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Cap-Formation Process of a Carbon Nanotube

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A new way to form carbon nanotubes (CNTs) has been found, where polyyne-containing carbon, prepared by reducing poly(tetrafluoroethylene) (PTFE), is irradiated by an electron beam in a transmission electron microscope (TEM). The in-situ TEM observation reveals that the CNTs grow from the bottom with being capped, and the cap is graphitized after the tubular shape is formed. Polygons other than a hexagon are assumed to be formed during the progress of graphitization to fit the half-sphere shape of the cap. The growth here is governed by neither the 'growth at the top' nor the 'growth with the open end' mechanism.
Keywords: carbon nanotube, cap, polyyne, electron beam, TEM.

1. INTRODUCTION

After finding CNTs [1-3], this material has attracted much attention for its unique one-dimensional structure leading to nanoelectronics. A variety of CNT-formation techniques, such as arc discharge, chemical vapor deposition, and laser evaporation, have been presented and are moving forward toward a CNT-device fabrication by a post-synthesis alignment [4-6]. The authors have been studying a new way to form CNTs by irradiating an electron beam onto polyyne-containing carbon without a metal catalyst [7-9], which is specifically designed for a CNT-device fabrication directly on a substrate.

The electron-beam process has been applied to construct carbon nanostructures, where graphite has been employed as a precursor. The formation processes have been well observed in an in-situ way over fullerenes [10-12] and onion-like carbons [13-15] by a TEM. On the other hand, a polyyne scheme for fullerenes (polyyne, or sp-carbon, works as an intermediate) has been presented [16], which inspired some researchers leading to successful formation of fullerenes by a laser beam [17-20]. The technique employed here is a combination of the electron beam and the polyyne scheme.

In this paper, a cap formation process is presented and discussed based on an in-situ observation by a TEM, supporting the 'closed-end' and the 'from-the-bottom' mechanism.

2. EXPERIMENTAL SECTION

The CNT formation is comprised of two processes: preparation of polyyne-containing carbons, and irradiation of an electron beam at 600°C under low pressure. The details and the characterizations have been presented in another publication [21].

The polyyne-containing carbon is prepared by electrochemically reducing PTFE (DuPont) films, using a two-electrode method (anode: magnesium, cathode: stainless steel) under argon at 0°C. The PTFE films (10 mm x 10 mm x 60 μm) are charged in a flask with a solvent containing supporting salts (tetrahydrofuran (THF): 30 ml, LiCl: 0.8g, $FeCl_2$: 0.48 g). A DC voltage (40 V) is applied between the anode and the cathode for 10 hr. After the reduction, the films are washed with THF and are dried in vacuum.

The films are analyzed by an IR spectrograph (MagnaIR 760, Nicolet), Raman (HoloLab 5000, Kaiser), and XPS (ESCA 750, Shimazu). The specimen is embedded in an epoxy resin (Araldite CY211, Ciba) and is cut by a microtome (UltraCut, Leica).

The growth and the observation are carried out in a TEM (H7100, Hitachi, 100 kV; ARM1250, JEOL, 1.25 MV). The specimen is heated up to 600°C prior to irradiating an electron beam.

3. RESULTS AND DISCUSSION

The authors have shown that polyyne-containing carbon is converted to CNTs [22, 23], as shown in Fig. 1, and carbon nanoparticles [24] by an electron beam, where in-situ TEM observations have cast light on their growth mechanisms providing informative insights. The CNT grows from the bottom with being capped from an early stage, where carbon is provided from the precursor at its bottom. The growth is comprised of two steps: quick formation of rod-like aggregates of carbon, and slow graphitization of the wall accompanied by a hollow formation in its inside. The hollow is formed by evaporating carbon fragments, which diffuse through the not-well graphitized wall. In addition, the cap formation process has been observed in an in-situ way, and is presented in this paper.

Generally speaking, the in-situ TEM observation on the CNT growth is accompanied by some technical difficulties. First, the specimen moves by thermal displacement and electron-beam bombardment, which demands quicker focusing and shooting than a well-experienced operator achieves. Second, the CNT is not well crystallized at an early stage, where a successful observation is limited manifesting one of setbacks of a TEM. The authors must have accepted some blurred pictures.

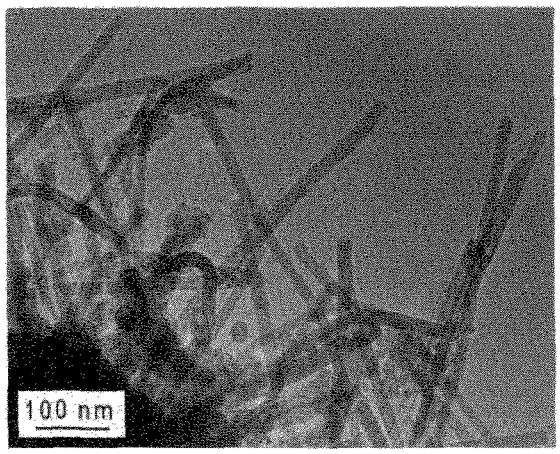

Fig. 1. CNTs formed on polyyne-containing carbon.

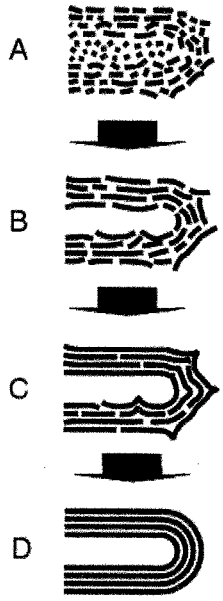

Fig. 2. Schematics of the cap formation on a CNT. The formation progresses from A to D.

The cap formation process is shown schematically in Fig. 2. Immediately after starting an electron-beam irradiation (in a few seconds), a CNT grows, which is a tubular-shape aggregate of carbon being stuffed by carbon fragments at its core, as shown A in Fig. 2. A cap is already formed at this stage, though it is not well graphitized and consists of partially-aligned graphenes (one sheet of graphite). The cap is constructed by small graphenes and is shaped like a polyhedral rather than a perfect semi-sphere.

By continuing the irradiation, the small graphenes develop larger by fusing and rearranging each other, as shown B in Fig. 2, whereas a hollow is formed by diffusion and evaporation of carbon fragments. At this stage, the wall is not well graphitized and allows fragments to diffuse through the wall. This stage is photographed in Fig. 3, where graphene layers are not well observed due to their premature graphitization.

Further, the graphitization progresses and the graphenes develop more, as shown C in Fig. 2. The photograph (Fig. 3) of this stage shows clearer graphenes than before, resulting from the better graphitization. The cap and the wall move violently and sometimes shape edges, which suggests vigorous fusing and rearranging of graphenes.

The graphitization is completed and leads to a half-sphere shape of the cap, as shown D in Fig. 2. The whole process takes from 45 to 60 min.

As far as the growth is observed, the 'open-end' growth [25-29] is not found, suggesting that the growth by this technique is governed by the 'closed-end' mechanism [30]. At an early stage, the carbon fragments coagulate rather being capped than being open-ended to attain a more stable state in surface energy.

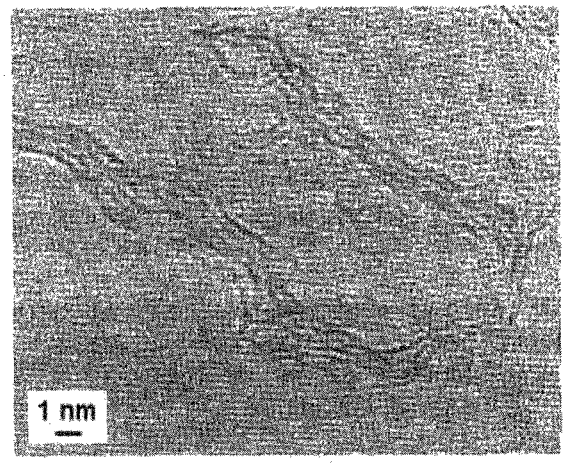

Fig. 3. A cap at the early stage of the CNT formation. This photograph represents B in Fig. 2.

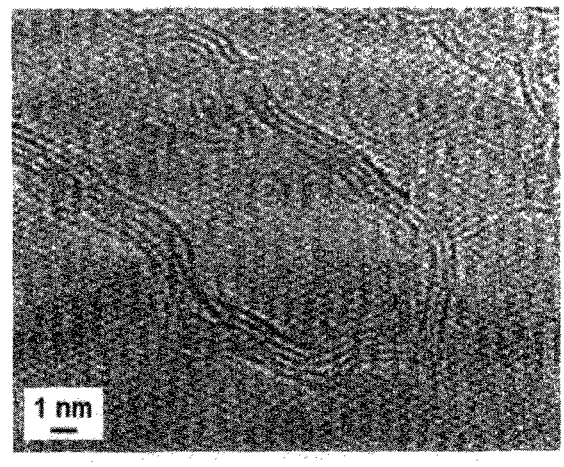

Fig. 4. A cap in the course of graphitzation. This photograph represents C in Fig. 2.

The cap must incorporate a pentagon, heptagon, octagon, ..., in place of a hexagon. At the early stage, the tube is an aggregate of carbon fragments, in which a hexagon dominantly exists than others. A pentagon and others are assumingly formed to fit the round shape in the course of graphitization at the latter stage.

The in-situ observation provides insights on the formation mechanism, which are inspiringly applied to designing the process and the precursor, as well as further understanding on the mechanism.

4. CONCLUSION

CNTs grow with being capped from an early stage of the formation. The cap and the wall graphitize in parallel. Polygons other than a hexagon are assumed to be formed at the latter stage to fit the round shape.

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