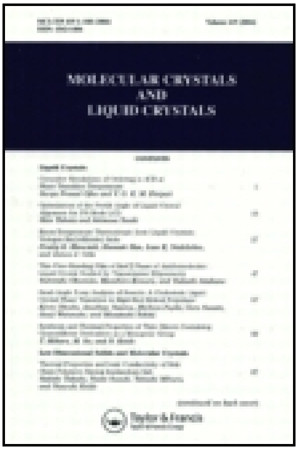

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Structure and basic properties of cup-stacked type carbon nanofiber

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STRUCTURE AND BASIC PROPERTIES OF CUP-STACKED TYPE CARBON NANOFIBER

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Structural characterization of novel nanofibers, so called "cup-stacked type carbon nanofibers" with large hollow core and their potential applications are described as compared with those of tubular type of nanotubes and nanofibers. This novel carbon nanofiber containing peculiar features provide the variety of carbon nanotubes and nanofibers from basic science to application field.

Keywords: cup-stacked type; truncated conical sheets; exposed edge

Recently, pyrolytic carbon nanofibers obtained by floating reactant method, which allow a three-dimensional dispersion of the hydrocarbon together with the catalytic particle resulting in a high yield and rather uniform diameter of the fibers, have been characterized in terms of the highly preferred orientation of their graphitic basal planes parallel to the fiber axis, with an annular ring texture in the cross section.

This structure gives rise to excellent mechanical properties, very high electrical and thermal conductivity, and a high graphitizability of the fibers [1,2]. These excellent physical properties have been evaluated and made possible to use commercially as either electrode itself or additive to electrode in various electrochemical systems, such as lithium-ion battery (LIB), electric double layer capacitor (EDLC).

This discussion was prepared with the benefit of the significant contributions of researchers at Faculty of Engineering of Shinsyu University and staffs at GSI Creos Corporation including S. Higaki, S. Shimizu, S. Ishiwata and T. Yoshinaga. The original fibers were prepared by Applied Sciences, Inc. through Nano Graphite Materials, Inc., whose efforts and service are gratefully acknowledged.

In this study, novel carbon nanofibers, also obtained by a floating reactant method, are characterized in terms of its structure, mainly, that is, "cups-stacked type nanofibers" with large hollow core and large portion of open edges, and their potential applications are described as compared with those of normal type of nanotubes and nanofibers. Present new type of one-dimensional tubular material has specific structural features in comparison with other seamless graphene tubules as shown in following structural models (Fig. 1(a) and (b)).

This type of fiber can be continuously produced and tailored by optimizing precise control of the fiber growth conditions, such as composition of the metallic catalyst, the gas as carbon feedstock, gas flow rate, reaction time and temperature.

FE-SEM and HR-TEM images at low magnification (Fig. 2(a) and (b)) reveal relatively long and straight carbon nanofibers with large hollow core along the fiber axis as compared with that of conventional tubular type, which are showing diameter ranging from 50 to 100 nm and length up to 200 μm. The fibers having long and straight outlook are also observed at conventional nanotubes and nanofibers, whereas this hollow core of cup-stacked type shows not only continuously large size, but also no bridge in the central hollow core that makes relatively thin wall thickness compared with large hollow core diameter. It is interested that this large hollow core structure suggests the possibility of practical use in inside of nano-scale fibers and tubes.

Other TEM images at high magnification (Fig. 3(a) and (b)) reveal stacking morphology of truncated conical sheets containing some angels to

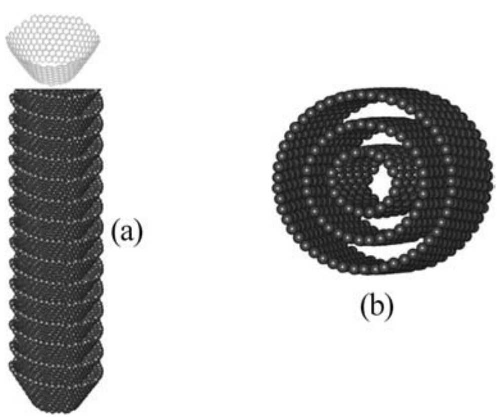

FIGURE 1 (a) Comparative structural models of cup-stacked type, and concentric type carbon nanotubes (b).

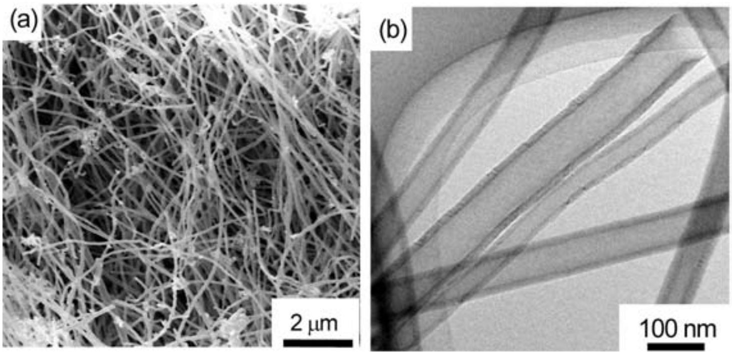

FIGURE 2 (a) FE-SEM image of cup-stacked nanofibers showing long and straight morphology; and (b) TEM images of cup-stacked type nanofibers with large hollow core.

fiber axis and because of this angles, a large portion of the graphene edges are exposed and opened at the apparent tube surface as well as inner hollow core. This also means there is a link between outer surface and inner channel through graphene layers.

While the deposition of pyrolytic carbon, which is inevitable in the chemical vapor deposition (CVD) process using catalyst, is observed, it

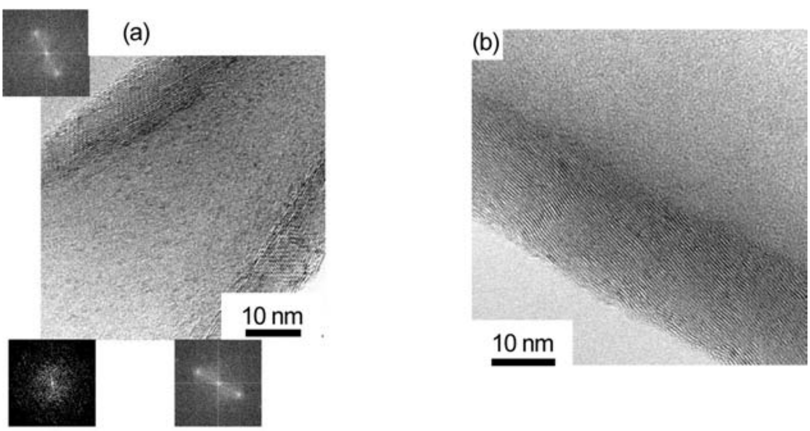

FIGURE 3 (a) Another TEM images of cup-stacked type nanofibers showing stacking morphology of truncated conical sheets containing some angles to fiber axis; and (b) TEM image showing relatively thin wall thickness compared with hollow core diameter.

is possible to optimize the chemical and physical reactivity by several surface modifications using oxidation, etching and sizing which are available from the applied technologies done for conventional carbon materials. These modifications step first to remove any loose surface residues or coatings and then modify the surface chemistry and micro-topography.

After such initial surface modifications, the surface of this cup-stacked type carbon nanofiber becomes comparatively reactive with the intended matrix materials on the tube surface as well as inner hollow core. This tube structure and surface accelerate adhesion strength between fiber and matrix materials such as polymers, resins, metals, rubbers and ceramics and this strength may be also supported physically like the anchor effect due to fine but uneven surface at the atomic level. In addition, this feature might be supported by several applied processes, adding the oxygen-containing functional groups or the activated hydrogen-containing functional groups, such as the phenolic hydroxyl group, carboxyl group, carbonyl group and lactone group. These functional groups give hydrophilic and high dispersion in liquid and lead to tremendous form stability, transferability and lubricancy at forming stage, and also suggest higher tensile strength, compressive strength, elongation and wear resistivity in composites.

These surface modifications should be well considered and studied in each application. Excessive adhesion strength is known to induce the composite materials brittle and lose fracture toughness that is negative factor for mechanical application. While excessive oxygen-containing functional groups or hydrogen-containing functional groups on the carbon surface tends to act as radical to reduce the electrical conductivity by catching π electrons as electric conductor [3,4].

The model of Figure 1(a) and TEM image of Figure 3(a) are also shown that several layers of truncated conical graphene sheets are stacking and placing each other like metal bellows. This bellows structure raises the flexibility of the configuration of this cup-stacked type carbon nanofiber at bulk phase for its bending, entangling, twisting and rotating, as well as bellows tubes in the several industrial applications. This structure can also suggest the possibility of the control of the length, mechanically. It is generally difficult to shorten or cut the length of the conventional carbon nanotubes and nanofibers by mechanical method that is ideal from industrial point of view, due to its configuration and covalent bonds on the surface of graphene sheets. Since the cup-stacked type shows the cup stacking each other by Van der Waals bonds, the cut of cup-stacked type can be considered as pull or release each cup from Van der Waals bonds. This means that cut, actually “pull” can be achieved by using applied technologies, such as ball milling, colloidal milling or roll milling.

These unique structural characteristics mentioned the above strongly suggest using this novel nanofiber in the composite materials, catalyst-carriers, field emission devices, gas storage components and filters. In addition, this cup-stacked type fibers with the shorter length obtained by applied technology induce higher dispersion and stability in matrix and that may accelerate higher luster and brighter color in ink and paint fields in comparison with carbon black filler contained ink and paint.

The characteristics and the structural features of the novel cup-stacked type carbon nanofibers are as following;

1) Long and straight nanofiber morphology.
2) Stacking morphology of truncated conical sheets containing some angles to fiber axis.
3) Exposed graphene edges on the apparent tube surface as well as inner hollow core.
4) Link between outer surface and inner channel through carbon layer.
5) Continuous large hollow core with no bridge in the central hollow tube.
6) Relatively thin wall thickness compared with hollow core diameter.
7) Anisotropic structure of the both ends of a tube.
8) Common structure as concentric type being possible by pyrolytic coating on the pristine tubes.

These structural characteristics can provide the variety of carbon nanotubes in basic properties, together with normal VGCFs, sub-micron VGCFs, Nanofibers and Carbon nanotubes. Actually, remarkable properties of vapor grown carbon fibers (VGCFs) have been already reported in the scientific literature for approximately thirty years [5–7], and now this novel structure can afford to expand the applications in various fields and possibly develop new industry in the 21st century.

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