Silica template synthesis of ordered mesoporous carbon thick films with 35-nm pore size from mesophase pitch solution

Li-Heng Kao, Tzu-Chien Hsu *

Institute of Materials Science and Engineering, National Sun Yat-sen University, Kaohsiung 80424, Taiwan

Received 22 May 2007; accepted 14 June 2007
Available online 19 June 2007

Abstract

Under a lower carbonization temperature and with a mesophase pitch solution as the carbon precursor, ordered mesoporous carbon thick films with 35-nm pore size have been synthesized using SiO₂ spheres as the template. The pore size of the mesoporous carbon thus fabricated was the smallest one ever reported using silica templates. XRD and Raman spectroscopy suggest a microstructure of carbon with low crystallinity. SEM and TEM patterns show a discernible morphology of an ordered hexagonal close-packing of the mesopores interconnected via holes of 6 nm in diameter. A fair BET surface area of 502 m²/g and a total pore volume of 0.861 cm³/g, along with the characteristic pore structure and hysteresis loop, are identified.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Ordered mesoporous carbon; Mesophase pitch solution; Silica template; Microstructure; Sol–gel preparation; Thick film

1. Introduction

Ordered mesoporous carbon materials have recently been studied extensively because of their potential applications in adsorption, catalysis, electrochemistry, and energy storage [1–4]. Among the various methods for fabricating porous carbon materials, the template method can uniquely afford a variety of porous frameworks with a wide range of pore size, well-defined morphology, and various chemical functionalities [5]. It has been reported that a zeolite template was used to prepare the microporous carbons (~0.1 nm), a periodic mesoporous silica (PMS) template for the mesoporous carbons (~3 nm), and a template of colloidal SiO₂ spheres for the macroporous carbons (>50 nm) [5–7]; this results in a gap of pore size in 3–50 nm range. There are gas and liquid routes to introduce the carbon precursors into the hard template; the former uses propylene or benzene as the carbon precursors via chemical vapor deposition; the latter uses sucrose or phenol oligomers [5,8]. Infiltrating into the interstitial regions of the hard template with desired carbon and non-carbon precursors has been recognized as a great challenge [9].

Using PMS (ordered) or colloidal SiO₂ spheres (random) as the template, the mesophase pitch powders have recently been adopted as the carbon precursors to prepare the mesoporous carbon materials; a highly graphitized carbon was reported as compared to those prepared by other carbon precursors [8,10,11]. These pitch powders were mixed with SiO₂ template, keeping the temperature slightly higher than their softening point and allowing the pitch particles to penetrate into the SiO₂ template and to form the silica-pitch composite; the mesoporous carbon was obtained after removal of the SiO₂ template.

In this work, thick films of ordered mesoporous carbon materials with 35-nm pore size having interconnected holes were fabricated using SiO₂ spheres as the template and a pitch solution as the carbon precursor. Combined with a micro-tube suction pump, this novel pitch solution approach offers an easy infiltration of carbon precursors into the interstitial regions of the hard template, making possible the fabrication of thick carbon films. It presents a facile and cost-effective fabrication process at a lower carbonization temperature in controlling the pore size of the porous carbon materials with unique microstructure and morphology.

2. Experimental section

2.1. Materials

Tetraethyl orthosilicate (TEOS, 98%, Arcos), anhydrous ethanol (C₂H₅OH, 99.9%, Arcos), and ammonia solution (NH₄OH, 28%,
crystallinity when compared to that of the crystalline graphite ($I_D/I_G = 0.1–0.3$). This result is consistent with the findings from XRD. The FE-SEM image (Fig. 3a) further reveals an ordered hexagonal close-packing of the mesopores with an average pore diameter of $\approx 35$ nm, which is the smallest one ever reported using silica templates. Worthy of note are the interconnected holes having a diameter $\approx 6$ nm (indicated by the upper arrow), which are located between the mesopores. There are also few scattered small openings with average diameter $< 15$ nm (indicated by the lower arrow). These occur at regular interstitial regions due mainly to incomplete infilling. A finer morphological feature identified by TEM showing the three-dimensional order of the interconnected mesopores is given in Fig. 3b. By measuring the average mesopore size from SEM image and comparing to the original particle size of the silica template, the shrinkage caused by the pyrolysis is found to be $\approx 33\%$ by volume.

A typical pair of isotherms is shown in Fig. 4, which represents a pore structure of type IV and a hysteresis loop of type H2, according to the definition by IUPAC. This ordered mesoporous carbon gives a fair BET specific surface area of $502 \text{ m}^2/\text{g}$ and a fair total pore volume of $0.861 \text{ cm}^3/\text{g}$, as compared to the reported data [6,7,10]. An extremely sharp rise of the capillary condensation takes place at a relative pressure of 0.953; whereas the capillary evaporation occurs at a much lower relative pressure of 0.877. This strongly indicates that the interconnected holes between the mesopores are much narrower than the mesopores themselves [7]. On the other hand, from the BJH analysis on the isotherms shown in Fig. 4 (inset), a broader pore size distribution with larger pore diameter (with maximum peak at 29.35 nm) can be found from the adsorption branch than those from the desorption branch (with maximum peak at 11.79 nm). This suggests an ink-bottle-like pore shape for the ordered mesoporous carbon.

4. Conclusions

We have demonstrated in this study a facile low-temperature fabrication route of ordered mesoporous carbon thick films with 35-nm pore size using silica spheres as the template and a pitch solution as the carbon precursor. With the aid of a micro-tube suction pump, problem of infilling the carbon precursor solution into the interstitial regions of the hard template is overcome, making possible the formation of thick carbon films with controllable pore sizes and with thickness up to few millimeters. Results from XRD and Raman spectroscopy suggest a low crystalline nature of the carbon material. An ordered hexagonal close-packing of the mesopores with 35 nm in diameter, interconnected by holes having 6 nm in diameter, is evidenced from SEM and TEM. The pore size of the mesoporous carbon from this study is the smallest one ever reported using the silica template. A pore structure of type IV with an ink-bottle-like pore shape and a hysteresis loop of type H2, exhibiting a BET surface area of $502 \text{ m}^2/\text{g}$ and a total pore volume of $0.861 \text{ cm}^3/\text{g}$, are identified from the nitrogen adsorption/desorption isotherm.