The influence of electron transport layer on charge dynamics and trap-state properties in planar perovskite solar cells

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S1. Experimental section

Laser-ablated FTO glass (Pilkington TEC-7, 7 Ω/sq) were successively rinsed with detergent, deionized water, acetone and ethanol by an ultrasonic bath for 20 min, respectively. Subsequently, the substrates were treated by oxygen plasma for 15 min. A thin compact TiO2 (c-TiO2) layer was deposited on substrates by spin-coating 0.15 M titanium diisopropoxide in 1-butanol at 2500 rpm for 40 s, and then sintered at 500 °C for 1 h in an oven. For SnO2 ETL, the SnO2·2H2O colloid precursor was purchased from Alfa Aesar (tin (IV) oxide, 15% in H2O colloidal dispersion), then 200 μL SnO2·2H2O precursor is diluted by 1000 μL ultrapure water before used. The final solution was spin coated onto FTO substrates at 3000 rpm for 30 s, and then baked on a hot plate at 150 °C for 30 min in air.

Briefly, the perovskite films are prepared by mixing CH3NH3I (1.1 M) and PbI2 (1.15 M), in DMF: DMSO (4:1, v:v). The perovskite precursor solution is spin-coated in a two-step program at 1000 and 5000 rpm for 10 and 30 s, respectively. During the second step, 200 μL of chlorobenzene was poured on the spinning substrate 15 s prior to the end of the program. Then, the as-fabricated films were baked at 100 °C for 1 h in a nitrogen filled glove box.

After the deposition of the perovskite layer, the hole transport layer (HTL) was coated at 4000 rpm for 30 s. The HTL solution was prepared by dissolving 72.3 mg of 2,2′,7,7′-tetrakis(N,N-di-p-methoxyphenylamine)-9,9-spirobifluorene in 1 mL of chlorobenzene, to which 28.8 μL of 4-tert-butylpyridine, 17.5 μL of 520 mg mL⁻¹ lithium bis(trifluoromethylsulphonyl)imide in acetonitrile and 28.8 μL of 300 mg mL⁻¹ tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)-cobalt(III) bis(trifluoromethylsulphonyl)imide in acetonitrile were added. Finally, an 80-nm-thick Au counter electrode was deposited by
thermal evaporation. Unless otherwise stated, all materials were purchased from Alfa Aesar and used as received.

**S2. Characterization of the perovskite films**

![Figure S1](image)

**Figure S1** Statistics of the perovskite grain sizes SEM images of two targeted perovskite films: (a) TiO₂ and (b) SnO₂, respectively.

![Figure S2](image)

**Figure S2** Cross-section SEM images of devices based on TiO₂ (a) and SnO₂ ETL (b), respectively.

**S3. Transient photovoltage and transient photovoltage decay trace**

![Figure S3](image)

**Figure S3** (a) The normalized transient photovoltage decay traces of diverse desired steady-state
photovoltages, and (b) is the corresponding normalized transient photocurrent decay traces.

The trace of TPV is fitted by bi-exponential function is described as: \( V(t) = V_{\text{base}} + A_1\exp(t/\tau_1) + A_2\exp(t/\tau_2) \), where \( V_{\text{base}} \) is the baseline, \( A_1 \) and \( A_2 \) are pre-exponential factors, and \( \tau_1 \) and \( \tau_2 \) are time constants. The charge carried lifetime is calculated as \( \tau_n = (A_1\tau_1 + A_2\tau_2)/(A_1 + A_2) \).\(^{1-3}\) The results of the TPC is also fitted by the by bi-exponential function. The corresponding charge carrier transport nearly exhibits a constant, which can by interpreted by the unique ambipolar transport property of the perovskite.

**S3. Time-resolved charge extraction trace**

![Figure S4](image)

**Figure S4** Representative kinetics trace of the overall photovoltage (\( V_{\text{ph}} \)) for an open-circuit perovskite solar cells device (thicker black line), and the charge extraction kinetics at indicated timing (thinner color lines) recorded by fast switching of the PSCs into short circuit.

The quantity of extracted charges (\( Q \)) can be readily obtained by the integration, 
\[ Q = R^{-1}\int V_{\text{ph}} \, dt \]
where \( R \) and \( V_{\text{ph}} \) stand for the sampling resistance (50 \( \Omega \)) and the photovoltage, respectively.\(^4,5\)

**References**

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