High-resolution Transmission Electron Microscopy of Heat-treated C$_{60}$ Nanotubes

R Kato$^1$, K Miyazawa$^1$, T Nishimura$^1$ and Z M Wang$^2$

$^1$National institute for Materials Science, Tsukuba, Ibaraki, 305-0044, Japan
$^2$Energy Technology Research Institute, AIST, Tsukuba, Ibaraki 305-8569, Japan

E-mail: KATO.Ryoei@nims.go.jp

Abstract. Fullerene nanowhiskers and nanotubes are single crystals consisting of C$_{60}$ molecules with a high aspect ratio of length to diameter. In this study, C$_{60}$ nanowhiskers and nanotubes were heat-treated at various temperatures up to 3000 °C. The structural characteristics of the heated samples were examined using transmission electron microscopy (TEM) and Raman spectroscopy. By the high-temperature heat treatment, the C$_{60}$ nanotubes turned to glassy carbon composed of randomly oriented ribbons with graphitic layers with an interlayer spacing which is close to that of the (002) planes of graphite.

1. Introduction

In 2001, Miyazawa et al. synthesized single crystalline non-tubular nanowhiskers consisting of C$_{60}$ molecules with a high aspect ratio of length to diameter, typically a diameter of sub-micrometer and a length of more than 100 µm [1]. Furthermore, tubular C$_{60}$ nanowhiskers, i.e., C$_{60}$ nanotubes were fabricated by the same method as the C$_{60}$ nanowhiskers [2]. The dried fullerene nanofibers have a face-centered cubic structure or a body-centered tetragonal structure [3], and the lattice constant of the C$_{60}$ nanofibers with the face-centered cubic structure is close to that of pristine C$_{60}$ crystal.

The as-prepared C$_{60}$ whiskers have a high electrical resistivity $>10^5$ Ωcm, but it is reported that the resistivity decreases with decreasing diameter [3, 4].

On the other hand, with respect to the thermal properties of C$_{60}$ nanowhiskers, the heated fullerene nanowhiskers could get a high specific surface area and a high electrical conductivity [5]. Asaka et al. examined the electrical conductivity of a C$_{60}$ whisker preheated in vacuum at 1100 °C in a TEM [6]. The preheated C$_{60}$ whisker was broken when a high current was applied. Interestingly, a whisker composed of multilayered carbon hollow nanocapsules less than 10 nm in diameter was produced. It was deduced that the formation of the capsules results from an increase in temperature due to the resistive Joule heating.

The whisker composed of carbon nanocapsules has a high specific surface area and a porous structure. Therefore the high temperature-treated fullerene nanowhiskers exhibit a high specific surface area and a good electrical conductivity. They are expected to be utilized as new electrode materials for fuel cells.
In this study, C$_{60}$ nanowhiskers and C$_{60}$ nanotubes, i.e., C$_{60}$ nanofibers, were heat-treated at various temperatures up to 3000 °C. The structural characteristics of the samples heat-treated at each temperature were examined using optical microscopy, scanning electron microscopy (SEM), TEM and Raman spectroscopy.

2. Experimental

The fullerene nanowhiskers were prepared by the liquid-liquid interfacial precipitation method [7]. Firstly, C$_{60}$ powder (99.95% pure C$_{60}$, MTR Ltd., USA) was dissolved in toluene by ultrasonication for 30 minutes. The toluene solution saturated with C$_{60}$ was filtered by a paper filter to remove undissolved C$_{60}$ powder. Isopropyl alcohol was gently added to the C$_{60}$-toluene solution to form the liquid-liquid interface in a glass bottle. The bottles were stored in an incubator for a few days.

The fullerene nanotubes were also fabricated by a similar liquid-liquid interfacial precipitation method [2, 8, 9], where a pyridine solution saturated with C$_{60}$ irradiated by visible light (436 nm) or ultraviolet light (302 nm) was used.

The grown C$_{60}$ nanofibers in a glass bottle were collected by centrifugal separation method or filtration. The prepared C$_{60}$ nanofibers were heated for 60 min at 900 °C in an evacuated fused silica tube set in a muffle furnace (Denken Co., Ltd., KDF-S70). The C$_{60}$ nanofibers heated at 900 °C were collected from the silica tube and further heated at 2000 °C, 2500 °C and 3000 °C, respectively, for one hour in Ar atmosphere using an ultra-high temperature furnace. The microstructure of samples was examined using a high-resolution transmission electron microscope (HRTEM, JEM-4010, JEM-2010, JEOL) and a microscopic Raman spectrophotometer (JASCO, NRS-3100, Japan) at a laser excitation wavelength of 532 nm.

3. Results and discussion

Figures 1 (a) and (b) show optical microscopy image of as-prepared C$_{60}$ nanotubes on a slide glass and scanning electron microscopy image of that on a silicon plate, respectively. The C$_{60}$ nanotubes exhibit metallic red brownish colour and grow to a length of more than 100 micrometer order and have a smooth surface.

Figure 2 shows the low magnification and high-resolution TEM images and electron diffraction patterns of the as-prepared or heat-treated C$_{60}$ nanotubes that were dispersed on TEM microgrids. The C$_{60}$ as-prepared nanotube has a single crystalline structure. But the C$_{60}$ nanotube heated at 900 °C

![Figure 1. (a), (b) Optical microscopy image of as-prepared C$_{60}$ nanotubes on a slide glass and scanning electron microscopy image of that on a silicon plate, respectively.](image)
Figure 2. (a) Conventional TEM (CTEM) image, (b) electron diffraction pattern and (c) high-resolution TEM image of an as-prepared C$_{60}$ nanotube. (d) CTEM image, (e) electron diffraction pattern and (f) high-resolution image of the C$_{60}$ nanotube heated at 900 °C.

shows an amorphous structure as shown Figs. 2 (e) and (f).

Figure 3 shows the Raman spectra of heat-treated non-tubular C$_{60}$ nanowhiskers, as-prepared C$_{60}$ nanowhiskers and graphite. The Raman spectrum of the as-prepared C$_{60}$ nanowhiskers dried in air at room temperature is very similar to that of pristine C$_{60}$[10]. Hence, those C$_{60}$ nanowhiskers without heat treatment are found to be composed of the C$_{60}$ molecules that are loosely bound via van der Waals bonding forces like the case of pristine face-centered cubic C$_{60}$ crystals. The change of Raman spectra for the heat-treated C$_{60}$ nanowhiskers is shown in Fig. 3. The peaks observed in the nanowhiskers without heat treatment are not found in the nanowhiskers heated at 900 °C. The peak at 1461 cm$^{-1}$ as shown in the spectrum of the as-prepared C$_{60}$ nanowhisker shows the A$_g$ (2) peak pentagonal pinch mode which is caused by the vibration of 5-membered rings of C$_{60}$ cage [11]. The disappearance of this peak suggests that the

Figure 3. Raman spectra of as-prepared C$_{60}$ nanowhiskers, the C$_{60}$ nanowhiskers heated at 900°C and 3000 °C, and graphite.
spherical shape of C$_{60}$ was destroyed by heat treatment. The spectrum of the sample heated at 3000 °C is similar to that of glassy carbon [12-14].

Figure 4 shows low-magnification images and high-resolution images of the C$_{60}$ nanowhiskers which were heated at 2000 °C, 2500 °C and 3000 °C, respectively. By the high-temperature heat treatment, the C$_{60}$ nanowhiskers turned to glassy carbon nanowhiskers composed of randomly oriented ribbons with graphitic layers. The crystallinity of glassy carbon increases with
increasing the temperature of heat-treatment. Therefore, the structure of nanowhiskers heated at high temperature became porous. However, the carbon nanocapsules which have fine circular shape couldn’t be observed [6]. We think that a rapid increase of temperature is a factor to form the carbon nanocapsules.

Figure 5 shows a bright field TEM image of a C$_{60}$ nanotube heated at 3000 °C. The heated nanotube retained their original tubular morphology. The inner structure of the heated nanotube is similar to the above heated nanowhisker. Owing to the tubular morphology, the C$_{60}$ nanotubes must have a specific surface area higher than the C$_{60}$ nanowhiskers. The tubular structure suggests that the C$_{60}$ nanotubes heat-treated at high temperature can be utilized as a new electrode material.

Figure 6 shows the distribution of layer number and interlayer spacing of the graphitic ribbons of the C$_{60}$ nanofibers heated at each temperature. The average interlayer spacings are close to the interlayer spacing of {002} planes of graphite. The maximum number of graphitic ribbons is counted to be 17 as shown Fig. 6. With decreasing the temperature of heat-treatment, the number of layers decreases and the average interlayer spacing increase as shown in Fig. 6.

Figure 7 shows the relationship between the number of layers (x) and the average interlayer spacing (y) as shown in Fig. 6. A linear relationship expressed by y = -0.001 x + 0.39 is obtained. It is deduced that the interlayer spacing of heat-treated nanotubes with 49 layers converges to 0.3354 nm of {002} spacing of highly oriented pyrolytic graphite [15].

4. Conclusion

The above research can be summarized as follows.

(1) The C$_{60}$ nanowhiskers and nanotubes became amorphous by the heat-treatment at 900 °C.

(2) The C$_{60}$ nanowhiskers heated at temperatures higher than 2000 °C exhibited the structure of glassy carbon composed of randomly oriented graphitic ribbons with interlayer spacings close to {002} planes of graphite. The heat-treated C$_{60}$ nanowhiskers became porous owing to the crystallinity development of graphitic ribbons.

(3) A linear relationship holds between the number of layers and the average interlayer spacing of graphitic ribbons of the heat-treated C$_{60}$ nanowhiskers and nanotubes.

(4) The tubular morphology of C$_{60}$ nanotubes can be retained by the heat treatment up to 3000 °C.

Acknowledgments

The authors are grateful to Mr. Hideo Tsunakawa (The University of Tokyo) for the use of HRTEM.

References

[1] Miyazawa K, Obayashi A and Kuwabara M 2001 J. Am. Ceram. Soc. 84 3037
[2] Minato J and Miyazawa K 2006 Diam. Relat. Mater. 15 1151
[3] Miyazawa K, Kuwasaki Y, Hamamoto K, Nagata S, Obayashi A and Kuwabara M 2003 Surf. Interface Anal. 35[1] 117-120.
[4] Larsson M P, Kjelstrup-Hansen J and Lucyszyn S 2007 ECS Transactions 2 27
[5] Miyazawa K, Minato J, Zhou H, Taguchi T, Honma I and Suga T 2006 J.Eur.Ceram.Soc. 26 429-434.
[6] Asaka K, Kato R, Maezono Y, Yoshizaki R, Miyazawa K and Kizuka T 2006 Appl. Phys. Lett. 88 051914-1-051914-3.
[7] Miyazawa K, Kuwasaki Y, Obayashi A and Kuwabara M 2002 J.Mater.Res. 17 83-88
[8] Ringor C L and Miyazawa K 2008 Diam. Relat. Mater. 17 529–534
[9] Miyazawa K and Ringor C 2008 Mater. Lett. 62 410-413
[10] Martin M C, Koller D, Rosenberg A, Kendzior C and Mihaly L 1995 Phys. Rev. B 51 3210-3213
[11] Eklund P C, Zhou P, Wang K A, Dresselhaus G and Dresselhaus M S 1992 J. Phys. Chem. Solids. 53 1391
[12] Diane S, Knight and William B White 1998 J. Mater. Res. 4 385
[13] Robertson J 1986 Advances in phys. 35 317
[14] Nakamizo M, Honda H and Inagaki M 1978 Carbon 16 281
[15] Murakami M, Nishiki N, Nakamura K, Ehara J, Okada H, Kouzaki T, Watanabe K, Hoshi T and Yoshimura S 1992 Carbon 30 255-262