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Communications

Formation of Ultrafine Carbon Tubes by Using an Anodic Aluminum Oxide Film as a Template

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Previously, we prepared a new type of thin graphite film by the carbonization of an organic polymer in the two-dimensional opening between the lamellae of a layered clay.¹⁻⁵ Then, we attempted to prepare a new type of porous carbon by using the three-dimensionally controlled pores of a zeolite as a space for carbonization of an organic polymer.⁶ Our next approach in the template carbonization technique is the preparation of a one-dimensional carbon such as carbon tubes by using a one-dimensional channel. It is well-known that carbon tubes of nanometer level not only have potential applications to various functional materials such as electronic devices and catalysts, etc., but also are of fundamental interest. Here, we have attempted to prepare carbon nanotubes and submicron tubes by using an anodic aluminum oxide film as a one-dimensional template. This template was originally used by Martin

et al. to synthesize nanocylinders or tubes of polymers,⁷ metals,⁸ and semiconductors.⁹

The following two anodic oxide films were used as a template. One was a commercially available membrane filter of 25 mm i.d. wide and 60 μm thick (Whatman Ltd., Anodisc 25), whose porosity consisted of an array of parallel and straight channels with a diameter of about 230 nm, perpendicular to the film surface. Another one was prepared by ourselves according to the method reported.¹⁰ The diameter and the thickness of this film were 15 mm and 75 μm , respectively, and the diameter of its straight channels was about 30 nm.

The anodic oxide film was placed in a vertical quartz reactor (i.d., 20 mm i.d.). The reactor temperature was increased to 800 °C under N_2 flow and then propylene gas (2.5% in N_2) was passed through the reactor at a total flow rate of 200 cm^3 (STP)/min. The thermal decomposition of propylene in the uniform straight channels of the anodic oxide film results in pyrolytic carbon deposition on the channel wall. After the desired period of time, the film was taken out of the reactor. Then the film was washed with an excess amount of 46% HF solution at room temperature to dissolve the anodic aluminum oxide. As a result, carbon was obtained as an insoluble fraction.

Scanning electron microscopic (SEM) observation of the carbon samples obtained with the two types of films revealed that in both cases the samples consisted of only cylindrical tubes whose length was exactly the same as the thickness of the corresponding film. Most of the tubes were connected at the both ends of each tube, because the carbon deposition also took place on the outer surface of the anodic film. But some of the tubes

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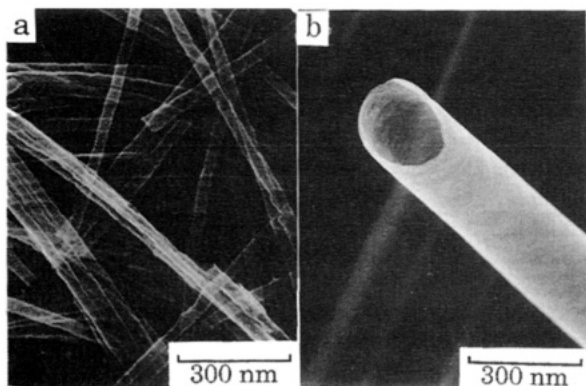


Figure 1. SEM photographs of the carbon tubes prepared by a carbon deposition for 1 h on an anodic oxide film. The channel diameter of the film: (a) 30 nm; (b) 230 nm.

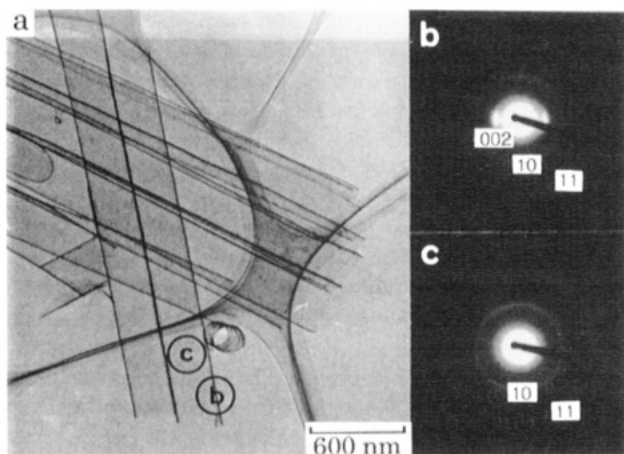


Figure 2. TEM images of the carbon tubes prepared under a carbon deposition period of 1 h by using the anodic oxide film with a channel diameter of 230 nm: (a) bright field image (a microscope grid is seen under the sample); (b) and (c) diffraction patterns from the areas indicated by circles in (a).

were separated from the others during the stirring in HF solution. Figure 1 shows the SEM photographs of such tubes. Their outer diameter is almost the same as the channel diameter of the corresponding film. It is noteworthy that the tubes from the anodic oxide film with the channels of 30 nm in diameter (Figure 1a) look transparent under the SEM observation with an acceleration voltage of 15 kV, indicating that the wall thickness of the tubes is very thin. The photograph of Figure 1b shows the open end structure of the carbon tube.

Figure 2a shows the transmission electron microscopic (TEM) photograph of the carbon tubes prepared under a carbon deposition period of 1 h using the anodic oxide film with the channels of 230 nm in diameter. The TEM observation confirmed that the shape of all the carbon samples obtained here are tubular. The wall thickness of the carbon tubes was roughly estimated from the TEM photograph (Figure 2a) to be 5 nm. It was found that the thickness of the sample with a carbon deposition period of 6 h was 45 nm. This finding indicates that the wall thickness increases with an increase in the deposition period. Figure 2b,c shows the

electron diffraction patterns for the carbon tube in Figure 2a. These two patterns were taken from different areas and they are indicated as a circle in Figure 2a. It is noted that, in the area b of Figure 2a, part of the electron beam passed through the tube wall in parallel, but no beam paralleled the wall in the area c. The pattern in Figure 2b presents a pair of small but strong arcs for 002, together with weak 10 and 11 diffraction rings. Such strong 002 arcs were also observed in the case of the carbon tubes using a film with a channel diameter of 30 nm. The appearance of the 002 diffraction not as a ring but as a pair of small arcs, indicates some orientation of the 002 planes in a carbon tube. On the other hand, such 002 arcs are not seen in the case of Figure 2c, where only 10 and 11 rings are observed. The presence of 002 arcs in Figure 2b and the presence of only 10 and 11 rings in Figure 2c suggest that the tube wall consists of cylindrically stacked 002 planes. It should be noted, however, that the degree of the crystallization in the 002 planes here is not very high, because the 002 diffraction was observed as arcs, not as clear spots.

We can conclude that carbon nanotubes and submicron tubes were prepared by the template carbonization method using an anodic oxide film. Carbon nanotube is now attracting much attention as a new carbon material. Such tubes have been prepared thus far mainly using an arc-discharge evaporation technique^{11,12} or by thermal decomposition of benzene vapor.^{13,14} The nanotubes prepared from these techniques are much more graphitic and finer than the present carbon tubes. These techniques do not, however, allow the preparation of uniform carbon tubes and the accurate control of the tube diameter and thickness. On the other hand, one can prepare carbon tubes with uniform diameter and thickness by the present method. Since the size of the channels in an anodic oxide film can easily be controlled by changing the current density during anodic oxidation, it is possible to control the diameter of the carbon tubes from ten to hundreds of nanometers. Furthermore, by changing the carbon deposition period, the wall thickness of the carbon tubes is controllable. Unlike the carbon nanotubes prepared by the other methods, all the carbon tubes obtained here are not capped at both ends. Thus, the encapsulation of other material into the present tubes would be very easy. This opens up a possibility for the formation of a novel one-dimensional composite with carbon.

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