Identification of primary structural units in fibrous nano-carbon

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Introduction

Selective synthesis of carbon nanofibers (CNFs) has been motivated by recognition on their particular structure and properties from trying to prevent deleterious carbon deposits in many processes relating hydrocarbon conversion. [1, 2, 3] Since discovery of carbon nanotube by high-resolution transmission electron microscopy [4], nano-sized carbon fibers have been extensively studied on their synthesis, growth mechanism, structure, and properties in the last decade.

In the catalytic preparation, the structure or morphology of CNFs and their relating properties are also controllable by selection of catalyst, carbon sources and reaction conditions. [3, 10, r11] The structural diversity of CNFs occurs by the anisotropic alignment of carbon hexagonal layers like the graphite, providing several particular structures such as platelet, herringbone-like and tubular CNFs according to the alignment direction to the fiber axis [11]. Overall CNF structure has been established generally on the basis of observation of the lattice fringe by TEM (transmission electron microscope) and the overall morphology by SEM (scanning electron microscope).

The hexagonal layer alignment of CNF is quite uniform at a certain direction, comparable to the graphite. However, the crystalline properties obtained by X-ray diffraction never show a single crystallinity, especially in terms of the average (002) plane stacking height (Lc(002)).[3, 11, 12]

Recently, we have found the presence of a structural unit constituting platelet CNFs by observation under TEM with a tilting method and STM (scanning tunnelling microscope) [12], and the presence of such a structural unit was supported by examination on the structural and surface modification of platelet CNFs according to graphitization and mechanical or acid treatments.[13]

We propose rod- and plate-type as constructive units of CNF through this study on two different CNFs such as platelet and herringbone CNFs synthesized by a catalytic method. Examination of CNF structure under STM provided a structural insight, which can never be obtained by conventional TEM or SEM.

Experimental Section

Preparation of CNF

Platelet CNF was synthesized from carbon monoxide over an iron catalyst, while herringbone CNF was obtained from ethylene over a copper-nickel catalyst. The catalysts were prepared by a method described previously.[14] Metals (Fe or Cu-Ni) were co-precipitated as carbonates from aqueous solution of corresponding nitrates by addition of ammonium bicarbonate at prescribed amount, followed by several steps such as calcination and reduction. Pure iron catalyst and a Cu-Ni (2/8 wt/wt) catalyst were prepared respectively.

The apparatus used for the preparation of CNF throughout this study has been previously described. [12, 13] In a conventional horizontal furnace, the catalysts were treated in a 10% He/He mixture for 1 ~ 2 h at the reaction temperature, before introduction of the reactant gases such as a CO/H_2 mixture or a C_2H_4/H_2 mixture, where the gas flow to the reactor was precisely controlled by mass flow controllers.

Scanning tunneling microscopy (STM) was performed using the Nanoscope III (Digital Instrument, CA, USA). STM images were acquired in a constant current mode, using tunneling currents in the range of 0.2 – 1.0 nA, bias voltage in the range of 0.1 – 1V, and scan frequencies of 1-2 Hz. Small portion of Platelet CNF was suspended in methanol before being dropped onto freshly cleaved surface of HOPG.

Results

Characteristics of CNFs Produced

CNFs produced from CO/H_2 (4/1 v/v) gas mixture at 600^{o}C over the iron catalyst showed selectively a platelet structure, which is characterized by hexagonal plane alignment parallel to the fiber axis (see Figures 1a and b). The platelet CNFs showed high degree of graphitization as examined in the X-ray diffraction, the interlayer distance (d_{002}), the height of hexagonal plane stacking (Lc002), and the lateral size of hexagonal plane (La110) being approximately 0.3363 nm, 28 nm, and 22 nm, respectively. The platelet CNF has the shape of a planar fibril and a polygonal pillar in minority where the lateral width of the longer part was around 80 ~ 350 nm.

Herringbone CNFs, which have hexagonal plane alignment angled to the axis, were selectively synthesized from C_2H_4/H_2 (4/1 v/v) mixture at 580^{o}C over the Cu-Ni (2/8 wt/wt) catalyst. The herringbone CNFs showed comparatively low graphitization degree of about 0.344 nm d_{002} and 3.5 nm Lc002. The fiber cross section appeared polygonal such as tetragonal, pentagonal and hexagonal. The diameter of the herringbone CNF ranged widely from 50 to 450 nm, but most of the fibers showed a herringbone- or feather-like texture (see Figures 1c and d).

Structural Units by Scanning Tunneling Microscopy of CNFs

The SEM and TEM pictures showed the structure and morphology of typical platelet or herringbone fibers, whereas observation of STM provided novel features of CNF structure.

The STM pictures of Figures 2a and b shows some parts of platelet CNFs as prepared, which consist of a number of small units as illustrated in the model of Figure 2c. After graphitization in argon at 2800^{o}C for 10 min, the structural feature of platelet CNFs was more distinctly verified. Graphitized platelet CNF was found to be constructed by parallel close-packing of a number of rod-shaped units with about 20 nm length and 3 nm width. (see Figures 2d and e), which have dome-like caps on the rod ends (see Figure 2e). Such dome-like caps may correspond to loop-shaped ends formed by graphitization of platelet CNFs as shown in the TEM picture of Figure 2f. Figure 2e also shows the hexagonal lattice of carbon atoms on the surface of an individual rod-shaped unit. If the platelet CNFs consist of such rod units indeed, the interaction force among rod units may be weaker than that among hexagonal planes composing a rod unit. Graphitized platelet CNFs were ball-milled in ethanol at ambient temperature, some rod units were found to be perfectly separated from the CNFs (see Figure 2g).

Differing from the nano-sized rod unit in shape, a nano-sized plate consisting of several hexagonal planes was also observed as a constructive unit of CNFs as illustrated with a model of hexagon-type plate stacking in Figure 3a. Under TEM, plate-type units provide similar (002) lattice fringe pattern. The STM pictures in Figures 3b and c show platelet CNFs as prepared consisting of mainly plate-type units or mixture with rod-type units. After graphitization, plate units appeared more distinct in their shape as shown in Figures 3d ~ i. In Figure 3d, the fiber is constructed by discontinuous stacking units (see Figure 3e), each of which probably consists of several carbon hexagonal planes. Similar hexagonal lattice of elemental carbon in Figures 3f and g suggests that the A and B face in Figure 3e are equivalent basal planes. The STM picture of Figure 3h shows obviously presence of plate units of which the transverse shape is polygonal and the surface is of carbon basal plane (see Figure 3i).

Herringbone CNFs as prepared were also found to have rod or plate-shaped units and their packing constituting the CNFs. In the fibers of about 130 nm diameters, a pair of rod assemblies was distinctly found to align angled to the fiber axis, forming the herringbone structure (Figures 4a and b). Some defects or pores appear to be naturally formed in the center of V-shape connection between rod assemblies (see Figure 4b). In several cases, rod-type units (Figure 4d) and plate-type units (Figure 4e) are mixed to form a fiber. The herringbone structure can be constructed by both rod- and plate-type units as illustrated in Figure 4f.

Discussion

In this work, novel hierarchical intermediates were found in the construction of CNF from elemental carbon. It has been known that elemental carbon in sp^2 bonding state provides several allotropes such as graphite, fullerene, and single walled or multi-walled carbon nanotubes. So far, the structures of platelet or herringbone CNFs have been understood based on a flat strip of carbon hexagons, differing from fullerene comprising exquisite combination of pentagon/hexagon and carbon nanotubes of curved carbon hexagons. However, this study showed structural units of macromolecular state such as rod- or plate-type units, of which the packing pattern may determine the bulk structure such as platelet or herringbone ones.

The structural concept through the study is schematically summarized in Figure 5. From TEM and STM results, single rod unit is approximately 2.5 nm in the average width (8~10 carbon hexagonal layers, see Figure 2f) and variable in the length depending on the fiber dimension. The rod-type unit resembles a very short carbon nanotube. The rod-type unit resembles a very short carbon nanotube. However, it is presumed that the cross sectional shape is not round but polygonal, especially hexagonal as shown in Figure 5. In cylindrical carbon nanotubes, the smallest intertubule distance is theoretically 0.339 nm due to its turbostratic stacking. High graphitization degree (d_{002} ~ 0.336 nm) of platelet CNFs requires a corresponding stacking such as the *ABAB* stacking (natural graphite). Hypothetical cross section of single rod unit provides graphite-like stacking if a number of rod units are close-packed as illustrated in Figure 5. The (002) lattice fringe of rod unit assembly is the same with that of the graphite under TEM.

In a previous study, we found that the concept of rod unit assembly was more rational than conventional one of hexagonal plane stacking, concerning changes of the bulk properties obtained by X-ray diffraction, BET surface area, and Raman spectroscopy depending on micro-structural modification of platelet CNF. The rod-type unit may dominate structural characteristics of CNFs, compared to the plate-type unit which appears to be close to rather graphite lattice layer in terms of the cross-sectional dimension and the stacking pattern except that it is a macromolecule formed by several graphite lattice layers.

The alignment of rod- and plate-type units such as in platelet or herringbone textures may depend on the nature and shape of the catalyst particle and orientation of carbon precipitating faces. However, it remains unsolved at present whether the formation of rod- and plate-type units is determined by intrinsic properties of carbon, or catalyst characteristics or interaction between catalyst and carbon. In the relation between rod- and plate-type units, several results of two unit mixture such as Figures 4c ~ e give an idea that rearrangement of several rod-type units can lead to formation of a plate-type unit, also because rod unit of hypothetical hexagonal cross section is expandable as illustrated in Figure 5.

Physical and chemical properties of bulk CNF should be also revaluated under recognition of the rod- and plate-type units and their assembly. Especially, the surface property of CNF consisting of such units is more controllable than that of graphene stacking. Surface roughness depending on uneven stacking in the unit assembly is expected to provide new spaces formed among the rods, and further to be controlled by synthetic technique as well as various post-treatments. For examples, the surface area of graphitized platelet CNF increased probably by uneven piling of loop-ends (or the caps of rod units as in Figures 2e and f) induced by ball-milling at ambient temperature. Also, growth rate control or intermittent growth at prescribed interval may provide formation of CNF with some preferable pores.

In conclusion, the rod- and plate-type units were found in platelet and herringbone CNFs, but a number of detailed description relating to the formation, structure, and dimension are still open to discussion. However, this three-dimensional concept of CNF structure is expected to improve performance of CNF in many practical applications through delicate designs and developed techniques under significant structural understanding.

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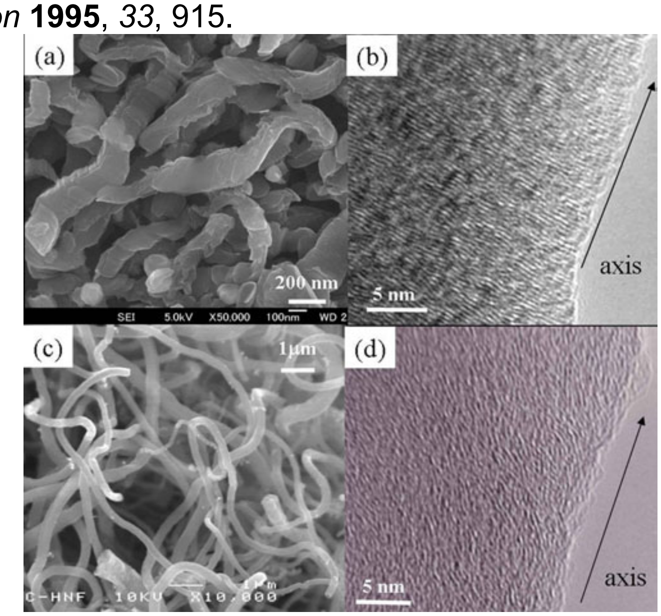

Figure 1. SEM and TEM pictures of platelet CNF (a, b) and herringbone (c,d) catalytically grown.

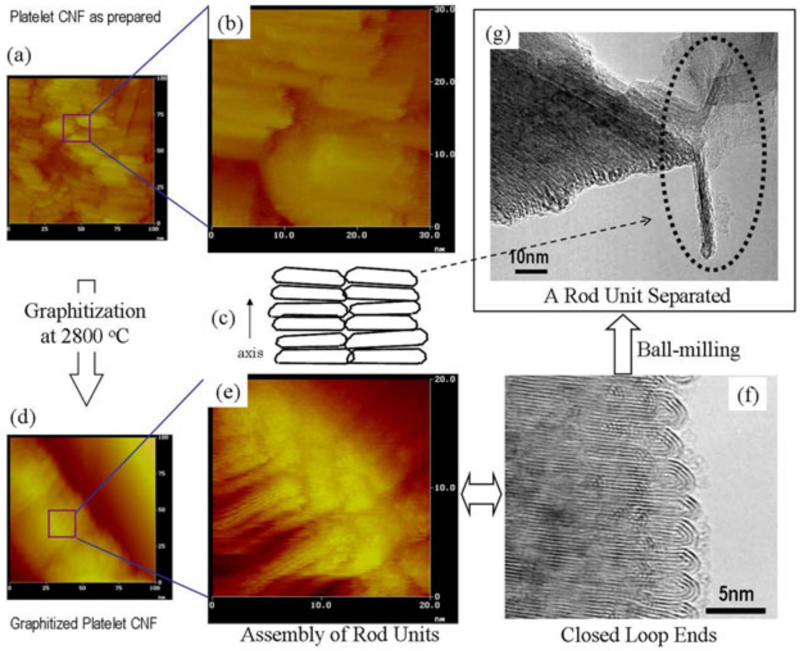

Figure 2. Rod-type unit as a constructive unit of platelet CNF: STM pictures of platelet CNF as prepared (a, b), a schematic model of rod-type unit stacking (c), STM pictures of graphitized platelet CNF (d, e), HR-TEM picture of graphitized platelet CNF (f), and HR-TEM picture of separated rod-type unit (g).

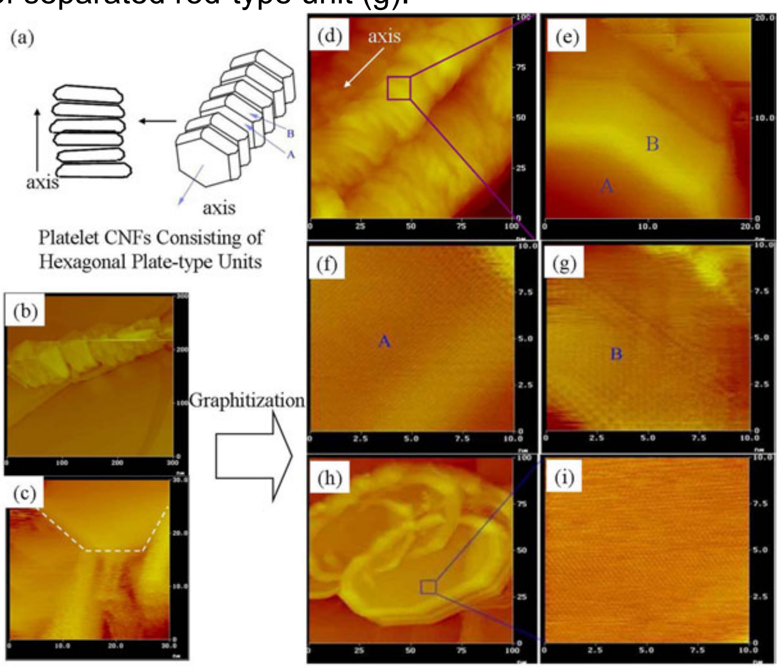

Figure 3. Plate-type unit as a constructive unit of platelet CNF: a schematic model of plate-type unit stacking (a), STM pictures of platelet CNF as prepared (b, c) and graphitized platelet CNF (d ~ i).

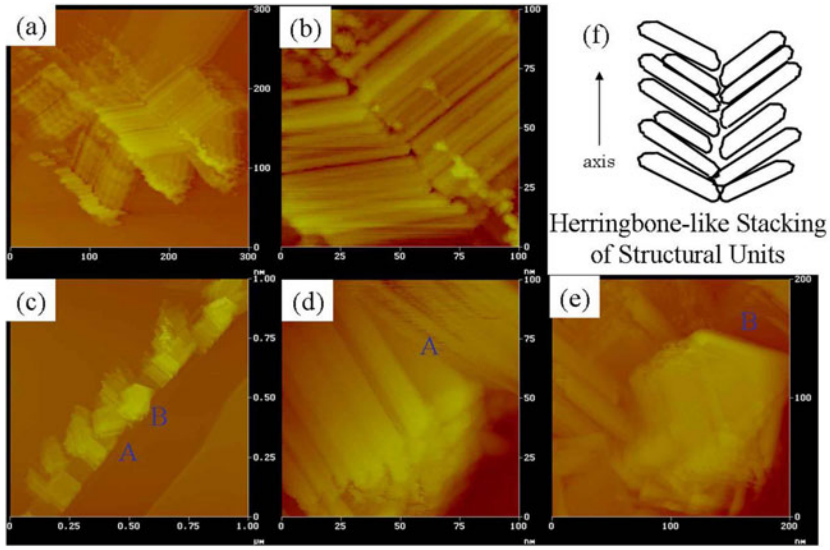

Figure 4. STM pictures of a herringbone CNF consisting of rod-type units (a, b) and another herringbone CNF (c - e) consisting of rod- (d) and plate-type units (e). A schematic model of unit stacking was illustrated (f).

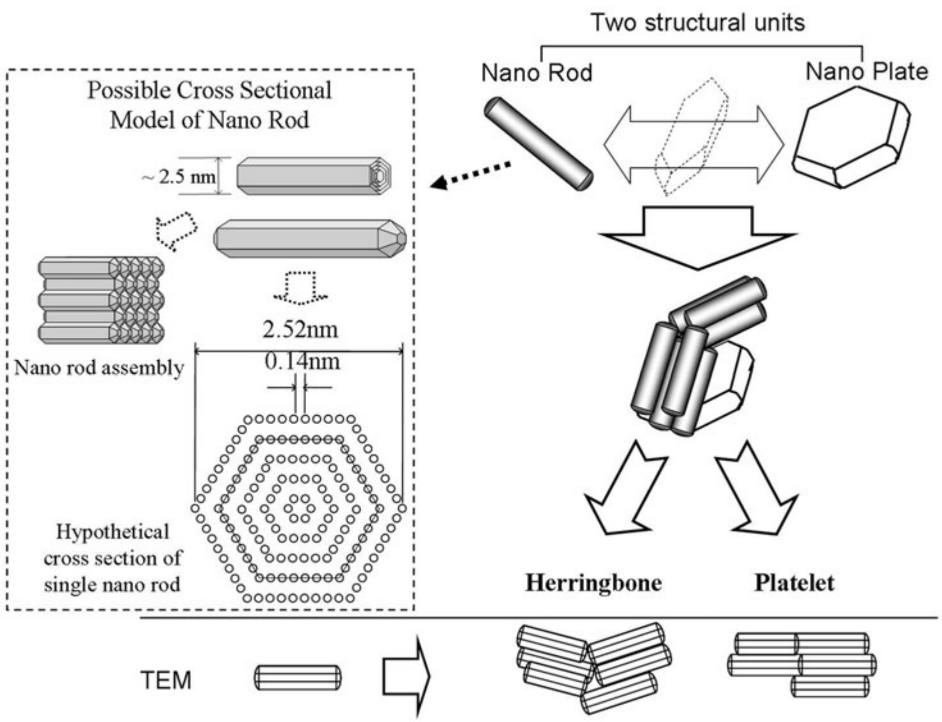

Figure 5. Hypothetical model of single nano-rod and the relationship of rod- and plate-type units.