

Promotion of Crystal Growth on Biomass-based Carbon using Phosphoric Acid Treatments

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The effect of phosphoric acid treatments on graphitic microcrystal growth of biomass-based carbons was investigated using X-ray diffraction, infrared spectroscopy, and Raman spectroscopy. Although biomass-based carbons are believed to be hard to graphitize even after heat treatments well beyond 2000 °C, we found that graphitic microcrystals of biomass-based carbons were significantly promoted by phosphoric acid treatments above 800 °C. Moreover, twisted spindle-like whiskers were formed on the surface of the carbons. This suggests that phosphorus-containing groups turn graphitic microcrystalline domains into graphite during phosphoric acid treatments. In addition, the porous texture of the phosphoric acid-treated carbon has the advantage of micropore development.

Keywords: Crystal growth; Biomass-based carbon; Phosphoric acid; Graphitic whisker

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INTRODUCTION

Carbon materials are widely used in various industrial fields. Several studies have been conducted on the promising physical properties of these materials. Various arrangements of groups of carbon atoms give carbon materials an extremely wide range of properties (*i.e.*, physical, chemical, and mechanical). The structure of carbons thus represents major features of carbon materials. From the Franklin model of carbon structure (Franklin 1950), there are so-called graphitizable carbons in which graphene layers show considerable planarity and stacking: for example, petroleum coke and asphalt. On the other hand, there are carbons that are always non-graphitic, even after heating well beyond 2000 °C. These are so-called non-graphitizable carbons. Charcoal, activated carbons, and other biomass carbons are examples of non-graphitizable carbons. In this study, we thus focus on a method that improves the crystallinity of carbons made from biomass materials. If graphitizable carbons are obtained from biomass materials, this provides economic and ecological advantages because of their sustainability.

Phosphoric acid treatment of cellulosic materials has become a widely used method for the large-scale manufacture of activated carbons in the last 20 years because of their environmental benefits and low energy cost advantages. Most of the studies that deal with phosphoric acid treatment were focused on the pore structure of the activated carbons during the treatment (Molina-Sabio *et al.* 2004; Corcho-Corral *et al.* 2006). There has been little research that has applied activated carbons to the materials manufacture field because the conventional researcher has been interested in application

of activated carbon products for adsorption of vapors, extraction of organics from water, decolorizing and so on.

In the conventional studies, lignocellulosic materials have been frequently used as a starting specimen for the manufacture of activated carbons. The chemical reactions between cellulose and phosphoric acid at high heat-treated temperature (HTT) have been reported by Puziy *et al.* (2006). In the case of reactions at $\text{HTT} < 450\text{ }^\circ\text{C}$, phosphate esters are formed by the reaction of cellulose with phosphoric acid. At $\text{HTT} > 450\text{ }^\circ\text{C}$, the structure begins to contract. With the elimination of phosphoric acid, the reduction in cross-link density allows the growth and alignment of aromatic clusters, producing a more densely packed structure. Meanwhile, an effect of phosphorus on the development of carbon crystallites was reported by Marinkovic *et al.* (1973; 1974), who studied the carbonization and graphitization of pyrocarbons incorporated with phosphorus. However, little is known about the effect of phosphoric acid on the crystalline growth of biomass-based carbons at high HTT. If a carbon material of high crystallinity is obtained at low cost, it can greatly contribute to the carbon material invention.

In the present study we attempted to use the carbonized biomass materials for the first time as a starting point. Then we tried to determine how phosphoric acid affects the crystalline growth of the biomass-based carbon. To accomplish this, two treatments, physical treatment using steam and chemical treatment using phosphoric acid, were selected to treat the biomass-based carbons under high HTT. The differences in their crystalline structures were then investigated using various structural analysis methods: not only spectroscopic (Infrared and Raman) but also X-ray diffraction (XRD) and small-angle X-ray scattering (SAXS). Bio-based carbons imparted crystalline structure will contribute to the new property and function of activated carbon as a new material.

EXPERIMENTAL

Materials

Commercially available bamboo charcoal was selected as the raw material in this study. The starting material was ground to obtain samples of 0.2- to 0.5-mm particle size for hardening-carbonization, in which the samples were carbonized at $850\text{ }^\circ\text{C}$ for 1 h in an electric furnace.

Methods

Sample preparation

To compare the growth of the crystalline structures of the biomass-based carbons, the samples were treated by two methods: physical treatment using steam and chemical treatment using phosphoric acid. For the physical treatment process, 10.0 g of carbonized bamboo charcoal was put into a cylindrical crucible situated in the middle position of a tube furnace and heated at a rate of $5\text{ }^\circ\text{C}/\text{min}$ to $850\text{ }^\circ\text{C}$ under a nitrogen flow of $2.0 \times 10^{-4}\text{ m}^3/\text{min}$. The sample was then treated at $850\text{ }^\circ\text{C}$ for 30 min with a steam flow of $2.0 \times 10^{-4}\text{ m}^3/\text{min}$. The sample was cooled to ambient temperature and kept in a desiccator for further characterization experiments. For the chemical treatment process, 10.0 g of carbonized bamboo charcoal was impregnated with 50 mL of 20% phosphoric acid solution. The mixture was held in a water bath at $80\text{ }^\circ\text{C}$ for 2 h and was then dried at $120\text{ }^\circ\text{C}$ until it reached a constant weight. The impregnated bamboo charcoal was put into a cylindrical ceramic container that was placed in a muffle furnace. The impregnated

material was heated from room temperature up to 850 °C at a rate of 5 °C/min and resided for 30 min. After cooling to around room temperature in the muffle furnace, the sample was washed repeatedly with warm deionized water until phosphorus was undetectable in the filtrate. Finally, the phosphoric acid-treated (H_3PO_4 -treated) samples were dried at 120 °C until they reached a constant weight.

The treated carbons were further heat-treated at 1500, 2000, and 2800 °C using a graphitizing furnace (Kurata, SCC-U-30/650 KRET-50; Japan) for 10 min to investigate the growth mechanism of graphitic microcrystals.

Characterization method

The information on the pore structure of the treated carbons was estimated with gas adsorption and small angle X-ray scattering (SAXS) measurements. The adsorption of N_2 , as a probe species, was performed at -196 °C using a Bel Sorp 18 (Bel Japan Co. Ltd., Japan). The nitrogen adsorption isotherms of the activated carbon samples were measured over the relative pressure (P/P_0) range from 0 to 1. The specific surface area and the micropore volume (V_{mic}) of the samples were estimated by Brunauer-Emmet-Teller (BET) analysis (Rouquerol *et al.* 1999) and the subtracting pore effect method (Kaneko *et al.* 1992) using α_s -plot. The total pore volume (V_{tot}) was calculated from the amount of nitrogen adsorbed at a relative pressure of 0.99. Mesopore volume (V_{mes}) was obtained by subtracting V_{mic} from V_{tot} . Pore size distribution was estimated based on the nitrogen adsorption isotherms.

SAXS measurements were performed using synchrotron radiation at the beam line BL11 of the SAGA Light Source with the approval of the Kyushu Synchrotron Light Research Center, Japan. The beam energy was 8.0 keV, and the camera length was 2,641 mm.

X-ray diffraction (XRD) measurements were used to investigate the crystalline structural changes of the treated carbons. The XRD patterns were recorded at ambient temperature on a Rigaku diffractometer (Rigaku RINT2100V, Japan). The data collection was performed on the diffraction angle 2θ from 5° to 45°. The accelerating voltage and current were 40 kV and 20 mA, respectively.

The organic functional groups of the treated carbons were characterized by Fourier transform infrared (FT-IR) spectroscopy using the KBr method. The FT-IR data were collected using a FTIR-620 (JASCO Co., Japan) spectrophotometer. The condition for the measurements was as follows: 32 scans with a 2 cm^{-1} resolution equipped with a TGS detector, and the wavenumber region investigated ranged from 4000 to 400 cm^{-1} . Raman spectra were recorded by using a Laser Raman spectrometer (JASCO Co., NRS-2000) with a 488 nm laser excitation (a spectral resolution of 1 cm^{-1}) to evaluate the degree of graphitization in the samples.

The surface of the treated carbons and the non-treated carbons after heat treatment at 2800 °C were observed using field emission scanning electron microscopy (FE-SEM: SU8000, Hitachi High-Technologies Co., Japan).

RESULTS AND DISCUSSION

Crystalline Structures

The growth of crystalline structures in the H_3PO_4 -treated carbons was investigated with XRD analysis, as shown in Fig. 1. The XRD profiles of the non-treated and treated

bamboo carbon prepared by steam or phosphoric acid at 850 °C are shown in Fig. 1a. The carbons prepared by the steam and the non-treated carbons showed halos, which indicate that the samples were almost amorphous. On the other hand, the carbon treated with phosphoric acid had a sharp peak at 2θ values of 24° from the 002 plane (a d_{002} spacing of 0.37 nm). This suggests that some graphitic microcrystals were grown during the phosphoric acid treatment and that the phosphorus tends to promote the crystal growth.

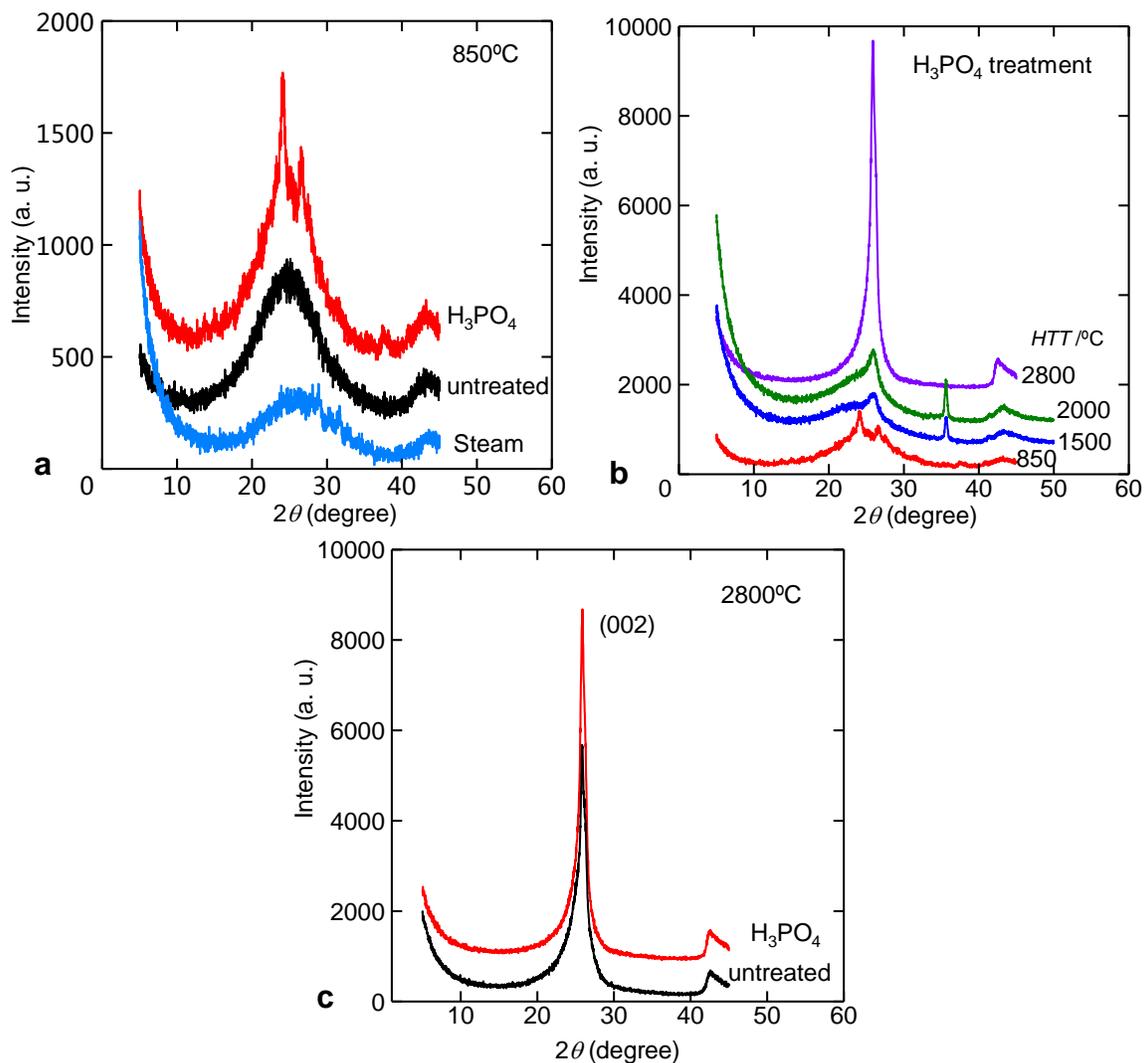


Fig. 1. X-ray diffraction profiles of (a) non-treated and bamboo carbon treated by steam or phosphoric acid at 850 °C, (b) H₃PO₄-treated carbon further heat-treated at 850 to 2800 °C, and (c) non-treated and H₃PO₄-treated carbon at 2800 °C

To further investigate the growth of graphitic microcrystals, the H₃PO₄-treated carbon was heat-treated at 1500, 2000, and 2800 °C (Fig. 1b). From the XRD profiles, the treated samples at 1500, 2000, and 2800 °C had a sharp peak at 2θ values of 26° from the 002 plane, originating from the graphitic structure. In the case of the heating temperature of 2800 °C, the peak intensity dramatically increased at $2\theta = 26^\circ$ (a d_{002} spacing of 0.34 nm), which was attributed to the graphite (Chung 2002). Increasing the heat-treated temperature resulted in a shift of the diffraction angle from 24° to 26°, which means that

the d_{002} space became narrower. This suggests that phosphorus penetrated into inter- or intra-crystalline and then gave rise to the swelling of the d_{002} space at 850 °C. When the heat-treated temperature increased, the space between the d_{002} spaces became gradually smaller due to the removal of phosphorus. The difference of the graphitic structures in the H_3PO_4 -treated carbon and the non-treated carbon heat-treated at 2800 °C can be seen in Fig. 1c. A sharp peak was also found at 2θ values of $\sim 26^\circ$ from the 002 plane for the non-activated carbon, which indicates that both samples had the same d_{002} spacing.

The coherent crystalline domain size along c axis (L_c) can be calculated from the Scherrer equation (Hamond 2009) as follows:

$$L_c = K\lambda/b\cos\theta \quad (1)$$

where the form factor (K) is 1.00, the X-ray wavelength (λ) is 0.154 nm, and b is the half width of the peak. The calculated coherent domain sizes L_c are 8.58 nm and 12.3 nm for the non-treated carbon and the H_3PO_4 -treated carbon, respectively. The larger value of the coherent domain size of the H_3PO_4 -treated carbon occurs because phosphorus promotes the further growth of graphitic microcrystals and then forms graphite.

Growth of Graphitic Microcrystals in H_3PO_4 -treated Carbons

The FT-IR spectra of the non-treated and treated bamboo carbon prepared by the steam or the phosphoric acid at 850 °C are shown in Fig. 2a. The IR spectra of the above samples contain a series of absorption bands of C-O and C-O-C stretching at 1080 cm^{-1} and 1180 cm^{-1} (Zawadzki 1989). The spectra also show a band at 1580 cm^{-1} due to aromatic ring stretching vibrations (Vinke *et al.* 1994). The intensity of the bands at 1080 to 1180 cm^{-1} in the H_3PO_4 -treated carbon was stronger than that in the steam treated carbon and the non-treated carbon. The absorption in this region is usually found in oxidized carbons (Zawadzki 1989; Vinke *et al.* 1994) and carbons treated with phosphoric acid (Laine and Calafat 1991; Jagoyen *et al.* 1992; Vinke *et al.* 1994; Solum *et al.* 1995; MacDonald and Quinn 1996). Broad bands at 1300 to 1000 cm^{-1} have been assigned to C-O stretching in acids, alcohols, phenols, ethers, and esters (Bellamy 1954). The absorption in this region is also characteristic for phosphorus and phosphocarbonaceous compounds (Bellamy 1954; Jagoyen *et al.* 1992; Socrates 1994; Solum *et al.* 1995).

The FT-IR spectra of the H_3PO_4 -treated carbon after being further heat-treated at 850, 1500, 2000, and 2800 °C are shown in Fig. 2b. With increasing heat-treated temperature, the absorption in 1300 to 1000 cm^{-1} and 1580 cm^{-1} disappeared at temperatures above 1500 °C. This indicates that the phosphorus and phosphocarbonaceous compounds were removed from the treated carbons at higher temperatures.

The Raman spectra of the samples under various heat-treated temperatures are shown in Fig. 3a and Fig. 3b. Carbon materials typically exhibit two broad bands in the Raman spectra, called D (disordered) and G (graphitic) around 1357 and 1582 cm^{-1} . The band located at 1582 cm^{-1} is attributed to the graphitic structure, whereas the band located at 1357 cm^{-1} originates from disordered structure in the carbon (Ferrari and Robertson 2000). The intensity ratio of D- and G-bands (I_D/I_G) can be used to extract structural information of the carbons. It is widely used to evaluate the quality of graphitic materials (Roy *et al.* 2003). In our measurements, at 850 °C (Fig. 3a), the value of the I_D/I_G ratio for the H_3PO_4 -treated carbons was found to be the smallest of the three samples. This

indicates that the graphitization degree of H₃PO₄-treated carbons was the highest even under a relatively lower HTT. However, at the temperatures of 1500 and 2000 °C (Fig. 3b), the value of the I_D/I_G ratio for the H₃PO₄-treated carbons increased as HTT increased, although the intensity of D and G bands were stronger than that in 850 °C. This suggests that the phosphorus was difficult to completely remove below 2000 °C, and they still remained along with the graphitic microcrystalline domains to keep the microcrystalline size small. This makes the I_D/I_G ratio high for the H₃PO₄-treated carbons at 1500 and 2000 °C.

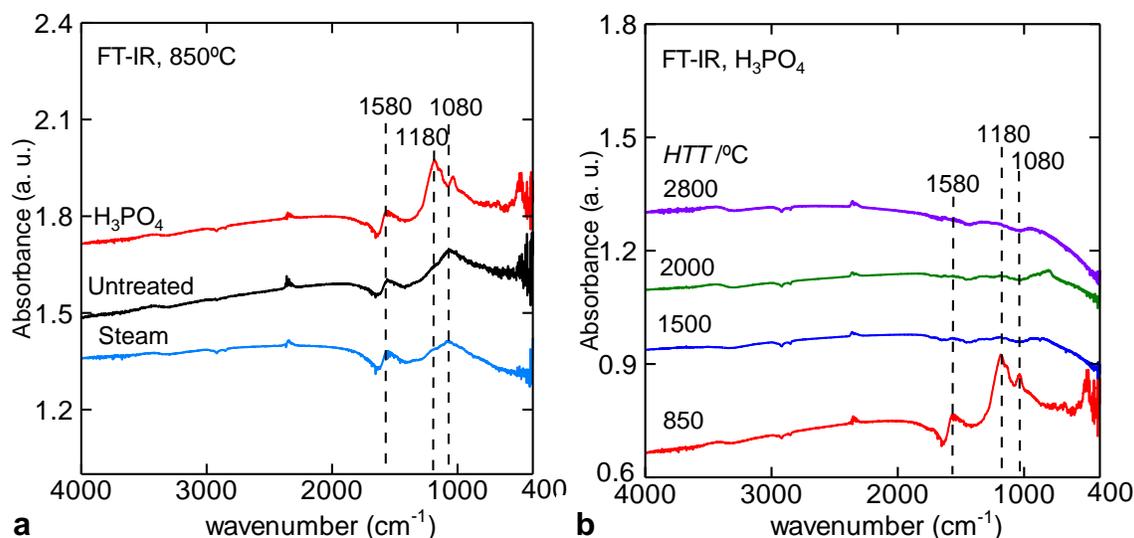


Fig. 2. FT-IR spectra of (a) non-treated and carbons treated by steam or phosphoric acid at 850 °C and (b) the H₃PO₄-treated carbons after further heat-treated at 850, 1500, 2000, and 2800 °C

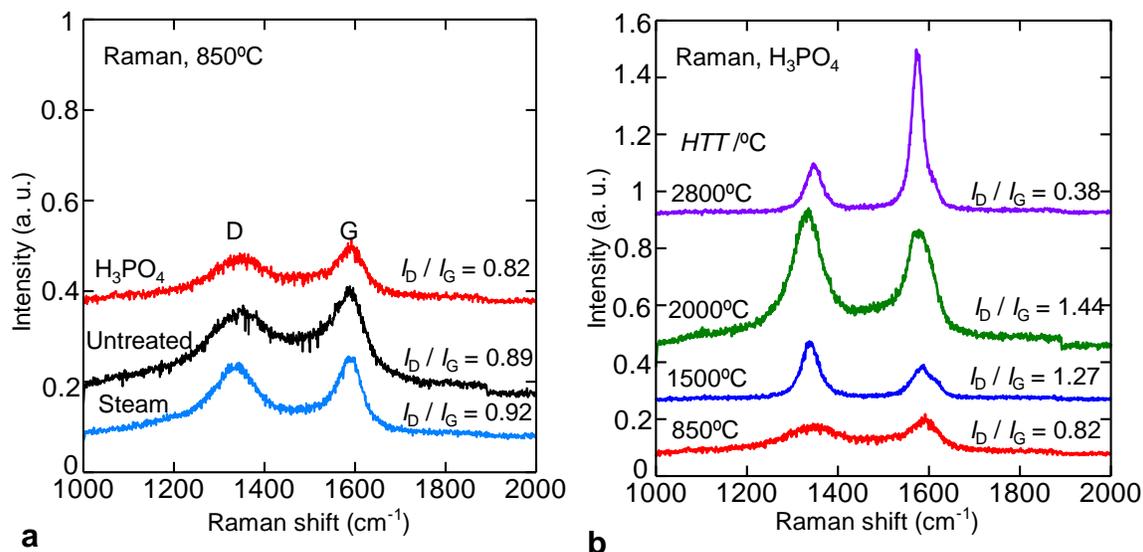


Fig. 3. Raman spectra of (a) non-treated and carbons treated by steam or phosphoric acid at 850 °C and (b) the H₃PO₄-treated carbons after further heat-treated at 850, 1500, 2000, and 2800 °C

In contrast, the value of the I_D/I_G ratio at 2800 °C (Fig. 3b) exhibits a noticeable decrease. This is possibly related to the fact that the phosphorus has been removed under high temperature treatment (2800 °C). The presence of phosphorus promotes the graphitic microcrystalline domains to form graphite. The results investigated above are consistent with the results of the XRD and FT-IR measurements.

Imamura *et al.* (1999) found that the introduction of phosphorus had an effect in promoting the development of graphitic crystallites at 3000 °C. Schönfelder *et al.* (1997) showed that phosphorus has a softening effect on the hard carbons derived from a polymer precursor by decreasing the strain on carbon layers, reducing interlayer spacing, and increasing the crystallite sizes. Also, we found a promoting effect of phosphorus on biomass-based carbons.

Growth in the microcrystals of the H_3PO_4 -treated carbons is illustrated in Fig. 4 as a function of HTT. The growth is divided into three regions. In region I, there were some graphitic microcrystals formed at 850 °C because of the assistance of the phosphorus. With increasing HTT, phosphorus was still difficult to remove below 2000 °C, and they still remained along the edge of graphitic microcrystalline domains to increase the amount of microcrystalline (region II). Until the HTT increased to 2800 °C (region III), the phosphorus was desorbed and the leaves of phosphorus promoted the graphitic microcrystalline domains to form graphite.

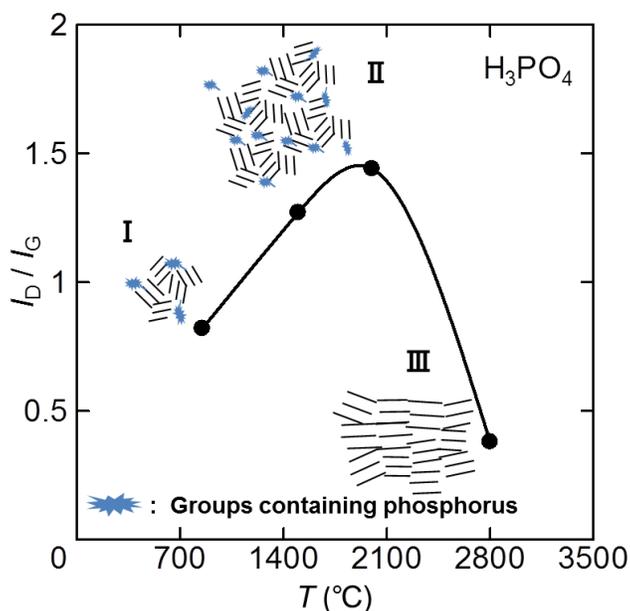


Fig. 4. Variation in I_D/I_G as a function of HTT for the H_3PO_4 -treated carbons

Whisker Emergence on the Surface of the H_3PO_4 -treated Carbons

The surface of the treated carbons and the non-treated carbons were observed by the use of a FE-SEM after heat treatment at 2800 °C (Figs. 5a and 5c). On the H_3PO_4 -treated carbons as shown in Fig. 5a, graphitic whiskers in the shape of a column with a twisted spindle head were grown on the carbon surface. On the contrary, there were almost no graphitic whiskers on the non-treated carbon surface as shown in Fig. 5c. These results were consistent with the results of X-ray diffraction in Fig. 1c. A few cases have been reported of accidental vapor phase carbonization of wood and the development of columnar or spindle-like deposits (Yoshida and Hishiyama 1982; Saito and Arima

2002; 2004). These deposits were arranged as conical stacked hexagonal layers (Saito and Arima 2004), assumed to be vapor-grown carbon that originated from vaporized pyrolysates generated from the wood cell walls during the high heat-treatment temperature. In this way, the findings in this study suggest that the phosphoric acid is related to the carbon deposits, and promoted the graphitic whiskers growth.

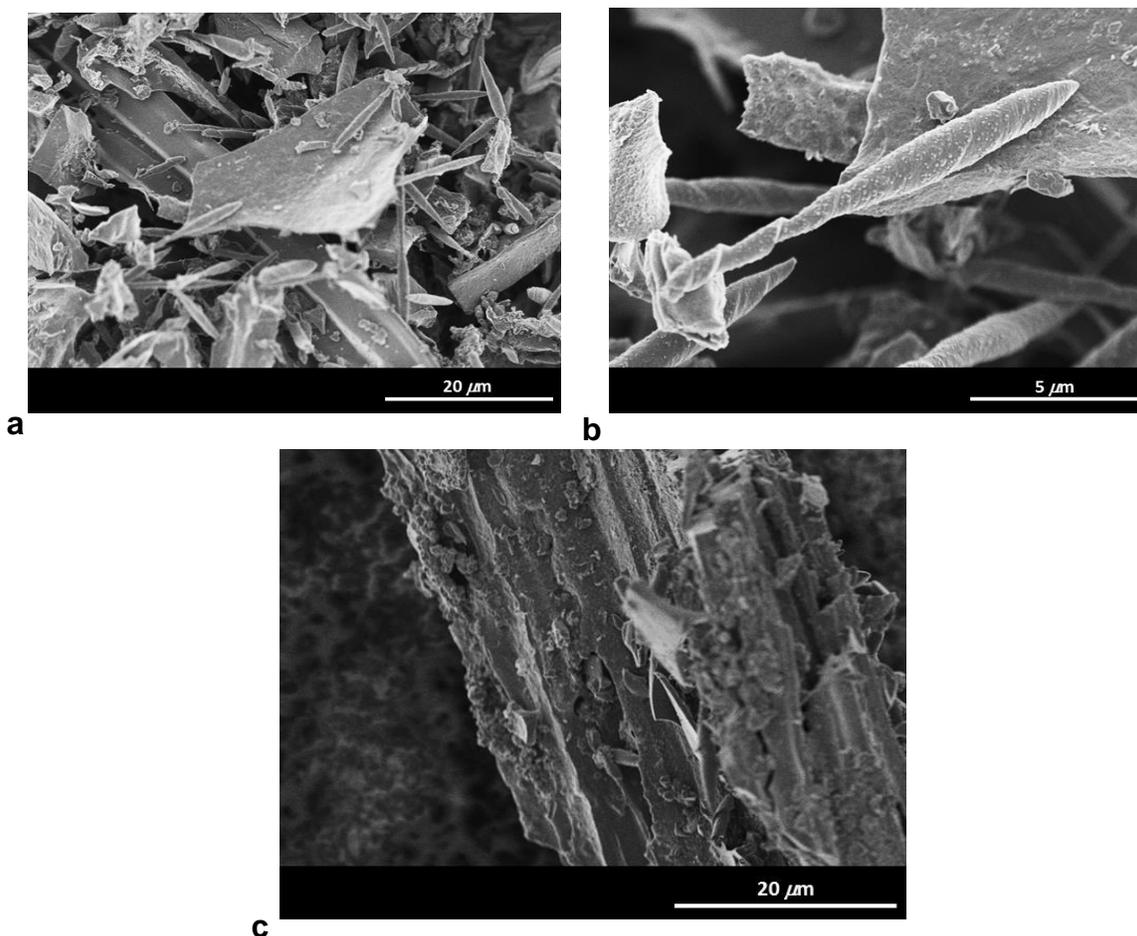


Fig. 5. FE-SEM micrographs of (a) the H_3PO_4 -treated carbons after heat treatments at $2800\text{ }^\circ\text{C}$, (b) graphitic whiskers on the surface of the H_3PO_4 -treated carbons, and (c) non-treated carbons after heat treatments at $2800\text{ }^\circ\text{C}$

Pore Characteristics of Treated Carbons

Figure 6 shows the nitrogen adsorption-desorption isotherms measured for the H_3PO_4 -treated carbons and the steam-treated carbons prepared at $850\text{ }^\circ\text{C}$. It shows that the H_3PO_4 -treated carbons had a shape of N_2 adsorption isotherm belonging to typical microporous carbons in the IUPAC classification (Sing *et al.* 1985) This indicates that the carbons had mainly microporous characteristics. The steam-treated carbons showed a hysteresis loop because they contained a mesoporous structure. The amount of N_2 adsorption onto the H_3PO_4 -treated carbons was larger than that of the steam-treated carbons, especially in the range of relatively high pressures. The adsorption isotherms can also be transformed into the BET surface areas and pore volumes as shown in Table 1. It was found that the surface areas and the pore volumes of the H_3PO_4 -treated carbon were larger than that of the steam treated one.

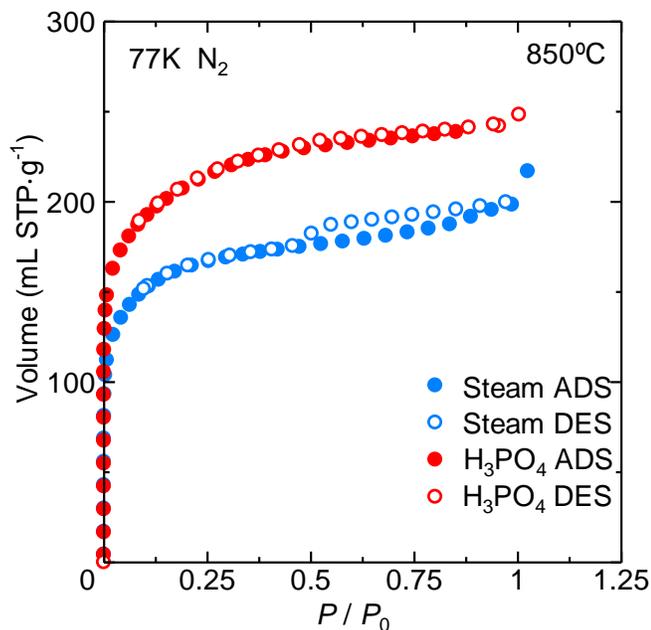


Fig. 6. Adsorption profiles of N₂ on the carbon treated at 850 °C

Table 1. Yield and Surface Properties of Bamboo Carbons Treated at 850 °C

	Yield (%)	Specific surface area (m ² /g)	Micro-pore volume (cm ³ /g)	Total pore volume (cm ³ /g)
Steam Treatment	43.9	610	0.237	0.310
Phosphoric Acid Treatment	55.2	766	0.322	0.381

Figure 7 shows the SAXS profiles of these carbons. The $I(q)$ and q are the scattering intensity and the absolute value of the scattering vector, respectively.

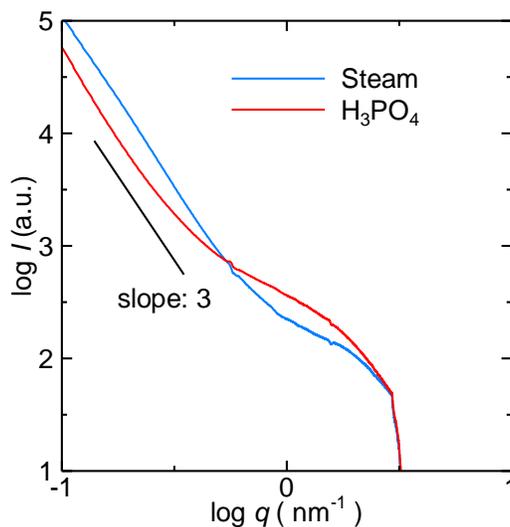


Fig. 7. SAXS profiles of bamboo carbon prepared by steam and phosphoric acid treatment

In the high- q range, a difference appeared in scattering curves for the treated carbons of the different methods. The pore size (d) of the treated carbon was calculated by the following expression:

$$d=2\pi/q \quad (2)$$

As a result, the SAXS profiles show that the H₃PO₄-treated carbon had more pores than the steam-treated carbon in the q range of 10^{-0.25} to 10⁻¹ nm⁻¹, which was in the pore size range of 2 to 11 nm. This is consistent with the results of the N₂ adsorption measurements.

CONCLUSIONS

1. The influence of phosphoric acid on the growth of microcrystals in biomass-based carbons was shown. At a relatively low temperature, some graphitic microcrystals were formed because of the phosphorus. With increasing heat-treated temperature, the phosphorus was difficult to remove below 2000 °C, and it still remained along the graphitic microcrystalline domains; thus the microcrystalline size was not changed. Finally, at the temperature of 2800 °C, the graphitization of the H₃PO₄-treated carbon exhibited a sharp increase, which was related to the phosphorus being removed under high-temperature treatment. This demonstrated that phosphorus can promote the graphitic microcrystalline domains to form graphite.
2. The appearance of the graphite was found to be a twisted spindle-like whisker in addition to the usual carbonization of wood. The present technique is useful to obtain the high crystalline carbons from biomass-based carbons at a low cost.

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