Development of graphite structure with heat treatment in a carbon sheet derived from cellulose nanofibrils of plant origin

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Commercially available pure cellulose paste of plant origin composed of nanofibrils was dispersed in ethanol or distilled water, and sheets made of the nanofibrils were prepared by filtration. The sheets were carbonized and then heat-treated at temperatures between 2400 and 3200 °C at atmospheric pressure, and the original paste was also carbonized and heat-treated at 3100 °C. The diameter of the cellulose nanofibrils was found to be 30-300 nm in the sheets, while no fibrous texture was observed in the original paste. Structural order of the carbonized sheets improved with increasing heat treatment temperature, and was especially remarkable for the sheet derived from nanofibrils dispersed in ethanol, though turbostratic components were observed even for the sheet heat-treated at 3200 °C. On the other hand, the 3100 °C-treated paste exhibited a typical turbostratic structure. The development of graphite structure in the carbon sheets is probably attributed to surface graphitization, the same as the graphitization of the carbonized sheets prepared from bacteria cellulose nanofibers by heat treatment at high temperatures reported previously. The structural development of the present heat-treated sheets was less than that of the heat-treated sheets prepared from bacteria cellulose nanofibers. The result could be attributed to the thicker diameters and lower crystallinity of the present precursor nanofibrils compared to those of the bacteria cellulose nanofibers.

KEYWORDS: Cellulose nanofibril, Plant pulp, Surface graphitization, Graphitic carbon nanofiber, Non-graphitizing carbon

1. Introduction

Cellulose-based carbon materials are essentially known to be one of nongraphitizing carbons¹⁾ and exhibit multiphase graphitization²⁾. In the case of cellulose films, the surfaces of carbonized films *i.e.*, the skins of 100-200 nm thick, were graphitized by simple heat treatment at high temperatures³⁾, and also the skin regions of about 70-80 nm thick of cellulose-based carbon fibers were graphitized by simple heat treatment at high temperatures⁴⁾. A mechanical stress was applied to the skin regions during the formation processes of the fibers and films. The stress enhanced the preferred orientation of cellulose molecules of the skin regions. After carbonization, so called basal structural units probably aligned along each surface of the fibers and films, so that the surfaces seemed to be graphitized by simple heat treatment at high temperatures.

On the other hand, Kim *et al.* reported that a 500 °C-treated sample of freeze-dried bacteria cellulose was graphitized by heat treatment at 2000 °C for 5 min *in vacuo*⁵⁾. Bacteria cellulose is known to be composed of crystalline cellulose nanofibrils⁶⁾. From the X-ray diffraction (XRD) measurements for the bacteria cellulose-derived carbons heat-treated at 2000 °C, however, the average crystallite size along *c*-axis L_c was obtained to be 3.7 nm and no separation of 100 and 101 diffraction peaks were observed⁵⁾. We found that sheets prepared from the bacteria cellulose nanofibers with 30-60 nm in diameter dispersed in ethanol or distilled water were graphitized by simple heat treatment at high temperatures up to 3200 °C after carbonization^{7),8)}. The sheets prepared in ethanol and carbonized were graphitized well in comparison with those in water because the separation of cellulose nanofibers dispersed in ethanol was better. For example, the interlayer spacing d_{002} and L_c were 0.3378 nm and 22 nm, respectively, for

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(Received January 10, 2013; Accepted April 3, 2013)

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<http://dx.doi.org/10.7209/tanso.2013.187>

the sample dispersed in ethanol and heat-treated at 3200 °C for 5 min. The development of graphite structure was thought to be attributed to the graphitization on the surface of nongraphitizing carbon, and the surface graphitization seemed to have a obvious effect on the insides of the carbon nanofibers because of very thin diameters^{7,8}). However, the structural improvement with heat treatment for the carbon sheets was less remarkable in comparison with that for typical graphitizing carbons. The limited graphitization behavior of the heat-treated sheets was attributed to their heterogeneous structure.

Recently, entangled cellulose nanofibrous network prepared from purified natural cellulose powder, which was derived from plant pulp, was investigated as a low cost precursor of carbon nanofibers^{9,10}). The cellulose nanofibrous network consisting of nanofibrils with 5-10 nm in diameter was made by a waterjet treatment of the plant pulp and freeze-dried technique. After a heat treatment at 2500 °C, some limited area of the fibrous region of the network exhibited development of stacking structure consisting of 10-20 carbon layers being extended to 50 nm at longest and roughly in parallel with other nanofibrils, though the structural parameters of the heat-treated network, such as the mean interlayer spacing and mean crystallite sizes, were not examined¹⁰).

Commercially available cellulose paste consisting of elemental nanofibrils, similar to the cellulose nanofibrous network as mentioned above, but with around 10-100 nm in diameters, has been obtained from plant pulp by smashing it to submicroscopic fragments mechanically^{11,12}). It was found that the 3000 °C-treated sample of the carbon nanofiber aggregate prepared from the cellulose paste was not graphitized¹²). The result seems to be due to the aggregation of the carbon nanofibers. The separation of cellulose nanofibrils is important factor for the development of graphite structure^{7,8}). The cellulose nanofibrils are very cohesive because of nanometer sizes. To prevent the cohesion of the cellulose nanofibrils, the nanofibrils have to be dispersed in ethanol or distilled water since cellulose, $(C_6H_{10}O_5)_n$, has hydroxyl radicals^{7,8}).

There has been no systematic experimental investigation of the structural development of carbon nanofibers obtained from cellulose nanofibrils of plant origin with simple heat treatment up to high temperature, such as 3100 °C. In addition, the cellulose nanofibrils of plant origin are easy to obtain because of commercially available ones, and they are very cheap in comparison with the bacteria cellulose nanofibrils, though their mean diameters are larger than those of the bacteria cellulose nanofibers. In the present study, the commercially available cellulose nanofibrils of plant origin were dispersed in ethanol or distilled water, and sheets made of the nanofibrils were prepared by filtration of the dispersed nanofibrils, and the structural development of the carbonized sheets with heat treatment was examined systematically.

2. Experimental

The cellulose nanofibril paste used in this study was a commercial product with trade name “Cellish FD-100G” produced by Daicel Fine Chemical Ltd.¹¹) The cellulose nanofibril paste was dispersed in ethanol or distilled water (hereafter Et or H₂O). Paper like sheets composed of the cellulose nanofibrils of about 1 mm in thickness were obtained by the same way as refs. 7 and 8. The cellulose sheets obtained were designated by the abbreviations of cellulose (Cel) and liquid used, *i.e.* Cel-Et and Cel-H₂O.

From the measurements of X-ray fluorescence, Cel-Et and Cel-H₂O were composed of C and O. C_{1s} and O_{1s} peaks were only observed by the measurements of X-ray photoelectron spectroscopy, and also Fourier transform infrared spectra show OH, CH, CO, C-C, CH₂ vibrations, corresponding to the molecular structure of cellulose.

Cel-Et and Cel-H₂O were carbonized at 900 °C for 1 h in an Ar flow, and then the sheets were heat-treated at temperatures of 3000 and 3100 °C and kept for 30 min, and at 3200 °C for 5 min in a high purity Ar flow at atmospheric pressure. The carbonized Cel-Et sheets were also heat-treated at temperatures of 2400, 2600 and 2800 °C and kept for 30 min in a high purity Ar flow at atmospheric pressure. The samples were designated by Cel-Et or Cel-H₂O followed by the heat treatment temperature (HTT), such as Cel-Et-3000. To examine the effect of the dispersion of the nanofibrils in ethanol or distilled water, the original cellulose nanofibril paste, Cel-Paste, was dried in air, and the solid sample was carbonized and then heat-treated at 3100 °C and kept for 30 min in a high purity Ar flow (denoted hereafter as Cel-Paste-3100).

The texture and structure of the heat-treated sheets were investigated by observations using a scanning electron microscope (SEM) and transmission electron microscope (TEM) and by measurements of first-order Raman spectra, XRD and DC electric resistivity. The Raman spectra were measured on five different areas of each heat-treated sample using an Ar ion laser of 514.5 nm in wavelength. The diameter of the laser beam was 1 μm. The ratio of the peak intensity of D band (a disorder-induced band) to that of G band (a Raman active lattice vibration band of graphite), I_D/I_G , and full width at the half maximum of the G band, G-FWHM, were determined for the heat-treated samples. To examine the crystallinity of the cellulose nanofibril precursor used in this study, the XRD measurements were carried out for the Cel-Et sheet. The XRD measurements were also performed for the sheets made of bacteria cellulose nanofibers^{5),7),8}) (Bact-Et) and animal cellulose nanofibers⁵) (Ani-Et) for comparison, which were dispersed in ethanol and filtered. For the heat-treated sheets of Cel-Et and Cel-H₂O and Cel-Paste-3100, the XRD profiles were measured separately in the regions of 20°-35° and 35°-85°, and the precise measurements were carried out between 49°-57°. From the XRD measurements of the heat-treated samples, the values of

the interlayer spacing d_{002} were evaluated by the same way as refs. 7 and 8. Electric resistivity along the longitudinal direction of each sheet, sheet resistivity ρ , was measured at room temperature in air by a conventional DC four terminal method for Cel-Et-3000, -3100 and -3200.

3. Results and Discussion

3.1 SEM

Figure 1 shows the SEM images of the original samples and the 900 °C- and 3000 °C-treated samples, *i.e.*, Cel-Et (a) and the extended image (c), Cel-Paste (b), Cel-H₂O (d), Cel-Et-900 (e), Cel-H₂O-900 (f), Cel-Et-3000 (g) and Cel-H₂O-3000 (h). In both of Cel-Et and Cel-H₂O, the nanofibrils were oriented along each sheet surface as shown in Figs. 1(a), (c) and (d), while no fibrous texture was observed in Cel-Paste as shown in Fig. 1(b). It can be estimated that the nanofibrils in Cel-Paste cohered each other strongly and made a thick lump. The diameters of the nanofibrils observed in Figs. 1(c) and (d) were about 30-300 nm, which were somewhat larger than the catalogue values of 10-100 nm¹¹⁾. The nanofibrils also stuck together

to some extent even in Cel-Et, but the separation of the nanofibrils in Cel-Et seems to be better than that of the nanofibrils in Cel-H₂O, as the same trend as that of the bacteria cellulose nanofibers in their sheets^{7),8)}. The diameter distribution of the present nanofibrils was broader than that of the bacteria cellulose nanofibers with 30-60 nm in diameter^{7),8)}.

The samples shrank after the heat treatment at 900 °C and the fibrous texture remained in Cel-Et-900, but not in Cel-H₂O-900, as shown in Figs. 1(e) and (f). The results indicate that the degree of separation of individual nanofibers depends on the sample treatment of cellulose nanofibers.

The samples shrank further after the high temperature heat treatments, and no individual nanofibers were observed in both of Cel-Et-3000 and Cel-H₂O-3000 as shown in Figs. 1(g) and (h). In the case of the 3100 °C-treated carbon sheets derived from Bact-Et, some individual nanofibers were still observed, while the individual nanofibers were hard to observe for the 3100 °C-treated sheets derived from Bact-H₂O and also for Bact-NT-3100⁸⁾. Bact-H₂O is a sheet composed of bacteria cellulose nanofibers dispersed in water and filtered, and Bact-NT-3100 is an original aggregate of bacteria cellulose nanofibers heat-treated at 3100 °C after carbonization. The cellulose nanofibers decomposed and were carbonized during the heat treatment up to 900 °C, but the decomposition was not finished at 900 °C. They further decompose during the heat treatment up to high temperatures, such as 2000 °C. In the course of the decomposition, the nanofibers tend to stick together if they touch together and entangle each other. The degree of separation of individual nanofibers depends on the sample treatment of cellulose nanofibers and also the origin of the nanofibers. The present cellulose nanofibrils are the commercially available ones which are obtained from plant pulp by smashing it to submicroscopic fragments mechanically, and the fragments entangle each other as shown in Figs. 1(a), (c) and (d). Therefore, during the decomposition and carbonization of the cellulose nanofibrils even in Cel-Et and Cel-H₂O, the nanofibers stick together in some degree, and by the high temperature heat treatment the nanofibers seem to make an aggregate. Consequently, no individual nanofibers were found on the surfaces of Cel-Et-3000 and Cel-H₂O-3000 by the SEM observations. On the other hand, the bacteria cellulose nanofibers are produced by acetic acid bacteria and are crystalline cellulose with rather uniform texture, though the nanofibers also somewhat entangle each other, but the degree of separation is much better than that in the present cellulose nanofibrils⁸⁾. Therefore, some individual nanofibers were still observed for the 3100 °C-treated carbon sheets derived from Bact-Et as mentioned above.

3.2 TEM

By the TEM observations, a fibrous texture was observed for all heat-treated Cel-Et and Cel-H₂O sheets as shown in Figs. 2(a), (b) and (c) for Cel-Et-3100 as examples. A graphitic area on Cel-Et-3100

Fig. 1 SEM images of the original samples and the 900 °C- and 3000 °C-treated ones. Cel-Et (a), original cellulose nanofibril paste dried in air (b), extended image of Cel-Et (c), Cel-H₂O (d), Cel-Et 900 (e), Cel-H₂O-900 (f), Cel-Et-3000 (g) and Cel-H₂O-3000 (h).

Fig. 2 TEM images of Cel-Et-3100. (a) and (b) are the bright field images, (c) and (d) are the 002 lattice fringes of graphitic parts, and (e) and (f) are those of turbostratic parts. The insets in (d), (e) and (f) are the FFT images of the 002 lattice fringes in (d), (e) and (f). Each of ①, ② and ③ indicates a diameter of each carbon nanofiber in (a), (b) and (c), respectively.

is shown in **Figs. 2(c)** and (d). Stacked hexagonal carbon layers, running parallel each other, extended along the axis of the carbonized nanofibril. Each of ①, ② and ③ indicates a diameter of each carbon nanofiber in and **Figs. 2(a)**, (b) and (c), respectively. The diameters of the 3100 °C-treated carbon nanofibers observed are distributed widely, being about 10-300 nm, which approximately correspond to those of the original cellulose nanofibrils of about 30-300 nm estimated from the SEM observations. For example, the diameter ① in **Fig. 2(a)** is about 100 nm, ② in **Fig. 2(b)** is about 20 nm and ③ in **Fig. 2(c)** is about 10 nm. On the other hand, the fibrous texture was not observed by the SEM observations as shown in **Fig. 1(g)** and (h) for the 3000 °C-treated carbon nanofibers as mentioned above. Even though the carbon nanofibers entangle each other, stick together and make an aggregate, the fibrous texture should remain, but the texture may not be obvious on the sample surface as observed using SEM. The difference between the SEM and TEM results seems to be attributed to the difference between the images formed by transmission

Fig. 3 Raman spectra for heat-treated samples of Cel-Et and Cel-H₂O and for Cel-Paste-3100.

electrons through specimens and those by the secondary electrons on the specimen surfaces.

The heat-treated sheets were found to be composed of graphitic and turbostratic components as shown in **Figs. 2(c)-(f)** as examples. The insets in **Figs. 2(d)-(f)** are the two dimensional fast Fourier transform (FFT) images of the 002 lattice fringes in these figures. Different types of the turbostratic areas are shown in **Figs. 2(e)** and (f). In **Fig. 2(e)**, carbon layers with small sizes tended to parallel along the axis of the carbonized nanofibril. Thin entangled turbostratic ribbons were observed in **Fig. 2(f)**. The regions exhibiting turbostratic structures seem to correspond to the inhomogeneous nanofibrils, inside of thick nanofibrils and disordered parts in the cellulose sheets.

3.3 Raman spectra

Raman spectra measured on the five different areas of the surfaces of each heat-treated sample differed from one another. The irradiated area of the Ar laser beam with 1 μm in diameter is large enough compared with the nanotexture of the carbonized nanofibrils, and the Raman spectrum relates not only to the surface structure, but also the orientation of carbon layers. Therefore, the Raman data were somewhat scattered by area to area. The Raman spectra measured on the five different areas were averaged, and the mean Raman spectrum for each heat-treated sheet of Cel-Et, Cel-H₂O and Cel-Paste-3100 are shown in **Fig. 3**. The D and D' bands in addition to the G band were observed for all heat-treated samples measured. The intensity of the D band for the heat-treated sheet of Cel-Et and also that of Cel-H₂O decreased with the increase of HTT. The results indicate that both carbon sheets prepared from Cel-Et and Cel-H₂O show improvement in structural order with HTT. On the other hand, the D

band of Cel-Paste-3100 was intense though heat-treated at 3100 °C, indicating non-graphitizing nature. Organic materials exhibiting solid phase carbonization, such as cellulose and furan resin, are basically known to be the precursors of nongraphitizing carbon, and the result for Cel-Paste-3100 is a typical case for the nongraphitizing carbon heat-treated at high temperatures^{1),2)}. The development of graphite structure on Cel-Et-3100 and Cel-H₂O-3100 seems to be attributed to graphitization behavior on the surface of nongraphitizing carbon, and the surface graphitization is effective against the carbon nanofibers with very thin diameters, *i.e.*, with high surface area^{4),7),8)}.

The values of G-FWHM and I_D/I_G were plotted as a function of HTT in Figs. 4(a) and (b), respectively. The values of G-FWHM and I_D/I_G for the heat-treated Bact-Et and Bact-H₂O and for Bact-NT-3100 are also plotted as a function of HTT in the figures for comparison⁸⁾. G-FWHM and I_D/I_G decreased with increasing HTT for the heat-treated Cel-Et and Cel-H₂O sheets, indicating structural improvement with increasing HTT. The G-FWHM and I_D/I_G

Fig. 4 FWHM of G-band G-FWHM (a) and intensity ratio I_D/I_G (b) as a function of HTT for heat-treated samples of Cel-Et and Cel-H₂O and for Cel-Paste-3100. The values of I_D/I_G and G-FWHM for the heat-treated Bact-Et and Bact-H₂O and for Bact-Paste-3100 are also plotted as a function of HTT in the figures for comparison⁸⁾.

for Cel-Paste-3100 are larger than those for Cel-H₂O-3100 and Cel-Et-3100. For examples, the values of G-FWHM and I_D/I_G for Cel-Et-3100 were 23.5 and 0.163, respectively, and those values for Cel-Paste-3100 were 29.4 and 0.493, respectively. The G-FWHM and I_D/I_G values for Cel-Et-3100 roughly correspond to the d_{002} value of 0.3414 nm and those for Cel-Paste-3100 correspond to d_{002} =0.3418-0.3420 nm using the relations between d_{002} and G-FWHM and between d_{002} and I_D/I_G for Kapton-derived carbon films¹³⁾, *i.e.*, the structure for both Cel-Et-3100 and Cel-Paste-3100 is expected to be turbostratic. We have to consider that the information of the Raman spectrum is limited to the surface of the specimen, *i.e.*, Raman spectrum reflects the structure, texture and orientation of carbon layers at the surface as mentioned above. Therefore, the Raman result of Cel-Et-3100 indicates that the influence of the surface texture on G-FWHM and I_D/I_G is large, and the surface structure, *i.e.*, degree of graphitization of the sample seemed to be underestimated. The Raman result is also probably due to the multiphase graphitization of Cel-Et-3100 being composed of graphitic and turbostratic structures. In addition, the present Raman results show that the G-FWHM and I_D/I_G values for the heat-treated Cel-Et, Cel-H₂O, Bact-Et and Bact-H₂O gave almost the same values at the same HTT above 3000 °C and also those values for Cel-Paste-3100 gave almost the same values as those for Bact-NT-3100. As will be described later, however, the results of the XRD measurements indicate that the structure development of the heat-treated Cel-Et and Cel-H₂O sheets is less than that of the heat-treated sheets of bacteria cellulose nanofibers⁸⁾. The present Raman results in Fig. 4 suggest again that the influence of the surface textures of the heat-treated sheets and lumps on G-FWHM and I_D/I_G is considerably large.

3.4 XRD

It was reported that no correlation was obtained between characteristics of the 002 diffraction profile of a charcoal and the crystallinity of the precursor cellulose in ref. 2. On the other hand, Kim *et al.* measured XRD patterns for *Cladophora* (algal cellulose), *Halocynthia* (tunicate cellulose, *i.e.* animal cellulose), *Acetobacter* (bacteria cellulose) and ramie fiber (China grass), and obtained a good correlation between the mean crystallite size of the initial cellulose nanofibrils and that of the resultant carbons heat-treated at 2000 °C⁵⁾. The order of the mean crystallite sizes of the cellulose nanofibrils were algal cellulose > animal cellulose > bacteria cellulose > ramie fiber. In the present study, we measured the XRD diffraction profiles of Cel-Et (from plant pulp), Bact-Et (from bacteria cellulose) and Ani-Et (from animal cellulose), and the profiles are shown in Fig. 5. The order of crystallinity was obtained to be Ani-Et > Bact-Et > Cel-Et and the result is consistent with that in ref. 5. The structural improvement of carbon nanofibers derived from cellulose nanofibrils with heat treatment probably progress more remarkably for the precursor nanofibrils with better crystallinity as pointed out in ref. 5. The less crystallinity

Fig. 5 XRD profiles of present Cel-Et (cellulose nanofibrils), Bact-Et (bacteria cellulose) and Ani-Et (animal cellulose).

of Cel-Et prepared from the commercially available cellulose paste is attributed to a plant pulp used and also to the production method *i.e.*, smashing the plant pulp to submicroscopic fragments mechanically¹¹⁾.

Fig. 6 shows the XRD profiles for the heat-treated samples. Separated 100 and 101 peaks were observed for all heat-treated Cel-Et and Cel-H₂O sheets as shown in **Fig. 6(a)**. On the other hand, only 10, 002 and 004 peaks were observed for Cel-Paste-3100, exhibiting typical turbostratic structure, which is consistent with the Raman results. The turbostratic 10 peak was also observed for the heat-treated sheets, but was very weak for the Cel-Et sheets heat-treated at temperatures above 2600 °C. A 112 peak, reflecting the stacking regularity of carbon layers in graphite, was observed for the Cel-Et sheets heat-treated at temperatures above 2600 °C and Cel-H₂O-3000, -3100 and -3200. The XRD results demonstrate that a relatively large region of the Cel-Et sheet and some region of the Cel-H₂O sheet are graphitized by heat treatment at high temperatures. These results are consistent with the results of the TEM observations and Raman spectra measurements.

The 102 peak was observed for the heat-treated Cel-Et and Cel-H₂O sheets. The 102 peak was also observed for the heat-treated sheets of bacteria cellulose nanofibrils and should be attributed to some arrangement and orientation of the nanofibers against each sheet plane⁸⁾. The values of the peak intensity ratio of 004 against 100 or 101, or against 102, for the heat-treated Cel-Et and Cel-H₂O sheets were incoherent to HTT and scattered, as the same as those for the heat-treated sheets derived from bacteria cellulose nanofibrils⁸⁾, and the incoherent values of the peak intensity ratios are probably due to the different orientation conditions of the nanofibers against sheet planes.

Asymmetrical 002 and 004 peaks were observed for the heat-treat-

Fig. 6 XRD profiles of 100-112(a), 002(b) and 004(c) for heat-treated samples of Cel-Et and Cel-H₂O and for Cel-Paste-3100.

ed Cel-Et and Cel-H₂O sheets except Cel-Et-3200 as shown in **Figs. 6(b)** and **(c)**, and some heat-treated sheets exhibited complex 002 and 004 peaks, which are different from the symmetrical 002 and 004 peaks for the heat-treated sheets of bacteria cellulose nanofibers⁸⁾. These results indicate multiphase graphitization of the heat-treated Cel-Et and Cel-H₂O sheets as observed generally for nongraphitizing carbons^{1),2)}. However, the 002 diffraction profiles are also different from those for charcoals after heat-treated at high temperatures, even from those for the samples derived from crystalline cellulose components of wood, which exhibited clear double 002 peaks²⁾. The present XRD data indicated that the structure development of the heat-treated Cel-Et and Cel-H₂O sheets is less than that of the heat-treated sheets of bacteria cellulose nanofibers⁸⁾, but better than the charcoals heat-treated at high temperatures²⁾, *i.e.*, the graphitized components in the heat-treated Cel-Et and Cel-H₂O sheets seem to occupy smaller regions than those in the heat-treated sheets derived from bacteria cellulose nanofibers, but larger regions than those in the heat-treated charcoals. The difference in improvement of graphitization should be due to the difference in the effect of the surface graphitization. The diameters of the nanofibrils in Cel-Et and Cel-H₂O were about 30-300 nm with a broad distribution of their diameters, while the diameters of the bacteria cellulose nanofibers were 30-60 nm^{7),8)}, and the sizes of the charcoal particles should be micrometric because the XRD measurements were made according to so-called Gakushin method¹⁴⁾.

The values of d_{002} for the heat-treated sheets and Cel-Paste-3100 are plotted as a function of HTT in **Fig. 7**. The values of d_{002} for the heat-treated Bact-Et and Bact-H₂O and for Bact-NT-3100 are also plotted as a function of HTT for comparison⁸⁾. Because of the asymmetrical or complex 002 peaks for the present heat-treated sheets,

Fig. 7 d_{002} plotted as a function of HTT for heat-treated sheets of Cel-Et and Cel-H₂O and for Cel-Paste-3100. The values of d_{002} for the heat-treated Bact-Et and Bact-H₂O sheets and for Bact-Paste-3100 are also plotted as a function of HTT for comparison⁸⁾.

the L_c values were not evaluated and the d_{002} values obtained are the mean values for turbostratic and graphitic components in each sample. d_{002} decreases with increasing HTT for both of the heat-treated Cel-Et and Cel-H₂O sheets. The tendency of the HTT dependence of d_{002} shown in **Fig. 7** is similar to those of G-FWHM and I_D/I_G shown in **Fig. 4**, except some respects due to the influence of surface texture on G-FWHM and I_D/I_G . The d_{002} values for Cel-Et-3100 and Cel-Paste-3100 are 0.3402 and 0.3436 nm, respectively, while from the G-FWHM and I_D/I_G data for Cel-Et-3100 and Cel-Paste-3100 the d_{002} values were estimated to be 0.3414 nm and 0.3418-0.3420 nm as described in Section 3.3¹³⁾. The difference in the d_{002} values for Cel-Et-3100 and Cel-Paste-3100 between the measured values and those estimated from the Raman data are probably due to following reason. Cel-Paste-3100 has a lump shape and the surface is rather smooth, so that the Raman spectrum reflects the improvement of structure on the surface mainly, while Cel-Et-3100 has a rough surface texture as shown in **Fig. 1(g)**, so that the texture and orientation of carbon layers at the surface affect the Raman spectrum considerably.

At the same HTT above 3000 °C, the d_{002} value for the heat-treated Cel-Et sheet is smaller than that for the heat-treated Cel-H₂O sheet and much smaller than that for Cel-Paste-3100, *i.e.*, the order of the degree of graphitizability is Cel-Et > Cel-H₂O > Cel-Paste, and the order is the same as that of the carbon nanofibers derived from bacteria cellulose, Bact-Et > Bact-H₂O > Bact-NT⁸⁾. However, the d_{002} values for the heat-treated Cel-Et and Cel-H₂O sheets and Cel-Paste-3100 are larger than those for the heat-treated Bact-Et and Bact-H₂O sheets and Bact-NT-3100, respectively. The structural improvement of carbon nanofibers derived from cellulose nanofibrils with heat treatment should progress more remarkably for thinner diameter, better separation and better crystallinity of the nanofibrils, and also narrower distribution of their diameters.

3.5 Electric resistivity

The ρ values for Cel-Et-3000, -3100 and -3200 are listed in **Table 1**. The ρ values for Bact-Et-3000, -3100 and -3200 are also listed in the table for comparison⁸⁾. The values for the Cel-Et samples are larger than those for the Bact-Et samples, but not so much different from those values. The results are in consistent with those of the XRD measurements. These ρ values also larger than the volume resistivity of a commercially available powder of vapor grown carbon

Table 1 Values of sheet resistivity ρ for Cel-Et-3000, -3100 and -3200. Values of the sheet ρ resistivity for Bact-Et-3000, -3100 and -3200 are also listed in the table for comparison⁸⁾.

ρ of sample	HTT		
	3000 °C	3100 °C	3200 °C
Cel-Et (Ω m)	3.53×10^{-4}	3.32×10^{-4}	2.84×10^{-4}
Bact-Et (Ω m)	2.71×10^{-4}	1.80×10^{-4}	1.34×10^{-4}

fibers heat-treated at high temperature, VGCF[®], ($1.2 \times 10^{-4} \Omega \cdot \text{m}$). If the good separation of each carbon nanofiber after heat-treated at high temperature is achieved, for example the cellulose nanofibrils prepared by freeze dry in an organic solvent, there is a possibility as electrical conductive additives for CFRP with high performance.

4. Summary

Structural order of carbon nanofibers improves with increasing HTT in the carbon sheets derived from cellulose nanofibrils of plant origin dispersed in ethanol or distilled water, especially those dispersed in ethanol, though a turbostratic component was also observed even for the sheet heat-treated at 3200 °C. On the other hand, a bulk carbon derived from the original cellulose nanofibril paste exhibited a typical turbostratic structure even after heat-treated at 3100 °C. The development of graphite structure in the carbon sheets is probably attributed to the surface graphitization, *i.e.*, a graphitization behavior on the surfaces of the carbon nanofibers and also on their insides because of the thin diameters of about 30-300 nm, as the same as the graphitization of the carbonized sheets prepared from the bacteria cellulose nanofibers with 30-60 nm in diameter dispersed in ethanol or distilled water by simple heat treatment at high temperatures^{7),8)}. The structure development of the heat-treated Cel-Et and Cel-H₂O sheets is less than that of the heat-treated sheets of bacteria cellulose nanofibers⁸⁾. The structural improvement of carbon nanofibers derived from cellulose nanofibrils with heat treatment should progress more remarkably for thinner diameter, better separation and better crystallinity of the nanofibrils, and also narrower distribution of their diameters.

Acknowledgment

One of the authors Y. K. acknowledges the financial support by a

Grant-in-Aid for Science Research No. 23560806 from the Japan Society for the Promotion of Science (JSPS).

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