

A template method to control the shape and porosity of carbon materials

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Abstract

Template silica materials with novel structures were synthesized by a sol–gel process and were used for the preparation of carbon replicas. Because the silica templates have thick skeleton walls and large textural pores, they can be molded to the required shape and size without cracking and shrinkage. By utilizing such templates, morphology and porosity control of the carbon materials were easily achieved. Carbon materials in various shapes including cylinders, triangles, squares, loops, and pentagons have been produced, and their skeleton pores can be tailored from 6.5 to 7.6 nm. In addition, the textural pore size of the carbon materials is tunable in the range of several micrometers.

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1. Introduction

Porous carbon materials with high surface areas and large pore volumes are widely employed in many fields of science and technology, including catalysis, purification, energy storage and separation [1,2]. Originally they were prepared by carbonizing various hydrocarbons such as wood, phenol resin [3], a copolymer of styrene and divinylbenzene etc. Generally these carbon materials were irregular and exhibited small pores or broad pore size distributions, which limited their applications. Modern industry needs carbon materials with a definite macroscopic morphology, a suitable pore size as well as a narrow pore size distribution.

Currently there is a tendency to use a template method for producing carbon materials. In 1997 Kamagawa and Yoshida [4] prepared swelling carbon beads using silica gel as template. Kyotani and coworkers [5,6] reported the preparation of ordered microporous carbons in zeolite nanochannels. Later Ryoo and coworkers [7–10] reported the synthesis of ordered mesoporous carbons of the CMK family using ordered mesoporous

silica particles such as MCM-48, SBA-1, and SBA-15 as templates. Pinnavaia and coworker [11] have prepared C-MSU-H using MSU-H as a hard template. Yoon et al. [12] synthesized carbon molecular sieves by carbonizing divinylbenzene polymer in the pores of trimethylsilyl chloride modified MCM-48. Hyeon and coworkers [13,14] demonstrated that mesoporous carbons could be prepared by using silica sols as templates. In addition, Hyeon and coworkers [15–17] also reported the preparation of carbon foam and carbon with bimodal pores by using approximate silica templates. Due to the ordered or homogeneous structures of the silica templates, the obtained carbon materials usually exhibited narrow pore size distributions.

Though carbon materials with narrow pore size distributions have been synthesized, most of them are in the form of powder and their pore sizes cannot be freely tailored due to the silica template limitation. For the development of their actual application, it is necessary to fabricate them into various macroscopic shapes with tunable pore sizes. Recently, several groups [18–21] have reported the synthesis of carbons with monolithic shape. Ryoo et al. [22] have attempted to adjust mesopore size of carbon materials. However, it is far from enough because various shaped carbons with tunable pore size in a wide range are required for different applications.

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A silica monolith, which was prepared by Nakanishi and Soga [23,24] via the combination of phase separation and sol–gel processes, exhibits both co-continuous structure and textural porosity; the co-continuous structure results from the interconnected silica skeletons and the interconnected textural pores with their size of several micrometers, while the skeleton pores exist in the silica skeletons with the pore size in the nanometer scale. Furthermore, the shape and textural pore/skeleton pore size of the silica monolith are easily controlled by the adjustment of the preparation conditions. The unique property of the silica monolith presents itself an attracting template for carbon replica.

Here, we adopted such a template and realized morphology and pore size control of carbon materials.

2. Experimental

2.1. Materials and reagents

Tetramethoxysilane (TMOS) was obtained from the Chemical Factory of Wuhan University (Wuhan, China). Acetic acid, ethanol, sulfuric acid, sucrose and poly (ethylene glycol) (PEG, $M_w = 10,000$) of analytical grade were purchased from Shanghai General Chemical Reagent Factory (Shanghai, China). Water was distilled from a quartz apparatus.

2.2. Preparation of silica monoliths

The silica monolith was prepared according to the previous reported method with modification [25]. Generally, TMOS, PEG and acetic acid were mixed together at 273 K until a homogeneous solution was obtained. Then it was transferred into containers with different shapes and incubated in a water bath for reaction. The temperature of the water bath was controlled accurately through a thermometer. The RSD of the temperature accuracy was ± 0.2 K.

Gelation within the containers for 20 h led to formation of wet silica gels. After being aged in situ for additional 48 h, the wet gels were flushed sequentially with massive water and ethanol to remove any possible residues. Subsequently, they were carefully dried and sintered at 873 K for 2 h. Finally rigid silica monoliths were obtained and were ready for further use. The details of the reaction parameters were summarized in Table 1.

2.3. Preparation of carbon monoliths

For the synthesis of carbon monoliths, the silica monoliths were impregnated with aqueous solution containing sucrose and sulfuric acid (sucrose: sulfuric acid: water = 2.5 g: 0.3 g: 10 ml). After being dried, it was thermally treated at 433 K for 5 h. Then the same procedures were repeated until no infiltration could be observed. Subsequently, the composite materials were carbonized at 1223 K for 5 h under inert atmosphere. Finally, the carbon monoliths were liberated by dissolving the silica framework in a boiling 1.0 mol/l NaOH solution.

2.4. Scanning electron microscope

Scanning electron microscope (SEM) experiments were performed with Hitachi (Tokyo, Japan) Model X-650 Scanning Electron Microscope instrument. Slices of cross sections were cut off from the silica monoliths and the carbon monoliths, and vapor-deposited with gold for scanning electron microscope analysis at 25 kV.

2.5. Surface area and pore size analysis

Nitrogen sorption experiments were carried out at 77 K using a Coulter (Florida, USA) SA 3100 Plus surface area and pore size analyzer. The monolithic samples were activated by evacuating in vacuum and heating to 473 K for 10 h to remove any physically adsorbed substances before analysis. The specific surface

Table 1
The starting compositions of reactants and codes assigned for monoliths and carbons

TMOS	PEG (g)	CH ₃ COOH (ml, pH 3.0)	Temperature (K)	Silica
Carbon-1				
6	0.9	10	313	Silica-1
Carbon-2				
6	1.0	10	313	Silica-2
Carbon-3				
6	1.1	10	313	Silica-3
Carbon-A				
6	1.1	10	308	Silica-A
Carbon-B				
6	1.1	10	313	Silica-B
Carbon-C				
6	1.1	10	318	Silica-C

area values were calculated according to the BET (Brunauer–Emmett–Teller) equation at P/P_0 between 0.05 and 0.2. The pore parameters (pore volumes and pore diameters) were evaluated from the desorption branches of isotherms based on BJH (Barrett–Joyner–Halenda) model.

2.6. X-ray photoelectron spectroscopy, gravimetric analysis and X-ray powder diffraction analysis

X-ray photoelectron spectroscopy (XPS) and gravimetric analysis were performed on a carbon monolith to determine the possible silica residue after NaOH treatment. XPS experiment was carried out with an X SAM 800 instrument (Katos, British). For the measurement, the carbon monolith was ground into powder. The gravimetric analysis was performed by a combustion method. In the process, a carbon monolith with known weight was exposed to air and underwent heat treatment at 1073 K for 3 h. After cooling in a desiccator, the residue was weighed and used to measure the silica content in the carbon monolith. X-ray powder diffraction (XRD) experiment was carried out on a Shimadzu Lab X-3000 (Shimadzu, Japan) to investigate the internal array of the carbon monoliths.

3. Results and discussion

3.1. The composition and atomic array of the carbon monoliths

A carbon monolith was chosen as a representative for XPS analysis to determine the silica residue. XPS at all areas including the surface and the interior show signals of carbon and oxygen, and Si element can be hardly detected, indicating that the silica ingredient has been removed from the silica–carbon composite. In order to confirm the conclusion, gravimetric analysis was adopted. After calcination, the carbon was totally burned off while the possible silica would be left. By weighing the carbon monolith and the residue, quantities result could be obtained. It was found from the result that the silica remains was only 0.1% (w/w) of the total carbon monolith. Therefore, we can believe that the silica component has almost been totally removed from the silica–carbon composite by NaOH corrosion. The XRD pattern of the carbon monolith shows no obvious Bragg lines in the region 2θ greater than 10° , suggesting the carbon is amorphous.

3.2. Shape control of the carbon monoliths

Fig. 1 shows a photograph of the silica monoliths and their corresponding carbon replicas in different morphologies. It can be seen that the carbon replicas are

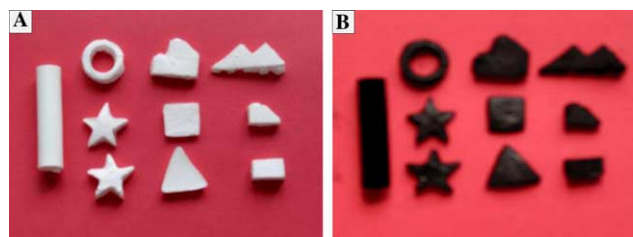


Fig. 1. Photograph of the silica templates (A) and the corresponding carbon replicas (B).

almost identical to their hard templates in shape and size. No cracking or shrinkage was observed for the silica templates and their carbon replicas.

Since the silica templates result from sol–gel conversion, it can be molded in different shapes. By choosing such templates, various shaped carbons can be easily obtained to achieve morphology control of carbon materials. Though the silica monolith produced from silica sols has been used as templates for preparation of carbon monoliths [18], the silica monolith generally suffered from cracking and shrinkage due to the lack of large-dimension-sized textural pores. Therefore, the carbons they obtained were generally in the monolith form with small size. However, using the templates we proposed, the shape and size of the final carbons could be freely tailored. For example, the dimension size of the cylindrical silica and carbon in Fig. 1 are 45 mm in length and 16 mm in diameter. This result can be ascribed to the novel structure of the silica templates we used. As mentioned above, the silica templates possess thick skeleton walls and large textural pores; the thick skeleton walls prevented the silicas from shrinkage, while the large textural pores decreased the capillary pressure, and thus avoided cleft of the silica materials. Therefore, the silica can be molded in different forms and sizes; then shape control of carbon materials can be achieved by the proposed method.

3.3. Textural pore size control of the carbon monoliths

Fig. 2 shows scanning electron micrographs for the Carbon-1, Carbon-2 and Carbon-3 that were prepared by using Silica-1, Silica-2 and Silica-3 (as shown in Table 1) as templates, respectively. From Fig. 2, the interconnected skeletons and interconnected textural pores can be easily observed, and the textural pore size and the skeleton size of the carbons decrease in the order of Carbon-1 > Carbon-2 > Carbon-3. This phenomenon can be ascribed to the characteristics of their silica templates.

As shown in Table 1, the silica templates were prepared with different PEG content. The PEG has dual functions in the sol–gel process. One is porogenic function and the other is phase separation inducing function. In previous papers, it has been demonstrated

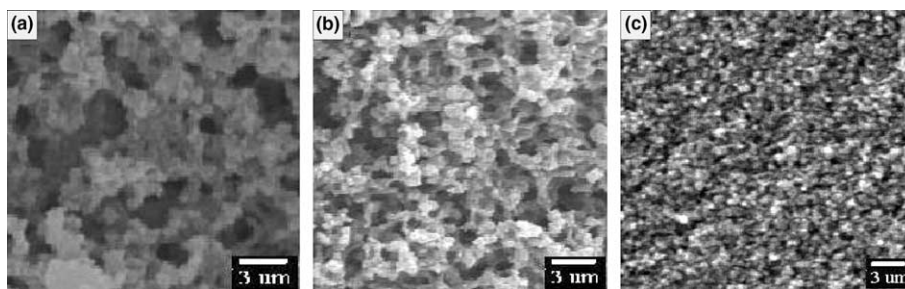


Fig. 2. Scanning electron micrographs for (a) Carbon-1, (b) Carbon-2 and (c) Carbon-3.

that the phase separation speed is inverse proportional to the PEG content [25,26]. The more the PEG content the slower is the phase separation speed. Slow speed of phase separation would result in fine silica skeletons and fine textural pores for the silica material. Therefore, increasing the PEG content leads to the decrease in the size of silica skeletons and textural pores. From Silica-1 to Silica-3, the PEG content for their preparation increased, and then the skeleton sizes as well as the textural pore sizes of them decreased (details please refer to reference [25]).

The micrometer-sized textural pores of these silica materials provide channels for liquid infiltration. Sucrose solution can easily penetrate into the pores and fill them. In the following drying and temperature treatment, the sucrose in the pores was dehydrolyzed by the sulfuric acid, leading to the formation of carbon residues adsorbed onto the silica surface. After repeated infiltration and dehydration, the sucrose carbon stuffed the textural pores of the silica templates. The further high temperature treatment made the sucrose carbon cross-link into a three dimensional solid network that occupied the textural pores of the silica templates. Subsequently, the silica templates in the composites were removed by an alkaline treatment, leading to the formation of carbon replicas with co-continuous structures. Therefore, the shapes and porosity of the carbons prepared by the proposed method can be predetermined according to the silica templates. Due to the decrease in the silica skeleton sizes from Silica-1 to Silica-3, the textural pore sizes of the carbons also decreased from Carbon-1 to Carbon-3. Therefore, the textural pores of the carbon materials can be easily tailored by choosing suitable templates.

3.4. Tailoring skeleton pores of the carbon monoliths

The skeleton pore sizes of the carbon monoliths were predetermined by the skeleton wall thickness of the silica templates. So controlling the skeleton wall thickness of the silica templates is an effective way for the preparation of carbon monoliths with various skeleton pore sizes. We have found that the sol–gel transition speed accounts for the skeleton wall thickness of the silica

materials; the increase in the speed of the sol–gel transition leads to a decrease in skeleton wall thickness of the silica monoliths. So silica monoliths were prepared at different temperatures, as shown in Table 1.

Fig. 3 shows the nitrogen adsorption and desorption isotherms of the silica monoliths synthesized under different temperatures. Obviously, the isotherm of Silica-A is type IV while the isotherms of Silica-B and Silica-C belong to type II. All the isotherms show capillary condensation at medium relative pressures, suggesting the skeleton pores in these silicas are mainly composed of mesopores. It can also be seen from Fig. 3 that, as the reaction temperature increases, the hysteresis loops of the isotherms shifts to higher relative pressures, which indicates that the skeleton pore sizes increase with the increase in the reaction temperature. The inset is the skeleton pore size distribution curves of the silica monoliths calculated from the desorption branches of the isotherms. Apparently, the major of the skeleton pores lie in the mesopore range.

By utilizing templates of Silica-A, Silica-B and Silica-C, carbon monoliths (Carbon-A, Carbon-B, and Carbon-C) with different skeleton pore sizes were easily synthesized. Their nitrogen adsorption–desorption iso-

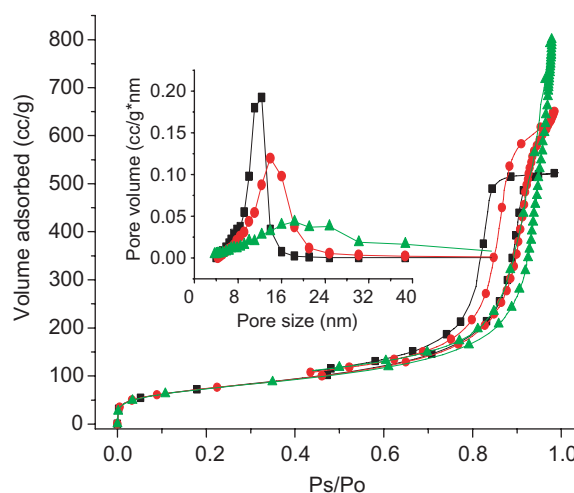


Fig. 3. Nitrogen adsorption–desorption isotherms for the Silica-A (—■—), Silica-B (—●—) and Silica-C (—▲—); Inset: pore size distribution curves from desorption branches for them.

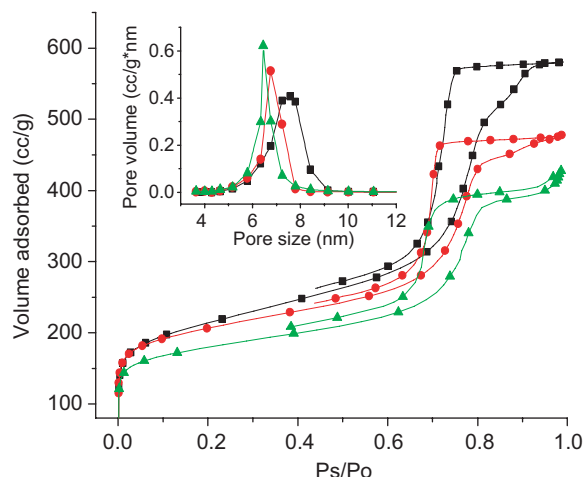


Fig. 4. Nitrogen adsorption-desorption isotherms for the Carbon-A (—■—), Carbon-B (—●—) and Carbon-C (—▲—); Inset: pore size distribution curves from desorption branches for them.

therms are shown in Fig. 4. Apparently, all the isotherms belong to type IV of the IUPAC classification with H1 hysteresis loops. Comparing with their silica templates, all the carbons show remarkable adsorption uptake at pressures below 0.05 P_o , which is the signal of the existence of micropores. Another apparent adsorption uptake at relative pressures of 0.5–0.9 is ascribed to the capillary condensation of nitrogen in the mesopores of the carbon skeletons. As the relative pressure further increases to P_o , no adsorption increase can be observed, suggesting absence of macropores in the carbon skeletons. It can be seen from Fig. 4 that the hysteresis loops for the carbons lie in different relative pressure ranges. The skeleton pore size distributions (PSDs) of the carbons calculated from the desorption branches of the isotherms were plotted in the inset of Fig. 4. In comparison to the silica templates, the PSDs of the carbons are generally narrower than those of the silica templates. These results imply that the silica templates have the uniform skeleton wall thickness but relatively inhomogeneous

skeleton pores. The mean skeleton pore size, BET surface area, pore volume for the silica templates and carbon replicas are listed in Table 2.

It can be seen from Table 2 that the mean skeleton pore sizes of the carbon monoliths decrease from Carbon-A to Carbon-C, which is a reflection of the skeleton wall sizes of their templates (Silica-A, -B, -C). Therefore, temperature control for silica preparation is an alternative method for preparation of carbon monoliths with different skeleton pore sizes.

4. Conclusions

A template method has been used for the preparation of carbon materials of various shapes and pore sizes. The shapes of the carbons are predetermined by the forms of the silica templates, while the skeleton pore size and textural pore size of the carbons are predicted by the skeleton wall thickness and the total skeleton size of the silica templates. By delicate template selection, carbon monoliths in cylindrical, triangular, square, loop, and pentagonal shapes can be synthesized, with their skeleton pore size varying from 6.5 to 7.6 nm and textural pores ranging from one micrometer to several micrometers.

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Table 2

The mean skeleton pore size, BET surface area and pore volume for the silica templates and the carbon replicas

Pore volume (ml/g)	Mean skeleton pore size (nm)	BET surface area (m ² /g)
Silica-A 0.80	12.3	270
Silica-B 1.01	14.0	267
Silica-C 1.24	18.3	260
Carbon-A 0.69	7.6	747
Carbon-B 0.52	6.8	716
Carbon-C 0.47	6.5	624

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