

Template-assisted synthesis of mesoporous tubular carbon nanostructure by chemical vapor infiltration method

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Abstract

A novel synthesis route for fabrication of tubule mesoporous carbon by chemical vapor infiltration method using a mesoporous silica template is reported. Powder X-ray diffraction and pore size analysis revealed that the nano-sized carbon material consists of three-dimensional framework structure and possesses a bimodal pore distribution with average pore diameters of 1.5 and 3.3 nm. The formation of the former pore is ascribed due to removal of the silica template, whereas the latter represents pore size of tubule carbon with ordered structure having an average wall thickness corresponding to about 1.3 layers of graphitic sheets, as verified by Raman spectroscopy and electron microscopy.

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1. Introduction

Porous carbon materials are potential candidates as supports for sensors or for electrocatalysts in proton exchange membrane fuel cells (PEMFCs) as well as adsorbents for fuel storage applications. In particular, owing to their unique physical and electrochemical properties, carbon nanotubes (CNTs) [1,2] and carbon mesoporous materials (CMMs) [3–6] have drawn much attention in R&D. Although various synthetic methods, viz. arc discharge [7], laser vaporization [8], and chemical vapor deposition (CVD) [9–11] have been developed in the past decade, utilization of a transition-metal catalyst is seemingly inevitable for CNT fabrication. On the other hand, CMMs were mostly synthesized through repeated carbonization process using mesoporous silicas as templates. More recently, Vix-Guterl and coworkers [12] reported a novel chemical vapor infiltration (CVI) process to deposit rod-type carbon within the channels of mesoporous MCM-48 (Mobil

Composite of Matters-48) silica having three-dimensional porous network with cubic (*Ia3d*) structure [13–16].

The objective of this study is to fabricate novel nano-sized mesoporous tubular carbon by CVI method using MCM-48 mesoporous silica as template. The structure and physical properties of this novel carbon material, denoted as CMT-1 (Carbon Materials from Taiwan-1), were characterized by X-ray diffraction (XRD), N₂ adsorption/desorption measurements, transmission electron microscopy (TEM), and Raman spectroscopy and will be compared to its analogue, namely CMK-1 (Carbon Materials from Korea-1).

2. Experimental

2.1. Material synthesis

The template material, namely mesoporous MCM-48 silica, was prepared following a hydrothermal synthesis procedure [15] with the following starting molar gel compositions: 5 SiO₂:1.5 NaOH:0.16 Brij-30 (C₁₂H₂₅(OCH₂CH₂)₄OH):0.84 C₁₆TMABr (hexadecyltrimethylam-

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monium bromide; $C_{16}H_{33}(CH_3)_3NBr$:400 H_2O . Briefly, aqueous solution of colloidal silica and sodium hydroxide was mixed with a homogeneous solution which consists of an ionic surfactant ($C_{16}TMABr$) and a neutral co-surfactant (Brij-30). The gel mixture was kept under hydrothermal condition (373 K) for 2 days. Subsequently, the pH of the gel was adjusted to 10 using glacial acetic acid, and then allowed for crystallization for additional 2 days. Finally, the resultant product was filtered, washed and then calcined in air at 833 K for 6 h to remove the surfactant.

The ordered mesoporous CMK-1 carbon material was obtained following the direct replication procedures reported earlier by Ryoo and co-workers [3,17–19]. First, MCM-48 was impregnated with sucrose solution in presence of sulfuric acid, carbonized at 373 K for 6 h, then at 433 K for additional 6 h. This procedure was repeated again before the sample was further subjected to graphitization by pyrolysis at 1173 K for 4 h under N_2 environment. The resultant CMK-1 material was obtained after removing the MCM-48 template by washing with ethanol and HF solution (1M) at 298 K for 24 h.

For the synthesis of CMT-1 material, a reaction chamber (not shown) different from conventional designs [12,20] was constructed such that the reactant gases, i.e. controlled mixture of acetylene (C_2H_2), hydrogen, and argon, can be introduced from the top of a smaller quartz tube aligned coaxially to a larger quartz tube containing the MCM-48 template sample at the bottom, thus allowing the mixture gases to flow directly through the sample bed during the CVI treatment before exhausting from the top of the chamber. The nano-sized tubular CMT-1 carbon material was synthesized by the following procedure: first, the MCM-48 template was placed into the home-designed reactor, followed by gradual heating (1 K/min) of the sample to 1073 K under vacuum. Then, a desired amount of acetylene, which served as the carbon source, was introduced into the reactor along with gas mixture of H_2 and Ar, typically under a controlled gas flow rate of $C_2H_2/H_2/Ar=50:50:50$ sccm/sccm/sccm, and allow for ca. 40 min reaction time. Subsequently, the carbonized composite was further subjected to graphitization at 1183 K for 3 h before it was eventually cooling down to room temperature. After removal of silica framework by etching with 1 M HF solution of 50% ethanol–50% H_2O , the final CMT-1 carbon material was collected by filtering and drying.

2.2. Characterization methods

The phase purities of all samples were examined by a small-angle powder X-ray diffractometer (Philips X'Pert PRO) using $CuK\alpha$ (0.154 nm) radiation (40 kV, 30 mA). Their textural properties, viz. Brunauer–Emmett–Teller (BET) [21] surface area, pore volume, Barrett–Joyner–Halenda (BJH) [22] pore size distribution and wall thickness, etc., of the samples were derived from N_2 adsorption/

desorption measurements (Micromeritics ASAP 2010) done at 77 K. TEM micrographs were taken with a Hitachi H-7100 instrument operated at 75–100 keV. Powdered sample in ethanol solution was dispersed and dried on copper grid for the TEM measurement. All Raman spectra were acquired on a spectrometer (Jobin Yvon HABRAM HR) equipped with a Helium/Neon laser at wavelength of 632.8 nm.

3. Results and discussion

3.1. Structure and physical properties

Fig. 1 displays the XRD patterns of synthesized MCM-48, CMK-1, and CMT-1 materials, which all show well-ordered mesoporous structures as revealed by the characteristic peaks at small 2θ angles. That the novel CMT-1 material synthesized by the CVI method exhibits [110] and [211] peaks at respective 2θ angles of ca. 1.4° and 2.5° , whereas the corresponding diffraction peaks for CMK-1 sample are at ca. 1.6° and 2.8° , clearly indicates that these two mesoporous carbon materials have a rather similar structure. The XRD pattern of CMK-1 is in good agreement with existing literatures [3,17–19]. The MCM-48 silica template exhibits a major [211] diffraction peak at $2\theta \sim 2.3^\circ$, also consistent with earlier reports [13–16]. Moreover, the N_2 adsorption/desorption curves obtained from MCM-48, CMK-1 and CMT-1 (Fig. 2) all exhibit a typical type-IV isotherm with a broad hysteresis loop,

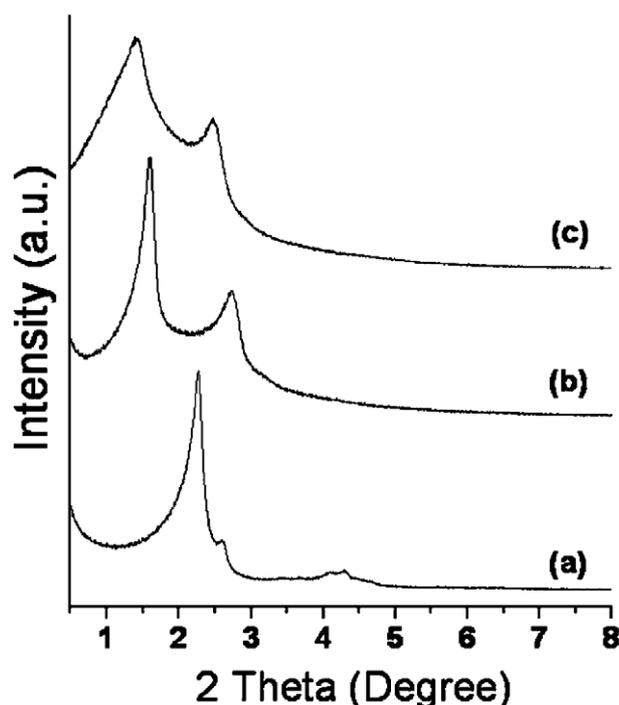


Fig. 1. XRD patterns of (a) MCM-48, (b) CMK-1, and (c) CMT-1.

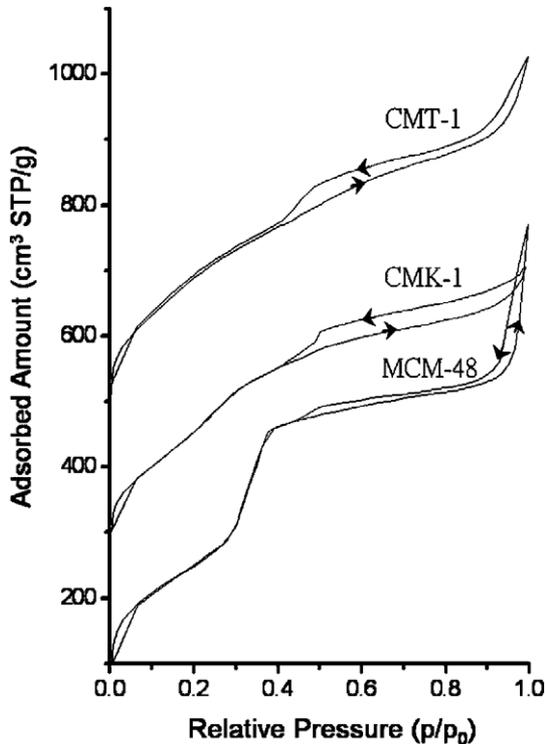


Fig. 2. N₂ adsorption/desorption isotherms (77 K) of mesoporous MCM-48 silica, CMK-1, and CMT-1. The isotherms for CMK-1 and CMT-1 carbons are shifted vertically by 200 and 400 cm³ STP/g, respectively.

characteristics of capillary condensation in mesoporous channels [23–25]. Further analyses based on desorption curves of the isotherms using BJH method [22] provide additional information on pore size distribution curves (Fig. 3), BET surface areas, and pore volumes of the samples, as depicted in Table 1. Additional *t*-plot analyses (not shown) further confirmed that these materials do not possess any

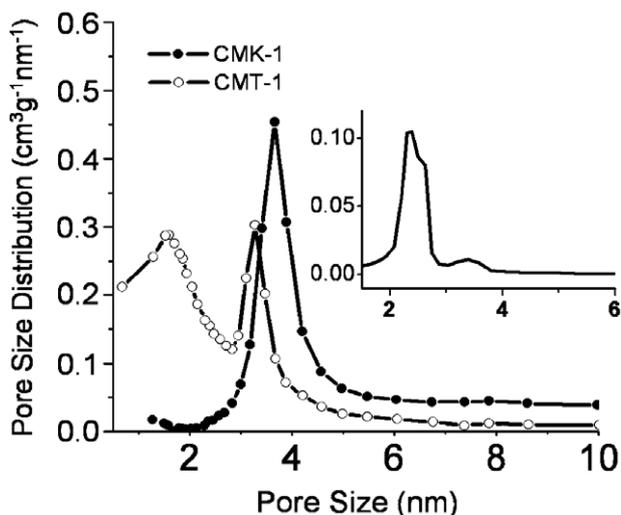


Fig. 3. BJH pore size distribution of CMT-1 (●), CMK-1 (○), and MCM-48 (inset).

Table 1
Textural properties of various mesoporous materials

Sample	Pore diameter (nm)	Surface area (m ² /g)	Pore volume (cm ³ /g)
MCM-48	2.4	923	0.68
CMK-1	3.6	1238	0.75
CMT-1	1.5; 3.3	1076	0.63

microporosity (pore size <1 nm). As can be seen from Table 1, these porous carbons replicated from MCM-48 possess high BET surface area over 1000 m²/g. However, unlike CMK-1 carbon, which shows only one type of mesopores with average pore size of ca. 3.6 nm, the novel CMT-1 carbon appears to possess two types of pores near 1.5 and 3.3 nm.

Additional investigations by Raman spectroscopy reveal that both CMK-1 and CMT-1 materials exhibit well-structured D-band and G-band near 1340 and 1600 cm⁻¹, respectively, as shown in Fig. 4. These characteristic bands observed for CMK-1 and CMT-1 indicate that these porous carbons possess typical graphite structures analogous to carbon nanotubes (CNTs) [26]. More specifically, the G-band can be attributed to graphitic structure and the D-band is normally ascribed due to structural defects or sp³ graphites requisite by a 3-D tubular structure [27].

The TEM images of MCM-48 and CMT-1 in Fig. 5 confirm that these mesoporous materials are indeed well-ordered, in consistent with the XRD results. Furthermore, the close-up TEM image near the edge of the CMT-1 sample particle (which is ca. 400–500 nm in size) in Fig. 5c clearly shows tubular carbons with average outer diameter of ca.

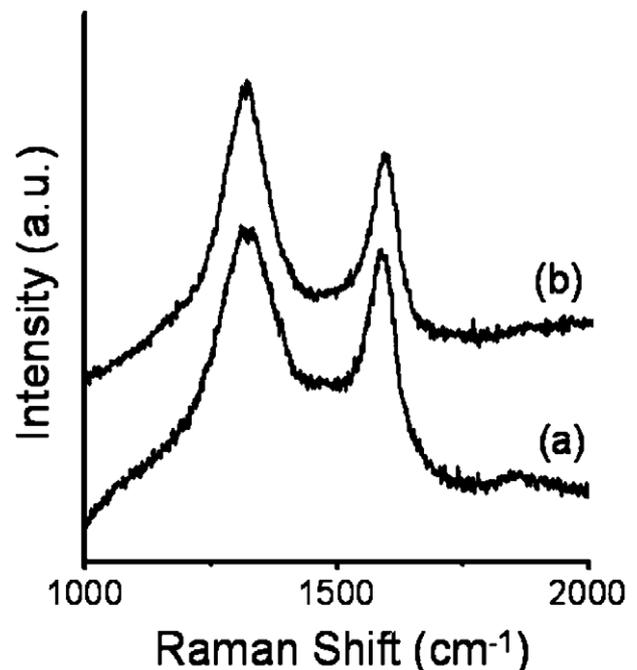


Fig. 4. Raman spectra of (a) CMK-1 and (b) CMT-1.

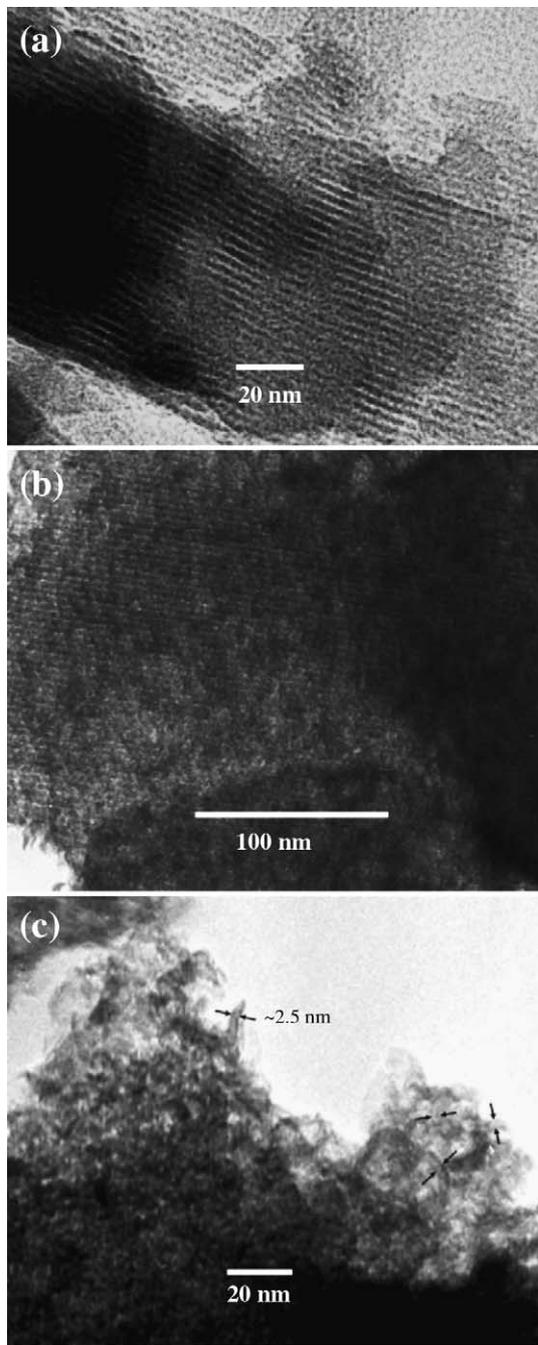


Fig. 5. TEM images of (a) MCM-48 template and (b) CMT-1 carbon along the [110] plane. (c) A close-up view near the edge of CMT-1 sample particle.

2.5 nm, which is also in excellent agreement with the N_2 adsorption/desorption data.

3.2. Estimation of wall thickness for CMT-1

Based on the BJH pore size distribution in Fig. 3 and Table 1, the averaged pore size of the MCM-48 silica template is ca. 2.4 nm, corresponding to a maximum outer diameter available for formation of the tubular CMT-1 carbon (Fig. 5c). Thus, as illustrated in Fig. 6, the two types of pores near 1.5 and 3.3 nm observed for the CMT-1 carbon can be respectively correlated to the inner diameter of the tubular CMT-1 and the wall thickness of the MCM-48 template. The latter represents the space between pore channels of MCM-48 and hence should be roughly equal to the pore size of CMK-1 (3.6 nm; see Table 1), which is a direct replica of MCM-48. Taking the well-known inter-layer distance of graphite sheets of ca. 0.336 nm [28], a simple calculation therefore leads to an estimated average thickness of the CMT-1 carbon tubules corresponding to about 1.3 graphite sheet layers, in good agreement with the TEM analysis.

4. Conclusions

We report herein the synthesis of a novel nano-sized, well-ordered mesoporous carbon, CMT-1, by the CVI method using MCM-48 silica as template. This new type of porous carbon was found to have a 3-D framework structure similar to conventional mesoporous CMK-1 carbon synthesized by direct replication using the same template but possesses a bimodal pore distribution and high surface area rendering for advanced applications, for example, as catalytic support for electrodes in PEMFCs and as carrier adsorbent for fuel storage.

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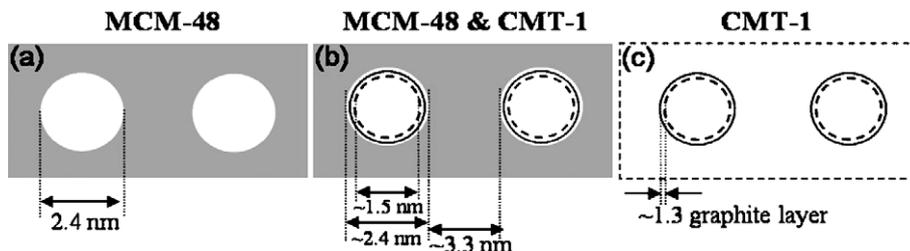


Fig. 6. Schematic illustrations of pore size and wall thickness for tubular CMT-1 carbon.

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