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1 Introduction

Sustainable storage technologies aiming to resolve the energy and environmental crisis have been a worldwide research target. Electrochemical capacitors, also known as supercapacitors (SCs), with the merits of environmental benignity, fast charge/discharge capacities, excellent cycling lives, safety, and low cost, have triggered increasing attention as promising energy storage devices.^{1–3} Generally, there are three prerequisites for SCs electrode materials, *i.e.*, high electrochemical energy storage abilities (electric double layer capacitance EDLC, pseudocapacitance), large electrolyte-accessible surface areas, and high conductivity.⁴

Metal–organic frameworks (MOFs) are crystalline porous materials constructed by linking metal-containing nodes with organic ligands,⁵ which are considered as excellent electrode

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

Bing Wang,^a Shuo Liu,^a Lin Liu, ^b^a Wen-Wei Song,^a Yue Zhang,^a Shi-Ming Wang^{*ab} and Zheng-Bo Han^{*a}

Metal-organic frameworks (MOFs) are promising electrode materials for supercapacitors; however, their electrochemical performances are limited by their low electrical conductivities. To address this problem, "conductive ink" poly(3,4-ethylenedioxythiophene) (PEDOT) was used to enhance the conductivity, while "electron sponge" polyoxometalate $[PMo_{12}O_{40}]^{3-}$ (PMo₁₂) with large electronic transfer capability was used as the capacitance contributor. Finally, MOFs (PCN-224) acted as the host of this composite that provided the electrical double-layer capacitor and a PCN-224@PEDOT/PMo12-CC-II hierarchical hollow micro-vesicle nanostructure was obtained via a simple one-step electro-codeposition. The microvesicle nanocomposite was interspersed in MOF hosts. Benefiting from the novel structure and the synergistic effect of three components, the optimal areal capacitance of the PCN-224@PEDOT/PMo12-CC-II electrode was 4077.8 mF cm⁻² at 5 mA cm⁻² (the concentration ratio of EDOT : PMo_{12} is 1 : 0.75), which is 32.9 times more than that of pristine PCN-224 (123.6 mF cm⁻²). Furthermore, a symmetric supercapacitor device was constructed by the PCN-224@PEDOT/PMo12-CC-II nanocomposite, which possessed an excellent energy density of 0.297-0.0192 mW h cm⁻² (at a power density of 0.324-5.128 W cm⁻²) and a good long-term cycle ability (84.59% for 10 000 cycles at 5 mA cm⁻²). This study presented a one-step electro-deposition synthetic strategy for the design and fabrication of the highcapacitance MOF-based electrode material, which showed great promise in the future design of highperformance materials for advanced energy production.

> materials for supercapacitors, which provide large electrolyteaccessible surface areas and EDLC.6,7 Yaghi et al. explored various MOF-based electrode materials for supercapacitors with high capacitances; a zirconium MOF (nMOF-867) exhibited exceptionally high capacitance.8 Samorì et al. reported MOF-UiO-66-NH₂ as the substrate and obtained superior capacitor performance aza-MOFs@COFs hybrid porous electrode materials through the aza-Diels-Alder cycloaddition reaction with an areal capacitance of 20.35 μ F cm⁻².⁹ Huang *et al.* utilized the *in* situ self-transformation method to prepare MnOx-MOF manganese hexacyanoferrate hydrate (MHCF) nanocube-based composite material with improved capacitor and rate performance (1200 F g^{-1}) .¹⁰ However, the poor conductivity of MOFbased composite materials hampered their wide application in capacitors. Contemporaneously, polyoxometalates (POMs), a kind of nanoscaled metal oxide clusters with diverse structures, are reputed as "electron sponges" with multi-electron redox properties.11-15 According to the literature, POM-based composites have proved to be promising capacitor materials. One disadvantage of most POMs is their good solubility in various solvents, which makes them easy to dissolve and be lost from the electrode. Combining soluble POMs with other insoluble components is the most effective way to solve this

[&]quot;College of Chemistry, Liaoning University, Shenyang 110036, P. R. China. E-mail: ceshzb@lnu.edu.cn

^bLight Industry College, Liaoning University, Shenyang 110036, P. R. China. E-mail: wangsm@lnu.edu.cn

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problem. However, similar to MOFs, POMs also suffer from low conductivity, which limits their performances as electrode materials. Some efforts have been made to enhance the conductivity of MOFs and POM-based electrode materials.16 For example, Lan reported a novel polyoxometalate-based metalorganic framework (POMOFs)/reduced graphene oxide (rGO) nanocomposite for battery and supercapacitor. rGO films can improve the conductivity of composite materials and are thus used as excellent supports to avoid the agglomeration of nano-POMOFs particles.¹⁷ Wang et al. introduced MXene to prepare the Co-MOF/Ti₃C₂T_r(a)Ni composite material, which increased the active sites and afforded a fast ion transport path while providing capacitance of 3741 F g^{-1} .¹⁸ The conductive polymer poly(3,4-ethylenedioxythiophene) (PEDOT) with high electric conductivity is often applied in SCs to enhance the conductivity, which can overcome the barrier of poor electric conductivity of MOFs and POMs.¹⁹⁻²³ Flexible and wearable devices have the advantages of lightweight, safety, and foldability. Some of the flexible solid-state supercapacitors (SSCs) feature high stability, exceptionally long cycle life, high power density, and low carbon footprint.24-26 Carbon cloth (CC) and ITO-PET, could be the substrates for flexible conductive electrodes.27 Therefore, we intent to use phosphomolybdic acid as the electron sponge, PEDOT to enhance the conductivity, and MOFs with high specific surface area porous channels to construct the composites with hierarchical pores and high conductivity. At the same time, CC was employed as the substrate to achieve flexible electrodes.

In this paper, we selected PCN-224, a kind of Zr-based MOF with high stability, as the electrical charge storing material. Carbon cloth, a highly conductive textile, was used as both the substrate and current collector with outstanding mechanical flexibility and strength.²⁸ PCN-224 is in situ grown on the carbon cloth and linked by electrodeposited PEDOT/PMo12. Finally, the composite electrodes (PCN-224@PEDOT/PMo12-CC-n) were obtained. In a three-electrode system, exceptional areal capacitance of 4077.8 mF cm⁻² at 5 mA cm⁻² for optimized PCN-224@PEDOT/PMo12-CC-II was achieved. Compared to PCN-224-CC, PEDOT/PMo12-CC, and PCN-224/PEDOT-CC, the areal capacitance showed 32.9, 2.7, and 2.0 times enhancement, respectively. Moreover, a flexible symmetric supercapacitor device was constructed, which yielded a remarkable areal capacitance of 218.5 mF cm $^{-2}$ (874 mF cm $^{-3}$). The high energy densities of 0.0297–0.0192 mW h cm $^{-2}$ (0.132–0.0853 mW h cm⁻³) were achieved at the power densities of 0.324-5.128 W cm^{-2} (1.358–21.934 W cm^{-3}). The superior capacitance retention (84.59% for 10 000 cycles at 5 mA cm⁻²) indicates outstanding cycling performance.

2 Experimental section

Materials

The commercial chemicals used in this study were commercially obtained without further purification and deionized water was used in the process of experiments. Zirconium chloride (ZrCl₄, \geq 99%),4-carboxybenzaldehyde, benzoic acid (\geq 99%), propionic acid (\geq 99%), pyrrole (Aldrich), phosphomolybdic acid (H₃PMo₁₂O₄₀·*n*H₂O), potassium hydroxide (KOH, \geq 96%), 3,4-ethoxylene dioxythiophene (EDOT, \geq 99%), *N*,*N*-dimethylformamide (DMF, \geq 99%), tetrahydrofuran (THF, \geq 99%), methanol (MeOH, \geq 99%), and sulfuric acid (H₂SO₄, \geq 98%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Carbon cloth was purchased from CeTech.

Preparation of the PCN-224-CC precursor

In order to graft carboxyl and hydroxyl groups on the carbon cloth $(1 \times 1.5 \text{ cm}^2)$, we activated it in the concentrated sulfuric acid and nitric acid mixture (VH₂SO₄ : VHNO₃ = 3 : 1) for 4 hours. ZrCl₄ (0.06 g), H₂TCPP (0.025 g), and benzoic acid (0.6 g) in DMF (4 mL) were ultrasonically dissolved in an 18 mL Teflonlined stainless-steel vessel and finally, carbon cloth was put into it. The vessel was sealed and heated at 120 °C for 24 h under autogenous pressure and then cooled to room temperature naturally. Cubic dark purple crystals were grown on the carbon cloth *in situ*, washed by DMF, and drying in vacuum overnight. The mass loading of PCN-224 was calculated to be about 1.85 mg cm⁻².

Preparation of PCN-224@PEDOT/PMo12-CC-n

Three pieces of PCN-224–CC as the working electrode was immersed in a three-electrode cell. The electrolytes contained 0.08 M LiClO₄ and different concentrations of EDOT : PMo_{12} in the ratio of 1 : 0.25, 1 : 0.75, and 1 : 1.5, respectively. Then, electrodepositions were further carried out at a scan rate of 50 mV s⁻¹, cycling of the potential between -1 and 1 V with Ag/AgCl as the reference electrode for 300 s, and Pt plate as the counter electrode at the RT. The obtained PCN-224@PEDOT/PMo₁₂–CC-(I, II, III) was washed with distilled water several times and vacuum-dried overnight.

Fabrication of the flexible supercapacitor device

A PVA/H₂SO₄ gel electrolyte was prepared by dissolving 1 g PVA in 10 mL 0.01 M H₂SO₄ aqueous solution at 85 °C and leaving the solution in air until it cooled down to room temperature. Subsequently, two pieces of the PCN-224@PEDOT/PMo₁₂-CC-II electrodes ($1 \times 2 \text{ cm}^2$) were chosen and each was half-immersed into the prepared PVA/H₂SO₄ gel electrolyte for 30 minutes; then, the supercapacitor device was assembled by sandwiching the PVA/H₂SO₄ membrane between the two electrodes. In order to avoid the occurrence of short circuits, the device was left standing under infrared light for several hours for the complete solidification of the electrolyte. The preparation of the PVA/ Na₂SO₄ gel electrolyte is given in the ESI.†

Materials characterization

The structure of the as-prepared samples was characterized by powder X-ray diffraction (PXRD) patterns that were recorded on a Bruker AXS D8 advanced automated diffractometer at 40 kV and 30 mA with Cu K α radiation ($\lambda = 1.54060$ Å). The Raman spectra were collected by a Renishaw confocal micro-Raman spectrometer equipped with a 532 nm laser operated at 0.1% power. X-ray photoelectron spectroscopy (XPS) was obtained by

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monochromated X-rays (Quantum 2000, USA) using Al K α radiation. Micromorphology and structural analysis were conducted using a scanning electron microscope (Hitachi SU8010 (SEM) system). EDS and elemental mapping patterns were acquired on the SEM instrument (Oxford Instruments). Transmission electron microscopy (TEM) images were obtained on a JEM-2100 apparatus. The contact angle was measured on a Theta/Attension Optical Tensiometer (SDA 100). The FT-IR spectra were recorded on a Nicolet 5DX spectrometer using KBr pellets in the 4000–400 cm⁻¹ range. The N₂ adsorption–desorption isotherms were measured using a BeiShiDe 3H-2000PS1 system at 77 K.

Electrochemical characterization

The electrochemical behavior was investigated in a threeelectrode system in 1 M H_2SO_4 aqueous electrolyte. The nanocomposite PCN-224@PEDOT/PMo₁₂–CC-II was used as a working electrode, and Pt plate and Ag/AgCl electrode were used as the counter and reference electrodes, respectively. Cyclic voltammetry (CV), galvanostatic charge–discharge (GCD) measurements, and electrochemical impedance spectroscopy (EIS) were carried out on a CHI660E electrochemical workstation at RT. The EIS data were collected with an alternate current voltage of 5 mV amplitude in the frequency range from 0.01 Hz to 100 kHz. The test of GCD was carried out from 0 to 1 V at 5, 10, 15, and 20 mA cm⁻². The methods applied for calculating the specific capacity, specific capacitance, energy and power density symmetric supercapacitor device is provided in the ESI.[†]

3 Results and discussion

Morphology and structural characterization

The preparation route of the PCN-224@PEDOT/PMo₁₂-CC-II flexible electrode is briefly illustrated in Fig. 1a. Firstly, PCN-

224 was coated on the surface of the CC fibres uniformly with the thickness of 0.5 µm via a facile solvothermal approach for 48 h. Subsequently, PEDOT and PMo₁₂ were weaved into the surface and channels of the PCN-224 by the electrochemical codeposition method. The isolated MOF crystals were interconnected and linked by the hollow micro-vesicles of PEDOT and PMo12, which acted as the bridges for electron transportation between the external circuit and the internal surface of the MOFs. As shown in Fig. 1b, the CC fibres showed a smooth surface and the diameter of the fibres was about 5 μ m, and the raw CC had a black color (as shown in the inset of Fig. 1b). After the solvothermal reaction, the black CC piece turned brown red (inset in Fig. 1c) and the fibres turned less smooth compared to the CC fibres, which evidenced that CC was entirely enveloped by PCN-224 (Fig. 1c). After the codeposition of PEDOT/PMo12, the micro-vesicles covered the surface of the fibres and the roughness of the fibre continued growing, which indicated that PCN-224-CC were further wrapped and weaved by the uniform hollow micro-vesicles (Fig. 1d). Meanwhile, the color of the electrode switched to dark blue, which originated from the color of PEDOT and reduced PMo12 (inset of Fig. 1d). Finally, the hierarchical hollow micro-vesicle nanocomposite PCN-224@PEDOT/PMo12-CC-II was assembled.

In order to evaluate the impact of the ratio of EDOT and PMo₁₂ in the depositing solution on the nanocomposites, the concentration ratio of EDOT/PMo₁₂ of 1 : 0.25 (I), 1 : 0.75 (II), 1 : 1.5 (III) in the solution for electrodeposition was used to prepare the PCN-224@PEDOT/PMo₁₂-CC-*n* (*n*: I, II, III). As the concentration of PMo₁₂ increased, the macroscopic size of the vesicles decreased from \sim 3 µm to \sim 1–2 µm and then increased to \sim 3–4 µm again. All the prepared nanocomposites were employed for supercapacitors. According to the experimental results, when the concentration ratio is 1 : 0.75 and the



Fig. 1 (a) Scheme for the *in situ* growth of the PCN-224@PEDOT/PMo₁₂-CC-II flexible electrode; (b) carbon cloth substrate; (c) hydrothermal preparation of PCN-224 $_{
m CC}$ -II (d) electrochemical co-deposition preparation of PCN-224@PEDOT/PMo₁₂-CC-II.

deposition time is 300 s, PCN-224@PEDOT/PMo₁₂-CC-II exhibited the best electrochemical performance, possessing an areal capacitance of 4077.8 mF cm⁻² at 5 mA cm⁻². As the control experiments, we also prepared PCN-224–CC (123.6 mF cm⁻²), PEDOT/PMo₁₂–CC (1532.3 mF cm⁻²), and PCN-224@PEDOT–CC (1985.2 mF cm⁻²) *via* the same method.

Moreover, for the sake of exploring more structural information about PCN-224@PEDOT/PMo12-CC-n, further amplified SEM and TEM images of this composite at different stages were recorded (Fig. 2c-f). The particle size of nano-crystalline PCN-224 in situ grown on CC was 150-300 nm (Fig. 2a and b). However, the surface of PCN-224@PEDOT/PMo12-CC-II showed uniform "red blood cell"-shaped hollow vesicles, which were composed of dense nanocapsules (Fig. 2c and d). The changes in appearance also revealed that the PEDOT/PMo₁₂ layer was successfully coated on the surfaces of PCN-224. From the TEM images of the sample, as shown in Fig. 2e and f, we can clearly see that the hollow vesicles were wrapped around PCN-224 and present a hierarchical hollow morphology. According to the literature²⁹ and our experiments, PMo₁₂ played an important role for forming the hierarchical hollow micro-vesicle morphology. The formation mechanism could be attributed to the following aspects: (1) though the EDOT monomer and PMo₁₂ were evenly dispersed in the solution for deposition, PMo12 and PEDOT did not enter PCN-224-CC at the same time during the electrodeposition process. When the potential changed from +1 to -1 V, PMo12 moved to the surface and penetrated to the pores of PCN-224-CC to accept electrons. As a result, the matrix exhibited a negatively charged surface. Actually, the negative charges were not continuous distributed on the surface but isolated by the PMo₁₂ nano-cluster. This was

the basis to form the hollow vesicles. (2) In turn, when the potential changed from -1 to +1 V, the positively charged PEDOT (S⁺) would be adsorbed by the negatively charged PMo₁₂ to form new positive surfaces. (3) Under the CV process, the surfaces grew alternately, leading to a hierarchical vesicle structure (Fig. 3); the corresponding opening hierarchical vesicle photo is shown in the inset in Fig. 2c. The advantage of this hierarchical vesicle is that PEDOT and PMO₁₂ can be tightly woven on the pores and the surface of MOFs, which had the dual effects of increasing the specific surface area of the electrode material and improving the conductivity of the material. The ratio of EDOT and PMo₁₂ in the deposition solution would also be affected by the size and quality of the vesicles. Different ratios of EDOT : PMO12 were employed to examine the relation between the concentration ratios of EDOT : PMo12 and the size of the vesicles. When the concentration of PMo_{12} is 0.4 g L⁻¹ and the EDOT: PMO12 mass ratio is 1:0.25, the vesicles for PCN-224@PEDOT/PMo12-CC-I were incomplete; a defect state can be clearly seen in Fig. S1a.[†] When the concentration of PMo_{12} increased to 1.2 g L⁻¹ and the EDOT : PMo_{12} mass ratio was 1:0.75, the vesicles of PCN-224@PEDOT/PMo12-CC-II appeared uniform, which are completely similar to the shape of red blood cells. If the concentration of PMo₁₂ is continually increased to 2.0 g L^{-1} and the EDOT : PMo₁₂ mass ratio is 1: 1.5, a large amount of amorphous PEDOT mixed with PMo₁₂ was deposited and agglomerated on the surface of PCN-224 to form PCN-224@PEDOT/PMo12-CC-III with large cavities (Fig. S1c[†]). The corresponding TEM images are shown in Fig. S1b and d.† It can be attributed to the polyoxometalate agglomerates and the local concentration was higher than that at other places, causing PEDOT to polymerize rapidly and form



Fig. 2 (a and b) SEM image of PCN-224–CC; (c and d) SEM image of PCN-224@PEDOT/PMo₁₂–CC-II with different magnifications, respectively; inset: the open hierarchical hollow micro-vesicles; (e and f) TEM images of PCN-224@PEDOT/PMo₁₂–CC-II; (g-(1–8)) EDS mapping for PCN-224@PEDOT/PMo₁₂–CC-II.



Fig. 3 Schematic representation of the PEDOT/PMo $_{12}$ micro-vesicle formation mechanism.

large cavities. To further understand the elemental dispersion in PCN-224@PEDOT/PMo₁₂-CC-II, EDS analysis was carried out. Uniform distribution of C, N, Zr, O, P, Mo, and S elements was observed, suggesting the homogeneous dispersion of PCN-224, PEDOT, and PMo₁₂ on CC (Fig. 2g).

The composition of PCN-224@PEDOT/PMo₁₂-CC-II was examined by powder X-ray diffraction (PXRD) (Fig. 4a). Obviously, the PXRD patterns of the as-synthesized samples PCN-224-CC and PCN-224@PEDOT/PMo₁₂-CC-II matched well with their simulated patterns, thus demonstrating their phase purities. The two appeared peaks located at 26° and 44° are derived from the CC substrate (JCPDS no. 26-1076). As expected,

PCN-224@PEDOT/PMo₁₂–CC-II displayed similar diffraction configuration as that of PCN-224 with decreased peak intensity, which indicated the successful enveloping of PEDOT/PMo₁₂. It is worth mentioning that no diffractive peaks for PEDOT were detected due to its amorphous nature, which matched well with the HRTEM results (Fig. S2†).

The FTIR spectra of PMo₁₂, PCN-224@PEDOT/PMo₁₂-CC-II, and PEDOT-CC are shown in Fig. 4b. Typical H₃[PM0₁₂O₄₀] peaks were exhibited, confirming that PCN-224 and PMo12 are assembled together. The characteristic bands of PMO₁₂ are 798, 876, 979, and 1068 cm⁻¹, which were ascribed to the stretching vibrations of Mo-O_d-Mo, Mo-O_c-Mo, Mo-O_d, and P-O_a, respectively, were matched with that of PCN-224@PEDOT/ PMo₁₂-CC-II (800, 843, 981, and 1084 cm⁻¹) with some shifts.³⁰⁻³² The results indicated that HPMo₁₂ was successfully loaded.33 Raman spectroscopy was performed to further understand the chemical composition of PCN-224@PEDOT/ PMo12-CC-II (Fig. 4c). The two intense peaks observed at 1423 and 1509 cm⁻¹ were attributed to the symmetric and asymmetric C=C stretching of PEDOT, respectively.34 In addition, small shoulders located at 1367 and 1563 cm⁻¹ were assigned to the overlaying between D and G bands of carbon cloth and the strong Raman peaks of PEDOT.35

Nitrogen adsorption measurements at 77 K were conducted to investigate the surface area and pore size distribution of the samples. The BET surface areas of PCN-224, PCN-224–CC, and PCN-224@PEDOT/PMo₁₂–CC-II were calculated to be 1628.5, 226.8, and 102.7 m² g⁻¹, respectively, which indicated the permanent porosity characteristic of PCN-224@PEDOT/PMo₁₂–



Fig. 4 (a) XRD patterns of the PCN-224–CC (green), PEDOT/PMo₁₂–CC (yellow), PCN-224@PEDOT/PMo₁₂–CC-II (purple), and activated CC (blue); (b) FTIR spectra of PCN-224@PEDOT/PMo₁₂–CC-II, PMo₁₂ and PEDOT–CC (purple, yellow, blue); (c) Raman shifts of PCN-224@PEDOT/PMo₁₂–CC-II; (d) N₂ adsorption–desorption isotherms for the samples (PCN-224, blue; PCN-224–CC, green; PCN-224@PEDOT/PMo₁₂–CC-II, purple); (e) pore size distribution for the PCN-224, PCN-224–CC and of PCN-224@PEDOT/PMo₁₂–CC-II (blue, green, purple); (f) Zr 3d high-revolution spectra of PCN-224@PEDOT/PMo₁₂–CC-II (i) and PCN-224–CC (ii).

CC-II even after co-electrodeposition (Fig. 4d). The pore size distributions were investigated by non-local density functional theory method; the results showed that the amount of the micropores in PCN-224 were significantly decreased and the pore size generated by the space between the MOF particles was also reduced (Fig. 4e). The decrease in the pore size and surface area indicated that PEDOT and PMo12 covered the open spaces between the particles as well as the internal micropores, which allowed the electron to access the internal surface of PCN-224. More importantly, though the pores in PCN-224 were partially blocked by PEDOT and PMo₁₂, the electrolyte could still enter the pores via diffusion, which was detected by further electrical performance evaluation. Furthermore, PCN-224 belongs to microporous crystalline materials as it has 2.4 nm size pores due to the defects of MOFs.36 These results revealed that PEDOT and PMo12-engineered PCN-224 retained the vesicle structure with large, open MOF areas, which may provide more active sites on the surface to contact with the electrolyte and shorten the electron transfer pathways.37 In addition, the interconnected network architecture enabled to increase the mechanical stability during the charge and discharge process.38 The PXRD, Raman, FTIR, and nitrogen adsorption measurement results indicated the successful enveloping of PEDOT and PMo12 around the surface and the inside of PCN-224 successfully.

X-ray photoelectron spectroscopy (XPS) was further performed to investigate the chemical compositions and valence states. With regard to PCN-224@PEDOT/PMo12-CC-II, the elements Zr, C, O, N, S, P, and Mo were detected in the full survey spectrum (Fig. S3a[†]). Five deconvoluted peaks (284.5, 286.2, 287.2, 287.8, and 290.1 eV) were obtained from the C 1s spectrum of PCN-224@PEDOT/PMo12-CC-II (Fig. S3b†), which were correspondingly assigned to C-C (C-S), C=C-O, C-O-C, C=O, and O-C=O, respectively. However, the corresponding peaks of PCN-224-CC (Fig. S4a[†]) shifted to lower binding energy area, which confirmed the successful deposition of PEDOT and the successful deposition of PEDOT. The high-resolution Mo 3d spectrum exhibited two different valence states, namely, Mo^{VI} and Mo^{IV} (Fig. S3d[†]). The acquired spectra demonstrate that both the Zr 3d and O 1s orbitals were electronically perturbed upon the incorporation of PEDOT/PMo12 into the PCN-224 structure. In Fig. 4f, a positive shifting of the Zr 3d_{5/2} orbital from 182.4 eV (PCN-224-CC) to 182.7 eV (PCN-224@PEDOT/ PMo12-CC-II) suggested that the Zr node in PCN-224 binds to the moiety of PEDOT/PMo₁₂, which can attribute to the defect sites in the synthesized MOFs, which is consistent with the pore size distribution results (Fig. 4e). As expected, the binding energy of O 1s (Fig. S3c[†]) also showed a positive shift (0.79 eV) compared to PCN-224 (Fig. S4b[†]), which agrees well with the result mentioned above. Comparing PCN-224@PEDOT/PMo12-CC-II with PCN-224-CC, N 1s spectrum shifted to higher binding energy, as shown in Fig. S3e and S4c.† The highresolution S 2p and P 2p spectra are shown in Fig. S3f and g.† These observations clearly indicated the re-establishment of the electronic structure of the PCN-224@PEDOT/PMo12-CC-II which would benefit the pseudocapacitive composite, behavior.39

Electrochemical performance

The electrochemical performances of the electrode materials were firstly studied by cyclic voltammetry (CV) in a threeelectrode system using H_2SO_4 solution (1 mol L^{-1}) as the electrolyte from -0.2 to 0.8 V (vs. Ag/AgCl) at different scan rates. At the same scan rate of 10 mV s⁻¹, different areas were reflected by the CV curves of different electrode materials. To investigate the functions of each component in the composite film, PCN-PCN-224@PMo12-CC, PEDOT/PMo12-CC, PCN-224–CC, 224@PEDOT-CC, PCN-224@PEDOT/PMo12-CC-I, II, and III electrodes were examined at the scan rate of 10 mV s⁻¹ (Fig. S5[†]). The capacity of the electrode was reflected by the area of the CV curves. PCN-224@PEDOT/PMo12-CC-II exhibited the largest area among the electrodes, which showed 2.02 times larger area than the area sum of PCN-224@PMo12-CC and PCN-224@PEDOT-CC. For activated PCN-224-CC and PCN-224@PMo12-CC, the CV areas were negligible. After introducing conductive PEDOT, the two-component electrode materials (PEDOT/PMo12-CC and PCN-224@PEDOT-CC) were still not ideal as the area was still smaller than the ternary component PCN-224@PEDOT/PMo12-CC-n. The areal capacitance of PCN-224@PEDOT/PM0₁₂-CC-II was 2218.6 mF cm⁻², which is 19.6 times that of PCN-224-CCand surpassed that of PCN-224@PEDOT-CC (947.2 mF cm⁻² at 10 mV s⁻¹) by 223%, thus indicating the enhanced capacitance from the EDLC due to the high surface area and porosity of PCN-224 and the pseudocapacitance of PEDOT/PMo12. The areal mass loading of PCN-224@PEDOT/PM0₁₂-CC-II was about 6.2 mg cm⁻² (the mass ratio of PEDOT/PMo12 is 1/0.75) and the thickness of PCN-224@PEDOT/PMo12-II was about 1.5-2 µm, as shown in Fig. S6.† The corresponding specific capacitance for PCN-224@PEDOT/PMo₁₂-CC-II was 518.6 F g^{-1} at 10 mV s^{-1} .

The CV curve of PCN-224@PEDOT/PMo12-CC-II exhibited a mirror-image current response and the presence of redox reaction peaks, which indicated the coexistence of both the EDLC behavior and pseudocapacitance (Fig. S5[†]). More importantly, this three-component composite exhibited higher enclosed CV curve area and a higher redox peak intensity compared to the two-component and single-component ones, which revealed a significant improvement of the capacitance and faster redox reaction kinetics processes. The areal capacitances at 10 mV s⁻¹ were only 113.2 mF cm⁻² for PCN-224–CC, 153.8 mF cm⁻² for PCN-224@PMo₁₂-CC, 647.4 mF cm⁻² for PEDOT/PMo₁₂-CC, and 947.2 mF cm⁻² for PCN-224@PEDOT-CC, which increased significantly to 2218.6 mF cm^{-2} for PCN-224@PEDOT/PMo12-CC-II; this is possibly due to the hierarchical hollow micro-vesicles structure with uniform morphology, which can provide a larger electrolyte contact area, thereby promoting electron transfer and ion diffusion. PCN-224@PEDOT/PMo12-CC-I and III gave areal capacitances of 1402.6 and 1526.7 mF cm^{-2} because the hierarchical vesicles were incomplete under the low concentration of PMo₁₂; thus, the electron transport was blocked. When using a higher concentration of PMo₁₂, the progress of the electrochemical reactions was weakened by the agglomerated vesicles and increased cavity (Fig. S1[†]). Three redox peaks were detected at

 $-0.01,\,0.31,\,and\,0.55$ V, which could be attributed to the 3-step redox processes of PMo_{12} (eqn (1)–(3)).40

$$PMo_{12}O_{40}^{3-} + 2e^{-} + 2H^{+} \rightleftharpoons H_2PMo_{12}O_{40}^{3-}$$
(1)

$$H_2 P M o_{12} O_{40}^{3-} + 2e^- + 2H^+ \rightleftharpoons H_4 P M o_{12} O_{40}^{3-}$$
 (2)

$$H_4PMo_{12}O_{40}^{3-} + 2e^- + 2H^+ \rightleftharpoons H_6PMo_{12}O_{40}^{3-}$$
 (3)

$$X(\text{PEDOT}) + X(\text{SO}_4^{2-}) \rightleftharpoons (\text{PEDOT}^{X+})(\text{SO}_4^{2-})_x + Xe^- \quad (4)$$

Obviously, compared with the other binary component electrodes, the capacitance of PCN-224@PEDOT/PMo₁₂-CC-II (2218.6 mF cm⁻²) was far larger than the sum of the capacitance of PCN-224@PEDOT-CC (153.8 mF cm⁻²) and PCN-224@PEDOT-CC (947.2 mF cm⁻²), which confirmed that PMo₁₂ and PEDOT synergize with each other to promote electron transfer and that the ternary components were indispensable. In the composite, the MOFs provided a large specific surface area, PMo₁₂ could promote electron transfer, and PEODT could increase the conductivity of the material as the conductivity of the electrode material containing PEDOT is 980 S cm⁻¹, as measured by the Four Probe Tester at room temperature, which was similar to that of pure PEDOT.⁴¹ The ratio of PEDOT/PMo₁₂ also affected the morphology, thereby affecting the performance.

As discussed above, different ratios of EDOT and PMo_{12} in the solution for electrodepositing would result in different morphologies of the composites. Furthermore, how the morphology affects the electrochemical performances should

be clarified. Therefore, the CV curves of PCN-224@PEDOT/ PMo₁₂-CC-n at different scan rates ranging from 10 to 100 mV s^{-1} were collected (Fig. 5a and S7[†]). The CV current densities of PCN-224@PEDOT/PMo12-CC-II increased linearly with the increase in the scanning rates, which indicated good electrochemical reversibility.42 The presence of three redox reaction peaks corresponded to the successive redox reactions process of the PMo₁₂ cluster, accompanied by the reaction process of PEDOT with the anions in the electrolyte while providing pseudocapacitance. The CV of PCN-224@PEDOT/PMo12-CC-I and III at the scan rates of 10, 20, 50, and 100 mV s⁻¹ are collected in Fig. S7a and b; † the decrease of the CV areas indicated that the performances of the corresponding electrode materials were lower than that of PCN-224@PEDOT/PMo12-CC-II, and the maximum areal capacitances of 1402.6 and 1526.7 mF cm⁻² for PCN-224@PEDOT/PMo₁₂-I/III electrode materials was obtained at the same scan rate of 10 mV s⁻¹ (Fig. S8[†]). The experimental results meant there were two functions of PMo12 in the composite materials. The first function was to adjust the morphology by changing the concentration. When the concentration of PMo_{12} was 0.4 g L⁻¹, defects were detected in the vesicles (Fig. S1a and b†), which resulted in a discontinuous electronic transfer path; when the concentrations of PMo12 was increased to 2.0 g L⁻¹, agglomerated vesicles and increased cavities (Fig. S1c and d[†]) weakened the progress of the electrochemical reactions, leading to a decrease in the capacitance. The second function was to effectively promote electron transfer and improve the capacitance performance.



Fig. 5 (a) Electrode cyclic voltammograms of PCN-224@PEDOT/PMo₁₂-CC-II under the scan rate of 10–100 mV s⁻¹ in a three-electrode system and (b) the relation of the concentration ratio effect on the areal capacitance at different vesicle sizes. (c) Galvanostatic charge/discharge curves of the PCN-224@PEDOT/PMo₁₂-CC-II electrode at different current densities in 1 M H₂SO₄. (d) The areal capacitance of PCN-224–CC (yellow), PCN-224@PEDOT/CC (blue), PEDOT/PMo₁₂-CC (green), and PCN-224@PEDOT/PMo₁₂-CC-II (purple) at different current densities in the three-electrode system configuration using H₂SO₄ as the electrolyte. (e) Nyquist electrochemical impedance spectra of PCN-224_CC (red-brown), PEDOT/Mo₁₂-CC (green), PCN-224@PEDOT/CC (blue), and PCN-224@PEDOT/PMo₁₂-CC-II (purple). (f) Schematic representation of electron and electrolyte conduction in PCN-224@PEDOT/PMo₁₂-CC-II, PCN-224, and PMo₁₂ interwoven by PEDOT.

Thence, the concentrations of PMo₁₂ and ratio of PEDOT/ PMo₁₂ were critical for the areal capacitance, which was mainly because the concentration of PMo₁₂ directly affected the change in the materials' morphology. When the appearance and size of the multilayer vesicles were relatively uniform, the concentration of the PMo₁₂ vesicles was 1.2 g L⁻¹ and the areal capacitance value was 2218.6 mF cm⁻². With the increase in the PMo₁₂ concentration, the vesicles did not show the expected gradual trend but displayed a form of extreme change, from large to small and then returned to the large size again. The best concentration ratio of EDOT : PMo₁₂ was 1 : 0.75; the composite presented uniform multi-layered vesicles of 0.8–1 μ m, while the other concentrations showed damage and agglomeration in the vesicles, which could explain why PCN-224@PEDOT/PMo₁₂-CC-II showed maximum capacitance (Fig. 5b).

The aforementioned experimental results showed that the appropriate surface areas and porosities, as well as good conductivities, facilitated electron or ion transport, resulted in the improvement of the electrochemical performance. This phenomenon indicated that the components and microstructures had a great influence on the performance of the electrode materials. In addition, the areal capacitance of the sample electrode materials PCN-224@PMo₁₂-CC, (PCN-224-CC, PCN-224@PEDOT-CC, PEDOT/PMo12-CC, and PCN-224@PEDOT/PMo12-CC-n) under different current densities were also investigated by galvanostatic charge-discharge (GCD). The GCD curves were slightly distorted from the ideal triangular shape (Fig. 5c) because of the pseudocapacitive contribution from PEDOT/PM012.43 Similar to the CV curves, the PCN-224@PEDOT/PMo12-CC-II still revealed the longest discharge time and showed an areal capacitance of 4077.8 mF cm⁻² at a current density of 5 mA cm⁻². In contrast, the capacity of PCN-224-CC, PCN-224@PMo12-CC, PEDOT/PMo12-CC, PCN-224@PEDOT-CC, PCN-224@PEDOT/PMo12-CC-I and III only gave an areal capacitance of 123.6, 395.1, 1532.3, 1985.2, 2402.6, and 2726.7 mF cm⁻² at the same current density, respectively (Fig. S9[†]). As far as we know, this value was higher than those of other MOF-based and polymer composite materials; the capacitance of PCN-224@PEDOT/PMo12-CC-II was about 2 times larger than the best reported MOF-based electrode material PANI-ZIF-67-CC (2146 mF cm⁻²), as shown in Table 1.

It can be seen in Fig. 5d that a more superior capacitance retention rate of 82.95% than that of PCN-224@PEDOT-CC (56.3%) and PEDOT/PMo12-CC (45.56%) was obtained from 5 to 20 mA cm⁻², which might be because hydrophilic PEDOT and PMo12 were weaved and inserted into the pores of PCN-224, which were accessible to the electrolyte and efficiently reduced the 'dead' mass in the electrode. The maximum areal capacitances of the samples were obtained at the same current density of 5 mA cm⁻², as shown in Table S1^{\dagger}. The contact angle of PCN-224@PEDOT/PMo12-CC-II was close to 0° in contrast to PCN-224-CC (~140.1°) (Fig. S10†).44 From the SEM/TEM images and the XRD patterns of PCN-224@PEDOT/PMo12-CC-II before and after the charge-discharge process, it can be concluded that the hierarchical micro-vesicles structures and the phase can still be maintained (Fig. S11[†]), and PCN-224@PEDOT/PMo₁₂-CC-II has excellent cyclic stability.

The comparisons of the Nyquist plots of the four electrodes revealed the origins of sizable capacitance (Fig. 5e) compared to PCN-224-CC, PCN-224@PEDOT-CC, PEDOT/PMo₁₂-CC, and PCN-224@PEDOT/PMo₁₂-CC-I-III electrodes; the hierarchical micro-vesicles PCN-224@PEDOT/PMo₁₂-CC-II demonstrated the lowest equivalent series resistance (1.31 Ω in the high frequency region), which confirmed that this wonderful structure of PCN-224@PEDOT/PMo₁₂-CC-II can accelerate the transport and diffusion of ions and electrons, accelerate charge transfer kinetics, and thus contribute to the boosting of the pseudocapacitance. In addition, the straight line of the PCN-224@PEDOT/PMo₁₂-CC-II low frequency region was nearly parallel to the imaginary axis, further demonstrating the ideal capacitive performance.^{45,46} The equivalent circuit of PCN-224@PEDOT/PMo₁₂-CC-II is shown in the inset of Fig. 5e.

Compared with the reported nanocomposite-based electrode materials in Table 1, the PCN-224 (a) PEDOT/PMo₁₂-CC-II composite material had higher performance, which can be attributed to the following reasons: (i) hierarchical hollow micro-vesicles structure can effectively adapt to the volumetric change caused by the electrochemical reaction process, thus improving the stability of the electrode materials. More importantly, it can provide effective diffusion channels for the electrolyte, thus efficiently reducing the dead mass of the

Туре	Morphology	Electrolyte	Scan rate/current density	Capacitance (mF cm ⁻²)	Ref.
NENU-5/PPv-0.15 ^{<i>a,b</i>}	Nanoparticle	3 M KCl	0.5 mA cm^{-2}	1090	54
PANI/CNTs/G/PETC ^{a,b}	CNTs	1 M H ₂ SO ₄	1.5 mA cm^{-2}	791	55
PANI-ZIF-67-CC ^{a,b}	Nanoparticle	3 M KCl	10 mV s^{-1}	2146	48
$ZIF-67-PPy-2^{a,b}$	Network	1 M Na ₂ SO ₄	10 mA cm^{-2}	2330	51
PEDOT-GO/U-C ^{a,b}	Curly fold	1 M KCl	10 mV s^{-1}	102	47
PEDOT/H-15G-CNTF ^{a,b}	Porosity	3 M KCl	10 mV s^{-1}	128	53
NENU-5/PPy/60 ^{a,c}	Nanoparticle	$1 \text{ M H}_2 \text{SO}_4$	20 mA cm^{-2}	2034.5	56
PCN-224@PEDOT/PMo ₁₂ -CC-I ^{a,b}	Breakage of hollow micro-vesicles	1 M H ₂ SO ₄	5 mA cm^{-2}	2402.6	This work
PCN-224@PEDOT/PMo ₁₂ -CC-II ^{a,b}	Hierarchical hollow micro-vesicles	$1 \text{ M H}_2 \text{SO}_4$	5 mA cm^{-2}	4077.8	This work
PCN-224@PEDOT/PMo12-CC-III ^{a,b}	Agglomeration hollow micro-vesicles	1 M H ₂ SO ₄	5 mA cm^{-2}	2726.7	This work
PCN-224@PEDOT/PMo12-CC-II ^{a,b}	Hierarchical hollow micro-vesicles	1 M Na ₂ SO ₄	5 mA cm^{-2}	3636.3	This work

Table 1 Comparison of PCN-224@PEDOT/PMo12-CC-II with other MOF-based and polymer composite electrode materials

^{*a*} In three electrode system. ^{*b*} Flexible electrode material. ^{*c*} Rigid electrode material.

electrode materials. (ii) Super stable PCN-224 with rich access channels. Moreover, the micropores not only cause the uniform dispersion of PMo₁₂ and prevent PMo₁₂ from dissolving in the electrolyte but also act as an electrochemical double layer capacitor, which favors charge storage/transport and the ionic diffusion. PMo₁₂ inside the framework took part in the redox reactions and provided pseudocapacitance because of the transformation of Mo^{VI} to Mo^{IV}, which was confirmed by the XPS results (Fig. S3d†). PEDOT can improve the conductivity of the materials greatly and promote electron transfer. In addition, the structure of PCN-224@PEDOT/PMo₁₂-CC-II was stable; the unique structure facilitates electron storage and transmission and ion diffusion. The schematic diagram of the mechanism is shown in Fig. 5f. (iii) Benefiting from the π - π conjugations



Fig. 6 Energy level diagram of PCN-224, PEDOT, and PMo₁₂.

effects, the synergy between PCN-224, PEDOT, and PMo_{12} can establish an effective electron transfer path. The unhindered electron transfer path is shown in the energy level diagram (Fig. 6). During the discharge process, electrons flowed from PMo_{12} through PEDOT to PCN-224 with the lowest CB energy level and the discharge process was completed smoothly. The charging process was reversed. This facile electron transfer helped to maximize the capacitance.

Device assembly and capacitance evaluation

To demonstrate the potential application of PCN-224@PEDOT/ PMo12-CC-II in supercapacitors, we fabricated a symmetric allsolid-state supercapacitor device. The same two pieces of PCN-224 @PEDOT/PMo_12-CC-II electrodes with an area of 1 \times 2 cm^2 were parallelly placed and PVA/H2SO4 gel was used as the separator and the solid electrolyte (Fig. 7a). The effective area of the device was approximately 2.0 cm². Its electrochemical behaviors were studied using CV in the potential range from 0 to 1.0 V with different scan rates from 5 to 50 mV s^{-1} , which exhibited a large closed area (Fig. S12a[†]). To further evaluate its electrochemical performance, GCD measurements at relatively high current densities from 0.5 to 5 mA cm^{-2} were carried out (Fig. 7b). With the increase in the current density, this solid device showed decreased capacitance. The areal capacitances of this device were 215.7–143.8 mF cm⁻² at different current densities from 0.5 to 5 mA cm⁻². The high energy densities of 0.0297-0.0192 mW h $\rm cm^{-2}$ (0.132–0.0853 mW $\rm \dot{h}~\rm cm^{-3})$ were achieved at the power densities of 0.324-5.128 W cm⁻² (1.358-21.934 W cm⁻³), which revealed that the device had potential applications in energy



Fig. 7 (a) Schematic representation of the PCN-224@PEDOT/PMo₁₂–CC-II flexible SSC; (b) GCD curves of the device at the current density of 0.5-5 mA cm⁻²; (c) Ragone plots of the assembled PCN-224@PEDOT/PMo₁₂–CC-II device and the comparisons of data covered by the literature;⁴⁷⁻⁵³ (d) cycling test *via* the GCD cycling process for 10 000 cycles (inset, an LED lit by the three devices); (e) the capacitance retention after bending the solid-state supercapacitor 500 times. The inset shows the digital photos and CV curves at different bending stages; (f) photographs of the three connected devices in series starting up one minifan.

storage. The relationships between energy densities and power densities under various current densities are given in the Ragone plots (Fig. 7c). The performance of this device exceeds the values achieved for other reported MOF-based supercapacitors.^{47–53} More importantly, superior capacitance retention (84.59% for 10 000 cycles at 5 mA cm⁻²) indicates the outstanding cycling performance (Fig. 7d).

When the neutral electrolyte Na₂SO₄ was selected, the CV curves (three-electrode system) of PCN-224@PEDOT/PMo12-CC-II in 1 mol L^{-1} Na₂SO₄ electrolytes at different scan rates (10– 100 mV s⁻¹) were recorded and are given in Fig. S13a.[†] The CV current densities linearly increased, which confirms again that PCN-224@PEDOT/PMo12-CC-II has good electrochemical reversibility. Similar to acidic electrolyte systems, the GCD curves were slightly distorted from the ideal triangle shape (Fig. S13b[†]) because of the pseudocapacitive contribution from PEDOT/PMo12. The maximum area capacitance of PCN-224@PEDOT/PMO12-CC-II is 3636.3 mF cm⁻² at a current density of 5 mA cm^{-2} (Fig. S13c[†]), which still showed higher areal capacitance compared to the literature shown in Table 1. We also assembled a symmetric flexible supercapacitor device with PCN-224@PEDOT/PMo12-CC-II and PVA/Na2SO4 gel electrolytes between the electrodes. The CV curves of the device had a large closed area and near rectangular shape at a scan rate of 5 to 50 mV s⁻¹ (Fig. S14a^{\dagger}). The GCD curves of this device are shown in Fig. S14b.[†] Based on the GCD curves at 0.5-5 mA cm^{-2} , the device exhibited an areal capacitance of 206.8–126.3 mF cm⁻². The high energy densities of 0.0288–0.0164 mW h cm^{-2} (0.125–0.0753 mW h cm^{-3}) were achieved at the power densities of 0.311-4.853 W cm⁻² (1.302-19.156 W cm⁻³).

The solid-state device possessed excellent mechanical flexibility, which can be bent into various angles without a notable loss of performance and its electrochemical performance was investigated by CV. Apparently, no obvious shape change was observed in the CV curves shown at angles of 0° , 30° , and 90° (inset of Fig. 7e); at the same time the solid-state supercapacitor was subjected to continuous bending tests for 500 times, with only 8.2% capacitance loss (Fig. 7e), which indicated the stable mechanical properties and promising utilization as a flexible energy-storage device. The PCN-224@PEDOT/PMo12-CC-II electrode also showed excellent stability after bending. As shown in Fig. S15b,† after 500 times of bending, the areal capacitance of PCN-224@PEDOT/PMo12-CC-II is 3662.8 mF cm⁻², which was 89.9% of the initial capacitance. Meanwhile, the characteristic peaks of PCN-224@PEDOT/PMo12-CC-II were clearly retained in the CV curves, which is shown in Fig. S15a.[†] We further explored the potential of the flexible supercapacitor devices for practical applications in series and in parallel (Fig. S12b[†]). Besides, a three-series device can successfully start up a minifan (Fig. 7f and ESI video[†]) and lighted up one blue light-emitting diode (LED) (inset of Fig. 7d), which displayed great potential for the practical applications of flexible supercapacitor devices.

4 Conclusions

A hierarchical hollow micro-vesicle nanocomposite comprised of the super-stable MOF, PCN-224 cross-woven by PMo₁₂ and PEDOT,

was constructed via simple electrodeposition. The unique hierarchical vesicle structure can accommodate the volume change of the electrode materials and offers an efficient way for electronic transmission. The introduction of PMo12 into the PCN-224 frameworks vastly accelerated electron transfer and promoted the kinetics of electrochemical reaction. PEDOT had high conductivity and mechanical strength, which were beneficial for the fabrication of high-performance flexible SCCs. Indeed, electrons flowed from PMo12 with a higher energy level through PEDOT to PCN-224 with the lowest CB energy level. Because of the facile electron transfer in the composite, PCN-224@PEDOT/PMo12-CC-II showed state-ofthe-art capacitance of about 4077.8 mF cm⁻², which is 32.9 times larger than that of pristine PCN-224 (123.6 mF cm^{-2}) and the other reported MOF-based supercapacitor. Meanwhile, the symmetric supercapacitor device based on PCN-224@PEDOT/PM012-CC-II was successfully developed, which exhibited an areal capacitance of 215.8 mF cm⁻² and which was far above that of other MOFbased supercapacitors. This work provides a new strategy to prepare MOF-based supercapacitor electrode materials and to extend the diversity of the supercapacitor family.

Conflicts of interest

There are no conflicts to declare.

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