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Morphology of C_{60} nanotubes fabricated by the liquid–liquid interfacial precipitation method

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Abstract

Single crystalline C_{60} fullerene nanowhiskers are formed by adding isopropyl alcohol gently to fullerene saturated solutions. The method is called the liquid–liquid interfacial precipitation method. In the present study, observation using transmission electron microscope was made for C_{60} nanowhiskers with hollow structure, i.e. C_{60} fullerene nanotubes fabricated by the modification of liquid–liquid interfacial precipitation method using pyridine as solvent. After adding isopropyl alcohol to the C_{60} solution in the glass bottles, ultrasonic dispersion was applied for 1 min and then the bottles were kept at 10 °C. Within 24 h, fibrous solids with the length larger than several millimeters and the diameters ranging from submicrons to 1 μm were precipitated. For the transmission electron microscope study, the samples were pulverized by the ultrasonic dispersion. Under the transmission electron microscope, tubular morphology was usually observed for the whiskers with the diameters larger than 200 nm and hardly observed for those with the diameters smaller than 200 nm; both the C_{60} fullerene nanotubes and the fullerene C_{60} nanowhiskers were in crystalline state. Since partly tubular structures were sometimes observed at the end of the C_{60} fullerene nanowhiskers, the mechanism for the formation of tubular morphology is suggested to be a dissolution process after the crystal growth. When the samples were kept in the glass bottles for several hours after the pulverization, closing of nanotubes at the ends was observed for relatively smaller nanotubes in diameter. For relatively larger nanotubes in diameter, zigzag thinning of tube wall edges was observed. It is thus expected that subsequent growth or dissolution occurred at the end of the pulverized C_{60} nanotubes, which may be an effective way to control the shape of tubes. The C_{60} nanotubes presented here will be useful as adsorbents, catalysts, and membranes.

Keywords: Fullerene; C_{60}; Nanowhisker; Nanotube; Liquid–liquid interfacial precipitation method; Transmission electron microscopy

1. Introduction

Since the discovery of the method to manufacture bulk fullerenes in macroscopic quantities, many crystallographic studies have been made [1]. Fullerenes are soluble in many solvents such as benzene, hexane, and CS_2, and crystallize to form solid solvates with these solvents. Some of these solvated structures are not air stable and rapidly loose solvent by evaporation [2]. Some other solvated crystals, on the other hand, are shown to be stable in air for 9 years at room temperature in the dark [3]. Depending on their structure, variety of morphologies is obtained for these solid solvates; they are sometimes large and well-defined polyhedral ones and are quite different from those expected for the pure solid C_{60} of the face-centered cubic structure [1,2].

Fullerene nanowhiskers are fibrous fullerene single crystals with diameters as small as submicrons [4]. The fabrication method of the fullerene nanowhiskers is quite simple and unique. They are precipitated at the liquid–liquid interface of fullerene-dissolved solution and isopropyl alcohol (liquid–liquid interfacial precipitation method [5]). By the liquid–liquid interfacial precipitation method, various fullerene nanowhiskers have been successfully fabricated such as C_{70} nanowhiskers [6], iodine-doped C_{60} nanowhiskers [7], and nanowhiskers of fullerene derivatives [8,9]. The structure of fullerene nanowhiskers is based on the face-centered cubic packing of fullerene molecules as well as the pristine C_{60} crystals. The growth axis of the fullerene nanowhiskers is parallel to $[\bar{1}10]$,

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i.e. a close-packed direction of face-centered cubic packing of fullerene molecules, with the slightly shorter intermolecular distance by a few %. This has been explained in relation with the van der Waals polymerization of fullerene molecules along the direction [10].

Recently, fullerene nanowhiskers with hollow structures, which may be called as fullerene nanotubes, have been found [10,11]. They have wall structures made of fullerene molecules. With the modification to the liquid–liquid interfacial precipitation method, the hollow fullerene nanowhiskers have been successfully fabricated either by mixing $(\eta^2\text{-}C_{60})Pt(PPh_3)_2$ with the C_{60} [12], or by using pyridine solution of C_{70} fullerenes [11]. However, the latter method was not directly applicable to the formation of pure C_{60} fullerene nanotubes because the precipitation of fibrous material hardly took place. The another way to obtain tubular structure was the careful sublimation of fullerene molecules by heating after the crystal growth of C_{60} fullerene nanowhiskers; however, heating process sometimes destroyed fullerene molecules leaving the shell of amorphous carbon [13]. When the application of the fullerene nanotubes is taken into account, it is desired to predict the property change of fullerene nanotubes with their composition of fullerene species. For this purpose, an establishment of the way to fabricate pure C_{60} fullerene nanotubes is needed.

In this paper, we propose a reproducible fabrication method of purer C_{60} fullerene nanotubes by the modification of liquid–liquid interfacial precipitation method. Since the diffusion state at the liquid–liquid interface seemed to affect the growth and the quality of products, controlled mixing was applied ultrasonically. Attempts to control the morphology of C_{60} fullerene nanotubes were also reported. Characterization by X-ray diffraction (XRD) and transmission electron microscopy showed that fullerene nanotubes were grown as solvated structure with hexagonal symmetry followed by the phase transformation into face-centered cubic structure due to the evaporation of solvent molecules. Unlike the other carbon substances, fullerene nanotubes are re-dissolved in proper solvents, and maybe useful not only as adsorbents and catalysts but also as templates for the various forms of materials such as fibers and membranes.

2. Experimental

As received, pristine C_{60} powder (MTR Ltd. 99.5%) was dissolved in pyridine. Twenty seven milliliters of isopropyl alcohol was added to each 3 mL of pyridine solution of C_{60} in the glass bottles; all solutions and bottles were kept at about 10 °C during the experiments. To obtain suitable diffusion at the interface, insertion of ultrasonic dispersion for 1 min was made after the addition of isopropyl alcohol.

Morphological observations were performed using an ordinary optical microscope and a transmission electron microscope (TEM; JEOL, JEM-2000EX). The specimens in the glass bottles were mounted either on the slide glass or onto the microgrids after the ultrasonic pulverization for 1 min. XRD spectra were obtained using an X-ray diffractometer (RIGAKU, RINT2000) with Cu Kα radiation. For the measurement, the specimens were directly mounted on a glass sample holder immediately after the sampling from the glass bottles to monitor the structural changes during the drying process.

3. Results

Although the precipitation of the fibrous material occurs within a day, completion of the growth seems to require several weeks. When the C_{60} nanowhiskers were sufficiently grown, the bundles of them were easily recognized by eye (Fig. 1(a)). Optical microscopy revealed the bundles consisted of fibers of about 1 μm in diameter and several millimeters in length (Fig. 1(b)). Dissolution in toluene, *m*-xylene, or pyridine that are known as good solvents of fullerenes well demonstrated that the specimens are really

(a)

(b)

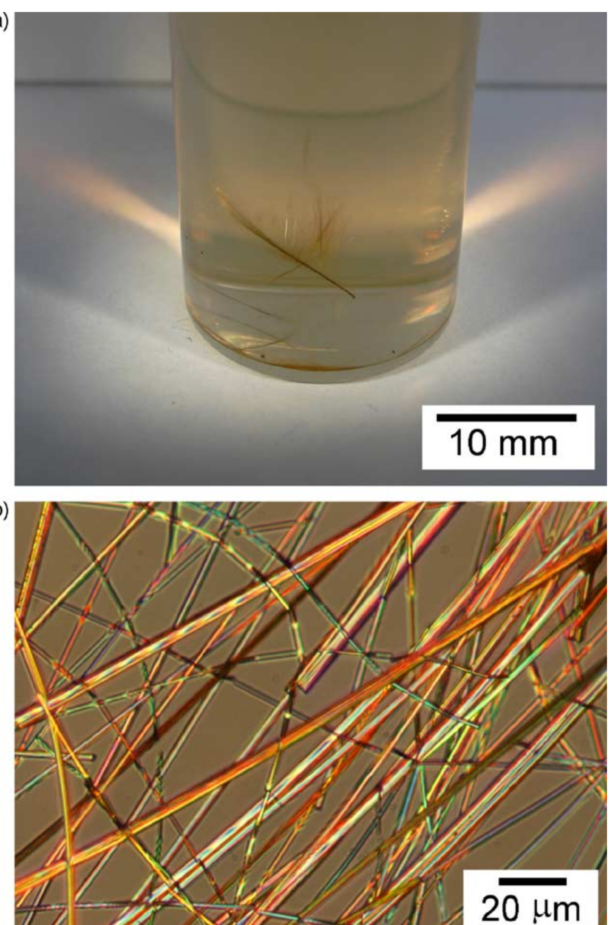

Fig. 1. (a) Photograph of C_{60} nanotubes grown by forming liquid–liquid interface between pyridine saturated with C_{60} and isopropyl alcohol and (b) optical photomicrograph of C_{60} nanotubes.