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Solvated structure of C_{60} nanowhiskers

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Abstract

This work characterizes the structure of C_{60} nanowhiskers prepared by the liquid–liquid interfacial precipitation method in the C_{60}-saturated *m*-xylene and isopropyl alcohol system. Transmission electron microscopy and X-ray diffraction measurement show that the C_{60} nanowhiskers had a hexagonal structure with cell dimensions $a = 2.407$ nm and $c = 1.018$ nm which is different from pristine C_{60}. The structure of the C_{60} nanowhiskers in solution is different from that of the solvated structure reported for the C_{60} nanotubes but similar to that reported for the C_{60} bulk crystal solvated with *m*-xylene. X-ray diffraction analysis also showed a shift to fcc structure after solvent evaporation. The C_{60} nanowhiskers prepared using toluene as solvent also showed a similar solvated structure, and a more rapid structural change into fcc upon drying was again observed.

Keywords: Carbon nanofibers; Fullerene; Infrared spectroscopy; Transmission electron microscopy; X-ray diffraction

1. Introduction

Crystalline fullerene solids precipitated from solutions sometimes show unexpected morphologies different from the ordinary face-centered cubic (fcc) packing of fullerene molecules [1,2], which may be attributed to the presence of solvent molecules between fullerene molecules. When isopropyl alcohol (IPA), which is known as a poor solvent of fullerenes, was gently added to a toluene solution saturated with C_{60}, needlelike or fibrous crystals were precipitated at the interface between the solutions [3]. Since their diameter was in the submicron range, they have been referred to as C_{60} nanowhiskers and the preparation method have been referred to as liquid–liquid interfacial precipitation (LLIP) method. To date, the LLIP method has been successfully used to fabricate fullerene nanowhiskers from C_{60} [3], C_{70} [4,5] and C_{60} derivatives [6,7]. The structure of the fullerene nanowhiskers have been understood based on the fcc structure. The whisker axis (growth axis) is parallel to one of the closest-packed directions of C_{60} molecules, i.e. $\langle 1\,1\,0 \rangle$ in the fcc structure. Since the intermolecular distance was observed to be shortened along this direction, a model was proposed where the '2 + 2' cycloaddition was assumed [3].

Most of the previous characterizations of the fullerene nanowhiskers were carried out on dried specimens [3–10] . However, fullerene molecules should be solvated when they are in true solution. It is known that many kinds of solvent form the structures of solid solvates with fullerenes [11–13] including toluene and *m*-xylene which are used in the LLIP method [9]. In addition, some of those solvated structures, depending on the kinds of solvent, have been shown to change into the fcc structure by the evaporation of solvent molecules in air [12,13]. It is thus expected that the fullerene nanowhiskers also have solvated structures when they are first precipitated from the liquid phase. However, few studies have examined the structure changes during drying of fullerene nanowhiskers from the LLIP method. In the present study, the C_{60} nanowhiskers were prepared by the LLIP method using *m*-xylene and toluene as

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solvents. Characterizations by Fourier-transform infrared (FTIR) spectroscopy, transmission electron microscope (TEM) observation, and X-ray diffraction (XRD) measurement confirmed the solvated structure and the structural change in air for both of the specimens. The results were compared with the previous observations.

2. Experimental

The C_{60} nanowhiskers were prepared by the liquid–liquid interfacial precipitation method using *m*-xylene (or toluene) as solvent [9]. A typical procedure is as follows. Five milliliters of *m*-xylene (or toluene) solution saturated with C_{60} was put into a glass bottle and then 5 mL of IPA was gently added. The bottles were capped and kept at a temperature lower than 21 °C for more than one month before the characterization.

Morphological observations were performed using an ordinary optical microscope and a TEM (JEOL, JEM-2000EX). The specimens in the glass bottles were mounted on slide glasses or onto copper microgrids with carbon film using a pipette. Infrared spectroscopy was performed for the C_{60} nanowhiskers and the pristine C_{60} powder with KBr using a FTIR apparatus (Valor III, JASCO, Tokyo, Japan). XRD spectra were obtained using an X-ray diffractometer (RIGAKU, RINT2000 Tokyo, Japan) with CuKα radiation.

3. Results and discussion

Fig. 1 shows an optical micrograph of the solid precipitates obtained by the liquid–liquid interfacial precipitation method in the C_{60}-saturated *m*-xylene and IPA system. As shown in the image the precipitates were submicron in diameter and reached several tens of micrometers in length, i.e. nanowhiskers.

Fig. 2(a)–(c) shows FTIR spectra taken for the pristine C_{60} powder, the nanowhiskers grown in the C_{60}-saturated *m*-xylene and IPA system, and *m*-xylene, respectively. The spectra of Fig. 2(a) and (b) showed sharp absorption peaks characteristic of C_{60} (527, 576, 1182, and 1428 cm^{-1}), indicating that the specimens were composed of C_{60} molecules. However, the broad bands at 690 and 767 cm^{-1} indicated by circles in the spectrum of Fig. 2(b) suggest the presence of *m*-xylene molecules (Fig. 2(c)) trapped in the structure.

Fig. 3 shows a TEM image of a typical C_{60} nanowhisker grown in the C_{60}-saturated *m*-xylene and IPA system. Under TEM the C_{60} nanowhiskers were loosely curved by the contact with the carbon film support, indicating a similar flexibility as reported for the C_{60} nanowhiskers prepared using toluene as solvent [5]. However, the selected area electron diffraction patterns (SAEDPs) usually showed no coincidence with the fcc-based structure. Fig. 4(a) is an example of SAEDPs taken for the enclosed part of Fig. 3. The pattern resembles to that reported for the iodine-doped C_{60} whiskers [10] rather than to those for the C_{60} nanowhiskers [3] or the C_{60} nanotubes [14]. The SAEDPs taken with rotations around the growth axis consistently indicated that the lattice planes with a *d*-spacing close to 1 nm exist normal

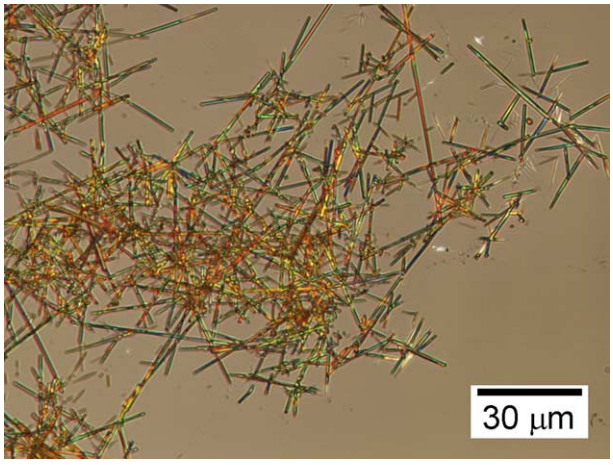

Fig. 1. Optical photomicrograph of C_{60} nanowhiskers prepared by the liquid–liquid interfacial precipitation method in the C_{60}-saturated *m*-xylene and isopropyl alcohol system.

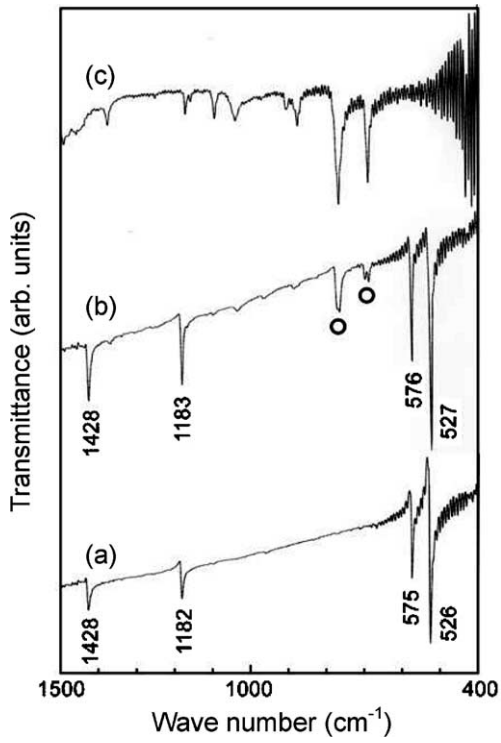

Fig. 2. FTIR spectra for (a) pristine C_{60}, (b) C_{60} nanowhiskers grown in the C_{60}-saturated *m*-xylene and isopropyl alcohol system, and (c) *m*-xylene.