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ORIGINAL ARTICLE

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Cone structure of hexagonal carbon sheets stacked in wood cell lumen

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Abstract Cone-shaped carbon particles were produced inside the cell lumen of sugi (Japanese cedar) charcoal treated at 2500°C. We succeeded in clarifying the structural and morphological features by separating the cone-shaped carbon from the carbonized cell wall by heating to 800°C in air. Cone-shaped carbon is less susceptible to oxidation than the carbonized cell wall. The isolated cone-shaped carbon and carbonized cell wall fracture were observed separately by transmission electron microscopy and selected area electron diffraction. Results revealed that the cone-shaped carbon has a very highly ordered cone structure with regularly stacked hexagonal carbon sheets, whereas the carbonized cell wall has a disordered structure of mosaic-like turbostratic carbon.

Key words Wood charcoal · Turbostratic carbon · Cone structure · Electron diffraction

Introduction

Wood charcoal is useful as fuel and as activated carbon because of the original porous structure of the wood. When wood charcoal is heated at high temperatures, hexagonal carbon planes are formed and grow in piles with a minimum interplane distance of 0.344 nm.[1,2] This distance is approximately 0.01 nm greater than the interplane distance of graphite, even though suffiently high temperature is used for graphitization. This fact indicates that carbonized wood charcoal is, potentially, a type of turbostratic carbon,[3] i.e., it has regularly stacked hexagonal carbon planes that are disordered in both translation and rotation with respect to each other. On the other hand, graphite is crystalline with hexagonal carbon planes stacked in an orderly manner, are regularly spaced, and do not show translation or rotation. The mismatch of adjacent carbon planes in turbostratic carbon causes larger repulsive forces between the carbon atoms of adjacent sheets than occur in graphite. Therefore, the hexagonal carbon plane distance in turbostratic carbon is greater than that in graphite. Normally, wood charcoal treated at high temperature consists of randomly arranged turbostratic carbon particles that do not rearrange to graphite.

Principally, solid-state carbonization of wood has been studied, although we recently found that vapor growth of highly ordered carbon material occurs in wood charcoal.[4] The newly found vapor-grown carbon material is a micron-sized, cone-shaped substance that is several micrometers in diameter and is 10–20 μm in length. It is noteworthy that the cone-shaped substance is formed not on the surface of the wood block but is formed in the cell lumen of Japanese cedar and bamboo by heating at 2500°C. Because the shape of the material does not originate from the anatomical structure of the parent wood and it consists of carbon, the cone-shaped substance appears to be a kind of vapor-grown carbon originating from gas pyrolysis inside the cell lumen. The vapor-growth system is not affected by spatial hindrance and potentially allows a large aggregation of defect-free crystalline product, whereas solid-state carbonization yields small crystallites with mosaic-like order. For example, many types of carbon fibers are known to be vapor-grown carbons catalytically formed by disproportionation of various hydrocarbons over metallic catalysts.[5–9] The vapor-growth system is useful for producing various carbon materials with characteristic ordered structures.

This study aimed to clarify the fine structure of cone-shaped carbon formed by vapor pyrolysis inside the cell lumens in wood. For structural studies of cone-shaped carbon, transmission electron microscopy (TEM) is appropriate, but it requires the cone-shaped carbon to be separated out. This was difficult because the cone-shaped carbon is

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micro-sized and completely enclosed by carbonized wood cell walls. In this study, the carbonized cell walls were successfully removed and the cone-shaped carbon extracted by oxidization during heating up to 800°C. The fine structure of the cone-shaped carbon was revealed by TEM and selected area diffraction.

Materials and methods

Materials

Samples were prepared as described in our previous report.[4] Briefly, sapwood of Japanese cedar (*Cryptomeria japonica* D. Don) was charcoalized at 300°–400°C for 3 h in an outdoor furnace and used as the starting sample. The samples were cut into 1.5 × 1.5 × 5 (L direction) cm sections and were secondarily carbonized using an electric furnace SCC-30/220 (Kurata Giken) at a heating rate of 10°C/min, and for 1 h at 1000°, 1500°, 2000°, or 2500°C. The furnace was evacuated to a high vacuum at a pressure of 10–20 Pa, but at temperatures higher than 2100°C, argon gas was introduced into the furnace intermittently to maintain the internal pressure at 0.005–0.01 MPa.

Thermogravimetry and differential thermal analysis

Powdered samples (1.4 mg) were weighed accurately and placed in platinum pans. Thermogravimetry (TG) and differential thermal analysis (DTA) measurements were performed with a Thermoplus TG8120 (Rigaku) at a heating rate of 5°C/min under air flowing at 350 ml/min. About 1.4 mg Al_2O_3 was used as a reference material.

Scanning electron microscopy

With scanning electron microscopy (SEM), the specimens were observed directly with no metallic coating because it is highly conductive. A JEOL 4000 SEM operated with an accelerating voltage of 5–20 kV was used.

TEM and electron diffraction

The residue obtained after TG/DTA analysis of the sample treated at 2500°C was examined by TEM and electron diffraction. Because the specimen possibly included some salts that may give extra diffractions, samples were thoroughly washed with 1% aqueous HF to remove any salts. According to SEM and energy dispersive X-ray (EDX) analyses, the specimen had the same configuration after washing as before washing and contained no salts. The washed specimen was mounted on a carbon-coated grid and used for the experiments. All TEM and electron diffraction analyses were performed with a JEOL 2000EX electron microscope operated at 200 kV. Selected area diffraction was performed on an area of 1 μm or 250 nm in diameter. Calibration of the electron diffraction patterns was achieved with gold (characteristic spacing d_{111} = 0.235 nm) sputtered directly onto the specimens.

Results

DTA/TG

Thermal analysis upon heating to 800°C in air was performed on Japanese cedar secondarily carbonized at 1000°, 1500°, 2000°, or 2500°C. Charcoal treated at lower than 2000°C did not contain cone-shaped carbon, but the sample treated at 2500°C did.[4] DTA and TG thermograms are shown in Fig. 1. All samples displayed exothermic peaks in the DTA diagrams and decreases in weight in the TG curves at the corresponding temperature. When similar thermal analysis was performed under nitrogen gas flow rather than under air, the exothermic peaks were not observed on heating. Thus, it is clear that the exothermic peaks (Fig. 1a) and the corresponding weight losses (Fig. 1b) are due to oxidation of the samples. With an increase in carbonization temperature, the exothermic peaks shifted to a higher temperature and the charcoal structure became

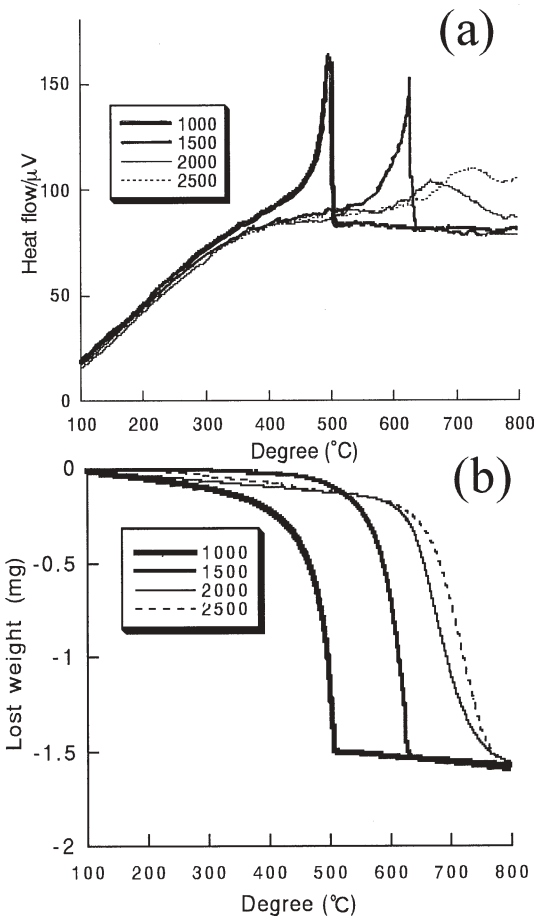

Fig. 1a,b. Thermograms of Japanese cedar secondarily charcoalized at 1000°, 1500°, 2000°, or 2500°C, under air flow. **a** Differential thermal analysis. **b** Thermogravimetry

themodynamically stable. Such a phenomenon has also been reported previously[10] and the peak position is considered to be a qualitative indicator of oxidation resistance. As shown in Fig. 1a, the sample that was carbonized at 1500°C had an exothermic peak at a temperature 130°C higher than that of the sample carbonized at 1000°C, although X-ray diffraction profiles of these specimens were identical.[4] This indicates that samples with similarly amorphous carbon patterns by X-ray diffraction were conspicuously thermodynamically different, depending on the carbonization temperature.

Only the sample carbonized at 2500°C produced a residue upon heating to 800°C in air, although the amount was too small to weigh, whereas all other samples produced no residue. The following part of this report describes the investigation of the residue.

SEM

A SEM image of the residue of the sample carbonized at 2500°C produced after heating treatment to 800°C in air is shown in Fig. 2. The residue consisted of both carbonized cell wall and cone-shaped carbon. Whereas most of the carbonized cell wall was burnt away and even the remnants were fragmentary, the cone-shaped carbon remained in a configuration similar to that observed before the heating treatment to 800°C in air (compare Fig. 2, top and bottom panels).

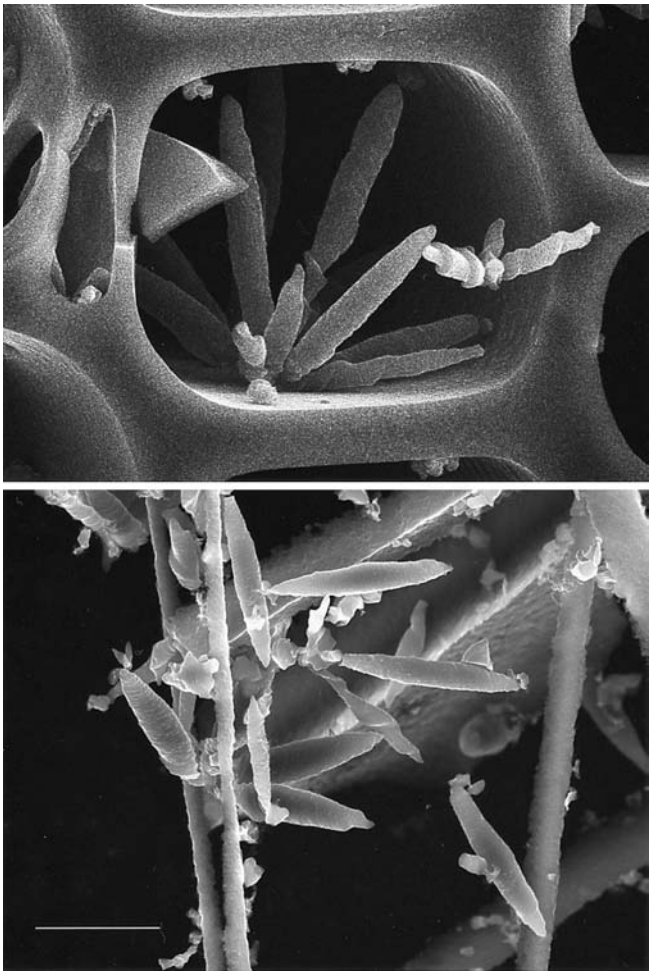

Fig. 2. Scanning electron microscopy (SEM) images of Japanese cedar treated at 2500°C. *Top* the cross section. *Bottom* after the sample was powdered and oxidized at 800°C. *Bar* 5 μm

TEM and electron diffraction analysis

The residue of the sample carbonized at 2500°C produced after heating treatment to 800°C in air was also examined by TEM (Fig. 3). The carbonized cell wall was easily observed by TEM after heating treatment to 800°C in air, which caused the cell wall to become thin, allowing transmission of the electron beam. An electron diffractogram of the thin area of the specimen is also shown. Diffraction occurred at a *d*-spacing of 0.35 nm and 0.21 nm, which is consistent with the results of X-ray diffraction of the whole specimen without separation into cell wall and cone-shaped carbon.[4] The observed *d*-spacing for the hexagonal carbon plane distance was 0.35 nm, which is significantly larger than that of graphite (0.335 nm), indicating that the cell wall carbonized at 2500°C is a type of turbostratic carbon. In the carbonized cell wall, the turbostratic carbon particles have no orientation, giving ring diffractions by irradiation of electron beams in any direction.

TEM observation of the cone-shaped carbon was successful. Specimens carbonized at 2500°C are inappropriate for TEM analysis because they include significant amounts of thick carbonized cell wall which shields the conical carbon and makes it barely discernible by TEM. The heating treatment to 800°C in air increases the probability of visualizing the cone-shaped carbon in a suitable condition for TEM analysis and allowed us to elucidate its fine structure. In Fig. 4, a lateral image of the end of the cone-shaped carbon is shown. In the selected area diffractograms, the

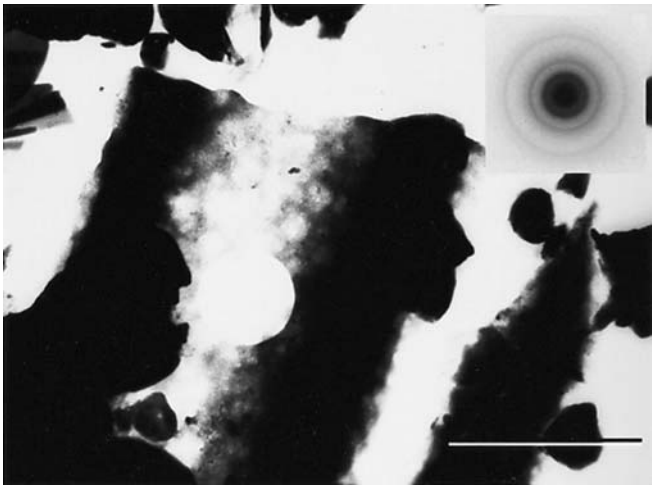

Fig. 3. Transmission electron microscopy (TEM) and electron diffraction images of part of the carbonized cell wall of Japanese cedar treated at 2500°C and observed after heating treatment at 800°C in air. Diffractions from the *circled area* in the image correspond to 0.35, 0.21, and 0.12 nm, from the center to the outer margin. *Bar* 2 μm

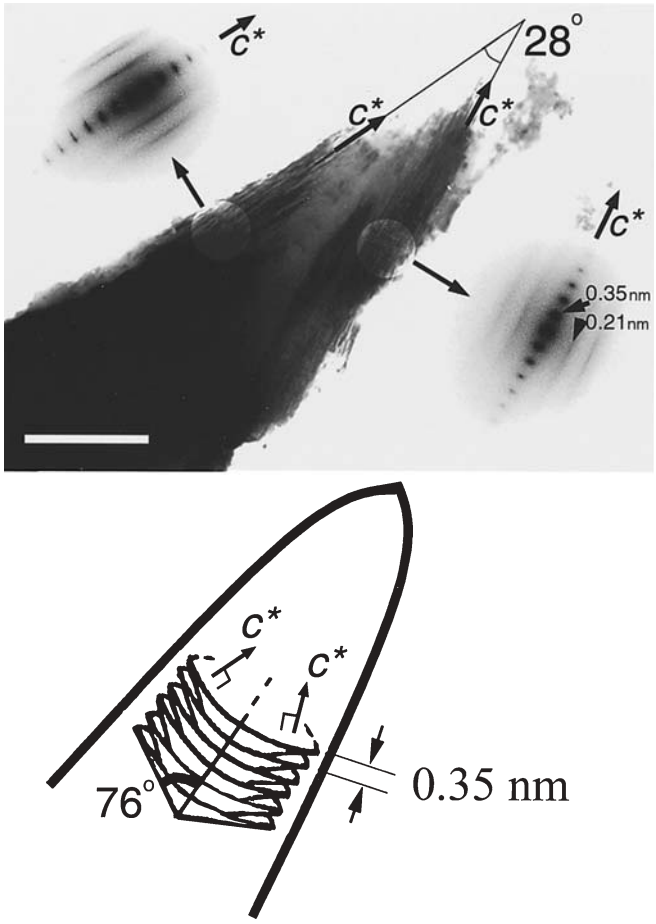

Fig. 4. TEM and electron diffraction images of the end of a cone-shaped carbon particle from Japanese cedar treated at 2500°C, observed after heating treatment at 800°C in air. *Bottom* schematic drawing of the arrangement of hexagonal carbon sheets inside the cone-shaped carbon particle. *Bar* 0.5 μm

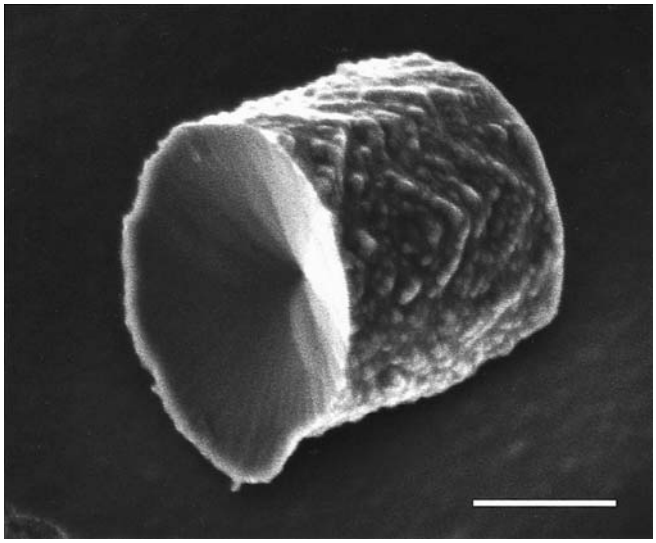

Fig. 5. SEM image of cleft cone-shaped carbon. *Bar* 1 μm

reflection of the intersheet distance of the hexagonal carbon sheets is 0.35 nm and appears as spots, indicating that the turbostratic particles are oriented as regularly stacked hexagonal carbon sheets inside the cone-shaped carbon. Diffraction of the distance of the hexagonal carbon sheet is observed until the sixth reflection, which indicates a very high degree of regularity in the hexagonal carbon sheet stacking direction (known as the "c^* axis"). On the other hand, diffraction at 0.21 nm appears perpendicular to the hexagonal carbon sheet diffraction, and is not a spot but a streak. Diffraction at 0.21 nm, which corresponds to (100) of graphite, is caused by the stacking period of the adjacent carbons on the hexagonal carbon sheet. The streaking phenomenon of diffraction is commonly observed with turbostratic carbon.[11]

The arrangement of the hexagonal carbon sheets in cone-shaped carbon was investigated from the image and the diffraction patterns shown in Fig. 4. The figure was observed in diffraction contrast where the diffracting part is observed as the dark image by cutting off the diffraction powers with an objective aperture. In Fig. 4, where the image and diffractograms are displayed in exactly the same directions, the direction of the diffraction of 0.35 nm from the center beam and that of the dark lines in the cone-shaped carbon image are similar. The direction corresponds to the c^* axis. The dark lines appearing symmetrically inside the cone-shaped carbon make an angle of 28° with each other, i.e., the longitudinal angle between the axis of the cone-shaped carbon and the carbon sheet is 76° (Fig. 4, schematic drawing). If the hexagonal carbon sheet is conical, the fracture of the cone-shaped carbon should be conical, because the intrasheet binding of carbon elements are very strong owing to the covalent bonds of the three σ-bonds of the sp^2 hybrid orbital, while the intersheet binding by van der Waals forces between the π-electron clouds is weak, as it is well known for the case of graphite. Figure 5 is a typical SEM image of cleft cone-shaped carbon with a conical fracture surface. The conical fracture shows that cone-shaped carbon consists of piled cones of hexagonal carbon sheets, consistent with the schematic drawing inferred by the TEM image (Fig. 4).

On the specimen, many round sections were also observed, which gave unique elliptical diffraction patterns (Fig. 6). The minor axis of the ellipses corresponded to the diameter of the normal diffraction rings of graphite, at 0.21 nm and 0.12 nm (corresponding to the intrasheet distances, (100) and (110) of graphite, respectively). The theoretical explanation of this peculiar diffraction, characteristic of turbostratic carbon, is described as follows:[11] both rotational and translational disorder with the piled up hexagonal carbon planes are necessary to make an ellipse. As a result of these phenomena, the distribution of scattering power in reciprocal space occurs as concentric cylinders, with radii equal to the distances from the origin of the hk0 reciprocal lattice points. Thus, the section of these cylinders by an Ewald sphere, which fulfils the Laue condition to produce a diffraction pattern, produces a series of ellipses with major axes proportional to $1/\cos\alpha$ where α is the angle between the direction of electron irradiation and the c^* axis. In Fig. 4, the (100) diffraction is a pair of parallel lines

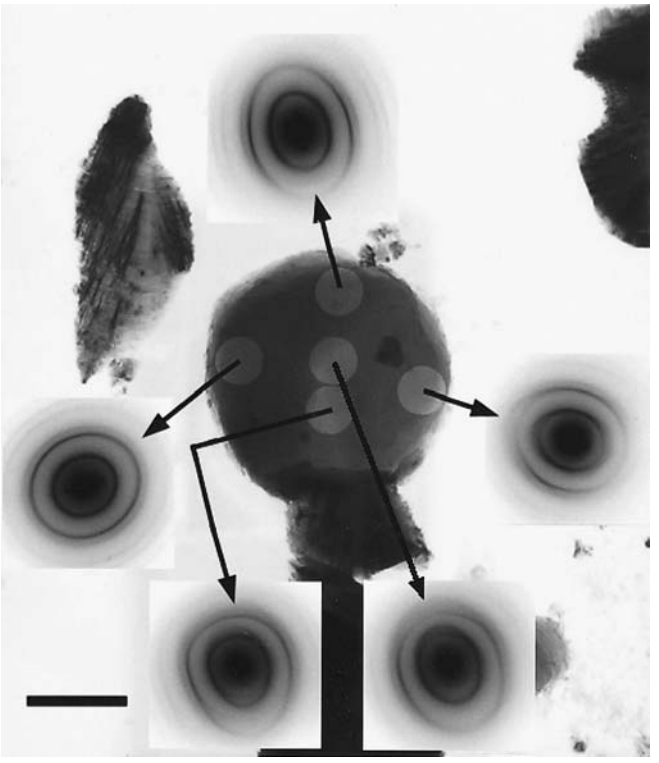

Fig. 6. TEM image of a fractured section from cone-shaped carbon and the diffractograms from the *circled areas*. *Bar* 0.5 μm

because the electron irradiation is perpendicular to the c^* axis ($\alpha = 90°$). On the other hand, in Fig. 6, all the diffraction patterns are ellipses, indicating that the c^* axes are tilted from the direction of the irradiation beam. When calculated with α, the carbon sheet is thought to be nearly concave or convex, making angles of 84°–85° with the longitudinal axis of the cone, the top of which appears slightly decentered in Fig. 6. The round section must be a cleft section of the cone-shaped carbon, with the hexagonal carbon sheets arranged conically.

Discussion

Cone-shaped carbon was revealed by TEM to be a conical structure composed of hexagonal carbon sheets. Heating to 800°C in air allowed detailed observation of the cone-shaped carbon, but it was essential to consider whether the oxidization process itself affected the structure of the cone-shaped carbon. Because graphitization scarcely occurs when heating to less than 1800°C,[12] it is considered that the inside of the cone-shaped carbon, where oxygen cannot attack, is not changed by heating, even though the surface of the cone-shaped carbon was oxidized. For cone-shaped carbon, a heating temperature of 800°C seems sufficiently low to avoid any change to the inner structure, which could be detected with electron diffraction. There is considerable difference between the carbonized cell wall and the cone-shaped carbon: the former is a disordered mosaic and the latter a strongly oriented cone structure, although both are turbostratic carbon with similar intersheet distances. This difference is thought to originate in the parent samples, regardless of the treatment at 800°C.

The cone-shaped carbon from wood is unique because the edge sites of the hexagonal carbon sheets are located on the lateral surface. In contrast, "graphite whisker", a type of vapor-grown carbon similar to cone-shaped carbon, has hexagonal carbon sheets parallel to their length and the side faces are covered by hexagonal carbon sheets. There are comparatively few reports of vapor-grown carbon fibers that have the edge sites of the carbon sheets facing the side surface. A cone-stacked structure similar to cone-shaped carbon has been reported in several papers but it was prepared by completely different procedures, e.g., heat treatment of iron–carbon alloy at 2800°C[13] or carbon black at 3000°C,[14] or pyrolysis of carbon monoxide at 1800°C.[15,16] It is necessary to establish for the cone-shaped carbon observed in this study whether the carbon is supplied by the pyrolysis of organic gas from the cell wall of the wood and is deposited by the activity of a catalytic metal as in the case of vapor-grown carbon fibers.

It is remarkable that cone-shaped carbon is less susceptible to oxidization than is the carbonized cell wall, although both are turbostratic carbon. In our case, the prime reason for the difference in oxidizability is considered to be the difference in packing. The carbonized cell wall has a mosaic-like structure of small turbostratic carbon particles randomly arranged, having a larger surface available for oxidation than the cone-shaped carbon which consists of turbostratic carbon closely packed in order. Further investigation of the physical properties of the surface of cone-shaped carbon must be achieved to determine its future applications.

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