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Synthesis of ordered mesoporous carbons with tunable pore size by varying carbon precursors via soft-template method

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ABSTRACT

Ordered mesoporous carbons (OMCs) with tunable pore size in the range of 3.6–6.2 nm were prepared using the mixture of phenol, resorcinol and phloroglucinol as carbon precursor and triblock copolymer F127 as template via self-assembly method. The OMCs had ordered 2-D hexagonal mesostructure with high specific surface areas (up to 1100 m^2/g) and pore volume (up to 0.84 cm^3/g). Nitrogen sorption results demonstrated that the pore size of OMCs can be tuned by varying the composition of carbon precursors and the mass ratio of carbon precursor-to-F127. Systematic research revealed that increasing amount of resorcinol and phloroglucinol in carbon precursors resulted in carbons with larger pore size but less ordered mesostructure. Compared with resorcinol, phloroglucinol facilitated a larger mesopore, while led to a worse mesostructure.

1. Introduction

The pore size of ordered mesoporous carbons (OMCs) has significant impacts on performances in many cases while they are used as catalyst support [1,2], hydrogen storage [3,4], CO_2 capture [5,6]. OMCs with various pore shapes and connectivity have been synthesized by nanocasting strategy with mesoporous silica as template [7–9]. Since the synthesized mesoporous carbon was the reversed replica of the silica template, the pore size of the resulting OMCs depends on the thickness of the silica walls, which is not easily tunable, and the pore diameters of OMCs are usually ca. 4 nm. In order to obtain smaller pore size, the mesoporous silica SBA-3 and HMS with thinner wall thickness can be used as template [10–12].

Recently, inspired by the successful preparation of ordered mesoporous silica via self-assembly, a series of OMCs have been prepared via organic–organic assembly using amphiphilic surfactant such as triblock copolymer F127, P123 et al. as soft template [13–17]. By using resol (prepared from phenol and formaldehyde with NaOH as catalyst) as carbon precursor, the pore size of the obtained OMCs is ca. 3 nm [14,18,19]. Similar to mesoporous silica, the pore size of OMCs from resol can be expanded from 3.1 to 4.1 nm by adding organic swelling agents. Moreover, OMCs with large pores can be prepared using unconventional block copolymers with large molecular weight, such as PS-P4VP [20], PEO-PS [21] and PEO-PMMA [22].

The pore size of OMCs from self-assembly decreases significantly during the carbonization due to structure shrinkage of the polymeric framework [14]. Resorcinol and phloroglucinol, as important derivatives of phenol, are also employed as carbon precursor in self-assembly method [23,24]. When using resorcinol or phloroglucinol as carbon precursor, a less shrinkage of polymer framework has been observed, which result in OMCs with larger pore size of ca. 5 nm [25]. Moreover, it has been reported that increasing concentration of acid [26,27] is in favor of reducing the shrinkage of polymer framework. OMCs with pore size ca. 6 nm are obtained under highly acidic conditions with resorcinol as carbon precursor. Likewise, a larger pore size of 19 nm is reported with phloroglucinol as carbon precursor, although the resulting mesoporous carbon has disordered mesostructure [27].

Furthermore, the mass ratio of carbon precursor-to-template has big influence on the pore size. Nishiyama et al. have pointed that the larger pore size has been obtained when increasing the amount of F127 template [25]. It is important for the applications of OMCs to tune the pore size systematically. However, it is still a great challenge to systematically tune the pore size of OMCs.

Herein we reported systematic control of the pore size of OMCs via self-assembly method by varying the carbon precursors. The mixtures of phenol (used as resol), resorcinol, and phloroglucinol

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are employed as carbon precursors. The pore size of OMCs can be tuned in the range from 3.6 to 6.2 nm. The resultant mesoporous carbons exhibited ordered 2-D hexagonal mesostructure with high specific surface areas and high pore volume. The effects of carbon precursors (phenol, resorcinol and phloroglucinol) on the pore size and ordered mesostructure of OMCs were investigated in detail.

2. Materials and methods

2.1. Chemicals

Triblock copolymer Pluronic F127 (M_w = 12600, EO_{106}-PO_{70}-EO_{106}) was purchased from Acros Corp. Phenol, resorcinol, phloroglucinol, formalin solution (~37 wt.%), sodium hydroxide, hydrochloric acid (12 M), and ethanol were purchased from Shanghai Chemical Corp. All chemicals were used as received without any further purification. Millipore water was used in all experiments.

2.2. Synthesis of resol precursors

Resol, a soluble low molecular weight resin, was prepared from phenol and formaldehyde in a base-catalyzed process according to the reported work [14]. The molar ratio of phenol/formaldehyde/NaOH was 1:2:0.1. In a typical procedure, 0.61 g of phenol was melted at 40–42 °C in a flask and then 0.13 g of 20 wt.% sodium hydroxide (NaOH) aqueous solution was added under stirring. After 10 min, 1.05 g of formalin (37 wt.% formaldehyde) was added dropwise below 50 °C. Upon further stirring for 1 h at 72–75 °C the reaction solution was cooled to room temperature. Then the pH value of the mixture was adjusted with 0.6 M HCl solution until it reached a value of about 7.0, and water was removed by vacuum evaporation below 50 °C. Finally the product was dissolved in ethanol to obtain resol solution in which the solid content was 20 wt.%.

2.3. Synthesis of OMCs

OMCs with different textural properties were synthesized by co-assembly of carbon precursors and triblock copolymer F127 via EISA (evaporation induced self-assembly) strategy. In a typical preparation, 4.0 g of block copolymer F127 was dissolved in 87.0 g of ethanol to afford homogenous solution. Next, 0.89 g of resorcinol and 1.02 g of phloroglucinol were added in sequence. After being stirred for 10 min, 202. μL of concentrated HCl (36–38 wt.%, 12 M), 2464 μL of formalin solution (37 wt.%) and 6.3 g of 20 wt.% resols solution were added in the above solution. The amount of HCl and formalin were fixed at 10 mol% and 200 mol% respectively to the total amount of phenol, resorcinol, and phloroglucinol. The formed homogenous solution was stirred at 30 °C for 60 min, followed by transferring into petri dishes. And it took 8–12 h at room temperature to evaporate ethanol and 24 h at 100 °C in an oven to thermopolymerize. The as-prepared products, flaxen to yellow transparent films, were scraped from the petri dishes and ground into fine powders. Carbonization was carried out in a tubular furnace at 900 °C for 3 h under nitrogen flow (flow rate of 100 mL/min) at the ramp of 1 °C/min below 600 °C and 5 °C/min between 600 and 900 °C. The carbon products were designated as *a*:*b*:*c*–*x*, where *a*:*b*:*c* represented the molar ratio of three carbon precursors of phenol, resorcinol, and phloroglucinol. And *x* was the mass ratio of total carbon precursors to block copolymer F127. For instance, the sample of 1:1:1-0.67 represented the OMCs obtained from the typical preparation described above in which contained 8.12 mmol of phenol, resorcinol and phloroglucinol respectively (total weight of 2.68 g) and 4.0 g of F127.

2.4. Characterization

Small angle X-ray diffraction (XRD) patterns were taken on a Bruker D8 X-ray diffractometer with Ni-filtered Cu K_α radiation (40 kV, 40 mA). The *d*-spacing values were calculated using the Braggs diffraction formula of $2d\sin\theta = n\lambda$, and the unit parameters were calculated from the formula $a = 2d_{10}/3^{1/2}$. The nitrogen adsorption–desorption isotherms were carried out at 77 K on a Micromeritics TriStar 3000 apparatus at −196 °C. Before analysis, the tested samples were degassed at 473 K for at least 6 h under vacuum. The surface area was calculated by the Brunauer–Emmett–Teller (BET) method and the pore size distribution curve was calculated by the Barret–Joyner–Halenda (BJH) method using adsorption branch of the isotherms. And the total pore volumes (V_t) were estimated from the adsorbed amount of nitrogen at a relative pressure P/P_0 of 0.995. The micropore volumes (V_m) was calculated from the *V*–*t* plot method using the equation of $V_m/cm^3 = 0.001547I$, where *I* represents the *y* intercepts in the *V*–*t* plots. The *t* values were calculated as a function of the relative pressure using the de Bore equation, $t/Å = [13.99/(\log(P_0/P) + 0.0340)]^{1/2}$. Transmission electron microscopy (TEM) experiments were conducted on a JEOL 2011 microscope (Japan) operated at 200 kV. The samples for TEM tests were suspended in ethanol and supported onto a holey carbon film on a Cu grid.

3. Results and discussion

3.1. Results

A series of OMCs have been prepared via self-assembly by using the mixtures of phenol, resorcinol and phloroglucinol as carbon precursors (Table 1). The carbon precursor compositions are varied by replacing part of phenol with resorcinol and phloroglucinol. The physicochemical properties of OMCs derived from different composition of carbon precursors are depicted in Table 1.

The XRD patterns (Fig. 1A) of all OMCs-1.0 synthesized with higher carbon precursor-to-F127 mass ratio (1.0) clearly show one intense diffraction peak near the 2θ values of 0.84–1.0, indicating an ordered mesostructure. Combined with TEM results (Fig. 3c and d), it proves that OMCs-1.0 have a hexagonal mesostructure as FDU-15 [14]. This indicates that replacing part of phenol with resorcinol and phloroglucinol has little effect on the mesophase of OMCs. While increasing the amount of resorcinol and phloroglucinol in carbon precursors, the diffraction peak shifts to lower 2θ value, corresponding to a larger unit cell parameter. As shown in Table 1, the unit cell parameter of OMCs increases from 9.4 nm to 10.5 nm by varying the molar ratio of phenol-to-resorcinol-to-phloroglucinol from 1:1:1 to 1:5:5. All the nitrogen sorption isotherms of the OMCs-1.0 (Fig. 2A) are of typical type IV with sharp capillary condensation steps and H_1-type hysteresis loops, indicating uniform mesopores with narrow pore size distributions (Fig. 2D). The pore size of OMC 1:1:1-1.0 calculated from the adsorption branch of isotherms by BJH model is 3.6 nm, which is slightly larger than that of FDU-15. It can be seen that the pore size of OMCs-1.0 increases from 3.6 nm to 6.2 nm with the increasing amount of resorcinol and phloroglucinol in Table 1, indicating that the use of resorcinol and phloroglucinol favors for large pore size. This can be attributed to the higher reactivity of resorcinol and phloroglucinol with formaldehyde, which formed more rigid polymer framework with higher crosslinking degree. Such rigid network preferably reduces the structure shrinkage during the carbonization, leading OMCs with larger pore size.

The influence of the mass ratio of carbon precursor-to-F127 on mesostructure is also studied. When the mass ratio of carbon precursor to F127 is decreased to 0.67, the XRD patterns of all of