

## Electronic Supplementary Information

# Tubular perovskite solar cell: an improvement of charge separation at perovskite/HTM interfaces

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## 1. Experimental

**Perovskite precursor preparation.** Methyl ammonium iodide ( $\text{CH}_3\text{NH}_3\text{I}$ ) was synthesized and purified according to literature.<sup>1</sup> The precursor in the fabrication of tubular perovskite was prepared by dissolving 0.1 mmol of  $\text{CH}_3\text{NH}_3\text{I}$  and 0.1 mmol of  $\text{PbI}_2$  (99%, Aldrich) into 2.80 mL of DMF (99.8%, Aldrich). After stirred at 70 °C for 12 h under  $\text{N}_2$  protection,  $\text{CH}_3\text{NH}_3\text{PbI}_3$  solution with the concentration of 19 wt% was obtained.<sup>2</sup> Similar procedures were employed in the preparation of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  precursor forming planar perovskite layer. Instead of DMF, a mixture of  $\gamma$ -butyrolactone (GBL) and DMSO (7:3 v/v) was employed as the solvent. The final concentration of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  in the mixed solvent is 40 wt%.<sup>3</sup>

**Solar cell fabrication.** FTO-coated glass substrates (15  $\Omega$ /square, Nippon Sheet Glass) were cleaned with de-ionized water, acetone, and ethanol sequentially. A 30-50 nm dense blocking  $\text{TiO}_2$  layer was fabricated by spin-coating an isopropoxide solution (350  $\mu\text{L}$  Titanium (IV) isopropoxide (97 %, Alfa Aesar) in 5 mL of ethanol with 0.013 M HCl) onto precleaned FTO substrate at 2000 rpm for 30s and sintering the resultant substrate at 500 °C for 30 min.<sup>4</sup> Afterwards,  $\text{TiO}_2$  colloidal solution (20 nm  $\text{TiO}_2$ : terpeneol: ethanol = 1: 1: 3, weight ratio) was spin-coated onto the blocking  $\text{TiO}_2$  (bl- $\text{TiO}_2$ ) layer at 2000 rpm for 30 s. The resultant colloid-deposited FTO substrate was sintered at 500 °C for 30 min for attaining a mesoporous  $\text{TiO}_2$  (mp- $\text{TiO}_2$ ) layer with the thickness of 200~300 nm. The mp- $\text{TiO}_2$  film was further treated with 50 mM  $\text{TiCl}_4$  solution at 70 °C and subsequently annealed at 500 °C for 30 min.

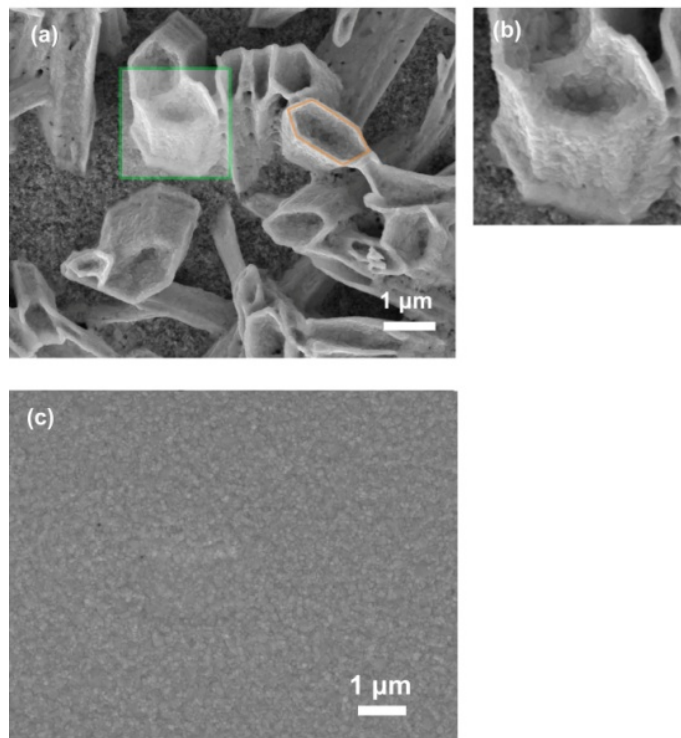
The deposition of tubular perovskite layer was carried out by spin-coating the perovskite/DMF precursor onto the surface of mp- $\text{TiO}_2$  film at 3000 rpm for 60 s and heated at 100°C for 10 min under  $\text{N}_2$  atmosphere. This protocol was also applied to form planar perovskite layer using the as-prepared perovskite/GBL/DMSO precursor. A slight difference is that the substrate was drop-casted with toluene before the step of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  solution casting. Afterwards, spiro-OMeTAD solution (72.3 mg of Spiro-OMeTAD, 17.5  $\mu\text{L}$  of lithium bis(trifluoromethanesulfonyl)-imide (LiTFSI)

solution (520 mg of LiTFSI in 1 mL of acetonitrile) and 28.8  $\mu\text{L}$  of 4-tert-butylpyridine all dissolved in 1 mL of chlorobenzene) was spin-coated onto the tubular and planar  $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{mp-TiO}_2/\text{bl-TiO}_2/\text{FTO}$  substrates at 2000 rpm for 30 s under  $\text{N}_2$  atmosphere.<sup>5</sup> Finally, spiro-OMeTAD deposited devices were covered with a thin graphite film with an active area of  $0.09 \text{ cm}^2$ . This graphite film was fabricated by coating a graphite paste onto a precleaned FTO substrate with a doctor-blade technique and then annealed at  $300^\circ\text{C}$  for 30 min. The graphite paste was prepared by stirring a mixture of graphite nanosheets (20 nm, Chenyang Graphite, China), terpineol and ethanol (1:5:1, wt%) vigorously for 30 min at room temperature.

**Device characterization.** The morphologies of tubular and planar perovskite films were recorded by using a Nova Nano SEM 230 field-emission scanning electron microscopy (FE-SEM, FEI). WAXS measurements were conducted by a D/max-2500 X-ray diffractometer (Rigaku, Japan) with Cu-K  $\alpha$  radiation at a scanning speed of  $1^\circ/\text{min}$ . Photoluminescence spectra were determined by a HITACHI F-4500 fluorescence spectrophotometer. The UV-vis absorption spectra were recorded by using a SHIMADZU UV-2600 spectrophotometer. Current-voltage ( $J$ - $V$ ) characteristics were measured by a computer controlled Keithley-2400 digital source meter (Keithley, USA). Cell illumination was performed by a standard solar simulator with a 300 W xenon lamp and an AM 1.5 filter (Oriel 91160-1000, Newport, USA). Light intensity was adjusted to 1 sun ( $100 \text{ mW cm}^{-2}$ ) by using a NREL-calibrated Si solar cell. The IPCE spectra were determined by a home-made IPCE measurement system, in which a DK240 monochromator (Spectral Products, USA) in combination with a 300-W halogen lamp was used to generate a light spectrum with a wavelength interval of 10 nm and a Keithley-2400 digital source meter was employed to record photocurrent responses. A Hamamatsu S1337-1010BQ silicon diode for determining incident light power was calibrated in National Institute of Metrology, China. Intensity modulated photovoltage and photocurrent spectroscopies (IMVS/IMPS) were measured by a Zennium electrochemical workstation (ZAHNER, Germany), in which a green light emitting diode (LED, 532 nm) was modulated to yield light frequency ranging from

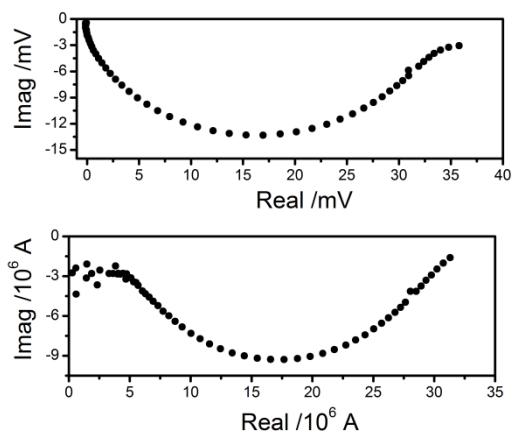
100 mHz to 10 kHz and illumination intensity from 1 to 40 mW cm<sup>-2</sup>. Electron densities were measured by charge extraction technique as reported.<sup>6</sup> Open circuit voltage decay measurements were carried out by LK2005A Electrochemical System (Lanlike, China) for monitoring voltage signals. The MATLAB software was employed to convert the voltage decay data to lifetimes. All the measurements were performed in air at room temperature on the devices without sealing.

## 2. Morphologies of Tubular and Planar Perovskite Layers



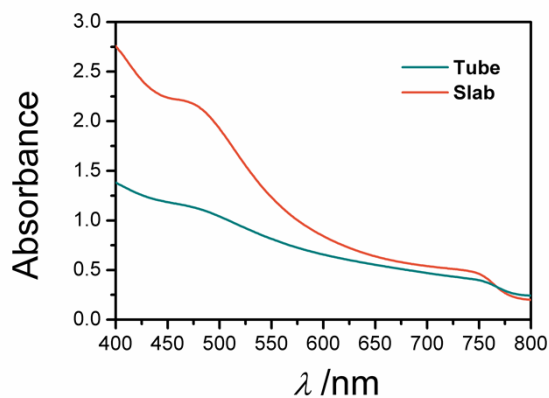
**Fig. S1** (a) SEM image of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite tubes coating onto mesoporous TiO<sub>2</sub> layer. Yellow hexagonal frame highlights the geometry of perovskite tube. (b) An enlargement of the green box in image a. (c) Top SEM view of planar CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> layer.

### 3. Nyquist Plots of IMPS/IMVS Responses



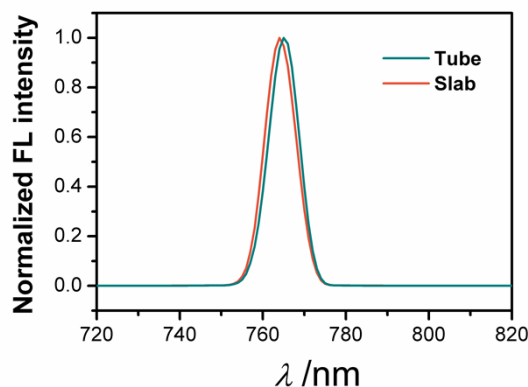
**Fig. S2** Typical Nyquist plots of (a) IMPS and (b) IMVS responses for tubular perovskite solar cells under illumination intensity of 10 mW cm<sup>-2</sup>.

### 4. UV-vis Spectra of Perovskite Films



**Fig. S3** UV-vis spectra of the devices with tubular and planar perovskite layers.

## 5. Normalized Fluorescence (FL) Spectra of Perovskite Films



**Fig. S4** Normalized fluorescence (FL) spectra of tubular and planar perovskite films.

### References

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