

Short Communication

One-step Nanocasting Synthesis of Ordered Mesoporous Carbon with Graphitic Frameworks

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A simple one-step nanocasting route has been demonstrated to synthesize ordered mesoporous carbon with graphitic frameworks. In the synthesis, the complicated carbon precursor impregnation step is no longer used and the carbon precursor (soybean oil) is incorporated into the mesopore channels in the hydrophobic domain of the triblock copolymers due to the coordination function through the preparation of the ordered mesoporous silica SBA-15. It was found that the as-prepared graphitic carbon material has an ordered 2D hexagonal mesostructure with a rod-like morphology, a high specific surface area ($813.7 \text{ m}^2 \text{ g}^{-1}$) and a large pore volume ($0.758 \text{ cm}^3 \text{ g}^{-1}$), giving the material wide potential applications as catalyst support, adsorbent and electrode material.

Keywords: mesoporous carbon; graphitic frameworks; soybean oil; one-step nanocasting.

1. INTRODUCTION

In recent years, the design and synthesis of ordered mesoporous carbons (OMCs) with extremely uniform pore structure, high specific surface area, and large pore volume have attracted considerable interests because of their potential applications as catalyst supports [1, 2], adsorbents [3, 4], hydrogen storage materials [5, 6], and electrode materials [7-10]. Generally, there are two main methods to synthesize OMCs, the conventional one is so-called chemical soft-template method which has been widely used in the synthesis of ordered mesoporous silicas (OMSs). However, OMCs prepared by this method requires higher demands on the synthesis conditions when compared with OMSs because of the nature of the phenolic-resin-based carbon precursors [11, 12]. Another more frequently used strategy is hard-template method (i.e. nanocasting) using OMSs as sacrificial scaffolds

in which carbon precursors are fabricated within the pore channels of OMSs, followed by carbonization and selective removal of the silica template. Based on this route, a large number of OMCs with varied mesostructures, different pore sizes, or even graphitic frameworks have been obtained [13-16], whereas an obvious disadvantage of this method is the fussy and time-consuming synthesis procedure.

Recently, some research groups independently reported the synthesis of OMCs from the direct carbonization of as-synthesized mesoporous silica/surfactant or mesoporous silica/surfactant/carbon precursor composites based on one-step nanocasting route [17-19]. However, to the best of our knowledge, there are no OMCs with graphitic frameworks prepared by this method. Our recent report has shown that we are able to synthesize ordered mesoporous carbon with graphitic frameworks through one-step solid-liquid grinding/templating route using natural seed fat as a carbon precursor [20]. Such materials are attractive to use as efficient supports for TiO_2 catalysts in the photoreduction of CO_2 with H_2O because of the high electron conductivity.

Herein, we report the synthesis of ordered mesoporous carbon with graphitic frameworks through a simple one-step nanocasting route. This synthesis was achieved using the similar procedure for the preparation of mesoporous silica SBA-15 except adding an appropriate amount of soybean oil (as a carbon source) in the initial reaction mixture, the soybean oil will be incorporated into the mesopore channels in the hydrophobic domain of the triblock copolymers due to the coordination function and will not affect the ordering of mesoporous SBA-15. Fig.1 shows the synthesis process of the graphitic ordered mesoporous carbon by one-step nanocasting route. Another advantage of this route is that the organic surfactant template does not need to be removed, which can be co-carbonized with the soybean oil under high temperature.

2. EXPERIMENTAL

2.1. Chemicals

Pluronic triblock copolymer P123 ($M_w=5800$, $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) was purchased from Aldrich. Tetraethoxysilane (TEOS), hydrochloric acid and hydrofluoric acid were purchased from Shanghai Chemical Corp. Soybean oil was obtained from Shanghai Wal-mart supermarket. All chemicals were used as received without further purification.

2.2 Materials preparation

Ordered mesoporous carbon with graphitic frameworks was prepared by a simple one-step nanocasting route (illustrated in Fig. 1). In a typical synthesis, an appropriate amount of soybean oil (SBO) and 2.4 g of triblock copolymer Pluronic P123 were added to 92.3 g of 1.5 M HCl aqueous solution (here the weight ratio of SBO/P123 can vary from 2 to 5), which was stirred at 35 °C for 4-6 h to get a transparent solution. Then, 5.17 g of tetraethoxysilane (TEOS) was added to the above solution under vigorous stirring. After stirring for 5-8 min, the mixture was kept in static conditions at the same

temperature for 24 h, followed by aging at 100 °C for 24 h. The solid products were collected by filtration, dried at 60 °C, and carbonized at 900 °C for 4 h under Ar flow, the silica template was removed with 10% hydrofluoric acid aqueous solution and this etching process was repeated three times, the resulting carbon materials were denoted as GMC-xSP (where x is the weight ratio of SBO/P123). Ordered mesoporous silica (SBA-15) with 2D hexagonal symmetry can be obtained if the composite was calcined at 550 °C in the air. For comparison, another carbon material has been prepared without soybean oil in the synthesis and named PC-1.

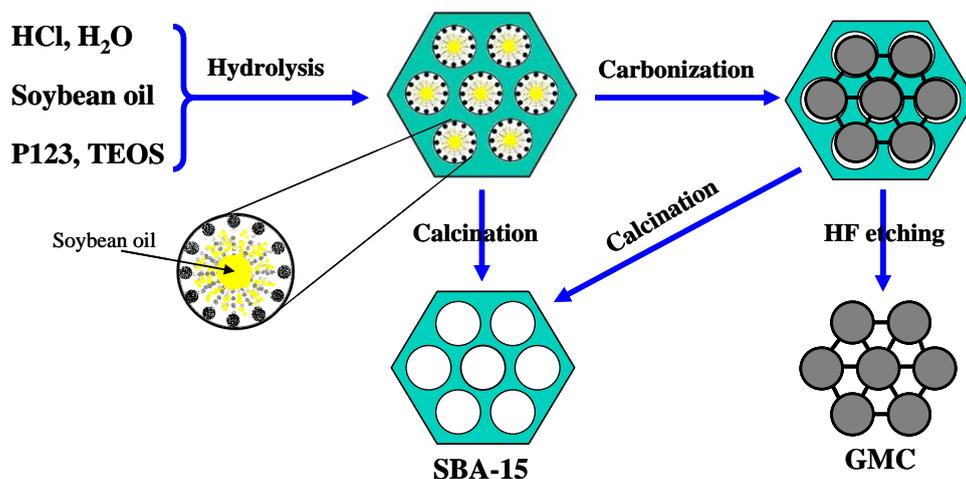


Figure 1. Schematic illustration of the synthesis process of ordered mesoporous carbon with graphitic frameworks by one-step nanocasting route.

2.3 Materials characterization

Small-angle X-ray diffraction (SXRD) patterns were collected in θ - 2θ mode using Rigaku D/MAX-2550VB/PC diffractometer (CuK α_1 radiation, $\lambda=1.5406\text{\AA}$), operated at 40 kV and 200 mA (scanning step: 0.02 ° per second). Wide-angle XRD patterns were collected in the same mode, but operated at 100 mA. Scanning electron microscopy (SEM) images were performed on a Philips XL-30 scanning electron microscope operating at an acceleration voltage of 25 kV. Transmission electron microscope (TEM) images were taken using a JEOL JEM-2010 electron microscope with an acceleration voltage of 200 kV. Nitrogen sorption isotherms were measured at -196 °C on a Micromeritics ASAP 2000 apparatus. Before measurements, the samples were degassed in vacuum at 200 °C for 6 h. The Brumauer–Emmett–Teller (BET) method was utilized to calculate the specific surface areas. The pore size distributions were derived from the desorption branches of the isotherms using the Barrett–Joyner–Halanda (BJH) method. The total pore volume (V_t) was estimated at a relative pressure of 0.98.

3. RESULTS AND DISCUSSION

Using the sample with initial SBO/P123 weight ratio of 3 (denoted as GMC-3SP) as an example, evidence for the formation of graphitic ordered mesoporous carbon is firstly provided by X-

ray diffraction (XRD) analysis. Fig. 2a shows the low-angle XRD patterns of the synthesized GMC-3SP, SBA-15 and PC-1 samples, both GMC-3SP and SBA-15 exhibit three obvious diffraction peaks in the range of $2\theta=1-2.3^\circ$ which can be respectively indexed to the (100), (110) and (200) reflections of the 2D hexagonal ($p6mm$) symmetry, indicating that the added soybean oil has not affect the ordering of mesoporous SBA-15 and the carbon material GMC-3SP is an exact reverse-replica of the silica template, as confirmed by the transmission electron microscope (TEM) images (see below). However, no low-angle peaks were detected in the sample PC-1, which means a disordered mesostructure as confirmed by previous study [21]. The wide-angle XRD pattern of GMC-3SP in Fig. 2b shows two intensive diffraction peaks which can be indexed as (002) and (101) diffractions for typical graphite carbons. The diffraction intensities and peak widths are comparable to those of our previous graphitic mesoporous carbon obtained by solid-liquid grinding/templating route [20], and much more intense than those of PC-1 with amorphous carbon.

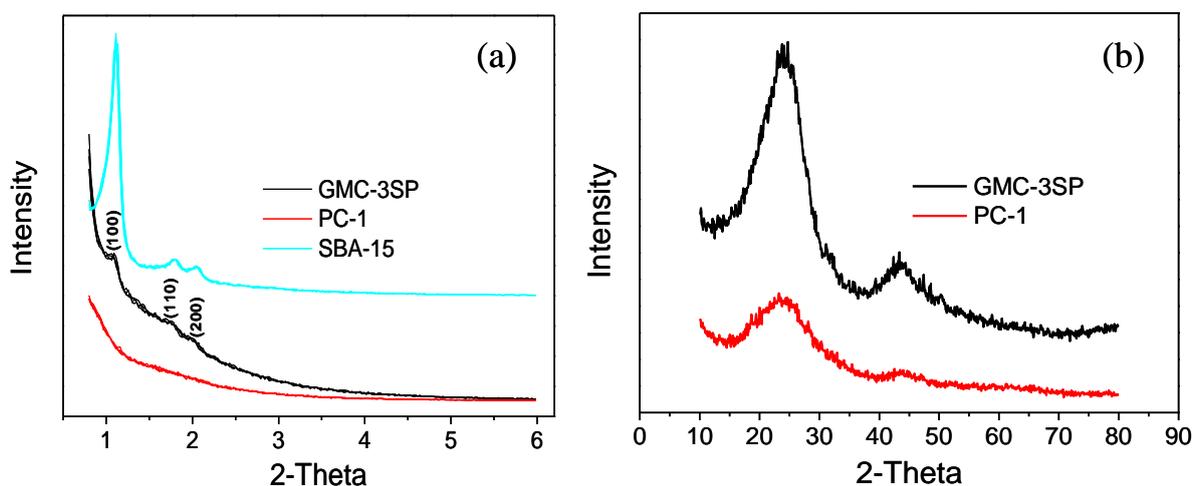


Figure 2. (a) Low-angle XRD patterns of GMC-3SP, SBA-15 and PC-1 samples, (b) wide-angle XRD patterns of GMC-3SP and PC-1.

Fig.3 shows the TEM images of the GMC-3SP sample, large domains with well-ordered hexagonal arrays of carbon rods and pore channels are clearly observed from the low-magnification image (Fig. 3a), which is similar to the structure of CMK-3 reported in the literature [1]. The high-magnification TEM (HRTEM) images along the [001] direction (Fig.3b) exhibits a distinct stacking of the irregular orientation of graphite layers, suggesting the formation of partial graphitized carbon frameworks. The corresponding selected area electron diffraction (SAED) pattern (Fig.3c) shows two distinct diffraction rings which can assigned to (002) and (101) crystal planes of graphite and further reveals the crystalline nature of the GMC-3SP. The representative scanning electron microscopy (SEM) image in Fig.3d shows that GMC-3SP has a rod-like morphology with a diameter of about 0.45 μm and a length of about 0.9 μm after removing the silica template.

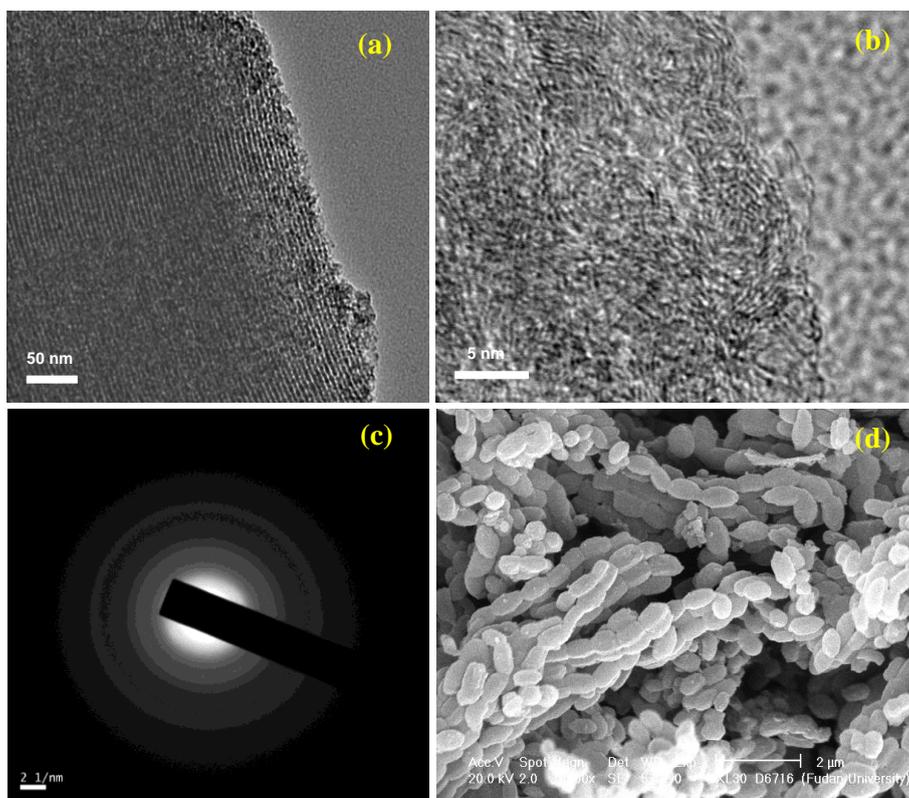


Figure 3. (a) TEM image and (b) HRTEM image of GMC-3SP sample, (c) the corresponding SAED pattern of the observed domain along [001] direction. (d) SEM image of GMC-3SP sample.

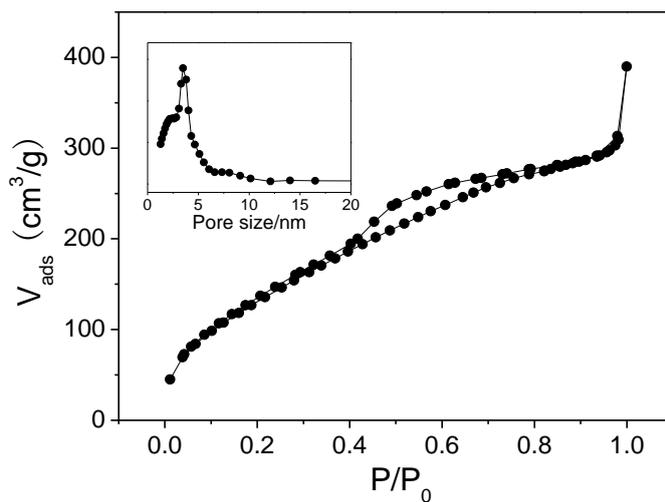


Figure 4. N₂ adsorption-desorption isotherm and corresponding pore size distribution curve (inset) of the GMC-3SP sample.

Fig. 4 gives the nitrogen adsorption-desorption isotherm and corresponding pore size distribution curve of the GMC-3SP sample. The isotherm exhibits a type-IV curve with an H₂ hysteresis loop at P/P_0 of 0.4-0.8, which is a characteristic of mesoporous non-siliceous materials

prepared by the hard template method. The pore size distribution curve (Fig. 4 inset) shows a uniform mesopore with a pore size of about 3.5 nm, which is consistent with the wall thickness of the template SBA-15. Furthermore, this graphitic ordered mesoporous carbon has a high Brunauer-Emmett-Teller (BET) surface area of $813.7 \text{ m}^2 \text{ g}^{-1}$ and a large pore volume of $0.758 \text{ cm}^3 \text{ g}^{-1}$, which are much higher than that of other graphitic mesoporous carbons derived from aromatic compounds, giving this material wide potential applications as catalyst support, adsorbent and electrode material.

4. CONCLUSIONS

In conclusion, ordered mesoporous carbon with 2D hexagonal ($p6mm$) symmetry mesostructure and graphitic frameworks was synthesized by a simple one-step nanocasting route. XRD, nitrogen sorption, SEM and TEM results reveal that the obtained carbon material possesses well-ordered mesostructure with partial graphitic pore walls, a rod-like morphology, a high specific surface area and large pore volume, these properties endow it with many potential applications as catalyst support, adsorbent and electrode material.

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