# Supporting Information

# Controlled fabrication of uniform hollow core porous shell carbon spheres by the pyrolysis of core/shell polystyrene/cross-linked polyphosphazene composites

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#### **Experimental details**

# Materials

Styrene (Shanghai, China) was purified using an inhibitor removal column and stored -5 <sup>o</sup>C prior to use. Hexachlorocyclotriphosphazene (HCCP) (Aldrich) was recrystallized from dry hexane followed by sublimation (60 <sup>o</sup>C, 0.05 mmHg) twice before use (mp=112.5-113 <sup>o</sup>C). Triethylamine (TEA), 4,4'-sulfonyldiphenol (BPS), 2,2-azobis(isobutyronitrile) (AIBN), polyvinylpyrrolidone (PVP), ethanol were purchased from Shanghai Chemical Reagents Corp. (Shanghai, China) and used without further purification.

#### Synthesis

Preparation of PS colloid spheres

PS colloid spheres were synthesized through common dispersion polymerization. The typical synthesis is described as follows. 10 mL of styrene, 3.0 g of PVP, 0.2 g of AIBN initiator, 75 mL of ethanol and 25 mL de-ionized water were charged to a three-necked 250 mL, round-bottomed flask equipped with a reflux condenser and a mechanical stirrer (200 rpm) in a thermoregulated water bath. Nitrogen was bubbled for 1 h to remove oxygen in the reactor. Subsequently, the reactants were heated to start the polymerization and were then kept at 70  $^{\circ}$ C under a gentle reflux. The polymerization was allowed to proceed for 24 h. After completion of polymerization, latex was repeatedly washed off with ethanol and de-ionized water and dried overnight in vacuum over at 50  $^{\circ}$ C.

# Preparation of PS/PZS composite spheres

To a 150 mL round-bottomed flask were added 0.12 g of PS colloid spheres, 0.12 g of HCCP, and 0.26 g of BPS (at a mass ratio of 1 : 1 : 2.2). Subsequently, 90 mL of ethanol was added. 6 mL of TEA was injected into the solution after ultrasonic irradiation for 10 min, and the solution was

reacted at room temperature for 6 h under ultrasonic irradiation (190 W, 40 kHz). The solution was then centrifugated and washed with ethanol several times. After drying overnight at 50 <sup>o</sup>C under vacuum, core/shell PS/PZS composites were obtained.

Preparation of HCPS carbon spheres

The as-obtained PS/PZS composites were placed in a ceramic boat, heated to the 600 °C at a programmed heating ratio of 2 °C·min<sup>-1</sup> and maintained for 2 h at this temperature, then to 1000 °C at 2 °C min<sup>-1</sup> and maintained at this temperature for 3 h in an electric furnace. The whole pyrolyzing process was under protection of nitrogen with a flow rate of 10 mL·min<sup>-1</sup>. The carbonized samples were cooled to room temperature in flowing N<sub>2</sub>.

# Characterization

The microstructures of PS colloid spheres, PS/PZS composite spheres and HCPS carbon spheres were characterized by field emission scanning electron microscopy (JEOL JSM-7401F) and transmission electron microscope (JOEL JEM-100CX). The transmission electron microscope was equipped with an energy dispersive X-ray analyser (EDX). Fourier transform infrared (FT-IR) spectra were measured by using a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer in the wave number range from 4000 to 400 cm<sup>-1</sup>. Elemental analyses were performed using a Perkin Elmer 2400-II. X-ray diffraction (XRD) pattern was recorded at a Bruker D8 Advance instrument. The Raman spectrum was investigated with a French Jobin Yvon High resolution 800 UV confocal laser micro Raman spectrometer; an argon-ion laser at 514.5 nm was used. Nitrogen adsorption was performed on a Quantachrome (NOVA 1000) sorption analyzer at 77 K. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method and the micropore size distributions were determined by micropore analysis method (MP method). A Perkin Elmer TGA 7/DX thermogravimetric analyzer was used to investigate the thermal stability of the PS colloid spheres at a heating rate of 10 °C·min<sup>-1</sup> under a nitrogen atmosphere.



**Fig. S1** TGA curve of the pure PS colloid spheres. PS spheres start their decomposition at  $360 \,^{\circ}\text{C}$  and burn-off at  $450 \,^{\circ}\text{C}$ , indicating that PS spheres template in our study could be removed via carbonization at high temperature.



**Fig. S2.**  $V_a$ -t plot for the HCPS carbon spheres



**Fig. S3** Typical TEM images of three types of the HCPS carbon spheres with shell thickness of  $\sim$  120 nm, 100 nm and 70 nm, respectively. Reaction conditions: the mass ratio of PS: HCCP: BPS of (a), (b) and (c) was 1: 1.4: 3.1, 1: 1: 2.2 and 1: 0.5: 1.1, respectively. By controlling the ratio, we could easily tune the shell thickness of HCPS carbon spheres.



Fig. S4 Typical FTIR spectra of the pure PS colloid spheres, pure PZS and PS/PZS composites.

Fig. S4 shows the typical FTIR spectra of the pure PS colloid spheres, pure PZS and PS/PZS composites. Obviously, all the characteristic absorption signals for PZS could be found in the spectrum of PS/PZS composites. They are the phenylene absorption of sulfonyldiphenol unit at 1591 and 1487 cm<sup>-1</sup>, the characteristic absorption of the P=N and P–N of cyclotriphosphazene at 1187 and 880 cm<sup>-1</sup>, the characteristic absorption of O=S=O at 1293 and 1152 cm<sup>-1</sup>, and the intense absorption of Ar–O–P at 941 cm<sup>-1</sup> proving the occurrence of polymerization between comonomers HCCP and BPS. In addition, the characteristic peaks of PS (3060, 3026, 2923, 2849, 1601, 1492, 1451, 756, 698 cm<sup>-1</sup>) could also be found in the spectrum of PS/PZS composites. The results indicated that polymerization of comonomers HCCP and BPS was finished on the surfaces of PS colloid spheres, which is consistent with the SEM and TEM characterization results (Fig. 1c and 1d).

In order to characterize the chemical structure of shell layer of PS/PZS composite spheres, hollow PZS spheres were prepared by dissolution in THF solvent to remove the core materials (PS colloid spheres). The elemental analysis for hollow PZS spheres gives the following results. Calcd for  $C_{30}H_{20}ClN_3O_{10}P_3S_{2.5}$  (PZS): C, 45.4; H, 2.8; Cl, 4.5; N, 5.3; P, 11.7; S, 10.1. Found: C, 45.2; H, 2.7; Cl, 4.0; N, 5.3; P, 11.8; S, 10.0. The result is similar to our previous report.<sup>[1-3]</sup> It could be concluded that the PZS layers (shell) should have highly cross-linked structure.



**Fig. S5.** SEM (a) and TEM (b) images of the porous carbon spheres obtained through the pyrolysis of the PZS microspheres.



**Fig. S6.** Typical  $N_2$  adsorption/desorption isotherms of the porous carbon spheres obtained through the pyrolysis of the PZS microspheres.

In this study, the loop of the hysteresis (Fig. 3 in the main text) was not closed at P/P<sup>o</sup>=0.43. To verify if the "surprising" adsorption/desorption isotherm is a common phenomenon for the porous carbon particles based on polyphosphazenes, a contrast experiment was carried out. In this experiment, poly(cyclotriphosphazene-co-4,4'-sulfonyldiphenol) (PZS) microspheres were first prepared without using PS micropheres as template, keeping the other experimental conditions

fixed. Then, porous carbon spheres were obtained through the pyrolysis of the as-prepared PZS microspheres at 1000  $^{\circ}$ C.

Fig. S5 shows the SEM and TEM images of as-prepared porous carbon spheres with an average diameter of 430 nm. Fig. S6 shows the typical  $N_2$  adsorption/desorption isotherms of the porous carbon spheres obtained through the pyrolysis of the PZS microspheres. Obviously, the hysteresis loop does not close at P/P<sup>o</sup><1, which is similar to that of the HCPS carbon spheres. We speculate that the "surprising" adsorption/desorption isotherms of the porous carbon particles should be related to their pore structure resulting from the incomplete carbonization of polyphosphazene, except for the aggregation effect of porous carbon particles. The detailed reasons are under investigation.

# Reference

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