Supplementary Information for:

Breaking down the confinement effect on perovskite growth to fabricate efficient, carbon electrode-based mesoscopic perovskite solar cells *via* low-temperature and all-air procedures

De'en Guo, Jiao Ma, Heng Peng, Xiaohan Yu, Junhao Xue, Haipeng Xie, Han Huang, Deming Kong, Conghua Zhou*

Hunan Key Laboratory of Super-microstructure and Ultrafast Process, Hunan Key Laboratory of Nanophotonics and Devices, Institute of Super-microstructure and Ultrafast Process in Advanced Materials (ISUPAM), School of Physics, Central South University, Changsha, Hunan 410083, China

* Corresponding author: chzhou@csu.edu.cn (C. Zhou)

Experimental Section:

1.1 Materials and Regents

FTO substrates (Advanced Election Technology), Graphite (99.85%, Sinopharm), Carbon black (Ketjen 600J), Zirconium oxide (ZrO_2, 99%, Sinopharm), ethanol (99%, Sinopharm), ethylene glycol (EG, 99%, Sinopharm), γ-Butyrolactone (GBL, 99.9%, Aladdin), TiO_2 nanocrystallites (P25, Degussa), lead iodide (PbI_2, 99.99%, Advanced Election Technology), methylammonium iodide (CH_3NH_3I) and $HOOC(CH_2)_4NH_3I$ (5-AVAI) (Xi'an Polymer Light Technology Corp) were all used as received. Deionized water was prepared in laboratory.

1.2 Materials Synthesis

Carbon paste was prepared by ball-milling graphite (2 g) and CB (*x* g, *x*=0.0625, 0.125, 0.25, 0.5, 0.75, 1.5 g) in 20 mL alcohol for 24 h. ZrO_2 sol was added as the binder. The speed of the planetary ball mill used is 300 r/min. For thick carbon-electrode, carbon paste is prepared by ball-milling 6g graphite and 1.5g CB in 30 mL ethanol. Perovskite precursor was prepared by dissolving 382 mg PbI_2, 10 mg 5-AVAI and 132.5 mg MAI in 0.9 mL GBL [1].

1.3 Device fabrication, and related material and device characterizations

Device fabrication process of the low-temperature, hole-conductor-free, mesoscopic perovskite solar cells (meso CPSCs) were produced by all air and low-temperature (150^oC) processes, following the method described in previous works[1]. For buried interface sample preparation, surface layer of carbon electrode was peeled off by tape, then a drop of polymethyl methacrylate (PMMA) chlorobenzene solution

is casted on the surface, being dried at 60°C, and then peeled off again, from the bottom substrate. Material characterization and device characterization methods were similar to that described elsewhere [2, 3]. As for external quantum efficiency (EQE) test, light-soaking was pre-performed, like that done in recording the current density – voltage characteristics.

Supplementary figures:

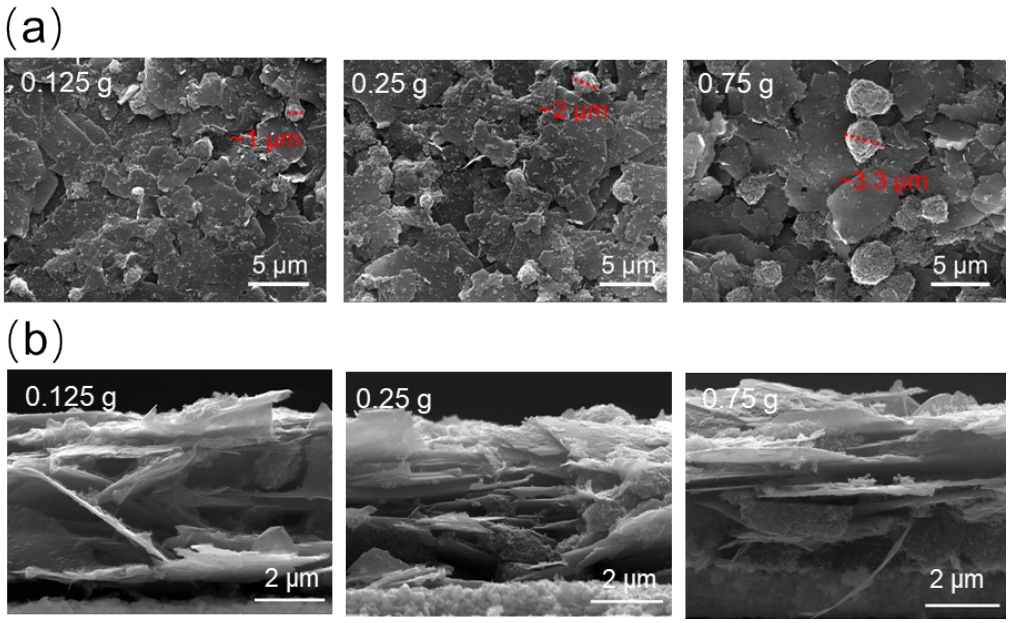

Fig. S1. (a, b) SEM images of surface and cross-section of carbon-electrodes with different CB masses.

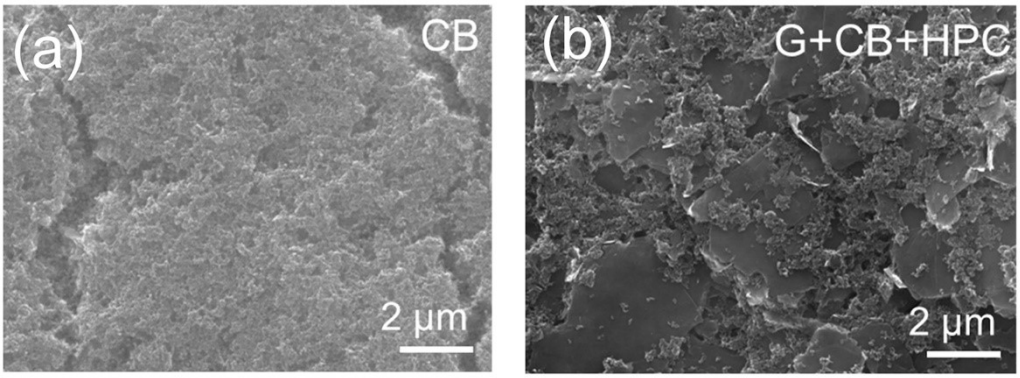

Fig. S2. Surface SEM images of carbon-electrode (CE)prepared by. (a) Carbon black (CB); (b) Graphite (G), carbon black (CB) and hydroxypropyl cellulose (HPC).

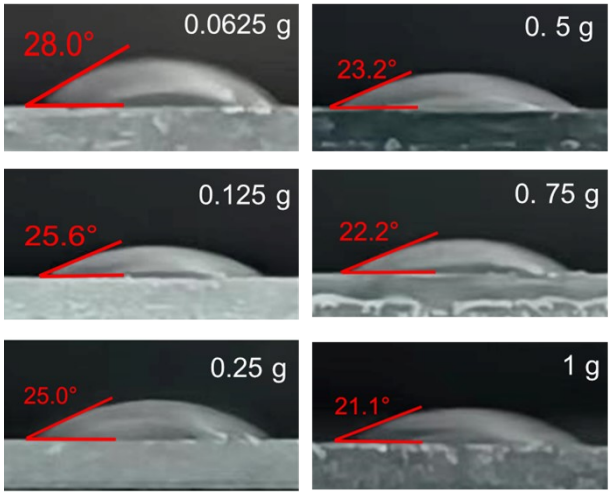

Fig. S3. Contact angle test on carbon-electrode prepared by different CB mass.

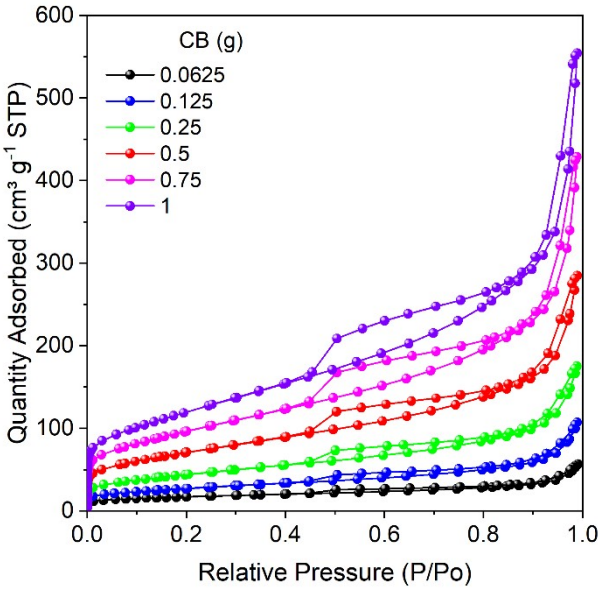

Fig. S4. N_2 adsorption-desorption isotherms of carbon-electrodes (CEs).

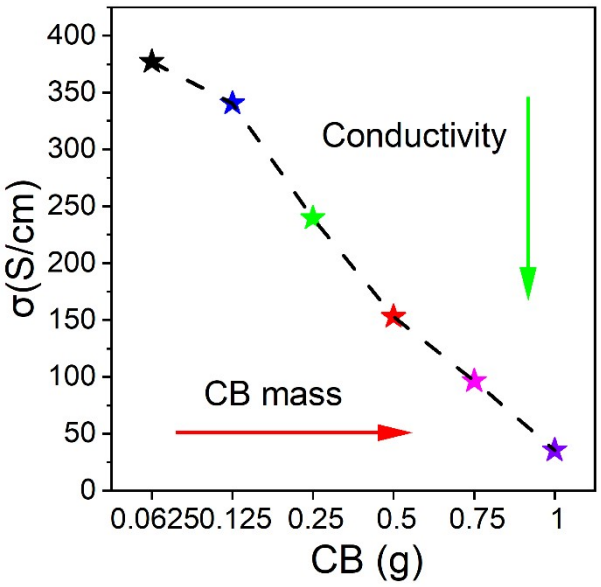

Fig. S5. Conductance test on CEs prepared with different CB mass.

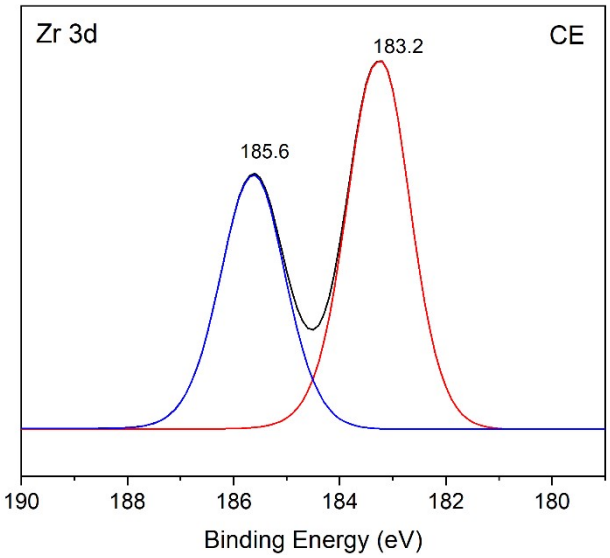

Fig. S6. XPS spectra of CE: Zr 3d.

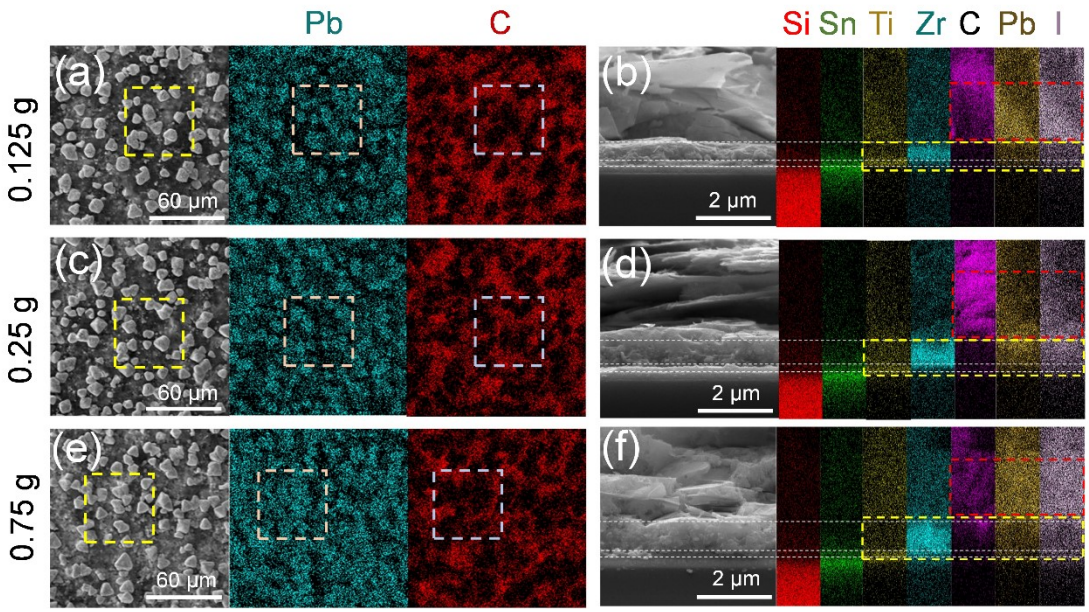

Fig. S7. SEM images of surface (left) and cross-section (right) of low-temperature mesoscopic perovskite solar cells (meso CPSCs) with carbon-electrodes prepared with different CB mass.

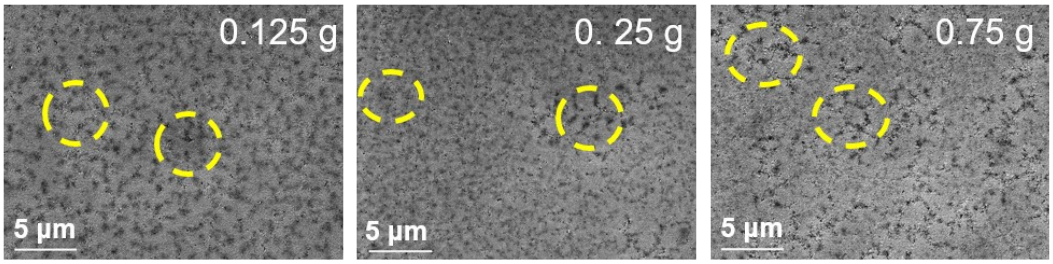

Fig. S8. SEM images of "PVSK/ETL" interface.

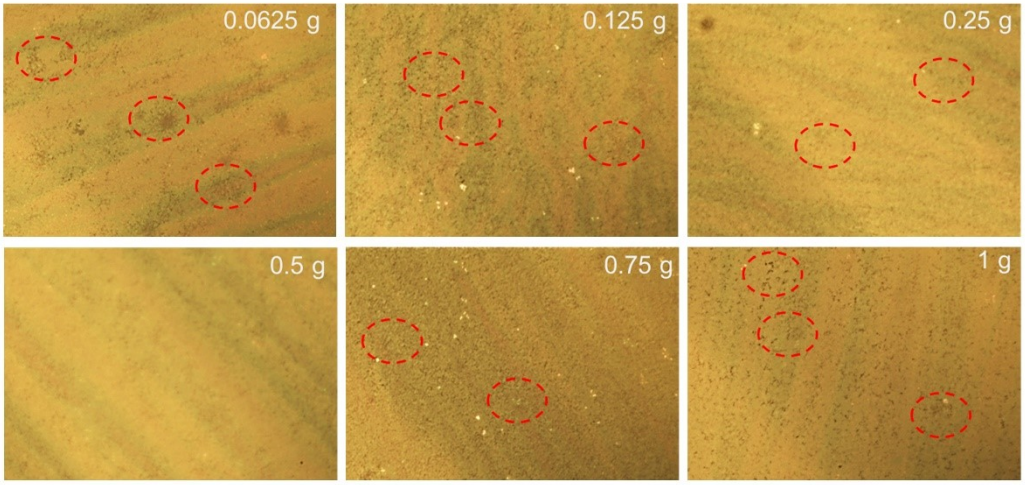

Fig. S9. Metallograph images of "PVSK / ETL" interface.

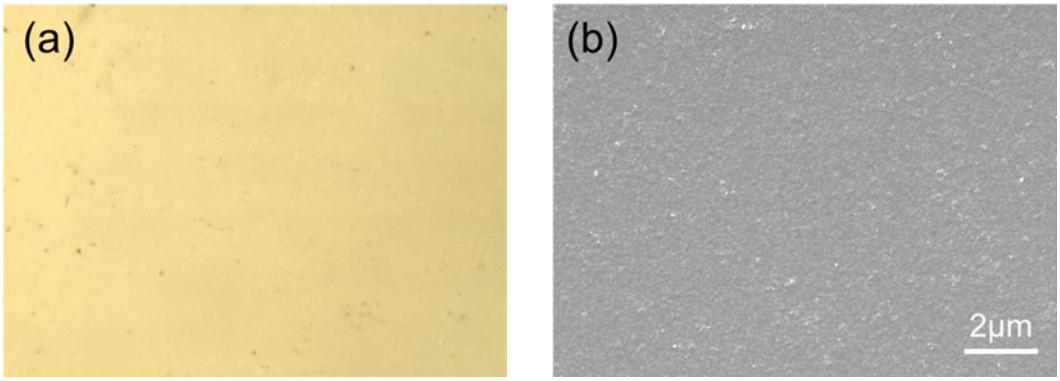

Fig. S10. (a) Top-view metallograph images and (b) SEM images of the FTO substrate after the PVSK incorporated layer has been peeled-off, so as to judge the quality of the buried interface.

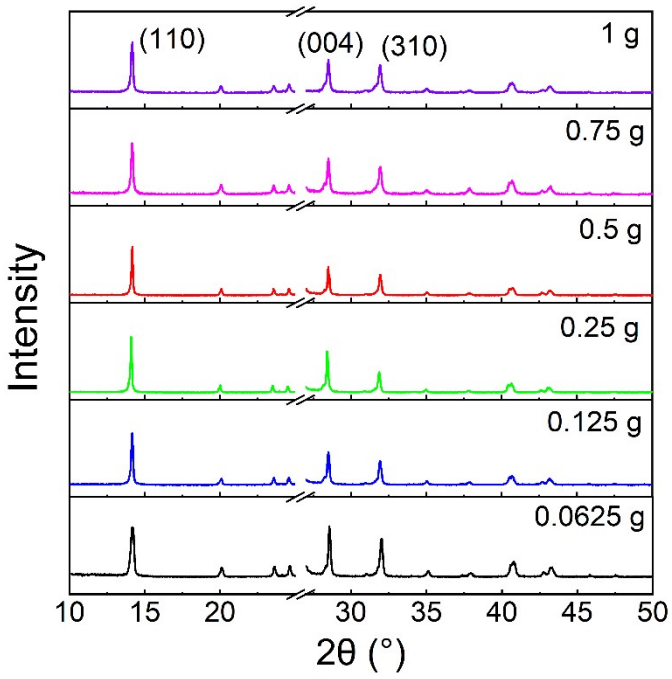

Fig. S11. XRD patterns of meso-CPSCs after CE has been partially peeled off. (X-ray is induced from the carbon-electrode).

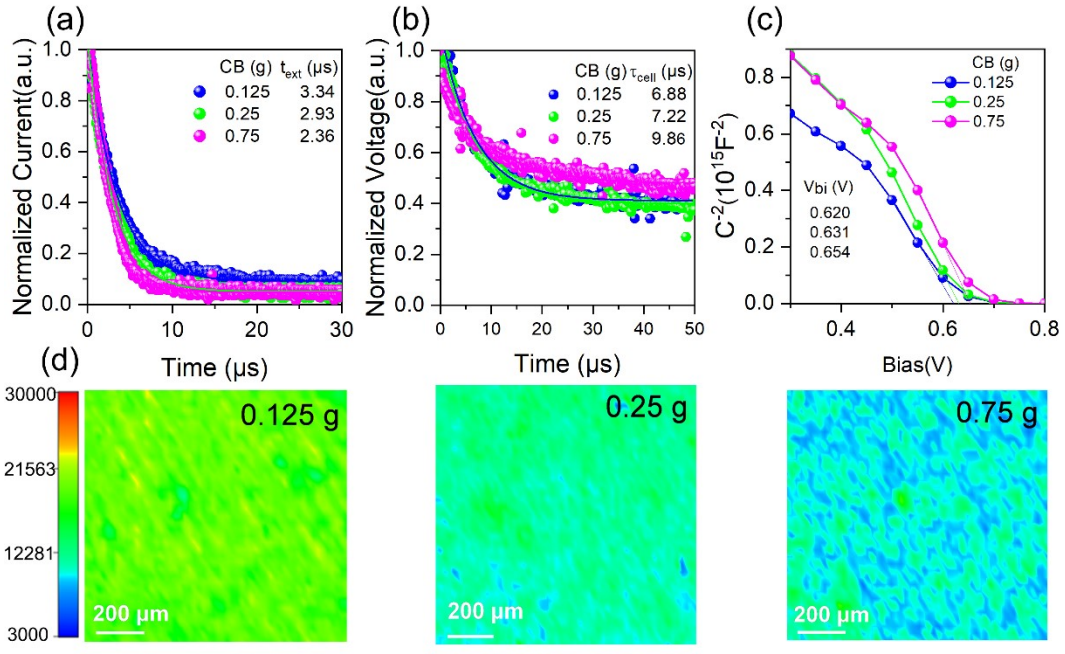

Fig. S12. (a, b) TPC / TPV decay curves; (c) Mott–Schottky analysis; and (d) PL mapping of meso-CPSCs (incident laser is guided from the FTO side).

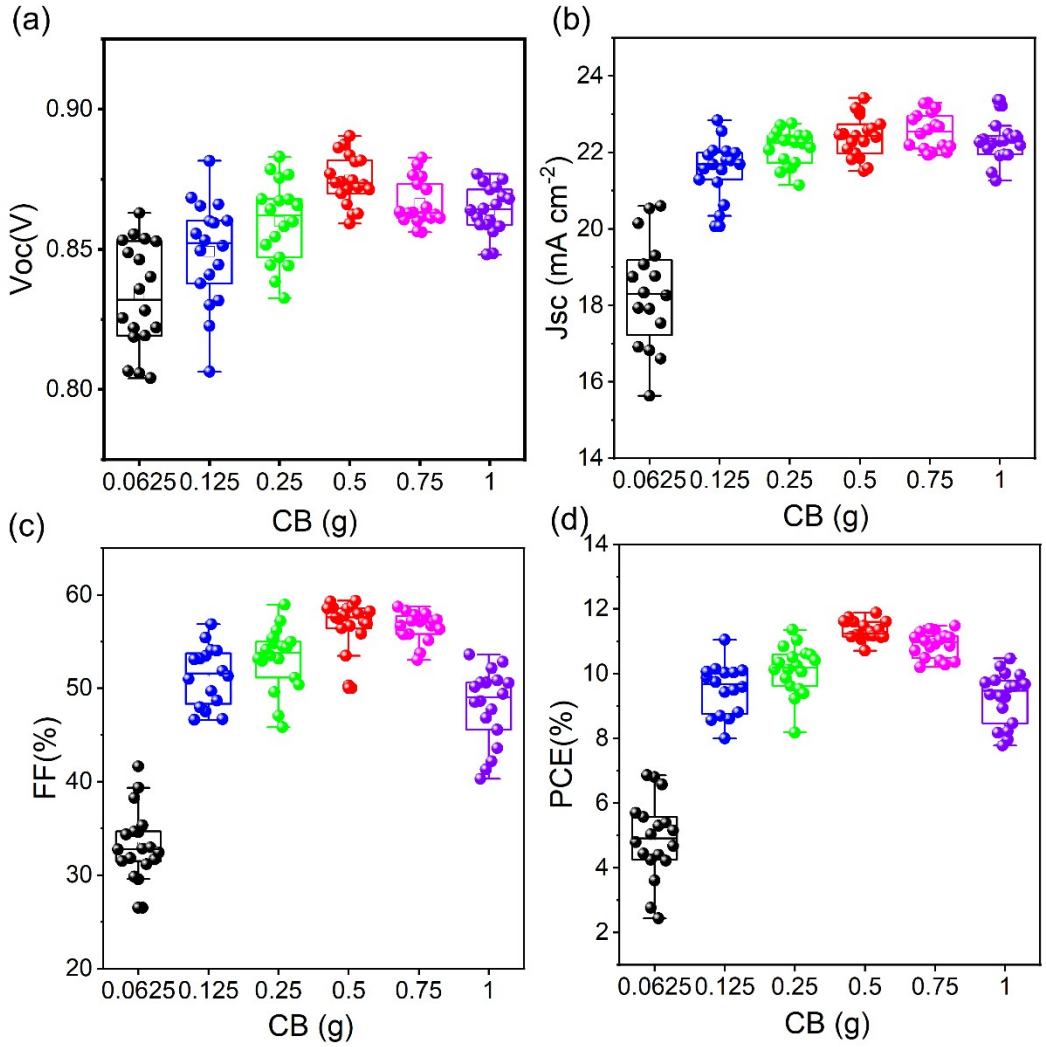

Fig. S13. Statistics on performance parameters (reverse scans): (a) V_{oc}; (b) J_{sc}; (c) *FF*; and (d) PCE.

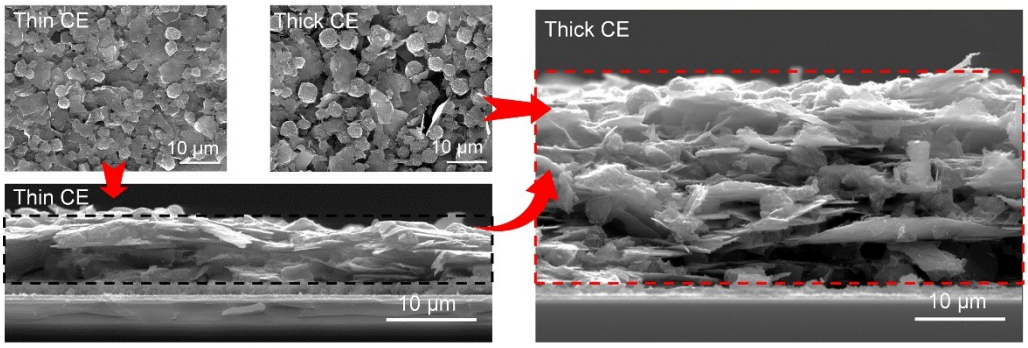

Fig. S14. Surface and cross-sectional SEM images of CEs.

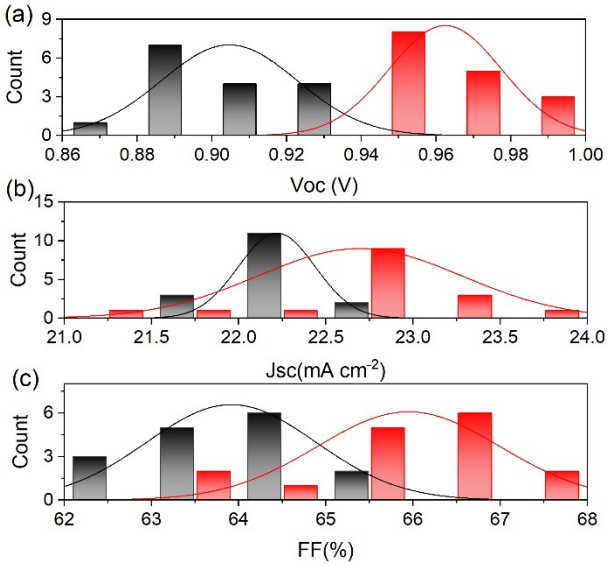

Fig. S15. Statistics on performance parameters with thin / thick CEs: V_{oc}, J_{sc}, *FF*.

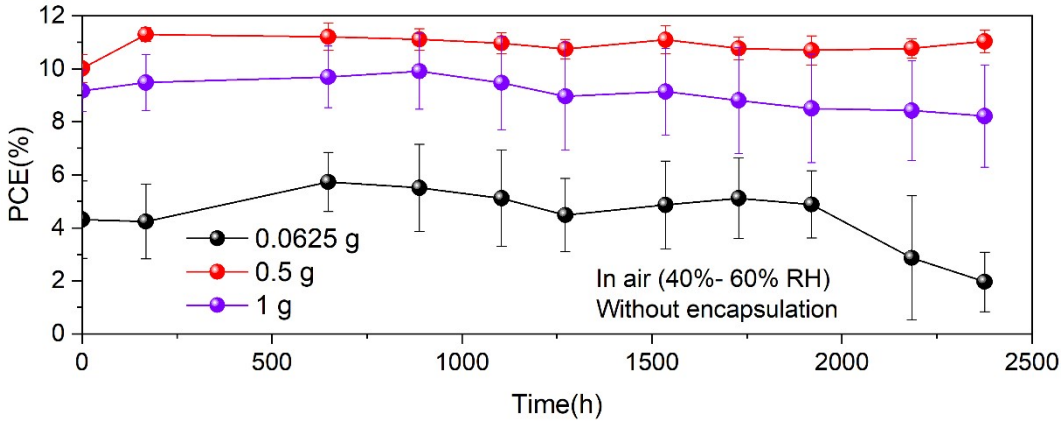

Fig. S16. Storage stability test of meso-CPSCs. (Relative humidity 40%~60%, no encapsulation is used).

References

1. D. Guo, X. Yu, Z. Fang, H. Peng, H. Xie, H. Huang, D. Kong and C. Zhou, *Sol. RRL*, 2024, **8**, 2400021.
2. D. Guo, J. Ma, S. Y. Lin, X. Guo, H. Huang, D. M. Kong, F. X. Xu, Y. L. Gao, W. H. Zhang, Y. Hu and C. H. Zhou, *Appl Phys Lett*, 2022, **120,** 263502.
3. J. Ma, S. Lin, M. Fang, Z. Fang, X. Yu, D. e. Guo, H. Xie, D. Kong, Y. Li and C. Zhou, *Small*, 2024, **20**, 2310196.