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

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A B S T R A C T

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 (Lc) and the largest number of graphene layers (Lc/d). Raman data show the intensity ratio of D to G peaks, which is related to the graphene size (Lc). Lc increases with increasing the carbonization temperature. In addition, as the carbonization temperature increases, the conductivity of MCNF increases due to larger values of Lc, L0, and Lc/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 (Ea) 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 (Lc), larger graphene size (L0), and larger number of graphene layers (Lc/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.

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 MCNFs carbonized at 1200 °C has the highest stacking height of graphene planes (Lc) and the largest number of graphene layers (L/δ). Raman data show the intensity ratio of D- to G-peak, which is related to the graphene size (Lc, L) increases with increasing the carbonization temperature. In addition, as the carbonization temperature increases, the conductivity of MCNFs increases due to larger values of Lc, Ld, and L/δ.

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 (Anodisc 13). Octadecltrichlorosilane (90%, Sigma–Aldrich) was used for the modification of PAM. Triblock copolymer of Pluronic F127 (BASF Chemical Co.), nitric acid (60%, Matsunden Chemical Co., Japan), ethanol (99.9%, %, Merck), and AlCl3 (98%, Junseii 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 μm) with octadecyltrichlorosilane (90%, Sigma–Aldrich) were dipped into the prepared hydrotropic 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 silica nanofibers due to the volume contraction induced by removal of the block copolymers. In order to minimize the empty space, the incorporation–calcination cycle was consequently repeated 3 times.

Then the templates were aluminated by using an aqueous solution of AlCl3 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 constant 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, JEOLJEM-3010) and field emission scanning electron microscopy (FE-SEM, JEOLJSM-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 (PAAnalytical, Pert Pro MPD) by using Cu Kα radiation source (λ = 1.5418 Å). The XRD data was used to determine the d spacing, Lc, and Ld. The d spacing (d002) was estimated by using the Bragg equation (1). The stacking size of Lc in the c-direction can be determined from the (002) peak and the graphene size of Ld can also be estimated from (10) peak by the Scherrer equation (2).

\[ n\lambda = 2d \sin \theta \] (1)
\[ L = \frac{\beta \cos \theta}{\lambda} \] (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 Lc and Ld 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 NH3 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 SiO2 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 N2 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 NH3, the device was exposed to NH3 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...
of MCNFs synthesized at different carbonization temperatures between 600 and 1400 °C. MCNFs synthesized at the carbonization temperatures from 600 to 1400 °C were denoted to be MCNF-600–MCNF-1400, respectively.

All images indicate the mesoporous carbon structures of the circularly-wound shape and an average pore diameter around 4.3 nm (inset of Fig. 2b). In our previous study, the major pore diameters estimated by the Barrett–Joyner–Halenda (BJH) method were of ~3.75 nm for all MCNFs, which were well correlating with the pore diameters estimated from the TEM image. The observed sorption isotherms of the MCNFs exhibited a characteristic hysteresis behavior that was a typical pattern for mesostructural materials. Moreover, MCNF-1200 showed the largest BET surface area (667 m² g⁻¹) and pore volume of 0.62 cm³ g⁻¹ [12,13]. Fig. 2(j) presents the interesting bobbin structure of the mesoporous carbon nanofiber, which is resulted from ultra-sonication in ethanol. The diameters of these carbon nanofibers are in the range of 150–220 nm, corresponding to the pore dimension of the utilized PAM. The SEM image of MCNFs are obtained after removal of the PAM template with HF solution and the longitudinal dimension of these nanofibers was around 60 μm, comparable to the thickness of the PAM utilized.

Structural changes during carbonization were confirmed by XRD and Raman spectra. Fig. 3 shows the XRD patterns of the graphitized MCNFs fabricated at different carbonization temperatures. MCNF-600, MCNF-900, and MCNF-1200 were characterized by the broad peaks at around 24° and 43° which correspond to the (002) and (10) diffractions of the carbon, respectively [20].

The corresponding interlayer distance, d₀₀₂, was calculated by the Bragg equation. And Lₐ and Lₐ were determined from the respective (002) and (10) diffraction peak profiles with the Scherrer equation. The d₀₀₂, Lₐ, and Lₐ values are listed in Table 1. As the carbonization temperature increases from 600 to 1200 °C, the Lₐ value of MCNF increases from 0.983 to 1.121 nm and the Lₐ value also increases from 1.511 to 4.232 nm. It suggests that the increase of carbonization temperature results higher degree of graphitization induced by the larger crystal domain since the (002) and (10) diffraction peaks (see Table 1) represent the stacking of parallel graphene layers and the size of graphene layer, respectively. The d₀₀₂ value of MCNFs decreases from 0.371 to 0.368 nm with increasing carbonization temperature. The d₀₀₂ value indicates the interlayer distance between the graphene layers, thus the number of graphene layer can be calculated by using Lₐ/d₀₀₂. The MCNFs with higher carbonized temperature has larger values for Lₐ, Lₐ, and Lₐ/d, suggesting higher graphitization of MCNFs and so more packing of graphene layers.

Information on the degree of graphitization of the prepared MCNFs can also be provided by Raman spectroscopy. Raman spectra of the MCNFs fabricated at different temperatures are presented in Fig. 4. All Raman spectra show two strong bands of D-band and G-band near 1350 and 1598 cm⁻¹, respectively [20–22].

As shown in Table 2, the position of G-peak shifted from 1605 to 1594 cm⁻¹ and the FWHM of G- and D-peaks became smaller with increasing of the carbonization temperature. The intensity
Table 1
XRD parameters of MCNFs at different carbonization temperatures (estimation of the parameters is described in the Supporting Information (Figs. S1 and S2)).

<table>
<thead>
<tr>
<th>Mesoporous carbon nanofibers</th>
<th>2θ (0 0 2) (°)</th>
<th>FWHM</th>
<th>d_{002} (nm)</th>
<th>L(100) (nm)</th>
<th>L(d)</th>
<th>2θ (10) (°)</th>
<th>FWHM</th>
<th>L(200) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600-MCNF</td>
<td>23.96</td>
<td>8.276</td>
<td>0.371</td>
<td>0.983</td>
<td>2.65</td>
<td>43.72</td>
<td>5.672</td>
<td>1.511</td>
</tr>
<tr>
<td>900-MCNF</td>
<td>24.04</td>
<td>8.151</td>
<td>0.370</td>
<td>0.998</td>
<td>2.70</td>
<td>43.42</td>
<td>4.660</td>
<td>1.837</td>
</tr>
<tr>
<td>1200-MCNF</td>
<td>24.18</td>
<td>7.261</td>
<td>0.368</td>
<td>1.121</td>
<td>3.05</td>
<td>43.47</td>
<td>2.023</td>
<td>4.232</td>
</tr>
</tbody>
</table>

Table 2
Characteristics of the D- and G-bands of MCNFs at different carbonization temperatures.

<table>
<thead>
<tr>
<th>Material</th>
<th>D-band</th>
<th>G-band</th>
<th>k(D)/k(G)</th>
<th>L(200) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Raman shift (cm⁻¹)</td>
<td>FWHM (cm⁻¹)</td>
<td>Raman shift (cm⁻¹)</td>
<td>FWHM (cm⁻¹)</td>
</tr>
<tr>
<td>600-MCNF</td>
<td>1364</td>
<td>177</td>
<td>1605</td>
<td>83</td>
</tr>
<tr>
<td>700-MCNF</td>
<td>1357</td>
<td>173</td>
<td>1605</td>
<td>79</td>
</tr>
<tr>
<td>800-MCNF</td>
<td>1353</td>
<td>170</td>
<td>1603</td>
<td>79</td>
</tr>
<tr>
<td>900-MCNF</td>
<td>1352</td>
<td>166</td>
<td>1601</td>
<td>76</td>
</tr>
<tr>
<td>1000-MCNF</td>
<td>1346</td>
<td>152</td>
<td>1598</td>
<td>73</td>
</tr>
<tr>
<td>1100-MCNF</td>
<td>1343</td>
<td>138</td>
<td>1598</td>
<td>69</td>
</tr>
<tr>
<td>1200-MCNF</td>
<td>1340</td>
<td>135</td>
<td>1594</td>
<td>62</td>
</tr>
<tr>
<td>1300-MCNF</td>
<td>1340</td>
<td>132</td>
<td>1594</td>
<td>59</td>
</tr>
<tr>
<td>1400-MCNF</td>
<td>1338</td>
<td>125</td>
<td>1594</td>
<td>55</td>
</tr>
</tbody>
</table>

The ratio of D- to G-peak (|I(D)/I(G)|) becomes larger from 0.74 to 1.18 as the carbonization temperature increases. These results are consistent with the characteristic changes occurring from amorphous carbon (a-C) to nanocrystalline graphite (nc-G) in the amorphization trajectory suggested by Ferrari and Robertson and co-worker [21]. L(200) is re-estimated from Raman data using the following Ferrari and Robertson equation (3):

\[
\frac{I(D)}{I(G)} = C^*\lambda L(200)
\]

where C* (514 nm) = 0.0055. The L(200) value estimated from the Raman data increases from 1.16 to 1.46 with increasing the carbonization temperature. As shown in Fig. 4, the increasing L(200) value is due to the relatively high value of the D-band intensity compared with the G-band intensity. The intensity of D-band is proportional to the probability of finding a sixfold ring in the carbon cluster in case of the small L(200) value less than 2 nm.

The L(200) obtained from XRD and Raman data both increases as the carbonization temperature becomes higher. However, the values of L(200) from both techniques of Raman and XRD are different. Such discrepancy is also reported in other works where the differences between the L(200) values obtained by Raman and XRD are 2 times by Vazquez-Santos et al. [23] and even 8 times by Baldan et al. [24]. It is because the line profiles cannot clearly be isolated from the adjacent peaks in case of XRD [25]. However, the L(200) values from the XRD peak still shows a similar trend to that obtained from Raman.

So far, the structural change of the MCNFs has been investigated according to the different carbonization temperatures. From now, it will be discussed how such structural properties of MCNFs manipulated by the different carbonization temperature influence their electrical properties.

The source/drain current–voltage (I_{SD}–V_{SD}) curves were measured at several temperatures for MCNFs carbonized at 600, 900 and 1200 °C, as shown in Fig. 5(a), (b), and (c), respectively. For

![Fig. 5](image-url)

Fig. 5. The I_{SD}–V_{SD} curves measured at several temperatures (T = 4, 77, 200 and 300 K) for MCNF-600 (a), -900 (b), -1200 (c). The upper inset of (a) shows a FE-SEM image of typical single MCNF device. The lower insets of (a), (b) and (c) show the plot of α versus T, where α is given by the relation of I_{SD} ∝ V_{SD}^{α}. (d) The G–T curves for MCNF-600, -900, and -1200, where G = dI_{SD}/dV_{SD} at V_{SD} = 0 V.
all MCNFs, the $I_{SD}$-$V_{SD}$ curve is linear at room temperature and the room temperature resistance is estimated to be 7.4 MΩ, 116 kΩ and 108 kΩ for MCNF-600, -900, and -1200, respectively. However, the $I_{SD}$-$V_{SD}$ curve became non-linear below about 260 and 230 K for MCNF-600 and -900, respectively, whereas its linearity was maintained down to 150 K for MCNF-1200. The differential conductance, $G = dI_{SD}/dV_{SD}$, at $V_{SD} = 0$ V is plotted as a function of temperature for MCNF-600, MCNF-900, and MCNF-1200 in Fig. 5(d). $G$ is described by the relation of $G \propto T^n$ with $n \approx 5.8$ and 2.4 for MCNF-600 and -900, respectively. In contrast, $G$ for MCNF-1200 decreases linearly with $T$ for $T > 150$ K, and then rapidly for $T < 150$ K, implying that the transport mechanism for MCNF-1200 is different from the one for MCNF-600 and -900.

It is because the interlayer distance between graphene layers decrease and more number of graphene layers exists at higher carbonization temperature, leading to the enhancement of the movement of the π electrons in the carbon cluster [26]. Additionally, the temperature dependence of $G = A - BT^{-1/4}$, which is predicted by the variable-range hopping theory [27,28], is reported for amorphous Ge, Si [29] or amorphous carbon films [30,31], where $A$ and $B$ are constants. Thus, to see whether the temperature dependence of $G$ shown in Fig. 5(d) is understood in terms of variable-range hopping or not, $G$ measured for MCNF-600, -900, and -1200 is replotted against $1/T^{1/4}$ in Fig. 6(a).

Indeed, a linear relationship is observed with $B \approx 36$ and $13 K^{1/4}$ for MCNF-600 and -900, respectively. Since the density of state $N(E_F)$ is proportional to $16\alpha^2/k_B^2$, where $\alpha^{-1}$ is the Bohr radius of localized electrons and $k_B$ the Boltzmann constant [32,33], $N(E_F)$ is estimated to increase with increasing the carbonation temperature, which is consistent with the results reported for the amorphous carbon films. These results conclude that the amorphous phases are dominant in MCNF-600 and -900, so that the temperature dependence of $G$ is explained by the variable-range hopping model. For MCNF-1200, however, $G$ does not follow the relation of $G \propto T^{-1/4}$, suggesting the $G$ is not governed by variable-range hopping any more, since the amorphous phases have changed to the crystalline phases at 1200 °C. Fig. 6(b) depicts the plot of $G$ versus $1/T$ for MCNF-600, -900, and -1200.

The activation energy of $E_a$ is estimated to be 0.040, 0.018 and 0.0072 eV for MCNF-600, -900, and -1200, respectively, although the data at low temperatures are deviated from the relation of $G \propto \exp(-E_a/k_BT)$. For conduction by electrons, the activation energy is the energy difference between the Fermi level and the conduction band. In an intrinsic semiconductor, the activation energy is approximately half of the band gap energy, since the Fermi level sits at mid-gap for an intrinsic material. So the band gap energy of MCNF-600, -900, and -1200 is estimated to be 0.080, 0.036 and 0.014 eV, respectively.

To investigate the gate voltage ($V_G$) dependence of the conductance, the $I_{SD}$-$V_{G}$ curves were measured for MCNF-600 and -1200, as shown in Fig. 7(a) and (b), where the highly doped Si substrate was used as a bottom gate. MCNF-600 exhibits a p-type semiconducting behavior, while MCNF-1200 shows an ambipolar semiconducting behavior. Such ambipolar property was also reported in the CNT with narrow band gap by Lin et al. [34]. These findings imply that MCNF-1200 has a narrower energy gap than MCNF-600, as in $E_a$. Therefore, the MCNFs have larger $L_p/d$ with higher carbonized temperature, which aids in the movement of the π electrons, which in turn, lower the electrical resistance value and increase the electrical conductivity.

The sensitivity of the single MCNF to NH₃ gas was measured by exposing several concentrations of NH₃ gas, as shown in Fig. 8. The MCNF-1200 shows the highest resistance to NH₃ gas. The resistivity of MCNF increases with adsorption of NH₃ molecules since
NH$_3$ acts as an electron donor [25]. The MCNF-1200 has the largest BET surface and pore volume through the biggest volume contraction compared with the others of the MCNFs carbonized at 600 and 900°C [13]. Therefore, the MCNF-1200 provides the largest cross section for gas adsorption, leading to the most enhanced sensitivity with respect to NH$_3$ gas.

4. Conclusion

This study shows that the controlled structural change of MCNFs influences their electrical properties. The structural control can be achieved by a simple tuning of carbonization temperature in the constrained nanopore space of PAM. According to the XRD and the Raman data, MCNFs experience characteristic structural change from a-C to nc-G as the carbonization temperature increases. Such structural change is ascribed to higher graphitization of MCNF and more packing of graphene layers, which are evidenced by larger values for $L_c$, $L_d$, and $L_c/L_d$. Conductivity of the single MCNF shows that MCNF-1200 has the ambipolar semiconducting behavior with low $E_0$ of 0.0072 eV, while MCNF-600 exhibits a p-type semiconducting property with $E_0$ of 0.040 eV. This study demonstrates that the low conductivity of amorphous carbon can be improved with a simple control of the carbonization temperature. Such enhanced conductivity of MCNF with high conductivity and large surface area is successfully utilized as a NH$_3$ gas sensor.

Acknowledgments

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.mseb.2014.04.001.

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