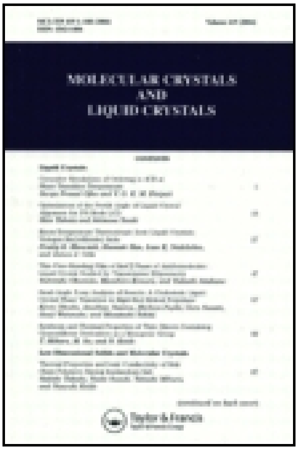

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Microstructural change of cup-stacked carbon nanofiber by post-treatment

Yoong Ahm Kim [a], Takuya Hayashi [a], Yasuo Fukaiand [a], Morinobu Endo [a] & Takashi Yanagisawa [b]

[a] Faculty of Engineering, Shinshu University, 4-17-1 Wakasato, Nagano-city, 380-8553, Japan

[b] GSI Creos Corporation, 2-3-1 Kudan minami, Chiyoda-ku, Tokyo, 102-0074, Japan

Version of record first published: 18 Oct 2010

To cite this article: Yoong Ahm Kim, Takuya Hayashi, Yasuo Fukaiand, Morinobu Endo & Takashi Yanagisawa (2002): Microstructural change of cup-stacked carbon nanofiber by post-treatment, Molecular Crystals and Liquid Crystals, 387:1, 157-161

To link to this article: http://dx.doi.org/10.1080/10587250215232

Mol. Cryst. Liq. Cryst., Vol. 387, pp. [381]/157–[385]/161
Copyright © 2002 Taylor & Francis
1058-725X/02 $12.00 + .00
DOI: 10.1080/10587250290113718

MICROSTRUCTURAL CHANGE OF CUP-STACKED CARBON NANOFIBER BY POST-TREATMENT

Yoong Ahm Kim, Takuya Hayashi, Yasuo Fukai, and Morinobu Endo
Faculty of Engineering, Shinshu University, 4-17-1 Wakasato, Nagano-city, 380-8553, Japan

Takashi Yanagisawa
GSI Creos Corporation 2-3-1 Kudan minami, Chiyoda-ku, Tokyo 102-0074, Japan

Structural changes of truncated graphitic conical graphene layers (cups) stacked carbon nanofiber by post-treatment, such as oxidation and heat treatment, are described in terms of microstructure and morphology.

Keywords: nanofiber; oxidation; heat treatment

In recent years, a catalytic thermal chemical vapor deposition (CVD) synthesis method has been extensively investigated as a promising method for the large-scale production of non-planar sp^2 carbon nanomaterials, including carbon nanotubes and nanofibers, especially using a floating reactant method [1–5]. Through a precise control of the synthetic conditions, it is possible to tailor the diameter, crystallinity and also the orientation of the cone angle with regard to the fiber axis [4–8]. In this study, novel carbon nanofibers with a large hollow core and having a large portion of open edges at the outer surface and also in the inner channels, due to the truncated graphene cone's morphology (cup-stacked or lamp-shade stacked), are modified by oxidation and also graphitization process. These structural characteristics and also their possible low-production cost using a floating reactant production system may make it possible to use this novel nanofiber in the fabrication of absorbent materials, catalyst-supports, field emitters, gas storage components and composite materials.

TEM image at low magnification reveal relatively long and straight carbon nanofibers with a hollow core along the fiber length (Fig. 1a), which exhibit diameters ranging from 50 to 150 nm and lengths up to 200 μm. One

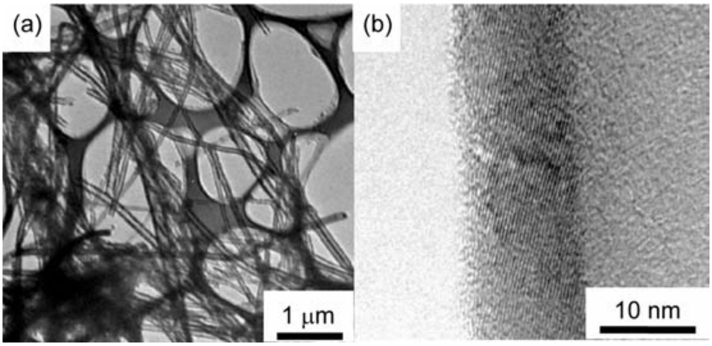

FIGURE 1 TEM images of nanofibers (a) at low resolution and (b) at high resolution.

of main characteristics of these fibers is a large hollow core. This nanofiber shows a truncated cone microstructure (Fig. 1b). The truncated cone angle (cup) with regard to the fiber axis, measured by electron diffraction (ED), taking the fast Fourier transform (FFT) of several TEM images, lies mainly between 45 and 80°.

The outer and also inner surfaces of the nanofiber have to be covered entirely by open edges, that is, the end face of the graphitic conical sheets from the point of view of the growth mechanism. Practically, the deposition of amorphous carbon on the catalytically-induced graphitic carbon phase, which is unavoidable in the synthetic process of nanofibers, and also the possible formation of loops between adjacent conical graphene sheets, might deteriorate the total chemical and physical reactivity of the nanofibers. To solve this problem, an air oxidation process is applied to prepare nanofibers with an increased fraction of open edge sites. Figure 2 shows Raman spectra for oxidized nanofibers at different temperatures. Modification of the surface of the nanofiber starts at 520°C, and then the optimal oxidation temperature is found to be at 530°C within our experimental conditions, based on a decreased half width at half-maximum (HWHM) and intensity of the D peak at 1355 cm^{-1} (the defect mode), the appearance of a shoulder peak at 1620 cm^{-1}, and also a decreased relative intensity (I_D/I_G). When oxidized at 540°C, structural disruption might occur, due to severe oxidation, based on an increased intensity of the D peak and also a large value of the relative intensity ($I_D/I_G = 0.9674$).

The graphitization process is known as one of the most efficient ways to modify the microstructure of carbons [9,10]. TEM images of graphitized nanofibers are shown in Figure 3. The most interesting change caused by the graphitization process is a morphological transformation from smooth wall tubule type to a reversing saw-toothed type with regular pitches

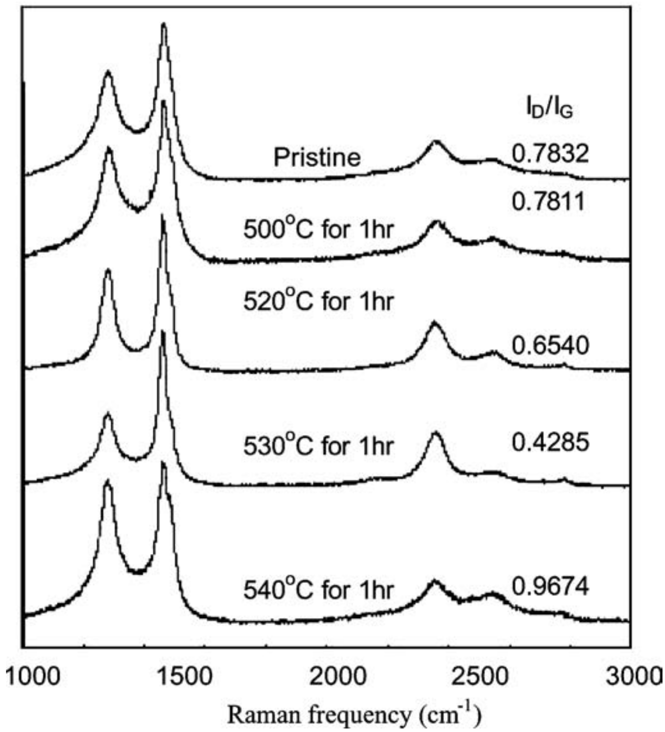

FIGURE 2 Raman spectra of oxidized nanofibers.

(Fig. 3a). The other features of the graphitized nanofibers are the long link formation along the outer and inner sides of the fibers in intervals of regular pitches (closure of open cups on both sides) and a loop formation between neighboring conical sheets (Fig. 3b). From the point of the graphitization mechanism, the degree of the decrease in interlayer spacing from 3.45 to 3.395 Å (from XRD analysis) is relatively smaller than that of CVD-based carbon materials. Actually the number of loops increases with increasing heat treatment temperature. Therefore, the formation of loops in both the inner and outer surfaces of the nanofiber might retard the three-dimensional stacking ordering caused by mass transformation, and also give indirect evidence for the carbonization and graphitization mechanism of hard carbon materials.

The novel nanofibers obtained by a floating reactant method consists of truncated conical sheets making various angles with regard to fiber axis with a large hollow core. It is found that air oxidation at 530°C for 1hour is the optimum condition to get an increased surface reactivity in nanofibers.

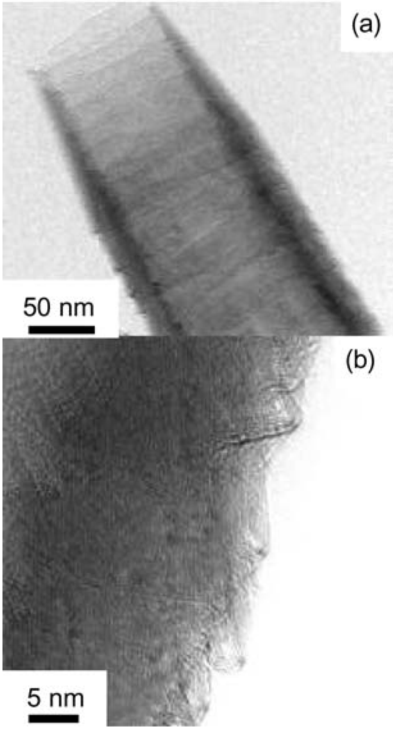

FIGURE 3 TEM images of graphitized carbon nanofibers.

The graphitization process results in a reversing saw-toothed type morphology and also in the formation of loops between neighboring conical sheets. These experimental results, as mentioned above, will spur both the research of applications fields from now on.

REFERENCES

[1] Dai, H. J., Rinzler, A. G., Nikolaev, P., Thess, A., Colbert, D. T., & Smalley, R. E. (1996). *Chem. Phys. Lett.*, *260*, 471.
[2] Rao, C. N. R., Sen, R., Satisshkumar, B. C., & Govindaraj, A. (1998). *Chem. Commun.*, *n15*, 1525.
[3] Andrews, R., Jacques, D., Rao, A. M., Derbyshire, F., Qian, D., Fan, X., Dickey, E. C., & Chen, J. (1999). *Chem. Phys. Lett.*, *303*, 467.
[4] Endo, M. (1988). *Chemtech*, *18*, 568.
[5] Tibbetts, G. G., Gorkiewicz, D. W., & Alig, R. L. (1993). *Carbon*, *31*, 809.
[6] Kamalakaran, R., Terrones, M., Seeger, T., Kohler-Redlich, Ph., Ruhle, M., Kim, Y. A., Hayashi, T., & Endo, M. (2000). *Appl. Phys. Lett.*, *77*, 3385.

[7] Endo, M., Kim, Y. A., Fukai, Y., Hayashi, T., Terrones, M., Terrones, H., & Dresselhaus, M. S. (2001). *Appl. Phys. Lett.*, *79*, 1531.
[8] Terrones, H., Hayashi, T., Munoz-Navia, M., Terrones, M., Kim, Y. A., Grobert, N., Kamalakaran, R., Dorantes-Davila, J., Escudero, R., Dresselhaus, M. S., & Endo, M. (2001). *Chem. Phys. Lett.*, *343*, 241.
[9] Kosaka, M., Ebbesen, T. W., Hiura, H., & Tanigaki, K. (1995). *Chem. Phys. Lett.*, *233*, 47.
[10] Endo, M., Nishimura, K., Kim, Y. A., Hakamada, K., Matushita, T., Dresselhaus, M. S., & Dresselhaus, G. (1999). *J. Mater. Res.*, *14*, 4474.