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Ultrasonic pulverization of fullerene nanofibers

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The liquid-liquid interfacial precipitation method can produce C_{60} nanotubes with a length of the order of millimeters. The C_{60} nanotubes dried in air showed a Raman profile close to that of pristine C_{60}. The C_{60} nanotubes are expected to be very useful to include various catalytic materials inside. The ultrasonic pulverization of the C_{60} nanotubes was examined in order to prepare short C_{60} nanotubes with open ends which make it easy to incorporate chemical substances. It was found that the ultrasonication of a few minutes is enough to prepare short C_{60} nanotubes with open ends.

Key words: fullerene nanowhisker, fullerene nanotube, nanofiber, C_{60}, ultrasonication

1. INTRODUCTION

Recently we showed that C_{60} nanotubes (C_{60}NTs) with porous wall were formed by a process of self assembly when isopropyl alcohol (IPA) was added to a C_{60}-saturated toluene solution containing a small amount of C_{60} platinum derivative "$(\eta^2\text{-}C_{60})Pt(PPh_3)_2$".[1] This process of "liquid-liquid interfacial precipitation method (LLIP method)" was first applied for preparing single crystalline C_{60} nanofibers,i.e., "C_{60} nanowhiskers (C_{60}NWs)", using a C_{60}-saturated toluene solution and IPA.[2] A combination of pyridine solution of C_{70} and IPA was also tested in the LLIP method, and the single crystalline nanotubes composed of C_{70}, "C_{70} nanotubes", were found to form using the LLIP method.[3] Further, C_{60}-C_{70} two-component nanotubes and single crystalline C_{60}NTs were similarly obtained.[3,4]

Owing to the tubular structure with a relatively large inner diameter of C_{60}NTs, the C_{60}NTs may be used to deposit various chemical substances. For example, KBr crystals could be deposited inside of the C_{60}NTs by infiltrating a methanol solution of KBr.[5]

Recently, platinum is widely used for polymer-electrolyte fuel cells (PEFCs) as the catalysts for hydrogen oxidation, and their recycling is a very important subject to save their limited source. The recycling of Pt from polymer electrolyte membrane fuel cells (PEMFCs) is usually performed by forming H_2PtCl_6.[6] On the other hand, the above liquid-absorbing property of C_{60}NTs is expected to be applied for recovering Pt from a waste liquid containing Pt. This paper will show that $PtCl_4$ can be deposited into the C_{60}NTs using an alcohol solution of $PtCl_4$, indicating that the C_{60}NTs have a potential usage for recovering various useful metals from waste solutions. Since the C_{60}NTs grow to a length of the millimeter order, preparation of short C_{60}NTs with open ends is necessary. This paper will show that the ultrasonication is an efficient method to make short C_{60}NTs.

2. EXPERIMENTAL PROCEDURES

The C_{60}NTs were prepared by the LLIP method combined with ultrasonication, using a pyridine solution with saturated C_{60} (99.5% pure C_{60}, MTR Ltd., USA) and isopropyl alcohol (IPA).[7] The C_{60}-pyridine solution was exposed to UV light (302 nm, UVP Model UVM-57, USA) or blue light (400 nm - 500 nm, Heraeus Kulzer GmBH, Technotray CU) for 12 h - 24 h in advance. The reddish purple color of the solution became brown by this exposure.

In the LLIP method, firstly, 1 mL of the C_{60}-pyridine solution was poured into a transparent glass bottle, and 9 mL of isopropyl alcohol was gently added to the C_{60}-pyridine solution to form a liquid–liquid interface in a water bath of 5 °C. Next, this glass bottle was ultrasonically stirred in a bath of iced water for 1 min, shaken by hand, and ultrasonicated also for 1 min (iuchi VS-150, 150W). The glass bottle was allowed to stand at 10 °C for seven days in an incubator with a transparent plastic window (SANYO MIR-153, SANYO Electric Co., Ltd., Japan) to grow C_{60}NTs.

The C_{60}NTs were pipetted into a glass bottle with isopropyl alcohol, and the glass bottle was ultrasonicated to pulverize the C_{60}NTs by using the same ultrasonic bath. The pulverized C_{60}NTs were mounted on a TEM copper mesh with carbon microgrids and dried in a vacuum desiccator at room temperature for 24 h to remove the solvents contained in the C_{60}NTs. An ethanol solution with saturated $PtCl_4$ was prepared and a few droplets of this solution were pipetted onto the TEM copper mesh to deposite $PtCl_4$.

The C_{60}NTs were observed by a high-resolution transmission electron microcopy (JEOL, JEM-4010, 400kV) equipped with an EDX system (Tracor Northern, WI) and a microscopic Raman spectrophotometer (JASCO, NRS-3100, Japan) at a laser excitation wavelength of 532 nm with a beam intensity of 1.1 mW.

3. RESULTS AND DISCUSSION

The C_{60}NTs grown in the glass bottle were pipetted onto a slide glass and observed as shown in Fig.1. The C_{60}NTs exhibit metallic red brownish color and grow to a length of millimeter order or more. Fig.1 shows the straightness and uniformity of the C_{60} nanotubes.

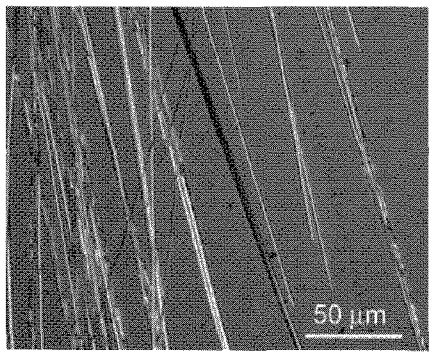

Fig.1 Optical micrograph of C_{60} nanotubes.

Fig.2 shows micro-Raman spectra for a single C_{60}NT at room temperature in air. Since the spectrum of the C_{60} nanotube has a profile with the peak positions very close to those of pristine C_{60},[8] it is found that the room-temperature dried C_{60}NTs are composed of the C_{60} molecules that are bonded via weak van der Waals bonding force. Our previous study on the C_{60}NWs that were prepared by use of toluene with saturated C_{60} and IPA and dried in air also showed that the constituent C_{60} molecules were bonded via van der Waals bonding force and well soluble in toluene.[9]

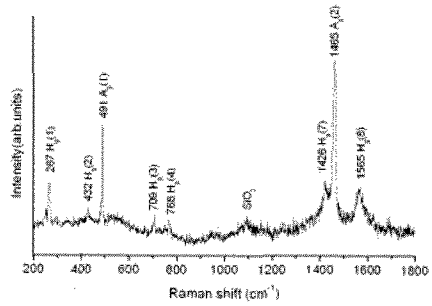

Fig.2 Micro-Raman spectra for a C_{60} nanotube dried at room temperature in air.

However, the loose bonding of C_{60} molecules in the C_{60}NTs is not a drawback. This fact is of importance in that the C_{60}NTs can be easily dissolved into organic solvents like toluene and that the dissolved C_{60} molecules can be recovered for recycling. We confirmed that the room-temperature dried C_{60} nanotubes can be redissolved in toluene by ultrasonication as shown in Fig.3. The color of toluene turns to reddish brown through the ultrasonication, proving the formation of toluene solution of C_{60}.

A low magnification TEM image for C_{60}NTs is shown in Fig.4. A breaking of the C_{60}NT (arrow) is observed at the marked place by circle. A magnified image for Fig.4 is shown in Fig.5.

As can be seen in the cross-sectional TEM image of the C_{60}NT of Fig.5, the C_{60}NT has a polygonal structure, showing a hexagonal cross section, which may correspond to the hexagonal crystal structure of the solvated C_{60}NTs.[10] Fig.5 also shows that the C_{60} nanotube was brittlely fractured. As compared with the C_{60}NWs which can be elastically bent with a small curvature radius, [12] the C_{60} nanotubes may be weaker in the fracture strength than the C_{60}NWs owing to their hollow structure and more porous structure of the tube wall than the C_{60}NWs. It can be known that the wall of C_{60} nanotubes has a more porous structure than C_{60}NWs from references 10 and 11, which also suggests that C_{60}NTs are weaker in strength than C_{60}NWs.

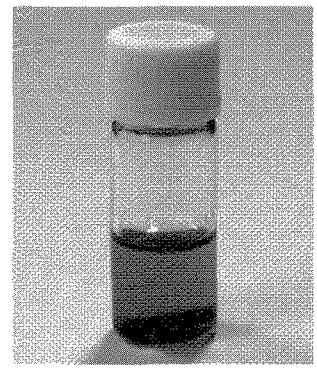

Fig.3 C_{60} nanotubes dissolved into toluene.

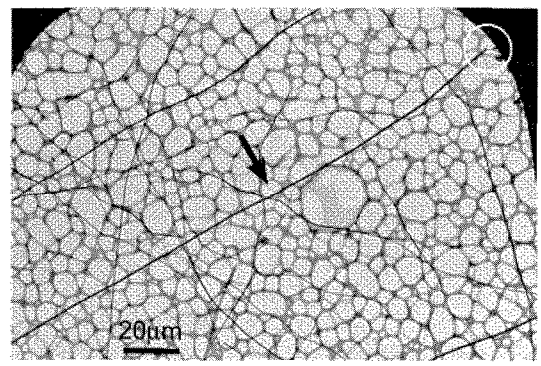

Fig.4 Low magnification TEM image for C_{60} nanotubes.

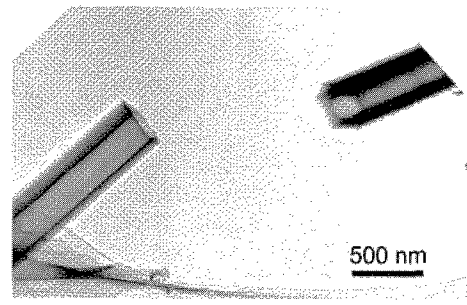

Fig.5 Magnified TEM image for a part of C_{60}NT indicated by a circle in Fig.4.

The C_{60}NTs with open ends are necessary for the infiltration of $PtCl_4$. Those C_{60} nanotubes with open ends were easily obtained by ultrasonication owing to the above brittleness of C_{60} nanotubes. Fig.6 shows an example of C_{60} nanotube with open ends that was shortly cut by ultrasonication in isopropyl alcohol for 3 min.

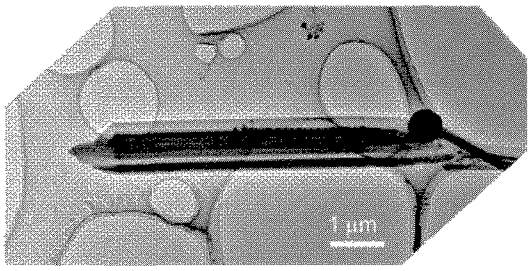

Fig.6 TEM image for a C_{60} nanotube with open ends prepared by ultrasonication.

The length of C_{60}NTs was changed depending on the ultrasonic pulverization time. Fig.7 and Fig.8 show the mean length of the pulverized C_{60}NTs is 7.5 ± 2.9 μm and 3.6 ± 1.3 μm for pulverization time of 1 min and 5 min, respectively. The length of C_{60} nanotubes becomes smaller with increasing the pulverization time. However, the mean length of pulverized C_{60}NTs is 7.1 ± 2.8 μm.in Fig.9 for the pulverization time of 30 min. Longer pulverizing time does not necessary lead to the formation of shorter C_{60} nanotubes. It is found that the ultrasonication duration of about 5 min or less is enough for the preparation of short C_{60} nanotubes.

The glass bottle contained also solid C_{60}NWs without hollow structure. The fullerene nanotubes form only when their outer diameter becomes larger than certain values, since the fullerene nanotubes have finite wall thicknesses.[3,10] Fig.10 shows an example which was pulverized for 3 min. The C_{60}NWs show no tubular structure since their diameter is too small to have the hollow structure.

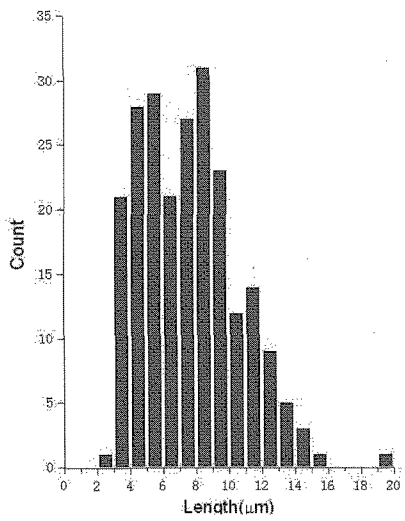

Fig.7 Histogram of the length distribution for the observed C_{60} nanotubes cut by ultrasonication for 1 min.

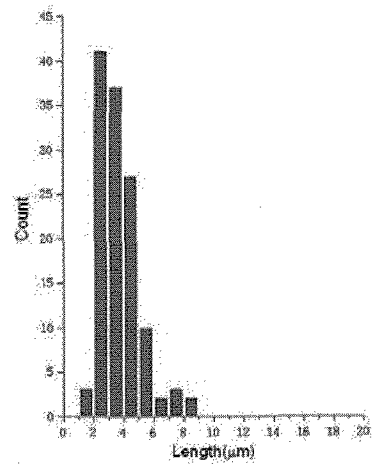

Fig.8 Histogram of the length distribution for the observed C_{60}NTs cut by ultrasonication for 5 min.

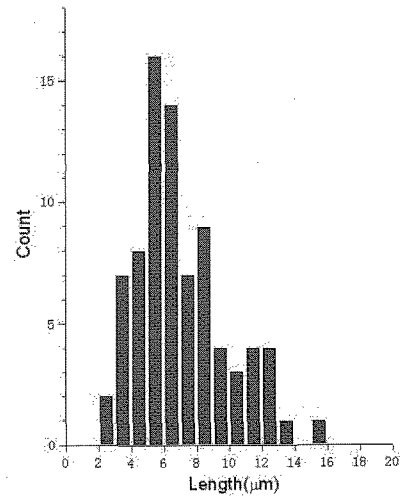

Fig.9 Histogram of the length distribution for the observed C_{60} nanotubes pulverized for 30 min.

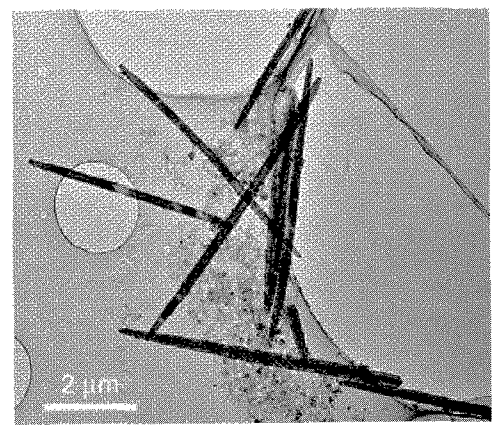

Fig.10 C_{60} nanowhiskers shortly cut by ultrasonication.

Using the ultrasonically pulverized C_{60}NTs, the infiltration of $PtCl_4$ into the C_{60}NTs was successfully performed as shown in Fig.11.

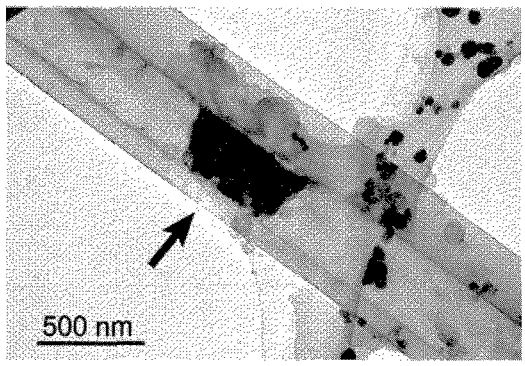

Fig.11 TEM image for a C_{60} nanotube with a $PtCl_4$ precipitation (arrow).

Most of the $PtCl_4$ precipitates could be deposited near the cut ends of C_{60} nanotubes.

The deposition of $PtCl_4$ was confirmed by taking an EDX spectrum as shown in Fig.12, where Pt and Cl from the $PtCl_4$ precipitate are detected.

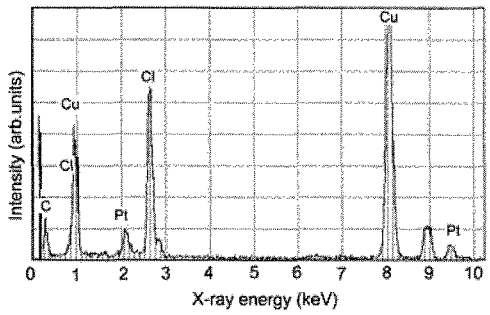

Fig.12 EDX analysis for the $PtCl_4$ precipitate (arrow) of Fig.11.

The infiltration of $PtCl_4$ into the inside C_{60}NTs was also tried by directly pipetting as-grown C_{60}NTs from a glass bottle into a 10 wt % isopropyl alcohol solution of $PtCl_4$, followed by ultrasonication. This process was conducted without drying the C_{60}NTs, retaining the liquid phase filling the inside of C_{60}NTs. In this case, no infiltration of $PtCl_4$ into the C_{60}NTs were observed by TEM.

As shown in the above, $PtCl_4$ can be infiltrated into the dried C_{60}NTs. The C_{60}NTs are expected to be used to deposit various chemical substances related with catalysts in the future. The C_{60}NTs are also expected to be used as future carriers to recover noble metals from liquid wastes.

4. CONCLUSIONS

The above research can be summarized as follows.

(1) The Raman spectroscopic analysis of the C_{60} nanotubes dried in air show profiles which are similar to pristine C_{60}, indicating that the C_{60} molecules in the dried C_{60} nanotubes are bonded via van der Waals bonding force.

(2) The ultrasonic pulverization can be effectively used to prepare short C_{60} nanotubes with open ends.

(3) $PtCl_4$ could be infiltrated into the C_{60} nanotubes by capillary phenomenon.

The present results will be developed for the preparation of catalyst carriers using the C_{60} nanotubes or for future recovery method of various noble metals from waste liquids.

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