Electrochemical Characteristics of Discrete, Uniform, and Monodispersed Hollow Mesoporous Carbon Spheres in Double-Layered Supercapacitors


Abstract: Core–shell-structured mesoporous silica spheres were prepared by using n-octadecyltrimethoxysilane (C18TMS) as the surfactant. Hollow mesoporous carbon spheres with controllable diameters were fabricated from core–shell-structured mesoporous silica sphere templates by chemical vapor deposition (CVD). By controlling the thickness of the silica shell, hollow carbon spheres (HCSs) with different diameters can be obtained. The use of ethylene as the carbon precursor in the CVD process produces the materials in a single step without the need to remove the surfactant. The mechanism of formation and the role played by the surfactant, C18TMS, are investigated. The materials have large potential in double-layer supercapacitors, and their electrochemical properties were determined. HCSs with thicker mesoporous shells possess a larger surface area, which in turn increases their electrochemical capacitance. The samples prepared at a lower temperature also exhibit increased capacitance as a result of the Brunauer–Emmett–Teller (BET) area and larger pore size.

Keywords: nanostructures · chemical vapor deposition · mesoporous materials · silica · supercapacitors

Introduction

Supercapacitors are very attractive power sources. They are essentially maintenance free, require a very simple charging circuit, experience no memory effect, and they possess a longer cycle life and are generally much safer than batteries.[1] More importantly, supercapacitors can be charged and discharged at high rates, and one of the most promising applications of supercapacitors is in electric vehicles. Supercapacitors have two energy-storage mechanisms: electric double-layer (EDL) capacitance and pseudocapacitance.

Currently, EDL capacitors contain activated carbon (AC) with a high surface area as the electrode materials, and the capacitance comes from the charge accumulated at the electrode/electrolyte interface. In contrast, pseudocapacitance is achieved by introducing a conducting polymer or metal oxide or surface functionalities into the electrode materials to trigger reversible Faradic redox reactions. Carbon materials such as AC usually exhibit good stability but limited EDL capacitance.[2,3] Hence, there is a need to identify more suitable carbon materials with high specific capacitance to replace AC.

Hollow spheres have attracted much attention as a result of their hollow inner space, which is useful in applications such as drug delivery,[4] catalysis,[5] electrochemistry,[6] photocatalysis,[7] adsorption,[8] environment protection,[9] energy storage,[10] and biomedical engineering.[11] Among the different kinds of hollow spheres, hollow carbon spheres (HCS) have been widely studied because of their chemical inertness, lightness, good mechanical properties, and economical sources.[12] There are several ways to synthesize HCS. Nano-casting methods are most widely used.[13] In this technique, templates are frequently employed because the resulting carbon spheres are monodispersed and the diameter can be controlled. Other methods such as chemical vapor deposition (CVD)[14–18] and hydrothermal methods[19–25] typically involve three steps including impregnation, carbonization, and template removal. Nevertheless, the template synthesis route is tedious and often expensive. Furthermore, most of the HCS obtained are not discrete and instead are aggregated. It is desirable to be able to produce monodispersed, discrete HCS by using a simple, cost-effective, and efficient technique. In our previous paper, we reported a two-step
method by which hollow mesoporous carbon spheres were synthesized from core–shell-structured silica sphere templates by using CVD without removing the hexadecyltrimethylammonium bromide (CTAB) surfactant.[24,25] By controlling the mesoporous shell thickness, HCS with different shell thicknesses were synthesized. The HCS were monodispersed and discrete, and it was postulated that CTAB served as the carbon seed in the subsequent CVD process. To further clarify whether the head [-(NH4)+Br-] or tail [-C18H33] of CTAB was the carbon seed, n-octadecyltrimethoxysilane (C18TMS) was chosen as the surfactant to synthesize the mesoporous wall of the silica spheres. Experimentally, only those having the tail structure, -C18H37, were successful in the carbonization process, which suggests that the tail was the actual carbon seed in the CVD process.

The specific capacitance of a supercapacitor is related to the specific surface area of the electrode materials and, at the same time, the specific surface area depends on the wall thickness of the HCS. In this study, three types of HCS with different wall thicknesses were synthesized and evaluated as electrode materials in supercapacitors. The objective was to elucidate the relationship between the wall thickness and specific capacitance of different types of HCS. The synthesis temperature also affects the specific capacitance, and the impact of this important parameter was also investigated. Our study revealed that a large Brunauer–Emmett–Teller (BET) area does not guarantee high specific capacitance and that only a suitable wall thickness of the HCS and the synthesis temperature yield improved specific capacitance.

**Results and Discussion**

**Synthesis and Characterization**

The synthetic process is illustrated schematically in Scheme 1. Silica spheres are first synthesized, and with the aid of the C18TMS surfactant template, the mesostructured C18TMS/silica composite is deposited on the silica spheres to produce well-dispersed core–shell mesoporous silica spheres. The materials with trapped C18TMS are placed in a horizontal quartz reactor, and after CVD and etching of the silica template by HF, hollow mesoporous carbon spheres are obtained. By varying the thickness of the mesoporous silica shell deposited on the bare silica spheres, HCS with different diameters are produced. The presence of C18TMS is very important, as it carbonizes the nanocarbon seeds that are used in the subsequent CVD process.

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**Abstract in Chinese:**

通过气相沉积法合成了一系列尺寸大小可控的介孔碳空心球，并以该碳空心球组装成双层电容器电极。实验结果表明，700度下得到的碳空心球的比容量最大。这主要归因于该条件下合成的碳球具有较大的比表面积。
the porous shell increased from 25 to 90 nm. The three kinds of core–shell silica spheres are shown in Figure 2a–c. After CVD and complete removal of the silica template, hollow mesoporous carbon spheres with different diameters were produced, as shown in Figure 2d–f. Comparing the silica spheres to the corresponding HCS, the shell thickness of the HCS increased slightly from 25 to 35 nm and from 45 to 60 nm. At 700°C, the same SiO$_2$@m-SiO$_2$-C18TMS template was used. Upon completion of the CVD reaction and removal of the silica components, HCS were also obtained. As shown in Figure 2g–i, HCS with a wall thickness of 25 nm were also synthesized, and the hollow spheres look very soft [HCS-25 (700°C)].

The N$_2$ adsorption–desorption measurement shown in Figure 3a shows that the hollow mesoporous carbon spheres have large BET specific surface areas. For HCS synthesized at 800°C with a shell thickness of 35 nm [i.e., HCS-35 (800°C)], the BET specific surface area of the hollow mesoporous HCS is 570 m$^2$ g$^{-1}$ and the total pore volume is 0.2152 cm$^3$ g$^{-1}$. By increasing the C18TMS and TEOS contents, the carbon shell thickness could be increased to 60 and 90 nm, respectively, and the BET specific surface areas of the HCS remarkably increased to 772 and 948 m$^2$ g$^{-1}$, respectively, with a total pore volume of 0.2898 and 0.3824 cm$^3$ g$^{-1}$, respectively, whereas the mean mesopore size was not affected significantly (Table 1). However, if the synthesis temperature was decreased to 700°C, the BET area of HCS-25(700°C) increased to 1230 m$^2$ g$^{-1}$. The pore size of HCS-25(700°C) is larger, and consequently, the specific surface area and total pore volume of the mesoporous carbon spheres could be easily tuned. The powder X-ray diffraction (XRD) patterns acquired from SiO$_2$@m-SiO$_2$ and SiO$_2$@m-SiO$_2$/C before and after HF treatment are depicted in Figure 3b. After CVD, SiO$_2$@m-SiO$_2$/C shows a strong and broad peak at approximately 20–30° arising from silica and pyrolytic carbon, which is indicative of the deposition of pyrolytic carbon on the SiO$_2$@m-SiO$_2$ spheres. After HF treatment, the peaks related to silica are absent, and the peak of pyrolytic carbon at 20=23° decreases significantly. The mesoporous HCS possesses a broad and strong peak at 20=20–30° arising from the SiO$_2$ and pyrolytic carbon, which is an indication of the deposition of pyrolytic carbon on the SiO$_2$@m-SiO$_2$ spheres. After HF treatment, the peaks related to the SiO$_2$ are absent, and the peak of pyrolytic carbon at 20=20–30° decreases significantly.
treatment for 24 h, the broad peak (20–30°) disappears and only two strong peaks emerge at 25.1 and 43°, and this shows that the silica was completely removed from SiO2@m-SiO2/C and that only the pyrolytic carbon structure remained in the sample. These two peaks appear at the same reciprocal spacing as (002) and (101) carbon reflections, respectively.

The bonding, order, and crystallinity of the materials were studied by Raman spectroscopy (Figure 4a). The presence of disordered graphitic materials is suggested by the two Raman modes. The peak at 1593 cm⁻¹ (G band) corresponds to the $E_g$ mode of hexagonal graphite and is related to the vibration of the sp²-hybridized carbon atoms in a graphite layer. This implies that the HCS are composed of graphitic carbon, and this is consistent with the TEM and XRD results. The D band at approximately 1359 cm⁻¹ is associated with the vibration of carbon atoms with dangling bonds in the plane with termination by disordered graphite. The TGA measurements in Figure 4b impart information about the carbon content as well as the quality of the carbon spheres, because the oxidation temperature affects the wall defects. Graphite starts to oxidize at 752°C, but the HCS were oxidized above 500°C. The HCS began to decompose at 593°C in air. As the temperature was further increased, the weight loss increased rapidly until all of the carbon spheres were exhausted at approximately 700°C. The ash content of the HCS after combustion at 900°C was 0% (w/w), which implies that the HCS have high purity.

The effects of C18TMS on the synthesis temperature of the HCS were also studied. C18TMS lowers the reaction temperature. At 800°C, CVD was successful for both kinds of silica spheres, with and without the surfactant. However, if the temperature was lowered to 700°C, the CVD reaction was successful only in the presence of the C18TMS surfactant. Lowering the temperature further to 600°C led to unsuccessful CVD, and 650°C was the lowest temperature for the production of HCS.

Figure 5a–c shows representative cyclic voltammetry (CV) traces recorded at various scanning rates from capacitors incorporating the HCS with different shell thicknesses. The current response (I) at various potentials was converted into specific capacitance ($C$) by using the equation $C = \frac{2I}{\nu m}$, in which $\nu$ is the scanning rate and $m$ is the mass of the active materials. It is well known that the capacitance of an ideal supercapacitor is independent of the charging–discharging rate and that the electrical charge stored in the capacitor is proportional to the voltage applied. Therefore, for a constant sweep rate (in mV s⁻¹), the current response remains constant in the CV measurements. An important characteristic of electrical energy storage in a capacitor is that the energy is retrievable upon discharging over the same potential range as that required to store the energy upon charging; otherwise, energy storage is limited.

Typical cyclic voltammograms were obtained from all of the HCS electrodes. The rectangular shape and humps in the CV curves indicate that the capacitive response is derived from the combination of the EDL capacitor and redox reactions. For the HCS synthesized at 800°C, the specific capacitance values are 47, 41, and 38 F g⁻¹ for HCS-35, HCS-60, and HCS-90, respectively, at a current density of 0.2 A g⁻¹. Figure 5d presents the relationship between the specific capacitance and charging–discharging current density. For a small current load, the specific capacitance of HCS-35 is higher than that of HCS-60 and HCS-90. However, in the high current load area, HCS-60 shows the highest specific capacitance. Comparing the specific surface areas to the specific capacitances of different HCS, no direct relationship between large surface area and higher specific capacitance is observed. However, higher specific capacitance is achieved only by controlling the shell thickness and pore size. As a result of diffusion, the lower mobility of the sulfate anions (effective size of ≈0.53 nm²) in the narrow pores of HCS-35 can be the main reason for the compromised performance of the materials.

Figure 6a presents the CV curves of HCS-25(700°C), and surprisingly, the specific capacitance reaches 120 F g⁻¹ at a scanning rate of 1 mV s⁻¹. This is much higher than the specific capacitance of HCS-60(800°C). The results suggest that a lower synthesis temperature increases the specific capacitance of the HCS. The improved capacitance can be ascribed to a proper pore-size distribution (PSD, Table 1) and the regular structure of HCS-25(700°C). A large pore is
better than a small one from the perspective of electrolyte transport in the mesoporous carbon structure. The calculated specific capacitance versus discharge current density relationship is also presented in Figure 6. As the temperature was decreased from 800 to 700 °C, the specific capacitance increased from 41 to 120 F g⁻¹, and the results are in agreement with the CV data acquired at the small scanning rate of 1 m V s⁻¹. HCS-25 synthesized at 700 °C also shows better behavior than commercial AC (CWZ-22, Gryfskand, Poland) with a BET surface area of 1000 m² g⁻¹ not only for a small current load but also for larger ones. These results are in agreement with the N₂ sorption–desorption data. The BET area of HCS-25 synthesized at 700 °C is larger than that of the sample produced at 800 °C. The pore-size distribution is also larger for HCS-25 synthesized at 700 °C than for the sample synthesized at 800 °C. A large BET area is favorable for storage of more electrolytes and, at the same time, larger pores enable more efficient transport of electrolytes in the mesoporous carbon. All of the above reasons lead to higher specific capacitance. Therefore, to produce HCS suitable for electrode materials in supercapacitors, not only the shell thickness and the pore size but also the synthesis temperature must be controlled. We also made a comparison between our results and the reported ones. The capacitance performance of HCS-25(700°C), 120 F g⁻¹, is higher than that of commercial AC [Norit A Supra Eur (NASE)], 80.5 F g⁻¹. However, the specific surface area of HCS-25(700°C) is only 1230 m² g⁻¹, which is lower than that of NASE (1525 m² g⁻¹), but the capacitance is higher for the latter material.[27]

Combining the results in Figures 5 and 6, for the same SiO₂@m-SiO₂-C18TMS(45 nm) template, HCS-25(700°C) behaves better than HCS-60(800°C). The better performance of HCS-25(700°C) is mainly due to the fact that the specific surface area (1230 m² g⁻¹) and pore size are larger than those of HCS-60 (800°C), because with larger pore sizes, the majority of the surface on the carbon spheres is readily accessible to the electrolyte. Consequently, a lower synthesis temperature favors higher capacitance. In addition to the EDL capacitor, minor pseudocapacitance contributes slightly to the capacitance, which comes from the carbon–oxygen (C–O) groups.[28] However, for the three kinds of HCS (800°C), a larger specific surface area does not lead to higher capacitance, which is related to the thickness of the HCS. Only a suitable wall thickness will produce higher capacitance, and hence, to prepare HCS with high capacitance, a lower synthesis temperature and suitable wall thickness are needed and must be controlled.

Conclusions

HCS are prepared by a simple SiO₂@m-SiO₂-C18TMS template method and used as electrode materials in supercapacitors. The capacitance can be effectively regulated by the morphology and structure of the HCS, which can be produced controllably with large specific surface areas in the range from 583 to 857 m² g⁻¹. The performance of HCS-25(700°C) is the best, as manifested by its high specific capacitance over a wide range of charging-discharging rates and by its high electrochemical stability, which is superior to that of AC. The large specific surface area, good mesoporosity, and regular structure are responsible for its excellent capacitance performance. A lower synthesis temperature also increased the capacitance, which results from a larger BET area. Good capacitance performance coupled with the con-
Synthesis of Core–Shell-Structured Silica Spheres (SiO2@m-SiO2-C18TMS) and their potential applications to supercapacitors. 

Convenient and cost-effective preparation of the HCS suggest their potential applications to supercapacitors.

**Experimental Section**

**Synthesis of Core–Shell-Structured Silica Spheres (SiO2@m-SiO2-C18TMS)**

In a typical synthesis of SiO2@m-SiO2-C18TMS with a shell thickness of 45 nm, a mixture of ethanol (125 mL), H2O (10 mL), the ammonium salt (5 mL), and TEOS (4 mL) was stirred for 12 h, and then different amounts of TEG/Si18TMS(0.7:1.7 v/v) were added. The mixture was stirred for 6 h and then separated by centrifugation and dried.

**Synthesis of Hollow Carbon Spheres**

The silica spheres were put in a tube furnace, in which the CVD was conducted. Ar was the carrier gas and ethylene served as the carbon source. The reaction temperature was 800 or 700 °C and the reaction time was 4 or 3 h. After CVD, a black powder was obtained, and the HCS were produced by subjecting the black powder to HF to remove the silica components.

**Characterization**

X-ray diffraction (XRD) was conducted with a Philips diffractometer by using CuKα radiation. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were performed with a FEI Tecnai F30 transmission electron microscope with a field emission gun operating at 200 kV to examine the dimensions and structural details of the HCS. The elemental compositions were determined by energy-dispersive X-ray spectrometry (EDS) in the HRTEM mode. The N2 adsorption–desorption isotherms were acquired at liquid-nitrogen temperature (77 K) with a Micromeritics ASAP 2010M instrument, and the specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method. The pore-size distribution (PSD) was determined by the Barret–Joner–Halenda (BJH) method. Raman scattering was conducted with a Renishaw micro Raman spectrometer (λ = 514 nm). Thermogravimetric analysis (TGA) was performed with 10 mg samples with a DTA-Q600 SDT TA instrument at a heating rate of 10 °C/min ramped from room temperature to 900 °C in air.

**Electrochemical Measurements**

The capacitance of the materials was determined by using a two-electrode Swagelok 1-type cell in the voltage range from 0 to 0.8 V with 1 M H2SO4 as the electrolyte. Electrodes with a diameter of 9 mm and a mass of 8–10 mg were pressed from a mixture of the active materials (80%), polyvinylidene fluoride (PVDF, 15%), and acetylene black (5%). Electrodes of a comparable mass were separated by glassy fibrous paper (Whatman GF/G) and placed between gold current collectors. The voltammetry experiments were conducted at a scanning rate from 1 to 100 mV/s, and the galvanostatic charge–discharge experiments were conducted at a current density from 0.2 to 20 A g−1 was used to estimate the specific capacitance C in farads (F) per gram of active materials on one electrode. The voltammetry results were presented as a function of C=f (E)., and VMP3 (Biologic, France) multichannel generators were used in the measurements.

Acknowledgements

The work was jointly financed by a statutory activity subsidy from the Polish Ministry of Science and Higher Education for the Faculty of Chemistry of Wroclaw University of Technology, the Polish National Science Centre within project No. 2011/03/D/ST5/06119 and the Hong Kong Research Grants Council (RGC) general research funds Nos. CityU 112510 and 112212.

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Received: January 23, 2013
Revised: April 16, 2013
Published online: August 8, 2013
Supporting Information

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asia_201300093_sm_miscellaneous_information.pdf
Table S1.

<table>
<thead>
<tr>
<th>HCS</th>
<th>DFT pore volume [cm³/g]</th>
<th>t-plot micropore volume [cm³/g]</th>
<th>t-plot micropore area [m²/g]</th>
<th>DFT PSD(nm)</th>
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<td>HCS-35</td>
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<td>1.47, 2.65</td>
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<td>0.295</td>
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<td>713</td>
<td>1.48, 3.97</td>
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<tr>
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<td>0.397</td>
<td>795</td>
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