

Confined pyrolysis for direct conversion of solid resin sphere into
yolk-shell carbon spheres for supercapacitor

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Experimental

Preparation of Y-CS samples.

The RF resin spheres was prepared by previous research [13]. Typically, monodisperse RF resins spheres were synthesized by using resorcinol and formaldehyde solution as precursors. Ammonia aqueous solution (NH_4OH , 0.1 mL, 25 wt%) was mixed with a solution containing absolute ethanol (EtOH, 4 mL) and deionized water (H_2O , 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/mesoporous silica nanohybrids (named RF@SiO₂-S (remain the surfactant) or RF@SiO₂-O (removing the surfactant)), 0.5 g of surfactant of Cetyltrimethyl ammonium Bromide (CTAB) was dissolved in 10 mL of H₂O, which was then added dropwise to a dispersion liquid containing 0.2 g of RF, 70 mL of H₂O and 0.8 mL of NH₃·H₂O (37 wt%). The derived mixture was then magnetically stirred for 30 min at 30 °C before 2 mL of TEOS, which was dissolved into 20 ml EtOH, was added dropwise. The mixture was kept at 30 °C for 12 h before the mesoporous silica-coated latex was harvested by centrifugation at 12000 rpm for 5 min. The precipitate was washed with copious amounts of H₂O and then dried at room temperature.

To prepare RF/silica nanohybrids (named RF@SiO₂-C) nanoparticles, 0.2 g RF nanoparticles was dispersed in 80 mL of ethanol solution containing 200 μL of aminopropyl-ethoxysilane (APTES) and stirred for 4 h. 2 mL of TEOS and 0.8 mL of

NH₃·H₂O were then introduced into the above solution under stirring and reacted at room temperature overnight. The solution became milky. The white product of RF@SiO₂-C nanoparticles was collected using centrifugation (9500 rpm) and rinsed several times with ethanol and dried at 25 °C for 10 h.

To achieve the Y-CS with different structure, the as-prepared RF@SiO₂-S, RF@SiO₂-O and RF@SiO₂-C 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. The pyrolyzed product was treated with aqueous HF solution (10 wt.%) to remove the silica and generate YCS-S, YCS-O and YCS-C, respectively.

In order to compare with the confined space, the RF sphere was directly carbonized under a nitrogen flow to obtain solid carbon spheres (denote as CS).

2.2 Characterization.

The morphology and microstructure of Y-CS samples and CS were investigated by a 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 ($P/P_0=0.97$). X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo Scientific ESCALab 250Xi system using an Al-K α radiation under a vacuum of 3×10^{-10} mbar. Thermogravimetric analysis (Pyris 1 TGA) was performed under air flow

from 20 to 800 °C at a heating rate of 10 °C min⁻¹.

2.3 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, a Pt wire and Hg/HgO was used as the counter and reference electrodes. Electrochemical performances were evaluated by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrical impedance spectroscopy (EIS) analysis. In the 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.

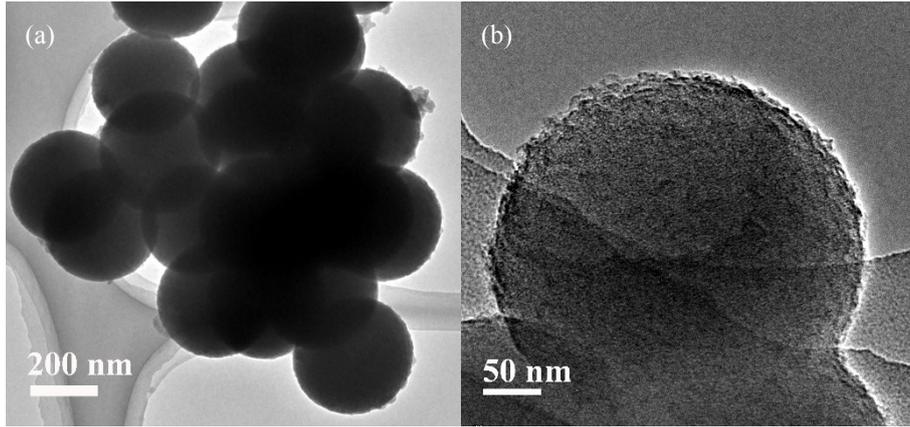


Fig. S1. TEM images of CS.

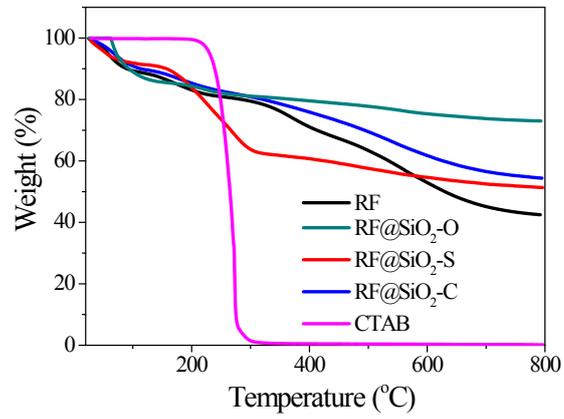


Fig. S2. TGA analysis of RF, CTAB and RF@SiO₂ samples.

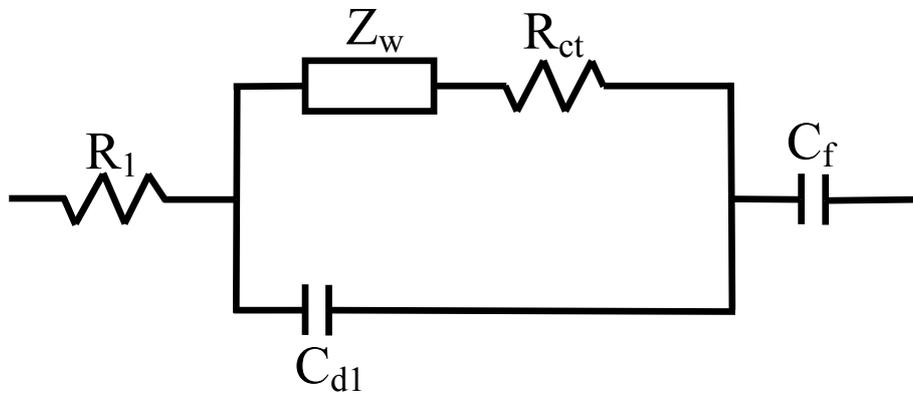


Fig. S3 The fitted equivalent circuits of the EIS.

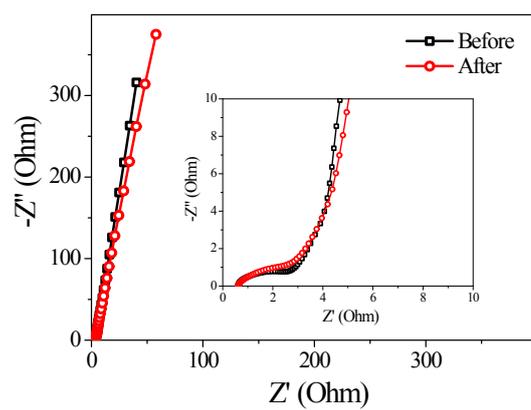


Fig. S4. Nyquist plots with fitting curves and the corresponding high frequency ranges (inset) of YCS-C in before and after the cycle test