Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

MOF/ PEDOT/ HPMo based polycomponent hierarchical hollow micro-vesicles for high performance flexible supercapacitors

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Summary

Experimental Section

Preparation of organic ligand

According to the previous reports, the tetrakis (4-carboxyphenyl) porphyrin (H_2TCPP) was synthesized with some modifications.[1-2] Typically, pyrrole (3.0 g, 0.043 mol) and methyl p-formylbenzoate (6.9 g, 0.042 mol) were added into a 250 mL three-necked flask with propionic acid (100 mL). The solution was refluxed at 140 °C for 12 h and then cooled down to room temperature. Filtering the precipitate, washed by ethanol, ethyl acetate and tetrahydrofuran, and finally drying in vacuum overnight. Then the obtained precipitate (1.95 g) was dissolved with THF (60 mL) and MeOH (60 mL) in a three-necked flask, then a solution of KOH (6.82 g) dissolved in H_2O (60 mL) was added. This mixture solution was refluxed at 80 °C for 12 h and subsequently cooled down to room temperature. Additional H_2O was added to make sure the solid was completely dissolved and then the solution was acidified with 1m HCl until no

more purple precipitate generated. The purple solid was filtrated, washed with water, and dried in vacuum.

Preparation of the PVA/Na_2SO_4 gel electrolyte

Na_2SO_4 (1 M, 6 g) and PVA powder (6 g) were added into 60 mL of deionized water, which was heated to 85°C under stirring until the mixture became clear. Two identical pieces of PCN-224@PEDOT/PMo_{12}-CC-II flexible electrodes (1 × 2 cm^2) were directly immersed in PVA/Na_2SO_4 gel electrolyte for 5 min. Afterward, the two as-prepared electrodes were symmetrically integrated into one flexible supercapacitor device.

Electrochemical Calculation

The specific capacitance calculated from Cyclic voltammetry (CV) examined in the range of -0.2 to 0.8 V at 10-100mV s^{-1}, areal capacitance (F cm^{-2}) calculated by equations (1):

$$C_s = \frac{\int IdV}{vs\Delta V} \quad (1)$$

where *C*s is the specific capacitance, *I* (A) is the instant current, *v* (V s^{-1}) is the scan rate, Δ*V* (V) is the range of a scanning region, *S* (cm^2) is the effective electrode area. The areal capacitance calculated by equation (2):

$$C_s = \frac{I\Delta t}{S\Delta V} \quad (2)$$

The Cs was evaluated from the galvanostatic charge-discharge (GCD) curves follow the equation (3), the energy density and power density were calculated by equation (3) and (4):

$$E = \frac{1}{2} \times C \times \Delta V^2 \quad (3)$$

$$P = \frac{E}{\Delta t} \quad (4)$$

The electrochemical measurements of flexible all-solid-state supercapacitor was evaluated by a two-electrode testing system. Where E ($mWh \cdot cm^{-2}$) is the energy density and power density is P ($mW \cdot cm^{-2}$), C ($F\ cm^{-2}$) is the specific capacitance, Δt is the discharge time.[3]

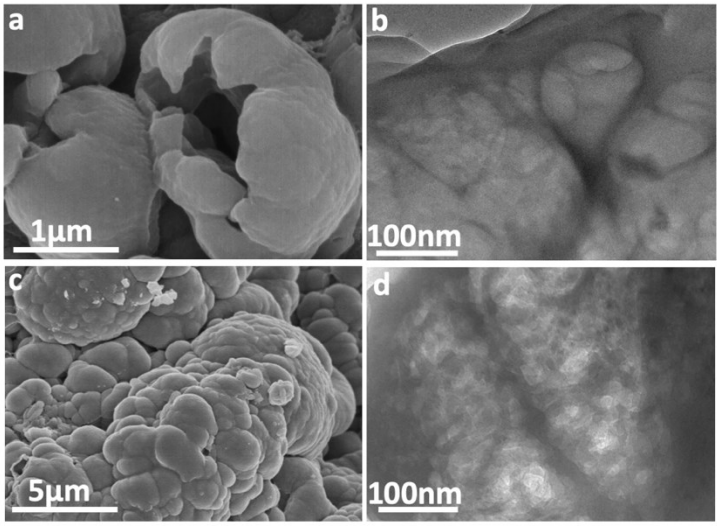

Figure S1. SEM and TEM images of PCN-224@PEDOT/PMo_{12}-CC-I (a-b) and III (c-d)

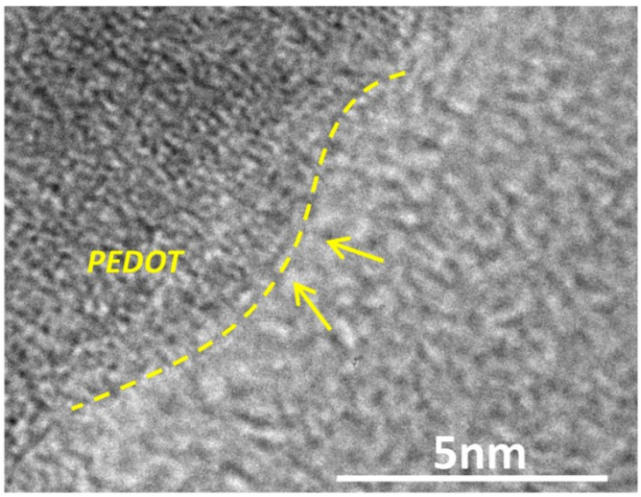

Figure S2. TEM image of PCN-224@PEDOT/PMo_{12}-CC-II

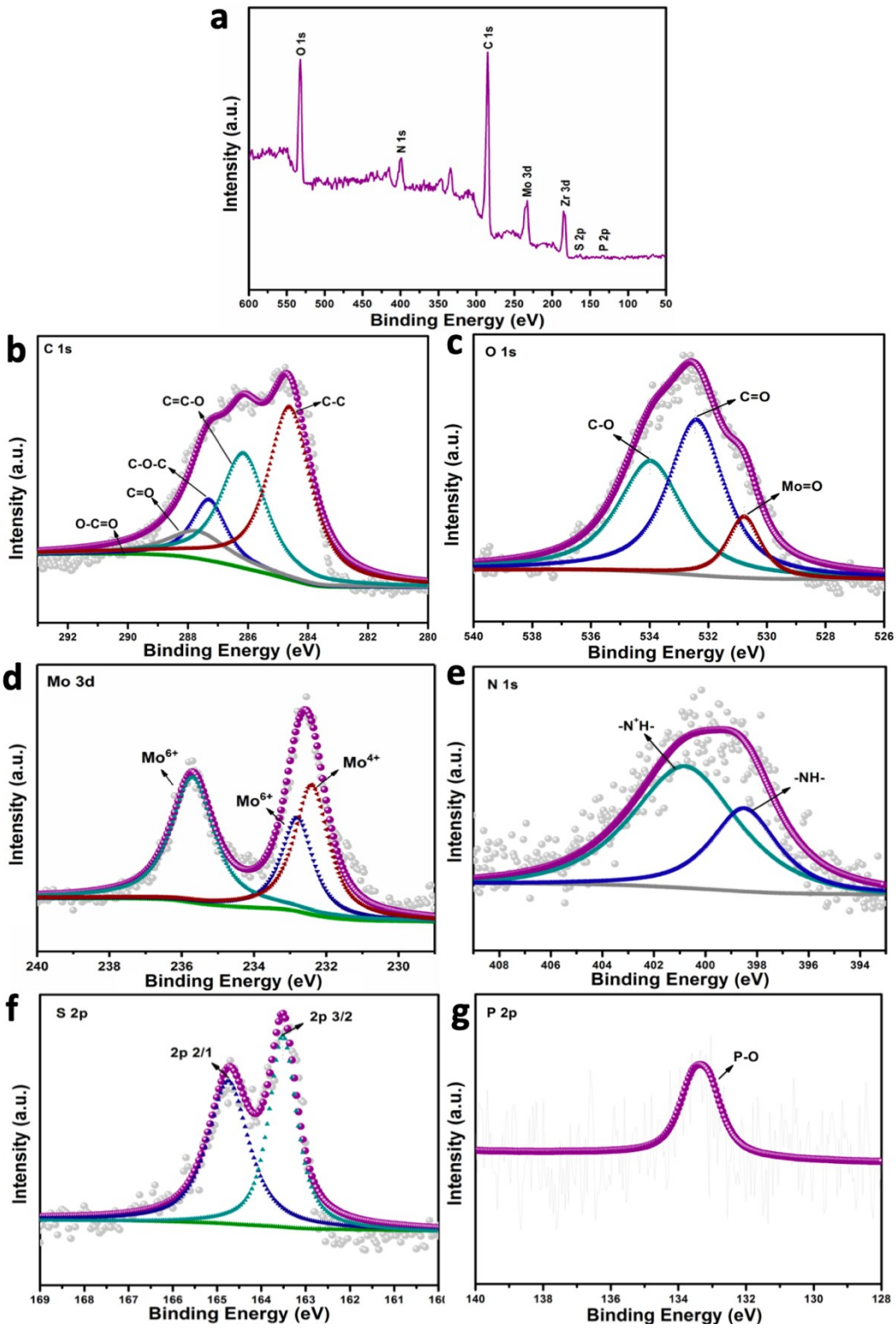

Figure S3. (a) XPS spectra of PCN-224@PEDOT/PMo_{12}-CC-II; (b) C 1s; (c) O 1s; (d) Mo 3d; (e) N 1s; (f) S 2p; (g) P 2p

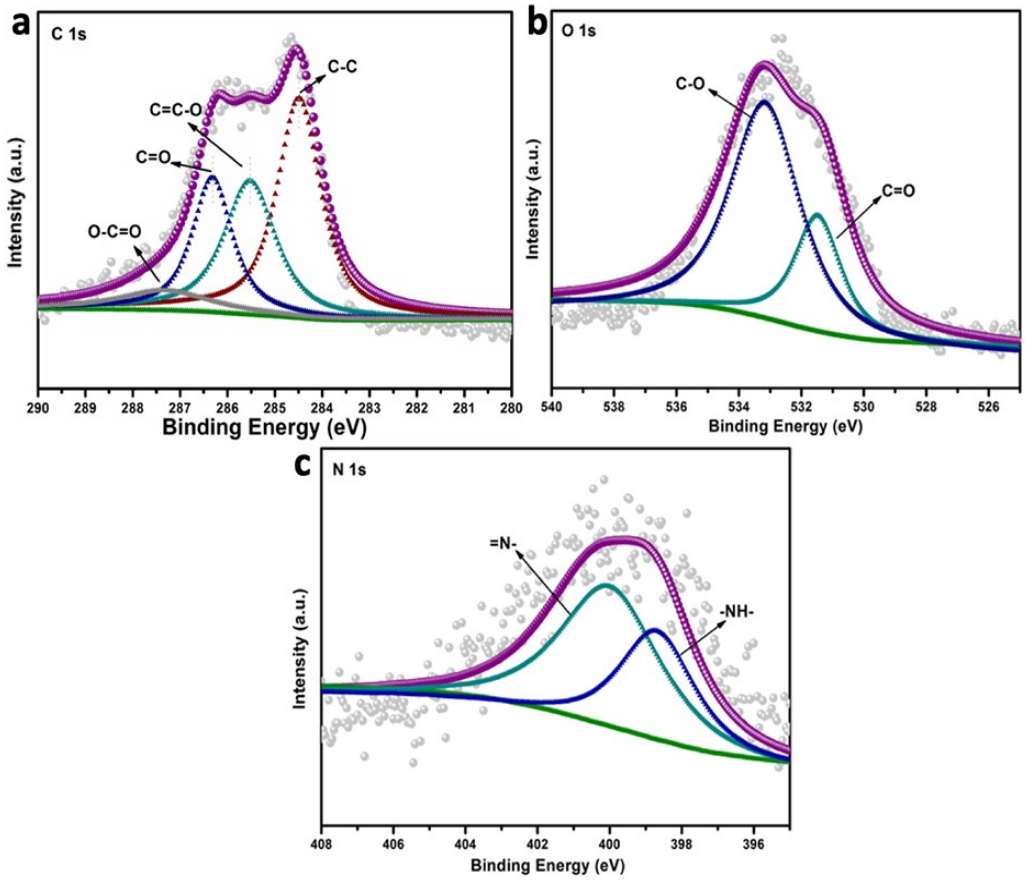

Figure S4. XPS spectra of PCN-224-CC; (a) C 1s; (b) O 1s; (c) N 1s

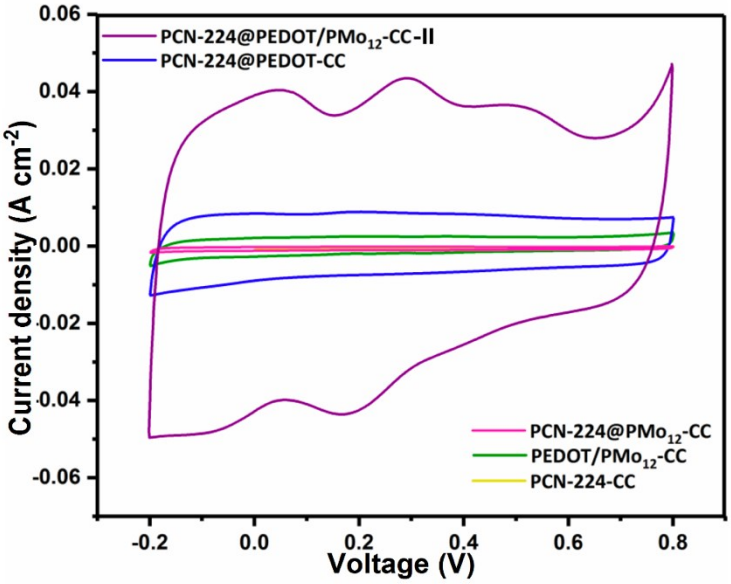

Figure S5. CV profiles of PCN-224@PEDOT/PMo_{12}-CC-II, PCN-224@PEDOT-CC, PCN-224@PMo_{12}-CC, PEDOT/PMo_{12}-CC and PCN-224-CC electrodes at 10 mV s^{-1}

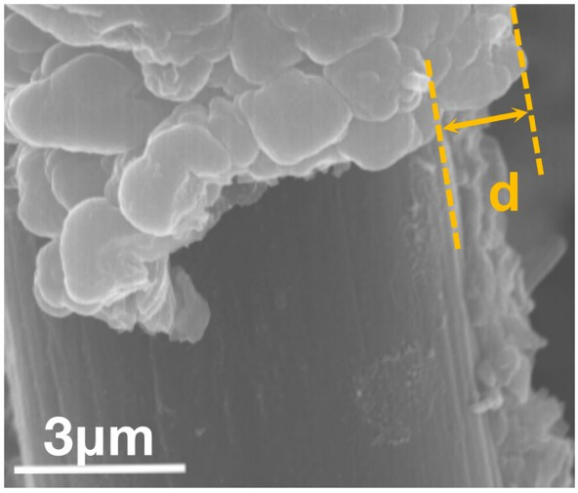

Figure S6. SEM image of the thickness of PCN-224@PEDOT/PMo_{12}

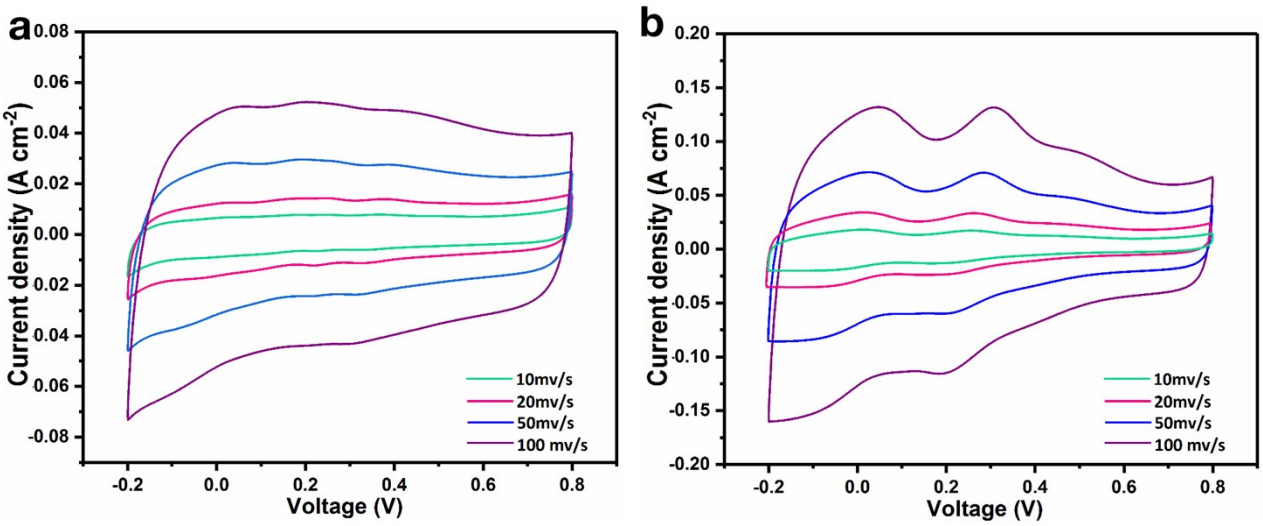

Figure S7. CV curves at various scan rates. (a) PCN-224@PEDOT/PMo_{12}-CC-I; (b) PCN-224@PEDOT/PMo_{12}-CC-III

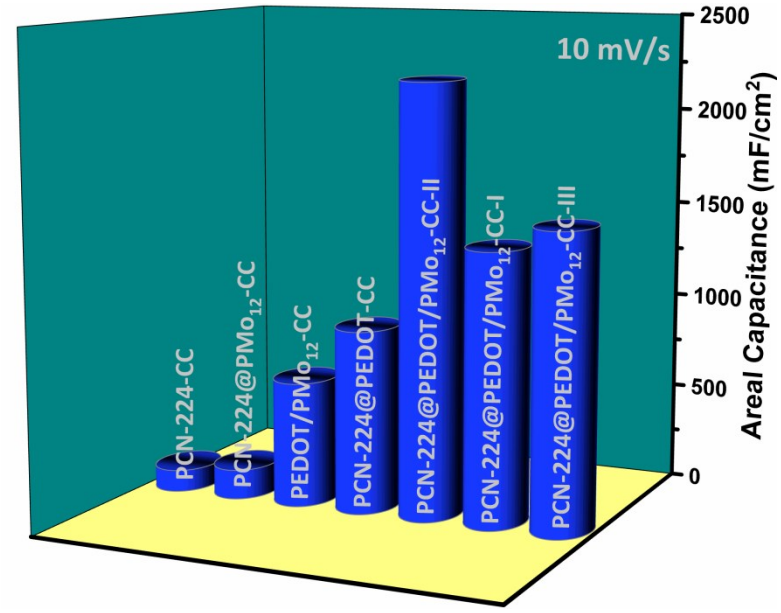

Figure S8. Areal capacitances calculated by CV curves at 10 mV·s^{-1} for sample.

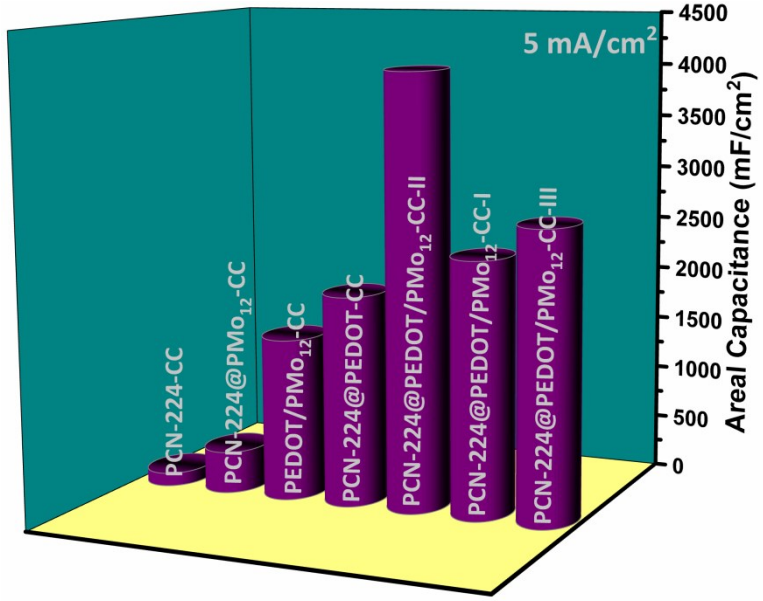

Figure S9. Areal capacitances calculated by GCD curves at a current density of 5 mA·cm^{-2}

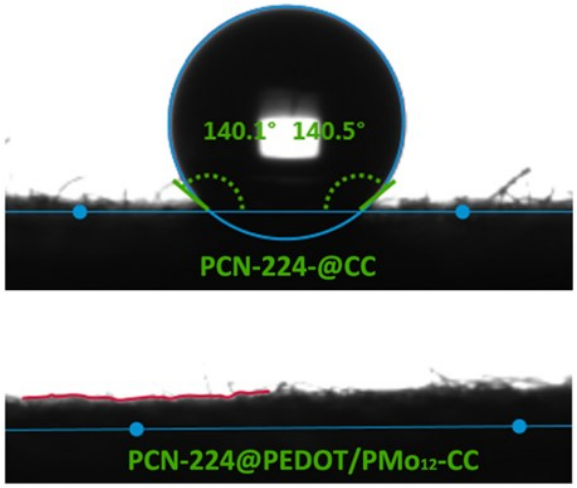

Figure S10. Contact angles of PCN-224-CC and PCN-224@PEDOT/PMo_{12}-CC-II

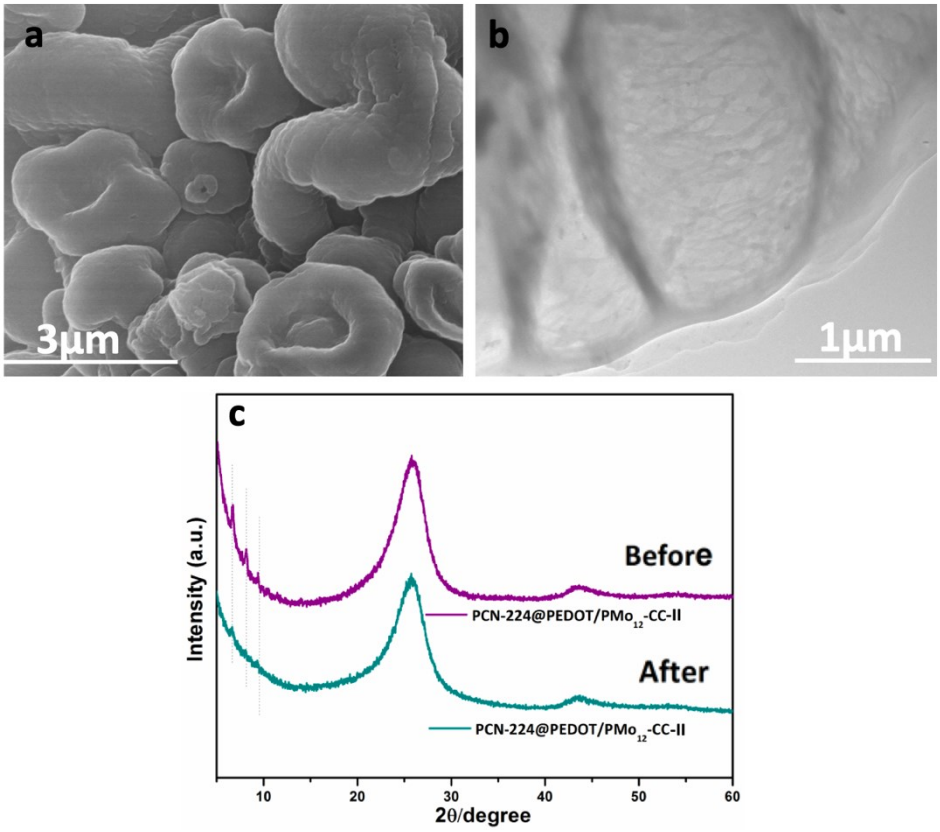

Figure S11. SEM (a), TEM (b) images and XRD patterns (c) of the PCN-224@PEDOT/PMo_{12}-CC-II electrode after the long-term charge-discharge process

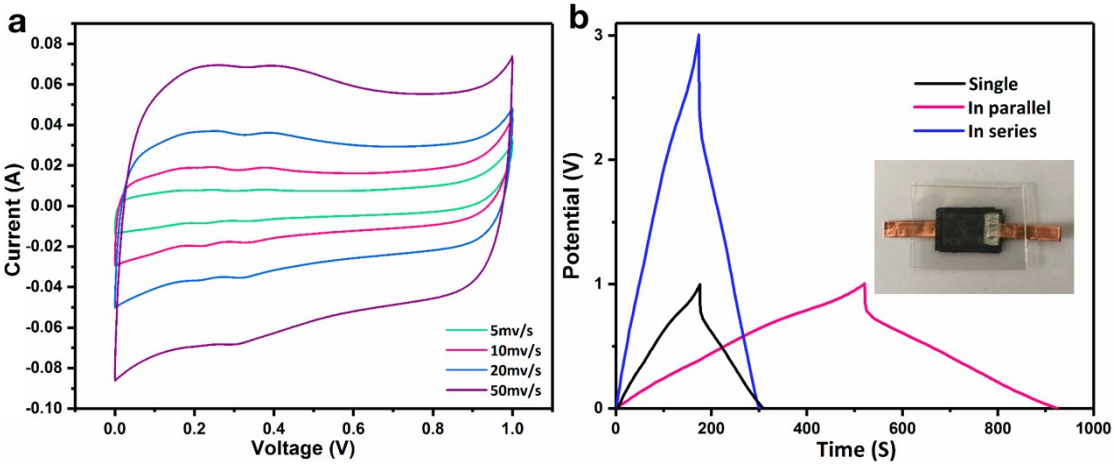

Figure S12. (a) CV curves and (b) GCD curves of the device (insert: optical image of the flexible supercapacitors device)

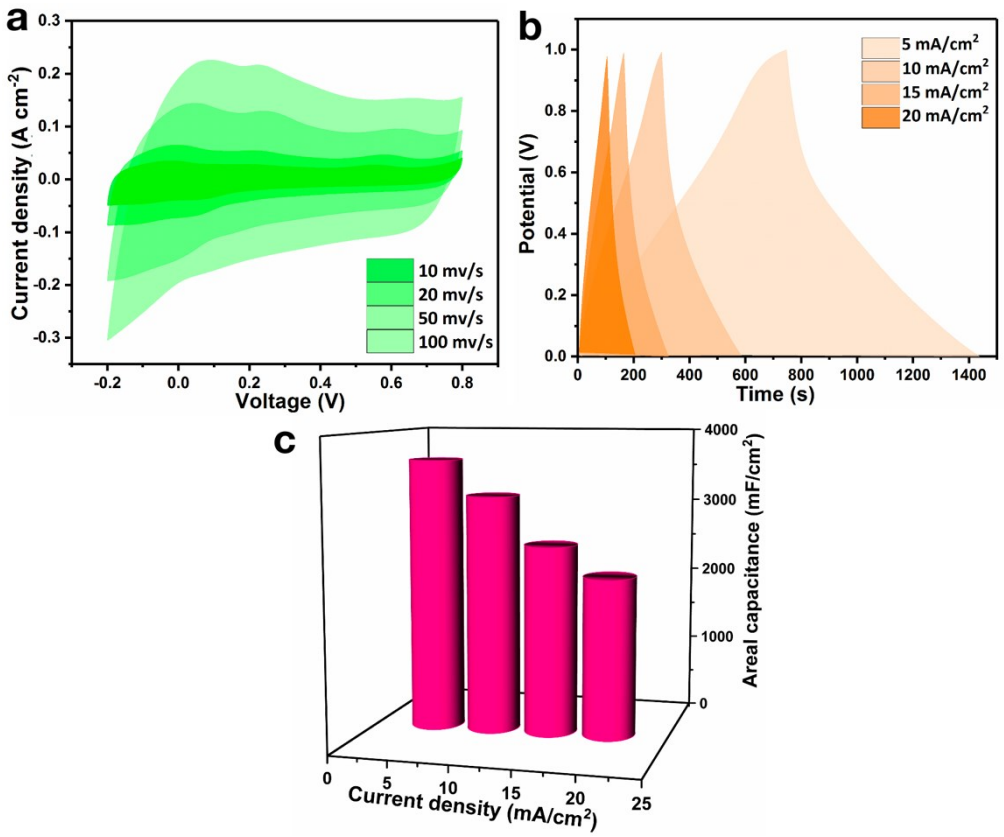

Figure S13. (a) CV curves and (b) GCD curves of the PCN-224@PEDOT/PMo_{12}-CC-II in the 1 mol/L Na_2SO_4 electrolyte. (c) Areal capacitances calculated by GCD curves at different current density

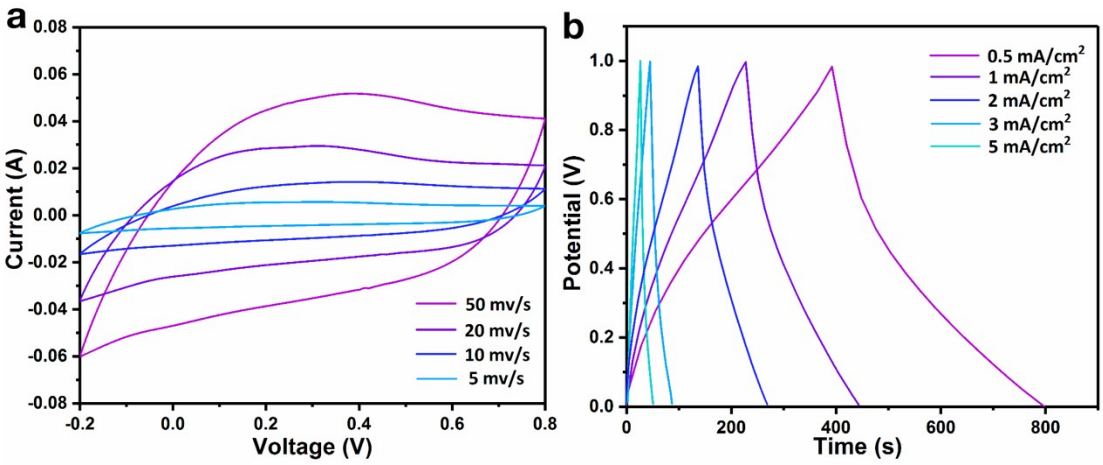

Figure S14. (a) CV curves and (b) GCD curves of the flexible supercapacitor device with the Na_2SO_4 gel electrolytes

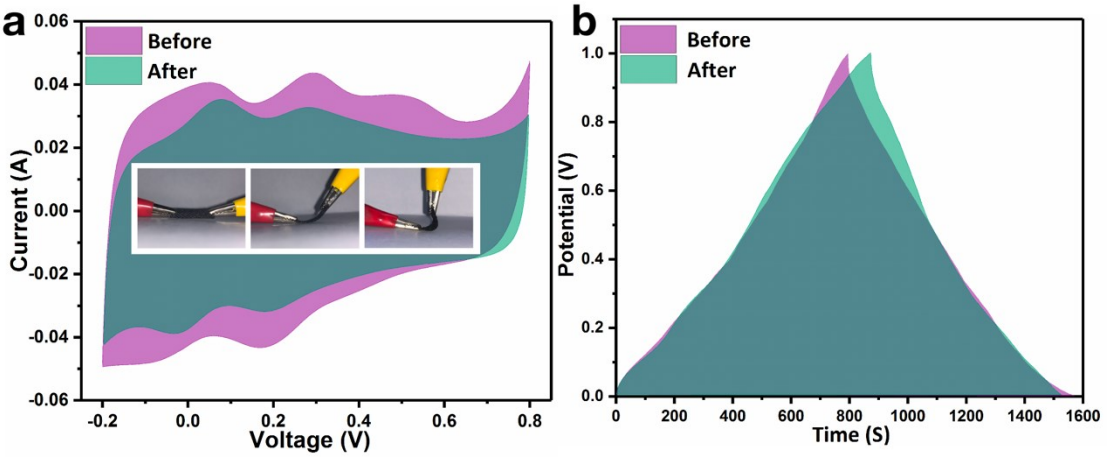

Figure S15. (a) CV curves (insert: optical image of the flexible electrode) and (b) GCD curves of the PCN-224@PEDOT/PMo_{12}-CC-II before and after the bending test

Table S1. The morphology and maximum areal specific capacitances of samples calculated by GCD curves at a current density of 5 mA·cm^2 in 1 M H_2SO_4 electrolyte

Type	**Morphology**	**Scan rate/ Current density (mA·cm^2)**	**Specific capacitance (mF·cm^{-2})**
PCN-224-CC	Nanoparticle	5	123.6
PEDOT/ PMo_{12}-CC	Agglomeration	5	1532.3
PCN-224@PEDOT-CC	Nanoparticle	5	1985.2
PCN-224@PEDOT/PMo_{12}-CC-I	Breakage of hollow micro-vesicles	5	2402.6
PCN-224@PEDOT/PMo_{12}-CC-II	Hierarchical hollow micro-vesicles	5	4077.8
PCN-224@PEDOT/PMo_{12}-CC-III	Agglomeration of hollow micro-vesicles	5	2726.7

Supporting video. A minifan started by three-series devices.

References

1 D. Feng, W. C. Chung, Z. Wei, Z. Y. Gu, H. L. Jiang, Y. P. Chen, H. C. Zhou, *J. Am. Chem. Soc.,* 2013, **135**, 17105-17110.

2 N. Huang, S. Yuan, H. Drake, X. Y. Yang, J. D. Pang, J. S. Qin, J. L. Li, Y. M. Zhang, Q. Wang, D. L. Jiang, H .C. Zhou, *J. Am. Chem. Soc*., 2017, **139**, 18590-18597.

3 B. G. Choi, J. Hong, W. H. Hong, P. T. Hammond, H. Park, *ACS nano*, 2011, **5**, 7205-7213.