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Three-dimensional conductive porous organic polymers based on

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

tetrahedral polythiophene for high-performance supercapacitors Tao Li,^a Wei Zhu,^a Rui Shen,^a Hui-Ying Wang,^a Wei Chen,^a Si-Jia Hao,^a Yunxing Li,^a Zhi-Guo Gu,^{a,b^a}

Porous organic polymer become a promising electrode material, but low surface area and poor electric conductivity limit its application in high-performance supercapacitors. The study reports a facile synthesis of two porous organic polymers (POP-1 and POP-2) via the condensation of tetra(4-aminophenyl)methane and 2-thenaldehyde or 2,2-bithiophene-5carboxaldehyde and its subsequent polymerization. The resulting porous organic polymers materials were characterized by FT-IR, ¹³C-NMR, X-ray single crystal diffractometer, SEM, TEM and N₂ adsorption-desorption measurements. The study shows that the POP-2 offers a diamond topological structure with regular morphology and the rich of pores, and a higher BET surface area (342 m² g⁻¹) compared with the **POP-1** (260 m² g⁻¹). The **POP-2** as an electrode material for supercapacitors also exhibits a much better electrochemical performance, including higher specific capacitance (332 F g⁻¹) and better cycle stability (capacity retention rate of more than 94% after 10000 successive cycles). The results verify that the structure and electrochemical properties of porous organic polymers materials can be effectively improved by altering monomers. The study also provides an approach for builiding various porous organic polymers materials for highperformance supercapacitors.

performance.

major challenge.

restacking and aggregation structures, which would obviously

limit the diffusion of ions, and then led to poor cycle life and low rate of charge-discharge.²⁹⁻³¹ It is necessary to design new

porous conductive polymers for improving the capacitance

polymers which have emerged as promising energy storage

because of their high specific surface area and controllable

pore structures, rapid ion diffusion properties, and variable

chemical functionality.³²⁻³⁴ Unfortunately, a key weakness of

porous organic polymers is poor electric conductivity, which

hindered their practical application in supercapacitors. To

effectively utilize porous organic polymer electrode materials,

either composites³⁵ or carbonization³⁶⁻³⁹ of porous organic

polymers was developed to improve their specific capacitance.

However, those methods led to a significant degradation from

the theoretical advantages of porous organic polymers, which

have largely limited their potential applications. Therefore, the

design and synthesis of conductive porous organic polymers in

supercapacitors applications is highly desirable. 3D conductive

porous network can provide much more open channels to allow efficient ionic transport and circumvent the severe

drawback of low dimensional conductive polymer materials.

However, the preparation of 3D porous organic polymers with

good electric conductivity and proper pore structure is still a

Porous organic polymers are a unique class of porous

Introduction

Supercapacitors have attracted a great deal of attention in academia and industry during the last few decades because of their merit of high power density, rapid charge-discharge rate, long cycle life, low weight, and high flexibility.¹⁻⁶ Therefore, various materials have been explored to fabricate electrodes, including carbon-based materials,⁷⁻¹² metal oxides,¹³⁻¹⁵ conductive polymers,¹⁶⁻¹⁸ and the composites of these materials.¹⁹⁻²² In particular, conductive polymers have received increasing attention owing to their unique conjugated structures, excellent electric conductivity and mechanical flexibility, and controllable physical properties.²³⁻²⁶ Some conductive polymers exhibit high specific capacitance due to good electric conductivity, e.g., 950 F g⁻¹ for polyaniline nanowires arrays,²⁷ and 380 F g⁻¹ for polypyrrole hydrogels.²⁸ However, the most of conductive polymers generally show low specific surface area and wide pore distribution owing to their 1 D structures. Even 2D conductive polymers with conjugated backbones still exhibit disappointed results due to the strong

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⁺ Electronic Supplementary Information (ESI) available: Experimental details, spectra and X-ray crystallographic data. CCDC 1818775. For ESI and crystallographic date in CIF or other electronic format see DOI:

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To develop 3D conductive porous organic polymers as electrode materials in supercapacitors, smartly choosing building blocks with targeted 3D framework is very necessary. The tetrahedral building blocks with sp³ hybridized carbon atoms enable the formation of 3D diamond structure.⁴⁰ We propose to design tetrahedral building blocks by introducing conductive units of thiophene, and then construct 3D porous organic polymers by polymerization. In this paper, tetrahedral building blocks were firstly synthesized via Schiff-base reaction of tetra(4-aminophenyl)methane (TAPM) and linear 2thenaldehyde (THE) or 2,2-bithiophene-5-carboxaldehyde (THC), and then two 3D conductive porous organic polymers POP-1 and POP-2 with diamond topological structures were formed by oxidative polymerization of tetrahedral building blocks (Fig. 1). Herein, the syntheses and characterizations of these polymers, and their applications as electrode materials for supercapacitors with remarkable electrochemical performance and excellent cycle stability were present.

Experimental section

Preparation of tetra (4-aminophenyl) methane (TAPM)

TAPM was prepared according to the reported method with slight modifications as follows.^{41,42} Tetraphenylmethane (16 g, 50 mmol) was added into nitric acid (60 mL) at -40 °C by vigorous stirring. Then acetic anhydride (25 mL) and acetic acid (45 mL) were slowly added, respectively, and stirred for 8 h. After filtration, the resultant precipitate was washed with water (3 \times 50 mL) and ethanol (1 \times 50 mL), the residue was collected and dried at 60 °C under vacuum to get tetrakis(4nitrophenyl)methane as yellow crystalline solid, yield 74%. Tetrakis(4-nitrophenyl)methane (5 g, 10 mmol), hydrazine monohydrate (20 mL) and Raney Ni (1.5 g) were added to THF (80 mL). The reaction mixture was heated at 60 °C for 24 h. After removal of the insoluble solid by filtration, the resultant filtrate was evaporated under reduced pressure to obtain white solid. The raw product was purified by flash column chromatography (petroleum ether/ethyl acetate/dichloromethane (6:1:0.9); silica gel, 200-300 mesh) to gain crystalline TAPM with 86% yield. Elemental analysis calculated (%): C 78.91, N 14.73, H 6.36; found: C 78.75, N 14.58, H 6.67; FT-IR (KBr, cm⁻¹): 3394, 3150, 3022, 1698, 1268, 1610, 1179, 859, 815, 711; 1 H NMR (DMSO-d₆, 400 MHz, δ ppm): 4.92 (s, 8H), 6.39 (d, 8H), 6.68 (d, 8H) (Fig. S1).

Preparation of POP-1

TAPM (100 mg, 0.26 mmol) and 2-thenaldehyde (THE) (0.14 mL, 1.4 mmol) were added to methanol (30 mL), the mixture was refluxed under N₂ for 24 h. The resultant yellow precipitate was collected by filtration and washed with methanol (5 × 20 mL), and then dried at 60 °C under vacuum for 12 h to obtain a yellow powder. The resultant crude product was recrystallized with CHCl₃ gave yellow crystals with 91% yield, namely MTH-1. Elemental analysis calculated (%): C



Fig.1 The structure of 3D porous organic polymers, (a) POP-1 and (b) POP-2.

71.40, N 7.40, H 4.26, S 16.94; found C 71.23, N 7.26, H 4.70, S 16.81; FT-IR (KBr, cm⁻¹): 1650, 1620, 1499, 1426, 1180, 1043, 1007, 961, 843, 706; ¹H NMR (DMSO-d₆, 400 MHz, δ ppm): 7.21 (m, 20H), 7.66 (m, 4H), 7.82 (m, 4H), 8.83 (s, 4H) (Fig. S2).

MTH-1 (0.76 g, 1 mmol) was dissolved in 40 mL of CHCl₃. Anhydrous FeCl₃ (2.27 g, 14 mmol) was previously dissolved in CH₃NO₂ (20 mL) and then slowly added into the monomer solution at 0 °C, the precipitation was immediately obtained, the solution was kept vigorously stirring for 24 h. The resultant precipitate was isolated by filtered, and washed with 1 M HCl (5 × 20 mL) and CH₃OH (3 × 20 mL), Soxhlet extracted by methanol 24 h, and then the precipitate was dried at 80 °C under vacuum for 12 h to afford bright brown powder corresponding **POP-1** with 85% yield. Elemental analysis for the calculated (%): C 72.08, N 7.18, H 4.29, S 16.45 and found C 71.89, N 7.11, H 4.67, S 16.33; FT-IR (KBr, cm⁻¹): 1650, 1620, 1498, 1424, 1194, 1045, 822, 733, 658, 584.

Preparation of POP-2

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Fig. 2 Schematic illustration of the constructed strategy in 3D porous organic polymers synthesis. (a) POP-1. (b) POP-2

POP-2 was prepared by a similar procedure to that described for **POP-1** except that 2,2-bithiophene-5-carboxaldehyde (THC) instead of the THE was used, yield the corresponding tetrahedral building block MTH-2 as yellow crystals with 93% yield. Elemental analysis calculated (%): C 67.49, N 5.16, H 3.72, S 23.63 and observed C 67.31, N 5.08, H 4.10, S 23.51; FT-IR (KBr, cm⁻¹): 1647, 1602, 1580, 1505, 1439, 1231, 1053, 792, 696, 584; ¹H NMR (DMSO-d₆, 400 MHz, δ ppm): 7.25 (m, 12H), 7.60 (m, 12H), 8.01 (m, 4H), 8.81 (m, 8H), 9.89 (s, 4H) (Fig. S3). The organic polymer **POP-2** was obtained as brown powder by oxidative polymerization of tetrahedral building block MTH-2, yield 86%. Elemental analysis calculated (%): C 68.01, N 5.07, H 3.72, S 23.20 and found C 67.82, N 5.02, H 4.18, S 22.98; FT-IR (KBr, cm⁻¹):1632, 1580, 1491, 1439, 1342, 1231, 1157, 1045.

Material characterization

The FT-IR spectra of samples were characterized using a NicoletiS10 instrument in the range 4000-500 cm⁻¹. X-ray diffraction (XRD) patterns were obtained on a Bruker D8 X-ray diffractometer. Scanning electron microscopy (SEM) images were collected using a Hitachi S-4800 field-emission SEM microscopy. Transmission electron microscopy (TEM) images were observed by JEOL Jem-2100 plus field-emission TEM microscopy. Thermogravimetric analysis (TGA) was carried out via Mettler Toledo TGA/DSC1/1100SF analyser. The surface area and pore size distribution measurements were conducted on a Micromeritics ASAP2020MP procedure. Solid-state nuclear magnetic resonance (¹³C-NMR) spectra were carried out on a Bruker AVANCE III 400 spectrometer. The liquid ¹H NMR spectra were recorded on Bruck 400 spectrometer, with the DMSO (2.50 ppm) as internal reference. The electric conductivity was performed by a Four-probe Tester at room temperature (ST2258A). The crystal structures were determined on a Siemens (Bruker) SMART CCD diffractometer using monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å). Cell parameters were retrieved using SMART software and refined using SAINT⁴³ on all observed reflections. The highly redundant

data sets were reduced using SAINT⁴⁴ and corrected for Lorentz and polarization effects. Absorption corrections were applied using SADABS⁴⁴ supplied by Bruker. Structures were solved by direct methods using the program SHELXL-97.⁴⁵ All of the non-hydrogen atoms except the anions were refined with anisotropic thermal displacement coefficients.

Electrochemical measurements

Cycle voltammetry (CV), galvanostatic charge-discharge (GCD) electrochemical impedance and spectroscopy (EIS) measurements were performed by an electrochemical workstation (CHI 660E). For the three-electrode systems, Hg/HgO electrode served as the reference electrode, platinum foil (1 cm^2) acted as the counter electrode, and the prepared electrode (1 cm^2) was used as working electrode. The working electrode was fabricated by mixing active material, acetylene black and poly(tetrafluoroethylene) in a mass ratio of 8:1:1, and then dispersed in ethanol under ultrasonication to obtain a homogeneous slurry. The slurry was coated on the Ni foam substrate (1 cm²). Similarly, in the two-electrode system, an asymmetric supercapacitor was assembled to test the device performance, with POP-2 acting as the positive electrode, activated carbon (AC) as the negative electrode. All the electrochemical tests were taken on using 3 M KOH aqueous electrolyte.

The specific capacitance of electrodes was calculated by the following equation (1) and equation (2): 46

$$E_{\text{inVD}} = I \int_{(U)}^{(U)} U(t) dt$$
(1)

$$C_{\rm int/D} = \frac{2E_{\rm int/D}}{U_{\rm max}^2} \tag{2}$$

Where $E_{int/D}$ stands for the discharge energy (W s), *I* represents the current density (A g⁻¹), *t* refers to the discharge time (s), *U* is the potential window (V) and $C_{int/D}$ is the specific capacitance (F g⁻¹).

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Fig. 3 The single-crystal structure of MTH-1 (ORTEP, 30% ellipsoids. All H atoms have been removed for clarity. C: grey; N: blue; S: yellow).

Results and discussion

POP-1 and POP-2 were prepared through a distinct and facile two steps strategy (Fig. 2). Firstly, tetrahedral building blocks MTH-1 and MTH-2 were synthesized by taking full advantage of tetrahedral TAPM and simultaneously introduced the conductive units of THE and THC. Secondly, the formed tetrahedral building blocks were polymerized by a simple oxidative polymerization approach. In this process, tetrahedral building blocks control the growing direction of the segments and the thiophene groups were linked to produce the extended 3D diamond network structures POP-1 and POP-2. Furthermore, the formed C=N bonds reduces the structural defects of 3D polymers, increases structural rigidity and further improves the stability of polymers.⁴⁷

To further demonstrate the structures of POP-1 and POP-2, a single-crystal structure of MTH-1 was collected. As can be seen from Fig. 3, four C=N bonds of building block were



Fig. 4 Spectra of FT-IR and NMR, (a) FT-IR of MTH-1 and POP-1; (b) FT-IR of MTH-1 and POP-2; (c) ¹³C NMR spectra of POP-1; (d) ¹³C NMR spectra of POP-2.

(a)	(b)
<u>500 nm</u>	
(c)	(d)
100 mm	

Fig. 5 (a) SEM images of (a) POP-1 and (b POP-2; (c) TEM images of (c) POP-1 and (d) POP-2.

formed between aniline and thiophene, and four Schiff-base arms extend along the tetrahedral direction with an average angle of 119°. Therefore, it is easy to infer that MTH-1 can be used as precursors to construct 3D porous organic polymers.

The formation of POP-1 and POP-2 were confirmed by FT-IR and NMR spectroscopic methods. In the FT-IR spectra, the absorptions at 1620 cm⁻¹ for MTH-1 and **POP-1** are assigned to the stretching vibration of C=N (Fig. 4a).⁴⁸ And the disappearance of the N-H stretching band (3394, 3150 and 3022 cm⁻¹ for TAPM) and C=O stretching band (1650 cm-1 for THE) in the FT-IR spectra of POP-1, suggest a completed conversion of starting materials during the polymerization.^{49,50} The similar analysis was performed on MTH-2 and POP-2, whereas peak at 1647 cm⁻¹ for MTH-2 is attributed to the stretching vibration of C=N, and the vibration peak of C=N shift slightly from 1647 to 1632 cm⁻¹ for **POP-2** (Fig. 4b), confirming the existence of imine bonds. The atomic precision construction of POP-1 and POP-2 were further verified by the ¹³C-NMR spectra. The characteristic peaks from 62 to 144 ppm in the spectra of POP-1 and POP-2 are assigned to the central sp³ carbon and benzene groups (Fig. 4c and 4d), which are consistent with the reported results.⁵¹ The peak at 152 ppm is attributed to thiophene, while the peak appearing at 154 ppm corresponds to a resonance of carbon for C=N band. These results unambiguously indicated the formation of organic polymers of POP-1 and POP-2.

To characterize the morphology of POP-1 and POP-2, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) measurements were utilized (Fig. 5). The SEM images of POP-1 and POP-2 show homogenous structure, consisting of the aggregation of grains with uniform dimension (Fig. 5a and 5b). In the TEM images, both POP-1 and POP-2 have a cross-linked network structure, which can be ascribed to the existence of well-ordered 3D frameworks (Fig. 5c and 5d, magnification TEM images in Fig. S4).

The permanent porous properties of POP-1 and POP-2 were investigated by N2 adsorption-desorption measurements at 77 K. The adsorption curves of POP-1 and POP-2 exhibited

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Fig. 6 N_2 adsorption-desorption isotherms of (a) POP-1 and (b) POP-2; Pore size distribution profiles of (c) POP-1 and (d) POP-2.

type-I and type-IV isotherms with a sharp uptake at low relative pressure (P/P₀<0.1), which is the characteristic of microporous nature (Fig. 6a and 6b).⁵² The slow increase in the range of $0.1 < P/P_0 < 0.8$, and the sharp increase at high pressure ($0.8 < P/P_0 < 1.0$) indicate the existence of mesoporous in both **POP-1** and **POP-2**. The Brunauer-Emmett-Teller (BET) surface areas of **POP-1** and **POP-2** were estimated to be 260 and 342 m² g⁻¹, respectively. The pore size of **POP-1** and **POP-2** were widely distributed and centred around the range of microporous and mesoporous (Fig. 6c and 6d). Compared with **POP-1**, **POP-2** provided a broad skeleton and pore owing to the introduction of longer building block.

The thermal stability of **POP-1** and **POP-2** were performed by TGA analysis under N₂ atmosphere and room atmosphere from 40 to 800 °C. **POP-1** and **POP-2** showed no discernible weight loss below 200 °C, and still retained 93% of their initial mass at 300 °C (Fig. S5). The results demonstrate that these 3D porous organic polymers possess high thermal stability, which may be attributed to the rigidity of skeleton and the conjugated diamond topology.

Four-probe measurements exhibited that the electric conductivity of **POP-1** and **POP-2** can reach up to 2.1×10^{-3} and 6.7×10^{-3} S cm⁻¹, respectively. The value of **POP-2** was comparable to reported organic polymers electrodes.⁵³⁻⁵⁶

Conductive ploythiophene units were embedded into the skeleton of polymers making the resulting POP-1 and POP with high BET surface area and proper pore size distribution good candidates for supercapacitors. CV measurements were carried out within the potential range of 0 to 0.6 V for POP-1 (Fig. 7a). The CV curves of POP-1 presented a pair of symmetric redox peaks with good reversibility, verifying that the POP-1 can be reversibly oxidized and reduced in 3 M KOH solution. It is noticeable that the peak current rapidly increases with scan rate and can maintain the shape of CV curves, suggesting a rapid reaction kinetics. By comparison, the CV curves of POP-2 showed similar redox peaks but with higher current density, demonstrating that POP-2 has a better electric conductivity compared with POP-1 (Fig. 7b). GCD



Fig. 7 Electrochemical performance characteristic of **POP-1** and **POP-2**, (a) CV curves of **POP-1** at different scan rates; (b) CV curves of **POP-2** at different scan rates; (c) GCD curves of **POP-1** at different current densities; (d) GCD curves of **POP-2** at different current densities; (e) Cycle stability of **POP-1** and **POP-2** at a current density of 1 A g⁻¹, inserts show GCD curves of the first ten cycles of **POP-1** and **POP-2** at the current density of 1 A g⁻¹, respectively; (f) Specific capacitance of **POP-1** and **POP-2** at different current densities.

measurements were then studied at different current density from 1 to 5 A g⁻¹ to investigate specific capacitance of **POP-1** and POP-2. It can be seen that the GCD curves show a sharp change near to 0.35 V, which reveals that the specific performance is predominantly pseudocapacitive in nature, in agreement with CV curves. The C_s values of **POP-1** could be calculated according to the formula of the specific capacitance, the values were 214, 190, 170, 151 and 135 F g^{-1} in the range from 1 to 5 A g⁻¹, respectively (Fig. 7c). Similar capacitance values were obtained for **POP-2**, the C_s values were 332, 290, 250, 218 and 200 F g⁻¹, respectively (Fig. 7d). Obviously, **POP-1** and POP-2 both showed high specific capacitance, which could be ascribed to an improved electric conductivity by introducing conductive polythiophene units. Moreover, the BET and capacitance values of TAPM are nearly zero. In comparison with POP-1, POP-2 exhibited a higher specific capacitance. The possibly resulted from extend conductive results polythiophene unit that can endow the sufficient space for charge transfer and the diffusion of ions.

The cycle stability of **POP-1** and **POP-2** was investigated by GCD cycle tests at 1 A g^{-1} . After 10000 cycles, **POP-1** maintained a specific capacitance of 197 F g^{-1} with capacitance retention of 92%, while **POP-2** maintained a specific capacitance of 312 F g^{-1} with capacitance retention of 94% (Fig. 7e). The good cycle stability of **POP-1** and **POP-2** can be ascribed to the rigidity of skeleton and the conjugated



Fig. 8 Nyquist plots of the electrodes based on POP-1 and POP-2. Insert exhibits the equivalent circuit.

diamond topology. The 3D rigid structure of **POP-1** and **POP-2** can effectively alleviate the volumetric swelling and shrinkage during for cycling, resulting in an enhanced cycle stability, which was also verified by GCD cycles (inserts of Fig. 7e). Furthermore, even at the current density of 5 A g⁻¹, the capacitance retention of **POP-2** also retain 60% of the initial C_s , indicating a high-rate stability (Fig. 7f). This may be associated with the excellent electric conductivity.

To further understand the electrochemical performance of the polymers, the Nyquist plots were analysed based on the equivalent circuit model (Fig. 8). R_e represents the total resistance including electrolyte, electrode and separator. *CPE* represents pseudocapacitor. R_{ct} represents the charge transfer resistance and Z_w is the Warburg impedance which is attributed to the ion diffusion and electrolyte penetration. Each EIS plot exhibits a semi-circle in the high frequency region and a straight part in the low frequency region. The semicircular arc is attributed to charge transfer resistance through



Fig. 9 (a) CV curves of single AC electrode and **POP-2** electrode at the scan rate of 10 mV s⁻¹ by a three-electrode system; (b) CV curve of **POP-2** at the scan rate of 10 mV s⁻¹ by a two-electrode system; (c) GCD curves of **POP-2** at different current densities by a two-electrode system; (d) The specific capacitance of **POP-2** at different current densities by a two-electrode system.

Table 1 Comparison of capacitive storage perf	formance with r	epresentative
porous organic polymers and related materials	5.	

Category		Materials	Specific	Capacitance	
			capacitance (F g ⁻ ¹)	retention (%)	
microporou	ıs	TAT-CMP-2	183	83	
polymers ⁶³					
microporous		KECMP-1	252	50	
polymers ⁶⁴					
$2D \text{ COF}^{65}$		ТаРа-ру	102	92	
2D COF ⁵⁸		TpPa-(OH)₂	416	88	
2D COF ⁶⁶		TThPP	82.79	85.7	
2D COF ⁶⁷		DAAQ-TFP	58	83.3	
Covalent		TpDAB	335	93	
polymer ⁵⁹					
Carbon	from	омс	159	-	
polymer ⁶⁸					
Carbon	from	HPPN-400-	129	99.93	
polymer ⁶⁹		30			
Carbon	from	C-HPU-1	209	99.8	
polymer ⁷⁰					
Carbon	from	ACOF1	234	99.8	
COF ⁷¹					
Composite		DAAQ-TFP-	197	80	
materials ⁷²		COF			
Composite		HCF fiber	63.1	96	
materials ⁷³					
Composite		G-PNF ₃₀	210	73.8	
materials ⁷⁴					

the electrode-electrolyte interface, and the straight line represents the diffusion properties of the electrolyte through the electrode surface.⁵⁷ The charge transfer resistance R_{ct} of **POP-1** and **POP-2** were evaluated to be 35 and 19 Ω, respectively. The transfer resistance of POP-2 was comparable to 2D COF TpPa-(OH) (37.5 Ω),⁵⁸ covalent polymer TpDAB (24.8 Ω),⁵⁹ and most of the reported porous organic polymers. Compared with POP-1, POP-2 possesses a higher electric conductivity. Moreover, POP-2 displayed a slope that is larger than POP-1, which suggested that the ion diffusion is faster than that of POP-1. The property of POP-2 is attributed to its proper pore structure.⁶⁰⁻⁶² The microporous offers a high surface area, while the mesoporous is benefit for decreasing ion transfer barrier, and can facilitate rapid ion diffusion and electrolyte penetration in the pore channels, which might improve the capacitance performance.

The specific capacitance of **POP-1** and **POP-2** electrode materials were found to be superior to those of the reported microporous polymers, ^{63,64} the most of covalent organic polymers, ^{58,59,65-67} and the carbon materials derived from porous organic polymers. ⁶⁸⁻⁷¹. The specific capacitance of **POP-2** is comparable to conductive polymers and composite electrode materials.⁷²⁻⁷⁴ Moreover, the excellent cycle stability was also demonstrated by capacitance retention (Table 1).

DOI: 10.1039/C8NJ00667A

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Fig. 10 Ragone plot of POP-2 electrode.

A two-electrode was further used to confirm the feasibility of POP-2 electrode for the practical application in supercapacitors, an asymmetric supercapacitor device (full-cell) was assembled in 3 M KOH aqueous electrolyte. CV tests of AC and POP-2 were performed by a three-electrode system (Fig. 9a). The AC (-1.0-0 V) and POP-2 (0-0.6 V) offer different potential ranges, their combination can obviously extend the potential range, which is benefit for improving the energy density of supercapacitors. The CV curves of the full-cell exhibited a pair of redox peaks in the potential range of 0-1.6 V (Fig. 9b). The result demonstrated that the combination of AC and POP-2 can extend the potential window of the supercapacitor, which is consistent with GCD curves of POP-2 at different current densities (Fig. 9c). The specific capacitance of the full-cell was calculated to be 107, 100, 94, 91 and 90 F g ¹ in the range from 1 to 5 A g⁻¹, respectively (Fig. 9d).

Energy density and power density of **POP-2** electrode in 3 M KOH aqueous electrolyte were calculated according to the following equation (3) and equation (4):

$$E = \frac{1}{2} C_{sp} V^2$$

$$P = \frac{E}{\Delta t}$$
(3)
(4)

Where *E* represents the specific energy (Wh kg⁻¹), *P* refers to the power density (W kg⁻¹), C_{sp} stands for the specific capacitance (F g⁻¹), *V* is the potential window (V) and Δt is the discharge time (s). Energy density of **POP-2** electrode was calculated to be 38 Wh kg⁻¹ at the power density of 1354 W kg⁻¹ (Fig. 10), which is much higher than other organic polymers electrode materials, indicating a promising electrode material for high performance supercapacitors.^{75,76}

The superior performances of **POP-1** and **POP-2** may be attributed to the following reasons. Firstly, 3D interconnected channels provide a large specific surface area and proper pore size distribution, which is conducive to charge transfer and the diffusion of ions. Secondly, the conductive thiophene units were embedded into polymers networks and formed extended π -conjugated skeleton. This can improve the electric conductivity of 3D porous organic polymers, and thus offers a minimized diffusive resistance to the ionic diffusion. Finally,

the inherently N,S-codoping in the 3D porous organic polymers improved the wettability and electric conductivity of the electrode materials, and enhanced the overall capacitance by enabling extra pseudocapacitance and double layer capacitance.

Conclusions

A new strategy to construct 3D conductive porous organic polymers was developed. By incorporating polythiophene units into 3D porous skeleton, **POP-1** and **POP-2** exhibited tunable pore structures, large specific surface areas, and high thermal stability. More significantly, they can be applied as promising electrode materials with high specific capacitance and excellent cycle stability. This work advances 3D porous organic polymers as a platform for electrode materials and supercapacitors applications. Optimization the electric conductivity and electrochemical performance studies on other porous organic polymers are now in progress in our laboratory.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21771089), the Fundamental Research Funds for the Central Universities (JUSRP51725B, JUSRP51513), the project for Jiangsu scientific and technological innovation team, and the MOE & SAFEA for the 111 Project (B13025).

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DOI: 10.1039/C8NJ00667A

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Published on 16 March 2018. Downloaded by University of California - Santa Barbara on 18/03/2018 14:27:44

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