Supplementary Information

Flexible Perovskite Solar Cells Based on Metal-Insulator-Semiconductor Structure

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Hysteresis analysis

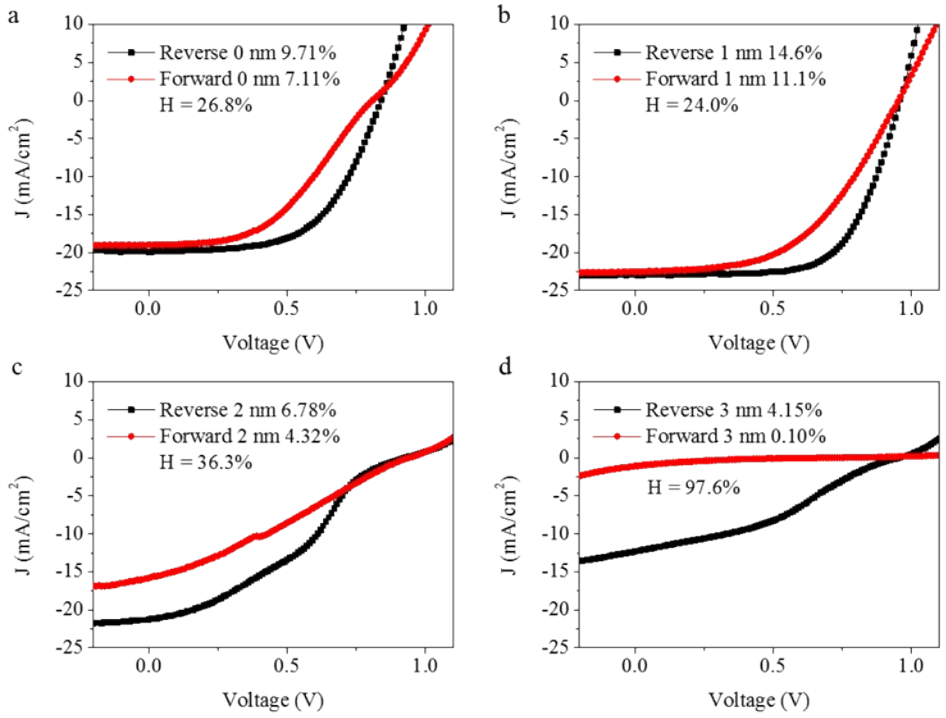

Fig. S1 Photovoltaic characterization of MIS-PSCs devices with different thickness of Al_2O_3 at forward (- 0.5 V ~ 1.5 V) and reverse (1.5 V ~ -0.5 V) scan: (a) 0 nm Al_2O_3; (b) 1 nm Al_2O_3; (c) 2 nm Al_2O_3; (d) 3 nm Al_2O_3 under illumination, with the scanning speed of 100 mV/s. H stands for the factor of hysteresis.

Hysteresis of the *J-V* curves base on different thickness of Al_2O_3 is analysis and result is shown as Fig. S1.We define a hysteresis factor, H, to compare hysteresis in different devices:

$$H = \frac{E_{Reverse} - E_{Forward}}{E_{Reverse}} \times 100\% \quad (1)$$

Where $E_{Reverse}$ and $E_{Forward}$ stands for power conversion efficiency of devices base on reverse (-0.5 V ~1.5 V) and forward (-0.5 V ~1.5 V) scan respectively

From the result we can see, devices with 0-1nm Al_2O_3 show smaller hysteresis than others. And hysteresis become serious with Al_2O_3 thickness increasing. We speculate that this may be caused by the carrier accumulation in the perovskite layer. In the MIS structure, perovskite layer is located between one insulate layer (Al_2O_3) and one conductive layer (spiro-OMeTAD). Under the external applied electric field, perovskite layer would accumulate charges of different polarity at the Al_2O_3 side, like shown in Fig. S2. This psudo-polarization causes hysteresis in *J-V* measurement. These accumulation charges will counteract the extra electric field and it would become more serious with the increasing of Al_2O_3 thickness. Thus lead to the hysteresis changes with different Al_2O_3 thickness.

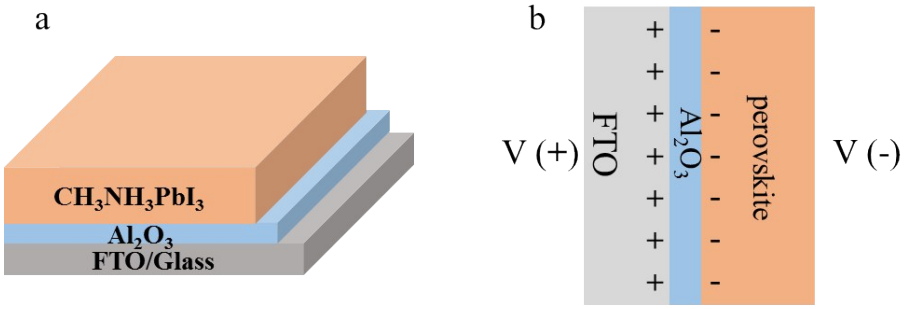

Fig. S2 Schematic diagram of MIS structure (a) and psudo-polarization in the perovskite layer (b).

Photoluminescence (PL) analysis

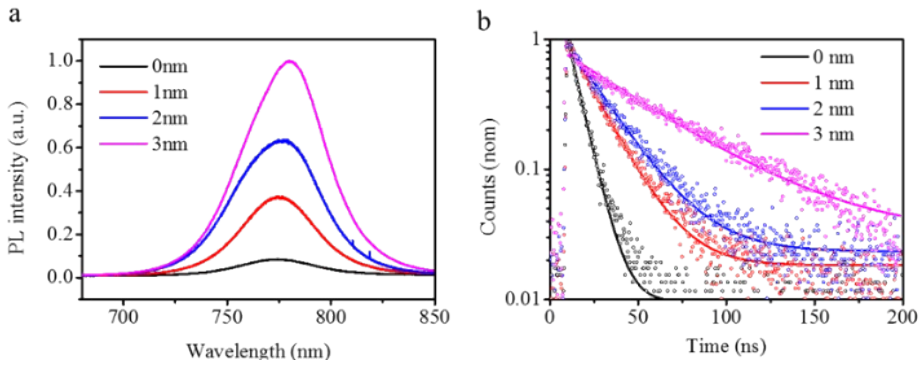

Fig. S3 PL measurement of the MIS structure under different thicknesses of Al_2O_3. (a) Time-integrated PL spectra. (b) Time-resolved PL decay transients measured at 770 ± 10 nm.

Photoluminescence was measured to compare the extraction ability of MIS structure under different thickness of Al_2O_3 to photon-generated carriers. The measured MIS-films were made by spin-coating perovskite onto a plasma-etched Al_2O_3/FTO glass substrate, with Al_2O_3 thickness varied from 0-3 nm. Fig. S3a shows the time-integrated PL spectra of the films. With a thinner Al_2O_3 layer, photon-generated carriers were extracted quickly by the tunnelling effect, which causes a big decline in the spectra peaks. Time-resolved transient PL measurements were also performed to detect the transfer of photo-generated carriers of each film. From Fig. S3b, the PL decay of the films with a 3 nm Al_2O_3 layer exhibits a time constant of τ = 85 ns. The thinning of the Al_2O_3 layer accelerates the PL decay, with observed time constants τ of 30 ns and 22 ns, for the Al_2O_3 layer of 2 nm and 1 nm, respectively, which show good ability of electron transfer ability. The lifetime of the $CH_3NH_3PbI_3$ film on FTO is only 7 ns, which is more due to its serious recombination at the interface of FTO/perovskite.

Experimental Section

Device fabrication. All of the materials were purchased from Sigma-Aldrich or J&K Scientific Ltd. unless expressly stated. CH_3NH_3I was purchased from Dyesol. Al_2O_3 layer is first deposited onto fluorine doped tin oxide (FTO)/glass or ITO/PEN (flexible

substrate) by ALD at 80^{o}C, with the rate of 1 Å/cycle. For each cycle, the depositon time is 12 s. 1~3 nm Al_2O_3 layers were deposited for 10, 20, 30 cycles, respectively. Before use, the substrate was preheated to 70°C. To get the perovskite solution, CH_3NH_3I and $PbCl_2$ were dissolved in anhydrous N,N-Dimethylformamide (DMF) at a 3:1 molar ratio with final concentrations of ~35 wt%. Then the as-prepared perovskite solution was spin coated onto the Al_2O_3/FTO or FTO substrate to get ~ 300 nm thick film with the spin coating speed of 2500 r.p.m. The film was dried at 50°C for 1 h, then annealed at 100°C for 90 min to form perovskite crystal. Then the hole transporting materials (HTM) was deposited by spin coating the solution of HTM at 3,000 r.p.m. for 60 s. The HTM formulation was prepared by dissolving 73 mg 2,2',7,7'-Tetrakis(N,N-p-dimethoxy-phenylamino)-9,9'-spirobifluorene (spiro-OMeTAD), 29.5 µl 4-tert-butylpyridine (tBP) and 18.5 µl of a stock solution of 520 mg/ml lithium bis(trifluoromethylsulphonyl)imide(Li-TFSI) in acetonitrile in 1 ml chlorobenzene. Finally, 80 nm of gold electrodes were deposited on top of the devices by evaporation at ~10^{-6} Torr.

***J-V* Measurement.** The current−voltage (*J*−*V*) characteristics were obtained using an Agilent B2900 Series precision source/measure unit, and the cell was illuminated by a solar simulator (Solar IV-150A, Zolix) under AM1.5 irradiation (100 mW cm^{-2}). For scan test, the *J-V* curves are tested with the rate of 100 mV/s. For steady-state test, the voltage is fixed on the maximum power point to test the current output for all the test time. The masked active area is 9 mm^2. For flexible solar cells, the masked active area is 16 mm^2.

PL. Steady-state photoluminescence spectra were measured using a green laser (514 nm in wavelength) guided by a micro-zone confocal Raman spectroscope (Renishaw inVia microRaman system) as the laser beam with a spot size diameter of 2 μm. The collected duration is ~1 ms. The time-resolved fluorescence spectra were recorded with a high resolution streak camera system (Hamamatsu C10910). All the samples were excited by 514 nm at room temperature with ~ 110 nJ cm^{-2}.

IS. The impedance spectrum and cyclic voltammograms were measured using a potentiostat/galvanostat (SP-150, Bio-Logic, France). The frequency can be tuned from 0.1 Hz to 1 MHz. And the voltage tuned from -0.2 V to 1.0 V.