Crystallinity and properties of C$_{60}$ nanotubes improved by annealing and alcohol-soaking

K Naito and K Matsuishi
Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan
E-mail: kiyoto@bk.tsukuba.ac.jp

Abstract. Well-uniformed C$_{60}$ nanotubes were grown at -20 °C with irradiation of red light using C$_{60}$-saturated pyridine solution and isopropyl alcohol by a liquid-liquid interfacial precipitation method without ultrasonic pulverization. We attempted to improve their crystallinity by two post-treatments; thermal annealing and alcohol-soaking. The crystallinity of as-grown and dried C$_{60}$ nanotubes, which was poor due to the evaporation of solvent molecules from crystals in the drying process, was improved by annealing around 220 °C for 5 hours in vacuum. Dramatic improvement of crystallinity of as-grown samples was achieved by soaking into methanol and then drying in air. Raman, infrared and X-ray diffraction results suggest that the methanol-soaked samples exhibit a solvated tetragonal structure. The crystallinity improved by methanol-soaking did not degrade after removal of methanol molecules from samples by thermal annealing. Photo-polymerization of the structurally-improved C$_{60}$ nanotubes was examined to investigate an effect of crystallinity on the polymerization kinetics.

1. Introduction
Fullerene crystals composed of C$_{60}$ molecules have been synthesized [1-3]. Miyazawa et al. have synthesized single crystalline whiskers with diameters smaller than 1 µm and a length of more than 100 µm by a liquid-liquid interfacial precipitation method [4, 5]. A C$_{60}$ nanowhisker with a diameter of 470 nm is flexibly bent with a curvature radius of 38 µm [5]. Recently, fullerene nanowhiskers with hollow structures, which are called as fullerene nanotubes, have been fabricated [6, 7]. They have wall structures made of fullerene molecules. Both fullerene nanowhiskers and nanotubes have drawn attention as a quasi-one dimensional nanomaterial due to their potential application to nanotechnology.

Fullerene nanowhiskers and nanotubes crystallize to form solid solvates with solvents. Especially, solvated structures of C$_{60}$ nanotubes are not air-stable and rapidly loose solvent molecules from the crystals by evaporation. This follows a rapid change in the structure, and consequently the crystallinity of the C$_{60}$ nanotubes is degraded. Such a structural degradation affects the properties of C$_{60}$ nanotubes. Hence, the preparation of C$_{60}$ nanotubes with good quality has been desired for evaluation of their intrinsic properties.

In this study, we synthesized C$_{60}$ nanotubes by a liquid-liquid interfacial precipitation method, and attempted to improve their crystallinity by thermal annealing in vacuum and alcohol-soaking processes. We characterized samples by X-ray diffraction (XRD), Raman scattering and Infrared (FTIR) measurements, and discussed their structures. Photo-polymerization of structurally-improved C$_{60}$ nanotubes was then examined to investigate an effect of crystallinity on the polymerization kinetics.
2. Experimental

C$_{60}$ nanotubes were prepared by a liquid-liquid interfacial precipitation method using C$_{60}$-saturated pyridine solution and isopropyl alcohol (IPA). Our typical procedure was as follows. 3 mL of pyridine solution saturated with C$_{60}$ was put into a glass bottle and then 27 mL of IPA was gently added. The bottle was capped and kept at -20 °C for more than one week. To obtain suitable diffusion at the interface, the glass bottle was shaken by hand. In our procedure, the ultrasonic pulverization which was reported necessary after the formation of liquid-liquid interface [6] was not executed. Since the photo-assisted growth of C$_{60}$ nanowhiskers was reported [8], we adapted this technique to the growth of C$_{60}$ nanotubes as well using red light from a Light Emitting Diode (LED) with the center wavelength of 627 nm. We attempted to improve the crystallinity of as-grown samples by thermal annealing and alcohol-soaking. The thermal annealing was performed in vacuum (about 1×10$^{-3}$ Pa by a diffusion vacuum pump system) at temperatures between 180 and 400 °C. Our typical alcohol-soaking procedure was as follows. As-grown samples were taken out of a glass bottle and soaked immediately into alcohols using a pipette for several hours. Then, the samples were dried completely in air. We examined several alcohols with different molecular weights; methanol, ethanol and 1-propanol for our soaking experiment.

Morphological observations were performed using an ordinary optical microscope, SEM (JEOL, JSM-5510) and TEM (JEOL, JEM-2010). To evaluate residual solvent molecules in samples, infrared absorption measurements were performed for pristine C$_{60}$ nanotubes and C$_{60}$ nanotubes after soaking into various alcohols using a FTIR apparatus (VM7, JASCO). XRD profiles were obtained using an X-ray diffractometer with CuK$_{α}$ radiation. Raman scattering spectra were measured in vacuum (about 1×10$^{-4}$ Pa by a turbo molecular pump system) using JASCO TRS-600 and an Ar$^+$ laser of the wavelength of 514.5 nm to investigate the influence of solvent molecules to the molecular vibrations of C$_{60}$ as well as to elucidate the photo-induced polymerization kinetics of C$_{60}$ nanotubes.

3. Results and discussion

3.1. Sample preparation

When C$_{60}$ nanotubes were sufficiently grown, bundles of nanotubes with several millimeters in length were easily recognized by eye as shown in figure 1(a). An optical micrograph of the sample in air is shown in figure 1(b). Figures 2(a) and 2(b) show a TEM image and a SEM image, respectively, of the C$_{60}$ nanotubes. The outer diameter is about 600 nm in figure 2(a) and about 3 µm in figure 2(b). Our observations revealed that the bundles consisted of nanotubes of about several hundred nanometers in outer diameter on average. We found that C$_{60}$ nanotubes could be synthesized without ultrasonic pulverization, although it had been thought necessary after the formation of liquid-liquid interface.

By the photo-assisted growth using the LED light (wavelength: 627 nm), C$_{60}$ nanotubes grew up to more than 20 mm in length. The observation suggests that the growth rate of C$_{60}$ nanotubes can be promoted by the red light illumination, as observed previously for C$_{60}$ nanowhiskers [8]. There was a size distribution in the outer diameter from about 250 nm to about 1500 nm. The average outer diameter was about 700 nm. The size distribution tends to become narrower with a lower growth temperature.

![Figure 1](image)
3.2. Improvement of crystallinity by annealing in vacuum and alcohol-soaking

Crystalline fullerene solids precipitated from solutions sometimes show morphologies different from the ordinary face-centered cubic (fcc) packing of fullerene molecules [9]. Fullerene molecules should be solvated when they are in solution. For fullerene nanotubes, they are known to crystallize in the solvated structure of hexagonal symmetry with cell dimensions $a = 1.541$ nm and $c = 1.00$ nm and to change into a fcc structure by the evaporation of solvent molecules after drying in air [10]. As a result, the crystallinity of as-grown and dried $C_{60}$ nanotubes is poor. Our as-grown samples exhibited a solvated hexagonal structure with $a = 1.540$ nm and $c = 0.99$ nm right after taking into air from the growth environment.

**Figure 2.** (a) TEM image, and (b) SEM image of the $C_{60}$ nanotubes grown at -20 °C under illumination of red light from a LED (wavelength: 627 nm).

**Figure 3.** Annealing temperature dependence of XRD profiles of $C_{60}$ nanotubes. Annealing was carried out in vacuum for 5 hours at the temperature indicated. The uppermost profile is for an as-grown sample just after drying in air.

**Figure 4.** XRD profiles of $C_{60}$ nanotubes soaked into alcohols and then dried in air. The uppermost profile is for the sample soaked into methanol and then annealed at 260 °C for 5 hours.
s
olution, and changed in 10 min in air to a poor crystalline structure as realized in the uppermost XRD profile in figure 3. FTIR spectra after dried in air showed very small peaks of intramolecular vibrational modes of pyridine (at 704 cm$^{-1}$) and IPA (at 954 and 1110 cm$^{-1}$) besides four intense peaks of C$_{60}$ molecules (at 527, 576, 1182 and 1428 cm$^{-1}$). This suggests the presence of a small amount of pyridine and IPA molecules in the as-grown/dried samples.

To improve the crystallinity of C$_{60}$ nanotubes, we performed thermal annealing in vacuum at temperatures between 180 and 400 °C at intervals of 20 °C. Figure 3 shows XRD profiles for the C$_{60}$ nanotubes annealed in vacuum at 180, 220, 300 and 400 °C together with that of the as-grown/dried sample. It is found that annealing around 220 °C in vacuum made the diffraction peaks the sharpest, resulting from structural relaxation and removal of residual solvent molecules from samples. The samples annealed in vacuum seem to exhibit the same structure as pristine C$_{60}$ powder (i.e., an fcc structure). However, the peaks that cannot be indexed by the fcc structure were observed as indicated by arrows in figure 3. The observation suggests the lowering of the symmetry of the fcc structure. We indexed the diffraction peaks by a tetragonal structure and obtained the lattice constants, $a = 0.995$ nm and $c = 1.437$ nm.

Figure 4 shows the XRD profiles for the C$_{60}$ nanotubes after alcohol-soaking followed by drying in air. Using methanol of the smallest molecular weight, the diffraction peaks became the sharpest among these alcohols. They can be indexed by a tetragonal structure, $a = 1.001$ nm and $c = 1.446$ nm. It should be noticed that by the methanol-soaking the diffraction peaks became sharper than those of the samples annealed at 220 °C shown in figure 3. Figure 5 shows the FTIR spectra of the C$_{60}$ nanotubes with the alcohol-soaking treatments. For the methanol-soaked sample, the absorption peak which originated from a vibrational mode of methanol was observed as indicated by an arrow in figure 5. Besides, very weak vibrational modes of pyridine and IPA are seen after the alcohol-soaking. This suggests that the solvents are removed from the solvated hexagonal structure of as-grown sample and methanol molecules diffuse into the C$_{60}$ lattice to form a solvated (C$_{60}$-methanol) tetragonal structure. We examined the soaking time dependence of Raman spectra for methanol-soaked samples. Figure 6 shows a change in the A$_g$ (2) pentagonal pinch mode of C$_{60}$ with increasing the soaking time. The A$_g$ (2) pentagonal pinch mode shifted to lower frequencies from 1467.9 to 1465.7 cm$^{-1}$ due to interaction between C$_{60}$ and methanol molecules, as the soaking time increased from 0.5 to 4 hours. Simultaneously, the XRD peaks became shaper as the soaking proceeded. These XRD, FTIR and

Figure 5. FTIR spectra of the C$_{60}$ nanotubes soaked into alcohols and then dried in air. The uppermost spectrum is for the sample soaked into methanol and then annealed at 260 °C for 5 hours.

Figure 6. Soaking time dependence of Raman spectra of the C$_{60}$ nanotubes with methanol-soaking treatments. Experiment was carried out at 77 K in vacuum to prevent samples from heating which may induce graphitization.
Raman results indicate that since the C₆₀ nanotubes are solvated with methanol to form a stable tetragonal structure, methanol molecules remain in the C₆₀ lattice stably in air at room temperature after methanol-soaking.

Our significant finding is that the improved crystallinity by methanol-soaking did not degrade after removal of methanol molecules from samples by annealing as seen in figure 4. The absorption peak from methanol disappeared after annealing at 260 °C for 5h, as shown in the uppermost spectrum in figure 5, indicating that the methanol molecules were certainly removed from the C₆₀ nanotubes. We found that the lattice constants were slightly changed to \( a = 0.998 \) nm and \( c = 1.442 \) nm after the annealing on the methanol-soaked sample.

3.3. Photo-induced transformation

We measured the Raman scattering spectra of C₆₀ nanotubes under laser irradiation of the 514.5 nm line from an Ar⁺ laser to investigate an effect of crystallinity on the photo-polymerization of C₆₀ nanotubes.

Figure 7 shows the relative intensity of the \( A₅(2) \) pentagonal pinch mode to the polymer mode which appears around 1461 cm⁻¹ due to polymerization of C₆₀ molecules as a function of laser irradiation time for methanol-soaked and non-soaked samples. Both samples were annealed at 260 °C for 5 hours in vacuum before laser irradiation. The time constants for the photo-polymerization of the C₆₀ nanotubes with and without soaking are 6.6 and 10 min, respectively. This indicates that the C₆₀ nanotubes soaked into methanol are easier to polymerize than non-soaked samples. We infer that the improvement of crystallinity in C₆₀ nanotubes promotes photo-polymerization, since the structurally-improved C₆₀ nanotubes by methanol-soaking followed by annealing has better crystallinity than the annealed C₆₀ nanotubes without alcohol-soaking as mentioned above from the XRD results.

4. Conclusion

We synthesized C₆₀ nanotubes using C₆₀-saturated pyridine solution and isopropyl alcohol by a liquid-liquid interfacial precipitation method. Well-uniformed C₆₀ nanotubes were grown successfully at -20 °C without ultrasonic pulverization. Using a photo-assisted growth technique with LED light of wavelength 627 nm, C₆₀ nanotubes grew up to more than 20 mm in length. We succeeded to improve their crystallinity by two post-treatments; thermal annealing and alcohol-soaking. The C₆₀ nanotubes annealed at 220 °C for 5 hours in vacuum made diffraction peaks the sharpest among the samples annealed at temperatures between 180 and 400 °C. This improvement is due to structural relaxation and removal of residual solvent molecules from samples. Dramatic improvement of crystallinity of as-grown samples was also achieved by methanol-soaking and then drying in air. Raman, infrared and X-
Ray diffraction results suggest that the methanol-soaked samples exhibit a solvated tetragonal structure. A significant finding is that the improved crystallinity by methanol-soaking did not degrade after removal of methanol molecules from samples by annealing. We examined the photo-polymerization of the structurally-improved C$_{60}$ nanotubes, and found that the C$_{60}$ nanotubes soaked into methanol were easier to polymerize than non-soaked samples.

Acknowledgments
We are grateful to K Nakama and T Yoshii at the Nippon Steel Glass Co., Ltd. for many useful discussions.

References
[1] Meng R L, Ramirez D, Jiang X, Chow P C, Diaz C, Matsuishi K, Moss S C, Hor P H and Chu C W 1991 Appl. Phys. Lett. 59 3402
[2] Yosida Y 1992 Japan. J. Appl. Phys. 31 L505
[3] Liu J Z, Dykes J W, Lan M D, Klavins P, Shelton R and Olmstead M M 1993 Appl. Phys. Lett. 62 531
[4] Miyazawa K, Obayashi and Kuwabara M 2001 J. Am. Ceram. Soc. 84 3037
[5] Miyazawa K, Kuwasaki Y, Hamamoto K, Nagata S, Obayashi A and Kuwabara M 2003 Surf. Interface Anal. 35 117
[6] Minato J, Miyazawa K and Suga T 2005 Science and Technology of Advanced Materials 6 272
[7] Miyazawa K, Minato J, Yoshii T, Fujino M and Suga T 2005 J. Mater. Res. 20 688
[8] Kobayashi K, Tachibana M and Kojima K 2005 J. Cryst. Growth 274 617
[9] Fleming R M, Kortan A R, Hessen B, Siegrist T, Thiel F A, Marsh P, Haddon R C, Tycko R, Dabbagh G, Kaplan M L and Mujsce A M 1991 Phys. Rev. B 44 888
[10] Minato J and Miyazawa K 2006 Diamond & Related Materials 15 1151