

Structural and electronic characteristics induced by carbonization control of mesoporous carbon nanofibers



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ABSTRACT

Mesoporous carbon nanofibers (MCNFs) are fabricated at various carbonization temperatures. The carbonization temperature plays a key role in determining the structural characteristics and the electronic properties of MCNFs. The band gap energies of MCNFs are estimated to be 0.080, 0.036, and 0.014 eV at the carbonization temperatures of 600, 900, and 1200 °C, respectively. The MCNF carbonized at 1200 °C has the highest stacking height of graphene planes (L_c) and the largest number of graphene layers (L_c/d). Raman data show the intensity ratio of D to G peaks, which is related to the graphene size (L_a). L_a increases with increasing the carbonization temperature. In addition, as the carbonization temperature increases, the conductivity of MCNF increases due to larger values of L_c , L_a , and L_c/d .

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1. Introduction

Porous carbons have become one of the important materials that are actively investigated. Especially, mesoporous carbon [1,2] materials with a high surface area and ordered mesostructure have quickly attracted wide attentions due to their potential applications of gas sensor, natural gas storage, fuel cells, and electrodes in electrochemical devices [3–7]. The first synthesis of mesoporous carbon with a silicate template was accomplished by Knox et al. [8]. Recently, a number of research groups have successfully demonstrated the arrays of mesoporous carbon nanofibers (MCNFs) with unique and tunable mesophases by using the replication of silica within the confined channels of porous alumina membranes (PAMs) [9–11]. We also reported the fabrication of MCNFs by using the template of mesoporous silica nanofiber within PAM templates [12,13]. These meso-carbon materials can be prepared with a quite simple process and the resultant MCNFs show a high surface area, narrow pore size distribution, and chemical/mechanical/thermal stabilities. A noticeable advantage of MCNFs over mesoporous powders of carbon (CMK) is that MCNFs have a long range (in μm scale) ordering that may be utilized to a sensitive nano-device of a single

fiber. Along with the single fiber nature, the properties of excellent mechanical strength, unique electrical property, and high chemical stability lead their potential application to energy storage, electric device, and molecular sensors. However, despite of such advantage, MCNFs show fewer cases of their applications in electrochemistry field compared to the mesoporous powders such as CMK-1 and CMK-3 [14–16].

Development of mesoporous carbon with high conductivity is one of the critical challenges for their practical applications. As an effort to achieve this development, in this study, the effect of carbonization temperature to the controllability of structural and electrical properties is investigated. The control of graphitic fraction and electrical conductivity by changing the carbonization temperature is also evaluated. We herein report that the activation energy (E_a) of the electrical conductance for the MCNFs decreases with the high carbonization temperature. Such higher conductivity with the MCNFs carbonized at high temperature is expected to be due to the larger crystalline graphite structure formed by higher stacking height of graphene planes (L_c), larger graphene size (L_a), and larger number of graphene layers (L_c/d). Also, we successfully demonstrate the controlled electrical property of MCNFs with the carbonization temperature. As for an application, the gas sensing property of MCNFs is investigated. The result indicates that the high sensitivity of gas sensor is obtained by MCNFs fabricated at the high carbonization temperature.

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structural characteristics and the electronic properties of MCNFs. The band gap energies of MCNFs are estimated to be 0.080, 0.036, and 0.014 eV at the carbonization temperatures of 600, 900, and 1200 °C, respectively. The MCNFs carbonized at 1200 °C has the highest stacking height of graphene planes (L_c) and the largest number of graphene layers (L_c/d). Raman data show the intensity ratio of D- to G-peak, which is related to the graphene size (L_a). L_a increases with increasing the carbonization temperature. In addition, as the carbonization temperature increases, the conductivity of MCNFs increases due to larger values of L_c , L_a , and L_c/d .

2. Experimental

2.1. Synthesis of MCNFs

Materials: Tetraethylorthosilicate (98%, TEOS) and furfuryl alcohol (99%; FA) were purchased from Aldrich and used without further purification. PAM was purchased from Whatman (Anodisk 13). Octadecyltrichlorosilane (90+%, Sigma–Aldrich) was used for the modification of PAM. Triblock copolymer of Pluronic F127 (BASF Chemical Co.), nitric acid (60%, Matsuden Chemical Co., Japan), ethanol (99.9%, Merck), and $AlCl_3$ (98%, Junsei Chemical Co., Japan) were used in the fabrication of MCNFs.

Fabrication procedure of MCNFs was also reported in the previous studies [12,13]. Mesoporous silica nanofibers fabricated within the nanochannels of PAM were utilized as a template. The modified PAMs (Anodisk 13, Whatman, diameter 200 nm, thickness 60 μ m) with octadecyltrichlorosilane (90+%, Sigma–Aldrich) were dipped into the prepared lyotropic precursor solution (1 g of Pluronic F127, 1.2 g of TEOS, 0.54 g of 0.3 M nitric acid, 2.3 g of ethanol) and stirred for 12 h before the introduction of the precursor solution. The sol infiltrated within the pores of the template was transformed into a gel by the aging process at 60 °C for 12 h [17,18]. The template composites were calcined under an air flow for 4 h at 450 °C (heating rate: 3 °C/min). The block copolymers incorporated within the mesoporous silica nanofibers were removed by the calcination. The calcination process results a little empty space between the inner surface of the nanochannels of PAM and the mesoporous silicate nanofibers due to the volume contraction induced by removal of the block copolymers. In order to minimize the empty space, the incorporation–calcination cycle were consequently repeated 3 times.

Then the templates were aluminated by using an aqueous solution of $AlCl_3$ to generate catalytic sites for the polymerization FA of a carbon precursor. The FA filled within the templates was polymerized by heating overnight at 90 °C. The templates filled with the polyfurfuryl alcohol were carbonized at several temperatures ranged from 600 to 1400 °C (heating rate 3 °C/min) for 2 h under argon flow with a temperature controlled furnace (Lenton LTF-14/50/180). Finally, the resulting MCNFs were immersed in HF (5 wt.%) solution at room temperature for 12 h in order to remove the template. The resultant MCNFs were washed with distilled water and ethanol, and then dried in vacuum oven at 60 °C.

2.2. Characterization

Structures of MCNFs were characterized by transmission electron microscopy (TEM, JEOL JEM-3010) and field emission scanning electron microscopy (FE-SEM, JEOL JSM-6700F). For TEM measurement, the samples were suspended in ethanol and supported on carbon-coated copper grid. X-ray diffraction (XRD) was used to determine the crystallite characterization and the structures of MCNFs. XRD patterns were obtained with a powder X-ray diffractometer (PANalytical, Pert Pro MPD) by using $Cu K\alpha$ radiation source ($\lambda = 1.5418 \text{ \AA}$). The XRD data was used to determine the d spacing, L_c , and L_a . The d spacing (d_{002}) was estimated by using the

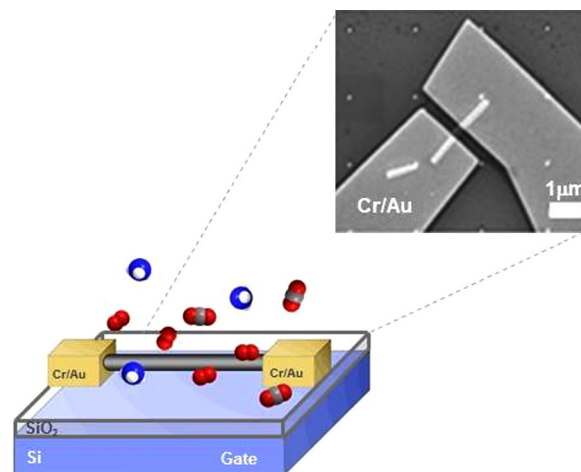


Fig. 1. Schematic drawing and SEM image of the conductivity measurement.

Bragg equation (1). The stacking size of L_c in the c -direction can be determined from the (002) peak and the graphene size of L_a can also be estimated from (10) peak by the Scherrer equation (2).

$$n\lambda = 2d \sin \theta \quad (1)$$

$$L = \frac{K\lambda}{\beta \cos \theta} \quad (2)$$

where θ is the scattering angle, λ is the wavelength of the X-rays used, and β is the full width at half maximum intensity (FWHM) (see Supporting Information, Figs. S1 and S2). K is the apparatus constant (≈ 0.9) and L is crystallite size [19]. And L_c and L_a were determined from the respective (002) and (10) diffraction peak profiles with the Scherrer equation.

FT-Raman spectra of the MCNFs samples were obtained by using a spectrometer (Jobin-Yvon T64000) equipped with liquid nitrogen cooled charged coupled device (CCD) detector. For FT-Raman measurements, the samples were excited with an argon laser (Lexel 95) operating at 514.5 nm.

2.3. Conductivity of a single mesoporous carbon nanofiber and its application to NH_3 gas sensor

To investigate the electrical properties of MCNFs, a single MCNF device was fabricated as follows: MCNFs were dispersed in ethanol and then spin-coated onto a degenerately doped Si substrate with a thermally grown 200 nm-thick SiO_2 layer. MCNFs were located by a FE-SEM and Cr/Au electrodes (5 Å/1000 Å) were made by using the electron beam lithography and lift-off techniques. To obtain a good contact between the MCNFs and the metal electrode, the pre-treatment step was done through rapid thermal annealing. It was performed at 800 °C for 2 min in N_2 atmosphere. A single MCNF device is illustrated in Fig. 1. Sensor measurements were performed using Agilent E5270 and were carried out in a vacuum chamber with BNC electrical feed-throughs for gas outlets. These measurements were made at room temperature and atmospheric pressure, with ultrahigh purity nitrogen as the carrier gas. The variation of current caused by the resistance change in a single MCNF was measured at a constant voltage of 0.5 V applied. In order to characterize the sensitivity of the MCNF-600, -900, and -1200 to NH_3 , the device was exposed to NH_3 gas concentration of 100 and 150 ppm during 90 s.

3. Results and discussion

The ordered mesoporous structure of carbon nanofibers was confirmed by TEM (Fig. 2). Fig. 2(a)–(i) present TEM images

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