A novel method to fabricate discrete porous carbon hemispheres and their electrochemical properties as supercapacitors†

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A simple and efficient method to produce discrete, hierarchical porous carbon hemispheres (CHs) with high uniformity has been successfully developed by constructing nanoreactors and using low crosslinked poly( styrene-co-divinylbenzene) (P(St-co-DVB)) capsules as precursors. The samples are characterized by scanning and transmission electron microscopy, Fourier transform infrared and Raman spectroscopy, X-ray diffraction, and N₂ adsorption and desorption. Considering their application, the cyclic voltammetry and electrochemical impedance spectroscopy characterization are tested. The experimental results show that the achievement of discrete and perfect carbon hemispheres is dependent on the proper amount of DVB in the P(St-co-DVB) capsules, which can contribute to the ideal thickness or mechanical strength of the shells. When the amount of DVB is 35 wt% in the precursors, a high Brunauer–Emmett–Teller surface area of 676 m² g⁻¹ can be obtained for the carbon hemispheres, and the extremely large pore volume of 2.63 cm³ g⁻¹ can also be achieved at the same time. The electrochemical test shows the carbon hemispheres have a higher specific capacitance of ca. 83 F g⁻¹ at 10 mV s⁻¹, compared to other carbon materials. So this method supplies a platform to extend the fabrication field of carbon materials and supplies more chances for the application of carbon materials including carbon hemispheres that are important components and substrates for supercapacitors.

Introduction

Carbon hemispheres (CHs), as halves of hollow carbon spheres (HCSs) in structure, can provide higher surface-to-volume ratios than HCSs¹,² besides excellent chemical and thermal stabilities,³⁻⁶ and are promising materials in a variety of applications such as adsorption,⁷ lithium ion batteries,⁸,⁹ fuel cells,¹⁰ electrical double-layer capacitors (EDLCs),¹¹,¹² and catalysis.¹³,¹⁴ The success of CHs in these applications relies on the availability of discrete CHs.

In the past few years, efforts in developing better supercapacitor electrode materials have gained considerable attention. Porous carbon materials have been widely adopted as the electrode materials for EDLCs due to their high specific surface area, excellent electrical conductivity, high chemical stability and low cost.¹⁵⁻¹⁹ Generally, the highly developed surface area and porosity are necessary for carbon electrodes to obtain high specific capacitance.²⁰⁻²² The literature has exhibited that the mesopore (2–50 nm) channels facilitate the electrolyte ion diffusion in the material, a noticeable volume of micropores (< 2 nm) can provide abundant adsorbing sites for the ions.²³ Wang and co-workers discovered that the hierarchical porous texture composed of macropores, mesopores and micropores displays great potential for advanced electrochemical capacitor applications.²⁴ So it is indispensable to fabricate functional materials with hierarchical pore structure for ideal supercapacitor electrode material.

By carefully considering the above mentioned aspects for the selection of carbon materials as EDLC electrodes with high performance, the discrete CHs with hierarchical pore structure should be used as a good electrode material. The success of CHs as EDLC electrodes relies on the availability of discrete CHs with hierarchical pore structure. Up to now, hollow carbon hemispheres (HCHs) or bowl-like hollow carbon particles have been prepared by templating and inverse-emulsion methods applying organic polymer precursors (resorcinol–formaldehyde, glucose).¹,²,²⁵ These HCHs are formed due to the depression of the shell of the hollow carbon spheres or the polymer precursors. However, these HCHs are indiscrète due to particle conglutination. In fact, an inevitable tendency of all carbon nanostructures during high-temperature annealing is the condensing and sintering, so the unsatisfied conglutinated bulky materials are inclined to be obtained in the end.²⁶ Considering these limitations, synthesis

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3cp52736k
of discrete, hierarchical porous CHs with high uniformity is a great challenge.

In this paper, a simple and efficient method to produce discrete, hierarchical porous CHs with high uniformity has been successfully developed by constructing nanoreactors and using low crosslinked poly(styrene-co-divinylbenzene) (P(St-co-DVB)) capsules as precursors. This construction route to the nanoreactors for each capsule by coprecipitation of the capsules and the SiO2 particles resolves the conglutination during high-temperature annealing, and the obtained CHs are discrete. Compared with the previous precursors, the P(St-co-DVB) capsules can completely cave in and form hemispherical structures at low temperatures due to their low crosslinking density and low glass transition temperature. More importantly, template-free construction of hierarchical pore structure in CHs has been achieved, showing a high Brunauer–Emmett–Teller surface area of 676 m\(^2\) g\(^{-1}\) and an extremely large pore volume of 2.63 cm\(^3\) g\(^{-1}\). And it shows high specific capacitance of ca. 83 F g\(^{-1}\) at 10 mV s\(^{-1}\), when it is used as the electrode material in the supercapacitor.

**Experimental**

**Preparation and sulfonation of the P(St-co-DVB) capsules**

Monodisperse core@shell poly(styrene-co-divinylbenzene) spheres (CSPSs) were synthesized via the soap-free emulsion polymerization in which the crosslinking agent (DVB) had delayed addition.\(^{27,28}\) The DVB amount for the CSPSs labeled as S15, S25 and S35 was 15, 25 and 35 wt%, respectively. CCl4 was used to remove the polystyrene (PS) core due to the close solubility parameters of CCl4 (8.6) and PS (8.7–9.1). 0.24 g of CSPSs was put into CCl4 (24 mL) in a three-necked flask in a thermostated water bath of 40 °C, and the mixture was vigorously stirred at a speed of 160 rpm. 10 h later, the product was collected and purified by centrifugation and redispersion in acetone by ultrasonication for three times. Finally, the P(St-co-DVB) capsules were obtained after drying at 40 °C. The P(St-co-DVB) capsules obtained from S15, S25 and S35 were marked as H15, H25 and H35, respectively.

The fine P(St-co-DVB) capsule powder (0.3 g) was added into concentrated sulfuric acid (98%), 30 mL and the mixture formed a suspension by stirring. The suspension was heated to 40 °C and kept at this temperature for 6 h. After it was cooled down to room temperature, the product was repeatedly centrifuged and washed with a large excess of ethanol until the pH value of the solution was close to 7. Finally, a yellow fine powder (sulfonated P(St-co-DVB) capsules) was obtained after drying at 40 °C. The sulfonated P(St-co-DVB) capsules obtained from H15, H25 and H35 were respectively labeled as SH15, SH25 and SH35.

**Construction of the SiO2 nanoreactors**

0.3 g of sulfonated P(St-co-DVB) capsules and 1.5 mL of tetraethyl orthosilicate (TEOS) were put into ethanol (20 mL) in a beaker and the mixture formed a suspension by adequate ultrasonic dispersion. 2 mL of ammonia was added dropwise into the suspension and the sol–gel procedure was kept for 8 h under vigorous stirring. Then the sulfonated P(St-co-DVB) capsules–SiO2 particles composite were formed by centrifugation and drying. The cumulative SiO2 acted as a nanoreactor to provide a nanospace for the high-temperature pyrolysis of the sulfonated capsules and also as a boundary to prevent polymer–carbon conglutination during high-temperature treatment.

**Preparation of carbon hemispheres**

The as-prepared sulfonated P(St-co-DVB) capsules–SiO2 composite was heated at 3 °C min\(^{-1}\) from room temperature to 370 °C and kept for 2 h under a nitrogen flow. The temperature was then raised to 800 °C at 5 °C min\(^{-1}\), and kept for 2 h. The pyrolyzed product was treated with dilute HF solution to remove the SiO2.

The CHs obtained from SH15, SH25 and SH35 were labeled as CH15, CH25 and CH35, respectively.

**Characterization**

The morphologies and structures of the samples were investigated using an FEI Quanta 200 scanning electron microscope (SEM), an FEI Tecnai G2 20 transmission electron microscope (TEM) with an accelerating voltage of 100 kV and a JEM-2100 TEM with an accelerating voltage of 200 kV. The elemental composition of the samples was analyzed using XPS. X-ray diffraction (XRD) spectra were measured using a Bruker Optics TENSOR 27 FT-IR spectrophotometer in the wavenumber range from 4000 to 400 cm\(^{-1}\). Nitrogen adsorption–desorption measurements were performed in a Micromeritics ASAP 2020 instrument at 77 K. The micropore volume and the pore size distribution were respectively calculated by the Dubinin–Radushkevich (D–R) equation and Density Functional Theory (DFT). The total pore volume was calculated at a relative pressure \(P/P_0 = 0.99\). The capacitance performance of the samples was evaluated at room temperature in a two-electrode system. A thin film electrode of each sample was prepared according to ref. 29. A suspension of CHs with a concentration of 1.0 mg mL\(^{-1}\) was prepared by ultrasonically dispersing CHs in ethanol. The suspension (20 μL) was then dropped onto a glassy carbon disk with a diameter of 5 mm. The CHs were covered with Nafion (Dupont, 5 wt%) (5 μL) when the suspension was dried. Two electrodes were immersed into a beaker containing 1 mol L\(^{-1}\) H\(_2\)SO\(_4\) solution, with a distance of 15 mm between the centers after they were dried thoroughly in air. The cell was then connected to CHI660D electrochemical analyzer for electrochemical characterization.

**Results and discussion**

The synthesis procedure for CHs using nanoreactors is illustrated in Scheme 1. Firstly, low crosslinked P(St-co-DVB) capsules are prepared by removing PS cores of monodisperse CSPSs using CCl4. Secondly, the capsules are sulfonated using concentrated sulfuric acid. The third step, which is crucial for obtaining discrete CHs,
involves the accumulation of the SiO$_2$ particles on the capsule surface by coprecipitation of the sulfonated capsules and the SiO$_2$ particles via hydrolysis of TEOS. The cumulated SiO$_2$ particles function as a nanoreactor to provide a nanospace and also as a boundary to prevent polymer–carbon conglutination. Finally, the discrete CHs with high uniformity are obtained after pyrolysis of the sulfonated capsules–SiO$_2$ particles composite and subsequent elimination of the nanoreactor silica.

A SEM photo of the H25 sample is shown in Fig. 1a. The experimental results indicate that a large number of P(St-co-DVB) capsules with diameters of about 450 nm are prepared, and the further sulfonation does not change the size and shape of the capsules (Fig. 1b). According to the TEM photo of the sulfonated P(St-co-DVB) capsules (Fig. 1c), the strong contrast between the dark edge and pale center is evidence of its hollow nature. In order to indicate the function of the SiO$_2$ as nanoreactors, the zeta potential of the sulfonated capsules is measured in aqueous solutions with different pH values. The experimental results are shown in Fig. 1d, and it shows the surface of the sulfonated capsules is negatively charged and the absolute values of the zeta potentials are close to 30. At the same time, according to the literature, we know the hydrolyzed silica moieties are also negatively charged. So the electrostatic repulsive interaction between the negatively charged capsules and the negatively charged silica moieties cannot induce the surface coating. Thus the silica nanoreactors are successfully constructed by coprecipitation of the sulfonated capsules and the SiO$_2$ particles around the low-crosslinked P(St-co-DVB) capsules.

Fig. 2a and b show the TEM photos of the CH25–SiO$_2$ composite. Apparently SiO$_2$ supplies the necessary conditions for the P(St-co-DVB) capsules, which contributes to the formation of the carbon hemispheres (CH). It is clear that the CHs formed inside the amorphous SiO$_2$ nanoreactors. After elimination of the nanoreactor SiO$_2$ using aqueous HF solution, a large number of discrete CHs with high uniformity are obtained (Fig. 2c and d). TEM photos of the CH25 sample indicate that the CHs have thin shells whose thickness is about 10 nm (Fig. 2d and e). The high resolution phase indicates that large amounts of micropores and worm-like channels are homogeneously dispersed in the carbon matrix of the shell (Fig. 2f).

Fig. 3 shows the FT-IR spectra of the samples with 25 wt% DVB. The FT-IR spectrum of the P(St-co-DVB) capsules is indicated in Fig. 3a. The peaks between 3100 and 2800 cm$^{-1}$ are ascribed to the stretching vibrations of C–H and –CH$_2$– of the PS, and the peaks between 1500 and 1400 cm$^{-1}$ are ascribed to C–H bending vibrations. The signals at 1510 and 838 cm$^{-1}$ are assigned to $p$-disubstituted phenyl rings and the signal at 6
795 cm\(^{-1}\) is assigned to \(m\)-disubstituted phenyl rings. The signals at 1493, 1028 and 760 cm\(^{-1}\) are assigned to monosubstituted phenyl rings (i.e., styrene units).\(^{33}\) The peak at 697 cm\(^{-1}\) is also from the PS component.\(^{34}\) Fig. 3b indicates the FT-IR spectrum of the sulfonated capsules. Sulfonation of the capsules results in the appearance of broad and strong peaks at 1050–1300 cm\(^{-1}\) assigned to sulfonic acid groups (\(-\text{SO}_3\text{H}\)) and peaks at 1630–1850 cm\(^{-1}\) assigned to carbonyl groups.\(^{33}\) Specially, the characteristic bands at 673, 1172 and 1214 cm\(^{-1}\) are assigned to the derived sulfonic acid group (\(-\text{SO}_3\text{H}\)). The band at 1128 cm\(^{-1}\) is related with the sulfone group (\(-\text{SO}_2\text{H}\)).\(^{35}\) The peaks at 1172 and 1006 cm\(^{-1}\) correspond to \(S=O\) stretching vibrations. Fig. 3c shows the FT-IR spectrum of the CHs prepared by carbonizing sulfonated capsules at 800 °C. The band at 1270–1220 cm\(^{-1}\) is assigned to \(\text{CH}_2\text{–S}\) wagging vibration. This indicates that these functional sulfonic acid groups are converted to sulfur bridges between the base polymers during pyrolysis. These newly formed bridging bonds provide extra crosslinking structure and enhance their thermal stability, resulting in formation of CHs after carbonization at 800 °C instead of the complete decomposition of the capsules.

Usually the DVB amount has the decisive effect on the thickness and mechanical strength of the shell of the P(St-co-DVB) capsules,\(^{27,36}\) so the morphology of the CHs prepared using the capsules with different DVB dosages as precursors is investigated. Fig. 4 shows SEM and TEM photos of the samples with 35 wt% DVB. Fig. 4a and b show the SEM and TEM photos of the SH35 sample. The experimental results indicate that the sulfonated spherical P(St-co-DVB) capsules are monodisperse and their diameter is about 420 nm. After carbonization at 800 °C, the sulfonated spherical capsules form perfect discrete CHs with high uniformity (Fig. 4c–e). A TEM photo of the CHs reveals that these CHs have thin shells and the thickness is about 16 nm, and the diameter is about 400 nm. The high resolution phase indicates that large amounts of micropores, and worm-like channels are homogeneously also dispersed in the carbon matrix of the shell (Fig. 4f). The EDS spectrum and the elemental composition of CH35 are shown in Fig. 5. The percentage composition of the C, O, and S elements in CH35 was respectively 85.8, 12.6 and 1.6 wt%.

Fig. S1 (ESI†) shows SEM and TEM photos of the samples with 15 wt% DVB. SEM photo of H15 indicates that the capsules have mushroom-like morphology due to the thin and weak mechanical strength shell.\(^{36}\) After carbonization, the sulfonated capsules form warped and wrinkled CHs (Fig. S1c, ESI†). The sharp deformation of these CHs is attributed to the thin and weak mechanical strength-shell that cannot maintain their hemispherical shape. It is suggested that the hemispherical structure of the CHs becomes more perfect with the increase in DVB amount from 15, 25 to 35 wt%, which could be ascribed to the augmentation of mechanical strength and thickness of the CH shells.

The XRD patterns of the CH powder samples obtained from the P(St-co-DVB) capsules with different DVB amounts are...
shown in Fig. 6a. The reflection peaks, indexed with [002], [100], correspond to primitive hexagonal graphite-2H with lattice constant \( a = 2.470 \) Å and \( c = 6.724 \) Å (PDF standard cards, JCPDS 41-1487, space group \( P6_3/mmc \) [194]). Two broad and weak reflection peaks indexed with [002], [100] could be observed for CH15. The wide reflection peaks indicate that no pronounced graphitization occurs at the carbonization temperature of \( 800^\circ \)C and these CHs are amorphous graphite phase. The XRD patterns of the CH25 and CH35 samples do not exhibit features associated with the [100] direction of graphite, and only show a very broad peak associated with the [002] direction, which indicate that their structure is highly disordered, with correlation between parallel graphene units but with very little short-range order (consistent with graphene-like basic units). The broad reflection peak at about 12° might be related to the microporous structure in the carbon matrix of the CHs.

The Raman spectra of the CH samples prepared from the P(St-co-DVB) capsules with different DVB dosages are shown in Fig. 6b. The D-band around 1350 cm\(^{-1}\) is associated with the vibrations of carbon atoms with dangling bonds for the in-plane terminations of disordered graphite. The G-band around 1580 cm\(^{-1}\) is attributed to an \( E_{2g} \) mode of graphite and is related to the vibrations of \( sp^2 \)-bonded carbon atoms in a two-dimensional hexagonal lattice, such as in a graphite layer. The low ratio of \( I_D/I_G \) is characteristic of a graphite lattice with perfect two-dimensional order in the graphitic layer. The intensity ratios of \( I_D/I_G \) corresponding to CH15, CH25, and CH35 are calculated to be 0.94, 0.92, and 0.91.

In order to obtain detailed information of the surface properties for the obtained CHs, we chose CH35 as the test subject. Fig. 7a shows the nitrogen adsorption–desorption isotherm of the porous CH35 carbon material with its textural parameters summarized in Table S1 (ESI†). The typical hystERIC-type IV nitrogen sorption isotherm indicates the presence of micropores and mesopores. The nitrogen adsorbed below \( P/P_0 \) of 0.02 is due to the filling of micropores, and the uptake from \( P/P_0 \) of 0.02–0.2 may be ascribed to the presence of super-micropores and small mesopores. An obvious hysteresis appears during desorption across a large relative pressure range, which indicates the presence of mesopores with a wide pore size distribution (PSD). Two regions could be observed in the PSD curve determined by the DFT method (Fig. 7b). One region is micropores with diameters of 1.0–1.6 nm and the other is mesopores and macropores of 4–87 nm. This experimental result indicates the hierarchical pore structure of the CH35. Besides, the CH35 sample has a high BET surface area of 676 m\(^2\) g\(^{-1}\), and an extremely large pore volume of 2.63 cm\(^3\) g\(^{-1}\).

Further the supercapacitor performance of the as-prepared CH35 was estimated by the two-electrode system and the experimental results are shown in Fig. 8. All the CV curves of the CH35 present a rectangular-like shape without a very oblique angle even at a scan rate as high as 100 mV s\(^{-1}\). As the scan rate increases, the specific capacitance decreases. The specific capacitance decreases sharply at small current densities below 20 mV s\(^{-1}\), which can be ascribed to the presence of micropores. A slow decrease in the specific capacitance can be observed in the current densities range from 20 to 100 mV s\(^{-1}\), which may be associated to the mesopores. Charge–discharge behavior of the CH35 electrode.

**Fig. 6** (a) XRD patterns of the CH powder samples, (b) Raman spectra of the CH samples.

**Fig. 7** (a) Nitrogen adsorption–desorption isotherm of the CH35 sample, (b) PSD derived from the DFT method.

**Fig. 8** (a) Cyclic voltammetry (CV) curves of CH35 at the scan rates of 10, 20, 30, 50, and 100 mV s\(^{-1}\). (b) The correlation of specific capacitance with scan rates for CH35. (c) Chronopotentiometry (CP) curves of CH35 at current densities of 0.2, 0.5, and 1.0 A g\(^{-1}\). (d) Nyquist plot at open circuit potential with amplitude of 5 mV for the CH35 sample with 1 M H\(_2\)SO\(_4\) as an electrolyte.
was tested at current densities from 0.2 to 1.0 A g\(^{-1}\). The charge–discharge curves exhibit an almost triangular shape at a current density of 0.2 A g\(^{-1}\) (Fig. 8c), implying a high degree of symmetry in charge and discharge.\(^{43,44}\) It can be observed that the higher current density can rationally result in the shorter charge–discharge time. The Nyquist plot of the carbon-based electrode (Fig. 8d) shows a straight line in the low frequency region, which is close to those of ideal capacitors. Further an inconspicuous loop can be found at high frequencies, and it is related to the charge transfer resistance and/or the different contact resistances.\(^{12}\) Similar experimental phenomena can be related to the charge transfer resistance and/or the different hierarchical pore structure can promote the mass transfer/diffusion of ions into the pores effectively. So it can be concluded that this method supplies an efficient route to obtain ideal carbon hemispheres that have potential application in energy storage devices.

**Conclusions**

A method to produce discrete, hierarchical porous CHs with high uniformity has been successfully developed by constructing nanoreactors and using low crosslinked P(St-co-DVB) capsules as precursors. The capsules with different amounts of DVB all form carbon hemispheres. The hemispherical structure of CHs becomes more perfect with the increase of DVB amount, which could be ascribed to augmentation of the mechanical strength and thickness of the CH shells. The obtained CHs have a hierarchical pore structure, and a high BET surface area of 676 m\(^2\) g\(^{-1}\) and an extremely large total pore volume of 2.63 cm\(^3\) g\(^{-1}\) can be obtained for CH35. And it shows a high specific capacitance of ca. 83 F g\(^{-1}\) at 10 mV s\(^{-1}\). The CHs with a hierarchical pore structure can promote the mass transfer/diffusion of ions into the pores effectively. Thus our method supplies an efficient route to obtain ideal carbon hemispheres that have potential application in energy storage devices.

**Acknowledgements**

This work was co-supported from the National Natural Science Foundation of China (No. 51202223, 51173170, 21101141), the Natural Science Foundation of Henan (No. 092300410048 and 092102310051), and the Program for New Century Excellent Talents in Universities (NCET).

**References**

32 S. S. Cao, X. Jin, X. H. Yuan, W. W. Wu, J. Hu and W. C. Sheng, 
34 Y. Yang, Y. Chu, Y. P. Zhang, F. Y. Yang and J. L. Liu, *J. Solid 
36 Q. Y. Yang, J. F. Chen, L. B. Wang, Q. Xu and L. H. He, 
*J. Colloid Interface Sci.*, 2011, 358, 437.
37 V. V. Bhat, C. I. Contescu, N. C. Gallego and F. S. Baker, 
38 X. G. Yang, C. Li, W. Wang, B. J. Yang, S. Y. Zhang and 
B*, 2006, 110, 18424.
40 F. Xu, R. J. Cai, Q. C. Zeng, C. Zou, D. C. Wu, F. Li, X. E. Lu, 
41 Q. Li, R. R. Jiang, Y. Q. Dou, Z. X. Wu, T. Huang, D. Feng, 
J. P. Yang, A. S. Yu and D. Y. Zhao, *Carbon*, 2011, 
49, 1248.
42 G. H. Sun, J. Wang, K. X. Li, Y. Q. Li and L. J. Xie, *Electro-
43 X. L. Wu, T. Wen, H. L. Guo, S. B. Yang, X. K. Wang and 
44 S. Yang, X. L. Wu, C. Chen, H. Dong, W. Hu and X. Wang, 