Supporting Information

Fabrication and Electrochemical Performance of Novel Hollow

Microporous Carbon Nanospheres

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Fig. S1 FTIR spectrum of SiO₂ nanoparticles and functionalized SiO₂ nanoparticles.



Fig. S2 SEM image of SiO_2 nanoparticles.



Fig. S3 Particle size distribution from SEM image analysis of (A) SiO₂ nanoparticles,(B) SiO₂@PS nanospheres, (C) SiO₂@xPS-24 nanospheres and (D) HCMNS-24.



Fig. S4 DLS curves of (A) functionalized SiO₂ nanoparticles, (B) SiO₂@PS nanospheres, (C) SiO₂@xPS-24 nanospheres and (D) HCMNS-24.

(1) Formation of carbocation ⁺CCl₃



(2) Formation of -CCl₂- crosslinking bridges



(3) Formation of -CO- crosslinking bridges



Fig. S5 Formation mechanism of -CO- crosslinking bridges based on the Friedel-Crafts reaction of polystyrene chain and carbon tetrachloride and subsequent hydrolysis.^[S1]



Fig. S6 FTIR spectrum of SiO₂@PS nanospheres and SiO₂@xPS-24 nanospheres.



Fig. S7 (A) N₂ adsorption-desorption isotherm and (B) DFT pore size distribution of SiO₂@*x*PS-24.



Fig. S8 DFT pore size distribution of carbonized SiO₂@*x*PS-24.



Fig. S9 Core size distribution of HMCNS-24 based on TEM image analysis.



Fig. S10 Shell thickness distribution of HMCNS-24 based on TEM image analysis.



Fig. S11 High-resolution TEM image of HCMNS-24.



Fig. S12 XRD pattern of HMCNS-24.







Fig. S14 SEM images of SiO₂@xPS nanospheres under different hypercrosslinking

reaction times: (A) 0.25 h, (B) 1 h, (C) 2 h, (D) 8 h, (E) 24 h and (F) 48 h.



Fig. S15 SEM images of (A) HCMNS-0.25, (B) HMCNS-1, (C) HMCNS-2, (D)

HMCNS-8, (E) HMCNS-24 and (F) HMCNS-48.



Fig. S16 BET surface areas of HCMNS-0.25, HMCNS-1, HMCNS-2, HMCNS-8,

HMCNS-24 and HMCNS-48.



Fig. S17 SEM images of HMCNSs obtained at various carbonization conditions, including (A) 700 °C, (B) 800 °C and (C) 1000 °C at 5 °C min⁻¹ for 3 h; (D) 1 h, (E) 2 h, (F) 10 h at 900 °C with 5 °C min⁻¹; (G) 1 °C min⁻¹, (H) 2 °C min⁻¹ and (I) 10 °C min⁻¹ at 900 °C for 3 h.



Fig. S18 (A) TEM image of $SiO_2@xPS-24$ without silica cores, (B) SEM and (C) TEM images of control carbon sample.



Fig. S19 (A) CV plots for the first 3 cycles at the scan rate of 0.1 mV s⁻¹, (B) rate performances at different current densities of HMCNS-24.



Fig. S20 (A) CV curves at the sweep rate of 25 mV s⁻¹, (B) Nyquist plots for HMCNS-24 and YP-50.



Fig. S21 DFT pore size distribution of YP-50. From the DFT pore size distribution curve, it can be clearly seen that YP-50 is microporous carbon material.



Fig. S22 SEM image of YP-50. From SEM image, it can be seen that the diameter of carbon particle of YP-50 is mainly micron-scale.



Fig. S23 Long-term cycling stability over 5,000 cycles for HMCNS-24 at a current density of 1A g^{-1} ; the inset shows the charging-discharging curves for the first and last five cycles.

Sample	$\frac{S_{BET}}{(m^2 g^{-1})}$	$\frac{S_{ext}}{(m^2 g^{-1})}$	$\frac{S_{mic}}{(m^2 g^{-1})}$	$\frac{V_t}{(cm^3 g^{-1})}$	$\frac{V_{mic}}{(cm^3 g^{-1})}$
SiO ₂ @xPS-24	287	127	160	0.22	0.07
carbonized SiO ₂ @xPS-24	396	317	79	0.24	0.15
HMCNS-24	1166	583	583	1.36	0.27
YP-50	1396	1022	374	0.73	0.47

Table S1 Pore structure parameters of typical samples.

Table S2 Comparison of the cycling performance of hollow or solid carbon spheres as

	Sample	Stable capacity (mA h g ⁻¹)	Current density (mA g ⁻¹)	Cycle number	Voltage range (V)	Ref.
Hollow carbon spheres	HMCNS	620	100	50	0-3	This work
	Hollow carbon nanospheres	310	372	200	0-3	S2
	Carbon hollow particles	330	0.15 (mA cm ⁻²)	5	0-1.5	S3
	Hollow carbon nanoparticles	443	50	75	0-3	S4
	Interconnected hollow carbon nanospheres	630	37.2	50	0-3	S5
	Hollow graphitic carbon nanospheres	391	37.2	60	0-3	S6
	Nanographene-constructed hollow carbon spheres	600	74.4	30	0-3	S7
	Hollow graphene oxide spheres	485	0.2 (mA cm ⁻²)	30	0-2.5	S8
	Hard carbon nano-spherules	475	0.2 (mA cm ⁻²)	20	-0.15-2.5	S9
Solid carbon spheres	Carbon nanospheres	420	60	60	0-3	S10
	Nitrogen-doped carbon nanoparticles	423	37.2	100	0-3	S11
	Porous carbon microspheres	450	50	50	0-2	S12

lithium-ion battery anodes in the references.

Sample		Current density	Capacitance retention ratio			
			Ref.		HMCNS-24 (This work)	
Hollow carbon spheres	Hollow carbon spheres	1-20 A g ⁻¹	75.7 %	S13	81.2 %	
	N- and O-doped hollow carbon spheres	0.5-5 A g ⁻¹	42.9 %	S14	87.8 %	
	Hollow carbon spheres	0.2-1 A g ⁻¹	60.6 %	S15	91.1 %	
	Hierarchical porous carbon hollow-pheres	0.5-10 A g ⁻¹	73 %	S16	81.9 %	
	Hollow carbon nanospheres	0.05-10 A g ⁻¹	81.8 %	S17	65.0 %	
	Hollow carbon nanospheres	0.1-10 A g ⁻¹	79.0 %	S18	73.4 %	
	Nitrogen-rich hollow porous carbon	0.5-10 A g ⁻¹	66.1 %	S19	81.9 %	
	N-doped hollow carbon spheres	0.5-10 A g ⁻¹	55.6 %	S20	81.9 %	
Solid carbon spheres	Solid carbon nanospheres	0.1-10 A g ⁻¹	75.7 %	S18	73.4 %	
	Mesoporous carbon spheres	0.5-30 A g ⁻¹	70.2 %	S21	65.2 %	
	Monodisperse Carbon Spheres	1-50 mV s ⁻¹	68.4 %	S22	81.3 %	
Activated carbon	YP-50	0.05-10 A g ⁻¹	23.6 %	This work	65.0 %	

Table S3 Comparison of the capacitance retention ratios of HMCNS-24 and other carbon spheres as high-performance supercapacitor electrode in the references.

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