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Surface Modification of Carbon Nanofiber with High Degree of Graphitization

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Mechanical and chemical treatments were found to improve the graphitization extent of graphitized platelet carbon nanofiber, which showed little change in graphitization parameters of X-ray diffraction even after heat treatment at 2800 °C. Such treatments also restored the surface area that was significantly decreased through the formation of loop-shaped ends on the surface of carbon nanofibers by the graphitization. Formation, distortion, and removal of loop-shaped ends corresponded to such morphological and structural changes of the platelet carbon nanofiber. Relaxation of high-energy edges of the hexagon at the graphitization and high reactivity of closed loop ends at the treatments were observed under TEM. This study also supports existence of the primary rodlike structural unit in carbon nanofibers.

Introduction

Carbon nanofibers (CNFs) have been recognized to be unique forms of carbon materials.[1−4] The diversity of CNFs has been recognized as variable alignments of laminated *c*-plane layers along the fiber axis, which provided typically three types of CNFs such as platelet (alignment perpendicularly to the fiber axis), tubular (alignment parallel to the axis), and herringbone (alignment angled to the axis) CNF.[4]

Graphitizable carbon materials are usually highly graphitized by the heat treatment over 2400 °C to be easily recognized by means of X-ray diffraction (XRD).[5,6] The platelet CNF was found to show highly graphitic structure comparable to that of the graphite even in its as-prepared form.[7−9] However, the interlayer spacing (d_{002}-spacing), the height of layered stackings (Lc(002)), and the mean basal plane diameter (La(110)) of the platelet CNF assessed by XRD were not much changed even after the graphitization over 2500 °C, whereas the electron diffraction patterns of TEM (transmission electron microscope) indicated certainly better alignment in the graphitized platelet CNF.[9] Such graphitization has been reported to induce formation of concentrically laminated loop ends via closing free edges on the surface of platelet CNF[8,9] as is similar with the case of graphite based carbon material.[10]

In this Letter, the present authors treated platelet CNF first thermally, then mechanically and chemically to follow the morphological and structural changes by TEM, XRD, and Raman spectroscopy. Structural changes caused by such treatments were notable in terms of structural understandings of CNFs. In a previous work,[9] we have proposed that the platelet CNF is constructed by uniform close-packing of rod-shaped primary units of 2−3 nm wide and 20−30 nm long, as described by TEM and STM (scanning tunneling microscope) images and the models in Figure 1. The peculiar behaviors of the platelet CNF through a series of treatments in this study were expected to confirm the unique structure of platelet CNF. Modification and removal of closed loop ends in graphitized platelet CNFs were expected to provide a highly graphitized CNF with novel surface functions.

Materials and Method

Platelet CNF (PCNF) was prepared from carbon monoxide and hydrogen mixed gases over Fe catalyst at 600 °C in a conventional horizontal tube furnace, as described in a previous work.[9] PCNF was graphitized (GPCNF) at 2800 °C for 10 min under an argon atmosphere. GPCNF was mechanically milled by using stainless steel balls (Diameter 2 mm) in ethanol for 72 h (GPCNF-M). GPCNF was treated in 10% HNO_3 at ambient temperature for 24 h (GPCNF-NA).

Fibers were measured by an X-ray diffractometer (Rigaku Geigerflex II, Cu Kα target, Rigaku Co. Ltd., Japan) to calculate the crystallographic parameters (d_{002}, Lc(002), and La(110)) according to the JSPS standard procedure.[11] The specific surface area was measured by the nitrogen isotherm using SOPTOMATIC 1990 (Fisons Instrument, Italy). High-resolution TEM (HR-TEM) were performed by using a JEM-2010F microscope (JEOL, Japan) with an acceleration voltage of 200 kV.

Results

Table 1summarizes the preparation conditions and some physical properties of CNFs. PCNF prepared at 600 °C showed a very high degree of graphitization in its as-prepared form, the values of interlayer distance (d_{002}) and the height of stacking (Lc002) being 0.3363 and 28 nm, respectively. PCNF showed 0.035 of H/C atomic ratio, suggesting C−H edges on the surface of as-prepared CNF.

Heat treatment of PCNF at 2800 °C (GPCNF) hardly improved its graphitization extent, as shown by its *d* spacing and Lc in Table 1, whereas no hydrogen was found in the

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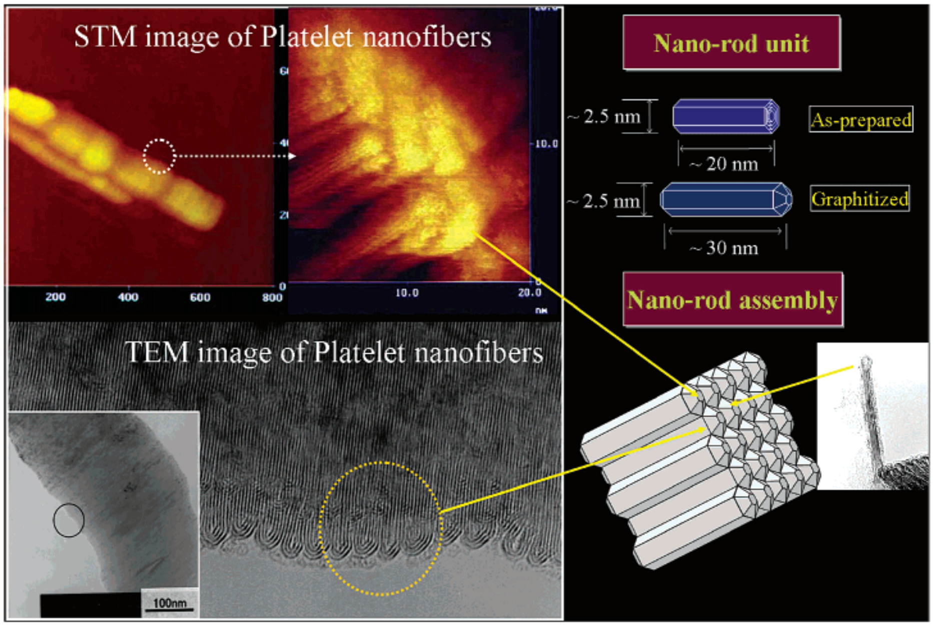

Figure 1. Primary structural unit of platelet CNFs: STM and TEM images of its packing in CNF, TEM images of a mechanically separated structural unit, and suggested models.

TABLE 1: Preparation Conditions and Some Physical Properties of Platelet CNFs Used in This Study

samples	preparation	H/C[a]	XRD properties d_{002} (nm)	XRD properties Lc(002) (nm)	surface area (m^2/g)
PCNF	as prepared	0.035	0.3363	28	91
GPCNF	graphitized at 2800 °C	0.000	0.3363	32	32
GPCNF-M	ball-milling for 72 h		0.3360	40	45
GPCNF−NA	10% HNO$_3$ for 24 h		0.3356	137	66

[a] The H/C ratio means the atomic ratio of hydrogen per carbon.

elemental analysis, indicating no C−H edge. The surface area decreased markedly from 91 to 32 m^2/g.

The milling of GPCNF increased slightly the graphitization extent and surface area, as shown in Table 1. HNO$_3$ treatment of GPCNF recovered the surface area up to 66 m^2/g, improving significantly the graphitization extent, as shown by 0.3356 nm of d_{002} and 137 nm of Lc(002).

TEM photographs of CNFs are shown in Figure 2. The edges of *c*-plane layers in the PCNF (Figure 2a) were closed to loop ends with concentrically laminated multilayers through graphitization at 2800 °C in Figure 2b, as previously reported.[8,9] It must be noted that every rod-shaped unit in its pile was covered with a cap as seen in Figure 1. Ball-milling distorted the alignment of the loop-ended structural units, as shown in Figures 2c and 3c, where some space appeared between the loop-ended structural units, possibly leading to an increase of the surface area. Comparing high magnification micrographs of Figure 3b,c, the semispherical head of the loop end was seen to swell slightly in size, or probably the interspacing of *c*-plane layers became denser after ball-milling treatment. In Figures 2d and 3d, the acid treatment definitely cut off the loop ends, consequently exposing the free edges. From the electron diffraction patterns (subimages of Figure 2a,b), improvement of the graphitization extent was confirmed after the heat treatment. Such well-aligned stacking appears to be preserved through milling and acid treatments as far as TEM was concerned (Figure 3b−d).

The recovery of free edges after the acid treatment was confirmed by Raman spectra of the CNFs, as shown in Figure 4. As shown in TEM photographs of Figures 2 and 3, the PCNF and GPCNF-NA exposed the edges on whole and major surfaces, respectively, whereas the surfaces of GPCNF and GPCNF-M were wholly covered by the loop ends. The order of the ratio, I_{1355}/I_{1580} (the intensity ratio of the 1355 cm^{-1} band against the 1580 cm^{-1} band) followed PCNF > GPCNF-NA > GPCNF ≈ GPCNF-M, which reflected the extent of free edges in TEM images.[12] The 1620 cm^{-1} bands of PCNF and GPCNF-NA were more emphasized than those of GPCNF and GPCNF-M, indicating edge-rich planes.[12] The full width at half-maximum of the 1580 cm^{-1} band, $\Delta\nu(1580)$, decreased slightly in the following order: PCNF > GPCNF > GPCNF-M ≈ GPCNF-NA, which is probably related to their graphitization extent.[12,13]

Discussion

In the present study, the surface of PCNF was observed under high-resolution TEM following a series of treatments such as graphitization, mechanical milling and chemical oxidation to clarify its microstructure. The heat treatment at 2800 °C (graphitization) induced the closed loop ends on the surface of PCNF as reported previously[8,9] and observed with other carbon materials.[10] Such loop ends have been proposed to be formed through folding of some planar hexagons at their edges, which looks like a multiwalled nanotube as described by Moriguchi et al.[10] However, uniform closed loop ends suggests that their formation is not accidental but based on the regularity in the substructure of PCNF. We have demonstrated in a previous work[9] that there exists a primary structural unit like a nanosized rod in PCNF, and the concentrically laminated loop end was found as a cap of nanosized carbon rod formed by graphitization. The nano rod consists of 8−10 pieces of hexagonal planes. The edges of such a set of planes appear to form regularly a closed loop end. The edges of the planes within the rod are connected with corresponding ones to form the concentric loops of hexagonal planes.

The heat treatment at higher temperatures than 2000 °C removes surface C−H bonds and stacks more densely hexagonal layers of PCNF prepared at 600 °C, forming chemically active dangling sites on the edges.[10] Thus, such edges must be stabilized by bonding each other in the manner as described above, even though such bonding must cause a large strain or

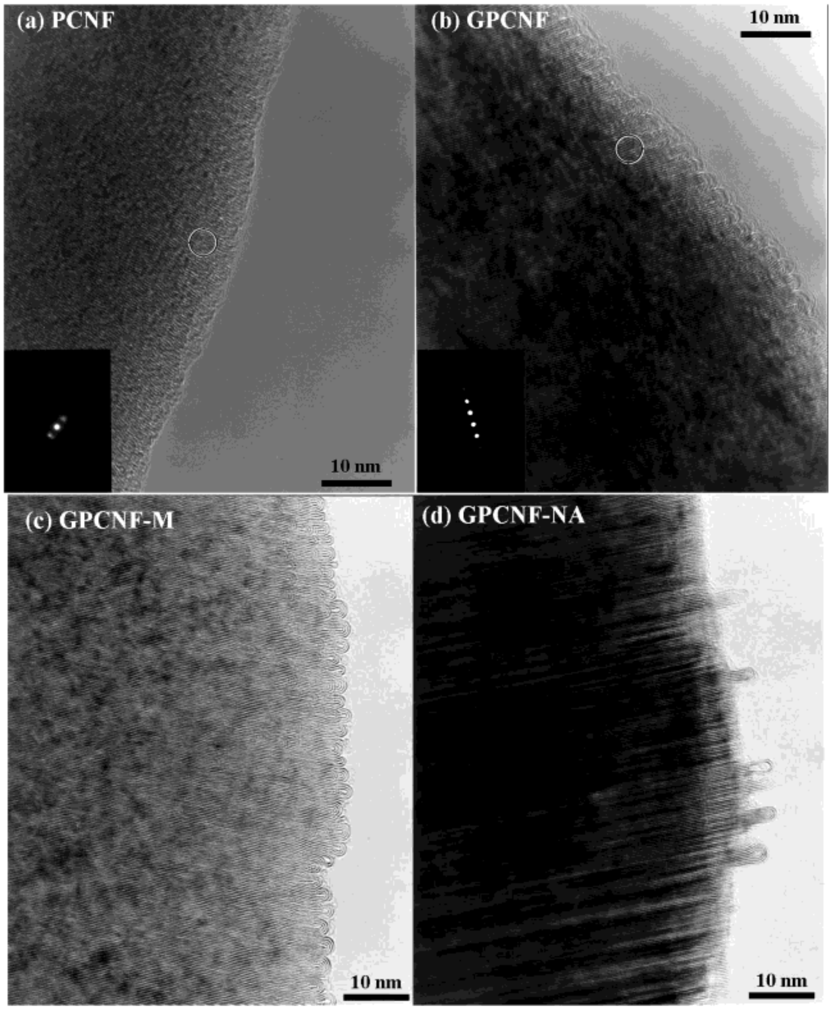

Figure 2. HR-TEM images of (a) PCNF, (b) GPCNF, (c) GPCNF-M, and (d) GPCNF-NA. Subimages of (a) and (b) show the electron diffraction pattern in circled parts of the main images.

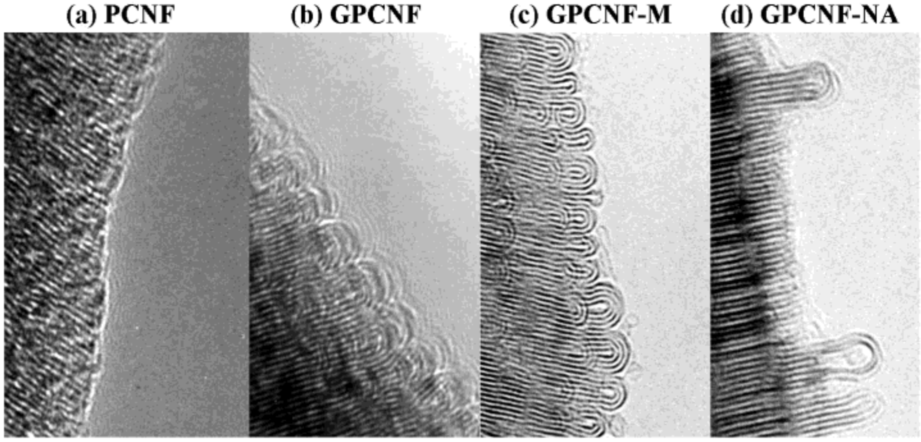

Figure 3. HR-TEM images of (a) PCNF, (b) GPCNF, (c) GPCNF-M, and (d) GPCNF-NA, which are magnified from a part of each image in Figure 1.

tension through formation of the sharp curvature in the concentric loop alignment of hexagon. Chemical reactivity and mechanical instability of such loop ends are expected at ambient temperature.

The mechanical treatment as well as the acid treatment indeed was found to modify the nanosized structure of GPCNF. Such changes appear to reflect a local strain at the surface of individual structural units, which is ascribed to formation of the closed loop ends. Although the overall alignment of hexagonal *c*-planes became certainly better in GPCNF, as shown under TEM observations and Raman spectroscopy, the formation of concentrically laminated loop ends from open edges may inhibit further decrease of interlayer spacing (d_{002}), inducing defects in graphitic packing of the nanosized structural units (little increase of Lc). The acidic oxidation cutoff the closed loop ends on the surface of GPCNF, consequently to improve overall alignment of hexagonal planes to be more graphitic, because a nanosized loop end must suffer a high reactivity. The distortion of the closed loop ends by milling at room temperature may reflect its high reactivity and tension.

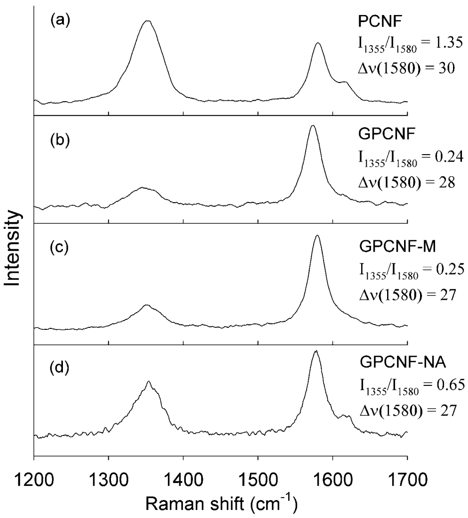

Figure 4. Raman spectra of (a) PCNF, (b) GPCNF, (c) GPCNF-M, and (d) GPCNF-NA.

The mechanical treatment at room temperature modified easily nanosized structure, which may reflect that the interaction between the primary structural units is weaker than that between *c*-planes in single crystal graphite. The loop ends unevenly piled up in the GPCNF-M show packing of the primary units more distinctly than those in the GPCNF. A slight increase of the surface area by ball-milling treatment suggests creation of new spaces among the primary structure units, which is similar to the external nanopores in the single-walled nanotube bundle[14] or the nanohorn assembly.[15] Uniform cutting-off of the loop ends looks like the cap-opening of carbon nanotubes.[16,17] However, it must be noted that the open edges were created by completely and uniformly cutting off the whole loop ends, not just the tip of the loop ends. Recovery of the surface area by cutting off loop ends suggests that free edges occupy a majority of active surface sites.[18]

It must be also noted that graphitization and acid treatment generated a novel CNF of many surface free edges as well as high graphitization extent close to the graphite single crystal, differing from conventional free edge-rich CNFs such as platelet and herringbone CNFs by catalytic methods[2,4] and recently orthogonal CNFs from mesophase pitch by a template method.[19]

In summary, heat treatment up to 2800 °C removes heteroatoms of the hexagonal edges of PCNF, producing the closed loop ends on its surface, which induce a local strain at the individual surface of primary structural units, limiting the graphitization extent despite better alignment and overall stacking. Such closed loop ends are mechanically distorted or chemically removed. The primary structural units must govern a series of structural changes in the surface as well as bulk of the CNF. Surface changes influence the graphitization extent and simultaneously the surface area of the graphitized CNF.

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