GRAPHITE PAPER PREPARED FROM BACTERIA CELLULOSE

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Introduction

Cellulose based carbon materials are known to be one of the nongraphitizing carbons, and cellulose based carbon fibers were not graphitized except the skin region by simple heat treatment at high temperatures [1]. Cellulose nanofiber paste consisting of elemental fibrils with 50-300 nm in diameters was obtained from wood pulp by smashing it to submicroscopic fragments mechanically. It was found that the carbon nanofiber aggregate prepared from the cellulose nanofiber paste was also nongraphitizing carbon [2]. On the other hand, recently, bacteria cellulose has attracted much attention as a new resource of cellulose for preparing fine clean paper and for the application to an artificial skin due to compatibility with organisms and for other technical use such as speaker corn. The bacteria cellulose is a secretion from acetic acid bacteria and pure cellulose nanofiber with 40 – 200 nm in diameters. In this study, we focused on the property as a carbon material when heat treated the bacteria cellulose at high temperatures.

Experimental

Nata de coco is mainly composed of bacteria cellulose, sugar and water. Nata de coco was smashed to a pulp by a liquidizer, and the bacteria cellulose was filtered out from the pulp. The bacteria cellulose was then dissolved in distilled water and stirred by an electromagnetic stirrer for 1 day and then filtrated. A paper like sheet composed of the cellulose nanofibers with about 1 mm in thickness was obtained after filtration and dried at 60°C in air for 12h. The sample is designated by PinW. The filtrated sample was dissolved again in ethyl alcohol and stirred for 1 day and then filtrated. A paper composed of cellulose nanofibers with about 1 mm in thickness was also obtained after filtration and dried at 60°C in air for 12h. The sample thus obtained is designated by PinE. PinW and PinE were carbonized at 900°C in Ar gas and then further heated to 2800°C in high purity Ar gas and kept for 1 min. The heat-treated samples are designated by PinW or PinE followed by the heat treatment temperatures. The heat treatments at 2800°C for PinE900 were made for three times for confirmation, and samples obtained are designated by PinE1, 2, 3 followed by 2800. The texture and structure of the heat treated carbon papers were investigated by the SEM observations and the XRD and Raman spectra measurements. The XRD measurements were conducted using CuKα radiation and the Raman spectra were measured using Ar ion laser with a wave length of 514.5 nm.

Results and Discussion

Figure 1 shows the SEM photo of PinE. The cellulose nanofibers are directed isotropically along a paper plane, but stacked parallel each other. By the X-ray fluorescence analysis, the chemical composition of PinE as well as PinW was found to be 50 wt% of C, 48 wt% of O, 2.3 wt% of N and traces of Cl, Na, S, Si, Mg, Ca and F. After carbonization at 900°C, the composition was 54 wt% of C and 46 wt% of O,

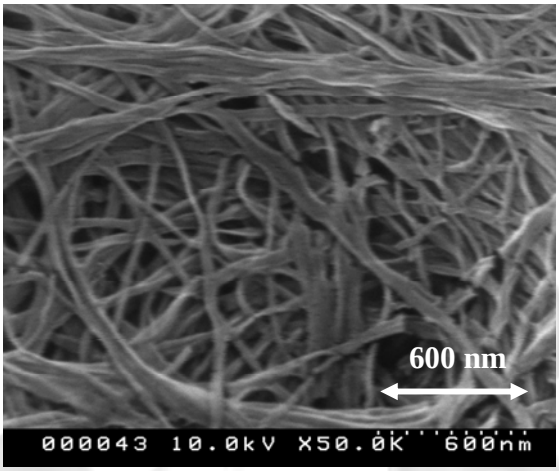

Fig. 1 SEM photo of cellulose nanofibers in PinE.

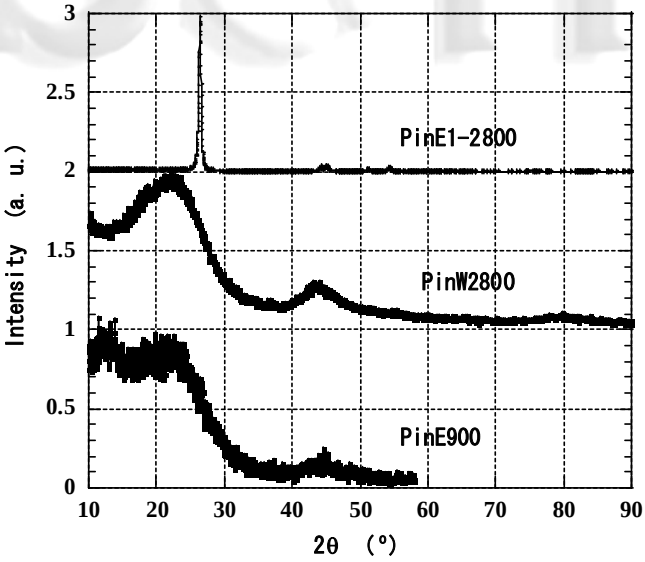

Fig. 2 X-ray diffraction profiles for PinE1-2800, PinW2800 and PinE900.

and almost 100 wt% of C for the 2800 °C-treated ones. On the other hand, the BET specific surface area of PinW900

evaluated from N_2 adsorption isotherm at 77K was 150 m^2/g, while it was 380 m^2/g for PinE900. The results show that the bulk density of PinE is lower than that of PinW, i. e., nanofibers in PinE exist more separately than those in PinW.

X-ray diffraction patterns for PinE1-2800, PinW2800 and PinE900 are shown in Fig. 2. The pattern for PinE900 as well as that for PinW900 shows usual pattern for the low heat-treated carbon. The pattern for PinW2800 exhibits typical one for nongraphitizing carbon heat treated at high temperatures, while that for PinE1-2800 indicates that PinE1-2800 is graphitized carbon. Almost the same results were obtained for PinE2-2800 and PinE3-2800. The values of the interlayer spacing d_{002} evaluated from the 004 lines for PinE1-2800 to 3-2800 were 0.3372 – 0.3375 nm and those of crystallite size Lc were 21 – 30 nm, though the residence time was only 1 min at 2800°C. Therefore, the carbon paper prepared from a paper composed of nanofibers of bacteria cellulose filtered from the solution in ethyl alcohol, PinE900, was recognized to be graphitizing carbon.

In Fig 3, detailed profile of PinE1-2800 in reflection mode shown in Fig. 2 and the diffraction pattern measured in transmission mode are shown. The results indicate that the carbon layers are oriented parallel in some degrees to the paper surface of PinE1-2800. The value of the mosaic spread for PinE1-2800, however, about 30°.

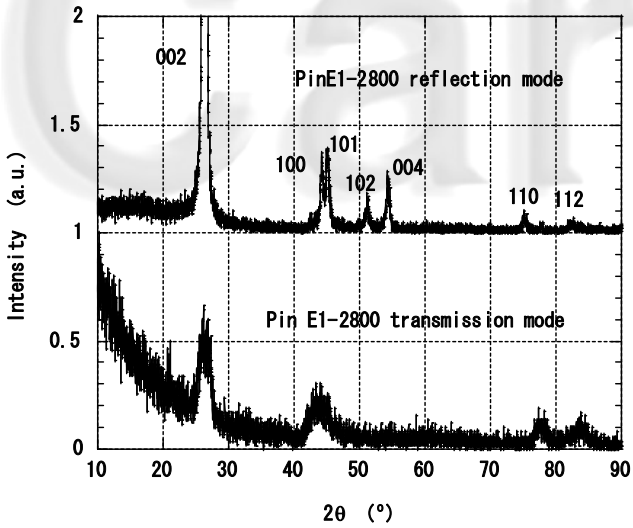

Fig 3 Detailed profile of PinE1-2800 in reflection mode and the diffraction pattern measured in transmission mode.

Raman spectra were measured for three different points on the surface of each PinE-2800 sample. The spectra were almost the same as each other for the three points. Figure 4 shows the Raman spectra as a function of Raman shift for PinE1-2800, 2-2800 and 3-2800. Each spectrum is the mean value of the spectra for the three points on each sample. The values of the ratio of the intensity of the D band to that of the G band I_D/I_G and those of the full width at the half maximum of the G band G-FWHM were evaluated to be 0.045 – 0.063 and 18 – 21, respectively, from Fig. 4. These results agree well with the results obtained from XRD, indicating that the carbon paper prepared from a paper obtained by filtration of bacteria cellulose in ethyl alcohol is graphitized carbon. As an example of the graphite papers, PinE3-2800 is shown in Fig. 5.

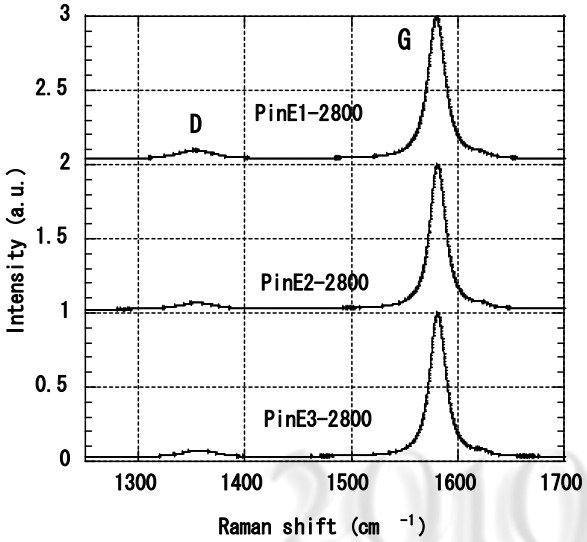

Fig. 4 Raman spectra as a function of Raman shift for PinE1-2800, 2-2800 and 3-2800. Each spectrum is the mean value of the spectra for the three points on each sample.

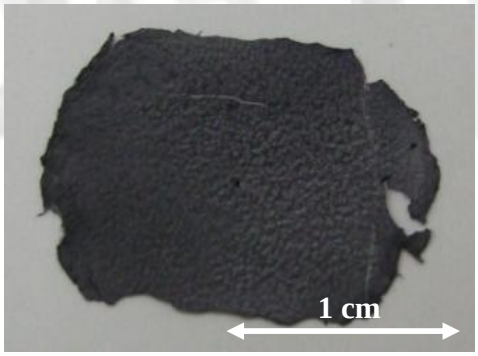

Fig. 5 Photograph of PinE3-2800.

Conclusion

Graphite papers with about 1 mm in thickness were obtained by the heat treatment at 2800°C for only 1 min, though cellulose-based carbon fibers have been known as nongraphitizing carbons.

References

[1] Y. Kaburagi, K. Hoshoya, A. Yoshida, Y. Hishiyama, Carbon **43** (2005) 2817.

[2] Y. Kaburagi, A. Yoshida, K. Hosoya, E. Shindou, Y. Hishiyama, Inter. Symp. on Nanocarbons, p.90, Nagano (2004).