

Using phenol–formaldehyde resin as carbon source to synthesize mesoporous carbons of different pore structures

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Abstract

In this research communication, we performed the phenol–formaldehyde (PF) resin as an alternative carbon source and various mesostructured silicas as the nano-templates to conveniently prepare the mesoporous carbons of high surface area ($850\text{--}1500\text{ m}^2\text{ g}^{-1}$), large pore size ($2.0\text{--}22.0\text{ nm}$) and great pore volume ($0.65\text{--}1.15\text{ cm}^3\text{ g}^{-1}$). It was reasonably supposed that there exist interaction matching between the negative-charged silica surface of the silica template and PF resin. Therefore, the PF oligomers could be homogeneously adsorbed into the nanochannels or cages of the mesoporous silicas via an impregnation process. Because the thermosetting PF resin only requires a simple heat treatment process at $100\text{ }^\circ\text{C}$ to form the cross-linked polymeric structure, the replication of the mesostructure of the mesoporous silica template could be readily achieved without adding any polymerization catalysts.

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1. Introduction

Mesoporous carbons with high surface area, large porosity and fine electric-conductivity have been regarded as an advanced material for many potential applications in nanotechnology [1]. Typically, a mesoporous-silica-templating technique has been widely employed for the mesoporous carbons synthesis in the previous reports. Due to concerns on pore-blocking effect of the nanochannels on the adsorption of carbon sources, the monomers (e.g. sucrose, furfuryl alcohol, acrylonitrile, and phenol–aldehyde monomers mixture) were usually used as the precursors to prepare mesoporous carbons [2–5]. However, appropriate catalysts are generally required for converting the precursor monomers into the rigid

polymeric framework to form the stable mesostructural replicas. Therefore, incorporation of the reactive species (e.g. aluminum oxide) onto the mesoporous silica template or addition of strong acid (e.g. H_2SO_4) in the reaction mixture is essentially needed. This results in a tedious process for carbon production. Therefore, selecting an appropriate carbon source for mesoporous carbons production is essential to extend the application of the carbon. The thermosetting phenol–formaldehyde resin has been widely used as the carbon source for industrial-scale production of the carbon fibers [6,7]. Resol-type phenol–formaldehyde (PF) resin can be converted into crosslinked polymeric framework via a simple heat-treatment process without adding any catalysts. Consequently, herein, we proposed a convenient way to prepare mesoporous carbons of different mesostructure with various mesostructural silica templates by using the commercial-grade PF resin as the carbon source.

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2. Experimental

The typical synthetic process of mesoporous carbon is as followed: 2.0–4.0 g of a commercial-grade PF resole resin PF650 (ca. 96 000 in molecular weight) was added into 10.0–50.0 g ethanol to form a homogeneous solution at pH around 8.0. This PF ethanol solution was mixed with 2.0–3.0 g of mesoporous silicas as solid template, and continuously stirred for a proper time of 12–48 h. Then, a glue-like mixture was formed after partial ethanol evaporated. That PF-resin and silica mixture was dried and cured at 100 °C for 12 h. The obtained solid product was ground into the powder and transferred to a quartz boat. The cured PF-resin, retained in the mesoporous silica, was carbonized in an oven under nitrogen atmosphere at a heating rate of 10 °C min⁻¹ from room temperature to 900 °C and soaking for 1–3 h before cooling. The silica framework was removed by HF (6.0 wt.%) etching. Filtrating, washing, and drying gave the mesoporous carbons. The mesoporous silicas utilized here are MCM-48, SBA-15, wormhole-like mesoporous silica and silica foams, the detail synthetic compositions and process for the mesoporous silicas were described elsewhere [8–13].

3. Results and discussion

Fig. 1 shows the representative transmission electron microscopic (TEM) images of the mesoporous carbons prepared

with the different solid templates. One can clearly see the well-aligned mesostructures of the carbons (i.e. denoted as the CMK-1 and CMK-3) templated with MCM-48 and SBA-15 mesoporous silicas in Fig. 1A and B, respectively. Fig. 1C reveals the disordered arrangement of the carbon channel prepared with wormhole-like mesoporous silica. The carbon spheres were obtained from the silica foam template, as shown in Fig. 1D. By analyzing the EDX data (see Fig. S-1), we verify that these TEM images are from the mesoporous carbon rather than from the residual silica template. With the examinations of the small-angle X-ray diffraction (XRD) (Fig. 2), we found the mesoporous carbons templated by MCM-48, SBA-15 and wormhole-like mesoporous silicas possess the representative XRD peaks ascribed to the CMK-1, CMK-3 and disordered mesostructure, respectively [2,9,10]. Due to the presence of the (1 1 0), (2 1 0), (2 2 0) diffraction peaks, the mesostructure of CMK-1 is a cubic structure of *I41/a*. In the CMK-3, there exist three obvious (1 0 0), (1 1 0) and (2 0 0) peaks that was ascribed to the *P6mm* hexagonal mesostructure. While, the wormhole-like mesoporous carbon of the disordered mesostructure shows only one broad peak. Accordingly, both the XRD data and TEM observation has indicated that the thermosetting phenol–formaldehyde resin is an alternative carbon source to replicate the mesoporous silicas of different mesostructures.

Fig. 3A illustrates the N₂ adsorption–desorption isotherms for these mesoporous carbon samples. For all the samples, a

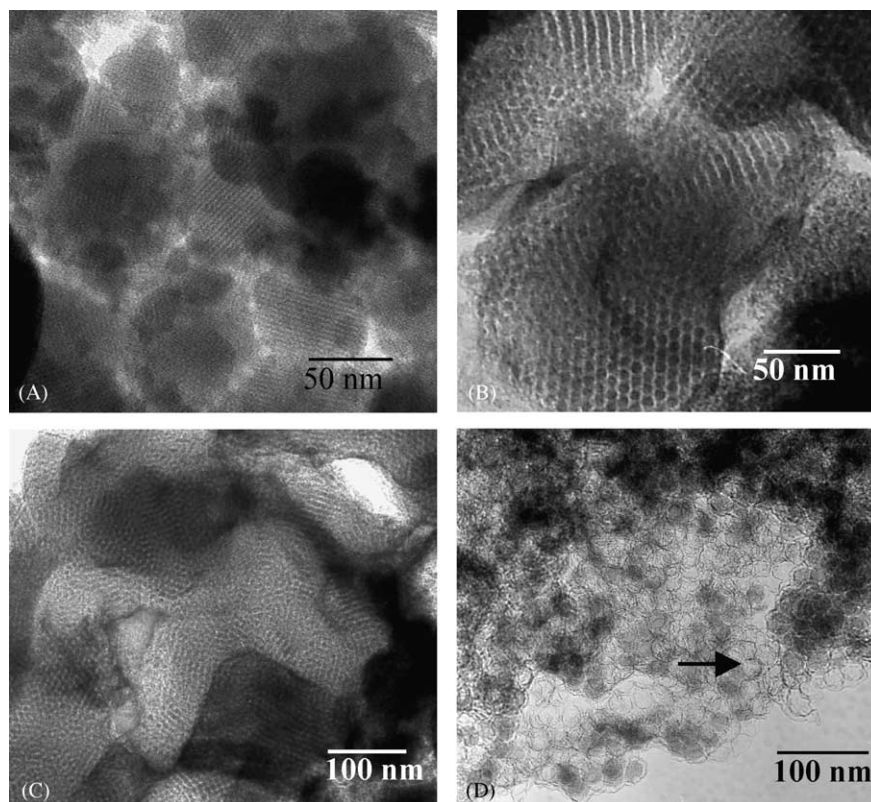


Fig. 1. Transmission electron microscopic (TEM) images of PF resin-made mesocarbons with different mesostructures. (A) CMK-1 carbon; (B) CMK-3 carbon; (C) wormhole-like mesocarbon; (D) Mesocarbon spheres and foams (denoted by an arrow).

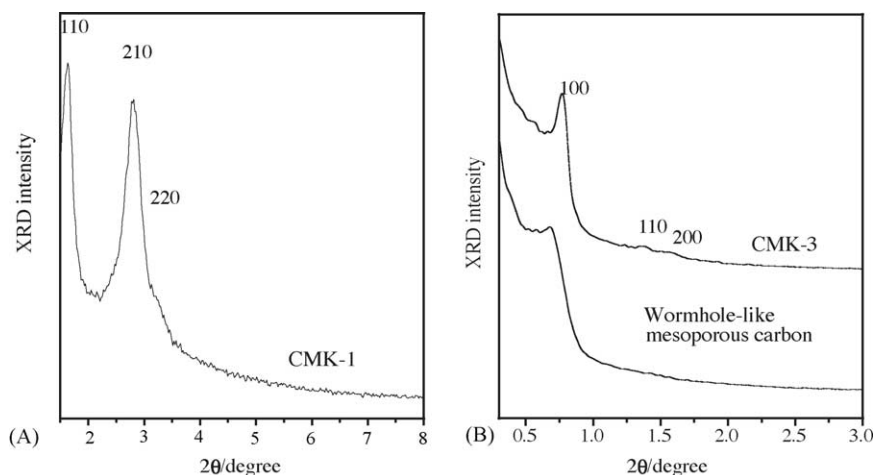


Fig. 2. The XRD patterns of the different PFresin-made mesoporous carbons. (A) CMK-1 mesoporous carbon; (B) CMK-3 and wormhole-like mesoporous carbons.

sharp capillary condensation occurring at P/P_0 in the range of 0.3–0.7 is clearly pronounced, which is attributed to the mesoporosity generated from the removal of the silica framework. Different from other mesoporous carbons, there exists an additional large hysteresis loops at P/P_0 around 0.90 in the mesoporous carbon sphere sample (denoted by an arrow). The extra adsorption would be resulted from the foam-like mesoporous carbon with diameter larger than 20 nm [3]. With a careful observation, one also can find the hollow mesoporous carbon foams (denoted by an arrow) accompanying with the mesoporous carbon spheres (Fig. 1D). The mesoporous carbon spheres and foams, thus, have bimodal mesoporosity (see the inset in Fig. 2A).

The physical properties of these aforementioned mesoporous carbons including surface area, pore size and pore volume were listed in Table 1. The PF-resin-made mesoporous carbons have the advantages of high BET

surface area ($850\text{--}1500\text{ m}^2\text{ g}^{-1}$), large pore size (about $2.0\text{--}22\text{ nm}$ calculated by BJH method) and great pore volume ($0.85\text{--}1.16\text{ cm}^3\text{ g}^{-1}$) as well as those made with other carbon sources. By examining the t -plots of these mesoporous carbon samples, we found the microporosity content (pore size $< 1.0\text{ nm}$) is relatively low (micropore volume $\sim 0\text{ cm}^3\text{ g}^{-1}$) in the CMK-1, CMK-3 and wormhole-like mesoporous carbon. However, the mesoporous carbon spheres and foams possess a micropore volume of around $0.1\text{ cm}^3\text{ g}^{-1}$. From these results, using the commercial-grade phenol–formaldehyde resin is a convenient way to prepare the high-quality mesocarbons. Both the surface area and pore volume are large enough to serve as high-capacity adsorbents.

To study the thermal stability and phase purity of carbons, the thermogravimetric weight changes recorded under air flow are commonly used [2,9]. As can be seen in

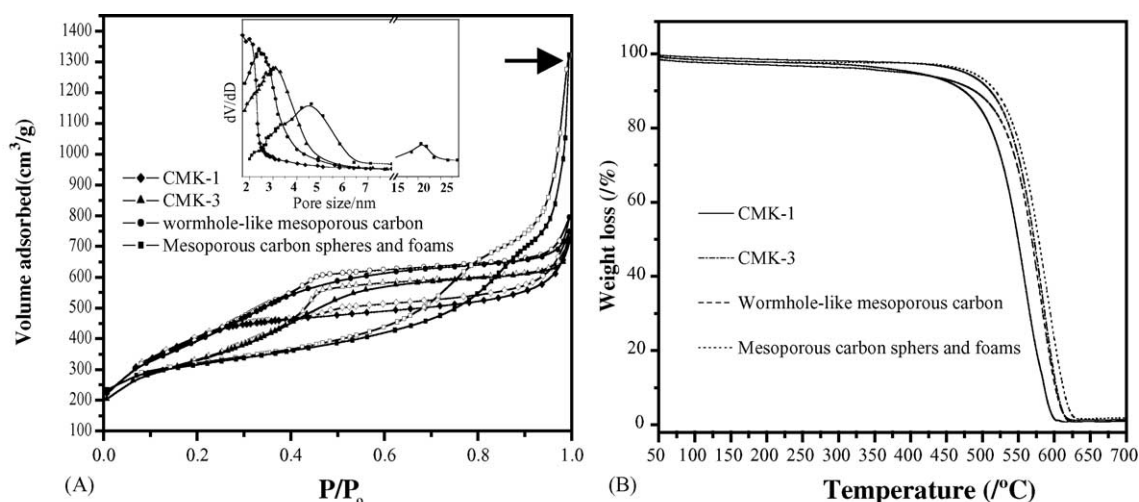


Fig. 3. The N_2 adsorption–desorption isotherms (A) and thermogravimetric curves (B) for the mesoporous carbons of different mesostructures. For TGA analysis, the heating rate was $10\text{ }^\circ\text{C min}^{-1}$ under air flow of $15\text{ cm}^3\text{ min}^{-1}$. The inset shows the BJH profiles of the mesoporous carbon samples in Fig. 3A.

Table 1

The physical properties of the PF-resin-made mesoporous carbons templated with the mesoporous silicas of different mesostructures

Entirety	d-Spacing (nm)	Pore size ^b (nm)	S _{BET} (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)
CMK-1	3.15	2.0	1477	0.85
CMK-3	10.85	3.3	1170	0.97
Wormhole-like mesoporous carbon	10.85	2.8	1182	1.00
Mesoporous carbon spheres and foams	X ^a	4.8 (22.0) ^c	850	1.16

^a The mesostructure of MCF is outside the detecting limit of the XRD instrument we performed.

^b The pore size was calculated from the N₂-adsorption isotherm by using BJH method.

^c The value in the parenthesis is the mesopore generated from the mesoporous carbon foams.

Fig. 3B, the mesoporous carbons prepared with the PF resin exhibit generally similar weight change profiles in thermogravimetric analysis. There exists a significant weight loss in a temperature range between 500 to 600 °C, corresponding to the gasification of the carbon. That narrow temperature range indicates a high structural homogeneity of these mesoporous carbons. Compared to other mesoporous carbons, the CMK-1 from MCM-48 decomposes at lower temperature. That is because the CMK-1 templated by smaller pore-size MCM-48 has smaller carbon nanodomains and higher surface area, which are more easily oxidized and combusted in air. Moreover, it should be noted that the percentage of the residues at 600 °C related to the unremoved silica template are quite low (<3.0 wt.%) in all these mesoporous carbons, indicating a considerably complete removal of the silica by HF-etching.

Accordingly, the advantage and convenience of the resin-filling process should be further expounded. Here we tried to explain the theoretical concept of the resin-filling process. Due to the presence of the hydroxyl-methyl groups (–CH₂OH as hydrogen-bonding donor) in the PF resin, the PF linear oligomers can behave as a multi-chelating polymer-chain to interact strongly with the Si–O[–] groups (i.e. as hydrogen-bonding acceptor) on the negative-charged mesoporous silica templates via the hydrogen-bonding interaction [14,15]. Thus, the adsorption of PF oligomers into the nanochannels is thermodynamically favorable. Under this circumstance, a simple impregnation can be unsophisticatedly conducted to allow PF oligomers homogeneously encapsulated into or deposited on the mesopores of the silica templates. Moreover, by raising the temperature to 100 °C the impregnated PF resin can isotropically polymerize to form a cross-linked frameworks of high rigidity, with precise replication the shapes and mesostructures of the silica templates. Upon properly tuning the resin/silica template ratio, the PF oligomers can be completely adsorbed into the mesopores without forming the template-free carbons.

Besides of mesoporous pure-carbons, a mixture of PF resin with other polymer precursors containing hetero-elements (such as N, O, S, etc.) would be performed to prepare the mesoporous carbons with tunable surface properties by introducing different hetero-elements and changing compositions [16]. These advanced mesoporous carbon materials with high composition-flexibility will be continuously developed.

4. Conclusion

In summary, we have used the cheap PF resin with high binding affinity with silica as a carbon source to conveniently prepare high-quality mesoporous carbons of different pore sizes, mesostructures and morphologies. The process enables a large-scale production of mesoporous carbons for potential applications. With a high-flexibility design on the solid silica templates [17,18], mesoporous carbons in various forms and dimensions would be efficiently prepared.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.matchemphys.2004.10.023](https://doi.org/10.1016/j.matchemphys.2004.10.023).

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