**Three-dimensional beehive-like hierarchical porous polyacrylonitrile-based
carbons as a high performance supercapacitor electrodes**

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Abstract: Three-dimensional beehive-like hierarchical porous carbons (HPCs) have been prepared by a facile carbonization of polymethylmethacrylate (PMMA)/polyacrylonitrile (PAN) core-shell polymer particle followed by KOH activation. The all-organic porogenic core-shell precursor was synthesized by a simple and green surfactant-free emulsion polymerization. The as-obtained HPCs show favorable features for electrochemical energy storage such as high specific surface area of up to $2085\text{ m}^2\text{ g}^{-1}$, high volume of pores up to $1.89\text{ cm}^3\text{ g}^{-1}$, hierarchical porosity consisting of micro, meso, and macropores, turbostratic carbon structure, uniform pore size and rich oxygen-doping (21.20 %). The supercapacitor performance of HPCs exhibit a high specific capacitance 314 F g^{-1} at a current density of 0.5 A g^{-1} and 237 F g^{-1} at a current density of 20 A g^{-1} , ultra-high rate capability with 83% retention rate from 1 to 20 A g^{-1} and outstanding cycling stability with 96% capacitance retention after 2000 cycles. The facile, efficient and green synthesis strategy for novel HPCs from polymer sources could find use in supercapacitors, lithium ion batteries, fuel cells and sorbents.

Keywords: Surfactant-free emulsion polymerization, KOH activation, Hierarchical porous carbons, Supercapacitors

1. Introduction

Supercapacitors, also known as ultracapacitors, are of great interest as high-power electrochemical energy storage devices due to the combination of high power density with a long cycle life and wide operational temperature range[1-4]. Generally, the electrode materials are the most important factor in determining the properties of supercapacitors[5]. Up to now, a large number of carbon materials as the electrode materials for supercapacitors have been investigated, such as activated carbon[6], carbide-derived carbons[7, 8], ordered mesoporous carbons [9, 10], carbon aerogels[11], carbon nanotubes [12-15]and grapheme[16, 17]. Among these different carbon materials, porous carbon materials are the most promising candidates because of their unique properties including high surface areas, stable physicochemical properties, good conductivity, low cost and availability[4, 18].

Recently, three-dimensional (3D) hierarchical porous carbon materials, especially 3D interpenetrating macroporous networks, can lead to a significant enhancement in electrochemical charge-discharge process by improving the poor ionic transport of electrolytes in electrode materials. The macrospores serve as ion-buffering reservoirs to reduce the diffusion distance[19-21], the mesopores provide ion-transport pathways with minimized resistance[10], and the micropores enhance the electrical double layer[7]. Until now, the carbon materials with hierarchical porous structure are of great potential in the supercapacitors, to which many efforts have been devoted [16, 22-24]. 3D hierarchical ordered porous carbons have been successfully prepared

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through templating method using silica sphere nano-array as a hard template, and were used as the electrode materials of supercapacitors[22]. However, the need to use dangerous hydrofluoric acid for efficient template dissolution could result in loss of chemical functionality of heteroatom-enriched carbon. Recently, hydrothermal carbonization is an increasingly popular route for the synthesis of porous materials from natural biomass because of its low cost, low temperature, environmental benignity without the need to use toxic chemicals, and a high content of functional groups in resulting materials. Unfortunately, activated carbons derived from natural precursors usually suffer from significant variation of their properties, which could be prohibitive for automotive applications of electrical double layer capacitors. Therefore, hierarchical porous carbon materials synthesis with green process, well-controlled properties and better capacitive characteristics are an urgent task for future development of supercapacitors application.

Herein, we present the fabrication of highly porous polyacrylonitrile (PAN)-derived carbons with 3D hierarchical pore structures in which mesopores and micropores are integrated into macroporous scaffolds using all-organic polymethylmethacrylate (PMMA)/PAN core-shell polymer as precursor. The all-organic porogenic precursor was synthesized by surfactant-free emulsion polymerization, which is a simple, green process without the addition and subsequent removal of the stabilizing surfactants. The mesopores and micropores were introduced by chemical activation with potassium hydroxide and PMMA acted as the macropores generator. In contrast with current soft-templating and hard- templating methods, our

procedure allows for a uniform filling of the template with heteroatom-enriched carbon source, and does not require the introduction of non-templated carbon sources. Moreover, the organic sacrificial cores used in our approach can be removed by simple thermal decomposition without interference with the heteroatom afforded functionality of nanocarbon. The three-dimensional hierarchical pore structures in the produced PAN-derived carbons exhibit well-defined template macropores, high surface area and an abundance of heteroatom-containing functional groups. Importantly, the electrodes thereof prepared have been electrochemically characterized and the results show that high-performance electrochemical energy storage supercapacitors can be obtained.

2. Experimental

2.1 Materials synthesis

The strategy for the fabrication of 3D hierarchical porous carbon materials was schematically illustrated in Fig.1. The macroporous carbon materials (MPCs) was synthesized using PMMA/PAN core-shell polymer particles as precursor. The precursor was prepared by two-stage surfactant-free emulsion polymerization. In the first stage, PMMA particles were prepared by polymerization of 10 mL of methylmethacrylate (MMA) and 10 mg of potassium persulfate (KPS) in 300 mL distilled water. The reaction was performed at 75°C for 4 h under protection of N₂ with intensive stirring. In the second stage, 150 mL of PMMA latex, 8 mL of acrylonitrile (AN) and 10 mg of KPS were mixed with 100 mL of distilled water. The reaction was

performed at 70°C for 2 h under protection of N₂ with intensive stirring. For the synthesis of MPCs, the dried PMMA/PAN powders were subjected to oxidative stabilization by heating in the presence of air to 250°C for 2h and were carbonized under N₂ atmosphere at 800°C for 30min (the products were denoted as MPCs). To prepare hierarchical porous carbon materials (HPCs) sample, the MPCs were mixed with KOH solution (1:4 by weight) and stirred for 2h. The resulting mixture was dried at 120°C under N₂ flowing and heated to 650-850°C. The activated carbon samples were washed with 10% acetic acid solution to remove residual inorganic salts and then an excess of distilled water, and the final 3D interpenetrating hierarchical porous carbon materials (named as HPCs- temperature) were created.

2.2 Materials characterization

Scanning electron microscopy (SEM) measurement of the samples was investigated using a FEI/Philips XL30 ESEM FEG field-emission scanning electron microscopy system. Transmission electron microscopy (TEM) images were recorded on a Hitachi H-8100 TEM system with an accelerating voltage of 200 kV. Infrared spectra were collected on a VERTEX. 70 Fourier transform infrared (FTIR) spectrometer (Bruker). X-ray diffraction (XRD) patterns of samples were recorded in the 2-Theta range from 10-80° using a Bruker D8 ADVANCE diffractometer (Germany) with Cu K α radiation. The Raman spectrum were scanned from 2000 to 600 cm⁻¹ using a Renishaw Raman system model 2000 spectrometer. X-ray photoelectron spectroscopy (XPS) measurement was performed on an ESCALAB-MKII spectrometer (VG Co.,

U.K.) with Al K α X-ray radiation as the Xray source for excitation. Nitrogen adsorption and desorption isotherms were measured at 77 K and a relative pressure p/p_0 of 3.3×10^{-7} –0.995 by using a Micromeritics-ASAP-2020. Brunauer–Emmett–Teller (BET) and density functional theory tests were performed to measure the specific surface area and pore size distribution.

2.3 Electrochemical measurements

Three-electrode cell system was used to evaluate the electrochemical performance. The reference electrodes and the counter electrode were saturated Ag/AgCl and Pt, respectively. The working electrodes were prepared by coating the slurry of the active materials (80wt.%), carbon black(10wt.%), and poly(vinylidene fluoride) binder(10wt.%) dispersed in an N-methyle-2-pyrrolidone solvent onto a nickel foam substrate. The electrodes were pressed at 10 MPa for 5 min. Finally, the electrodes were dried at 80°C in vacuum for 24 h. The cyclic voltammetry (CV), galvanostatic charge/discharge and electrochemical impedance spectroscopy measurements were carried out with CHI760D electrochemical workstation. The electrochemical impedance spectroscopy was measured in the frequency ranging from 10^{-2} Hz to 10^5 Hz with voltage amplitude of 5 mV. Besides, all the tests were measured in 6 mol L⁻¹ KOH electrolyte at room temperature. The specific capacitances were calculated from the slope of the discharge curve by the following equation:

$$C = \frac{I\Delta t}{\Delta V_m}$$

, where C is the specific capacitance (F g⁻¹), I is the discharge current (A), Δt is the

discharge time (s), ΔV is the potential window (V), and m is the mass of active material (g) [25, 26].

3. Results and discussion

3.1. Morphology, porous texture and elemental composition

The PMMA-PAN core-shell polymer particle was prepared by surfactant-free emulsion polymerization, which is a simple, green process without the addition and subsequent removal of the stabilizing surfactants. SEM images (Fig. 2a) clearly demonstrate that PMMA-PAN core-shell polymer particle exhibited highly uniform spherical shape about 280 nm in diameter. PMMA-PAN powders were converted into MPCs by preoxidation and carbonization. During the preoxidation treatment, the PAN were chemically stabilized to assure preservation of PAN nanostructure upon carbonization and activation. After carbonization, the sacrificial PMMA nanoparticle cores were thermally decomposed, leading to the formation of uniformly distributed spherical macropores evident in the SEM image shown in Fig.2 (b). As observed, the pore size of macropores is ca.160 nm. The mesopores and micropores were introduced by chemical activation with potassium hydroxide. SEM images of HPCs-750 (see Fig.2c) showed the activated sample preserved interconnected uniform macropores in a 3D framework. TEM (see Fig. 2d) revealed that the HPCs-750 has a highly uniform macroporous structure. The high-resolution transmission electron microscope (HR-TEM) images (Fig. 2e) further revealed that HPCs-750 had a porous carbon structure with a large fraction of worm-like micro- and small mesopores.

The pore texture properties of HPCs were further investigated by nitrogen adsorption-desorption isotherms. As shown in Fig.3(a), the nitrogen adsorption-desorption isotherms of HPCs-750 presented a characteristic type-IV sorption isotherm with saturation at a relative pressure (p/p_0) of ca. 0.1 and a pronounced hysteresis in the p/p_0 rang 0.4-1.0, implying the presence of a large number of microporous and small mesopores[27]. The total amount of N_2 adsorbed quantity at $P/P_0 \approx 0.99$ is $\approx 956 \text{ cm}^3 \text{ g}^{-1}$, which corresponds to the total pore volume of $1.48 \text{ cm}^3 \text{ g}^{-1}$. The pore size distributions of HPCs were displayed in Fig.3 (b, c, d). It clearly revealed that the as-prepared materials possessed abundant microporous ($<2 \text{ nm}$) and mesopores (2-50 nm). As the activation temperature increases to 750°C , microporous volume has a noticeable increase. Activation at higher temperatures of 850°C leads to the noticeable broaden in the pore size distribution and increase in volume of small mesopores in the range of 2–3nm.

Table 1 summarizes the porosity characteristics of all carbon materials. The total BET specific surface area of the carbons was found to increase with activation temperature from 1014 to 1579 and to $2085 \text{ m}^2 \text{ g}^{-1}$. Such features with 3D hierarchical ordered porous would be beneficial to the ion diffusion and the contact of electrode materials with electrolyte, thus leading to high performance when they were used as the electrode materials for supercapacitors[1, 28-30].

XPS was then used to determine the surface chemical properties of as-prepared products carbon materials. The wide XPS spectra (see Fig.4a) confirmed three peaks, at 284.8, 401.3 and 533.4 eV , corresponding to C 1s, N 1s, and O 1s, respectively,

further confirming that the existence of abundant foreign atoms in HPCs-750. To understand the electronic states of the elements in as-prepared carbon materials, we paid more attention to the higher-resolution spectra (see Fig.4b, c, and d). A deconvoluted C 1s spectrum of the as-prepared material was fitted with four peaks. The main peak at 284.6 eV could be assigned to sp^2 hybridized carbon, indicating that most of C atoms are aromatic carbon. As shown in Table 3, reasonable amounts of both nitrogen and oxygen were detected in all samples. For nitrogen, a fluctuation of the content (from 2.25 to 0.95 atom %) was observed. Besides variation of the nitrogen species, the oxygen content decreased from 21.20 to 12.64 atom % as the carbonization temperature increased from 650 to 850 °C.

3.2 Structure characterization

The structure and composition of the materials were further studied by FTIR spectroscopy, XRD and Raman spectroscopy. FTIR spectrum (see Fig.5a) of PMMA/PAN core-shell particles showed the absorption band at 2244 cm^{-1} corresponding to the $C\equiv N$ stretching vibration for PAN and 1725 cm^{-1} corresponding to the $C=O$ stretching vibration for PMMA. Moreover, the appearance of the $C=C$ stretching vibration absorption band at $1580\text{-}1650\text{ cm}^{-1}$ demonstrated the aromatization during the carbonization and activation process[5]. These features would be propitious to improve the electronic conductivity of the as-prepared materials [5, 29]. Fig.5 (b) shows the XRD pattern of the carbonized and activated samples. The MPCs exhibited two characteristic peaks at $\sim 25^\circ$ and $\sim 43^\circ$, which correspond to the (002) and (100)

planes of graphite , respectively [31, 32]. However, the XRD pattern of the HPCs-750 showed the relatively broad and low intensity, which indicated that the as-prepared materials possessed a low degree of graphitization [33]. The Raman spectrum displayed two broad bands centered at 1350 cm^{-1} (D band) and 1584 cm^{-1} (G band) [34], indicating the 3D carbon materials appeared a high degree of structural disorder (see Fig.5c) [33, 35].

This kind of porous carbon material has several advantages. First, a high surface area is benefit to form considerable electric double layers. Second, the special structural characteristics demonstrate multiple advantages for supercapacitor applications, including hierarchical porous to facilitate ion transport, a turbostratic carbon structure to improve electrical conductivity and uniform pore size to optimize charge storage. Third, enriched oxygen and nitrogen surface functional groups to improve wettability as well as provide extra pseudo-capacitance. Fourth, surfactant-free emulsion polymerization followed by KOH activation is a green and low-cost synthesis process of the porous carbon materials.

3.3 Electrochemical characterizations

Activation temperature has an important influence on the electrochemical behavior. Prior to using the products as the electrode materials for supercapacitors, we first optimized the activation temperatures. Fig.6 (a, b) shows the CV curves at 5 mV s^{-1} and galvanostatic charge/discharge at 1 A g^{-1} of the samples at different activation temperatures. The value based on the mass load of an electrode were 216 F g^{-1} , 287 F g^{-1} and 247 F g^{-1}

g^{-1} for HPCs-650, HPCs-750 and HPCs-850, respectively. The Nyquist plots (see Fig. 6c) of all samples exhibit the typical features of the porous electrodes with a relatively short 45° Warburg region and an almost vertical line at low frequencies, which are more obvious as the activation temperature increases. In the high- to mid-frequency region, the intercept of the semicircle with the real axis corresponds to the interfacial charge transfer resistance (R_{ct}), indicating the excellent operation rate of the capacitor, responding to the resistance of $\sim 1.68 \ \Omega$, $\sim 1.30 \ \Omega$ and $\sim 1.25 \ \Omega$ for HPCs-650, HPCs-750 and HPCs-850, respectively. We clearly see that R_{ct} is evidently the lowest in the sample activated at the highest temperature, likely due to the wider pores. A short real axis intercept in the high-frequency region for all the plots indicates a low equivalent serial internal resistance (R_s , $\sim 0.4 \ \Omega$) included material resistance (electrode materials and electrolyte) and contact resistance. The equivalent circuit model is displayed in the inset of Fig. 6c.

Generally, the sample with larger surface area exhibited higher performance [36, 37]. It could explain why the specific capacitance of HPCs-750 (with a surface area of $1579 \text{ m}^2 \text{ g}^{-1}$) higher than of HPCs-650 (with a surface area of $1014 \text{ m}^2 \text{ g}^{-1}$). Besides, the reason why HPCs-850 (with a surface area of $2085 \text{ m}^2 \text{ g}^{-1}$) has lower specific capacitance than that of HPCs-750 may be ascribed to the broadening of the pore size distribution and the reduction of foreign atoms with the increase of activation temperature. The increase in capacitance is relatively limited because not all pores in the carbon materials are electrochemically accessible to form the electrical double-layer when they are immersed in electrolytes. Generally, narrowing pore size

distribution leads to an increase in capacitance due to the increase in surface area of regular pore distributions vs. broad distribution of pores [38, 39]. As observed, HPCs-750 has a narrower pore size distribution (< 2 nm) and larger specific capacitance than HPCs-850, which contained small mesopores in the range of 2–3 nm (Fig. 3c,d). Besides, research has shown that elemental nitrogen and oxygen would considerably improve the wettability of electrode materials with electrolytes, as well as introduce large additional pseudo-capacitance through the faradic reactions at the electrode interfaces [29, 40, 41]. XPS revealed that HPCs-750 contained a larger amount of oxygen and nitrogen elemental than HPCs-850 (see Table2).

We further investigated the electrochemical properties of HPCs-750 in details. Fig.7 shows the electrochemical performance analyzed through CV, galvanostatic charge/discharge and electrochemical impedance spectroscopy. Fig 7(a) presents the CV curves of HPCs-750 to evaluate the influence of the pore structure parameters on the ion transport behaviors. The CV profiles were obtained at different scan rates from 5 to 100 mV s^{-1} . For an ideal double-layer capacitor or supercapacitor where the kinetic processes of the ion transfer are not limited. It will be a rectangular-shaped curve of current versus voltage if the responding current keeps a constant at a certain scan rate in the CV measurements[42]. All CV curves of HPCs-750 presents a rectangular-like shape, indicating a near-ideal capacitive behavior with good rate performance. Additionally, the curves show an asymmetric shape with a small hump in the range of -0.7 – -0.6 V, characteristic of Faradaic pseudo-capacitance due to redox reactions, and which is ascribed to the N and O functional groups (see below). The

following redox reactions involving N and O are possible, among others [43,44],

where $>\text{C}$ stands for the carbon network. To further investigate the relationship between the functional groups and pseudocapacitance, we paid more attention to the higher-resolution N1s and O1s spectra. The N1s spectra (Fig. S1) can be deconvoluted into three peaks located at ~ 402.2 , ~ 400.3 and ~ 398.5 eV, which are assigned to quaternary pyridinic nitrogen (N-Q), pyrrolic/ pyridine (N-5), and pyridinic (N-6), respectively[45,46]. N6 or N5 nitrogen at the edges of the graphitic layers is mainly responsible of the pseudocapacitance, unlike the N-Q quaternary nitrogen located inside the carbon sheets [43,47]. As shown in Table S1, N6+N5 functional groups were clearly dominant (78 %) and so we can assume that N species present accounted for the observed pseudocapacitance. The high-resolution O1s spectra shown in Fig. S2 clearly exhibit the presence of several oxygen-based groups including C=O quinone type groups (O-I) ($\sim 530.7.4$ eV), C-OH phenol groups and/ or C-O-C ether groups (O-II) (~ 532.2 eV), and chemisorbed oxygen (COOH carboxylic groups) and/or water (O-III) (~ 533.6 eV)[43].

Fig.7 (b, c) shows the charge/discharge curves of HPCs-750 with a series of current density from 0.5 to 20 A g⁻¹. They show good symmetry and linear slopes, even at

large current densities of 20 A g^{-1} , which is in accordance with the performance of the electrical double-layer capacitors. Fig. 7d summarizes the effect of the increasing current loads (from 0.5 A g^{-1} to 20 A g^{-1}) in galvanostatic charge–discharge tests on the specific capacitance. Sample HPCs-750 exhibit ultra-high rate capability with 83% retention rate from 1 to 20 A g^{-1} .

In order to confirm the performance durability of the as-prepared HPCs-750, galvanostatic charge-discharge tests at the constant current density of 5 A g^{-1} up to 2000 cycles were carried out (see Fig.8). Remarkably, the as-prepared carbon materials hold the high specific capacitance retention of 96% even after 2000 cycles.

4. Conclusions

In summary, we have proposed a green, facile and efficient strategy to prepare 3D hierarchical pore structure carbons using PMMA-PAN core-shell polymer particles as precursors followed by carbonization and activation. The as-obtained HPCs possess a 3D architecture with mesopores and micropores integrated into macroporous scaffolds, have a large surface area ($1014\text{--}2085 \text{ m}^2 \text{ g}^{-1}$) and high-level of oxygen containing groups (12.46–21.2%). These unique properties have favourable multiple synergistic effects, beneficial for excellent supercapacitor performance. Importantly, when used as the electrode materials for supercapacitors, the as-prepared carbon materials have exhibited excellent electro-chemical properties with high specific capacitance of 314 F g^{-1} at a current density of 0.5 A g^{-1} and ultra-high rate capability with 83% retention rate from 1 to 20 A g^{-1} . Concurrently, no significant changes in the specific

capacitances were observed during 2000 charge-discharge cycles. Accordingly, this porous carbon could find use in the high-performance supercapacitors.

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Table1. Porosity properties of HPCs activated at various temperature.

Sample	HPCs-650	HPCs-750	HPCs-850
$S_{\text{BET}}(\text{m}^2 \text{g}^{-1})$	1014	1579	2085
$V_{\text{total}}^1(\text{cm}^3 \text{g}^{-1})$	0.90	1.48	1.89

1) Total pore volume measure at $p/p_0=0.995$.

Table 2. The atom ratio of the elements by XPS peak analysis.

Element	HPCs-650	HPCs-750	HPCs-850
C (Atom %)	76.55	82.93	86.41
N (Atom %)	2.25	1.62	0.95
O (Atom %)	21.20	15.45	12.64

Table S1: Contributions to N1s bands in XPS patterns of HCNs-750 materials

Binding energy (eV) and area of the peak (%)			
	Pyridinic (N-6)	Pyrrolic (N-5) or pyridonic	Quaternary N-Q
HCNs-750	398.5	400.3	402.2
	(21.8)	(56.2)	(22.0)

Table S2: Contributions to O1s bands in XPS patterns of HCNs-750 materials

Binding energy (eV) and area of the peak (%)			
	O- I	O-II	O- IV
HCNs-750	530.7	532.2	533.6
	(24.1)	(54.1)	(21.8)

Fig.1

Fig.2

Fig.3

Fig.4

Fig.5

Fig.6

Fig.7

Fig.8

Fig.S1

Fig.S2