Fullerene nanowhiskers and related fullerene nanomaterials

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Abstract. Since the discovery of C60 nanowhiskers in a colloidal solution of PZT in 2001, various low-dimensional fullerene nanomaterials such as fullerene nanotubes and fullerene nanosheets have been synthesized by the liquid-liquid interfacial precipitation method (LLIP method) as well as the C60 and C70 nanowhiskers. The LLIP method is an excellent process to synthesize the quasi one-dimensional fullerene nanomaterials. This paper first reviews the typical fullerene nano and micro materials that have been prepared by the LLIP method and then show that the LLIP method is also applicable to the synthesis of composite C60 nano and micro whiskers containing wide compositions of C60 derivative molecules.

1. Introduction

A variety of novel low-dimensional fullerene nanomaterials have been synthesized since the discovery of C60 nanowhiskers (C60NWs) in a colloidal solution of lead zirconate titanate (PZT) added with C60 in 2001 [1]. The C60NWs can be classified into the category of “fullerene nanofibers (FNFs)”. The FNFs are the thin fibers with diameters less than 1000 nm and are composed of various fullerene molecules that include endohedral fullerenes and fullerene derivative molecules with functional groups. The FNFs have the aspect ratios of length/diameter greater than three and can take single crystalline, polycrystalline or amorphous structures. The FNF can have a very wide range of length from a few micrometers to several millimetres or more. The FNFs can contain impurity elements and solvents in their matrices as well.

The fullerene nanowhiskers (FNWs) are the needle-like crystals that are composed of fullerene molecules and have diameters less than 1000 nm, and hence constitute a part of FNFs. On the other hand, the fullerene nanotubes (FNTs) are the FNFs with a tubular structure [7], and can take single crystalline, polycrystalline or amorphous structures. Fullerene nanorods and fullerene nanowires are classified into the category of FNFs. Recently, short FNWs are sometimes called “fullerene nanorods” [2, 3, 4] and the fullerene nanofibers are occasionally called “fullerene nanowires” [5].

One of the most efficient and widely used methods to prepare FNFs is the liquid-liquid interfacial precipitation method (LLIP method) that can even produce single crystalline fullerene nanotubes and fullerene nanosheets as well as the non tubular FNWs [6,7,8,9].

In general, the heterogeneous nucleation of crystals more easily occurs than the homogeneous nucleation in solutions. Substrates are used for such a purpose to enhance the nucleation of crystals. The interface formed between two liquid phases also can be used for the above purpose. The LLIP method produces the crystal nuclei of fullerenes by laying an alcohol on a fullerene-saturated solution from which FNFs grow. The LLIP method was firstly applied for the C60NWs prepared by use of a
C60-saturated toluene solution and isopropyl alcohol (IPA) [6]. A supersaturation state for C60 is realized by adding IPA to the toluene solution of C60 owing to the interdiffusion between toluene and IPA. The crystal nuclei produced at the liquid-liquid interface grow and C60NWs appear. The alcohols act as the nucleators of fullerene nano crystals. By changing the combination of solvents, tubular fullerene nanofibers can be obtained. Single crystalline nanotubes composed of C60 or C70 can be fabricated by using their pyridine solutions and IPA [7, 8].

The LLIP method can also be applied to prepare “fullerene nanosheets”, single crystalline thin sheets made of C60 [9]. A variety sizes of C60 nanosheets have been synthesized by a modified LLIP method, using a C60-CCl4 solution and alcohols (isopropyl alcohol, ethanol, methanol). The diameter of C60 nanosheets changes depending on the kind of alcohols from 7.5 µm (CCl4/IPA) to 500 nm (CCl4/methanol). The self-standing single crystalline C60 nanosheets may be used as organic semiconductor films. The LLIP method is also applicable to the synthesis of various crystals other than fullerene crystals. For example, asymmetric NaCl crystals can be synthesized by the LLIP method using the interface formed between a water solution of NaCl and 1-butanol [10].

Furthermore, the LLIP method has been developed to “the liquid-membrane-liquid interfacial precipitation (LMLIP) method”, where an alcohol is injected into a fullerene-saturated solution through a membrane with fine through-holes. Cha et al., showed that vertically aligned microtubes of C60 can be fabricated by injecting IPA into a toluene solution of C60 through a porous alumina membrane [11]. The surface of alumina membranes supplies the nucleation sites of C60 from which the C60 microtubes grow.

Not only the monocomponent FNFs but also multicomponent FNFs can be prepared by use of LLIP method. The first example was the two-component fullerene nanotubes with a composition of C60 - 15 mol% C70 that were prepared by use of IPA and a pyridine solution saturated with a powder mixture of C60 and C70 [7]. The properties of fullerene nanofibers are expected to be variously modified by adding fullerene derivative molecules to the matrix of fullerene nanofibers as well. The first synthesis of FNFs containing fullerene derivatives was the C60 nanowhiskers added with (η2-C60)Pt(PPh3)2 molecules [12,13]. Owing to the large size of (η2-C60)Pt(PPh3)2, C60 powders containing more than 1 mol% (η2-C60)Pt(PPh3)2 could not produce the C60 nanowhiskers, while capsular or tubular C60 needle-like crystals appeared. This result shows an existence of a solubility limit of C60 derivative molecules to the matrix of C60 nanowhiskers. Hence, it is of importance to prepare the C60 nanowhiskers containing various C60 derivatives with various compositions in order to examine the extent and possibility of LLIP method. The present paper will show Raman spectroscopic analyses of C60 nanowhiskers containing four kinds of C60 derivatives and discusses their structural characteristics deduced from the Raman spectroscopy data.

2. Experimental

Various two-component fullerene whiskers containing the C60 derivatives as shown in Fig. 1 were prepared by the LLIP method.

![Fig. 1](https://via.placeholder.com/150)

_C60 derivatives used for the preparation of two-component C60 whiskers._

The LLIP process was done by using m-xylene for the good solvent of C60 and the C60 derivatives and IPA for the poor solvent. The high-performance liquid chromatography (HPLC) analysis was done by dissolving the C60 whiskers into m-xylene. Fractions were separated on an octadecylsilyl
(ODS) column (150×4.6 mm). The elution was performed using a mobile phase of ethyl acetate : toluene = 9:1 at a flow rate of 0.5 ml min⁻¹. The prepared fullerene whiskers were observed by an optical microscope and also examined by Raman spectroscopy at a laser excitation wavelength of 532 nm (JASCO, NRS-3100, Japan).

3. Results and discussion

The prepared fullerene whiskers were found to have the compositions smaller than those of the starting powders as shown in Fig.2. The compositions analyzed by HPLC deviate from the nominal starting compositions with increasing those values. Comparing the C₆₀ derivatives 2 and 3, the deviation from the stoichiometry line is larger for the C₆₀ derivative 3 with a larger substituent group, which suggests that the dissolution of C₆₀ derivative molecules into the matrix of C₆₀ fullerene whiskers becomes more difficult with increasing the substituent size.

As shown in Figs. 3 and 4, various morphologies of fullerene crystals were obtained by the LLIP method using the C₆₀ powders containing the C₆₀ derivatives 1-4. Thin fullerene nanowhiskers are mostly observed in Fig.3 (a), Fig. 3(b) and Fig. 4(a), while thicker needle-like crystals or the precipitates with irregular shapes are shown in Fig. 3(c), Fig. 3(d), Fig. 4(b), Fig. 4(c) and Fig. 4(d). This result shows that the addition of higher concentration of C₆₀ derivatives with larger sizes suppresses the growth of FNWs in general. This fact is consistent with our previous result of the preparation of C₆₀ nanowhiskers containing (η²-C₆₀)Pt(PPh₃)₂ [12].

![Fig. 2 Compositions of the C₆₀ whiskers prepared by use of the C₆₀ powders containing C₆₀ derivatives 1 - 4.](image)

![Fig. 3 Optical micrographs of the fullerene whiskers and precipitates with the compositions, (a) C₆₀ - 4.3 mass % C₆₀ derivative 1, (b) C₆₀ - 3.5 mass % C₆₀ derivative 2, (c) C₆₀ - 4.1 mass % C₆₀ derivative 3, and (d) C₆₀ - 4.0 mass % C₆₀ derivative 4.](image)
The Raman spectroscopy is a powerful tool to study the chemical bonding states of C$_{60}$. Pure C$_{60}$ molecules excite two $A_g$ peaks and eight $H_g$ peaks [14]. The $A_g(2)$ peak is sensitive to the deviation from the $I_h$ symmetry of C$_{60}$ and locates in the vicinity of 1469 cm$^{-1}$ in pristine C$_{60}$. Fig. 5 compares the $A_g(2)$ peaks of as-prepared C$_{60}$NWs and those of the C$_{60}$NWs heated at various temperatures in vacuum to remove the contained organic solvents. The C$_{60}$NWs were prepared by use of a C$_{60}$-saturated pyridine solution and isopropyl alcohol [7]. The $A_g(2)$ peaks of the as-prepared C$_{60}$NWs show a Raman shift of $\sim$1460 cm$^{-1}$, while the heated C$_{60}$ NWs show the $A_g(2)$ peaks close to pristine C$_{60}$. Although the downward shift of $A_g(2)$ peak to 1460 cm$^{-1}$ indicates a polymerization of C$_{60}$ molecules [15], the origin of peak shift may be also explained by an interaction between the C$_{60}$ molecules and the solvent molecules contained in the as-prepared C$_{60}$NWs. It is suggested that C$_{60}$ molecules of the as-prepared C$_{60}$NWs are deformed from their pristine $I_h$ structure owing to their interaction with the contained solvent molecules.

As shown in Fig. 6, every C$_{60}$ derivative powder shows the split $H_g(1)$ peaks at around 255 cm$^{-1}$ that are excited by the C$_{60}$ cages deformed from the $I_h$ symmetry of pristine C$_{60}$. However, those extra peaks are very weak or cannot be detected in the composite fullerene whiskers as shown in Fig. 7. The $A_g(2)$ peak is also sensitive to the deviation from the $I_h$ symmetry, and is close to 1460 cm$^{-1}$ in each profile of Fig. 6. However, like the case of $H_g(1)$ peaks, the $A_g(2)$ peaks are at around 1467 cm$^{-1}$ in Fig. 7. This result shows that the solid-soluted C$_{60}$ derivative molecules are weakly bound to the surrounding C$_{60}$ molecules and that the C$_{60}$ cages in the composite whiskers are also weakly bound by van der Waals bonding forces like the case of pristine C$_{60}$ crystals. These observations suggest that the C$_{60}$ derivative molecules dissolved into the matrices of C$_{60}$ whiskers do not significantly alter their
mechanical properties in a wide range of compositions and that the above C\textsubscript{60} - C\textsubscript{60} derivative composite whiskers have the Young’s moduli similar to pristine C\textsubscript{60}NWs. The Young’s modulus of C\textsubscript{60}NWs ranges from 32 - 54 GPa, which corresponds to 160 - 650 % of C\textsubscript{60} bulk crystals [16].

4. Conclusions

The LLIP method is an excellent technique to prepare various morphologies of low-dimensional fullerene nanomaterials like fullerene nanowhiskers, fullerene nanotubes, fullerene nanosheets and vertically aligned fullerene microtubes at room temperature.

The LLIP method can produce also the multicomponent FNWs containing various C\textsubscript{60} derivatives. However, the growth of FNWs is found to be inhibited by the addition of higher concentration of C\textsubscript{60} derivatives with larger substituents.

The functional groups of the C\textsubscript{60} cages located on the surface of FNWs will be further modified by attaching a variety of molecules like dendrimers. Hence, numerous kinds of quasi one-dimensional fullerene nanomaterials are expected to be produced in future. The low-dimensional fullerene nanomaterials are now establishing a new big scientific field of carbon.

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