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Ordered mesoporous carbons from the carbonization of sulfuric-acid-treated silica/triblock copolymer/sucrose composites

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Abstract

Ordered mesoporous carbon materials were successfully synthesized by the carbonization of sulfuric-acid-treated silica/triblock copolymer/sucrose composites. In the current approach, triblock copolymer P123 and sucrose were employed as both structure-directing agents for self-assembly of tetraethyl orthosilicate and carbon precursors, and sulfuric acid was used to cross-link P123 and sucrose in the as-synthesized composites in order to improve the carbon yield. When the weight ratio of sucrose relative to P123 was 1:4, ordered mesoporous carbon (C-S) with hexagonally arranged pore centered at 3.0 nm was synthesized. However, when the weight ratio was increased to 1:2, the obtained carbon material (C-S-1) exhibited low-ordered pore structure. In addition, thermogravimetric analysis revealed that C-S consisted of ca. 26 wt.% sucrose carbon and ca. 74 wt.% P123 carbon, and there was noticeable interaction between sucrose and P123, where P123 was a key substance for the formation of ordered mesostructure, and sucrose was responsible for the increased carbon yield.

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1. Introduction

Ordered mesoporous carbon (OMC) materials, fabricated using periodic inorganic silica templates, possess controllable pore size distribution and high surface area and have versatile applications in sorption and electrochemical reactors [1]. Generally, a long and complicated multi-step synthetic procedure (such as repeated impregnating) is involved in OMC formation. Therefore, several researchers independently reported some simple synthesis pathways. Yu et al. [2] synthesized an ordered mesoporous carbon using as-synthesized surfactant-included MCM-48 silica as hard template, and the surfactant molecules were used as carbon source. Thermogravimetric analysis indicated that the obtained carbon consisted of ca. 70–88% divinylbenzene (DVB) carbon and ca. 30–12% surfactant carbon.

Kim et al. [3] reported a simple synthesis route from the carbonization of silica/triblock copolymer composites. In this process, P123 ($EO_{20}PO_{70}EO_{20}$, the abbreviation of poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) triblock copolymer) was employed as both a carbon precursor and a structure-directing agent. Sulfuric acid was used as a catalyst for cross-linking of P123 in order to prohibit the prior formation of single nanotubes on the walls of the mesopores [4] and get an inverse replica of the mesostructure. Moreover, because of the deficiency of carbon source, the formed mesocellular carbon foam possessed ultra-large mesopores. Recently, several research groups have attempted to prepare mesoporous carbons by mixing micelle, another organic matter and silica source. Moriguchi et al. [5] reported the direct synthesis of mesoporous carbon material by in situ polymerization of DVB in the hydrophobic phase of a hexagonally arrayed micelle/silica nanocomposite. Lee et al. [6] synthesized a uniform mesoporous carbon directly from

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the carbonization of P123/phenol-resin/silica nanocomposite. Although the carbons obtained via the above two routes owned uniform mesopores, their pore structure was disordered and wormhole-like. To the best of our knowledge, studies on the surfactant as a carbon precursor are very scarce, and there is no report on ordered porous carbons obtained by removing the silica after the carbonization of silica/surfactant/polymer composites yet.

In our continuous efforts to develop a simple synthetic procedure for ordered mesoporous carbons, we used a combination of P123 and sucrose as both structure-directing agents and carbon precursors, where sucrose is a cheap and environmentally friendly carbon precursor. It is more important that both P123 and sucrose can be cross-linked together by sulfuric acid in order to improve the carbon yield. Herein, we report the new and simple route for OMCs directly from the carbonization of sulfuric-acid-treated silica/triblock copolymer/sucrose composites, followed by silica removal. The effects of the weight ratio of sucrose relative to P123 on the pore structure were investigated in detail by X-ray diffraction (XRD), nitrogen adsorption/desorption measurement and transmission electron microscopies (TEM and HRTEM). The transformation mechanism of sucrose and P123 to carbon was also elucidated by thermogravimetric analysis.

2. Experimental

2.1. Preparation of carbon materials

2.1.1. Direct synthesis of mesoporous carbon from sulfuric-acid-treated silica/P123/sucrose composite

Fig. 1 illustrates the synthesis strategy. First, sol–gel polymerization of silica in the presence of P123 and sucrose genera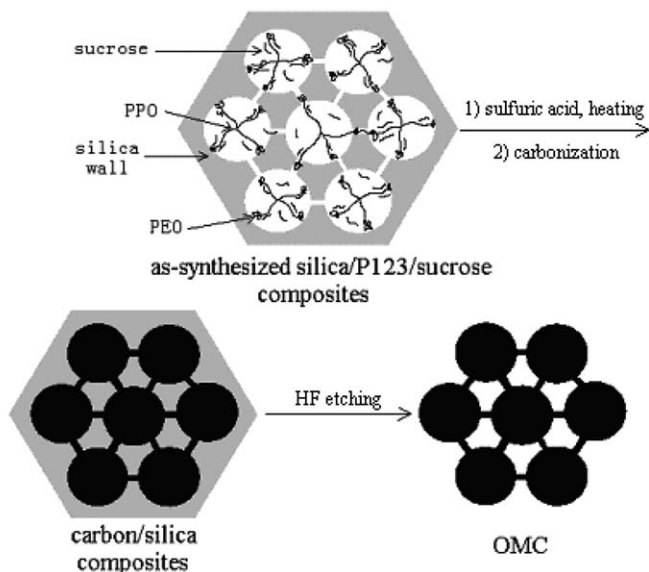tes silica/P123/sucrose composite. Subsequently, the composite is pre-treated by sulfuric acid and carbonized in order to convert the as-synthesized composite into carbon/silica composite. Finally, OMC is obtained by removal of the silica template. The key step is that P123 and sucrose are together partially cross-linked during the acid pre-treatment. That is, oxygen atoms of P123 [3,7,8] and sucrose [9] molecules are mostly eliminated in the form of H_2O because of dehydrating catalytic property of sulfuric acid.

The detailed synthetic procedure is as follows: (1) 4 g triblock copolymer P123 (Aldrich) and 1 g sucrose were together dissolved in 160 ml of 2 M hydrochloric acid solution at 40 °C. After 3 h, 9.2 ml tetraethyl orthosilicate (TEOS) was added under stirring, and the resultant solution was aged at 100 °C for 24 h. The molar ratio of TEOS:H_2O:HCl:P123:$C_{12}H_{22}O_{11}$ was 1:212:7.7:0.017:0.071. The resultant precipitate was filtered, washed and then dried at room temperature to obtain as-synthesized silica/P123/sucrose composite; (2) the composite (1 g) was mixed with a solution containing 10 ml of de-ionized water and 1 ml of sulfuric acid (98 wt.%). After stirring at room temperature for 12 h, the mixture was dried at 160 °C for 6 h; (3) the resulting dark brown material was carbonized under pure N_2 atmosphere at 850 °C for 2 h to realize the complete carbonization of P123 and sucrose; (4) the silica/carbon composite was treated by diluted HF solution to remove the silica and get the desired OMC, which is designated as C-S (the 'S' indicates sucrose). In addition, the silica template was obtained by calcining the as-synthesized composite in air at 550 °C in order to completely remove sucrose and P123, the resulting silica is designated as OMS. For the purpose of investigating formation mechanism of C-S, we synthesized C-S-1. The difference between C-S and C-S-1 is the weight ratio of sucrose relative to P123. C-S-1 was obtained when the weight ratio was increased to 1:2.

2.1.2. Direct synthesis of mesoporous carbon from sulfuric-acid-treated silica/P123 composite

The overall synthetic procedure is similar to that described for the synthesis of C-S, except no addition of sucrose. The resulting carbon [3,8] is designated as C-P (the 'P' indicates P123).

2.2. Characterization of materials

XRD patterns were recorded on a Rigaku D/max-2500B2+/PCX system operating at 40 kV and 20 mA using Cu Kα radiation ($\lambda = 1.5406$ Å). The interplanar spacing of ordered mesopores d is calculated from the Bragg's equation: $\lambda = 2d_{(hkl)}\sin\theta$ [10]. The unit cell parameter a_0 is calculated from $a_0 = 2 \times 3^{-1/2}d_{100}$ [11]. Nitrogen adsorption and desorption isotherms were performed at −196 °C on a Quantachrome NOVA 4200e volumetric adsorption system. The pore size distribution curve was calculated by the BJH (Barrett–Joyner–Halenda) method from the desorption branch. The specific surface area was calculated from the adsorption data in the relative pressure interval

Fig. 1. Proposed ordered mesoporous carbon formation mechanism.