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Liquid phase synthesis of the nanowhiskers of fullerene derivatives

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Abstract : Needle-like crystals and fine whiskers of $C_{60}[C(COOC_2H_5)_2]$ were successfully fabricated by the liquid-liquid interfacial precipitation method (LLIP method) that uses the phenomenon of crystal nucleation at the interface formed between two liquid phases. The center-to-center distance D between two adjoining C_{60} cages of $C_{60}[C(COOC_2H_5)_2]$ molecules was close to that of the C_{60} nanowhiskers, indicating that the C_{60} cages are linked along the close-packed direction without having the malonic groups between them. The nanowhiskers of C_{60} with dissolved C_{60} derivatives have been also successfully fabricated by using the toluene solutions of C_{60}-9mass% $C_{60}C_3H_7N$ and C_{60}-5mass%$C_{60}[C(COOC_2H_5)_2]$. It has been proved that the LLIP method is a very promissing method for preparing the C_{60} nanowhiskers with mixed fullerene derivatives.
Key words : Nanowhiskers, C60, fullerene, fullerene derivatives

1. INTRODUCTION

The "C_{60} nanowhiskers" were discovered in 2001 in a colloidal solution of lead zirconate titanate (PZT) with added a small amount of C_{60}.[1,2] This experiment were done in order to lower the firing temperature of PZT thin films by adding C_{60}.[3] The nanowhiskers of C_{60} and C_{70} with submicrometer diameters can be easily fabricated by using the liquid-liquid interfacial precipitation method (LLIP method).[4] The C_{60} and C_{70} nanowhiskers can grow into long whiskers with a very high aspect ratio that can be called "fullerene nanofibers".

One of the most important advantages of fullerene molecules is that they can be modified by a variety of functional groups like hydroxyl, amino, alkyl, phenyl, cyano, epoxy groups and so on.[5] C_{60} has been known to work as an efficient source of active singlet oxygen $^1O_2$, and is expected to exhibit a bioactivity which is applicable to various pharmaceuticals.[6] Although C_{60} is a promising bioactive material, it is necessary for C_{60} to be water-soluble in order to exhibit its bioactivity in water.[7] It is expected that the C_{60} nanowhiskers with functional groups form a very big group of new fullerene derivatives which could be used as useful bioactive agents and also as catalysts when their surface is modified by suitable metals and oxides.

This paper gives the first trial to prepare the nanowhiskers composed of fullerene derivatives. For this purpose, $C_{60}[C(COOC_2H_5)_2]$ (C_{60}-malonate ester mono-adduct) was used.

Furthermore, it is expected that the LLIP method is applicable to preparing C_{60} nanowhiskers with dissolved fullerene derivative molecules by using a C_{60} solution with mixed fullerene derivative molecules. This paper shows the morphology and microstructure of the C_{60} whiskers with dissolved $C_{60}[C(COOC_2H_5)_2]$ or $C_{60}C_3H_7N$ molecules.

2. EXPERIMENTALS

Firstly, a concentrated toluene solution of $C_{60}[C(COOC_2H_5)_2]$ was prepared. 3mL of this solution was poured into a transparent 10mL-glass bottle, and isopropyl alcohol (IPA) was gently added to the toluene solution to form a liquid-liquid interface between the toluene solution and IPA. The bottle was capped and kept still for seven days at room temperature.

Similarly, the C_{60} nanowhiskers with dissolved fullerene derivatives were also prepared by using the concentrated toluene solutions of C_{60}-5mass% $C_{60}[C(COOC_2H_5)_2]$ and C_{60}-9mass% $C_{60}C_3H_7N$ (C_{60}-*N*-methylpyrrolidine). The composition of the C_{60} whiskers with dissolved fullerene derivatives were analyzed by HPLC(high-pressure liquid chromatography).

The microstructure of the fine precipitates formed in the bottle were put on a micro grid and observed by a high-resolution transmission electron microscope (HRTEM, JEM-4010, 400kV).

3. RESULTS AND DISCUSSION

3.1 Surface morphology and microstructure of the needle-like crystals and (nano)whiskers of $C_{60}[C(COOC_2H_5)_2]$

As compared with the nanowhisker synthesis of C_{60} and C_{70},[4] the nanowhiskers of $C_{60}[C(COOC_2H_5)_2]$ were more difficult to form. Three kinds of precipitates were mostly observed. Fig.1, Fig.2 and Fig.3 show lens-shaped precipitates, a needle-like crystal with diameters of about 5 μm and a huge needle-like crystal, respectively. Most of the precipitates formed in the glass bottle had the lens-shaped morphology.

The magnified surface image (Fig.4) shows that the needle-like crystal of Fig.3 has a layered structure. This

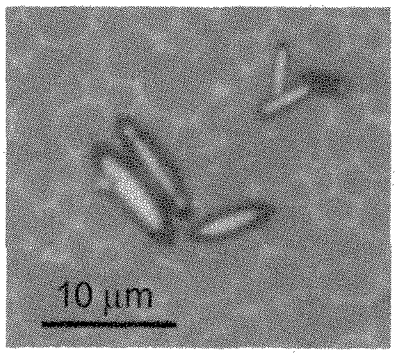

Fig.1 Optical micrograph of the lense-shaped precipitates of $C_{60}[C(COOC_2H_5)_2]$ formed in the solution.

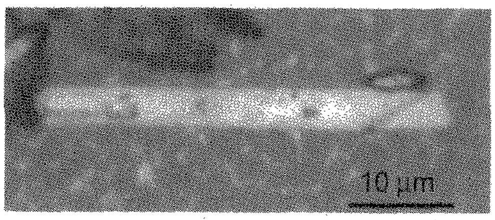

Fig.2 Optical micrograph of a needle-like crystal of $C_{60}[C(COOC_2H_5)_2]$.

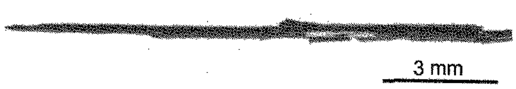

Fig.3 Optical micrograph of a huge needle-like crystal of $C_{60}[C(COOC_2H_5)_2]$.

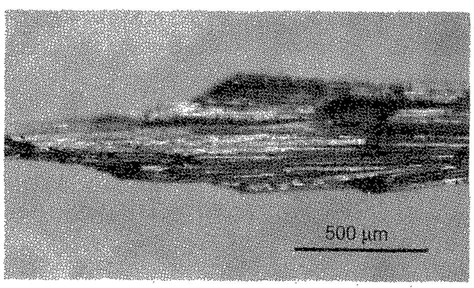

Fig.4 Magnified optical micrograph of a needle-like crystal of $C_{60}[C(COOC_2H_5)_2]$.

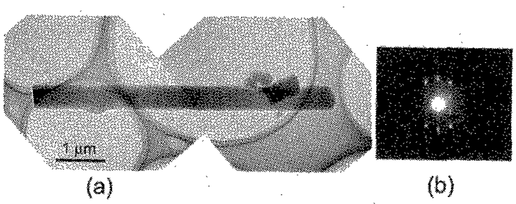

Fig.5 (a) TEM image of a nanowhisker of $C_{60}[C(COOC_2H_5)_2]$ and (b)its electron diffraction pattern showing the single crystallinity of the whisker.

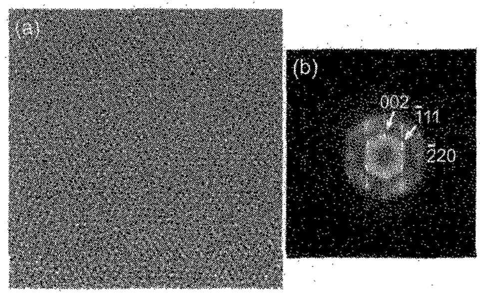

Fig.6 (a)HRTEM image and (b)its FFT pattern for the $C_{60}[C(COOC_2H_5)_2]$ nanowhisker of Fig.5.

Table 1 The d-spacings calculated from the FFT pattern of Fig.6 (b).

(hkl)	d(nm)	pristine C_{60} [8]
$(\bar{1}11)$	0.842	0.818
(002)	0.888	0.709
$(\bar{2}20)$	0.481	0.501

Table 1 shows the lattice plane spacings calculated from the FFT pattern of Fig.5, assuming a fcc structure. The $(\bar{1}11)$ and (002) plane spacings are expanded than those of pristine C_{60}, but the spacing of $(\bar{2}20)$ planes that are perpendicular to the growth axis is shrinked about 4% from that of pristine C_{60}. This shrinkage of the $(\bar{2}20)$ plane spacing means that the center-to-center distance (D) between two adjoining C_{60} cages is smaller than that of pristine C_{60}. This result suggests that the C_{60} cages in the $C_{60}[C(COOC_2H_5)_2]$ nanowhisker are linked along the whisker growth axis without having the malonic functional groups between the adjoining C_{60} cages.

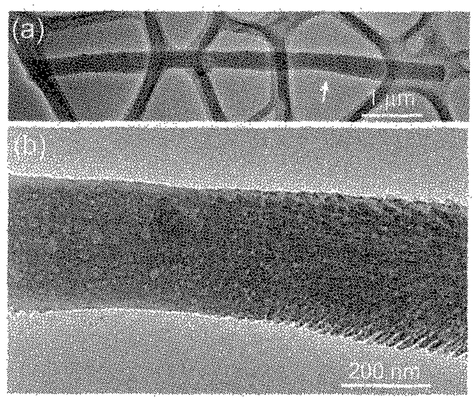

Fig.7 (a)TEM image of a nanowhisker of $C_{60}[C(COOC_2H_5)_2]$ and (b) magnified image of the arrowed part.

layered structure is characteristic to the C_{60} nanowhiskers that are composed of thin layers with a thickness of about 10 nm.[4]
A nanowhisker of $C_{60}[C(COOC_2H_5)_2]$ is shown as Fig.5, and Fig.6 shows its HRTEM image.

Although the nanowhisker of Fig.5 became amorphous during observation by TEM, a smooth surface was retained. However, a deposition of organic substances on the whisker surface was observed as shown in Fig.7 (a), when the whisker was irradiated by a concentrated electron beam. It is considered that the whisker was heated by the beam and that the constituent loosely bonded $C_{60}[C(COOC_2H_5)_2]$ molecules were evaporated and deposited on the whisker surface, and then, the whisker became porous (Fig.7 (b)).

3.2 Microstructure of the C_{60} nanowhiskers with dissolved $C_{60}[C(COOC_2H_5)_2]$ and $C_{60}C_3H_7N$

Very fine long nanowhiskers of C_{60}-5.1mass% $C_{60}[C(COOC_2H_5)_2]$ were obtained as shown in Fig.8.

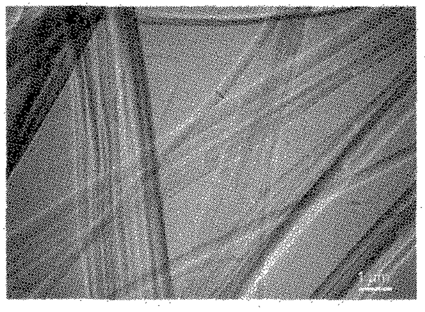

Fig.8 TEM image of C_{60}-5.1mass% $C_{60}[C(COOC_2H_5)_2]$ nanowhiskers.

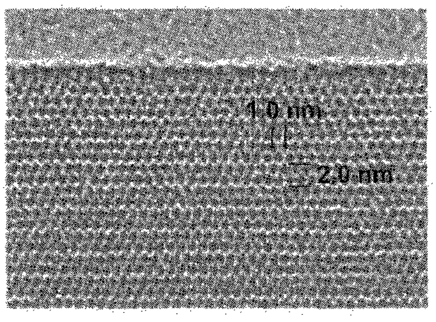

Fig.9 HRTEM image of a C_{60}-5.1mass% $C_{60}[C(COOC_2H_5)_2]$ nanowhisker.

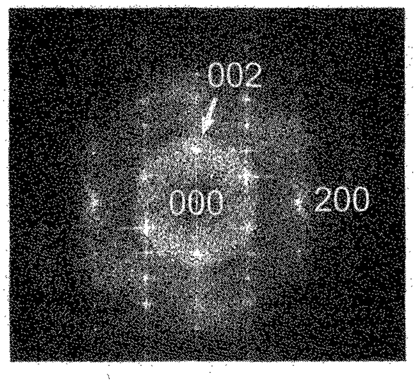

Fig.10 FFT pattern for the HRTEM image of Fig.8.

The single crystallinity of the nanowhiskers can be confirmed by the bending contours continuously running across the whisker growth axis. The whisker has a very smooth surface and a high crystallinity.

The FFT pattern of Fig.10 prepared by using the HRTEM image of Fig.9 can be best fitted by assuming a body-centered tetragonal (bct) lattice with a=1.00nm and c=2.03 nm. These lattice constants are accidentally close to those of the iodine-doped C_{60} nanowhiskers that showed a=1.01 nm and c=2.10 nm.[9] It is conjectured that the bct structure with the lattice constants of a=~1.0nm and c=~2.0 nm is a stable form of C_{60} nanowhiskers.

Single crystalline C_{60} nanowhiskers with dissolved $C_{60}C_3H_7N$ molecules were also successfully produced by the LLIP method as shown in Fig.11.

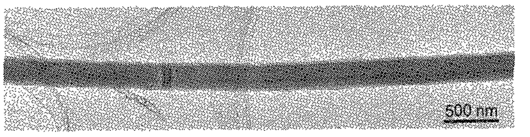

Fig.11 TEM image of a nanowhiskers of C_{60}-12.3mass% $C_{60}C_3H_7N$.

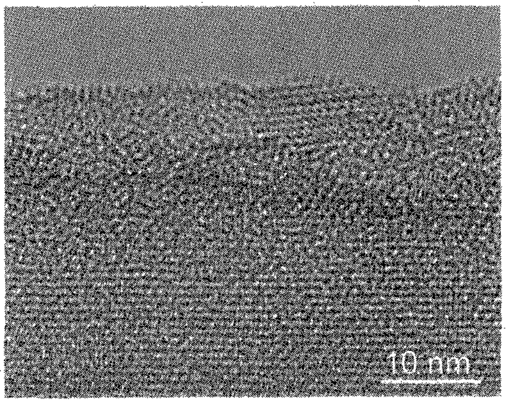

Fig.12 HRTEM image of a C_{60}-12.3mass% $C_{60}C_3H_7N$ nanowhisker.

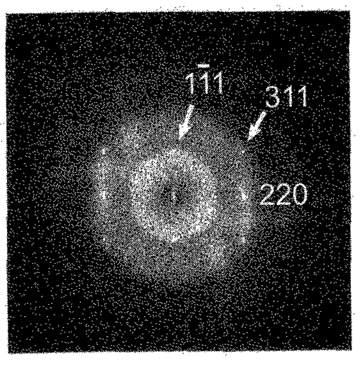

Fig.13 FFT pattern for the HRTEM image of Fig.12.

A HRTEM image of Fig.12 shows that the surface of the whisker with a thickness of ~10 nm is disordered, which is different from the case of the C_{60}-5.1mass% $C_{60}[C(COOC_2H_5)_2]$ nanowhiskers with the smooth surface.

The lattice plane spacings for the nanowhisker were analyzed by using the FFT pattern of Fig.13 and tabulated as Table 2. The FFT pattern can be indexed with a cubic system with the lattice constant a=1.38 nm. This lattice constant is 2.6 % smaller than that of pristine C_{60} crystals. This small lattice constant suggests that solidification of $C_{60}C_3H_7N$ molecules into the inner side of the whisker was not easy and that they were segregated on the whisker surface.

These result gives us an useful information for controlling the surface structure of the C_{60} nanowhiskers by using suitable C_{60} derivatives.

Table 2 Lattice-plane spacings (d.nm) obtained from the FFT pattern of Fig.13.

(h k l)	Fig.12	pristine C_{60}
$(1\bar{1}1)$	0.795	0.818
(220)	0.488	0.501
(311)	0.418	0.427

4. CONCLUSIONS

(1) The nanowhiskers of $C_{60}[C(COOC_2H_5)_2]$ were prepared by using the concentrated toluene solution of $C_{60}[C(COOC_2H_5)_2]$ and isopropyl alcohol. Huge needle-like crystals of $C_{60}[C(COOC_2H_5)_2]$ with a layered structure were also formed.
(2) The intercluster distance between the $C_{60}[C(COOC_2H_5)_2]$ molecules along the whisker growth axis was close to that of C_{60} nanowhiskers.
(3) The C_{60} nanowhiskers containing fullerene derivative molecules were successfully fabricated by the liquid-liquid interfacial precipitation method.

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