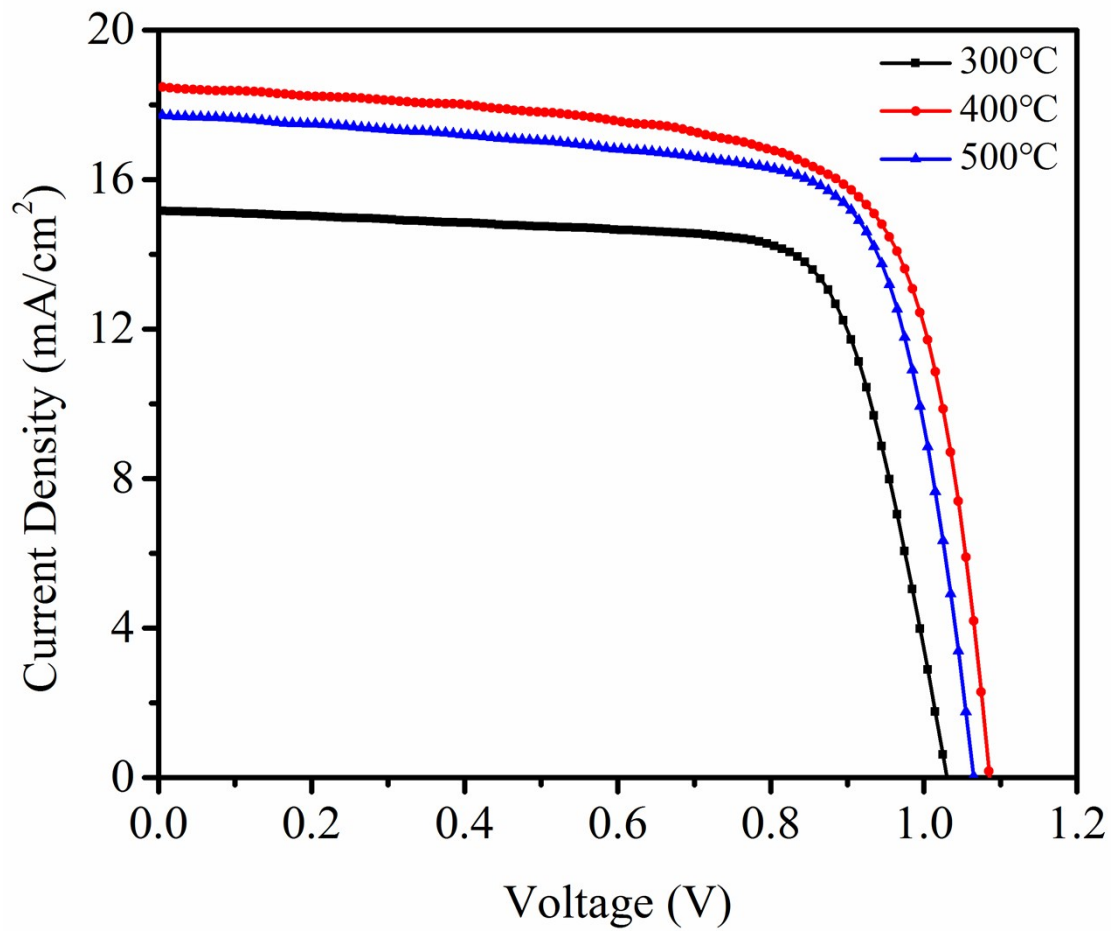


Fig. S1 The J-V curves of the perovskite solar cells (PSCs) based on the NiO_x hole transport layer (HTL) with different annealing temperature.

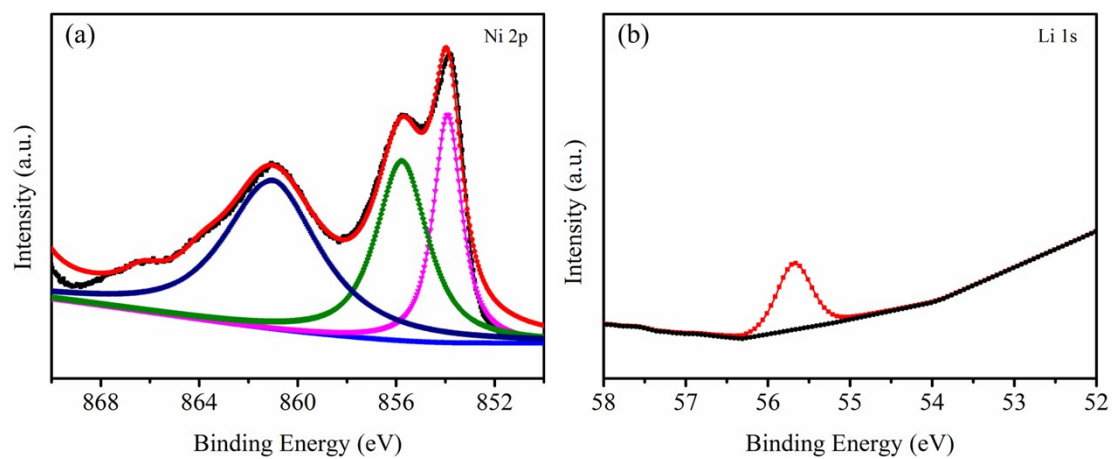


Fig. S2 XPS spectra of (a) Ni 2p and (b) Li 1s peaks for Li-treated NiO_x film.

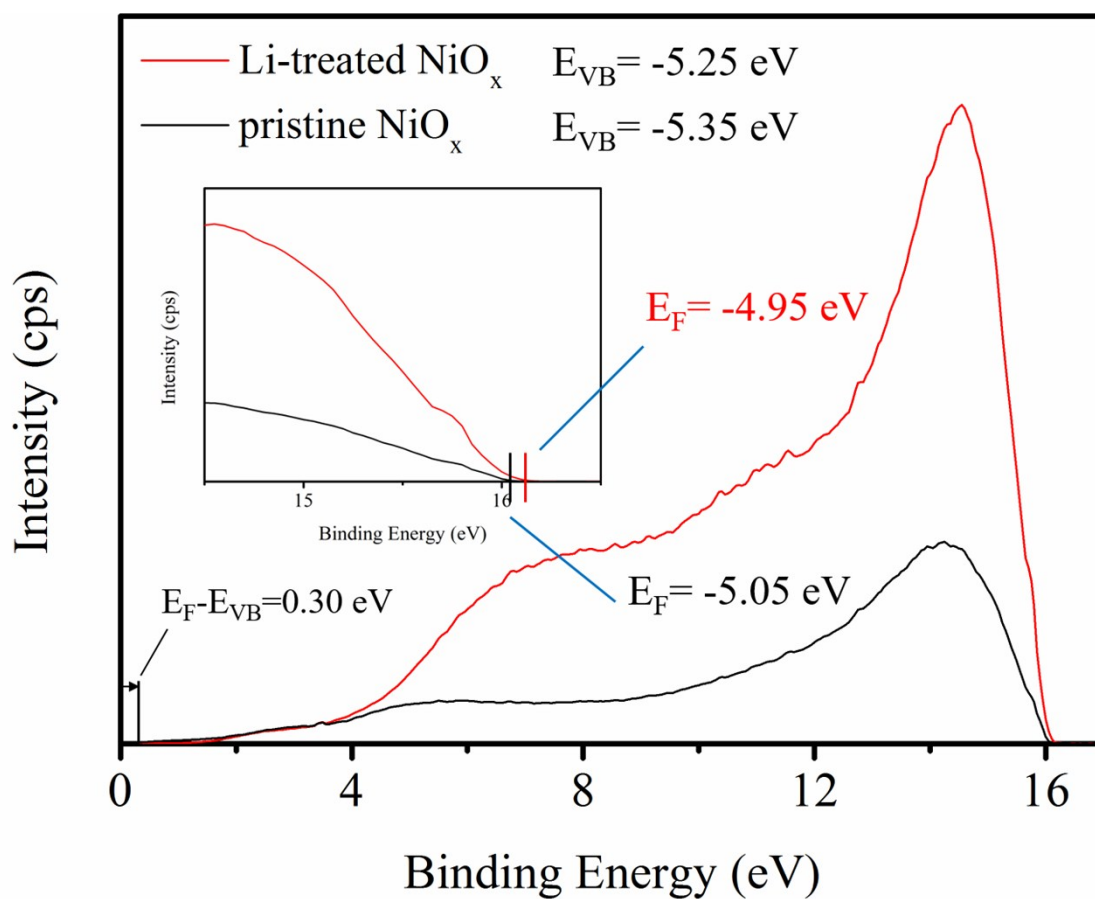


Fig. S3 Ultraviolet photoelectron spectra of the pristine NiO_x and Li-treated NiO_x films. Inset is the magnification of secondary cut-off region near binding energy 16 eV.

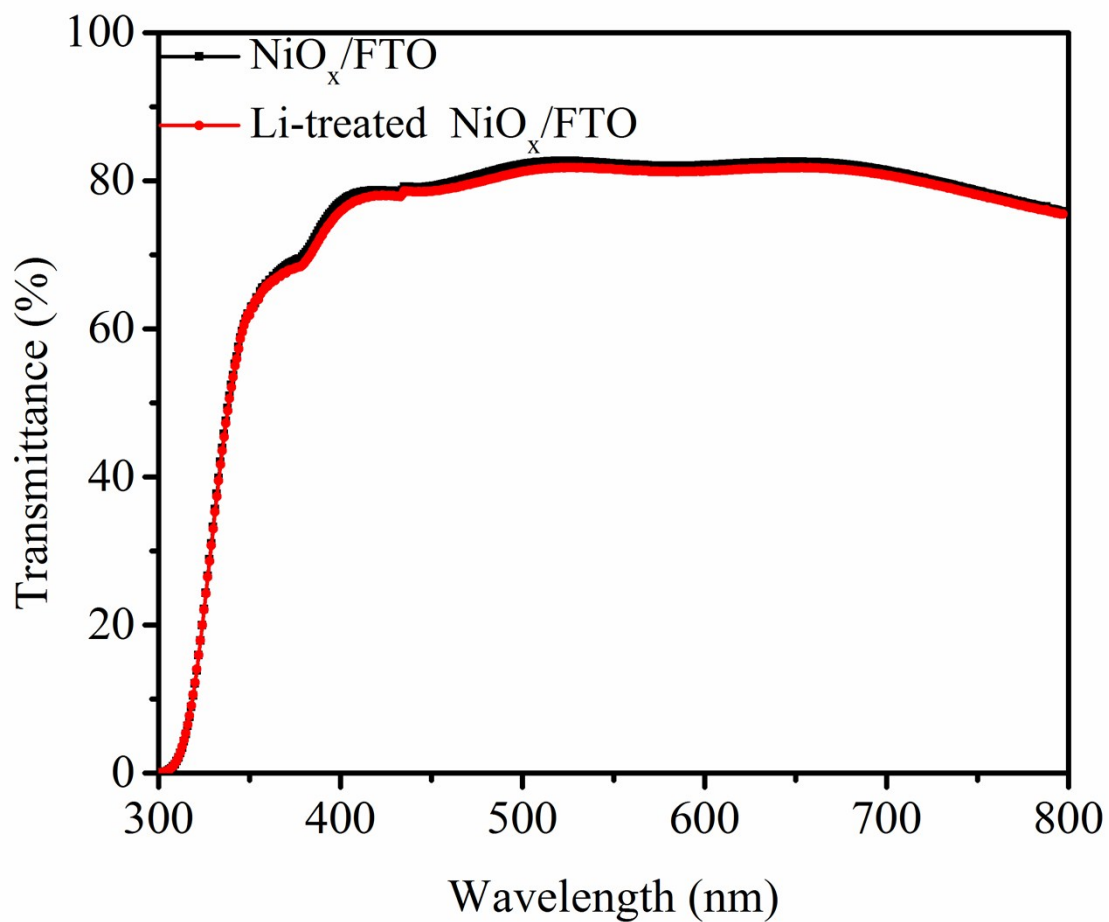


Fig. S4 Transmission spectra of FTO with NiO_x film and Li-treated NiO_x film.

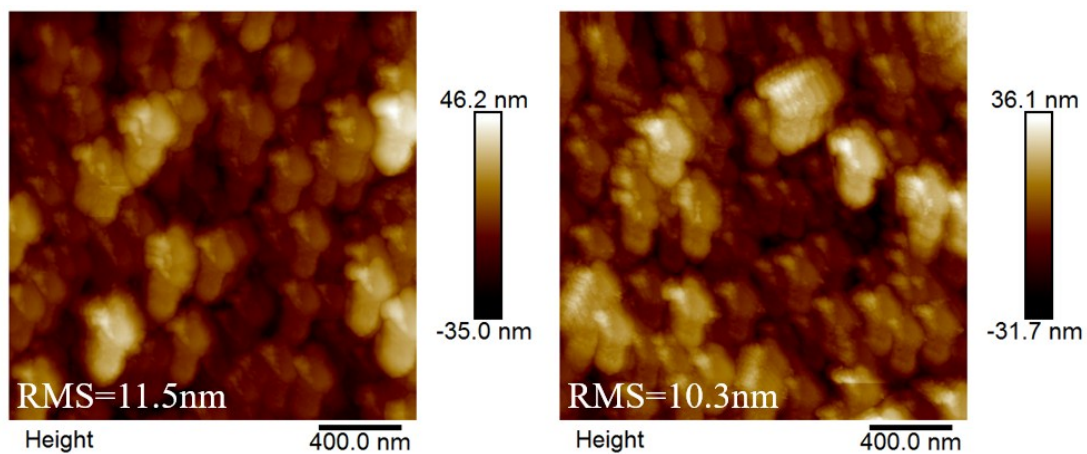


Fig. S5 AFM images of FTO substrates with NiO_x film and Li-treated NiO_x film.

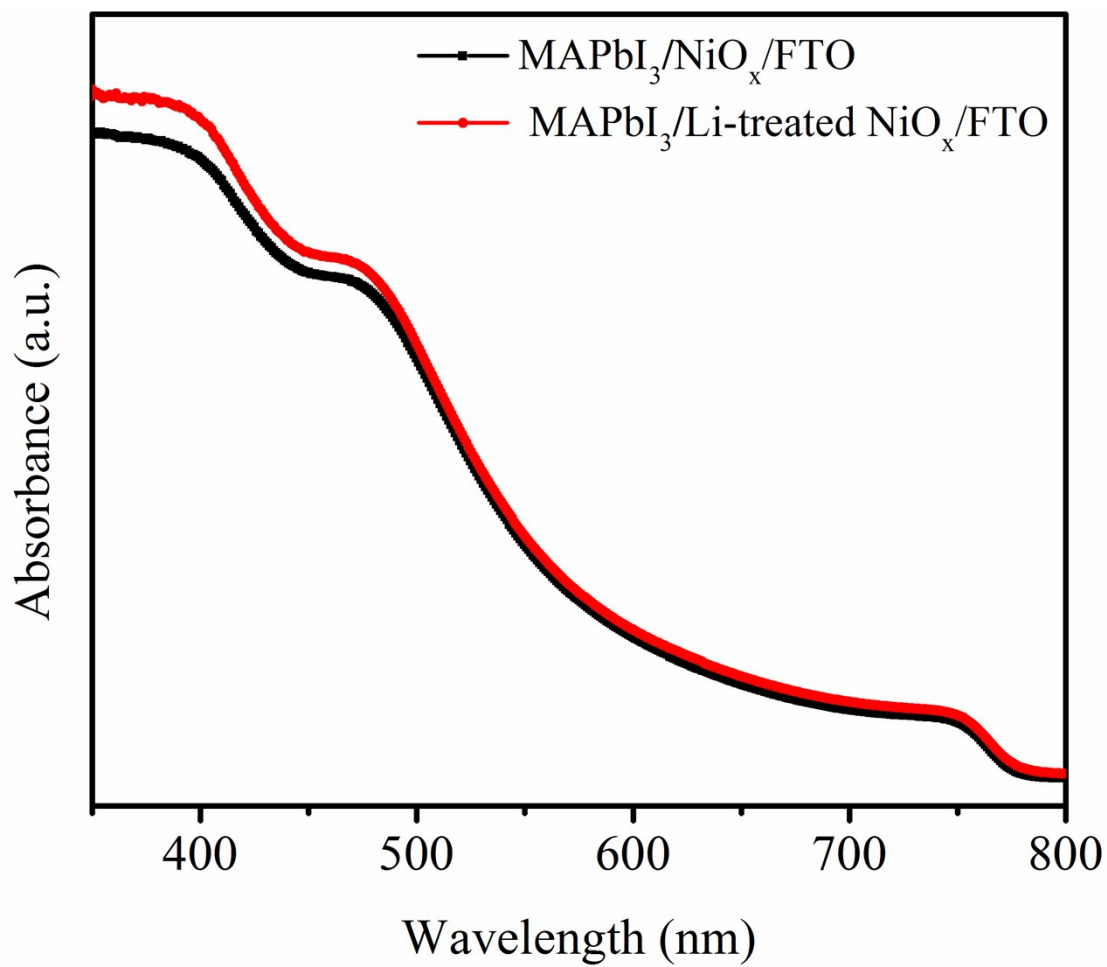


Fig. S6 UV-VIS absorption spectra of perovskite layers on the NiO_x and Li-treated NiO_x substrates.

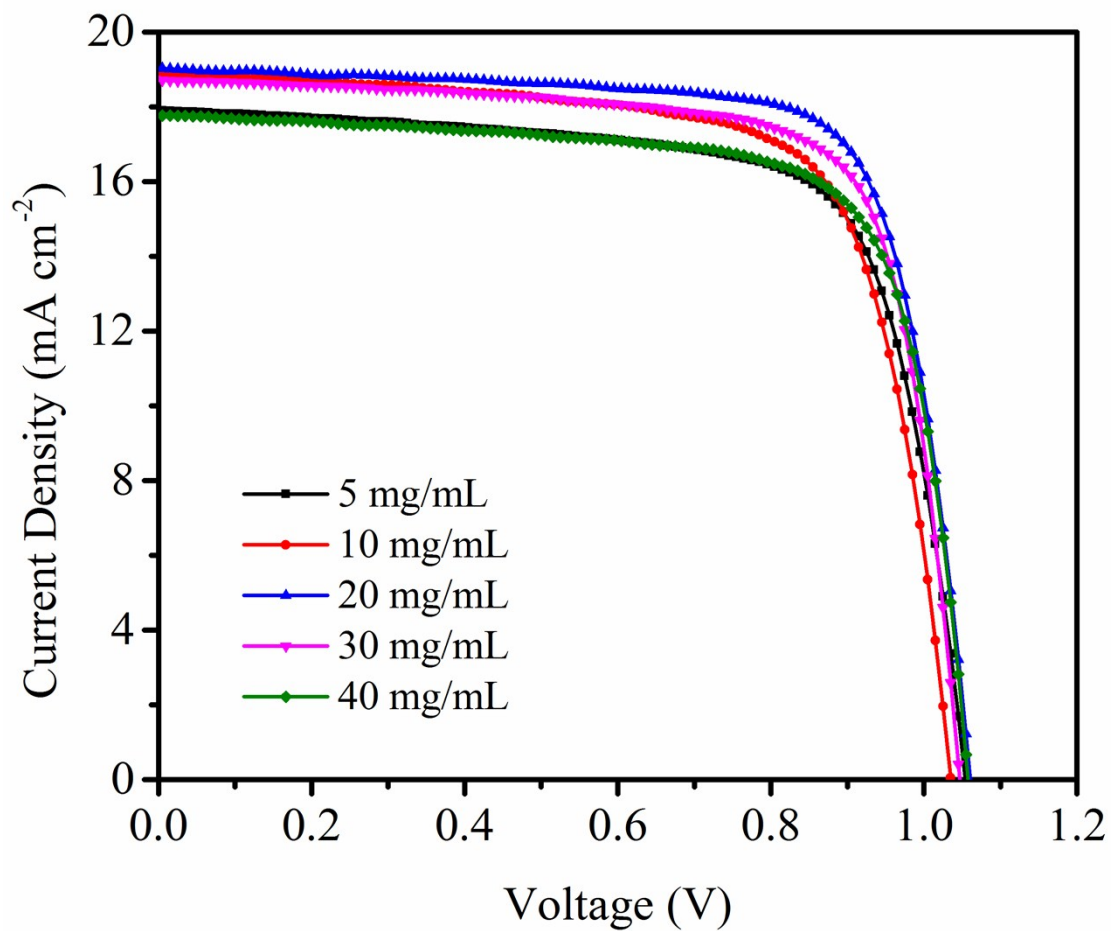


Fig. S7 The J-V curves of the PSCs based on the NiO_x HTL treated with different concentration of Li-TFSI solution.

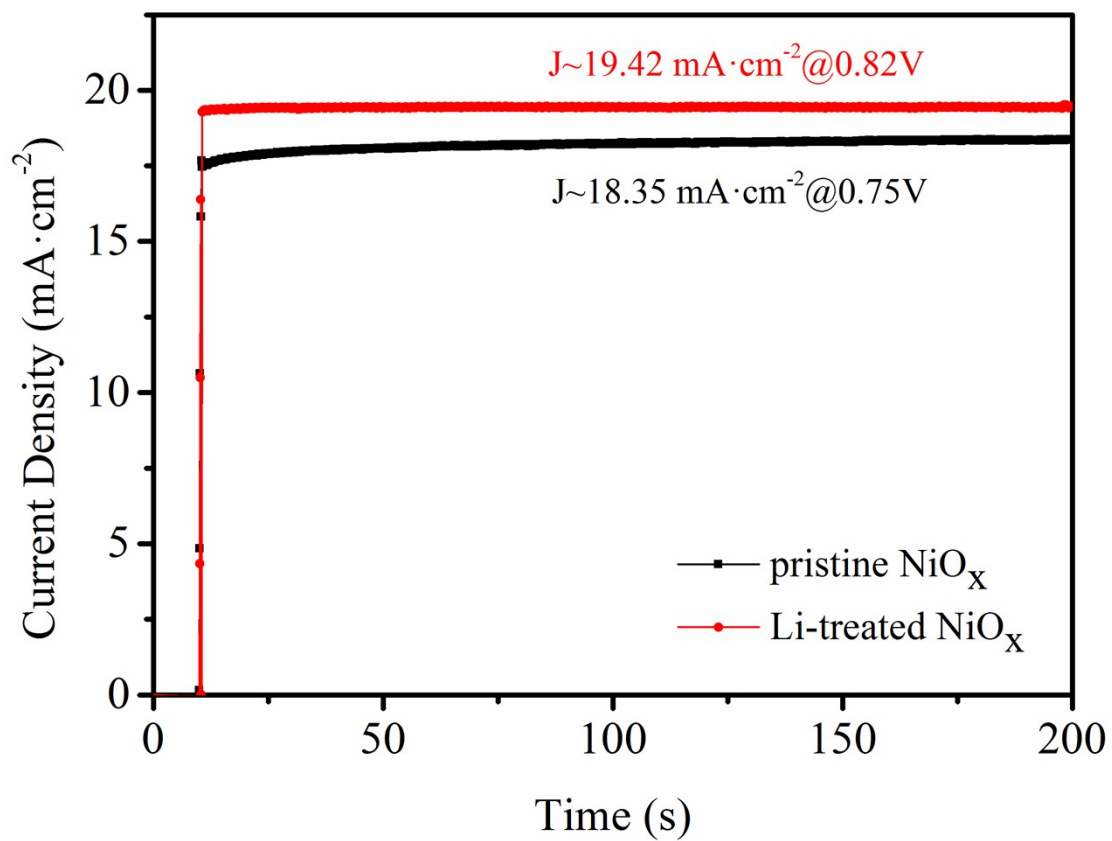


Fig. S8 Steady-state current density curves of the PSCs based on the Li-treated NiO_x and pristine NiO_x as a function of time.

Table S1 device performance parameters for different annealing temperature of NiO_x films. Average photovoltaic parameters with standard deviations were obtained based on 15 cells for each set.

Temperature (°C)	V _{oc} (V)	J _{sc} (mA cm ⁻²)	FF (%)	PCE (%)
300	1.03±0.01	15.82±1.64	71.20±2.80	11.63±1.11
400	1.04±0.01	17.83±0.47	72.50±1.10	13.54±0.44
500	1.07±0.01	18.15±0.52	66.90±3.40	13.02±0.65

Table S2 Electrical properties of NiO_x film modified with different concentration of Li-TFSI solution.

Li-TFSI salt treatment concentration	Conductivity (S cm ⁻¹)	Carrier Density (cm ⁻³)
0 mg/mL Li-TFSI	3.6×10^{-4}	3.63×10^{14}
5 mg/mL Li-TFSI	4.2×10^{-4}	3.95×10^{14}
10 mg/mL Li-TFSI	6.6×10^{-4}	6.55×10^{14}
20 mg/mL Li-TFSI	7.0×10^{-4}	2.52×10^{15}
30 mg/mL Li-TFSI	4.1×10^{-4}	1.38×10^{15}
40 mg/mL Li-TFSI	3.5×10^{-4}	1.16×10^{14}

Table S3 device performance parameters for different concentration of Li-TFSI solution treatment. Average photovoltaic parameters with standard deviations were obtained based on 30 cells for each set.

Li-TFSI concentration	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	PCE (%)
5 mg/mL	1.05 ± 0.02	17.77 ± 1.13	0.71 ± 0.03	13.41 ± 0.99
10 mg/mL	1.05 ± 0.01	18.14 ± 1.82	0.74 ± 0.03	14.04 ± 1.67
20 mg/mL	1.06 ± 0.01	18.83 ± 0.78	0.76 ± 0.01	15.26 ± 0.61
30 mg/mL	1.05 ± 0.02	18.39 ± 1.31	0.74 ± 0.03	14.43 ± 1.25
40 mg/mL	1.04 ± 0.02	17.55 ± 2.43	0.73 ± 0.03	13.51 ± 1.88

Reference

1. Z. Zhu, Y. Bai, X. Liu, C. C. Chueh, S. Yang and A. K. Jen, *Adv. Mater.*, 2016, **28**, 6478-6484.