

One-step hydrothermal synthesis of ordered mesostructured carbonaceous monoliths with hierarchical porosities†

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Hierarchical carbonaceous monoliths with ordered 2-D hexagonal mesostructures have been successfully synthesized by using phenolic resols as precursors and mixed triblock copolymers as templates via a one-step hydrothermal approach.

Among the various nanostructured materials, porous carbon monoliths have attracted great interest in many fields, such as electrochemistry, energy storage, separation and chromatography, mainly due to their high thermal and chemical stabilities, large surface areas and substantial advantages concerning mass transport.^{1–3} Since the hierarchical structure of multi-level pores can greatly benefit mass flow transportation, great interest has been focused on the design and synthesis of carbon monoliths that have tailored porosity and pore interconnectivity.⁴ Various approaches towards the synthesis of hierarchically-structured carbon monoliths with ordered mesopore channels have been conducted using the “nanocasting” strategy, which involves multiple steps: first, the synthesis of mesoporous silica monolith templates with hierarchical porosities by a surfactant self-assembly process, then replication of the silica template with carbon sources, and finally removal of the silica template.^{5–7} However, this nanocasting strategy is somewhat fussy and costly given its complicated multiple step synthetic procedures, and sacrificial use of both surfactants and monolithic silica templates.

Recently, ordered mesoporous carbon materials with various symmetries have been successfully synthesized by an organic–organic self-assembly strategy via a solvent evaporation-induced self-assembly (EISA) method,^{8–10} or by common aqueous reaction routes under atmospheric pressure at relatively low temperatures.^{11,12} However, these methods are problematic for large-scale industrial production because of long processing times and the large vessels used for the interface assembly of mesostructures. Hydrothermal synthesis is a more efficient approach under controlled temperature and pressure that has been extensively exploited in a variety of inorganic syntheses of zeolites, nanomaterials, catalysts and ion-conductors.^{13–15} In addition, this powerful method is

faster and more energy efficient than conventional aqueous chemical processing conditions.

Herein, we report a facile, one-step, hydrothermal synthesis of carbon monoliths with hierarchical porosities, built up from ordered mesopores and interconnected macropores. Mixed triblock poly(propylene oxide)–poly(ethylene oxide)–poly(propylene oxide) (PEO–PPO–PEO) copolymers of Pluronic F127 and P123 were employed as templates, and phenolic resols were used as carbon precursors (Fig. 1). The synthesis was carried out under hydrothermal conditions, in the presence of a base catalyst, in an aqueous medium, at 100 °C, for 10 h. The resultant carbonaceous monoliths were formed in high yield (around 90 wt% based on the carbon precursor), and were thermally stable and crack-free. It is interesting that the monoliths showed hierarchically porous structures, with interconnected macropores of around 3 μm, ordered 2-D hexagonally-arranged mesopores of around 3 nm and micropores in the mesopore walls. Microspherical and body-centered cubic mesoporous carbons with irregular shapes could also be obtained by only employing F127 as the template (see ESI†). Our results also show that the high temperature synthesis approach could be useful for the large-scale industrial production of mesoporous carbonaceous materials.

The synthesis of monoliths was carried out in an autoclave with an aqueous solution containing the triblock copolymer templates. Typically, 1.0 g of phenol and 3.5 mL of a formaldehyde solution (37 wt%) were dissolved in 5 mL of a 0.5 M NaOH solution and stirred at 70 °C for 0.5 h. Then, an aqueous solution of mixed PEO–PPO–PEO (0.75 g P123 and 1.25 g F127 in 10 mL of water) was added to the above solution, and the mixture continuously stirred at 70 °C for an additional 3 h. After that, the solution was poured into an autoclave and transferred into an oven at 100 °C for 10 h. The polymeric monolith was

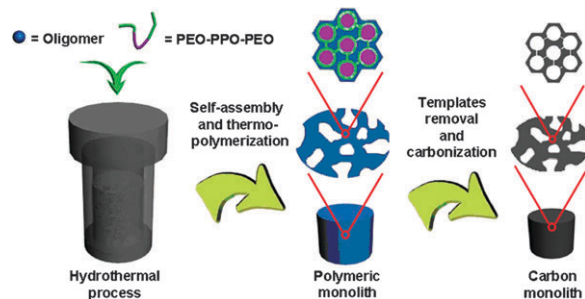


Fig. 1 Schematic representation of the hydrothermal synthesis route towards carbon monoliths with hierarchical porosities.

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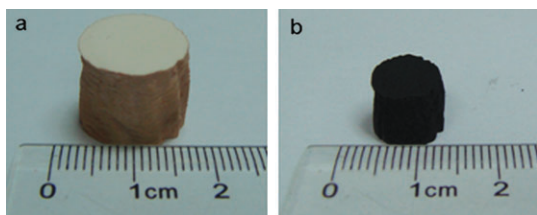


Fig. 2 Representative photos of (a) the as-synthesized polymeric monolith and (b) the carbon monolith after calcination at 600 °C under a nitrogen atmosphere for 3 h.

collected by filtration, washed with water and dried in air. The obtained monolith sample was calcined at 600 °C for 3 h in a nitrogen flow to obtain mesoporous carbonaceous monoliths. To obtain carbon spheres, 2.0 g of F127 was used as the template in the hydrothermal synthesis, and the other processes were performed according to the above procedure. To obtain ordered 3-D body-centered cubic mesostructured carbon, 2.0 g of F127 was used as the template, and the autoclave was placed in a 100 °C oil bath with vigorous magnetic stirring. A detailed characterization of the products is given in the ESI.†

Photographs of our typical, as-synthesized polymeric monoliths and calcined carbon materials show a good bulk macroscopic appearance (Fig. 2), and both are very stable and crack-free. The color of the as-synthesized polymeric monolith is buff, and it turns to black after calcination at 600 °C. The sizes of the monoliths can be easily adjusted by choosing autoclaves with different inner diameters. A typical, as-synthesized monolith in Fig. 2a is large, with a length of ~1.0 cm and a diameter of ~1.4 cm. The high yield of carbonaceous monoliths and the relatively rapid speed of the procedure suggest that this high temperature synthetic approach could be useful for the large-scale industrial production of mesoporous carbonaceous materials. Mesoporous carbon monoliths obtained after carbonization at 600 °C for 3 h under a nitrogen atmosphere exhibit a black color and a similar column-like shape (0.9 cm in diameter and 0.6 cm in height), with comparably smaller sizes to the polymeric monolith. The volume shrinkage was calculated to be about 75% during the carbonization process. A preliminary mechanical strength test showed that the carbon monolith is quite rigid and does not crack under a pressure of 0.2 MPa. The mesostructure obtained from the organic–organic self-assembly method possesses an integral framework and is mechanically stable, as shown by Meng *et al.*¹⁰ Scanning electron microscopy (SEM) images (Fig. 3a and b) show that the structures of the as-synthesized monoliths are constructed from interconnected particles. These particles build up a 3-D disordered macroporous framework, with sizes in the range of 2–5 μm. After carbonization at 600 °C, the macropore size slightly increases, although the structure contracts to about 75%. The macroporosity could also be revealed by Hg porosimetry (Fig. 4). The carbon monolith after calcination at 600 °C showed an average macropore size of 3 μm, with a relatively narrow size distribution and a correspondingly high total macropore volume of 1.14 cm³ g⁻¹. Transmission electron microscopy (TEM) images of the calcined sample (Fig. 3c and d) reveal that these building blocks are of an ordered 2-D hexagonal mesostructure. The cell parameter, *a*, is estimated from the TEM images to be ~10.0 nm.

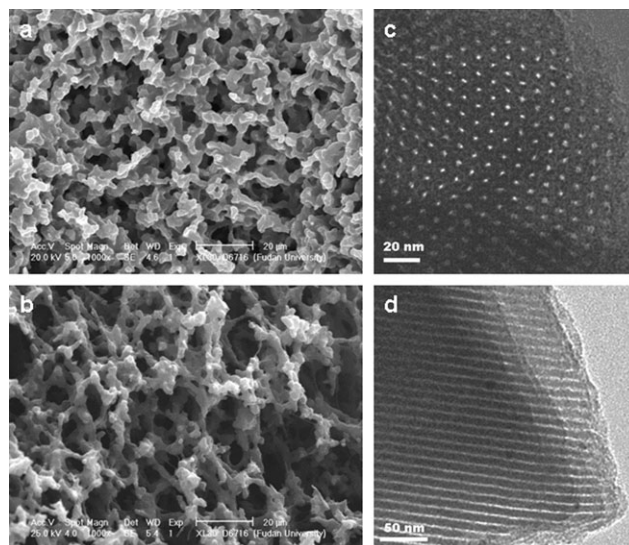


Fig. 3 SEM images of the (a) as-synthesized and (b) calcined monolith samples. TEM images of the hierarchical carbon monolith with its ordered hexagonal mesostructure viewed from the (c) [10] and (d) [11] directions.

The ordered periodic arrangement of mesopores could be further confirmed by their small angle X-ray scattering (SAXS) patterns (Fig. 5a). The pattern of the as-synthesized carbonaceous monolith exhibits two scattering peaks. After carbonization at 600 °C, the SAXS pattern becomes more resolved. Three resolved scattering peaks are observed, which can be indexed as 10, 11 and 20 reflections associated with a 2-D hexagonal mesostructure (space group of *p6mm*). The cell parameter, *a*, is calculated to be 10.0 nm, which is in good agreement with TEM observations. Shrinkage of the mesoporous framework is about 24%, which is much less than the macroscopic contraction. N₂ adsorption–desorption isotherms of mesoporous carbon monoliths (Fig. 5b) show typical type-IV curves, with a clear condensation step at *P/P*₀ = 0.3–0.5, suggesting a uniform mesopore. The specific BET surface area is calculated to be as high as 620 m² g⁻¹. The micropore area is 360 m² g⁻¹. The micropore and mesopore volumes are 0.16 and 0.20 cm³ g⁻¹, respectively. The Barrett–Joyner–Halenda (BJH) mesopore size distribution, calculated from the adsorption branch, is quite narrow, with a mean value of 3.0 nm.

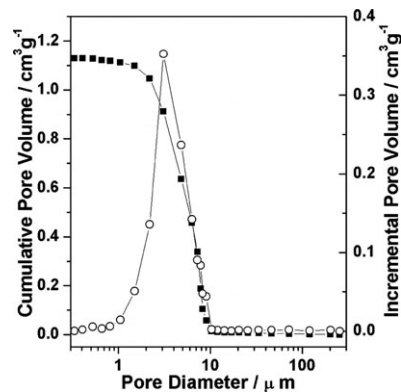


Fig. 4 Hg porosimetry curves of mesoporous carbon monoliths after carbonization at 600 °C under a nitrogen atmosphere.

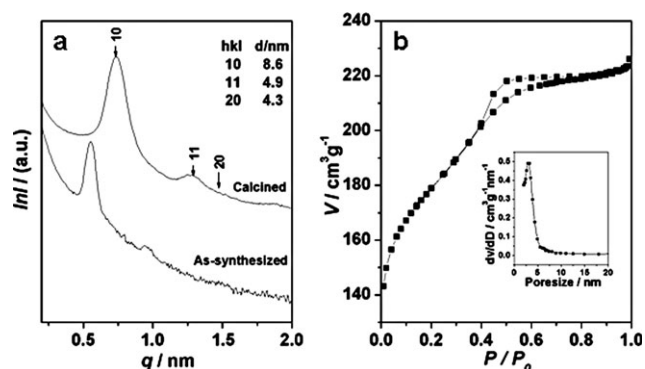


Fig. 5 (a) SAXS patterns of as-synthesized and calcined carbonaceous monoliths and (b) N_2 sorption isotherms with the pore size distribution (inset) of the mesoporous carbon monolith after calcination at $600\text{ }^\circ\text{C}$.

Fig. 1 illustrates the hydrothermal synthetic process for preparing carbonaceous monoliths with hierarchical porosities through the organic–organic self-assembly of triblock copolymers and phenolic precursors. In the first stage, the polymeric, water-soluble resol precursors are involved in a supramolecular templating process with triblock copolymers in an aqueous medium. The phenolic oligomers show more compatibility with the PEO blocks of amphiphilic PEO–PPO–PEO templates compared to the aqueous environment, and can be self-assembled into ordered mesostructures. Fast polymerization under hydrothermal conditions causes the macro-domains to be divided into a phenolic resin/PEO–PPO–PEO-rich phase and a water-rich phase. In the mixed F127–P123/resin/water system, the resin domains partially aggregate and further polymerize to form a rigid co-continuous structure, where both the resin and aqueous phases are continuous and highly interconnected. After drying in air, the aqueous phase domains can turn to the interconnected macropore system.¹⁶ When only F127 is used as the template, it tends to form dispersed, less ordered microspheres in 80% yield (ESI Figs. S1 and S2†). Our results show that the diameters of the microspheres are not very uniform, around $8\text{ }\mu\text{m}$, and vary with F127 content and the hydrothermal treatment time. The spherical morphology implies that the higher EO/PO ratio of F127 can effectively stabilize the resin domain by greatly reducing the interface free energy. While under vigorous stirring, the SAXS, SEM and TEM image results (ESI Figs. S3 and S4†) show that the products have an ordered body-centered cubic mesostructure with an irregular shape. The mesopore size is uniform, with a mean value of 3.8 nm . This can be explained by a uniform templating effect and a higher surface free energy caused by shearing forces.

The removal of triblock copolymer templates leads to the formation of mesopores. It has also been found that mesoporous carbonaceous materials templated by the triblock copolymers inherently possess microporosity within the phenolic walls, due to a strong affinity between the PEO block and the precursors.^{17,18} With the cross-linking of the phenolic resins, the PEO segments are embedded into the pore walls and then removed by calcination, resulting in the formation of micropores within the carbonaceous walls. The resultant

carbon monoliths have a unique hierarchical construction of interconnected macropores, ordered mesopores and micropores in the pore walls after removal of the template.

In summary, we have demonstrated a simple one-step hydrothermal method for the synthesis of carbonaceous monoliths with hierarchical porosities, by employing F127–P123 mixed triblock copolymers as templates and phenolic resols as carbon precursors at $100\text{ }^\circ\text{C}$. The monoliths show an ordered 2-D hexagonal mesostructure with a uniform pore size ($\sim 3\text{ nm}$) and 3-D irregular macroporous scaffolds with a size of $\sim 3\text{ }\mu\text{m}$. The high temperature synthesis approach is very efficient, with a high yield of 90 wt%. This may be useful for the large-scale industrial production of ordered mesoporous carbonaceous materials. This approach allows the one-pot formation of both ordered mesostructures and irregular 3-D scaffolds, which will be of considerable importance for the facile production of hierarchical porous carbon materials.

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