Short communication

Facile synthesis of bimodal nanoporous carbons by templating selective Swelling-induced mesoporous block copolymers

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HIGHLIGHTS

- Hierarchical nanoporous carbons with mesopores and micropores were synthesized.
- Mesoporous block copolymers were utilized as the synthesized templates.
- A capacitance of 165 F/g was maintained at 5 A/g after 10,000 cycles.
- Outstanding performances are attributed to the hierarchical nanoporous structures.
- The fast ion transport pathway and low resistance of charge diffusion are obtained.

GRAPHICAL ABSTRACT

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ABSTRACT

There is a strong need for simple and efficient strategies to produce nanoporous carbons with hierarchical porosities for a number of applications such as supercapacitors. Here we demonstrate the ease preparation of nanoporous carbons with both microscale and mesoscale porosities by infiltrating oligomeric phenol–formaldehyde resols into mesoporous block copolymer (BCP) templates followed by thermopolymerization and carbonization. The mesoporous polymeric templates are produced by an extremely simple and highly flexible selective swelling method which involves only the immersion of the BCP film into hot ethanol for a few hours and the subsequent air drying of the BCP films. The produced carbons exhibit mesoporous structures with thin pore walls containing micropores, implying a hierarchical porosity of the porous carbons. Such hierarchically porous carbons work as supercapacitors exhibiting a capacitance as high as 173 F/g at 1 A/g. Additionally, an excellent high-rate and steady capacitance of 165 F/g at 5 A/g is maintained after 10,000 cycles. The excellent performances are originated from the fast ion transport pathways and the low resistance of charge diffusion enabled by the hierarchical structures. This work suggests a new path to synthesize nanoporous carbons with hierarchical porosities which are expected to find more applications including but not limited to supercapacitors.

1. Introduction

Supercapacitors, also known as electrochemical capacitors, have been well developed as promising candidates for electrochemical energy storage due to their high power density, superior lifetime and rapid charge–discharge capability [1–3]. Owing to the
merits of low cost, excellent electrical conductivity and chemical inertness, carbon-based electrode materials, for instance, carbon fibers [4], graphene networks [5], and carbon nanotubes [6], have been widely utilized to fabricate supercapacitors. Such carbon-based supercapacitors rely on the electrochemical double-layer capacitance (EDLC), in which the energy charge and release can be achieved by the charge separation at the electrode–electrolyte interface [7]. Therefore, the capacitance of the carbon-based supercapacitor is greatly affected by the specific surface areas of electrode materials [8]. Furthermore, the specific surface area of carbon materials is mainly contributed by micropores [9]. However, the tortuous nature of micropores in carbon monoliths hinders the transport of ions and is liable to lead to high resistance, resulting in poor performances of the supercapacitors [8].

Nanostructured carbons with hierarchical porosities are then proposed to improve the ion transport by shortening micropore pathways via producing mesopores in microporous carbons where micropores are drilled in the mesopore walls [10]. Such porous carbons possess the rapid mass/charge transport due to the interconnected structures and hierarchical porosities [11]. Typically, such porous carbons are prepared by the carbonization of biosourced precursors, which suffer from ill-defined porosities and require an additional time-consuming activation treatment [12]. Alternatively, template-assisted synthesis has been proved to be one of the most efficient methods to synthesize hierarchically porous carbons to meet the needs of supercapacitors [13,14]. Because the carbon replicas are faithfully endowed with the reverse pore geometries of templates, it is much easier to control pore sizes and pore shapes of the produced porous carbons from the templating strategy [15–17]. However, this method requires to use templates with well-defined porosities, and usually sophisticated and time-consuming procedures are necessary to prepare these delicate templates [18]. For instance, colloidal crystals are frequently used as templates for the production of nanostructured carbons [19–22]. In the construction of the colloidal crystals, one first needs to have monodispersed polymeric spheres which are synthesized via strictly controlled emulsion polymerization, and then assemble these spheres into densely packed films by a slow evaporation process. Considering that the templates have to be removed either by thermal degradation or chemical etching the delicate fabrication of the templates makes the production of the porous carbon not only complicated in process but also costly in resources and timing. Therefore, it is highly demanding for templates with well-controlled porosities which can be efficiently and reproducibly obtained through simple methods, for the preparation of carbons-based supercapacitors.

Recently, we developed an extremely simple method to produce mesoporous polymers with interconnected pores with sizes in the range of ~10–50 nm. In this method, one simply needs to immerse amphiphilic block copolymers, for example, polystyrene-block-poly(2-vinyl pyridine) (PS-b-P2VP), with any dimensions in hot ethanol for a few hours. After removing the copolymers from the ethanolic bath and air drying, three-dimensionally interconnected mesopores are formed throughout the entire thickness of the copolymers. These pores are produced via the selective swelling-induced pore generation mechanism in which the P2VP microdomains are selectively swollen by ethanol and subsequently caviated with the evaporation of ethanol [23,24]. Considering the mesoscale pore size, open and impregnatable porosity, and more importantly, the easy preparation, we expect that these selective swelling-induced porous polymers may serve as a type of easily accessible templates for the synthesis of nanoporous carbon toward high-performance supercapacitors.

Herein, we report the preparation of the bimodal porous carbon with 3D hierarchical architecture by impregnating oligomeric phenol–formaldehyde resols into thus produced mesoporous PS-b-P2VP films followed by thermopolymerization and carbonization. The copolymer templates are degraded and converted to mesopores in the course of the thermal treatment. Interestingly, micropores are also produced by the carbonization of the PS-b-P2VP/resols composites. Therefore, we obtain nanostructured carbons containing both mesopores and micropores. Such a bimodal porosity offers the nanostructured carbons enhanced capacitive behaviours compared to other carbon supercapacitors with comparable surface areas.

2. Experimental

2.1. Chemicals and materials

Polystyrene-block-poly (2-vinyl pyridine) block copolymer (PS-b-P2VP, $M_{P2VP} = 50$ kg/mol, $M_{P2VP} = 16.5$ kg/mol, polydispersity = 1.09) was purchased from Polymer Source, Inc. Canada, and was used as received. Formaldehyde solution (37 wt%) was obtained from Shanghai Chemical Crop. Phenol was purchased from Guangdong Chemical Crop. Chloroform (≥ 99.8%) and ethanol (≥ 99.8%) were obtained from Sigma Aldrich Reagent Co., Ltd. All chemicals were used without further purification.

2.2. Preparation of hierarchically porous carbons

Resols were synthesized from phenol and formaldehyde by a base-catalyzed polymerization method, as described elsewhere [9,25]. 3 mL 10 wt% chloroform solution of PS-b-P2VP were added into a ceramic crucible with a bottom area of 2.0 cm² to form a solid film after the evaporation of chloroform. The PS-b-P2VP film was dried at 60 °C overnight and then swollen by ethanol at 60 °C for 15 h to generate mesopores in the film. 3 mL 15 wt% resols (dissolved in ethanol/water with the weight ratio of 1/1) were added into the crucible and then placed in vacuum for approximately 12 h at room temperature to allow the resols to fill into the mesopores of the film. It was found that 3 mL resol solutions could completely penetrate into the mesoporous PS-b-P2VP film, leaving no solid resin layers on the film surface. Subsequently, the resol-filled BCP film was heated at 80 °C for 20 h to thermopolymerize the resols [26]. The as-produced brown film was peeled off from the crucible and was then calcined at 450 °C under $N_2$ for 3 h with an increase rate of 1 °C/min to decompose block copolymers, and then the temperature was increased to 900 °C at the rate of 3 °C/min for 3 h to carbonize the resin.

2.3. Characterizations

Field emission scanning electron microscopy (FESEM) was used to acquire morphologies of the sample at the accelerating voltage of 5 kV. For transmission electron microscopy (TEM) characterization, the porous carbon was ground into powders which were dispersed in ethanol followed bysonication under the power of 100 W for 30 min. A droplet of the suspension was dropped onto TEM grids. TEM observations were carried out on a JEM-2100 microscope operated at 200 kV. $N_2$ adsorption–desorption isotherms of the porous carbon were obtained at 77 K using an ASAP 2020 Micromeritics surface area and porosity analyzer. Before the measurements, the monolithic carbons were degassed at 300 °C in vacuum for 12 h.

2.4. Electrochemical measurements

A three-electrode system was applied to investigate the electrochemical performance of the carbon film. The as-prepared hierarchical porous carbon was grounded into powders and mixed
with polytetrafluoroethylene (PTFE) (Shanghai 3F New Materials Co., Ltd.) with a weight ratio of 7:3. Subsequently, the mixture was compressed to produce a film which was then placed between two layers of nickel foam to form working electrodes and further dried at 120 °C for 24 h. A platinum foil was utilized as the counter electrode. An Hg/HgO electrode filled with 1 mol/L KOH was served as the reference electrode, and a 6 mol/L KOH solution was used as the aqueous electrolyte at room temperature. Cyclic voltammetry (CV) curves were recorded on a Princeton Applied Research PARSTAT 2273 (Advanced Measurement Technology Inc., USA) advanced electrochemical system. The galvanostatic charge and discharge tests were carried out on a NEWARE BTS computer-controlled galvanostat (Shenzhen, China). The specific capacitance (C) of the electrodes can be calculated via the equation described as:

$$C = \frac{(I \times \Delta t)}{(M \times \Delta V)}$$

where M (g) is the mass of the electrode, ΔV (V) is the operating potential window, I (A) is the galvanostatic discharge current, and Δt (s) is the discharge duration.

Electrochemical impedance spectroscopy (EIS) was carried out from 10^5 Hz to 0.01 Hz using a PARSTAT 2273 advanced electrochemical system. All electrochemical measurements were carried out at room temperature.

3. Results and discussion

In this work, we used cylinder-forming block copolymer. According to the phase diagram of BCP, it would take the morphology of P2VP cylinders embedded in PS matrix. However, as we did not make any alignment to the BCP, P2VP cylinders would be randomly oriented with the coexistence of both perpendicular and in-plane orientation. Upon swelling, the adjacent P2VP cylinders were swollen and merged to form another continuous phase in the PS matrix, which turns to be the continuous porous phase after drying [23,24]. As displayed in Fig. 1, the as-prepared monolithic film is converted to a porous template with bicontinuous structures by the swelling process (panel a). The bicontinuous PS-b-P2VP template is subsequently infiltrated with resols to yield the PS-b-P2VP/resols composite (panel b). After thermopolymerization for a period of time, the composite can be carbonized to generate the porous carbon containing both mesopores and micropores (panel c).

In this work, 10 wt% chloroform solution of PS-b-P2VP was added to a ceramic crucible with a bottom area of 2.0 cm² to allow the solvent rapidly evaporate in air. After complete removal of chloroform, the PS-b-P2VP monolithic film was immersed into ethanol at 60 °C for 15 h. In this process, as a selective solvent to P2VP, ethanol penetrated into the hydrophilic P2VP microdomains and swollen the block copolymer to a high degree following the swelling-induced pore generation strategy, producing a bicontinuous porosity in the template [23]. In the swelling-treated monolithic film, a large quantity of mesopores with the average pore size around 30 nm can be clearly observed from the SEM image (Fig. 2a) which is highly consistent to our previous work [23]. Thus-produced porous films did not contain any micropores as BET analysis revealed a very low surface area (~42 m²/g) of the film after swelling [23]. We already demonstrated that the porous PS-b-P2VP films have great potential to be used as templates to produce mesoporous materials. We utilized electrodeposition to fill gold into the pores of the film to produce mesoporous gold replicas after dissolving away the PS-b-P2VP templates [23]. Moreover, we also coated Al₂O₃ or TiO₂ onto pore walls of the swelling-treated PS-b-P2VP films by atomic layer deposition and then burned off the PS-b-P2VP films, producing metal oxides networks of interconnected hollow tubes [27,28]. In the present work, to obtain the

![Fig. 1. Schematic diagram of the synthesis process of the hierarchically porous carbons. (a) The monolithic mesoporous PS-b-P2VP film subjected to ethanol swelling at 60 °C for 15 h. The P2VP phases are marked red and the PS phases green. (b) Infiltration of the porous PS-b-P2VP film with resol solutions, followed by thermopolymerization. (c) The nanostructured carbon with bimodal porosity obtained by the carbonization of the resol-filled PS-b-P2VP composite. The micropores are presented as white holes and not drawn to scale. The digital photos of the corresponding samples are presented in the bottom. The chemical structure of the PS-b-P2VP template and resol are also included in this figure. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image-url)
reverse carbon structures from the bicontinuous PS-b-P2VP tem-
plate, 15 wt% ethanol/water solutions of resols were infiltrated into
the mesoporous PS-b-P2VP film in vacuum. The successful infiltra-
tion was directly verified by the color of the sample which was
transformed from white to brown (the bottom of Fig. 1). After
resols infiltration, the produced PS-b-P2VP/resols composite was
thermopolymerized and further thermally treated to decompose
the block copolymer template and to carbonize the composite.
Generally, the removal of the BCP template will produce meso-
porous structures with the pore size distributing from 20 to
40 nm just as the mesoporous gold, Al₂O₃ and TiO₂ networks that
we reported before [23, 27, 28]. Undoubtedly, the mesopores with
the pore size from 20 to 60 nm are observed from the SEM image
in our porous carbons (Fig. 2b). The generation of the bigger pores
with a diameter of larger than 40 nm is probably attributed to the
collapse of the mesoporous network with thin pore walls in the
carbonization process. In addition, it should be noted that, in the
carbonization process of resin, the release of fragments of resin
with low molecular weights can induce the generation of microp-
ores [8]. However, micropores are not visible in the hierarchical
carbon network probably due to the limited resolution of the
SEM image. To further investigate the micropores, TEM was uti-
lized to characterize the details of the porous carbon. As displayed
in Fig. 2c and d, numerous micropores with the average pore size

![Fig. 2.](image)

(a) The SEM image of the mesoporous PS-b-P2VP film as the template; (b) The SEM image of the produced porous carbons by carbonizing the resol-impregnated PS-b-P2VP films; (c and d) TEM images with different magnifications of produced porous carbons. (a) and (b) have the same magnifications and the scale bars are shown in (a). The inset in (d) is the high-resolution TEM of the porous carbon.

![Fig. 3.](image)

(a) Nitrogen adsorption–desorption isotherm at 77 K, and (b) Micro- and (c) mesopore size distribution of the as-synthesized porous carbon.
smaller than 1 nm have been yielded within the carbon skeletons. The average thickness of the micropores-drilled mesopore walls was further measured as thin as 13 nm which is highly consistent with the SEM image (Fig. 2c).

Nitrogen adsorption measurements were carried out to characterize the hierarchically porous structure of the produced carbon materials. Fig. 3 reveals the nitrogen adsorption–desorption isotherm and pore size distribution of the as-synthesized porous carbon. The adsorption isotherm profile demonstrates well-defined capillary condensation steps (Fig. 3a), which represents the typical absorption behaviours of microporous materials with the nitrogen adsorption completed at a low relative pressure ($P/P_0 < 0.1$), indicating the porosity of the porous carbon primarily consists of micropores [12]. There is a hysteresis loop at the relative pressure between 0.8 and 1.0, revealing the existence of mesopores in the porous carbon [29]. The pore size distribution clearly reveals that the pores of the porous carbon exhibit a bimodal feature: the larger mesopores centered at around 23 and 44 nm copied from the mesoporous PS-b-P2VP template, and micropores from the carbonization of resin (Fig. 3b and c) [25]. These results are in good consistence with the SEM and TEM images. Moreover, the porous carbon exhibits a BET surface area of 692 m$^2$/g, and a high pore volume of 0.73 cm$^3$/g as a result of the generation of large mesopores.

Because of the presence of N in the BCP templates and O in the resols one may argue that these heteroatoms may be left in the produced carbons, which might contribute to improving the performance of a supercapacitor [8]. We performed elemental analysis on the produced porous carbon and found that the content of carbon was higher than 99%. Therefore, the presence of heteroatoms, if any, would be in very small fraction in our porous carbon and would not noticeably change the capacitor performance of the porous carbon. N and O in the template and precursors are expected to be evaporated away in the carbonization process performed at 900 °C [25].

The electrochemical properties of the porous carbon were performed with a three-electrode system. Fig. 4a demonstrates the cyclic voltammetry (CV) curves of the carbon electrode with various scan rates (5 mV/s, 10 mV/s, 20 mV/s, 50 mV/s) within a potential window from −1.0 to 0.0 V (vs. Hg/HgO). The CV curves showed a quasi-rectangular shape for the porous carbon, indicating the common capacitive energy storage mechanism of carbonaceous materials [30]. The rectangular CV curves are still maintained at high scan rates implying the quick ion transport and good charge propagation due to the hierarchical pore structures in the porous carbon electrode [8,30]. The galvanostatic charge–discharge curves of the mesoporous carbon were carried
out at current densities from 1 A/g to 10 A/g (Fig. 4b). The charge–discharge curves reveal an approximately isoceles-triangular shape, suggesting the electric charge in the porous carbon electrode is generally stored in the electric double layer. With more pores more electric double layers will be formed to accommodate more charges, thus increasing the capacity of the porous carbon. The symmetrical charge–discharge curves are consistent with the above CV curves, indicating the excellent responses of the porous carbon electrode within the whole potential range [31]. Additionally, the porous carbon electrode possesses nearly identical charge and discharge durations, implying the excellent reversibility of the carbon electrode.

The Nyquist plot of the porous carbon over the frequency range from 10^4 Hz to 0.01 Hz in the 6 M KOH electrolyte is shown in Fig. 4c. The near-vertical line in the low frequency region reveals the approximately ideal capacitance of the porous carbon. A small semicircle in the high frequency region is related to the charge-transfer process. The x-intercept at the real axis is treated as the electrolyte resistance [32], which is determined as 0.45 Ω indicating the low equivalent series resistance (ESR) [33]. The specific capacitance as a function of discharge current density ranging from 1 to 10 A/g was illustrated in Fig. 4d. The specific capacitances are slightly decreased from 173 to 172, 168, 165 and 160 F/g with current densities increasing from 1 to 2, 4, 5 and 8 A/g, respectively, and retain stable at 10 A/g with the specific capacitance of 160 F/g. The specific capacitance remains 92.5% of the capacitance when the current density increases from 1 A/g to 10 A/g, indicating the outstanding rate performance of the porous carbon supercapacitor. Fig. 4e demonstrates the cycling performance of the porous carbon at a current density of 5 A/g. The electrode displays a highly stable electrode performance as expected due to the electric double layer capacitance. The specific capacitance remains at approximately 165 F/g after 10,000 cycles which is higher than that of other porous carbon supercapacitors with similar BET surface areas [34,35].

As there is no heteroatom present in the produced porous carbon as we mentioned previously, the pore structures rather than the heteroatoms are responsible for the superior performance of our supercapacitors. So we hold the opinion that the 3D interconnected hierarchical structures are capable of promoting the fast ion transport pathway and the low resistance of charge diffusion, and further increase the effective surface area mainly contributed by micropores [10]. It is due to these results that the improved capacitance and the superior electrochemical stability of the hierarchical porous carbon with bimodal pore structures are guaranteed.

4. Conclusions

In summary, a simple and facile template-assisted method has been reported to fabricate hierarchically porous carbons. Mesoporous PS-b-P2VP templates can be easily produced by directly swelling in hot ethanol for certain period of durations. Phenol-formaldehyde resols are proved to be successfully infiltrated into the mesoporous PS-b-P2VP templates followed by thermopolymerization and carbonization to generate hierarchically porous carbons containing both mesopores and micropores. Furthermore, the produced porous carbons have been designed as supercapacitors with excellent electrochemical performance. Excellent capacitance retention at a current density as high as 10 A/g is realized due to the presence of mesopores which activate micropores by facilitating the ion transport. Superior cycling stability is also ensured as no decay in specific capacitance of the porous carbon electrode can be detected after 10,000 cycling at 5 A/g. As a result, our hierarchical porous carbons could have great potential in supercapacitors and also other applications.

Notes

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References


