

Electronic Supporting Information

Nanofibrous Microspheres via Emulsion Gelation and Carbonization

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Experimental Section

Materials and reagents: Perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA, 97%), 5-aminoisophthalic acid (94%), imidazole (ACS reagent, $\geq 99\%$), triethylamine (TEA, $\geq 99\%$), glucono- δ -lactone (GdL), polystyrene (Mw 35 and 192 KDa), o-xylene ($\geq 99\%$), Sorbitan monooleate (span 80), melamine (MM, 99%), and non-ionic surfactant Pluronic F-127 (F-127) were purchased from Sigma-Aldrich and used without further purification. Standard analytical grade solvents and de-ionized water were used routinely.

Fabrication of nanofibrous carbon microspheres: The perylene diimide derivative with four carboxylic acid groups (PDI-COOH) was synthesized following a procedure reported previously.¹ Briefly, 0.20 g of PTCDA, 0.23 g 5-aminoisophthalic acid and 1.60 g of imidazole were heated at 127 °C for 6 hours under nitrogen atmosphere. Then 20 cm³ of ethanol was poured into the hot mixture, refluxed for 6 hours and kept for overnight to precipitate out. The precipitate was filtered and washed with ethanol. The product was dried at 60 °C under vacuum oven to get 0.32 g deep red powder (yield: 88%).

To form the hydrogel microspheres, 5.0 g of span 80 was dissolved in 10 cm³ of o-xylene with 10% polystyrene (Mw 192KDa) as the oil phase. 10.0 cm³ stock solutions of PDI-COOH (40 mM) were prepared by dissolving PDI-COOH in TEA solution with a molar ratio of PDI-COOH:TEA of 1:6 (denoted as T). 0.5 cm³ of the solution and 0.5 cm³ water or 80 mM MM in water were added to a test tube, followed by addition of 26 mg GdL (4 molar equivalents). 0.5 M NaCl solution (0.1 cm³) and the aqueous precursor solution (1 cm³) were added into the oil phase (o-xylene solution, 8 cm³) dropwise with stirring using a EUROSTAR 20 digital stirrer (IKA, Germany). After that, the color of the emulsion changed, which indicated that the process of the gelation has been completed. The emulsion was washed using cyclohexane, ethanol, acetone and cyclohexane in turn.

The F-127 templating gels were formed by mixing 0.5 cm³ of PDI-COOH in TEA solution with 0.5 cm³ aqueous 80 mM MM solution containing 0.05 mg cm⁻³ F-127. GdL was subsequently added (26 mg

cm⁻³ based on the mixed solution) to initiate the gelation at room temperature. The formed microspheres was washed using cyclohexane, ethanol, acetone and cyclohexane in turn.

All the hydrogel microspheres were washed, frozen in liquid nitrogen, and then freeze-dried in a freeze-dryer (Vis Advantage) for 12 h. Finally, the as-obtained dry samples were pyrolysed in a Nabertherm furnace (model R 50/500/12) under an N₂ atmosphere at 2 °C min⁻¹ to 200 °C for 2 h, 3 °C min⁻¹ to 800 °C for 3 h to form the black product. 1.0 g dry samples could yield approximately 0.23 g of carbon materials.

Characterization: The fiber structure was observed by a Hitachi-S4800 scanning electron microscope (SEM) with an energy dispersive X-ray (EDX) microanalysis detector (INCA7200, Oxford Instrument). A small piece was cut from the monolith using a blade and then adhered to a stud using double-sided carbon tape. The non-conductive samples were coated with gold using a sputter-coater (EMITECH K550X) for 2 minutes at 25 mA before SEM imaging. The Brunauer-Emmett-Teller (BET) surface area and pore volume by N₂ sorption at 77 K were determined using a Micromeritics ASAP 2020 adsorption analyzer. Samples were degassed for 10 h at 150 °C before N₂ sorption analysis. The surface of the samples was studied on a VG ESCA LAB-220i XL X-ray photoelectron spectrometer (XPS) with an exciting source of Al. The macropore size distribution of porous materials were determined by mercury intrusion porosimetry (MIP) using a Micromeritics Autopore IV instrument. Measurements were performed on 20 mg portions of the dry materials and the pressure range was between 0.1 and 60,000 psi.

Electrochemical measurements: The working electrode was prepared by mixing an active material (85 wt%) with acetylene black (10 wt%) and poly(vinylidene difluoride) (PVDF) (5 wt%) in ethanol. The slurry was coated on a piece of nickel foam current collector (1 cm²) with pressure and dried at 100°C for 12 h. The loading of the nanofibrous carbon microspheres on Ni foam is around 1 mg cm⁻². A three-electrode cell system was used to evaluate the electrochemical performance by cyclic voltammetry (CV, CHI 660D electrochemical analyzer) at room temperature. The electrolyte used was 6 M KOH aqueous solution. A platinum foil and an AgCl/Ag electrode were used as the counter and the reference electrodes,

respectively. The capacitance value was obtained from the CV curves according to the equation: $C_{avg} = \int idV / 2(\Delta V \nu m)$, where $\int idV$ is calculated by integrating the total area in the CV plot, i is the response current density, ΔV is the potential by measuring its voltage span from the CV plot, ν is the potential sweep rate, m is the mass of active materials, the value divided by 2 because both the charge and discharge process exists in a cycle. The specific capacity from galvanostatic charge-discharge was calculated by the equation: $C_g = (I\Delta t) / (m\Delta V)$ where I is the current loaded (A), Δt is the discharge time (s), ΔV is the potential change during the discharge process, and m is the mass of active material in a single electrode (g). The Ragone plot was obtained using the galvanostatic charge-discharge results from the 3-electrode system. The energy density (E) was calculated by $E = (C\Delta V^2) / 2$ while the power density (P) was calculated by $P = (Q\Delta V) / (2t) = E/t$.

Reference

P. K. Sukul, D. Asthana, P. Mukhopadhyay, D. Summa, L. Muccioli, C. Zannoni, D. Beljonne, A. E. Rowan and S. Malik, *Chem. Commun.*, 2011, **47**, 11858-11860.

Table S1. Pore characteristics of nanofibrous carbon microspheres NCM-MF, NCM-M and NCM as measured by N₂ sorption.

Item	NCM-MF	NCM-M	NCM
BET Surface Area (m ² g ⁻¹)	427	431	303
t-Plot Micropore Area (m ² g ⁻¹)	313	234	197
t-Plot External Surface Area (m ² g ⁻¹)	114	197	106
Total pore volume of pores (m ³ g ⁻¹)	0.36	0.44	0.29
t-Plot micropore volume (m ³ g ⁻¹)	0.17	0.13	0.10
Adsorption average pore width (nm)	3.4	4.0	3.8

Table S2. The specific capacitance of different nanofibrous carbon microspheres at different scan rates.

Scan rate (mv s ⁻¹)	Capacitance (F g ⁻¹)		
	NCM	NCM-M (with MM)	NCM-MF (with MM and F-127)
2	38	153	247
5	32	142	230
10	26	136	222
20	24	129	210
50	22	120	183
100	12	109	163

Table S3. Change of specific capacitance with current density by galvanostatic charge/discharge testing for the NCM-MF electrode (the carbon microspheres prepared from MM + F-127 templating system).

Current density (A g ⁻¹)	Capacitance (F g ⁻¹)
1	284
2	256
4	229
6	214
8	198
10	189
20	156

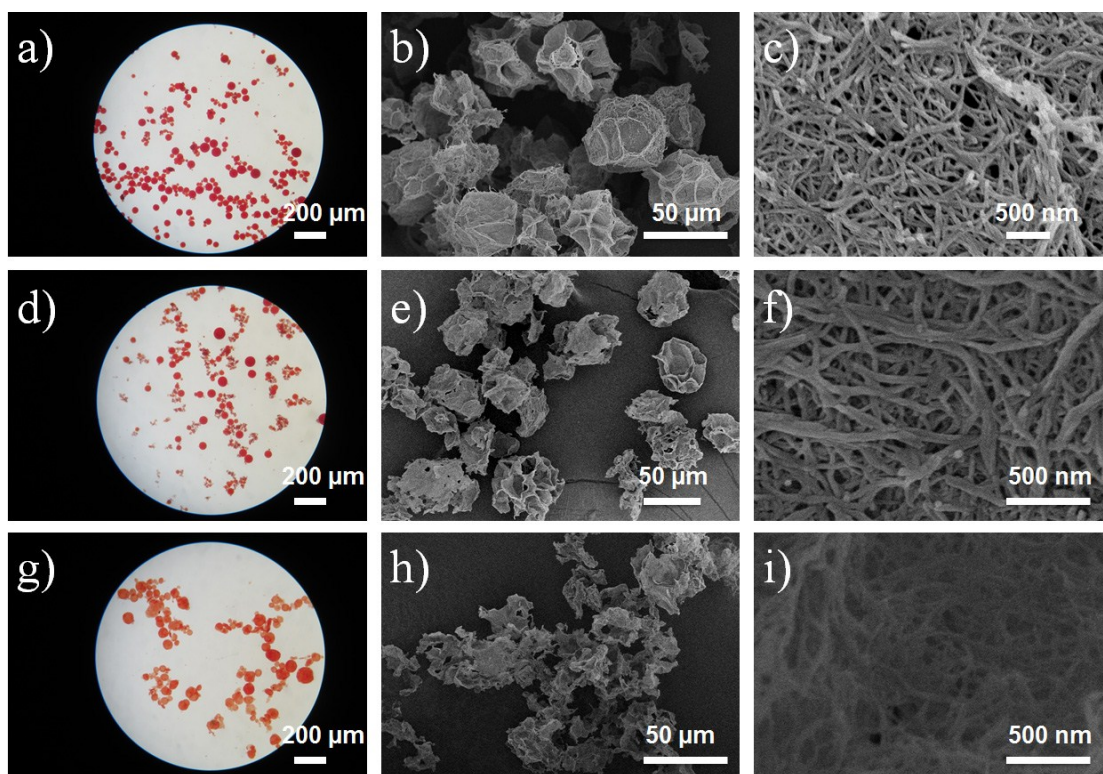


Fig. S1 Optical images and SEM images of freeze-dried hydrogel microspheres prepared from T + GdL precursor solutions at different PDI-COOH Concentrations: 20 mM (a-c), 10 mM (d-f), 5 mM (g-i) with the volume ratio of water phase/oil phase (1/4) and 50% span 80.

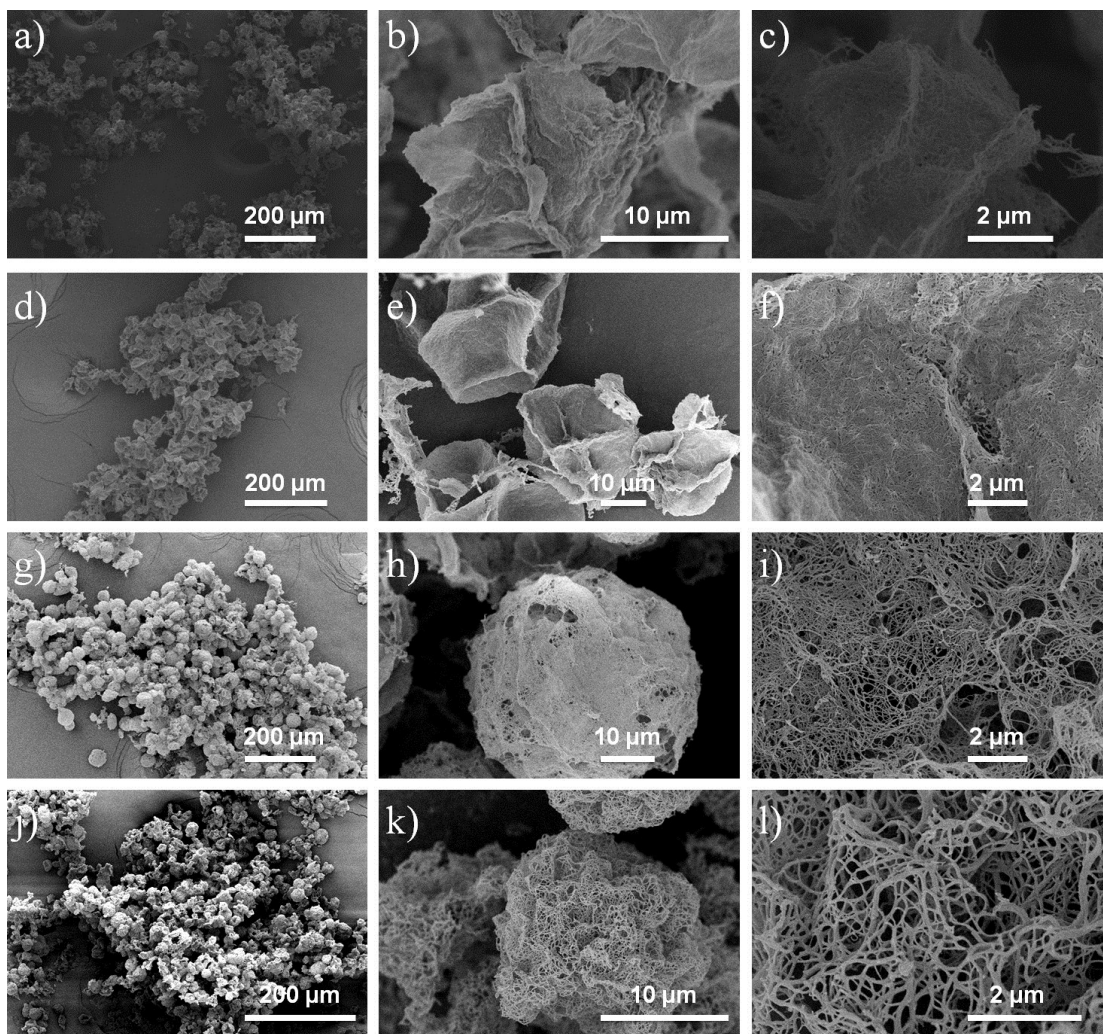


Fig. S2 SEM micrographs of freeze-dried hydrogel microspheres prepared from T + GdL using emulsions containing 5 mM PDI-COOH solution with the volume ratio of water phase/oil phase (1/4) and 50% Span 80, without any polystyrene (a-c), with polystyrene 35 (d-f), with polystyrene MW 192 (g-i), and with polystyrene MW 192 and 1.25% 0.5 M NaCl (j-l) .

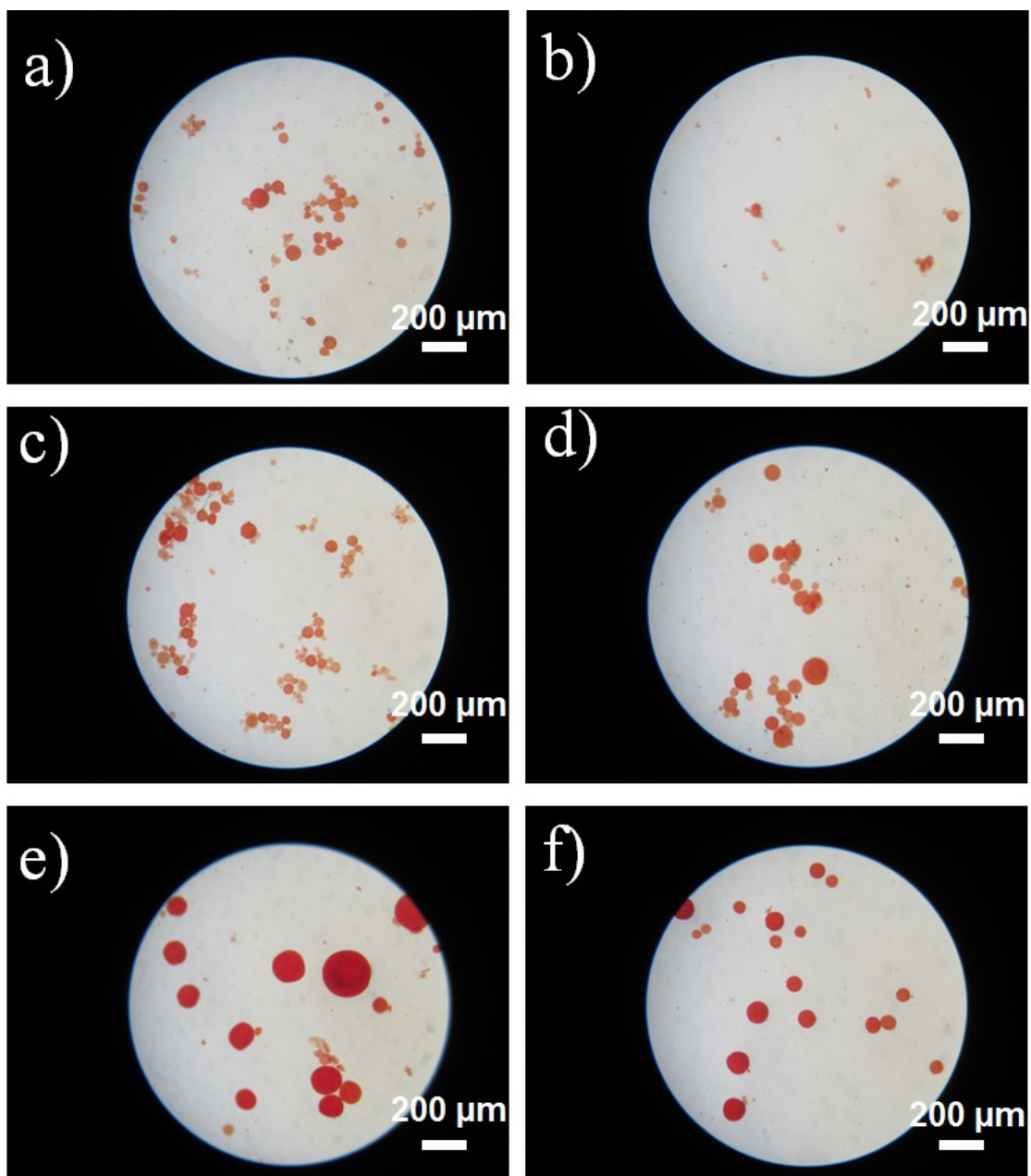


Fig. S3 Optical images of the T + GdL hydrogel microspheres formed under the same conditions (5 mM PDI-COOH solution and 10% polystyrene MW192) using different concentrations of Span 80: 5% (a), 10% (b), 20% (c), 30% (d), 40% (e), 50% (f).

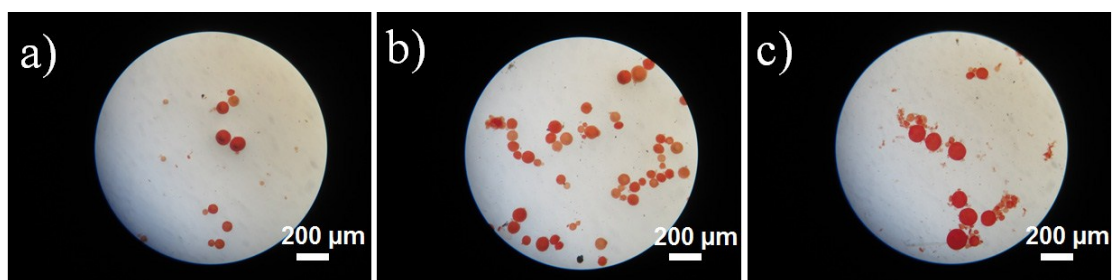


Fig. S4 Optical images of the T + GdL hydrogel microspheres formed under the same conditions (5 mM PDI-COOH solution and 50% span 80) with different concentrations of polystyrene MW 192: 5% (a), 10% (b), 15% (c).

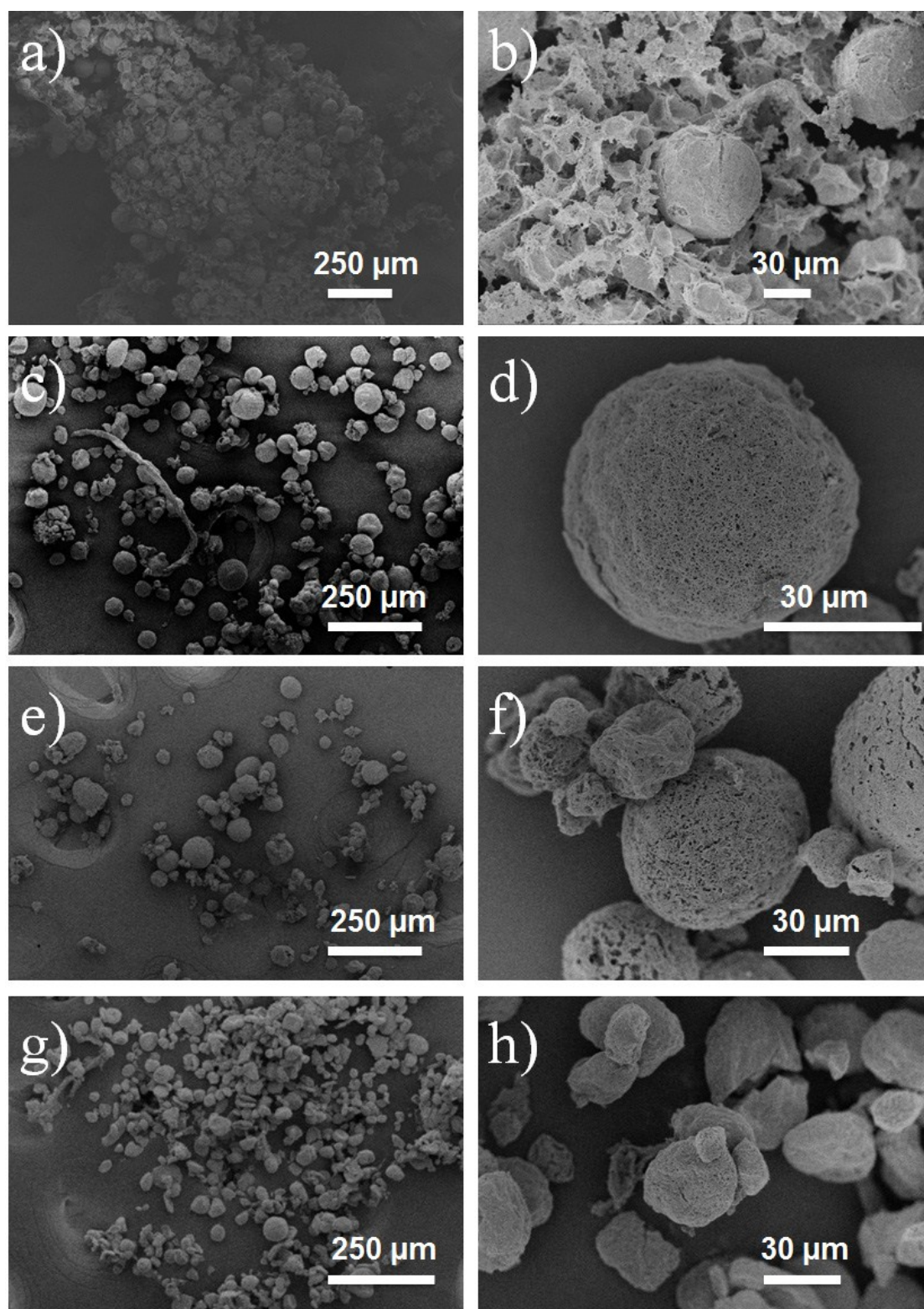


Fig. S5 SEM micrographs of freeze-dried samples T + GdL hydrogel microspheres prepared under same conditions (20 mM PDI-COOH solution, 50% span 80, 10% polystyrene 192) with different volume ratios of water/oil phase: 1/4 (a, b), 1/8 (c, d), 1/9 (e, f), 1/10 (g, h).

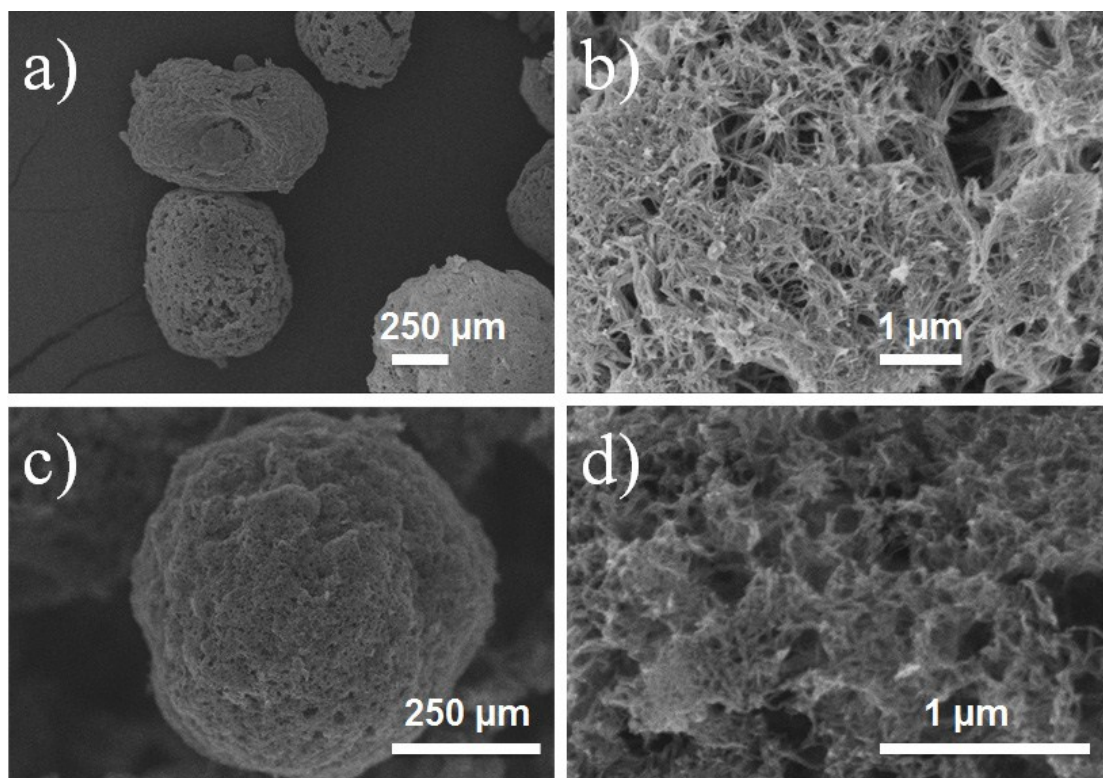


Fig. S6 SEM micrographs of freeze-dried samples (a, b) and carbonization samples (c, d) for NCM-M prepared under same conditions (20 mM PDI-COOH solution, 50% span 80, 10% polystyene 192, 1.25% 0.5 M NaCl with volume ratios of water/oil phase1/8).

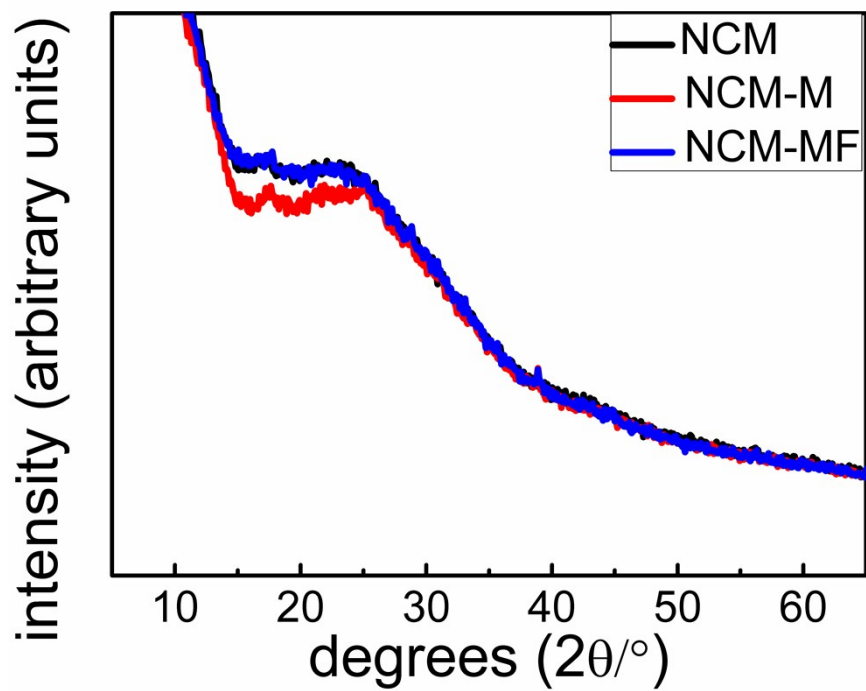


Fig. S7 PXR D patterns of carbonization samples NCM (black), NCM-M (red) and NCM-MF (blue).

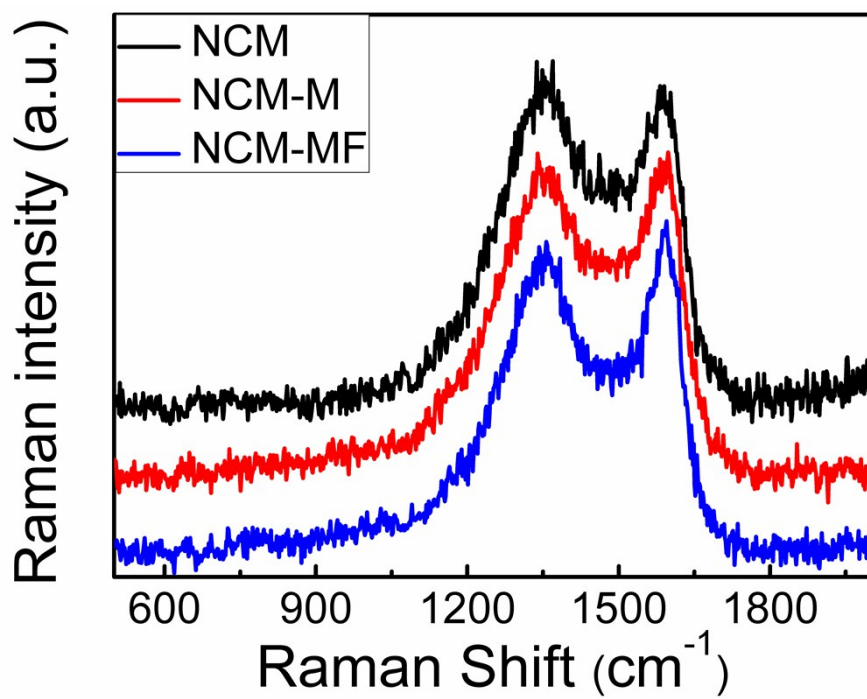


Fig. S8 Raman spectrum of carbonization samples NCM (black), NCM-M (red) and NCM-MF (blue).

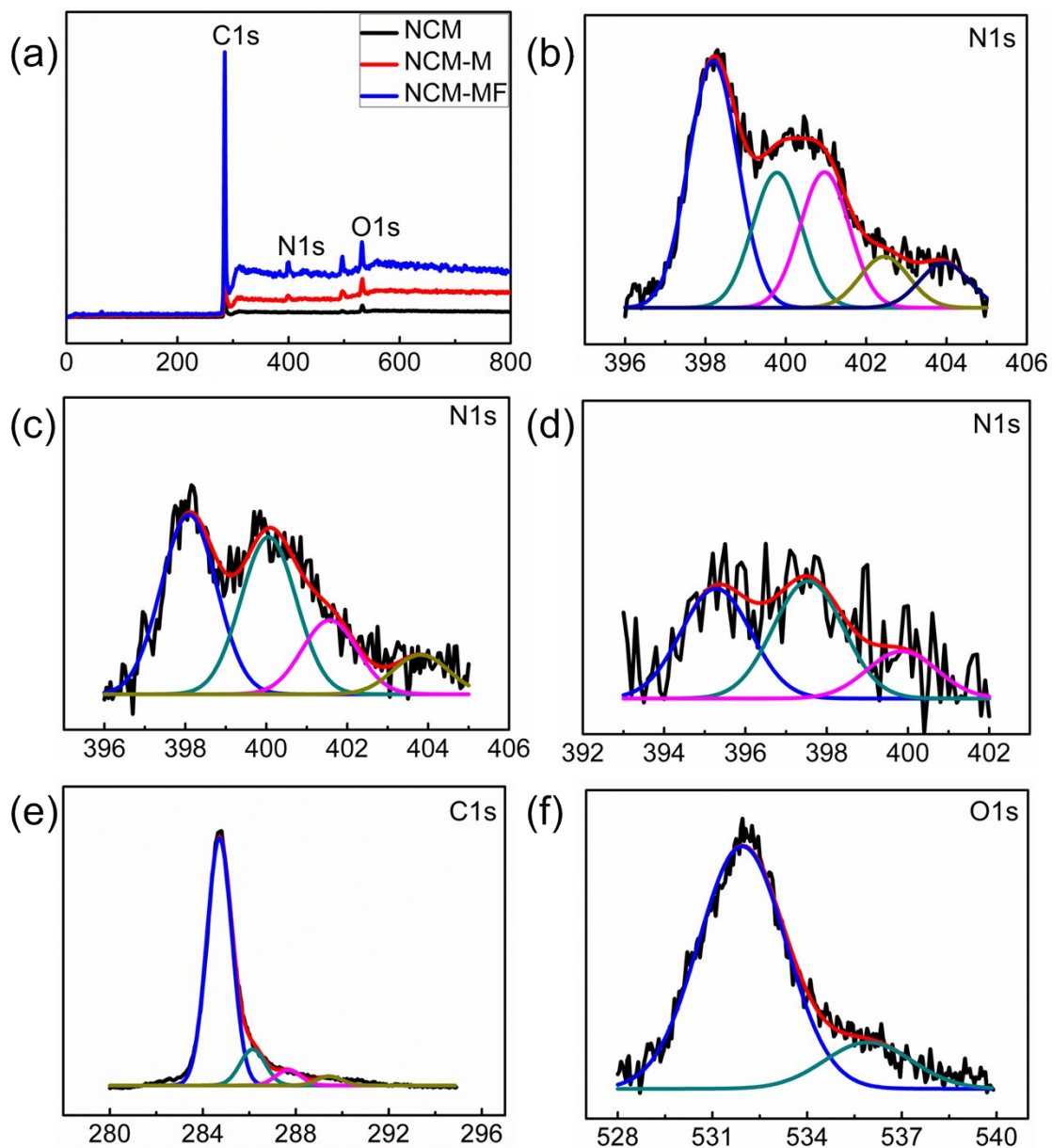


Fig. S9 XPS spectra of the calcined samples NCM (black), NCM-M (red) and NCM-MF (blue) (a), and the corresponding closer view and peak fitting for N1s of NCM-MF(b), NCM-M (c), NCM (d), and C1s (e), O1s (f) of the calcined NCM-MF.

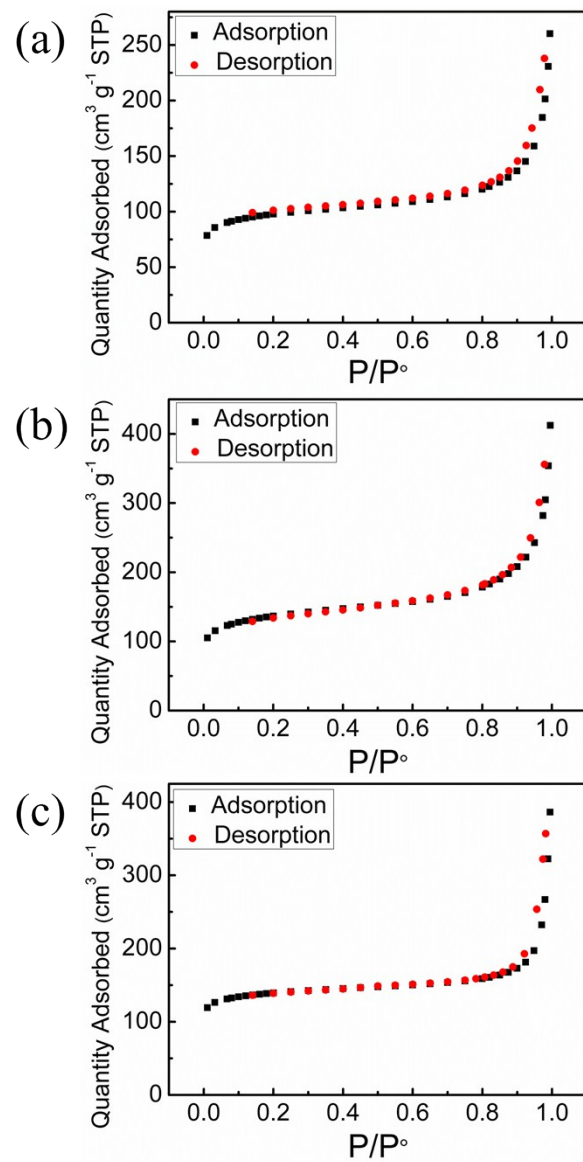


Fig. S10 N₂ gas sorption isotherms of samples (a) NCM, (b) NCM-M, and (c) NCM-MF.

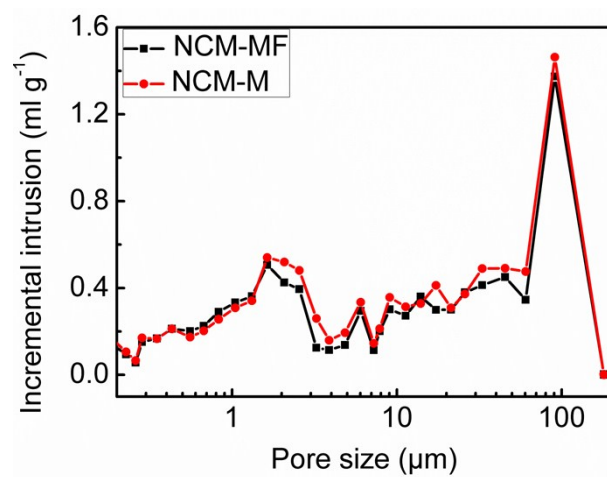


Fig. S11 Porous materials characterization of samples NCM-M and NCM-MF by Hg intrusion porosimetry.

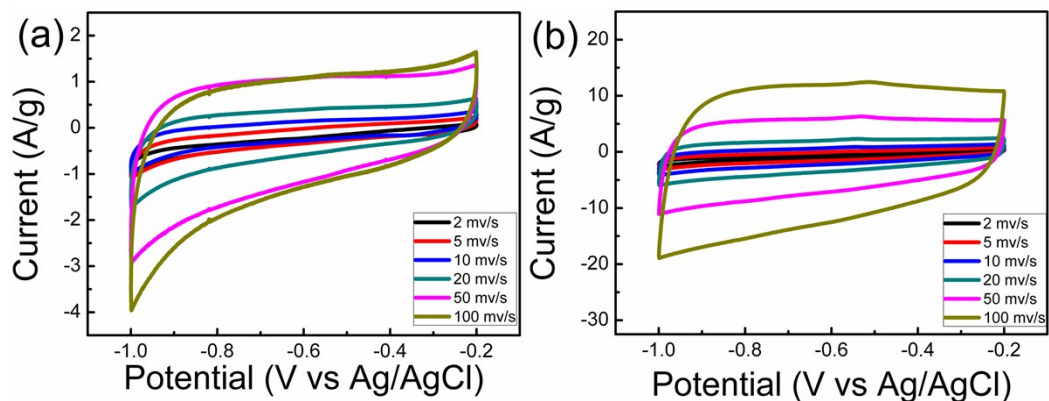


Fig. S12 Cyclic voltammograms using different scan rates of carbonization samples NCM (a) and NCM-M (b), All the tests were carried out in 6 M aqueous KOH solution in the voltage window of -1.0 V -0.2 V . The carbon microspheres slurry was coated on Ni foam as working electrode, Pt sheet as counter electrode, and Ag/AgCl electrode as reference electrode.

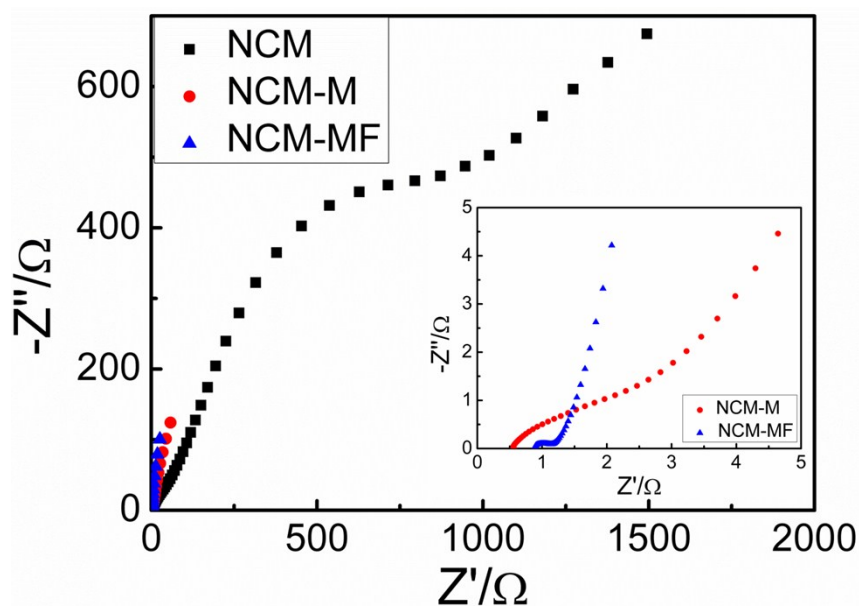


Fig. S13 Impedance spectra (Nyquist plots) of electrodes with different composites: NCM (black), NCM-M (red) and NCM-MF (blue).

The graph shows the frequency response of the electrode/electrolyte system and is a plot of the imaginary component (Z'') of the impedance against the real component (Z'). Each data point is at a different frequency with the lower left portion of the curve corresponding to the higher frequencies. The more vertical the curve corresponds to a cell more closing to an ideal capacitor. The equivalent series resistance (ESR) of the electrode can be obtained from the x intercept of the Nyquist plot. Samples NCM-M and NCM-MF show a very small ESR at about 0.6 and 0.9 Ω , respectively. The Nyquist plots of the three samples exhibited a semicircle over the high frequency range, followed by a near 45° sloped line in the low frequency region. Large semicircles observed for these electrodes are indicative of high interfacial charge-transfer resistance, which can be attributed to the poor electrical conductivity of these materials. The 45° sloped portion of the Nyquist plots is the Warburg resistance resulting from the frequency dependence of ion diffusion/transport in the electrolyte. The larger Warburg region of these electrodes indicates greater variations in ion diffusion path lengths and increased obstruction of ion movement (*Chem. Mater.* 2010, **22**, 1392 - 1401). The sample NCM shows the largest semicircle, indicating the electrode has a very large interfacial charge-transfer resistance. Compared with sample NCM-M, NCM-MF shows a relatively small semicircle, which indicates a remarkable decrease of interfacial charge-transfer resistance in the small microspheres with finer nanofibers. In addition, the very small Warburg region on the Nyquist plot of sample NCM-MF exhibits short diffusion path length of the ions in the electrolyte. This may be illuminated by the small carbon nanofiber microspheres with uniform and thin nanofiber structure.

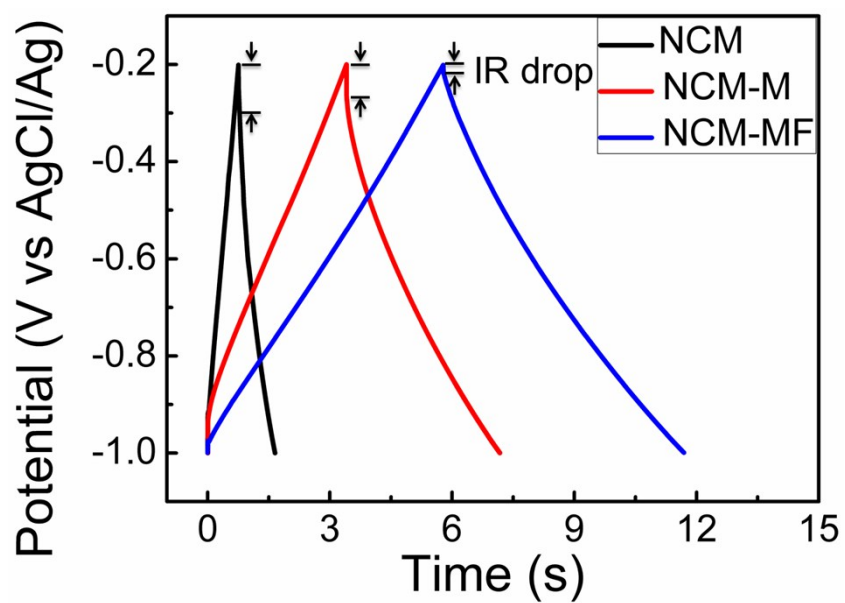


Fig. S14 Constant current charge-discharge curves of samples NCM (black), NCM-M (red), NCM-MF (blue). All the tests were carried out in 6 M aqueous KOH solution in the voltage window of -1.0 V -0.2 V . The carbon microsphere slurry was coated on Ni foam as working electrode, Pt sheet as counter electrode, and Ag/AgCl electrode as reference electrode. The current density is 20 A g^{-1} .

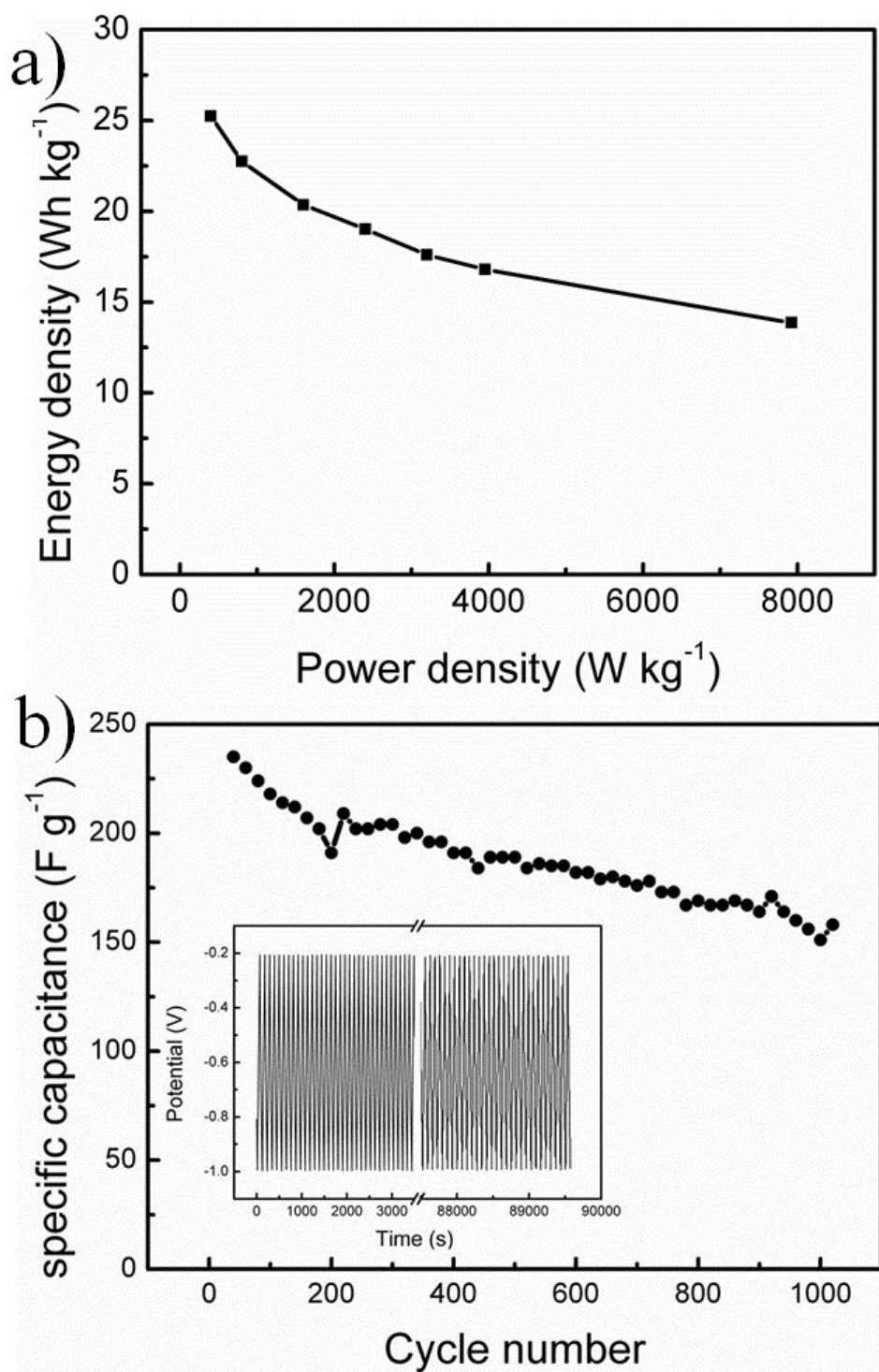


Fig. S15 (a) The Ragone plot of the prepared supercapacitor based on the electrode prepared with the carbonized NCM-MF and (b) the corresponding cycling stability test at a current density of 4 A g⁻¹.