

Template Synthesis of Three-Dimensional Cubic Ordered Mesoporous Carbon With Tunable Pore Sizes

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Abstract Three-dimensional cubic ordered mesoporous carbons with tunable pore sizes have been synthesized by using cubic *Ia3d* mesoporous KIT-6 silica as the hard template and boric acid as the pore expanding agent. The prepared ordered mesoporous carbons were characterized by powder X-ray diffraction, scanning electron microscopy, transmission electron microscopy, and nitrogen adsorption–desorption analysis. The results show that the pore sizes of the prepared ordered mesoporous carbons with three-dimensional cubic structure can be regulated in the range of 3.9–9.4 nm. A simplified model was proposed to analyze the tailored pore sizes of the prepared ordered mesoporous carbons on the basis of the structural parameters of the silica template.

Keywords Template synthesis · Mesoporous carbon · Mesoporous silica · Pore size control · KIT-6

Introduction

In recent years, ordered mesoporous carbons (OMCs) with uniform pore sizes, high surface areas, and large pore volumes have been of wide interest for applications in

many fields, such as catalyst supports, adsorbents, fuel cells, and electrodes for supercapacitors [1–3]. The hard template method has been successfully developed in the synthesis of OMCs. Since the emergence of numerous mesoporous silica materials, OMCs with various pore structures and narrow pore size distributions have been achieved by replicating the structures of mesoporous silica materials. The first OMC, CMK-1, was synthesized by Ryoo et al. [4] using MCM-48 silica (*Ia3d*) as a hard template. After that, ordered mesoporous silica materials with diverse symmetries, such as SBA-15 (*p6mm*) [5, 6], SBA-16 (*Im3m*) [6], KIT-6 (*Ia3d*) [7, 8], and FDU-12 (*Fm3m*) [9], were also employed to prepare OMCs.

The hard template synthesis procedure of OMCs involves impregnation of the silica template, carbonization of the carbon precursor, and removal of the silica template [1]. The structure of the OMC, such as the pore shape and the pore size, was determined by the silica template. It is believed that OMCs with tunable pore size distributions would be beneficial for various applications. Ryoo et al. reported the synthesis of mesoporous silicas with controllable pore wall thicknesses of 1.4–2.2 nm, which were further used as templates to synthesize OMCs with tailored pore diameters of 2.2–3.3 nm [10]. Alvarez et al. [11] modulated the pore sizes of mesoporous carbons within the range of 2–10 nm by changing the synthesis temperature of the silica template. However, the synthesis procedures of silica templates with different properties were tedious and difficult to precisely control.

Recently, Lee et al. [12] reported the synthesis of two-dimensional (2-D) hexagonal OMCs with controllable pore sizes in the range of 3–10 nm using MSU-H silica as the hard template and boric acid as the pore expanding agent, which was considered to be a facile method for the pore size control of OMCs. The pore expansion was realized by

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the spontaneous phase separation of the boron species from the boron and carbon precursors to the silica surface. Besides, the pore size was determined by the amount of the boric acid added to the carbon precursor. Herein, on the basis of this method, we report the synthesis of three-dimensional (3-D) cubic OMCs with tunable pore size distributions using KIT-6 silica as the template and boric acid as the pore expanding agent. Compared with MSU-H silica, KIT-6 silica exhibits 3-D cubic structure with *Ia3d* symmetry, which consists of the interpenetrating bicontinuous channel networks. We demonstrated that the aforementioned synthesis pathway could be generalized to prepare OMCs with various structures and symmetries using different mesoporous silicas as templates. Moreover, we quantitatively analyzed the pore expansion mechanism using a simplified model on the basis of structural parameters of the silica template.

Experimental Section

Chemicals

The poly(alkylene oxide)-based triblock copolymer Pluronic P123 (EO₂₀PO₇₀EO₂₀, MW = 5,800) and tetraethyl orthosilicate (TEOS, 98 wt%) were purchased from Aldrich Chemical Inc. Other chemicals were purchased from Shanghai Chemical Corp. All chemicals were used as received without further purification.

Synthesis of KIT-6 Silica

The synthesis of mesoporous KIT-6 silica with cubic *Ia3d* symmetry was performed according to the literature procedure reported elsewhere [8]. Typically, 5 g of Pluronic P123 was dissolved in 180 g of distilled water and 9.9 g of HCl solution (35 wt%) under vigorous stirring at 35°C. After complete dissolution, 5 g of *n*-butanol (99.4 wt%) was added. Following further stirring for 1 h, 10.75 g of TEOS was added immediately. Subsequently the mixture was left stirring at 35°C for 24 h and transferred into an autoclave, which was sealed and maintained at 100°C for another 24 h under static conditions. The resulting solid product was filtered and dried at 100°C overnight. After a brief ethanol/HCl washing, the final sample was dried at 70°C and calcined at 550°C for 6 h in air.

Synthesis of Ordered Mesoporous Carbons

Ordered mesoporous carbon materials were synthesized using the recipe described previously [4, 12]. KIT-6 and sucrose were used as the template and the carbon precursor, respectively. Various amount of boric acid were added to

the carbon precursor while keeping the sucrose concentration constant. The carbon replicas were designated as OMC-*x*, where *x* stands for the molar ratio of boric acid to sucrose. In a typical synthesis of OMC-1, 0.113 g of boric acid (99.5 wt%), 0.625 g of sucrose (95 wt%), and 0.071 g of sulfuric acid (98 wt%) were dissolved in 2.5 g of distilled water. After 0.5 g of KIT-6 silica was added, the mixture was heated at 100°C for 6 h, and subsequently at 160°C for another 6 h. The resulted composite was impregnated again with an aqueous solution consisting of 0.075 g of boric acid, 0.413 g of sucrose, 0.047 g of sulfuric acid, and 2.5 g of distilled water. After the heat treatment at 100°C and 160°C once again as before, the composite was carbonized at 900°C for 3 h under N₂ flow. Finally, the OMC-1 material was obtained by the removal of the silica template using 5 wt% HF solution at room temperature.

Characterization

Low-angle X-ray diffraction (XRD) was carried out on a Bruker D8 advance X-ray diffractometer using Cu K α radiation. Scanning electron microscopy (SEM) images were obtained with a Hitachi S-4800 scanning electron microscope operating at 10 kV. Transmission electron microscopy (TEM) images were taken on a JEOL JEM-2100 microscope operated at 200 kV. Nitrogen adsorption–desorption isotherms were measured on a Micromeritics ASAP 2010 volumetric adsorption analyzer at 77 K.

Results and Discussion

Figure 1 illustrates the XRD patterns of the KIT-6 silica and the carbons with tailored pore sizes. The KIT-6 silica exhibits well-resolved *hkl* reflections, which is characteristic of highly ordered 3-D cubic *Ia3d* symmetry. The OMCs with different pore sizes also exhibit cubic structure, which is similar to that of the KIT-6 silica template. Moreover, the d_{211} spacings of all OMC samples only varied slightly when the molar ratio of boric acid to sucrose was increased from 0 to 12. Figure 2 shows SEM and TEM images of KIT-6 and OMC-4. As can be seen in the Fig. 2a and b, the morphology of the OMC-4 is close to that of the mesoporous silica template. The cubic structures of the silica and carbon products were further demonstrated by the representative TEM images of KIT-6 and OMC-4 shown in Fig. 2c and d, respectively.

N₂ adsorption–desorption isotherms and the corresponding pore size distributions determined from the adsorption branches for KIT-6 silica and the OMCs are shown in Fig. 3. All samples represent type IV isotherms with a sharp capillary condensation step, which is

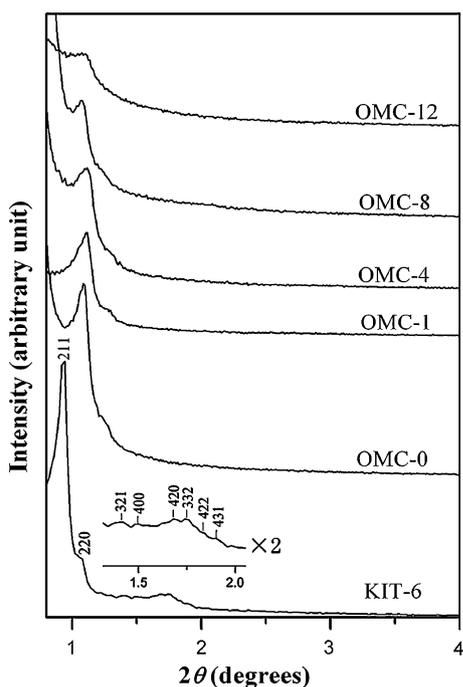


Fig. 1 XRD patterns of KIT-6 silica and the OMCs

indicative of a uniformity of mesopore size. For the OMC-0 replica of KIT-6 with no boron content in the carbon precursor, the capillary condensation step occurs at a relative pressure of about 0.4, which is consistent with the results reported elsewhere [13–15]. As the boron content increases, the position of the step gradually shifts to higher relative pressures, which reflects the effect of the boric acid on the pore size control. The systematic increase of the mesopore size with increasing the boron content in the carbon precursor was further confirmed by the pore size distribution curves of the prepared OMCs shown in Fig. 3b. All carbon replicas exhibit narrow pore size distributions except OMC-12, which has some deterioration of the mesostructure as convinced by the XRD pattern in Fig. 1. The structural properties of KIT-6 silica and the OMCs are summarized in Table 1. The prepared OMCs with tailored pore sizes possess the pore diameters of 3.9–9.4 nm.

We proposed a simplified model to quantitatively analyze the pore expansion of the as-synthesized OMCs. Figure 4 illustrates the schematic drawing of the pore expansion model for the synthesis of the OMC with tailored pore size. The d_0 and a_0 is the pore diameter and unit cell parameter of KIT-6 silica, respectively, and the w_0 is the wall thickness of KIT-6 silica, which is equal to $a_0/2 - d_0$. It is assumed that the boric acid and the sucrose are separated after the co-infiltration of the boric acid together with the sucrose, although the spontaneous phase separation of the boron species will occur during the

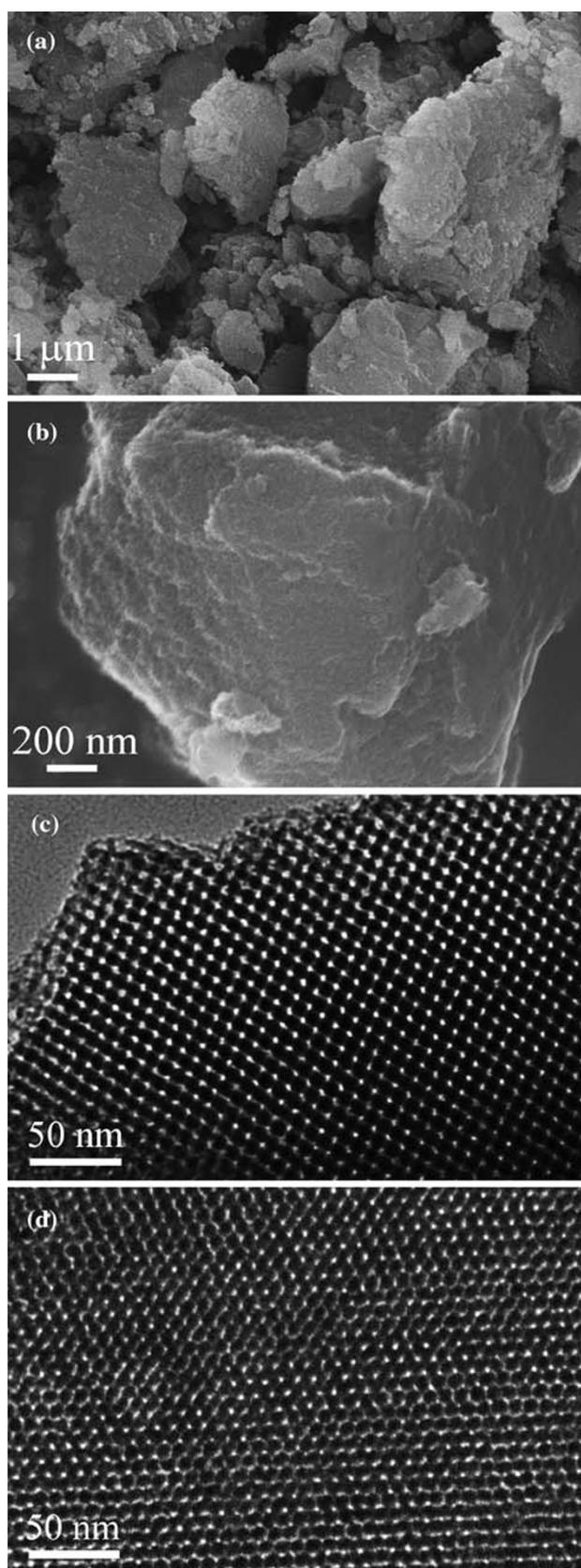


Fig. 2 SEM images of **a** KIT-6 and **b** OMC-4. TEM images of **c** KIT-6 and **d** OMC-4

Fig. 3 **a** N₂ adsorption–desorption isotherms for KIT-6 silica and the OMCs. The sorption isotherms for the OMC-0, OMC-1, OMC-4, OMC-8, and OMC-12 have been shifted vertically by 50, 550, 750, 1,200, and 1,450 cm³/g, respectively. **b** The corresponding pore size distributions for KIT-6 silica and the OMCs calculated from adsorption branches using the BJH algorithm

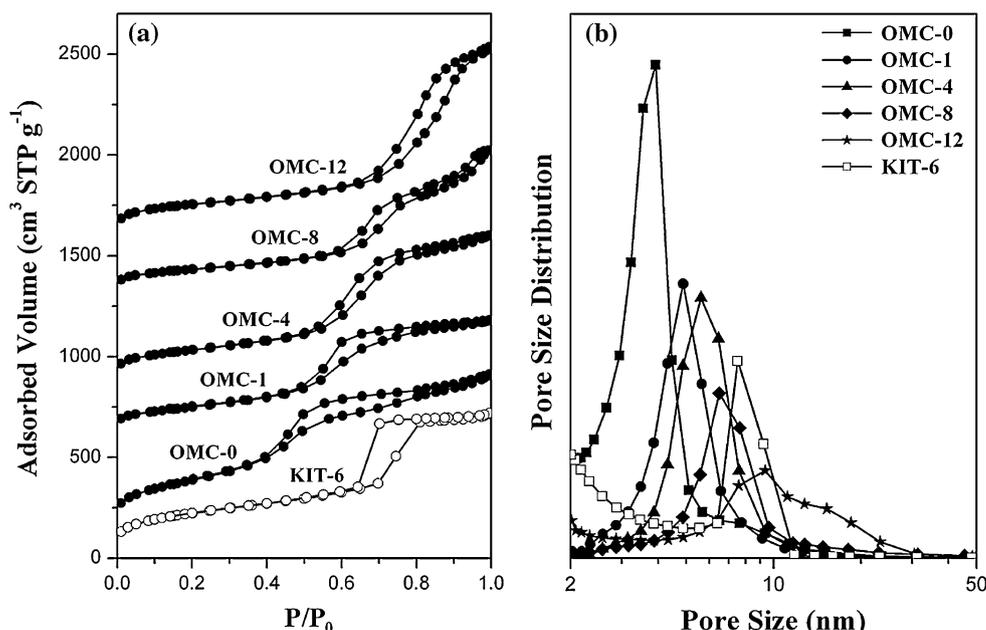
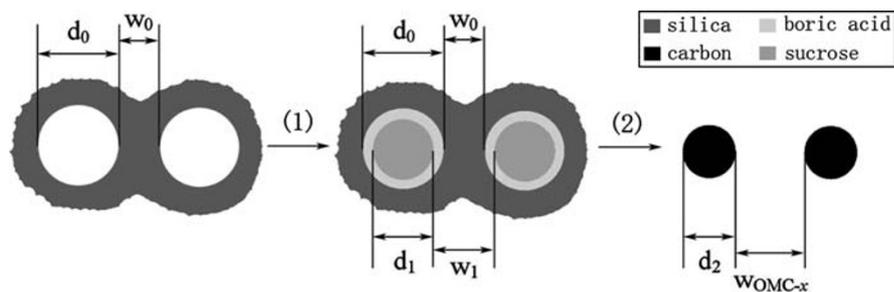


Table 1 Structural properties of KIT-6 silica and the OMCs

Samples	<i>a</i> ₀ (nm)	<i>d</i> ₀ (nm)	<i>S</i> _{BET} (m ² /g)	<i>S</i> _{micro} (m ² /g)	<i>V</i> _{tot} (cm ³ /g)	<i>V</i> _{micro} (cm ³ /g)
KIT-6	22.4	7.5	790.2	105.4	1.11	–
OMC-0	19.9	3.9	1,188.3	217.9	1.33	0.10
OMC-1	19.4	4.9	692.7	200.1	0.98	0.09
OMC-4	19.4	5.7	955.8	435.6	1.32	0.21
OMC-8	20.1	6.6	779.2	404.2	1.27	0.19
OMC-12	20.1	9.4	1,017.9	550.5	1.68	0.27

XRD unit-cell parameter *a*₀ is equal to 6^{1/2}*d*₂₁₁; *d*₀ is the pore diameter calculated from the adsorption branch of the isotherm using the BJH method; *S*_{BET} is the specific surface area using the BET method; *S*_{micro} is the micropore surface area; *V*_{tot} is the total pore volume at relative pressure of 0.99; *V*_{micro} is the micropore volume

Fig. 4 Schematic drawing of the simplified pore expansion model for the synthesis of the OMC with tailored pore size. 1 Co-infiltration of boric acid and sucrose. 2 Carbonization and removal of the silica template. The pore interconnectivity existed in the silica and the carbon replica is not shown



carbonization process [12]. On the assumption that *x* is the molar ratio of boric acid to sucrose, according to the relationship between the volume ratio and the molar ratio, we can deduce that the *d*₁ is equal to (1 + 0.2*x*)⁻³*d*₀, and then the distance *w*₁ is equal to *w*₀ + *d*₀ - *d*₁. In the synthesis of the OMC using the sucrose as the carbon precursor, the shrinkage of the carbon structure during the carbonization process was evidenced by the data reported elsewhere and the percentage of shrinkage of the structure *η* was estimated to be 10–15% [12, 13]. Thus, the diameter

of the carbon rod *d*₂ is estimated to be (1 - *η*)*d*₁ after the carbonization process, and the pore diameter of OMC-*x* with tailored pore size is expressed as:

$$w_{\text{OMC-}x} = w_0 + [1 - (1 - \eta)(1 + 0.2x)^{-3}]d_0 \quad (1)$$

According to the Eq. 1, the pore diameters of OMC-1, OMC-4, OMC-8, and OMC-12 are estimated to be 4.85–5.2, 5.65–5.96, 6.3–6.57, 6.71–6.96 nm, respectively. The estimated values are mainly coincident with the data shown in Table 1 except for OMC-12, which exhibits a greatly

broader pore size distribution due to the structural deterioration.

On the basis of the unit cell parameter and the pore diameter of KIT-6 silica, we estimated the pore diameter of the prepared OMC. OMCs with more precisely controlled pore sizes can be synthesized according to the estimated values calculated from the Eq. 1 with proper molar ratio of boric acid to sucrose. It should be noted that the aforementioned derivation is simplified. The practical volume changes during the carbonization and the spontaneous phase separation of the boron species were neglected. Moreover, the pore size analysis performed using the BJH method is applicable for cylindrical mesopores [16, 17], whereas the inverse carbon replica of KIT-6 exhibits rod-type structure [7]. It results in the overestimation of the pore widths of the prepared OMCs, which was also ignored in the derivation.

Conclusions

In summary, we synthesized 3-D cubic OMCs with tunable pore sizes in the range of 3.9–9.4 nm by using KIT-6 silica as the hard template and boric acid as the pore expanding agent. The pore expansion method reported by Lee et al. was demonstrated to be effective on the preparation of OMCs with different pore symmetries and tunable pore sizes. According to a simplified model, we deduced the carbon pore size equation that is expected to direct the synthesis of OMCs with tunable pore sizes on the basis of this synthesis pathway. The present work is expected to be helpful for the synthesis of OMCs with other pore structures by using other kinds of silica templates. Further, the

practical application of the prepared 3-D cubic OMCs in energy storage is under investigation and will be reported in the future.

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