Electronic Supplementary Information

Facile Fabrication of Novel Highly Microporous Carbons with Superior Size-Selective Adsorption and Supercapacitance Properties

Zhenghui Li, Dingcai Wu, Yeru Liang, Fei Xu, Ruowen Fu*

Materials Science Institute, PCFM Lab and DSAPM Lab, School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou 510275, P. R. China

Experimental

Sample preparation

In a typical process, 12.0 g of anhydrous aluminium chloride ($AlCl_3$) was added into 100 ml of carbon tetrachloride (CCl_4) in a three-neck flask. Then the mixture was refluxed with magnetic stir for 40 min at 75 °C. Subsequently, a solution of 5.0 g of linear polystyrene resin dissolved in 100 ml of CCl_4 was added to undergo a Friedel-Crafts crosslinking reaction. After 30 min, 100 ml of ethanol-water solution (95 wt. % ethanol/water = 80 ml/20 ml) was added slowly to stop the reaction. The product was filtered off, washed with the 95 wt.% ethanol/5 wt.% dilute hydrochloric acid mixture (150 ml/50 ml) and pure water, followed by drying at 100 °C for 8 h. After that, the as-obtained *x*PS was carbonized at 900 °C for 3 h in N_2 flow with a heating rate of 2 °C/min, leading to formation of HMC. To investigate the nanostructure evolution, *x*PS was also treated at 320 and 460 °C to obtain *x*PS-320 and *x*PS-460, respectively. For fabrication of *u*HMC, the procedure is exactly the same as that of HMC except that the used disposable polystyrene foam tableware, which was washed prior to utilization, was employed as the raw material.

* Corresponding author. E-mail: wudc@mail.sysu.edu.cn

Structural Characterization

The thermogravimetric analysis (TGA) was performed with a heating rate of 5 °C/min in N_2 flow. Fourier transform infrared (FTIR) spectra were measured using a Bruker Equinox 55 FTIR spectroscopy. The morphologies of the samples were observed by a JSM-6330F scanning electron microscope (SEM) and a JEM-2010HR transmission electron microscope (TEM). The Raman spectrum was obtained with a Renishaw inVia Raman spectrometer. A Micromeritics ASAP 2010 surface area and porosity analyzer was used to investigate the pore structure. The BET surface area (S_{BET}) was analyzed by Brunauer-Emmett-Teller (BET) theory. The micropore surface area (S_{mic}) was determined by t-plot method. The total pore volume (V_t) was calculated from the amount adsorbed at a relative pressure P/P_0 of 0.997. The pore size distribution was analyzed by original density functional theory (DFT) with non-negative regularization and medium smoothing.

Adsorption Characterization

Adsorption amounts of captopril and VB12 on carbon materials were obtained by measuring their concentrations before and after adsorption. 45 mg of carbon powder was added into a conical flask, and then 75 mL of captopril or VB12 solution (200 mg L^{-1}) was added quickly. After that, this suspension was shaken with a rate of 150 rpm at 30 °C. At intervals, 0.5 mL of supernate was taken out and diluted to 5 mL. The concentration of adsorbate was measured by UV-Vis spectra. The wavelength for captopril and VB12 is 220 and 360 nm, respectively. The adsorption capacity (C) was calculated according to the equation $C=(c_0V_0-c_1V_1)/(mS_{BET})$, where c_0, V_0, c_1, V_1 and m represent the initial concentration, initial volume, concentration and volume after adsorption, and weight of carbon materials, respectively. The selectivity (S) is obtained according to the equation $S=C_{cap}/C_{VB12}$, where C_{cap} and C_{VB12} are the molar saturation adsorption capacity at 24 h for captopril and VB12, respectively.

Electrochemical Characterization

The electrochemical performances of HMC were measured in 6 M KOH using a sandwich-type two-electrode testing cell at ambient condition. HMC electrodes in the form of round sheet were obtained by pressing a mixture film of 92 wt% HMC and 8 wt% polytetrafluorethylene into a nickel foam current collector. The mass of HMC in each electrode is about 10 mg. Galvanostatic charge–discharge test was executed at a current density of 10 mA g^{-1} over a voltage range of 0-1.0 V using Arbin BT2000 instrument. Cyclic voltammetry (CV) measurement was performed at a sweep rate of 2 mV s^{-1} with an IM6e electrochemical workstation from -1V to 0V. The specific capacitance (C_m) was calculated according to the equation $C_m=2 \times I_m t/\Delta V$, where I_m, t and ΔV represent the current density, the discharge time and the discharge voltage, respectively. The capacitance per surface area (C_s) was calculated according to the equation $C_s=C_m/S_{BET}$, where S_{BET} is the BET surface area.

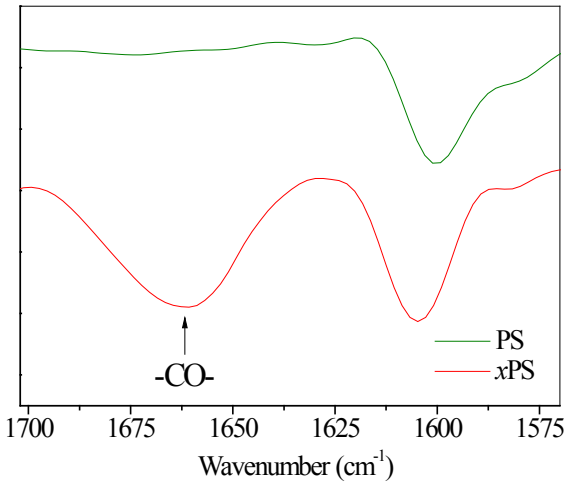
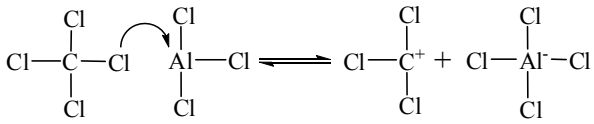
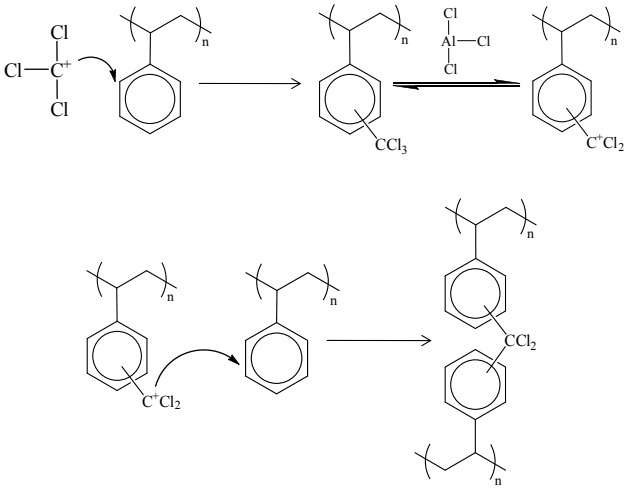


Fig. S1 FT-IR spectrums of PS and *x*PS.

(1) Formation of carbocation $^{+}CCl_3$



(2) Formation of -CCl_2- crosslinking bridges



(3) Formation of -CO- crosslinking bridges

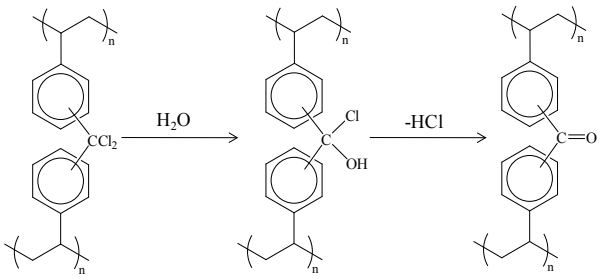


Fig. S2 Formation mechanism of -CO- crosslinking bridge.[1]

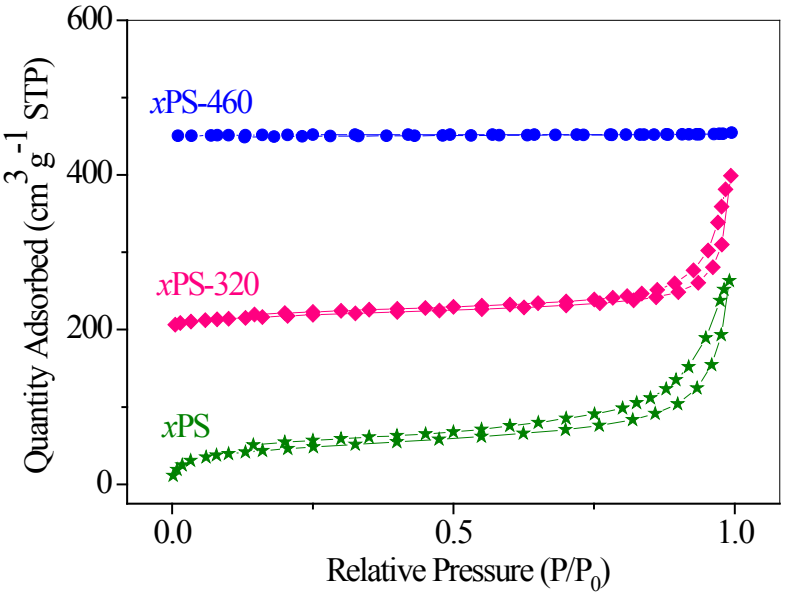


Fig. S3 N_2 adsorption-desorption isotherms of *x*PSs.

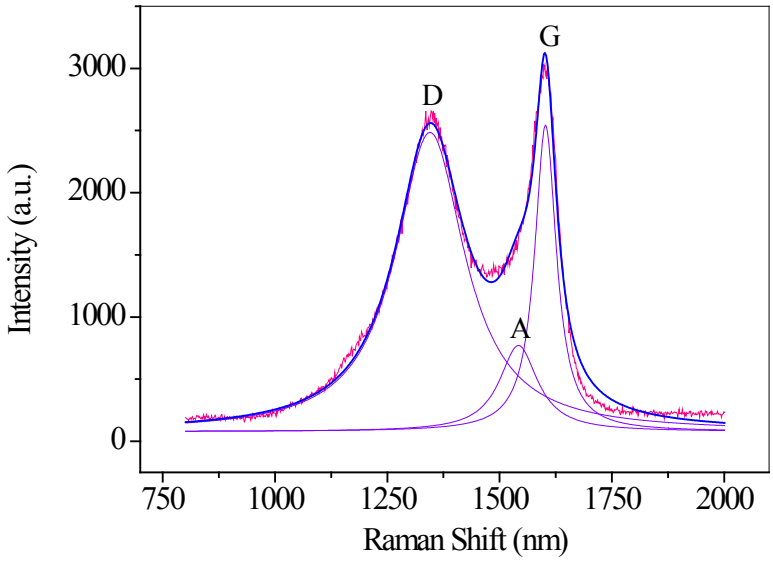


Fig. S4 Raman spectrum of HMC. In the Raman spectrum, the band around 1602 cm^{-1}, 1542 cm^{-1}, and 1345 cm^{-1} can be denoted as G (graphitic) peak, A (amorphous) peak and D (disordered) peak, respectively.[2] The microcrystalline planar crystal size L_a can be calculated using the empirical formula found by Tuinstra and Koeing ($L_a = 4.35\ I_G/I_D$ (nm), where I_G and I_D are integrated intensity of G and D peak, respectively). For HMC, L_a is equal to 1.39 nm, indicating that HMC reveals a graphite-like microcrystalline structure.

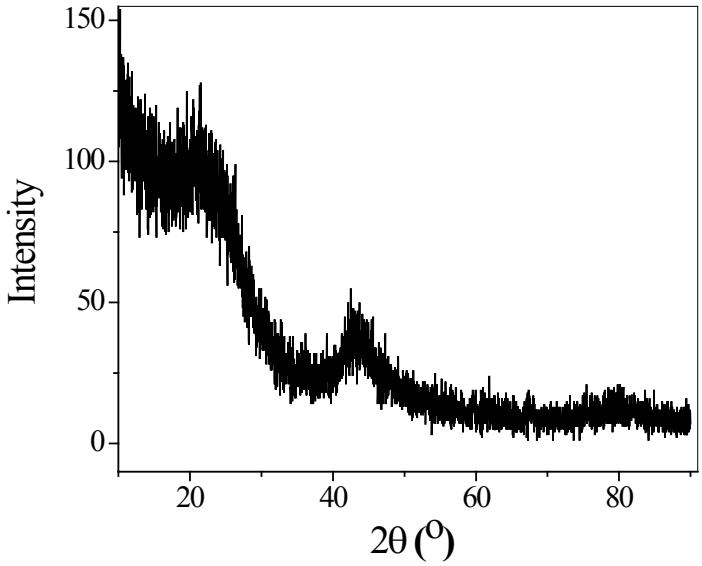


Fig. S5 XRD pattern of HMC. HMC displays a broad and weak (002) diffraction peak at 22°, indicative of a graphite-like microcrystalline structure.

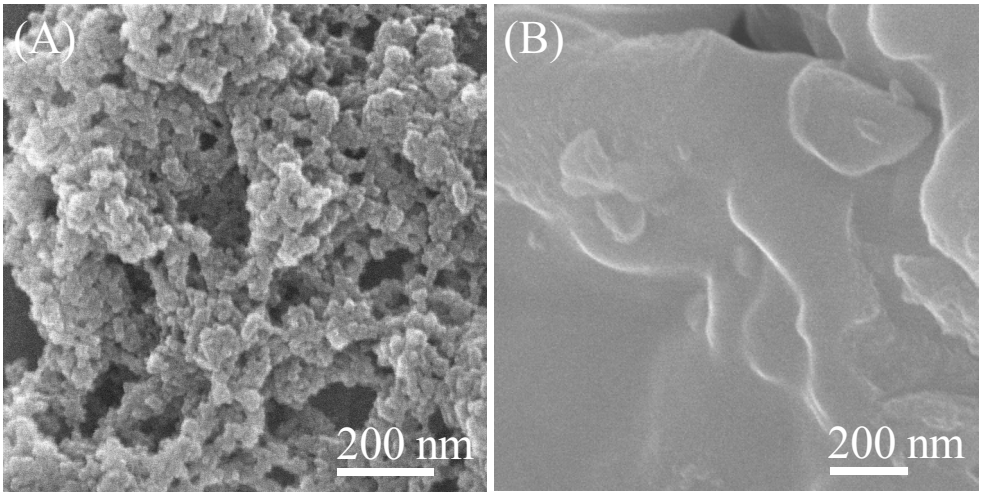


Fig. S6 SEM images of (a) the lowly crosslinked PS (*ux*PS) and (B) its related carbon product (*u*HMC) prepared using the used disposable polystyrene foam tableware as the raw material.

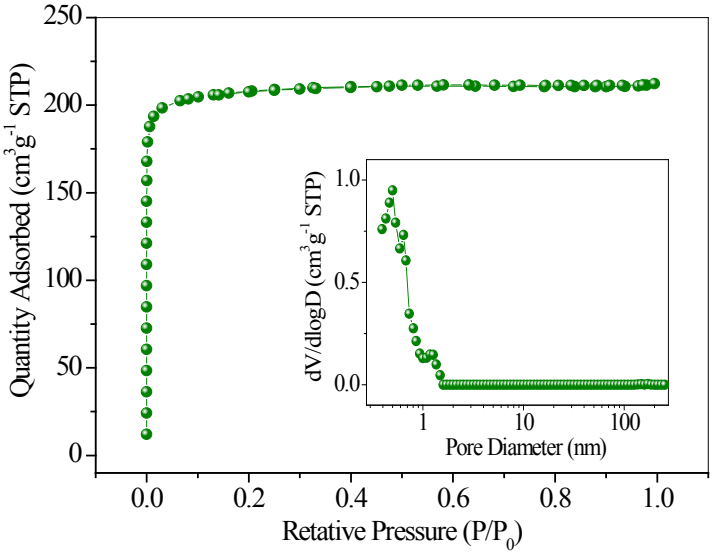


Fig. S7 N_2 adsorption-desorption isotherm and DFT pore size distribution (inset) for *u*HMC.

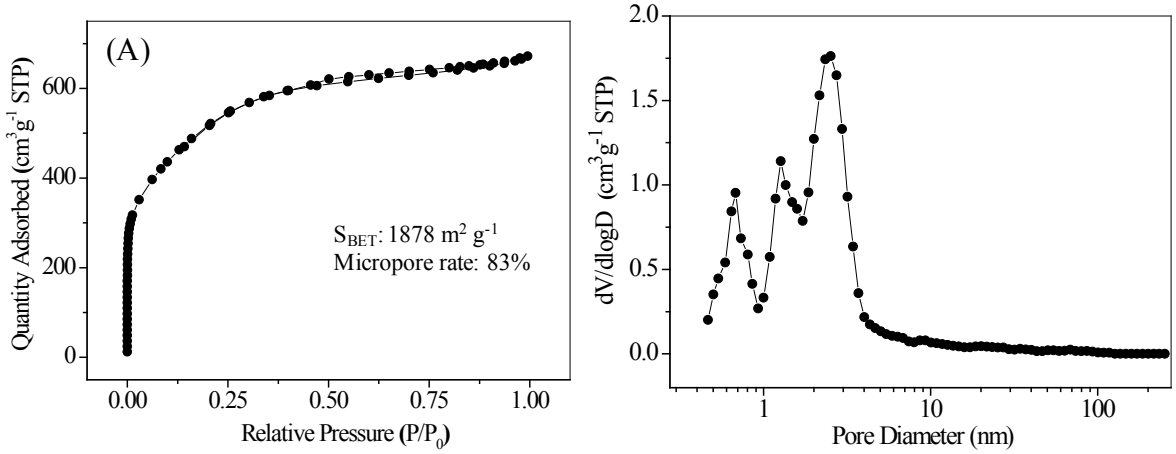


Fig. S8 (A) N_2 adsorption-desorption isotherm and (B) DFT pore size distribution for AC.

Table S1 Micropore rates of some typical microporous carbons.*

No.	Sample	S_{BET} ($m^2 g^{-1}$)	Micropore rate (%)		Reference
			Surface area	Volume	
1	**HMC**	**1108**	**97**	**93**	**This study**
2	PP carbon	1320-2260	-	46~59	3
3	PAN carbon	580	-	74	3
4	PFA carbon	590	-	65	3
5	N-C-1	1363	48	35	4
6	N-C-4	1329	49	42	4
7	CF900-4	1616	-	74	5
8	CFB900-4	1722	-	68	5
9	**AC**	**1878**	**83**	**71**	**This study**
10	Acticarbone 3S	1013	-	54	6
11	Norit SX 1G	1047	-	59	6
12	Norit SX2 POCH	835	79	-	7
13	AC	1585	-	41	8
14	AC-C4	1308	-	47	8
15	AC-K5	3190	-	64	8
16	AC-P600	2095	74	65	9
17	AC-P650	3246	47	39	9
18	AC-P700	3432	42	34	9
19	C34	1083	-	42	10
20	C46	1600	-	42	10
21	ACM-A	2652	69	72	11
22	ACM-C	403	78	85	11

23	DUT-38-A-850-6	2635	-	76	12
24	DUT-38-A-950-4	3104	-	60	12
25	K9-3/15	1576	-	83	13
26	K7-3/15	2438	-	70	13
27	K7-5/30	2875	-	54	13
28	popcarbon-600	589	86	-	14
29	popcarbon-750	773	84	-	14
30	popcarbon-900	1417	70	-	14
31	CS	430	-	87	15

* Samples 2~8 are microporous templated carbons, sample 9-27 are activated carbons, and samples 28~31 are other microporous carbons.

Table S2 Parameters of Raman spectrum of HMC.

Sample	Peak center (cm^{-1})			% Peak area*			L_a (nm)
	D	A	G	D	A	G	
HMC	1345	1542	1602	67.7	10.7	21.6	1.39

* Peak area = area of peak X/(total area of peaks D, A and G), where X=D, A, G.

Table S3 Structural formula of captopril and VB12.

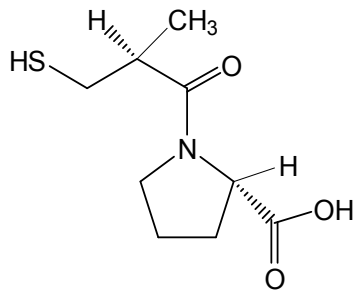
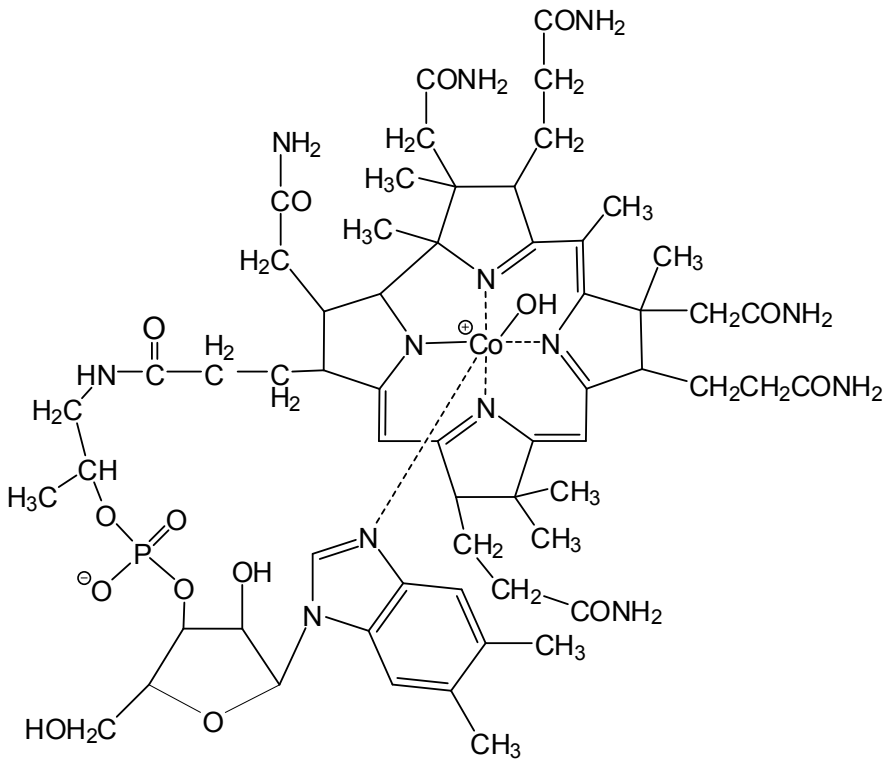
captopril	
VB12	

Table S4 The capacitance per surface area (C_s) of some typical microporous carbons.

No.	Sample	Measurement condition	Electrolyte	C_s (μF cm^{-2})	Reference
1	**HMC**	**10 mA g^{-1}**	**6M KOH**	**15.0**	**This study**
2	XC-72	5 mV s^{-1}	2M H_2SO_4	8.8	16
3	Maxsorb	5~50 mV s^{-1}	30% KOH	10.1~2.2	17
4	M30	1 mHz	30% KOH	2.4	18
5	SACF-20	1 mHz	30% KOH	2.7	18
6	A10	1 mHz	30% KOH	3.1	18
7	M10	1 mHz	30% KOH	4.1	18
8	TiC CDC	5 mV s^{-1}	1M H_2SO_4	4.8~12.2	19
9	ZrC CDC	5 mV s^{-1}	1M H_2SO_4	6.3~11.8	19
10	P-KOH-AC	10 mV s^{-1}	1M $NaNO_3$	9.3	20
11	CF	0.5~5 mA	1M H_2SO_4	9.4~8.8	21
12	CF01	0.5~5 mA	1M H_2SO_4	10~9.5	21
13	W-KOH-AC	10 mV s^{-1}	1M $NaNO_3$	10.9	20
14	LA/1	-	6M KOH	11.6	22
15	SA/S/1	-	6M KOH	11.9	22
16	CF03	0.5~5 mA	1M H_2SO_4	12.9~12.4	21
17	KJA	-	6M KOH	13.7	22
18	DCG-5	5 mV s^{-1}	2M H_2SO_4	16.5	16
19	CMS	5 mV s^{-1}	2M H_2SO_4	17.3	16

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