Experimental

Materials

Unless stated otherwise, all materials and reagents were purchased from Aladdin and used without further purification.

Preparation of carbon paste

MWCNT with average length of 1.3 μm and CB having average particle size of 30 nm were vigorously agitated for 3 h to obtain homogenous carbon powers. Carbon paste was prepared by mixing 50 mg of MWCNT and CB powders (0 mg, 12.5 mg, 15 mg, 20 mg) in 0.2 mg of terpineol. Upon persistent agitation for 30 min at room temperature, the carbon paste was made for PSC applications.

Preparation of TiO_2 photoanode

A fluorine doped tin oxide (FTO) glass with sheet resistance of 12 ohm square^{-1} was etched by 2.0 M HCl and Zn powders to obtained desired patterns and then rinsed by deionized water, acetone and ethanol.[1] Subsequently, an ethanol solution of titanium isopropoxide (0.5 M) and diethanol amine (0.5 M) was spin-coated onto FTO glass at 7000 rpm for 30 s, and then annealed at 500 ^oC for 2 h in air to obtain the compact TiO_2 (*c*-TiO_2) layer. The mesoscopic TiO_2 (*m*-TiO_2) layer was deposited onto *c*-TiO_2 layer by spin-coating TiO_2 paste[2,3] at 2000 rpm for 30 s, and then annealed in air at 450 ^oC for 30 min. Subsequently, the as-prepared FTO/*c*-TiO_2/*m*-TiO_2 photoanode was immersed in a 0.04 M $TiCl_4$ aqueous solution at 75 ^oC for 30 min. After rinsed with deionized water and ethanol, the photoanode was further calcined at 450 ^oC in air for another 30 min.

Assembly of all-inorganic PSCs

All the processes for fabricating all-inorganic PSCs were performed at room temperature (10~20 ^oC) and in ambient air (Relative humidity: 30~60%). In details, a DMF solution of 1.0 M $PbBr_2$ was spin-coated onto the as-prepared TiO_2 photoanode layer at 2000 rpm for 30 s, and dried at 80 ^oC for 30 min. Subsequently, a methanol solution of 0.07 M CsBr was spin-coated onto $PbBr_2$ layer at 2000 rpm for 30 s, followed by drying at ambient air, the film was heated at 250 ^oC for 5 min. By repeated depositing CsBr layers for five times, high-impurity $CsPbBr_3$ film was obtained. Finally, the carbon back-electrode was covered onto $CsPbBr_3$ film by coating carbon paste with a doctor-blade method.

Photovoltaic measurements and characterizations

The photocurrent density-voltage (*J*-*V*) curves of solar cell device were characterised by a CHI660E electrochemical workstation under one simulated solar light in ambient atmosphere. The solar simulator equipped with a 100 W xenon arc lamp and the incident light intensity was controlled at 100 mW cm^{-2} by calibrating with a standard silicon solar cell. A power source (Newport 300 W xenon lamp, 66920) with amonochromator (Newport Cornerstone 260) in the 300-850 nm wavelength range at room temperature to obtained the external quantum efficiency (EQE) spectra. The cross-sectional view of the all-inorganic PSC device were characterized on a field-emission scanning electron microscopy (FESEM, Japan Hitachi field emission S4800). The time-resolved delay PL spectra were measured on a Horiba spectrometer excited by 385 nm laser, and the PL characterizations were performed on a FluoroMax-4 Spectrofluorometer.

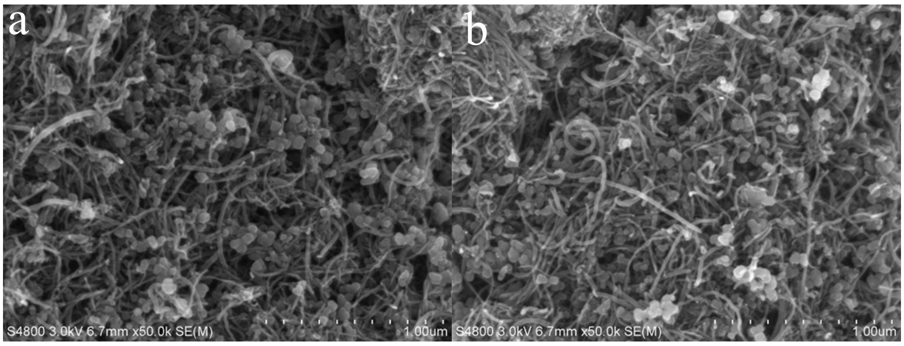

Fig. S1. The top-view SEM images of (a) 30 wt% CB and (b) 40 wt% CB carbon electrodes.

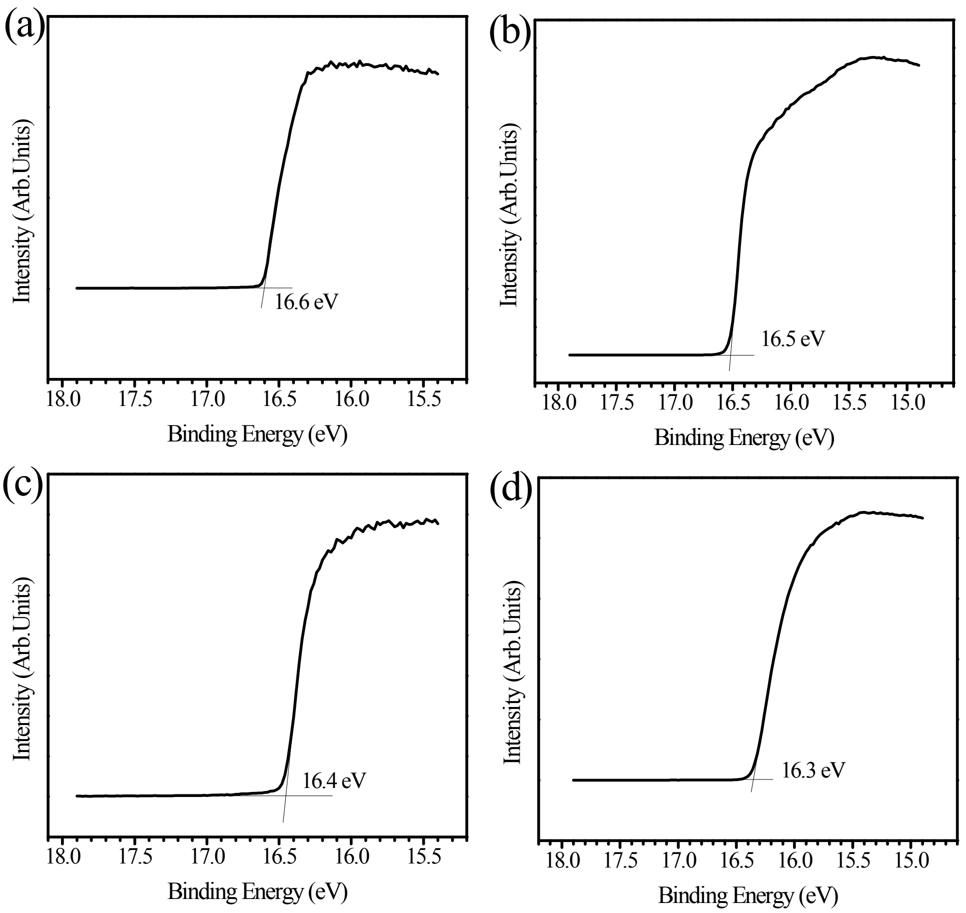

Fig. S2. The UPS spectra of carbon electrodes at different CB dosages: (a) 0 wt%, (b) 25 wt%, (c) 30 wt% and (d) 40 wt%.

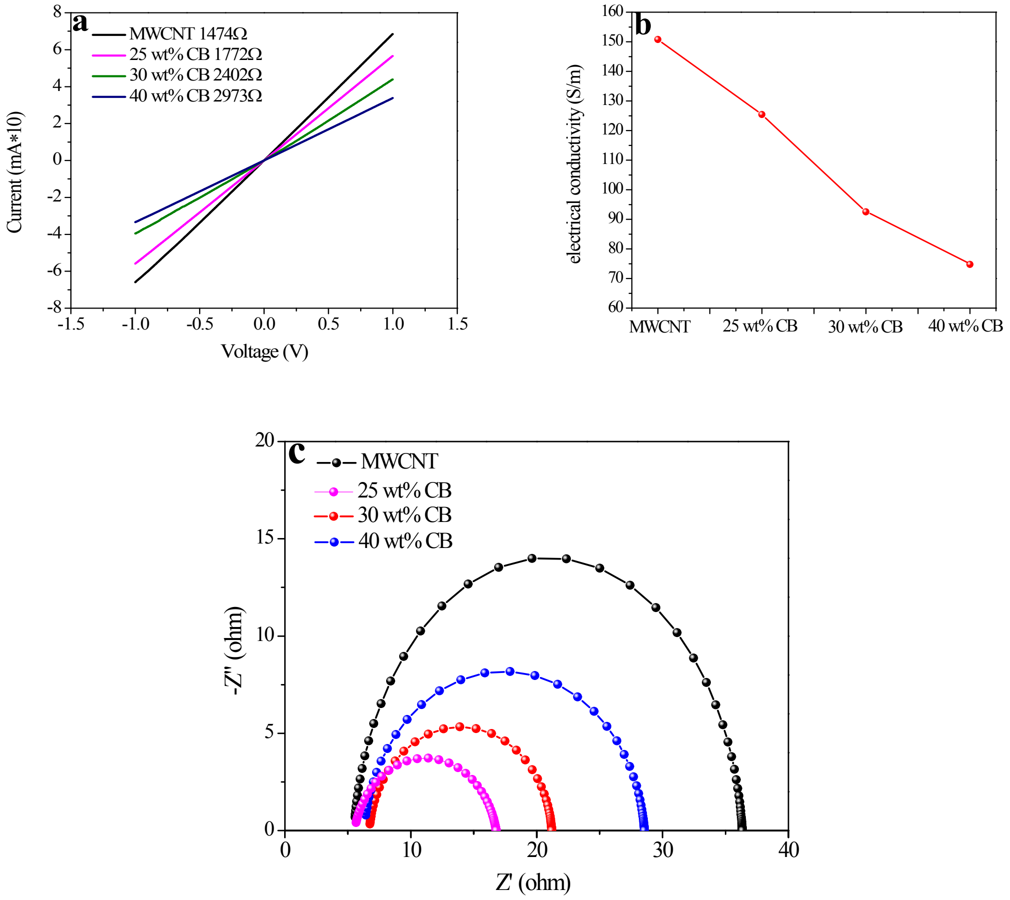

Fig. S3. (a) The *I-V* lines of carbon electrodes at different CB dosages to obtain the ohmic resistances: 0 wt%, 25 wt%, 30 wt% and 40 wt%. (b) The electrical conductivity of carbon electrodes at different CB dosages : 0 wt%, 25 wt%, 30 wt% and 40 wt%. (c) Nyquist EIS spectra of the devices with configuration of FTO/TiO_2/$CsPbBr_3$/carbon.

Table S1. The EIS data of inorganic PSCs.

Devices	R_s (ohm cm^2)	R_{ct} (ohm cm^2)
FTO/TiO_2/$CsPbBr_3$/MWCNT	5.49	30.85
FTO/TiO_2/$CsPbBr_3$/25 wt% CB	5.53	11.26
FTO/TiO_2/$CsPbBr_3$/30 wt% CB	6.30	22.26
FTO/TiO_2/$CsPbBr_3$/40 wt% CB	6.71	14.50

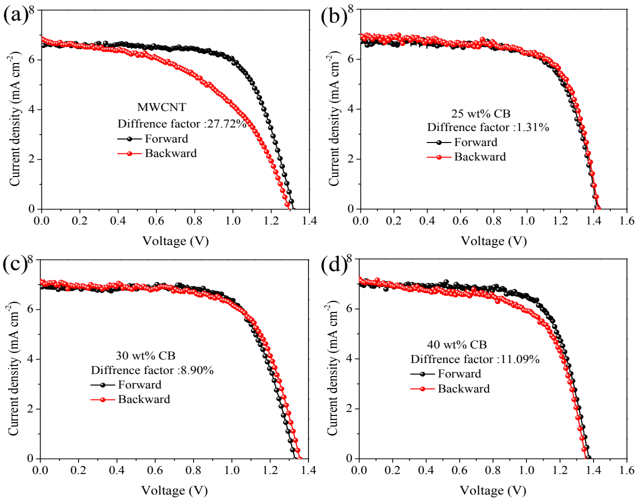

Fig. S4. The *J-V* curves of carbon electrode tailored all-inorganic PSCs from reverse and forward scan directions. All the devices are not encapsulated.

The charge accumulation at interfaces always creates hysteresis in PSCs, as shown in Fig. S4, all the devices are measured from reverse and forward scan directions (reverse: 0-1.6 V, foreword: 1.6-0 V) to study their hysteresis effects. Difference factor (DF) is used to remark the difference of PCE from reverse and backward scans.

$$\text{Difference factor} = (\eta_{\text{reverse}} - \eta_{\text{forkward}}) / \eta_{\text{reverse}}$$

where η_{reverse} and η_{forkward} are the PCE values from reverse and forward scans, respectively. As shown in Fig. S3, the DF is as large as 27.72% for the PSC using MWCNT-only electrode, and it is reduced to 8.90% and 11.09% by mixing 30 and 40 wt% CB with MWCNT, respectively. The *J-V* curves are almost overlapped by adding 25 wt% CB, yielding a low DF of 1.31%.

Notes and references

1 T. Liu, K. Yu, L. Gao, H. Chen, N. Wang, L. Hao, T. Li, H. Hea and Z. Guo, *J. Mater. Chem. A*, 2017, **5**, 17848-17855.
2 Y. Duan, Q. Tang, R. Li, B. He and L. Yu, *J. Power Sources*, 2015, **274**, 304-309.
3 T. Liu, X. Mai, H. Chen, J. Ren, Z. Liu, Y. Li, L. Gao, N. Wang, J. Zhang, H. He and Z. Guo, *Nanoscale*, 2018 **10**, 4194-4201.