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RAPID COMMUNICATION

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Onion-like graphitic particles observed in wood charcoal

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Introduction

Onion-like graphitic particles were first observed by Iijima in ark-discharge-deposited carbon blacks.[1] When the microstructure of the carbon blacks produced by vacuum evaporation of graphite was studied, onion-like structures were found by high-resolution electron microscopy. These structures were also found by Ugarte after irradiating carbon soot with high-energy (300kV) electron beams for a prolonged period.[2] Other techniques have also been reported to produce similar structures from other substances.[3] Although onion-like graphitic particles are now a well-defined allotropic nanophase of carbon,[4] they have not been found in wood charcoal thus far.

This report describes their growth during evolution in wood charcoal. The microstructure of carbonized microfibrils, which were observed in regions close to the groups of onion-like graphitic particles, are also presented in this paper.

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Materials and methods

Materials

The materials used were taken from 20-year-old Japanese cedar (*Cryptomeria japonica* D.Don) logs. Cylinder-like specimens with diameters of 30mm and heights of 60mm were cut from the logs and then carbonized up to 700°C using a laboratory-scale electric furnace. The temperature was increased at a heating rate of 4°C/min in an argon gas atmosphere. After the target temperature was obtained, the temperature was kept constant for 30min and then allowed to cool naturally.

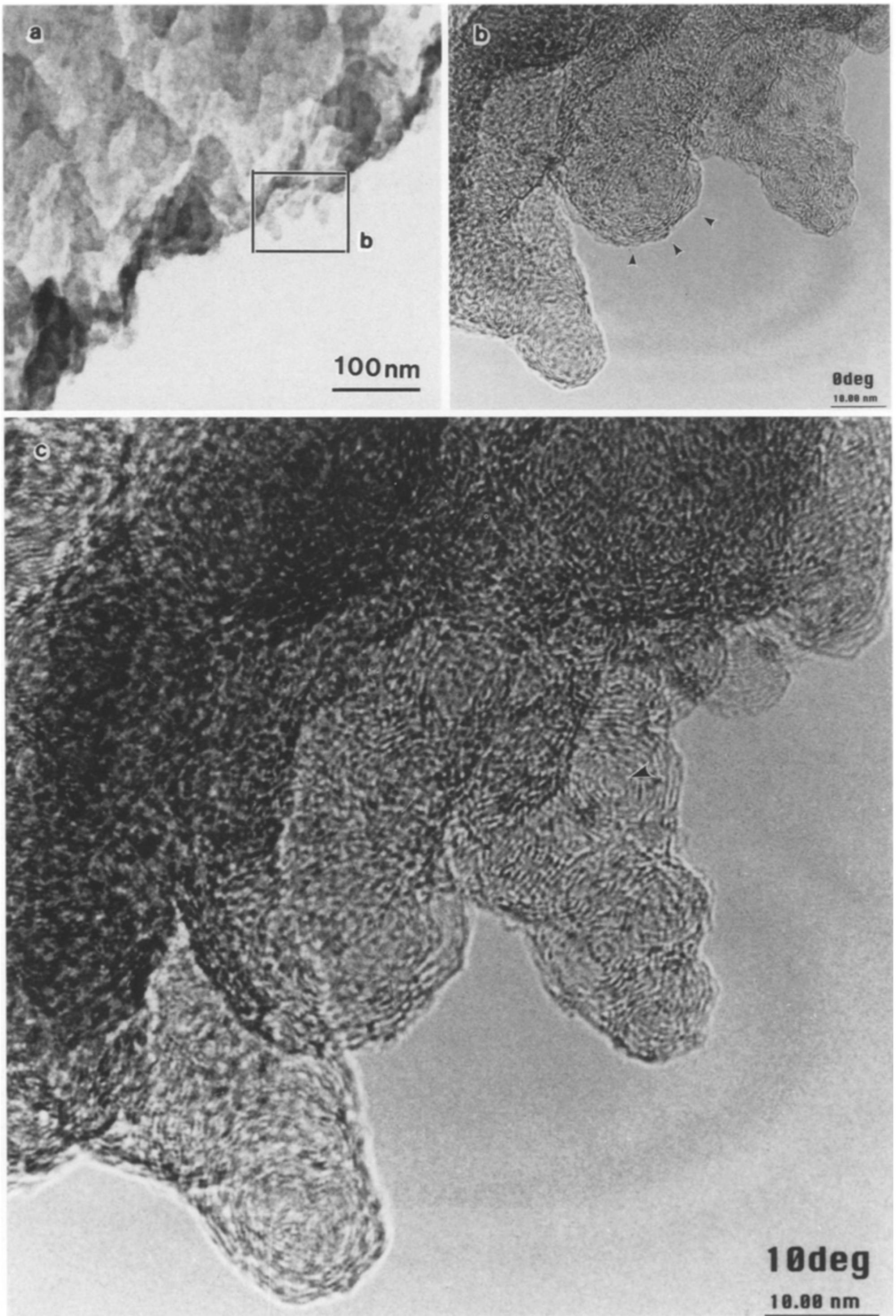
Observation by transmission electron microscopy

The specimen for transmission electron microscopy (TEM) was prepared using a precision ion polishing system (Gatan, model 691). The microstructures of the wood charcoal were analyzed by TEM (Philips CM200) operated at 200kV. The radiation of the electron beam was 100 A/cm^2. No structural change was observed under these measuring conditions.

Results and discussion

Typical TEM photographs of wood charcoal carbonized at 700°C for 30min are given in Fig. 1. Figure 1a is an external view of the area where onion-like graphitic particles were observed. Figure 1b is an enlarged image of the area indicated by the rectangular enclosure in Fig. 1a, from which different sizes of graphitic particles were observed. This micrograph shows also approximately spherical shapes of those particles with concentric fringe images. One large particle, shown by three arrowheads in Fig. 1b, is sandwiched between two groups of round-pointed clusters located in the upper right and lower left portions. Examination of the specimens tilted at 10 degrees indicated that they are nearly spherical, as shown in Fig. 1c. The diameter

Fig. 1. Onion-like graphitic particles in wood charcoal carbonized at 700°C for 30min [transmission electron microscopy (TEM)]. **a** High-resolution electron micrograph of spherical graphitic particles at a 0-degree tilt, which is an enlarged image of the rectangular area indicated by the enclosure in **c**. **b** Same image as in **a** but at a different tilt (10 degrees). **c** Reduced image of **a** including the surrounding area



of the largest particle is about 24nm. Those of the small particles ranged from 6.5 to 13.0nm.

Although it is difficult to see the innermost layer of the spherical particles in Fig. 1b, it was measured to be 1nm by changing the tilt to 10 degrees, as shown by an arrowhead in Fig. 1c. This size corresponds to that of the innermost concentric ring shell (0.8–2.0nm) for the 60-carbon cluster proposed by Smally's group.[5]

Polygonization is a typical morphological feature of graphitized carbon.[6] However, the sizes of the particles observed in this study were not uniform, and the distance between graphitic fringes (0.5–0.6nm) was larger than that of graphite (0.34nm). This gives evidence that these onion-like graphitic particles are still in the process of evolution to more complete graphitic particles. The structure of the onion-shaped particles is similar to that of graphitic

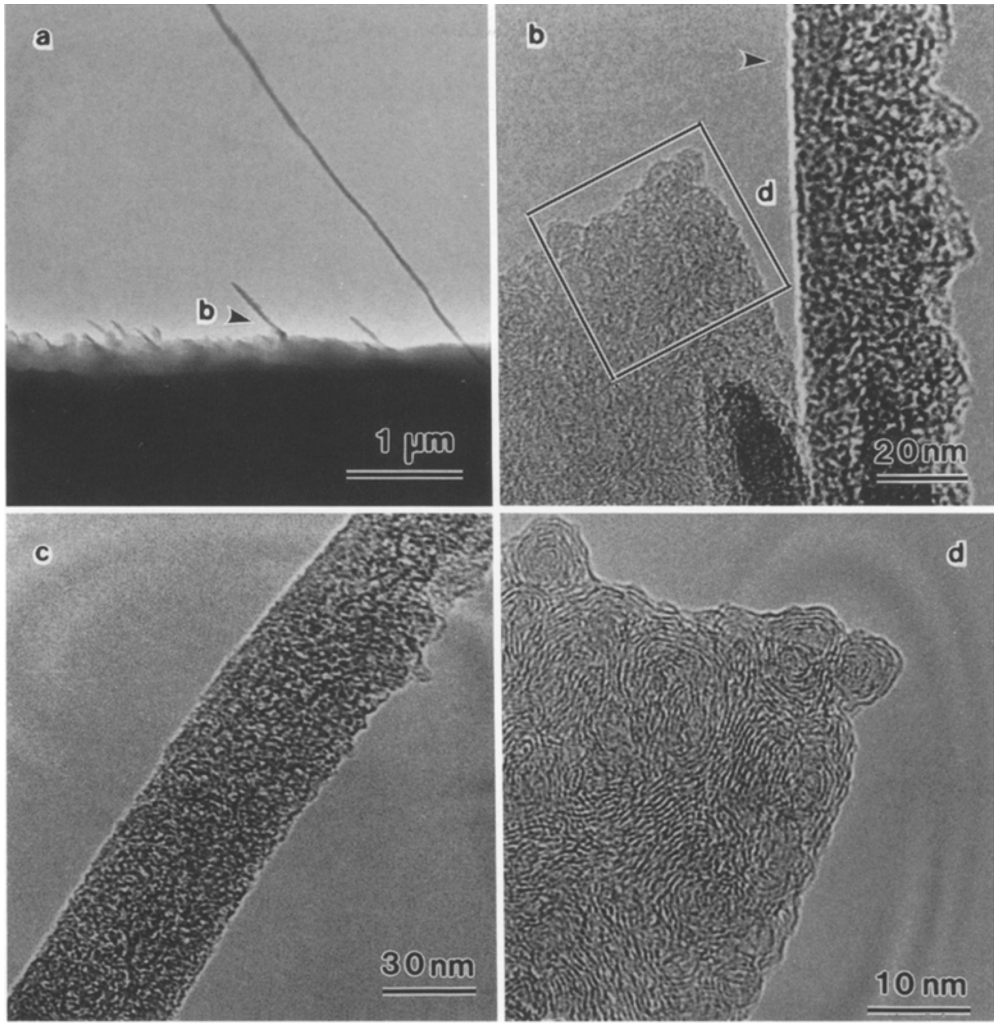


Fig. 2. Carbonized microfibrils and graphitic particle area in wood charcoal heated at 700°C for 30min (TEM). **a** Brightfield TEM image of oriented carbonized microfibrils. **b** Microfibrils and graphitic particle area shown in **a**. **c** Microtexture of carbonized microfibrils with little damage. **d** Enlarged view of graphitic particles with onion-like structures are seen

particles produced in a diamond after undergoing 5-min irradiation in a previous study.[3]

Typical photographs of carbonized microfibrils and graphitized particles taken by TEM are presented in Fig. 2. Figure 2a shows carbonized microfibrils aligned parallel to each other. These microfibrillar structures are speculated to be aggregated carbonized microfibrils based on the constant alignment and width similar to that of microfibrils in the original wood.

These results were obtained by selective argon ion milling of matrix around the microfibrils owing to differences in rigidity. The microstructures of microfibrils are quite different from those of the adjacent areas, including onion-like graphitic particles.

Figure 3 represents a cross section of carbonized microfibrils and the surrounding area. The upper part of Fig. 3, representing microfibrils surrounded by lignin, is modified from Fengel's model.[6] This model leads to the assumption that lignin easily changes its structure to onion-like graphitic particles by carbonization based on its three-dimensional network, which differs from that of cellulose molecules composed mostly of a crystalline region.

The right edge of the microfibril, indicated by an arrowhead in Fig. 2b, is not as sharp as the left edge owing to movement of the microfibrils during argon ion milling. As shown in Fig. 2b, c, the microstructures in microfibrils are random, as are typical characteristics of nongraphitized carbon. The layered structure isotropically winds within a short range. Both edges of the lower part of the microfibril in Fig. 2c are sharp, indicating that the original width of the carbonized microfibrils was retained. However, graphitic particles grew in the region close to the carbonized microfibril (Fig. 2d). It was observed that random microstructures in the microfibrils coexisted with the graphitic particles. The fact that cellulose microfibrils are surrounded by lignin in raw wood suggests that lignin is the potential source of a precursor for Fullerenes. The diameter of the graphitic particles in the image is 7 nm, and the distance between layered structures in the particles is 0.5–0.6 nm. The general understanding of different thermal behavior between cellulose and lignin can explain the appearance of both random structures in the carbonized microfibrils and the onion-like graphitic particles in the lignin area. It is scientifically interesting and technologically important to study the trans-

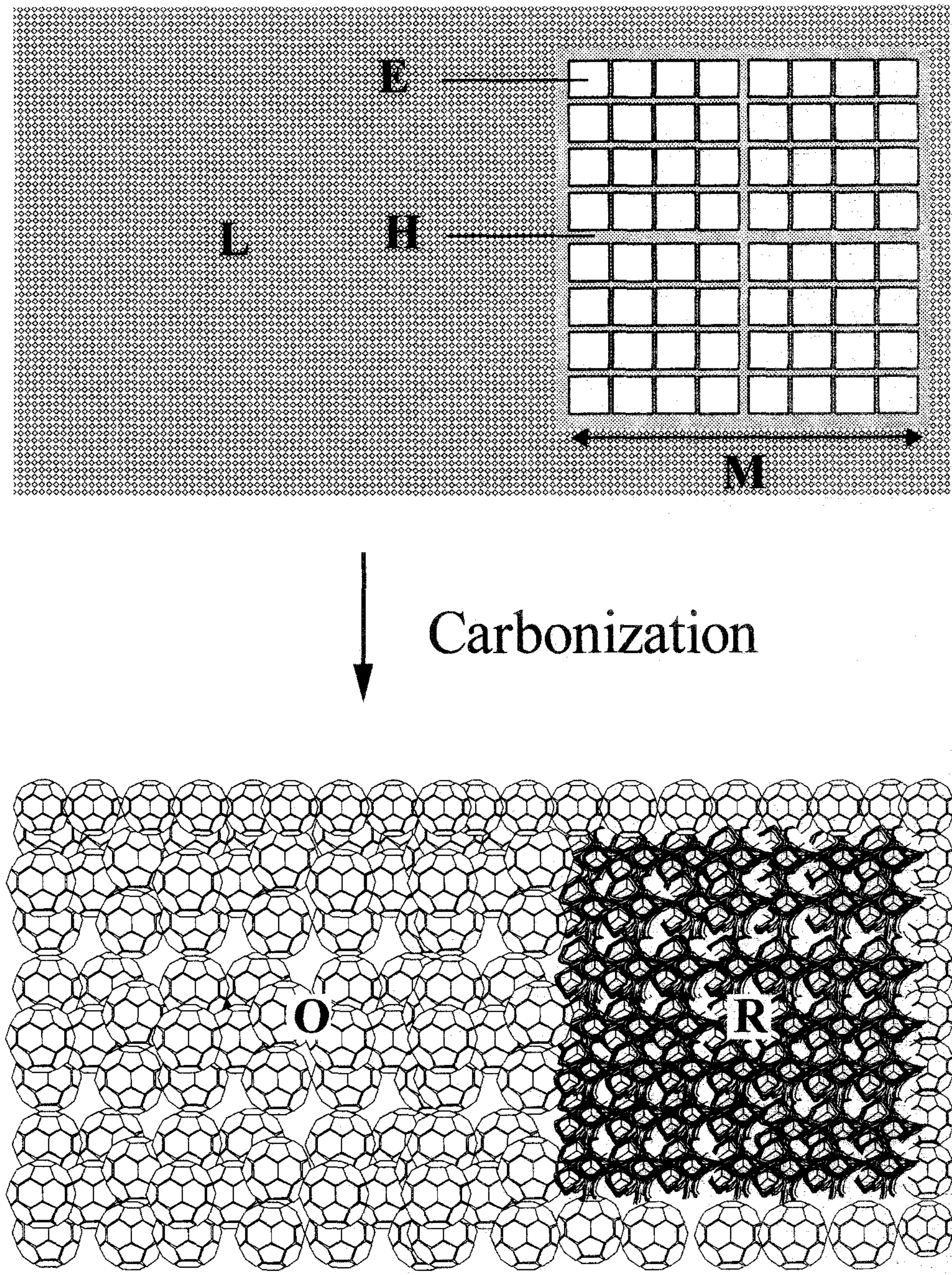


Fig. 3. Cross section of a carbonized microfibril and the surrounding matrix of lignin.[7] *E*, elementary microfibrils; *H*, hemicellulose; *M*, microfibril; *L*, lignin; *O*, onion-like graphitic particles; *R*, random structure

formation of lignocellulosic components to onion-like graphitic particles by thermal conversion.

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