

Electronic Supplementary Information

Easy synthesis of hollow core, bimodal mesoporous shell carbon nanospheres and their application in supercapacitor

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Experimental details

Materials

Poly(propylene oxide)-*block*-poly(ethylene oxide)-*block*-poly(propylene oxide) triblock copolymer Pluronic F127 (PEO₁₀₆PPO₇₀PEO₁₀₆) was purchased from Sigma-Aldrich Corp. Tetraethyl orthosilicate (TEOS), phenol, formaldehyde solution (37 %), NaOH, HCl, HF solution (40%) and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received without any further purification. Doubly distilled water was used in all experiments.

Synthesis

Preparation of phenol-formaldehyde (PF) resins

The resins precursors were prepared according to the literature method with some modification.^{S1} 65 mmol of phenol was melted at 41 °C and added with 6.5 mmol of 20 wt% NaOH solution. Then, 130 mmol of formaldehyde solution (37 wt%) was added and the reaction mixture was stirred at 72 °C for 1 h. after cooling to room temperature, the pH of the mixture was adjusted to neutral by using HCl solution. After water was removed by vacuum evaporation below 50 °C, the final product was dissolved in ethanol (20 wt% ethanol solutions).

Preparation of HCMSs

1.15 g of block copolymer F127, 5.0 g of the prepared PF resins and 1.04 g of TEOS were dissolved in 2.0 g ethanol and stirred for 2 h at 40 °C. Next, 0.5 g of 0.2 mol/L HCl and monodisperse silica nanospheres with an average diameter of ~360 nm prepared by the Stöber method were added in sequence. After stirring several hours for effective coating of triconstituent, the mixture was filtered under stirring and transferred into dishes. It took 5 h at room temperature to evaporate the ethanol and 24 h at 100 °C in an oven to thermopolymerize, respectively. The coating-evaporation-polymerization step was repeated again. Then, the resulted samples (called as-made samples) were scraped from the dishes and calcined in a tubular furnace at 850 °C for 2 h under N₂ to get carbon-silica/silica nanospheres core/shell composites, named as CSSNs. After CSSNs were immersed in 10 wt% HF solutions for removal of silicas, the HCMSs were obtained.

Characterization and electrochemical measurements

Nitrogen sorption isotherms were measured at 77 K with a Micromeritics ASAP 3020 analyzer (Micromeritics, USA), before measurements, the samples were degassed in a vacuum at 200 °C for at least 5 h. The Brunauer-Emmett-Teller (BET) method and the Barrett-Joyner-Halenda (BJH) model were utilized to calculate the specific surface areas (BET), the pore volumes and pore size distributions, respectively. The total pore volumes (V_t) were estimated from the adsorbed amount at a relative pressure P/P_0 of 0.994, Transmission electron microscopy (TEM) measurements were taken on a JEOL 2010 microscope (JEOL, Japan) operated at 200 KV, Scanning electron microscopy (SEM) measurements were taken on a Sirion 200 microscope (FEI, USA) operated at 5 KV. Fourier transform infrared (FT-IR) experiments were performed with EQUINOX55 (Bruker, Germany) using KBr pellets of the solid samples. Raman spectra were obtained with Labram-HR (Jobin-Yvon, France) using a He-Ne laser with an excitation wavelength of 632.8 nm, weight changes of products were monitored using SDT Q600 analyzer (TA, USA) from room temperature to 850 °C under air with a heating rate of 10 °C /min.

A composite electrode was prepared by using Nafion as adhesive. 3 mg of the HCMSs were mixed with 1 mL of ethanol solution containing 0.5 wt% Nafion, after sonication, 5.0 μL of the resulted mixture was spread onto a glassy carbon electrode (3 mm diameter) and then dried at room temperature to remove the ethanol. Cyclic voltammetry (CV) was conducted in an LK2005

electrochemical workstation (Lanlike, China) using a conventional three electrode electrochemical cell under the potential window of 0.1-0.8 V. A Pt and saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The 2.0 mol/L H₂SO₄ solution was employed as electrolyte.

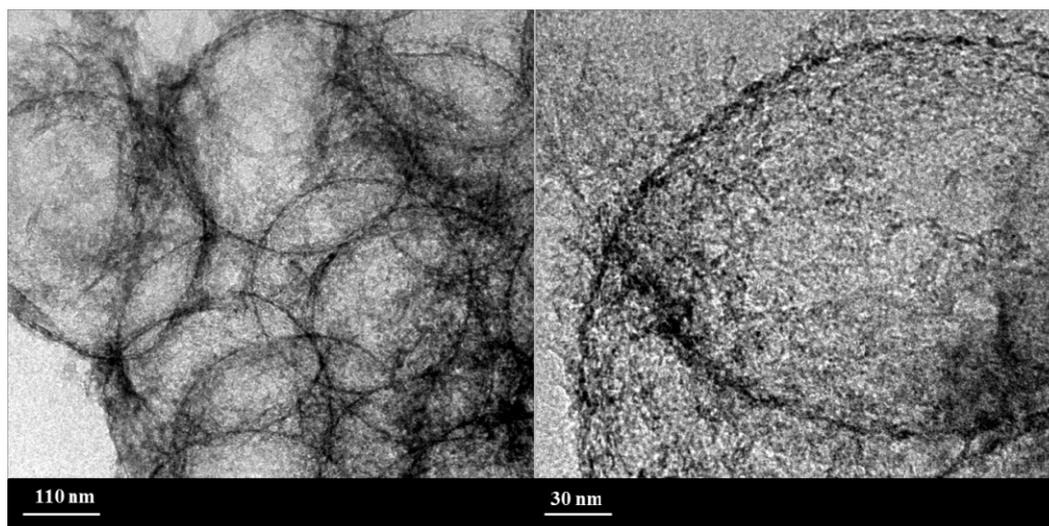


Fig. S1 TEM images of HCMSs at different magnification

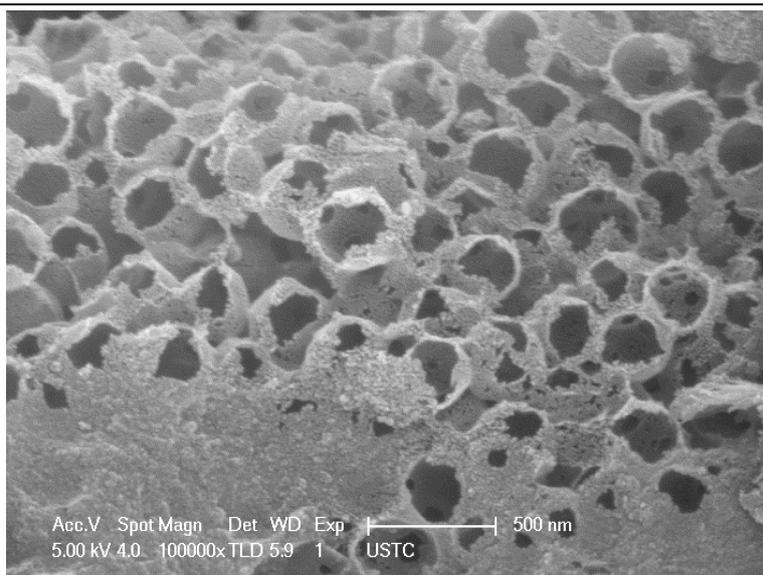


Fig. S2 SEM images of the hollow carbon samples when the Coating-Evaporation-Polymerization step was operated once.

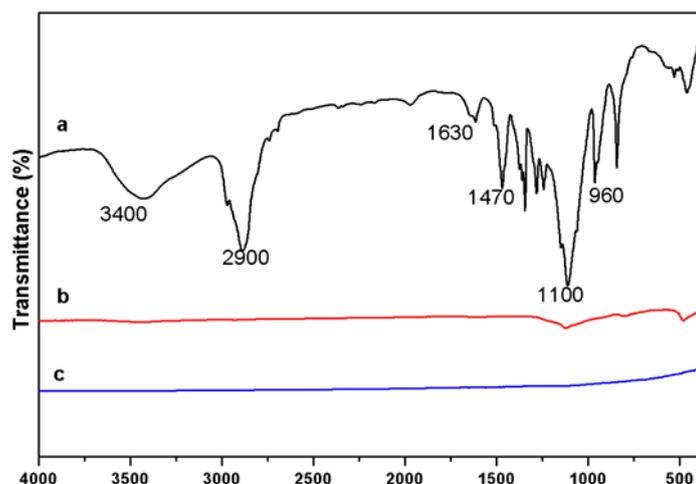


Fig. S3 FT-IR spectra of (a) as-made; (b) CSSNs and (c) HCMSs

FT-IR spectra (Fig. S3 a) of as-made nanocomposite shows the bands at $\sim 3400\text{ cm}^{-1}$ and weak bands at $\sim 1630, 1470\text{ cm}^{-1}$ attributed to the characteristic stretching vibration of phenolic resins.^{S2} The bands at around 2900 and 1100 cm^{-1} ascribed to the C-H and C-O stretching of F127^{S3, S4} and the overlap with Si-O-Si vibration.^{S5} The band at $\sim 960\text{ cm}^{-1}$ attributed to Si-OH vibration. After calcination at $850\text{ }^{\circ}\text{C}$ under nitrogen, the intensity of bands at around $\sim 3400, 2900, 1630$ and 1470 cm^{-1} decreases dramatically (Fig. S3 b), further suggesting decomposition of F127 templates and calcinations of phenolic resins, the retained band at 1100 cm^{-1} attributed to Si-O-Si indicates the coexistence of carbon and silica. After HF etching, the band of the resulted HCMSs at 1100 cm^{-1} disappears (Fig. S3 c), indicating the complete removal of silica by HF solution.

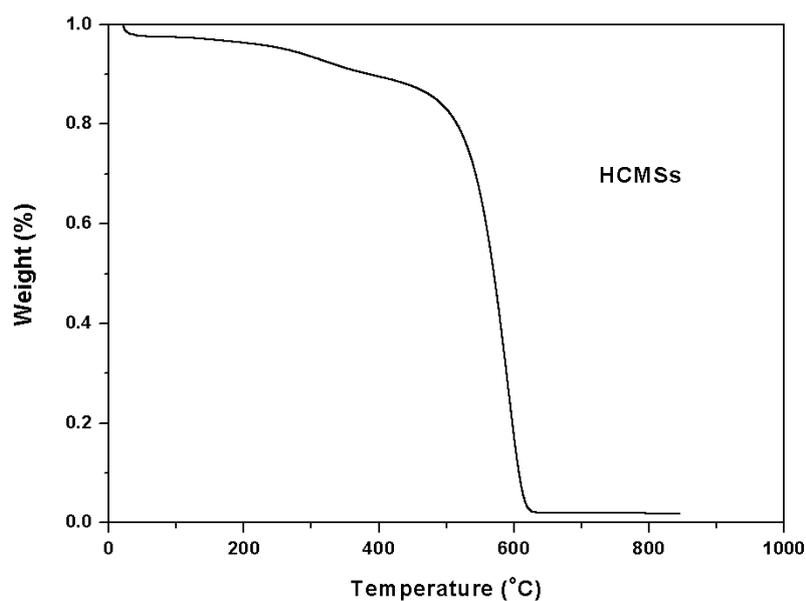


Fig. S4 Thermogravimetric (TG) curve of HCMSs recorded in air.

TG measurement shows that the HCMSs can completely combust (~98.1%) in air at temperature range from 400 to 600 °C. It indicates that silicas have been successfully removed from the CSSNs samples, which is accordance with the FT-IR result.

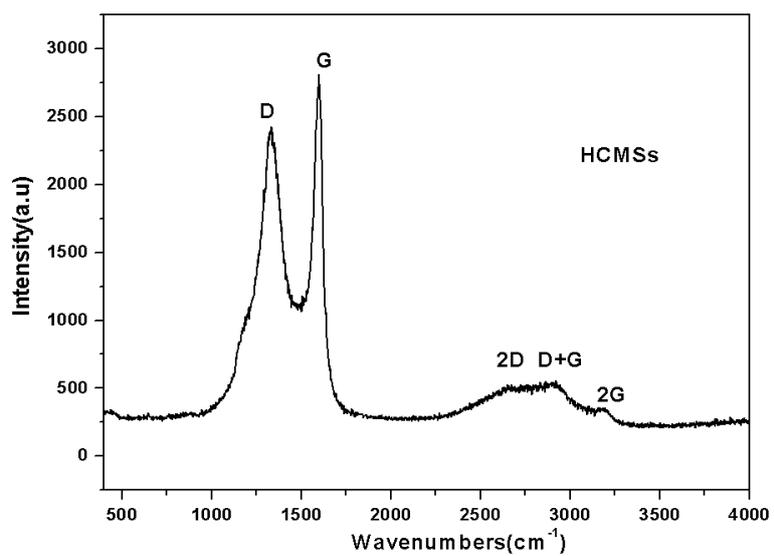


Fig. S5 Raman spectra of HCMSs

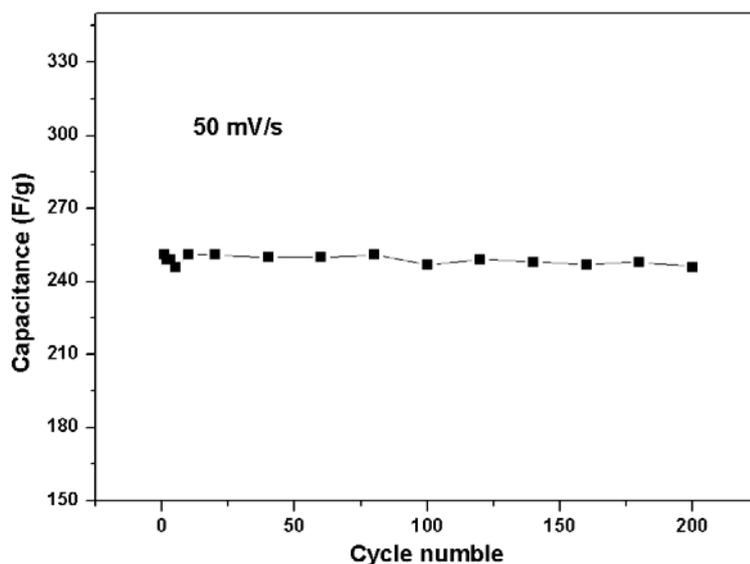


Fig. S6 The cycling performance of HCMSs capacitors, obtained at scan rate of 50 mV/s between 0.1 and 0.8 V.

References

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