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Supporting information

A Facile Route for Nitrogen-Doped Hollow Graphitic Carbon Spheres with Superior Performance in Supercapacitors

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Preparation of the Nitrogen-Doped Hollow Graphitic Carbon Spheres

The NHGCSs were obtained by pyrolysis of solid melamine-formaldehyde (MF) resin spheres, which were synthesized by hydrothermal treatment of the melamine and formaldehyde aqueous solution. In a typical experimental procedure, 1.2g melamine(99.5%) and 9.4g formaldehyde solution(37%) were added into 19.4g deionized water with vigorous stirring at 60°C about 10 min to form a clear solution, then maintained 10 min at 90°C. The solution was sealed in a Teflon-lined autoclave (50ml) followed by hydrothermal treatment at 180°C for 6 h. The white precipitate was collected by centrifugation (4000 rpm), then washed repeatedly with distilled water and ethanol for several times, and dried at 80°C overnight. The MF spheres were heated in a quartz tube at 800 °C for 5h with a heating rate of 1 °C min⁻¹ under high purity N₂ flow (30 cm³/min⁻¹), after that the furnace was naturally cooled to room temperature.

Material characterization

Scanning electron microscopy (SEM) micrographs were acquired using a Hitachi S-4800 instrument. Transmission electron microscopy (TEM) was performed with a JEM-2100 electron microscope (JEOL, Japan). The solid-state NMR ¹³C{¹H} SEDOR (Spin Echo Double Resonance) measurements were carried out using Varian Infinity Plus 400. XRD analysis was conducted on Rigaku D/max-III B with copper radiation (CuKα, 0.15406nm). Raman spectra were performed on a Jobin Yvon HR 800 micro-Raman spectrometer at 457.9 nm. The XPS measurements were performed on a VG ESCALAB MK II (VGScientific, UK).

Electrochemical measurements

Cyclic voltammetry and cyclic chronopotentiometric measurements were carried out in a one-compartment cell in 2 M H₂SO₄ solution using a three-electrode configuration on a CHI 760B (Shanghai Chenhua, China) electrochemical workstation. Carbon spheres mixed with acetylene black and poly(tetrafluoroethylene) at a mass ratio of 85:10:5 were pressed onto stainless steel mesh and were used as working electrodes (the active mass is 1.88mg and the active area is 0.36cm²). Platinum foil with the size of 2.5×2.5 cm² and Ag/AgCl were used as counter electrode and reference electrode, respectively. The specific gravimetric capacitance was calculated from the discharge process according to $C_g = I\Delta t / m\Delta V$, where C_g is the specific gravimetric capacitance (F g⁻¹), I is the charge/discharge current, Δt is the time for a full discharge, m is the mass of the active material, and ΔV is the voltage change after a full discharge.

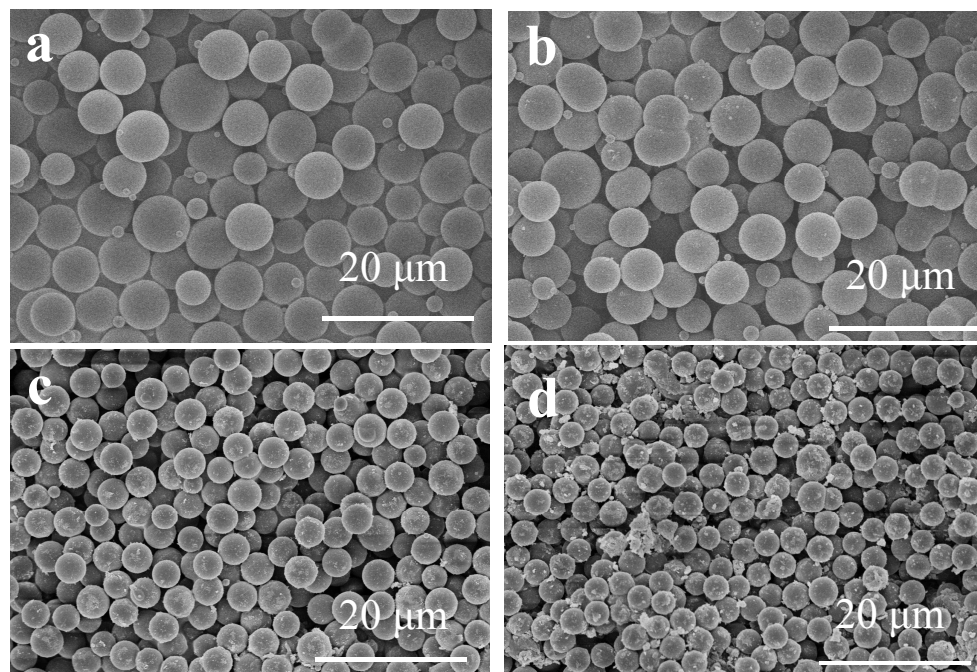


Fig. S1 SEM images of MF microspheres obtained at different hydrothermal temperatures: a) 120°C, b) 140°C, c) 160°C, d) 200°C.

Table. S1 Synthesis parameters and morphology of melamine formaldehyde resins

Sample		Hydrothermal temperatures(°C)	Hydrothermal treatment time (h)	pH of solution	Molar ratio of formaldehyde to melamine	Morphology
MF-1		120	6	5.5	12:1	microsphere
MF-2	Effect of temperatures	140	6	5.5	12:1	microsphere
MF-3		160	6	5.5	12:1	microsphere
MF-4		180	6	5.5	12:1	microsphere
MF-5		200	6	5.5	12:1	microsphere
MF-6		180	0.5	5.5	12:1	Microsphere, colloidal particles
MF-7	Effect of time	180	1	5.5	12:1	Microsphere, colloidal particles
MF-8		180	2	5.5	12:1	Microsphere, colloidal particles
MF-9		180	3	5.5	12:1	microsphere
MF-10		180	12	5.5	12:1	microsphere
MF-11		180	6	2.0	12:1	colloid
MF-12	Effect of pH	180	6	4.0	12:1	colloid
MF-13		180	6	7.0	12:1	microsphere
MF-14		180	6	9.0	12:1	microsphere
MF-15	Effect of molar ratio	180	6	5.5	6:1	microsphere
MF-16		180	6	5.5	3:1	microsphere
MF-17		180	6	5.5	1.5:1	microsphere

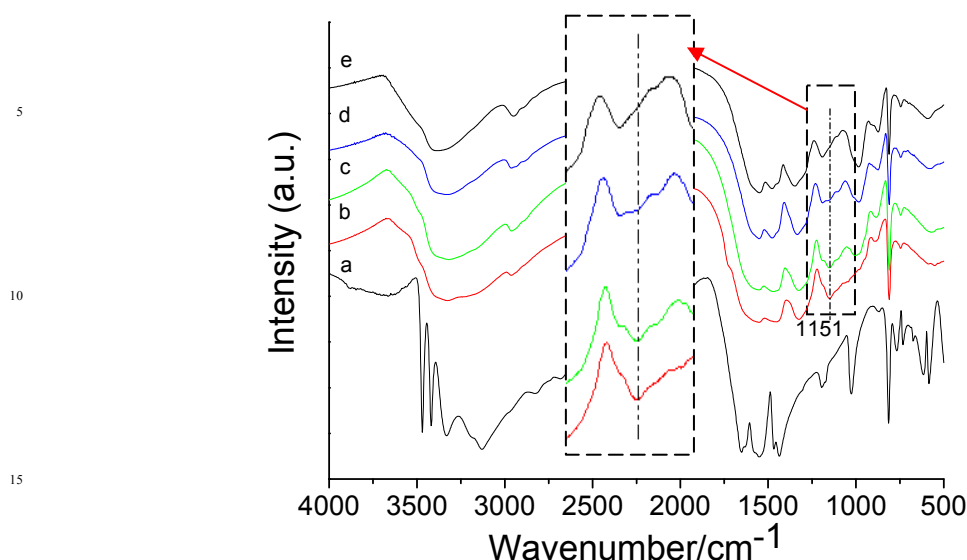


Fig. S2 Fourier transform infrared (FT-IR) spectra: a) melamine, b) as-synthesized MF-17, c) MF-16, d) MF-15, e) MF-4.

The FT-IR of the melamine and MF spheres are shown in Figure S2. The absorbance peaks at $3134\text{--}3470\text{cm}^{-1}$ and 1652cm^{-1} can be attributed to the stretching and bending vibration of primary amine group $\text{H}\text{--}\text{N}\text{--}\text{H}$, respectively. The bands at $1420\text{--}1600\text{cm}^{-1}$ are assigned to the triazine ring vibration in melamine molecular (Figure.S2a). The FT-IR spectra of the typical MF-4 (Figure.S2e) shows that the bands at $3134\text{--}3470\text{cm}^{-1}$ and 1652cm^{-1} disappear, which suggests that the hydrogen atoms in the NH_2 groups of the melamine are substituted by methylol groups ($\text{--CH}_2\text{OH}$). A broad peak at 3380cm^{-1} points to free hydroxyl groups in the resin or the stretching vibration peak of secondary amine group $\text{N}\text{--}\text{H}$.¹ New peaks appear at 2950cm^{-1} and 1340cm^{-1} , which can be assigned to the C–H stretching vibration of the methylene group and the C–N stretching vibration of the secondary and tertiary amines. The broad peaks near 1550cm^{-1} and 1460cm^{-1} are still present, which are assigned to the triazine unit. For the other MF resin spheres prepared under different molar ratios, the similar IR spectrum has been observed. It is emphasized that there is a peak observed around 1151cm^{-1} in the sample MF-17, which is related to C–O ether bond stretching vibration. This peak gradually disappears from MF-17 to MF-4, indicating the disappear of ether linkages in the condensed compounds.

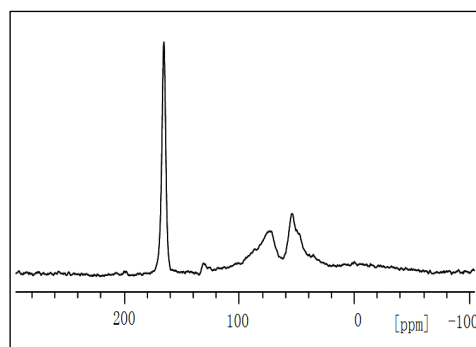


Fig. S3 $^{13}\text{C}\{^1\text{H}\}$ CPMAS-NMR spectra of MF-4.

Solid-state $^{13}\text{C}\{^1\text{H}\}$ CPMAS NMR is used to further explore the chemical structure of the hydrothermal prepared MF-4 resin (see Fig. S3). An intense signal at around 166 ppm is observed, which can be assigned to the carbons of the triazine nucleus whose hydrogen atoms in the NH_2 are disubstituted and monosubstituted by the methylol groups.² The broad peak at 73ppm can be assigned to the methylol groups,³ which indicates that there remains a small part of un-reacted methylol groups in the melamine resins during condensation. The signal at 53 ppm is quite intense, which is associated with methylene linkages. The C/N molar ratio of the melamine resins is derived from elemental analysis (Table. S2). The C/N molar ratio of the as-prepared MF is 0.99, a little less than the calculated value of 1.0 for a fully condensed network with methylene linkages, which indicates that the amino groups are not totally substituted. This deduction coincides with the observed NMR results. From the above discussions, it can be concluded that the chemical structure of melamine resin obtained in this paper is different from those reported MF resins which are mainly cross-linked through ether linkages.⁴ The MF-4 resin prepared by hydrothermal method is composed of triazine rings that uniquely connected through methylene linkages.

There are no ether linkages that can be found. Furthermore, from the elemental analysis results (table S2), we can also conclude that there are about one sixth methylol group remains unreacted on a triazine ring.

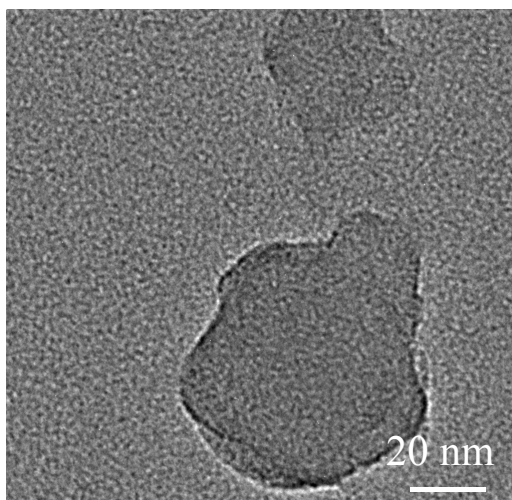


Fig. S4 TEM image of MF colloidal nanoparticles

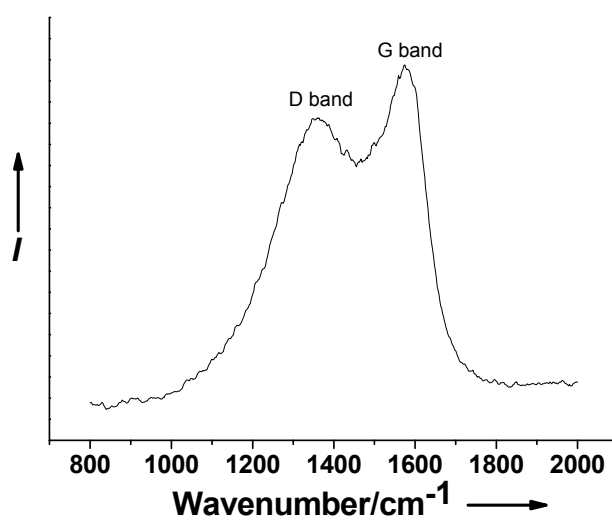


Fig. S5 Raman spectrum of the hollow carbon spheres.

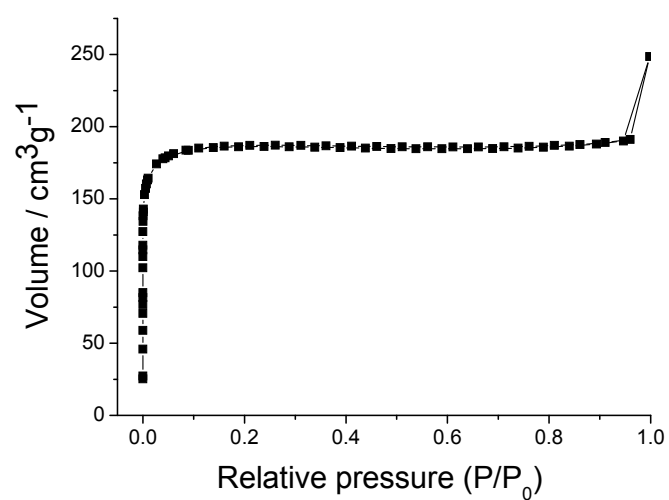


Fig. S6 Nitrogen adsorption/desorption isotherm of the hollow carbon spheres.

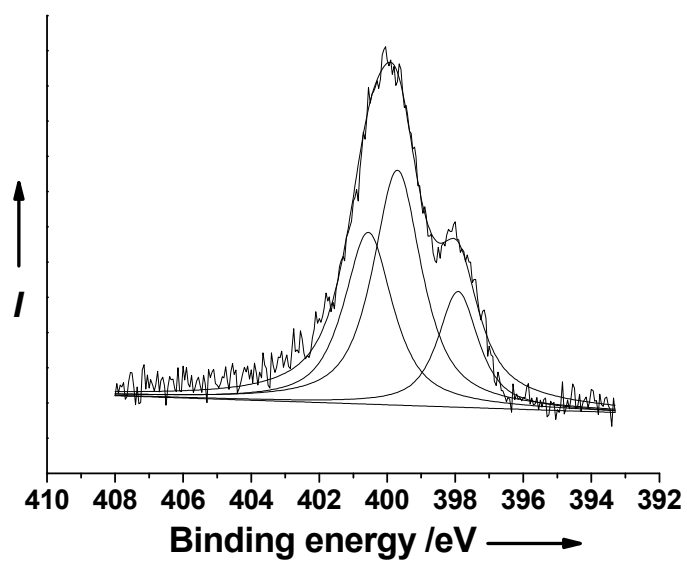


Fig. S7 N1s XPS spectra of the hollow carbon spheres.

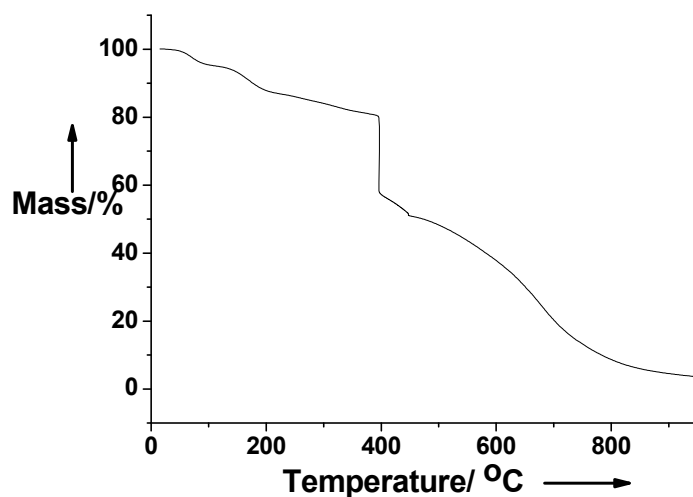


Fig. S8 TG curve of the MF-10 resin performed in N₂ atmosphere.

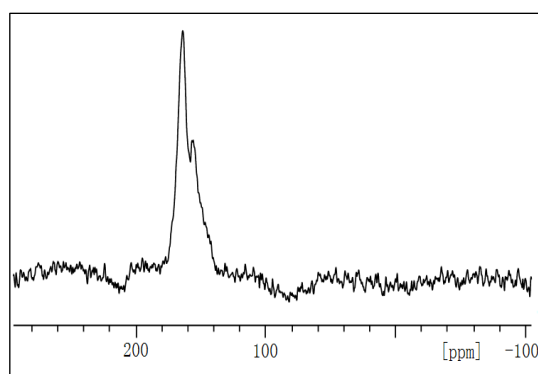


Fig. S9 ¹³C{¹H}CPMAS-NMR spectra of MF-10 resin after heated at 400 °C for 5 hours.

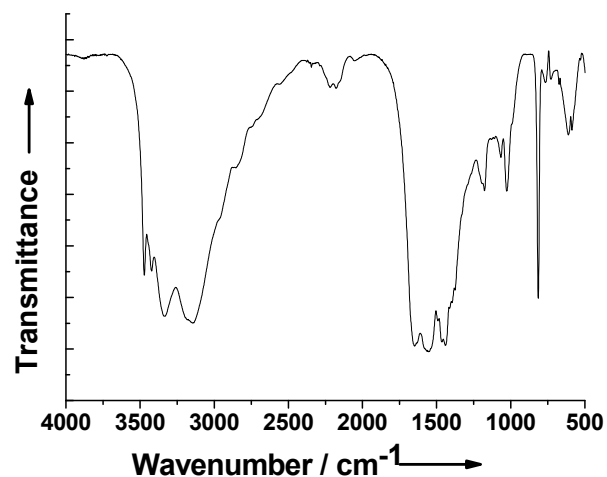


Fig. S10 Fourier transform infrared (FT-IR) spectra of the powder collected at the cold end of tubular furnace after the MF resin was heated at 400°C for 5 hours.

Table. S2 Carbon, nitrogen, hydrogen, oxygen contents [wt.%] and the C/N molar ratio in the MF-4 resin treated at various temperatures obtained from elemental analyzes.

Sample(°C)	80	150	300	400	500	600	700	800
C	35.62	34.86	38.61	45.32	50.91	59.97	76.68	80.66
N	41.79	44.5	50.23	41.63	34.03	21.39	12.34	6.02
H	5.096	4.935	4.31	2.305	2.26	2.283	1.276	1.14
O	17.494	15.705	6.86	10.745	12.6	16.357	9.704	12.18
C/N (mol)	0.9943	0.914	0.8968	1.27	1.67	3.27	7.25	15.63

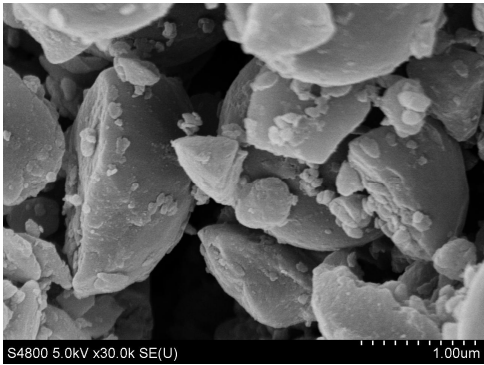


Fig. S11. SEM image of the solid carbon spheres (after grinded) obtained by heating the sample of MF-17 at 800°C for 5 hours.

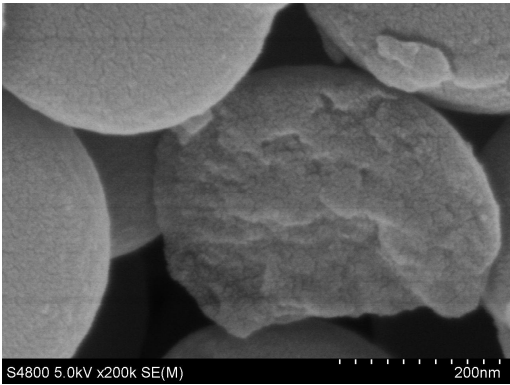


Fig. S12 SEM image of the solid carbon spheres obtained according to the method reported by B. Friedel.⁵

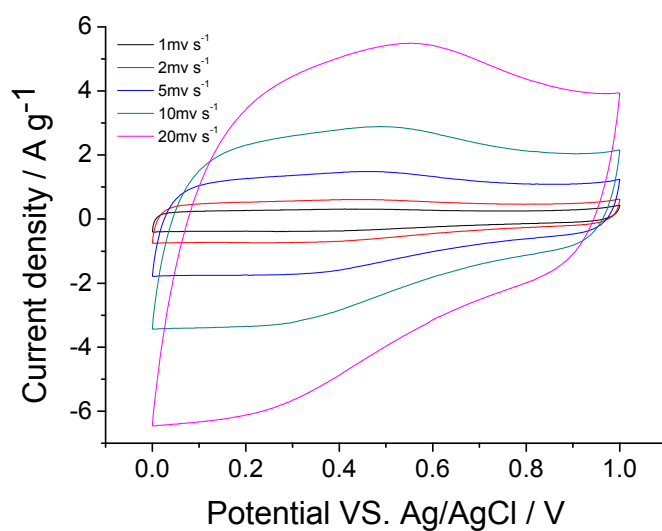


Fig. S13 Cyclic voltammograms of the NHGCSs at different scan rates in 2 M H₂SO₄.

References

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