

Supporting information

Spacer layer design for efficient fully printable mesoscopic perovskite solar cells

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Experimental section

Spacer paste

Synthesis of 5 nm ZrO₂. This method was referred to literature.¹ ZrOCl₂•8H₂O was mixed with hydriane and stirred for 6 hours, then hydrothermal reaction at 200 °C for 24 hours. After cooling to room temperature, the precipitation was washed with deionized water for three times, then with absolute ethanol for three times.

Synthesis of 10 nm ZrO₂. ZrOCl₂•8H₂O was dissolved in ethylene glycol. Ethylenediamine was slowly added into the solutions under continuous rigorously stirring for 6 hours. Then hydrothermal reaction at 220 °C for 24 hours was carried out. After cooling to room temperature, the precipitation was washed with deionized water for three times, then with absolute ethanol for three times.

Synthesis of 20 nm ZrO₂. Zirconium(IV) isopropoxide isopropanol was dissolved in triethanolamine. In another beaker, 0.02 mol ethylenediamine was added into 100 mL water. The ethylenediamine solutions was slowly added into Zirconium(IV) isopropoxide and triethanolamine solution under continuous rigorously stirring for 6 hours.. Hydrothermal reaction of the resulted solution first at 100 °C for 4 hours and then 250 °C for 24 hours was carried out. After cooling to room temperature, the precipitation was washed with deionized water for three times, then with absolute ethanol for three times.

Spacer paste was made by blending spacer building blocks, ethyl cellulose, and α -terpineol homogeniously by milling with zirconia beads. The weight ratio of spacer

building blocks: ethyl cellulose: α -terpineol is 1:0.5:4.

Perovskite precursor. The MAI was prepared according to the reported procedure.² A hydroiodic acid (30 mL, 57 wt% in water) and methylamine (27.8 mL, 40% in water) were stirred in the ice bath for 2 h. Then the resulting solution was evaporated at 50 °C and produced synthesized chemicals (MAI). The precipitate was washed three times with diethyl ether and recrystallized three times with absolute ethanol. Finally, the products were dried under vacuum. 5-AVAI was synthesized in a similar way except that MA was replaced by 5-AVA. To prepare $(5\text{-AVA})_x\text{MA}_{1-x}\text{PbI}_3$ perovskite precursor, the synthesized MAI (0.154 g), 5-AVAI (0.0123 g) and PbI_2 (0.462 g) were mixed in 0.8 mL GBL at 60 °C for overnight.

Fabrication of perovskite solar cells

The laser-patterned conductive glass was washed by ultrasonicing in detergent, deionized water, absolute ethanol for 30 minutes, respectively. Then the compact TiO_2 layer was deposited with aerosol spray paralysis at 450°C. Screen-printing technique was used to print TiO_2 , spacer, and Carbon films layer by layer onto the conductive glass coated with compact TiO_2 . Before screen-printing, paste was diluted with α -terpineol. The weight ratio of paste to α -terpineol is 1:1.5, 1:2 for P25 and spacer paste, respectively. TiO_2 and spacer film was sintered at 500 °C for 30 minutes before printing the next layer. TiO_2 , and Carbon film were controlled to be 1.0 μm and 15.0 μm , respectively. After annealing at 400 °C for 30 minutes and cooled to room temperature, 4 μL perovskite precursor solutions were dropped onto the surface of TSC films, and then the films were annealed at 50 °C for 30 minutes. All the procedures above were completed in air conditions with humidity of 40-50% RH.

Characterizations and measurements

A Belsorp-mini II instrument was used for nitrogen adsorption measurements. Samples were degassed at 110 °C for 4 h once the final temperature had been reached prior to analysis typically measured at 77 K consisting of an adsorption and desorption branch. Specific surface areas were calculated via the Brunauer–Emmett–Teller (BET) model.

All the $J-V$ curves in this study were recorded using a Keithley 2400 source meter unit. The device photocurrent was measured under AM1.5 illumination condition at an intensity of 100 mW cm^{-2} . The active area of solar cell is $0.64\text{-}0.80 \text{ cm}^2$. The area of aperture is 0.13 cm^2 . The illumination intensity of the light source was accurately calibrated with a standard Si photodiode detector equipped with a KG-5 filter, which can be traced back to the standard cell of the National Renewable Energy Laboratory (NREL). The EQE spectra performed here were obtained from an IPCE setup consisting of a Xenon lamp (Oriel, 450 W) as the light source, a monochromator, a chopper with a frequency of 100Hz, a lock-in amplifier (SR830, Stanford Research Corp), and a Si-based diode (J115711-1-Si detector) for calibration. The X-ray diffraction (XRD) measurements employed a X'pert PRO X-ray Diffractometer and detected through the top of nanoparticles on glass substrate. Time resolved PL measurements were measured at 760 nm using excitation with a 482 nm light pulse at a frequency of 4 MHz from the Horiba Jobin Yvon Fluoromax-4 fluorimeter. The lifetime was obtained by fitting the PL measured from spacer/perovskite films with an exponential decay function. The size and morphology of the spacer nanoparticles were determined by a JEOL JEM-1200EX transmission electron microscope (TEM) at 120 kV, Tecnai GF30 transmission electron microscope. Sample of TSC/perovskite composite film were prepared by Ar ion sputtering and placed on the surface of a copper grid.

Insulating resistance of spacer film. Spacer films were screen printed on laser patterned FTO glass, after sintering at 500°C for 30 minutes, carbon film was printed on spacer film. $I-V$ curves between carbon electrode and FTO glass was measured after sintering carbon film at 400°C for 30 minutes. Top-view and cross-sectional images of film, cross-sectional images of devices were recorded with field emission scanning electron microscopy.

Impedance Measurements. Before carrying out measurement under 1.0 sun, at least 20 minutes illumination is needed to stabilize the device. The device was put into Faraday box. The impedance measurements were performed using a Princeton Applied Physics power suite. A dc potential bias was applied and overlaid by a sinusoidal ac potential perturbation of 15 mV over a frequency range of 4 MHz to 0.05 Hz (for the

measurements under illumination, the lowest frequency is 0.01 Hz). The applied dc potential bias was changed by ~ 100 mV steps from 1.1 V to 0 V.

Table S1.

Figure S1-S5.

Table S1. Crystal size of infiltrated perovskite and average pore diameter of spacer layer.

Spacer	Crystal size of infiltrated perovskite by XRD (nm)	Average pore diameter from BET (nm)	Surface area from BET ($\text{m}^2 \text{g}^{-1}$)
S5	4.3	-	-
S10	3.9	8.7	96.5
S20	6.2	36.0	31.3
S60	11.5	39.9	17.7
S100	12.6	25.7	13.2

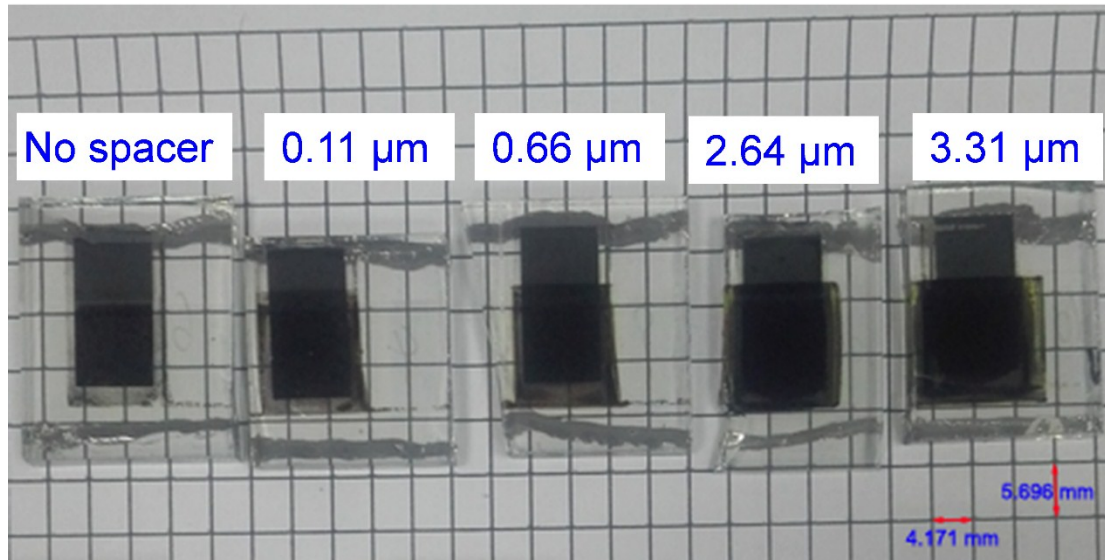


Figure S1. The photographs of devices used to measure the IS spectra without mesoporous TiO_2 layer.

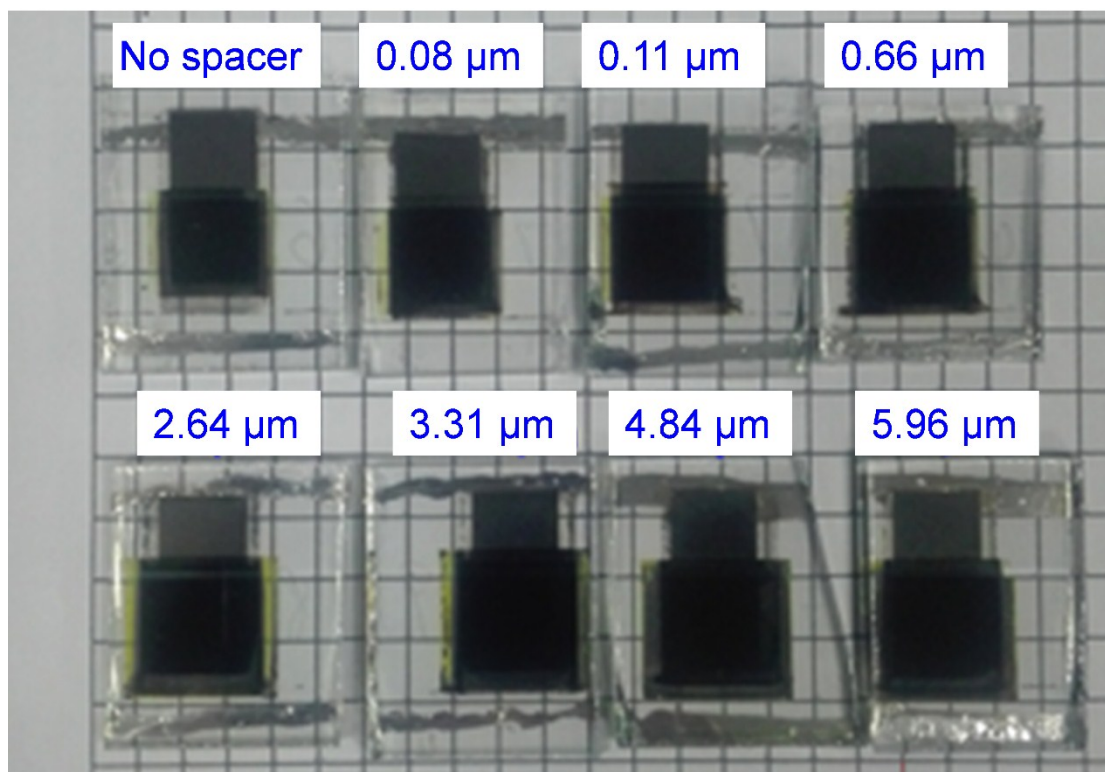


Figure S2. The photographs of devices used to measure the IS spectra with different thickness of spacer layer.

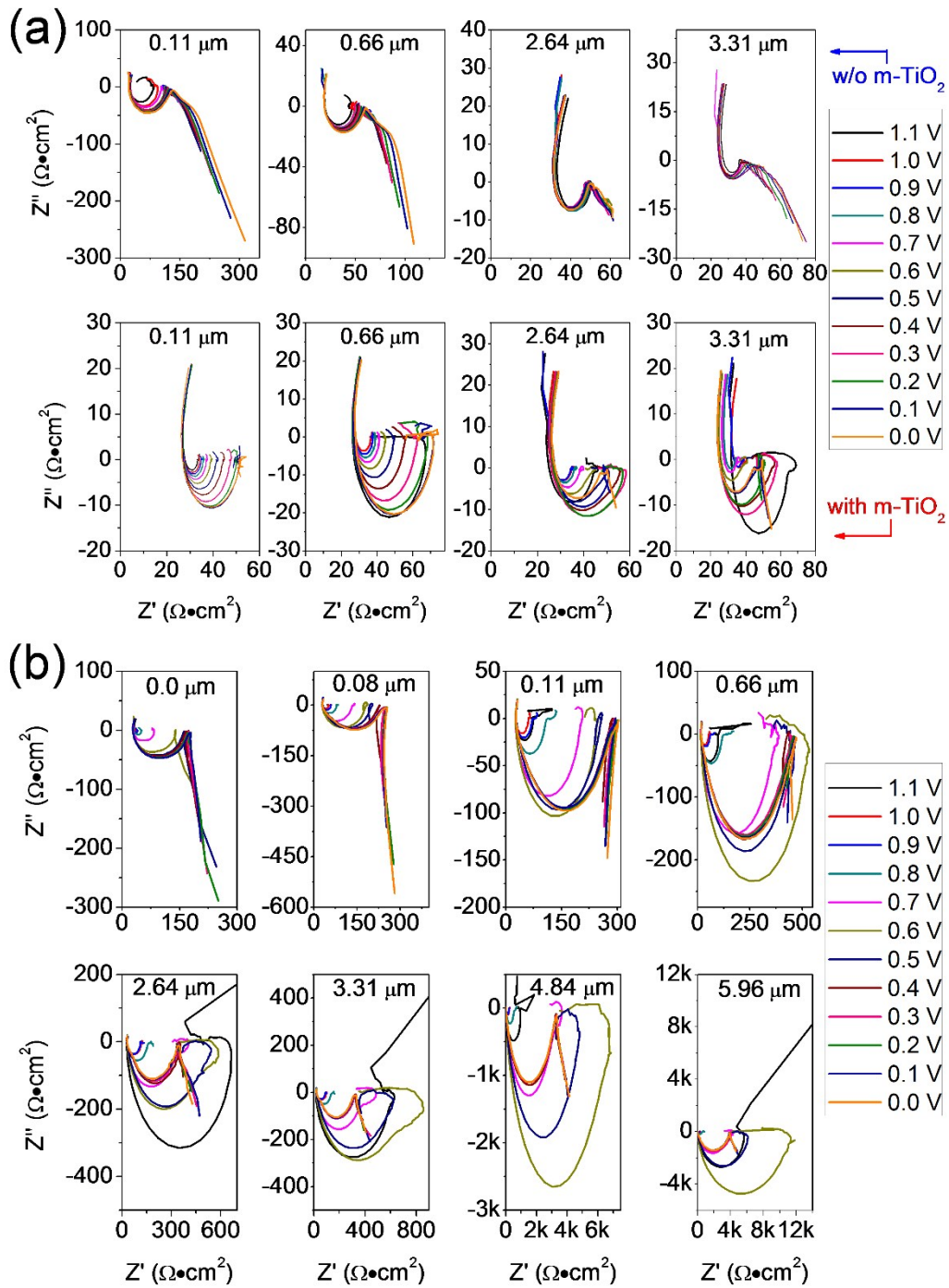


Figure S3. (a) Comparison of Nyquist plot of the FP-MPSC device with or without mesoporous TiO_2 film when different spacer film thickness was employed measured at between 1.1 V and 0 V, under one sun illumination. (b) Nyquist plot of the FP-MPSC device with different spacer film thickness measured at between 1.1 V and 0 V, under 0.1 sun illumination. Inset figures in Nyquist plot are thickness of spacer film.

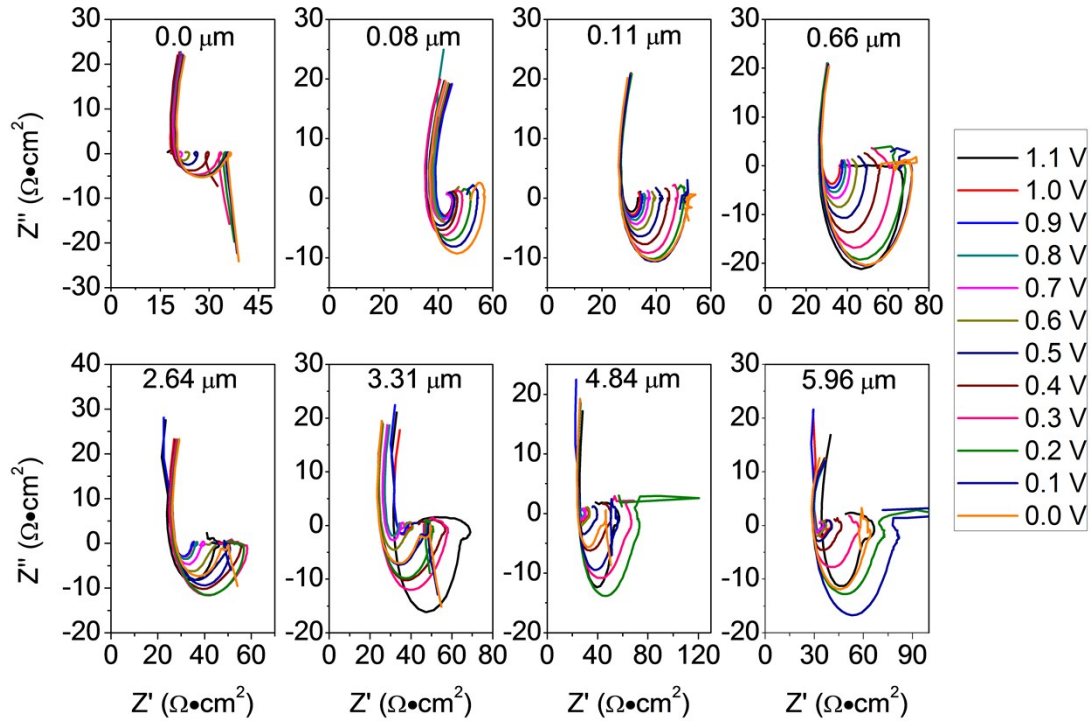


Figure S4. Nyquist plot of the FP-MPSC device with different spacer film thickness measured at between 1.1 V and 0 V, under one sun illumination. Under 1.0 sun, high frequency zone (10k-100k Hz) is not influenced by meso-TiO₂, but low frequency resistance (0.05-100 Hz) was largely decreased for all thickness of spacer film when meso-TiO₂ was used (figure 5a). High frequency resistance kept almost unchanged in investigating spacer film thickness range. This is very different from the high frequency resistance measured under 0.1 sun. Illumination induced resistance change indicates that resistance of perovskite confined in spacer film decreased so sharply that increasing thickness of perovskite/spacer composite film did not apparently increase resistance of perovskite. This also explains previous observed results that the slow response of photocurrent to illumination, and stabilized power output usually needs to be reached after about 3 minutes soaking under AM1.5G illumination. It is expected that more concentrated illumination may further decrease the resistance of perovskite.

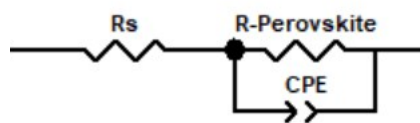


Figure S5. Circuit model used to fit high frequency part of impedance spectra.

References

- 1 H. Zhu, D. Yang, Z. Xi and L. Zhu, *J. Am. Ceram. Soc.*, 2007, **90**, 1334-1338.
- 2 H. S. Kim, C. R. Lee, J. H. Im, K. B. Lee, T. Moehl, A. Marchioro, S. J. Moon, R. Humphry-Baker, J. H. Yum, J. E. Moser, M. Gratzel and N. G. Park, *Sci. Rep.*, 2012, **2**, 591.