Reconstructed transparent conductive layers of fluorine doped tin oxide for greatly weakened hysteresis and improved efficiency of perovskite solar cells

Chemicals and reagents

Lead iodide, N,N-dimethylformamide (DMF), 4-tert-butylpyridine (4-tBP), Dimethyl sulfoxide (DMSO), Lithium bis(trifluoromethylsulphonyl) imide (Li-TFSI), Acetonitrile and Chlorobenzene were from Sigma Aldrich. Spiro-OMeTAD was from Shenzhen Feiming Science and Technology Co. Ltd. Formamidinium iodide (FAI) and methylamine bromide (MABr) were from Xi’an Polymer Light Technology Corp. The FTO substrates were from OPV Tech.

Electrochemical reduction and post annealing of FTO

The electrochemical reduction of FTO was conducted in a three-electrode system, where the working electrode, counter electrode and reference electrode were FTO glass, Pt foil and saturated calomel electrode (SCE), respectively. The electrolyte solution was 1 M Na$_2$SO$_3$ aqueous solution. A series of different potentials were applied to reduce the FTO. The optimal reduction was conducted at the potential of -1.56 V for 2.5 min. After the reduction, the FTO glass was immediately washed thoroughly with deionized water to remove the residual solution. The reduced FTO was then heated at 470 °C for 60 min in an oven.

Perovskite film preparation
The hybrid organic/inorganic perovskite was prepared by a two-step interdiffusion method. The precursor solutions used in the two-step interdiffusion method were prepared as follows. 599.3 mg of PbI$_2$ and 101.5 mg of DMSO were dissolved into 1 mL DMF to form a transparent solution of 1.3 M lead iodine as the first-step solution. The second-step solution was prepared by dissolving FAI/MABr (68 mg/12 mg) into 1 mL isopropyl alcohol. In order to make perovskite film, the PbI$_2$ solution was spin-coated onto the substrate at 3000 rpm for 30 s. The second step solution was then dripped on it and spin-coated immediately at 3000 rpm for 30 s. Afterwards, the film was heated on a hotplate in ambient atmosphere at 150 °C for 20 min to form a shiny smooth perovskite film.

*Solar cell fabrication*

Different FTO substrates were washed sequentially in detergent, ethanol, acetone and isopropanol each for 15 min. The spin-coating of the perovskite films on the FTO substrates and followed thermal annealing were conducted in an argon-filled glove box. The subsequent spin-coating of Spiro-OMeTAD solution was conducted at 5000 rpm for 30 s. Prior to depositing the back electrode, the coated substrates were kept in a desiccator to oxidize the Spiro-OMeTAD overnight. The Spiro-OMeTAD solution was prepared by dissolving 72.3 mg of Spiro-OMeTAD, 28.8 μl of 4-tBP and 17.5 μl of Li-TFSI/acetonitrile (520 mg mL$^{-1}$) sequentially into 1 mL chlorobenzene. 80 nm thick Au back electrode was deposited by thermal evaporation at a pressure of 5×10$^{-4}$ Pa. The active area of the cells was 0.09 cm$^2$.

*Perovskite device characterization*
The J-V curves were measured in reverse scan and forward scan (1.3→0 V, 0→1.3 V, 0.2V/s) using electrochemical workstation. The light density of the lamp (Newport, 91192) was measured by a standard silicon solar cell to be 95 mW cm². External quantum efficiency (EQE) was tested by SOLAR CELL IPCE TEST SYSTEM MODEL: QTEST STATION 1000AD from CROWNTECH, INC. The stability test was carried out by measuring the current density at the maximum power point (MPP) voltage of the device. The voltages selected for the O-R-FTO and FTO case are 0.83 V and 0.78 V, respectively.

Structure characterization

X-ray diffraction patterns were recorded on a Rigaku diffractometer using CuKα irradiation. X-ray photoelectron spectroscopy was used to determine the chemical states of the elements by Thermo Escalab 250. The optical absorption spectra were measured on a UV–vis spectrophotometer (JASCO-770) in the diffuse reflectance mode. The SEM images were recorded by the scanning electron microscopy (Nova NanoSEM 430). Photoluminescence emission spectra (471 nm excitation) were measured with a fluorescence spectrophotometer (Edinburgh Instruments, FLSP-920) at room temperature.
Fig. S1 XRD patterns of the pristine FTO, electrochemically reduced FTO (R-FTO) and re-oxidized FTO (O-R-FTO).

Fig. S2 SEM images of (a) the pristine FTO, (b) electrochemically reduced FTO (R-FTO) and (c) re-oxidized FTO (O-R-FTO).

Fig. S3 SEM images of the perovskite films on (a) the FTO, (b) R-FTO and (c) O-R-FTO substrates.
Fig. S4 J-V curves of PSCs based on O-R-FTO substrates with different electrochemical reduction durations (30 s, 60 s, 120 s, 150 s, 180 s, 210 s) at -1.56 V.

Fig. S5 Cross-section SEM images of (a) the pristine FTO and (b) the reconstructed FTO (O-R-FTO).
**Fig. S6** The depth dependent XPS spectra of F 1s upon Ar\(^+\) sputtering in the optimal O-R-FTO.

**Table S1** Photovoltaic parameters of the devices based on the pristine FTO and O-R-FTO substrates

<table>
<thead>
<tr>
<th>Sample</th>
<th>(J_{sc}) (mA cm(^{-2}))</th>
<th>(V_{oc}) (V)</th>
<th>FF</th>
<th>(PCE_{\text{forward}})%</th>
<th>(PCE_{\text{reverse}})%</th>
<th>(J_{\text{EQE}}) (mA cm(^{-2}))</th>
<th>Average PCE (%)</th>
</tr>
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<tbody>
<tr>
<td>FTO</td>
<td>18.82</td>
<td>0.97</td>
<td>0.731</td>
<td>9.0</td>
<td>14.0</td>
<td>18.88</td>
<td>13.1</td>
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<tr>
<td>O-R-FTO</td>
<td>21.13</td>
<td>1.04</td>
<td>0.675</td>
<td>15.1</td>
<td>15.7</td>
<td>21.05</td>
<td>14.3</td>
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</table>
**Fig. S7** Current densities (blue curves) and PCEs (red curves) of the devices based on O-R-FTO (solid line) and FTO substrates (dot line) measured at their corresponding maximum power points (MPPs).

![Graph showing current densities and PCEs](image)

**Fig. S8** Schematic of the energy band alignments and corresponding carrier dynamics at the FTO/perovskite and O-R-FTO/perovskite interfaces.

![Schematic of energy band alignments](image)

**Table S2** Fitting results of the recorded TR-PL spectra based on the pristine FTO and O-R-FTO substrates. The bi-exponent model below was used to fit the time resolved photoluminescence (Fig. 5b).

\[
Fit = A + B_1 e^{-t/\tau_1} + B_2 e^{-t/\tau_2}
\]

<table>
<thead>
<tr>
<th>Sample</th>
<th>A</th>
<th>B₁</th>
<th>B₂</th>
<th>τ₁ (ns)</th>
<th>τ₂ (ns)</th>
</tr>
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<tbody>
<tr>
<td>FTO</td>
<td>295.97</td>
<td>203.98</td>
<td>406.15</td>
<td>1.92</td>
<td>136.25</td>
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<tr>
<td>O-R-FTO</td>
<td>235.42</td>
<td>391.90</td>
<td>245.66</td>
<td>1.86</td>
<td>93.71</td>
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