

Supporting Information:

**Confined space pyrolysis strategy for controlling the structure of hollow
mesoporous carbon sphere with high supercapacitor performance**

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Detail Experimental Section

Synthesis of HMCS

The RF resins spheres was prepared by previous research.¹ Typically, monodisperse RF resins spheres were synthesized by using resorcinol and formaldehyde solution as precursors. Ammonia aqueous solution (NH₄OH, 0.1 mL, 25 wt%) was mixed with a solution containing absolute ethanol (EtOH, 4 mL) and deionized water (H₂O, 24 mL), then stirred for more than 1 h. Subsequently, resorcinol (0.2 g) was added and continually stirred for 30 mins. The formaldehyde solution (0.28 mL) then added to the reaction solution and stirred for corresponding time at 30 °C. To prepare RF/silica nanohybrids (named as RF@SiO₂) nanoparticles, the above produced solution was added in to the mix solution of 50 mL H₂O, 20 mL EtOH and 1mL NH₄OH (25 wt%) followed by stirring about 5min. Then, 100 µL of aminopropyl-ethoxysilane (APTES) was added and vigorously stirring (1 h). 1 mL of TEOS was then introduced into the above solution accompanying by stirring and reacted at 30 °C for overnight. The product of RF@SiO₂ nanoparticles was collected using centrifugation (9500 rpm) and rinsed several times with ethanol and dried at room temperature. The as-prepared RF@SiO_{2-x} (where the *x* represents the RF polymerization time with 1, 6 and 12 h) nanoparticles were heated at 2 °C min⁻¹ from room temperature to 800 °C and kept at this temperature for 3 h under a nitrogen flow to obtain HMCS@SiO₂. The pyrolysis product was treated with aqueous HF solution (10 wt.%) to remove the silica and generate HMCS-*x*. Under the same reaction conditions for synthesis of RF@SiO_{2-x} core-shell spheres to obtained HMCS-*x*, the RF polymerization time with 1, 6 and 12 h

in the synthesis of HMCS-1, HMCS-6 and HMCS-12, respectively.

In order to investigate the effect of compact silica shell in HMCS structure, the RF sphere prepared by polymerization time with 12 h was directly carbonized at 800 °C for 3 h under a nitrogen flow. After removing the silica shell, the solid carbon sphere was obtained (denoted as CS). Furtherly, the RF sphere prepared by polymerization time with 12 h and treated by hydrothermal process. Under the same reaction conditions with HMCS, the HMCS-H was prepared to investigate the affection of degree of polymerization for the cavity and porous structure. Under the same reaction conditions with HMCS, changing the adding TEOS amount with 0.5 and 2.0 ml, the HMCS-S@SiO₂ and HMCS-Y@SiO₂ were achieved and then corresponding HMCS-S and HMCS-Y were obtained respectively.

Characterizations.

The morphology and microstructure of samples were investigated by transmission electron microscopy (TEM, JEOL JEM-2100). Nitrogen adsorption-desorption isotherms were carried out on a Micromeritics TriStar 3020 instrument at -196 °C. The Brunauer-Emmett-Teller (BET) method was employed to calculate the specific surface area, while the Barrett-Joyner-Halenda (BJH) method was applied to analyze the pore size distribution using the desorption branch of isotherm. The total pore volume was obtained from the amount of N₂ adsorbed at the relative pressure ($P/P_0=0.97$).

Electrochemical Measurements

The working electrode was prepared by coating the viscous slurry (samples, carbon black and polytetrafluoroethylene with the mass ratio of 8:1:1 in ethanol) onto Ni foam

current collector. The mass of active material loaded on each working electrode was 4~5 mg after drying at 100 °C for 24 h. Electrochemical measurements were carried out in both three-electrode and two-electrode system using an electrochemical workstation (CHI 760E, Chenhua Instruments, China) with 6 M KOH solution as the electrolyte. For three-electrode system, a Pt wire and Hg/HgO was used as the counter and reference electrodes. For the fabrication of supercapacitor devices, two work electrode were immersed in 6 M KOH and were separated by a filtration paper, then tested by the current collector. Electrochemical performances were evaluated by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrical impedance spectroscopy (EIS) analysis. In three-electrode system, the specific gravimetric capacitance according to the GCD measurements: $C=I\Delta t/\Delta Vm$. For the two-electrode system, the specific capacitances (C , F g⁻¹), energy density (E , Wh kg⁻¹) and power density (P , W kg⁻¹) were calculated by the following equations: $C=4 I\Delta t/\Delta Vm$, $E=0.5 C(\Delta V)^2$ and $P=E/\Delta t$, where I (A), Δt (s), ΔV (V) and m (g) are GCD current, discharge time, voltage window, and mass of active material, respectively.

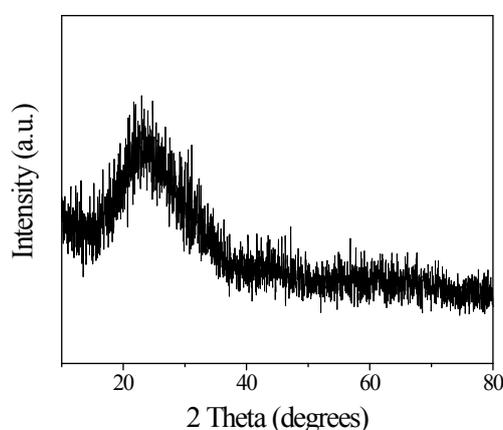
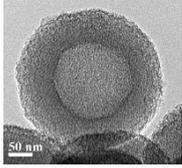
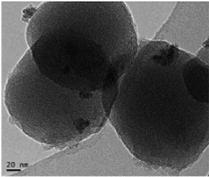
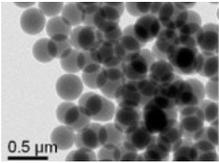
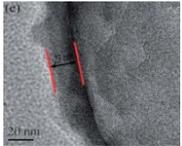
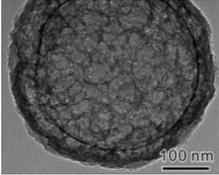
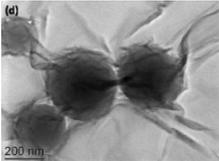
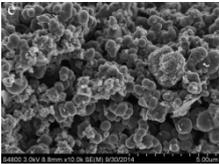
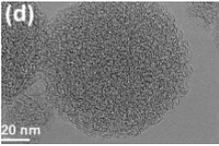
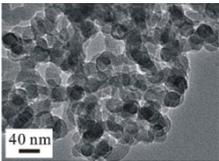
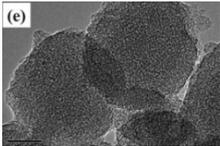
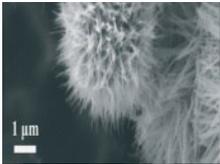
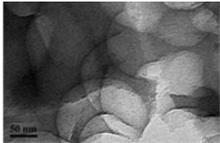
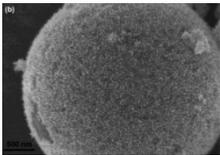
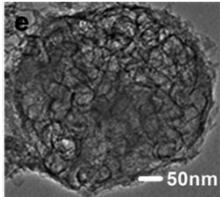
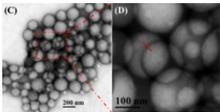
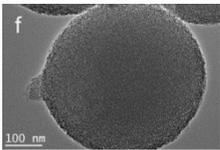
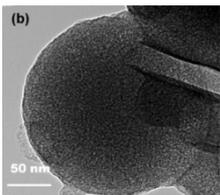
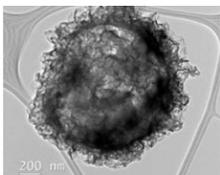
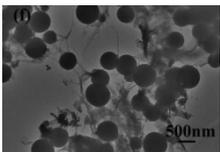


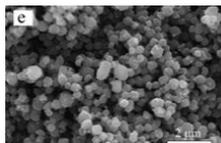
Fig. S1. XRD spectra of HMCS-Y.

Table S1. Comparison of the gravimetric capacitances for sample HMCS-12 with previous reported carbon spheres.

Samples	Morphology	SSA $\text{m}^2 \text{g}^{-1}$	Electrolyte	C_s F g^{-1}	I/m^a A g^{-1}	Ref.
HMCS-12		1425	6 M KOH	352	0.5	This work
Carbon spheres		2502	6 M KOH	230	1	2
Carbon spheres		1184	1 M H_2SO_4	388	1	3
N-doped HCS		213	6 M KOH	213	0.5	4
Core-shell HCS		1286	1 M KOH	210	1	5
Composite of graphene and carbon spheres		677	1 M NaCl	289	0.5	6
Carbon spheres		403	6 M KOH	228	1	7
Carbon spheres		1576	1 M H_2SO_4	154	2 ^{c,d}	8
Carbon spheres		1439	6 M KOH	269	1	9

Carbon spheres		735	6 M KOH	182	0.5	10
Carbon spheres		NA	1 M Na ₂ SO ₄	225	2°	11
Carbon spheres		2823	6 M KOH	316	0.2	12
Carbon spheres		2440	6 M KOH	231	1	13
Carbon spheres		687	6 M KOH	268	1	14
HCS		331	6 M KOH	266	1	15
Carbon spheres		1291	6 M KOH	274	0.5	16
Carbon spheres		1519	6 M KOH	371	0.5	17
HCS		NA	3 M KOH	318	0.5	18
Carbon spheres		NA	2 M H ₂ SO ₄	315	1	19

Carbon spheres



1200

6 M KOH

356

0.2

20

a: current density; b: active samples; c: mV s^{-1} ; d: two-electrode system; NA: not available.

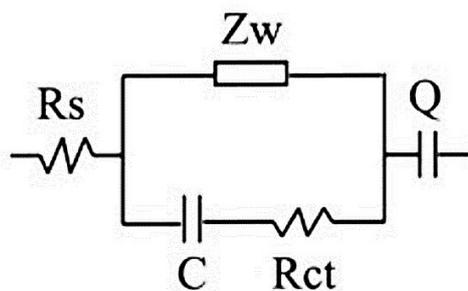


Fig. S2. The fitting equivalent circuit model of EIS.

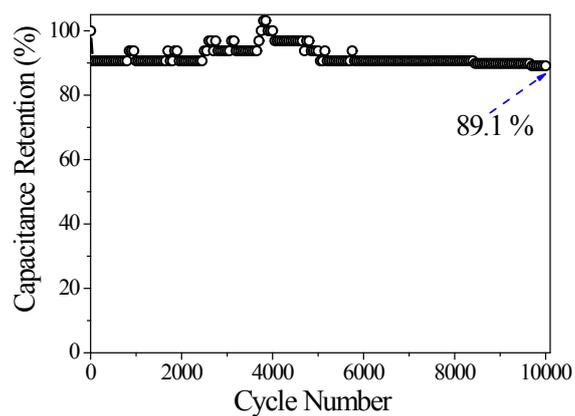


Fig. S3. Cycling stability of HMCS-12 over 10000 cycles.

Table S2. Comparison of the energy density for sample HMCS-12 with previous reported carbon materials.

Samples	Electrolyte	Energy Density Wh Kg ⁻¹	Power Density W Kg ⁻¹
HMCS-12	6 M KOH	26.3	1264.1
hierarchical porous carbon nanosheets	6 M KOH	22.8	198.8
Phosphorus, Nitrogen and Oxygen co-doped carbon spheres	1 M H ₂ SO ₄	10.0	750.0
Phosphorus-doped 3D hierarchical porous carbon	6 M KOH	8.5	100.0
Graphene-like porous carbon nanosheets	6 M KOH	20.9/12.1	467/34500
Heteroatom-doped porous carbon	6 M KOH	21.4	700
carbon spheres	6 M KOH	10.7	151.8
microporous carbon spheres	1 M NaCl	13.9	125
Sulfur-doped nanoporous carbon spheres	6 M KOH	24/11.6	45/5000

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