# **Supporting information for manuscript**

# Spacer improvement for efficient and fully printable mesoscopic

## perovskite solar cells

Tongfa Liu<sup>a</sup>, Yaoguang Rong<sup>ab</sup>, Yuli Xiong<sup>a</sup>, Anyi Mei<sup>a</sup>, Yue Hu<sup>a</sup>, Yusong Sheng<sup>a</sup>,

Pei Jiang<sup>a</sup>, Xiaomeng Hou<sup>a</sup>, Miao Duan<sup>a</sup>, Yanjun Guan<sup>a</sup>, Li Hong<sup>a</sup>, Hongwei

Han<sup>a</sup>\*

<sup>a</sup>Michael Grätzel Center for Mesoscopic Solar Cells, Wuhan National Laboratory for Optoelectronics, Huazhong University of Science and Technology, Wuhan 430074,

Hubei, P. R. China;

<sup>b</sup>Nanjing University of Information Science and Technology, School of Physics and Optoelectronics Engineering, 219 Ningliu Road, Nanjing, Jiangsu, P. R. China;

\*E-mail: hongwei.han@mail.hust.edu.cn;

#### **Experimental Section**

### **Material and Sample Preparation**

(1) Spacer paste. For the synthesis of TiO<sub>2</sub>@ZrO<sub>2</sub> (T@Z) nanoparticles, TiO<sub>2</sub> nanoparticle was first synthesized by hydrothermal method according to previous report. Then, 3 g TiO<sub>2</sub> nanoparticles were re-dispersed in ZrOCl<sub>2</sub> aqueous solution by stirring for 5 minutes, which was subsequently precipitated by hydrazine. The mole ratio of TiO<sub>2</sub>/ZrO<sub>2</sub>/N<sub>2</sub>H<sub>4</sub> is 1/0.2/0.2. After hydrothermal reaction at 200 °C for 24 h, the resultant materials were washed by deionized water three times. The above encapsulation procedure was repeated for another three times. The resultant materials were dispersed in 100 ml of absolute ethanol, 5 g (per 1 g of T@Z) of a 10 wt% ethanolic solution of ethyl cellulose (10 cps and 46 cps with w/w of 50/50), and 5 g (per 1 g of T@Z) of terpineol. After the addition of each component, the mix was stirred for 10

min and homogenized by ultrasonic irradiation. The paste was finally produced by a three-roller mill grinder (EXAKT) after concentrating the mixture solution in a rotary evaporator (concentration conditions: water bath temperature of 35 °C, pressure of 5 mbar, time of 2 hours). P25 paste was formulated by the same method except that T@Z nanoparticles were replaced by commercial P25 powder. (2) Perovskite precursor. The MAI was prepared according to the reported procedure <sup>5</sup>. 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  $(5-AVA)_xMA1-_xPbI_3$ , the synthesized MAI (0.154 g), 5-AVAI (0.0123 g) and PbI<sub>2</sub> (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 ultrasonicating in detergent, deionized water, absolute ethonal for 30 minutes, respectively. Then the compact TiO<sub>2</sub> layer was deposited with aerosol spray paralysis at 450°C. Screen-printing technique was used to print TiO<sub>2</sub>, T@Z or conventional ZrO<sub>2</sub>, and Carbon films layer by layer onto the conductive glass coated with compact TiO<sub>2</sub>. Before screen-printing, paste was diluted with terpineol. The weight ratio of paste to terpineol is 1:1.5, 1:2 for P25 and spacer paste, respectively. TiO<sub>2</sub> and conventional ZrO<sub>2</sub> or T@Z film was sintered at 500 °C for 30 minutes before printing the next layer. TiO<sub>2</sub>, ZrO<sub>2</sub> and Carbon film were controlled to be 1.0 µm, 1.0 µm and 10.0 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

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<sup>-2</sup>. The active area of solar cell is 0.64-0.80 cm<sup>2</sup>. The area of aperture is 0.13 cm<sup>2</sup>. Scanning mode employs voltage step of 1 mV and delay time of 2 s for all devices. 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 T@Z nanoparticles were determined by a JEOL JEM-1200EX transmission electron microscope (TEM) at 120 kV, Tecnai GF30 transmission electron microscope. Samples of T@Z nanoparticles were prepared by placing a drop of a T@Z nanocrystals reaction solution diluted by ethanol on the surface of a copper grid. 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.



Figure S1. TEM images of T@Z nanoparticles in low (a) and high (b, c) resolutions.



Figure S2. (a) Time-resolved PL spectra of perovskite/spacer. (b) XRD of perovskite grown in two spacer.



Figure S3. SEM images of  $5nm ZrO_2$  film. (a) and (b) surface view and cross section (c) view of  $5nm ZrO_2$  film.



Figure S4. Roughness profiles of different spacer films, cross sectional SEM images of spacer printed on P25 (TiO<sub>2</sub>) film in large scale.



Figure S5. Illustration of setup designed to measure insulating properties of spacer.



**Figure S6.** Cross section SEM images of devices based on different spacer films. Cross section of (a)T@Z and (b) conventional based devices. (c) and (d) are high resolution images in red box areas.



Figure S7. PCE (a), FF (b),  $V_{oc}$  (c),  $J_{sc}$  (d) histograms of devices with T@Z (red color) and

conventional (black color)spacer.



Figure S8. Performance of devices based on T@Z with different thickness.



**Figure S9.** (a) Histogram of the power conversion efficiency of fully printable mesoscopic perovskite solar cells based on  $TiO_2@ZrO_2$  spacer.(b) Photostability (AM 1.5G 100 mW cm<sup>-2</sup>) of fully printable mesoscopic perovskite solar cells based on  $TiO_2@ZrO_2$  spacer.There is no encapsulation and no UV-filter in the test. The relative humidity is about 40%.

Spacer layer	$V_{oc}$	$J_{sc}$	$\overline{FF}$	PCE
	[mV]	mA cm <sup>-2</sup> ]	I'I'	[%]
TiO <sub>2</sub> (best device) <sup>a)</sup>	597	15.35	0.68	6.19
5nm ZrO <sub>2</sub> (best device)	860	17.74	0.66	10.1

Table S1. PV data of devices with different spacer film.

a) aperture area is  $0.16 \text{ cm}^2$ .