## Cost-efficient Clamping Solar Cells Using Candle Soot for Hole Extraction from Ambipolar Perovskite

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## **Supplementary Materials**

**Materials and Methods:** Unless otherwise stated, all chemicals were purchased from Sigma-Aldrich or J&K and used as received.

**Preparation of candle soot film, candle soot powder and corresponding solid tape.** Candle soot film was directly deposited by putting a FTO glass in the candle flame for several minutes. Black candle soot powder was collected by scrapping the aforementioned film off. The soot powder was further calcinated at 1000 °C in argon gas to enhance the conductivity. Calcinated candle soot was dispersed in ethanol to make a slurry (10 wt%) firstly, which was then pasted on a Cu foil and dried at 80 °C for 10 min to obtain carbon solid tape.

**Device fabrication.** CH<sub>3</sub>NH<sub>3</sub>I was prepared according to a reported procedure. The FTO glasses were cleaned in detergent solution, deionized water, acetone, ethanol in order and dried with clean air. After UV-O<sub>3</sub> cleaning, a 80 nm thick TiO<sub>2</sub> compact layer was pattern-deposited on FTO by a home-made ultrasonic spray deposition system at 500 °C using titanium diisopropoxide bis(acetylacetonate)

solution (0.05 M, ethanol) as precursor and air as carrier gas. After cooling to room temperature, the substrates were treated in a 0.04 M aqueous solution of  $TiCl_4$  for 30 min at 70 °C, rinsed with deionized water and baked at 500 °C for 20 min.

A mesoporous  $TiO_2$  layer of about 400 nm (thickness) was deposited by spin coating at 5,500 r.p.m. for 30 s using a pre-prepared  $TiO_2$  paste diluted in ethanol (1:4, weight ratio). After sequent baking treatment (125 °C, 10 min; 350 °C, 20 min and 500 °C, 30 min) and cooling to room temperature, the substrates were transferred into a home-made glove-box, which supplied a dry and closed working condition (note: lead is a highly poisonous metal, regardless if inhaled or swallowed).

PbI<sub>2</sub> was dissolved in *N*.*N*-dimethylformamide at a concentration of 460 mg mL<sup>-1</sup> and kept at 70 °C too. After the TiO<sub>2</sub> coated substrates were pre-heated to 70 °C to remove the water vapor, the PbI<sub>2</sub> solution was then spin coated on top of the TiO<sub>2</sub> layer at 5,000 r.p.m. for 20 s, gently dried in air, and heated up to 70 °C for 15min. For the 1<sup>st</sup> and 2<sup>nd</sup> generation clamping solar cell, the cooled PbI<sub>2</sub> substrates were dipped into a solution of CH<sub>3</sub>NH<sub>3</sub>I in 2-propanol (20 mg mL<sup>-1</sup>) for 2 min, rinsed with 2-propanol, then gently dried under a flow of dry air and heated to 70 °C for 15 min to get CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> film. A piece of FTO-candle soot film and the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> film were directly clamped together to make the 1<sup>st</sup> generation clamping solar cells. For the 2<sup>nd</sup> generation clamping solar cells, a calcinated carbon soot electrode of 10 µm thick was rolling transferred onto the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> film using the asprepared carbon tape by a home-made rolling transfer equipment (the compression pressure is estimated to be about 10 MPa), with another piece of FTO glass covered for clamping solar cell. After rolling transfer, the calcinated candle soot thin film was strongly attached on the perovskite thin film and will not peel off even flushed with compressed air. In the case of the 3<sup>rd</sup> generation clamping solar cells, the calcinated candle soot electrode was rolling transferred onto the PbI<sub>2</sub> film instead of perovskite film and then it was subjected to CH<sub>3</sub>NH<sub>3</sub>I bath soaking. The perovskite will chemically embed carbon soot to yield an interpenetrating interface.

**Material and device characterization.** Powder or film X-Ray diffraction (XRD) data was collected on an X'pert Pro (PANalytical) with Cu Kα radiation. Film thickness was determined by a Tencor Alpha-Step 200 surface profiler system and confirmed by three consecutive measurements. Conductivity and Hall Effect was conducted used compressed candle soot disc inHL5500PC (Bio-Rad). Morphologies of as-deposited candle soot and perovskite-related films were directly examined on JEOL6700F Scanning electron microscope (SEM) at an accelerating voltage of 5 kV. Transmission electron microscope (TEM) and high resolution transmission electron microscope (HRTEM) observations were carried out on a JEOL 2010 transmission electron microscope operating at 200 kV.

The 2<sup>nd</sup> and 3<sup>rd</sup> generation CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> + C films for photoluminescence (PL) test were prepared on glass slide using similar procedures in device fabrication, however, only a little of candle soot powder was deposited on the film. Single-particle PL and Raman measurements were conducted on a Renishaw 2000 laser Raman microscope equipped with a 514.5 nm and 20mW argon ion laser with a 1 µm spot size for excitation. For time-resolved PL (TRPL) measurements, a tunable Ti:sapphire femtosecond-pulsed laser was used as the excitation light source, with an excitation wavelength of 400 nm and an incident light intensity of 1 W cm<sup>-2</sup>. A Hamamatsu C5680-04 streak camera was used for the TRPL experiments. The TRPL measurements were performed in the vacuum.

**Solar cell performance evaluation.** The solar light simulator (Newport solar simulator, model number 6255, 150 W Xe lamp, AM 1.5 global filter) was calibrated to 1 sun (100 mW cm<sup>-2</sup>) using a silicon reference solar cell equipped with KG-5 filter. A black metal shading mask (0.15 cm<sup>2</sup>) was used to define the illumination area of the cells to be tested and tightly packaged to prevent light incident from the edges. Current density-voltage (J-V) characteristic curves were recorded using an IM6x electrochemical workstation (ZAHNER-Elektrik GmbH & Co., KG, Germany). Incident-photo-to-current conversion efficiency (IPCE) spectra were recorded using IPCE kit developed by ZAHNER-Elektrik in AC mode with frequency of 1 Hz.



## C Candle soot

RESISTIVITY

Meas	+++ Vm		Sym	Factor	R-sheet
43	1.97e-02	-1.96e-02	2.03	0.96	1.49e+04
41	4.00e-02	-3.97e-02	2.08	0.96	1.47e+04
21	1.76e-02	-2.08e-02	2.07	0.96	1.47e+04
23	3.73e-02	-4.23e-02	2.02	0.96	1.49e+04

## d Calcinated candle soot

RESI,					
Meas	+++ Vm		Svm	Factor	R-sheet
43	2.23e-02	-2.22e-02	2.00	0.96	14.1
41	4.44e-02	-4.48e-02	2.01	0.96	14.1
21	2.20e-02	-2.25e-02	2.01	0.96	14.1
23	4.47e-02	-4.45e-02	2.00	0.96	14.1

Figure S1 | Characterization of the as-prepared and calcinated candle soot. a, A typical scanning electron microscope (SEM) image of the calcinated candle soot film, without obvious morphology change during calcination. b, Infrared spectroscopy results of the as-prepared and calcinated candle soot. Original conductivity test results of c, the as-prepared candle soot thin film (thickness: 40  $\mu$ m) and d, calcinated candle soot thin film (thickness: 100  $\mu$ m).



**Figure S2** | **a**, Absorbance spectra of PbI<sub>2</sub> and CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> films on a mesoporous TiO<sub>2</sub> film, insets present an obvious color change from shinny yellow to dark brown. **b**, X-ray diffraction (XRD) data clearly illustrate the phase transformation from PbI<sub>2</sub> to CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>. **c**, Cross-sectional SEM image of the as-prepared CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> film. **d**, Cross-sectional SEM image of FTO/TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/C device.

Figure S2a shows the transformation absorbance spectra from  $PbI_2$  to  $CH_3NH_3PbI_3$  on a mesoporous  $TiO_2$  film. Actually, the as-deposited  $PbI_2$  film majorly absorbs light bellow 520 nm and shows a shiny and transparent yellow color, after  $CH_3NH_3I$  bath treatment, the  $PbI_2$  is converted into  $CH_3NH_3PbI_3$ , enlarging the absorbance curve to near 800 nm, with dark brown appearance. Figure S2b represents the XRD data monitoring the phase transformation from  $PbI_2$  to  $CH_3NH_3PbI_3$ ,  $PbI_2$  shows three characteristic diffraction peaks at 12.77°, 38.74°, and 52.44°, which can be associated with (001), (003) and (004) planes. After transformation,  $CH_3NH_3PbI_3$  presents three new characteristic diffraction peaks at 14.10°, 28.44°, and 43.00° can be assigned as the (110), (220), and (330) planes, respectively. Figure

S2c, the cross-sectional SEM image of the as-prepared CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> film, displays a uniform film with a thickness of about 400 nm and many angular convex on the top layer. Figure S2d represent a typical cross sectional SEM image of a FTO/TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/C device, revealing well-defined layer stacking configuration.



Figure S3 | TEM images of the  $3^{rd}$  generation  $CH_3NH_3PbI_3 + C$  thin film in different positions, showing that the C nanoparticles are well connected or embedded in  $CH_3NH_3PbI_3$  nanoparticles.



**Figure S4** | Long term stability evaluation of one  $3^{rd}$  generation clamping solar cell. The solar cell was stored in dry air (20 % moisture) without encapsulation for one month before the stability testing.

In general, according to our previous experience, our C/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> clamping solar cell is more stable than spiro-MeOTAD based devices. As shown in Figure S4, after one month storage, the cell showed only ~15% decay of PCE, solely from the decrease of  $V_{oc}$  and FF. Remarkably,  $J_{sc}$  was kept essentially constant. As the candle soot is environmental stable, the performance decay can be mainly attributed to the instability of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>, which is found to be sensitive to water. It is believed that the long term stability of our clamping solar cell can be promoted by proper encapsulation, which is underway in our laboratory.



Figure S5 | J-V curve of perovskite solar cell with Au cathode, and the cell configuration can be represented as FTO/TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/Au.



Figure S6 | Performance of graphite/perovskite clamping solar cell. a, SEM image of graphite plates, revealing a tens of micrometer in diameter graphite nanostructure. b, The current density – voltage (J-V) of the graphite/perovskite clamping solar cell, presenting a poor power conversion efficiency of 0.99 %. c, Illustration diagram of graphite/perovskite clamping solar cell, showing poor interface contact between graphite plate and perovskite layer.

Solar cell with different cathode	$V_{\rm oc}({ m V})$	$J_{ m sc}$	FF	PCE
		(mA cm <sup>-2</sup> )		(%)
FTO	0.50	2.39	0.31	0.37
Pt sheet	0.40	0.50	0.15	0.03
Ag sheet	0.40	1.35	0.29	0.16
Carbon paper	0.65	1.50	0.15	0.15

**Table S1** | Solar cell performance summaries of the clamping solar cell families with the configuration of FTO/TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/clamping cathode.

To extend the concept of clamping solar cell, various materials and substrates, such as FTO glass, Pt and Ag sheets, etc., were clamped to CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> photoanode to make photovoltaic devices. In general, we can observe photovoltaic effect. However, similar to Figure S5c, macroscopic FTO glass, Pt and Ag sheets cannot form good interface contact with CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> film. In other words, there may be only few macroscopic contact points that can extract holes form CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> film, resulting in poor photovoltaic performance.



**Figure S7** | Performance of the solar cell devices fabricated by the simple clamping approach using Spiro-MeOTAD as hole transporter with the cell configuration of FTO/TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/Spiro-MeOTAD/FTO.



**Figure S8** | Performance testing results of the  $3^{rd}$  generation clamping solar cells fabricated with different thicknesses of the candle soot films.



**Figure S9** | Impedance spectroscopy characterization of the three generation clamping solar cells: (A) Complex plane impedance plots; (B) Enlarged spectra in the dashed boxes in (A). Equivalent circuit used for modeling is inserted in (B), where  $R_s$  is the series resistance,  $R_c/C_c$ , resistance/capacitance associated with carbon electrode, and  $R_{rec}/C_{rec}$ , resistance/capacitance related to C/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> interface.



**Figure S10** | Mott–Schottky curve for the  $3^{rd}$  generation FTO/TiO<sub>2</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/C solar cells. A linear fit (shown as the red line) shows that the built-in potential is 0.85 V, which is in good agreement with the  $V_{oc}$ .