Nano-structural Understandings on Carbon Nanofibers Based on Primary Structural Units

Seongyop Lim,* Seong-Ho Yoon, Isao Mochida
Institute for Materials Chemistry and Engineering, Kyushu University, Kasuga, Fukuoka 816-8580, Japan
Corresponding author e-mail address: lim9@asem.kyushu-u.ac.jp

Introduction

Unique properties of carbon nanofibers (CNF) depends on its microstructure and bulk morphology, which are governed by catalysts, carbon sources and synthesis conditions in the catalytic growth of CNF. Hence, exact understanding of the structure of CNF is important to achieve best performance of the CNF in practical applications.
In a previous work [1], the present authors have proposed that the platelet CNF is constructed by uniform close-packing of rod-shaped primary units of 2~3 nm wide and various length of 20~100 nm long.
In this study, the present authors treated platelet and herringbone CNFs first thermally, then mechanically and chemically to follow the morphological and structural changes by TEM, XRD, and Raman spectroscopy, in order to investigate its exact nano-structure and the possibility of applications.

Materials and Method

Platelet CNF (PCNF) was prepared from carbon monoxide and hydrogen mixed gases over Fe catalyst at 600^{o}C in a conventional horizontal tube furnace as described in a previous work.[1] Herringbone CNF (HCNF) was prepared from a ethylene and hydrogen mixture over a CuNi catalyst at 600^{o}C.
PCNF and HCNF were graphitized (GPCNF and GHCNF) at 2800^{o}C for 10 min under argon atmosphere. GPCNF was mechanically milled by using stainless steel balls (Diameter 2 mm) in ethanol for 72 h (GPCNF-M). GPCNF and GHCNF were treated in 10% HNO_3 at 200^{o}C for 24 h (GPCNF-NA and GHCNF-NA).
Fibers were measured by an X-ray diffractometer (Rigaku Geigerflex II, CuKα target, Rigaku Co. Ltd., Japan) to calculate the crystallographic parameters (d_{002}, Lc(002) and La(110)) according to the JSPS standard procedure.[2] 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 JEM-2010F microscope (JEOL, Japan) with an acceleration voltage of 200kV.

Results

Table 1 summarizes the preparation conditions and some physical properties of CNFs. PCNF prepared at 600°C showed 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 nm 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^{o}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 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).

Table 1. Preparation conditions and some physical properties of CNFs

Samples	Preparation	H/C §	XRD properties		Surface area (m^2/g)
			d_{002} (nm)	Lc(002) (nm)	
PCNF	As prepared	0.035	0.3363	28	91
GPCNF	Graphitized	0.000	0.3363	32	32
GPCNF-M	Ball-milling	-	0.3360	40	45
GPCNF-NA	HNO_3	-	0.3356	137	66

§ The H/C ratio means the atomic ratio of hydrogen per carbon.

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 multi-layers through graphitization at 2800°C in Figure 2b as previously reported [1]. 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 increase of the surface area. Comparing high magnification micrographs of Figures 3b and 3c, the semi-spherical 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 cut off definitely the loop-ends, consequently to expose the free edges. From the electron diffraction patterns (sub-images of Figures 2a and 2b), improvement of the graphitization extent was confirmed after the heat treatment.

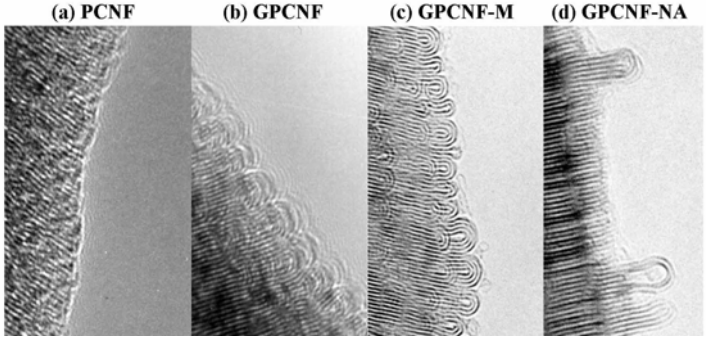

Figure 2. TEM images of PCNF (A), GPCNF (B), GPCNF-M (C), and GPCNF-NA (D).

Such structural changes were also found with HCNF as shown Figure 3. Figure 3A shows HCNF as prepared, of which the graphene alignment is relatively disordered, exhibiting no pattern of the electron diffraction (see sub-image of Figure 3A) and low graphitization degree as shown in Table 1. After graphitization (GHCNF), the alignment of graphene was much increased, the loop end being formed on the edge (see Figure 3B). Nitric acid treatment of GHCNF (GHCNF-NA) made the loop end removed, the open edge being exposed as shown in Figure 3C. The surface of GHCNF-NA appeared to be less rough than that of GHCNF.

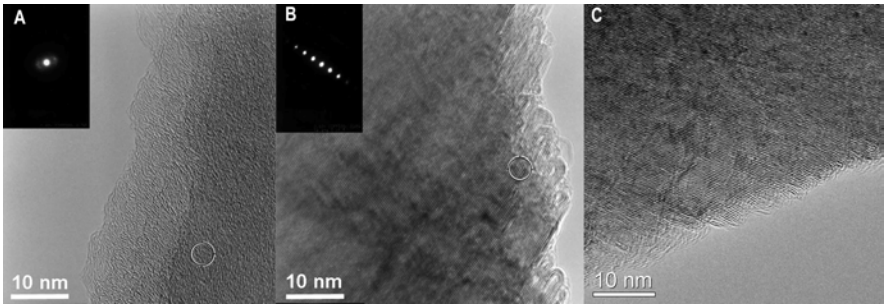

Figure 3. TEM images of HCNF (A), GHCNF (B), and GHCNF-NA (C).

Discussion

The heat treatment at 2800°C (graphitization) induced the closed loop-ends on the surface of CNF. The heat treatment at higher temperatures than 2000°C removes surface C-H bonds and stacks more densely hexagon layers of CNF prepared at 600°C, forming chemically active dangling sites on the edges [3]. 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 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.

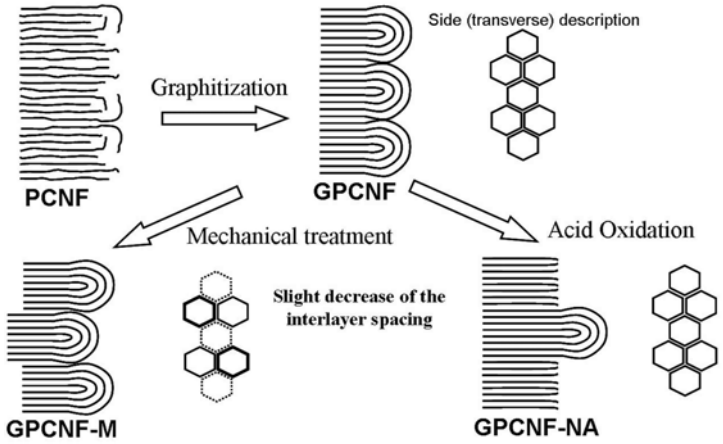

Figure 4. Schematic suggestion of structural changes of CNF through various treatments on the basis of carbon nano-rod.

The mechanical treatment as well as the acid treatment indeed was found to modify the nano-sized structure of GPCNF (or GHCNF). 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, 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 nano-sized structural units (little increase of Lc). The acidic oxidation cut off the closed loop-ends on the surface of GPCNF, consequently to improve overall alignment of hexagonal planes to be more graphitic, since the loop-end in a nano size must suffer a high reactivity. The distortion of the closed loop-ends by milling at room temperature may reflect its high reactivity and tension.

The mechanical treatment at room temperature modified easily nano-sized 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. 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 [4] or the nanohorn assembly [5]. Uniform cutting-off of the loop-ends looks like the cap-opening of carbon nanotubes [6,7]. However, it must be noted that the open edges was created through cutting off the whole loop-ends completely and uniformly, not just tip on the loop-ends. Recovery of the surface area by cutting-off loop-ends suggests that free edges occupy a majority of active surface sites [8].
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 herring-bone CNFs by catalytic methods and recently orthogonal CNFs from mesophase pitch by a template method [9].

Conclusion

The structural changes of CNF through some treatments reflected the stabilization of carbon nano-rods in their systematical stacking or the bulk structure of CNF. Consequently, surface changes influence the graphitization extent and simultaneously the surface area of the graphitized CNF.

REFERENCES

[1] Yoon SH, Tanaka A, Lim S, Korai Y, Mochida I, Ahn B, Yokogawa K, Park CW. Carbon 2003: International Conference (Oviedo, Spain): Spanish Carbon Group, 2003; 76.
[2] Iwashita N, Park CR, Fujimoto H, Shiraishi M, Inagaki M. Specification for a standard procedure of X-ray diffraction measurements on carbon materials. Carbon 2004; 42 (4): 701-714.
[3] Moriguchi K, Munetoh S, Abe M, Yonemura M, Kamei K, Shintani A, Maehara Y, Omaru A, Nagamine M. J Appl Phys 2000; 88: 6369-.
[4] Maruyama, S, Kimura, T. In Kim JH, editor, 2000 Proceedings of The ASME Heat Transfer Division, Vol. 2, New York: ASME press, 2000: 405-409.
[5] Murata K, Kaneko K, Steele WA, Kokai F, Takahashi K, Kasuya D, Yudasaka M, Iijima S. Nano Lett 2001; 1 (4): 197-.
[6] Ajayan PM, Iijima S. Nature 1993; 361 (6410): 333-.
[7] Ugarte D, Chatelain A, de Heer WA. Science 1996; 274: 1897-.
[8] Hoffman, W. P. Chemi-Sorption Processes on Carbons. In Marsh H, Rodriguez-Reinoso F, editors, Sciences of Carbon Materials, Alicante (Spain): Universidad de Alicante, 2000: 437-483.
[9] Jian K, Shim H-S, Schwartzman A, Crawford GP, Hurt RH. Advanced Materials 2003; 15(2): 164-.