Review

Synthesis of fullerene nanowhiskers using the liquid–liquid interfacial precipitation method and their mechanical, electrical and superconducting properties

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Abstract
Fullerene nanowhiskers (FNWs) are thin crystalline fibers composed of fullerene molecules, including C60, C70, endohedral, or functionalized fullerenes. FNWs display $n$-type semiconducting behavior and are used in a diverse range of applications, including field-effect transistors, solar cells, chemical sensors, and photocatalysts. Alkali metal-doped C60 (fullerene) nanowhiskers (C60NWs) exhibit superconducting behavior. Potassium-doped C60NWs have realized the highest superconducting volume fraction of the alkali metal-doped C60 crystals and display a high critical current density ($J_c$) under a high magnetic field of 50 kOe. The growth control of FNWs is important for their success in practical applications. This paper reviews recent FNWs research focusing on their mechanical, electrical and superconducting properties and growth mechanisms in the liquid–liquid interfacial precipitation method.

Keywords: fullerene nanowhisker, fullerene nanotube, fullerene nanosheet, fullerene nanofiber, LLIP method, superconductor

1. Introduction

Fullerene molecules consist of closed cage-type structures that are composed of carbon atoms. The best-known fullerene is C60, which was discovered by Kroto et al in 1985 [1]. The second well-known molecule is C70, which was also identified in [1]. The C60 molecule is analogous to a soccer ball with 12 pentagons and 60 vertices where carbon atoms are located, and has 30 six-membered ring/six-membered ring joints with double bonds of carbon and 60 five-membered ring/six-membered ring joints with single bond of carbon.

Polymerization of C60 molecules can occur via [2 + 2] cycloaddition reactions, which form four-membered rings between adjacent C60 molecules. This cycloaddition mechanism involves a change of carbon hybridization from sp2 to sp3 [2].

Various properties of C60 have been studied by forming thin films on suitable substrates. Bulk samples can also be prepared by sintering at high temperatures. The [2 + 2] cycloaddition polymerization of C60 molecules is known to occur in the presence of ultraviolet or visible light illumination [3, 4], high-pressure sintering [5–8], and electron beam irradiation [9, 10]. The hardness of high-pressure sintered C60 reaches 200–300 GPa [11, 12].

However, fine needle-like crystals (whiskers) comprising C60, ‘C60 (fullerene) nanowhiskers (C60NWs)’, were found in
a colloidal solution of lead zirconate titanate (PZT) with C₆₀ added [13–15].

Fullerene nanofibers are linear and thin, with diameters less than 1000 nm [16, 17]. Fullerene nanosheets are thin two-dimensional substances. In this paper, we define fullerene nanosheets to be less than 1000 nm in thickness. Fullerene nanofibers and nanosheets can include a variety of fullerene molecules and their derivatives including C₆₀, C₇₀, Sc₃N@C₈₀ [18], C₆₀(COOOC₂H₅)₂ [19–21] and (η²-C₆₀)Pt(PPh₃)₂ [22].

The aspect ratio of fullerene nanofibers is defined to be greater than three [16]. Fullerene nanofibers are described as either non-tubular or tubular [23–27]. Non-tubular crystalline fullerene nanofibers are called fullerene nanowhiskers (FNWs). FNWs with both single-crystal and polycrystalline structures have been reported [53].

Fullerene nanofibers can incorporate either one or multiple types of fullerenes. This enables formation of both monocomponent and multicomponent structures. Examples of monocomponent structures include C₆₀NWs, C₇₀ (fullerene) nanowhiskers (C₇₀NWs), C₆₀ or C₇₀ (fullerene) nanotubes (C₆₀NTs or C₇₀NTs), [23, 25, 28], and FNWs composed of C₆₀(COOOC₂H₅)₂ molecules (C₆₀(COOOC₂H₅)₂NWs). Examples of multicomponent fullerene nanofibers include two-component C₆₀–C₇₀ NWs [29], two-component C₆₀–C₇₀ NTs [23], two-component C₆₀–C₆₀(COOOC₂H₅)₂ NWs [19], and two-component C₆₀–(η²-C₆₀)Pt(PPh₃)₂ NWs [22]. Figure 1 shows the classification of fullerene nanofibers.

Fullerene nanofibers and nanosheets can be synthesized using the ‘liquid–liquid interfacial precipitation (LLIP) method’ [30], which has been widely applied [31–38]. In this review, we discuss the LLIP method to synthesize fullerene nanofibers and nanosheets and the applications in which these materials have been investigated.

The terminology ‘FNW’ represents all needle-like crystals comprising fullerene molecules with diameters less than 1000 nm. The words ‘nanorod’ and ‘nanowire’ are replaced with ‘nanowhisker’ to avoid confusion as was described in review paper [16].

2. Synthesis of FNWs

2.1. LLIP method

The LLIP method is commonly used to synthesize fullerene nanofibers and nanosheets [30]. This method relies on diffusion of a poor solvent of fullerenes such as isopropyl alcohol (IPA) into a fullerene-saturated toluene solution. An aliquot of a C₆₀-saturated toluene solution is added to a glass bottle. Following this, an appropriate amount of IPA is added gently to the solution to form a liquid–liquid interface [8]. The resulting mixture is kept at ambient temperatures, typically below 25 °C. During the slow mixing of toluene and IPA, the liquid–liquid interface becomes supersaturated in C₆₀ and allows nucleation of C₆₀NWs to occur. This supersaturated state is maintained as IPA diffuses into toluene and assists in the growth of C₆₀NWs. This procedure is named ‘static LLIP method’ [30, 39]. The glass bottle is kept still in an incubator, where the C₆₀NWs self-assemble into a shape similar to a cotton ball. The LLIP method can also be used in combination with ultrasonic mixing, manual mixing, or injection [24, 39, 40]. Ultrasonication induces rapid mixing of good solvents and poor solvents, causing formation of fine fullerene nuclei that grow into fullerene nanofibers or nanosheets.

The static LLIP method can involve either layering a poor solvent onto a good solvent or vice versa, and can be combined with manual mixing, supersonic mixing, mixing by injection of liquid, or ultrasonic mixing of liquid droplets [41]. These methods are collectively named the ‘dynamic LLIP method’.

Cha et al and Miyazawa et al reported the diaphragm LLIP method (DLLIP method), which involves injecting a poor solvent for fullerene into a fullerene solution through a porous membrane [40, 42, 43]. As an example, if IPA is slowly injected into a C₆₀-saturated toluene solution through
an anodic aluminum oxide membrane with nanosized pores, vertically grown microtubes of C₆₀ are produced. All methods that mix two solvents to form fullerene nanofibers and nanosheets can be classified as LLIP processes.

Using the DLLIP method, the influence of alcohol chain length (methanol, ethanol, and IPA) on the length of C₆₀ whiskers was investigated using toluene as a good solvent for C₆₀. Amer et al reported that the length of C₆₀ whiskers decreased when the chain length of the alcohol (poor solvent) increased [44]. The temperatures at which the C₆₀ whiskers were grown was not reported; however, the above result suggests that the chain length of the alcohol influences the desolvation energy of solvated C₆₀ molecules that governs the rate-limiting process of surface reaction [45].

2.2. Growth mechanism of FNWs using the LLIP method

The Young modulus of C₆₀NWs has been examined using a transmission electron microscope equipped with an atomic force microscope [46]. The Young modulus of C₆₀NWs increases with decreasing diameter [46–49]. This phenomenon is thought to occur because C₆₀NWs have a core–shell structure with a porous interior region and a dense surface region [48, 50]. Kizuka et al found that C₇₀NWs containing solvent molecules had a higher density of lattice defects in their interior regions, which caused a reduction in the Young modulus [51]. Additionally, the Young modulus of C₇₀NTs was found to increase with decreasing diameter [25]. These studies conclude that by decreasing the diameter of fullerene nanofibers, crystallinity is increased, which in turn leads to an increase in the Young modulus.

In the LLIP process, FNWs grow from seed crystals [52–54]. The size of the initial C₆₀NW nuclei is influenced by the degree of supersaturation of C₆₀ in solution, which is determined by the mixing ratio of both good and poor solvents [39]. C₆₀NTs grow in both directions along their growth axis from the seed crystals [53, 54]. However, the seed crystals should disappear by the core dissolution mechanism to form a through-hole structure [55].

The re-growth of C₆₀NTs was observed in ultrasonically pulverized C₆₀NTs [53]. The ultrasonically fractured C₆₀NTs have steep wall edges, on which C₆₀ molecules accumulate and crystallize [53]. This preferential accumulation of C₆₀ in areas with a small radius of curvature, such as the hexagonal vertices, is an important growth mechanism of fullerene nanotubes [53, 54].

The growth of C₆₀NWs is influenced by numerous factors, including time, temperature, light, solvent species, the ratio between good and poor solvents, and contained impurity water [39, 56–59]. The growth mechanism of C₆₀NWs in C₆₀-saturated toluene and IPA has been studied closely. The activation energy of growth (52.8 kJ mol⁻¹) was calculated by varying the temperature and measuring the length of C₆₀NWs. This value is approximately four times greater than the value obtained for the diffusion of C₆₀ in a mixed solution of toluene and acetonitrile (13.1 kJ mol⁻¹, 4:1 v/v) [56, 60]. The high activation energy indicated that the growth of C₆₀NWs is rate limited by the desolvation process of C₆₀ molecules bonded with solvent molecules on the crystal surface.

The dynamic LLIP process involves a fullerene solution being forcibly mixed with a poor solvent for fullerene. This process generates microscopic liquid–liquid interfaces between the fullerene solution and the poor solvent of fullerene, where supersaturated solutions lead to rapid nucleation of fine fullerene crystals. The formation of granular, linear, or sheet fullerene crystal morphologies depends on the growth kinetics, which may be governed by the degree of supersaturation, solvent species, and temperature.

Size control of fullerene nanofibers is critical for practical applications. Wakahara et al reported that the diameter of C₆₀NWs varied with the size of the glass bottles used in their synthesis. Linear relationships between the area of the liquid–liquid interface and the diameter of C₆₀NWs were observed when the total volume of solution was fixed [61]. Changes in the lengths and diameters of C₆₀NWs upon varying the solution volume have been examined [62]. These C₆₀NWs were prepared by dynamic LLIP in a C₆₀-saturated toluene and IPA system. After the initial formation of a liquid–liquid interface by layering an equal amount of IPA on a C₆₀-saturated toluene solution, the solution was manually mixed by shaking 30 times. The relationships between solution volume and mean length, diameter and aspect ratio are shown in figures 2(a)–(c) [62]. The aspect ratio, as derived from the y-intercepts of figures 2(a) and (b) (5.02 μm/387 nm) yielded a value of 13.0, almost identical to the value derived from the y-intercept of figure 2(c) (13.1). Hence, it is reasonable to consider the size of C₆₀NW nuclei can be estimated using the relationships shown in figures 2(a)–(c).

The relationship between the solution volume and number of C₆₀NWs per unit volume is shown in figure 2(d). The number density, as calculated from the nominal content of C₆₀ and the mean size of C₆₀NWs in solution [62], increased as the solution volume decreased. This implies that the volume fraction of liquid–liquid interfaces increases when the solution volume is decreased. A power law relationship (\(y = 1.12 \times 10^3 x^{-0.567}\)) was fitted to the data with an approximate index of −0.5, showing that the number density of C₆₀NW nuclei in solution is inversely proportional to the square root of the solution volume.

A model describing the changes in the liquid–liquid interface upon manual mixing is shown in figure 3. The initial layered interface (figure 3(a)) is assumed to form a sinusoidally modulated interface (figure 3(b)) upon the manual mixing. The amplitude of this interface increases along the height of the glass bottle, a section of this waveform is highlighted by the blue rectangle (figure 3(c)). This highlighted section is modeled by a cylinder with height \(h\), radius \(r\), basal area \(S\), and volume \(V\) (figure 4(a)). The front of the liquid–liquid interface travels vertically with a velocity \(v\).

The following equations hold.

\[ V = Sh, \]

\[ h = pr, \] where \(p\) is a constant,
The front of liquid–liquid interface is assumed to move along the height $h$ with a time $t$.

$$t = h/v.$$  

(4)

As the liquid–liquid interface front moves, interdiffusion between C$_{60}$-saturated toluene solution and IPA occurs (figure 4(b)). If the values of both $t$ and $\Delta r$ are assumed to be small, the area of the interdiffusion zone ($\Delta S$) is approximated as follows:

$$\Delta S = 2\pi r \Delta r.$$  

(5)

The volume of interdiffusion $\Delta V$ is:

$$\Delta V = b h \Delta S.$$  

(6)

If $\Delta r$ is assumed to be proportional to $(D t)^{1/2}$ with a coefficient of interdiffusion $D$ [63], it is calculated as in equation (7) with a constant $a$.

$$\Delta r = a t^{1/2}.$$  

(7)

Hence, combining (4), (5), and (7),

$$\Delta S = bh^{1/2}, \text{ where } b = 2\pi ra(1/v)^{1/2}.$$  

(9)

If $N$ is defined as the number of C$_{60}$NW nuclei per unit volume in the zone of interdiffusion, the mean number of C$_{60}$NW nuclei contained in a unit volume of a cylinder ($\rho$) can be calculated by combining equations (1), (3), (6), and (9):

$$\rho = (N q V)^{-1/2}.$$  

(12)

This model suggests that the mean number density of C$_{60}$NW nuclei is inversely proportional to the square root of the solution volume, which was indeed confirmed experimentally (figure 2(d)).

3. Electrical and superconducting properties of C$_{60}$NWs

C$_{60}$NWs display n-type semiconducting behavior and are used in a diverse range of applications, including field effect
transistors (FETs) [64], solar cells [65, 66], photocatalysts [67], chemical sensors [27], and photosensors [68]. However, Wakahara et al. recently synthesized ambipolar FETs with C60/cobalt–porphyrin hybrid nanosheets using a LLIP method [92].

The carrier mobility of C60NWs in a FET was determined to be $2 \times 10^{-2} \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ under vacuum [64]. However, the as-synthesized solution-grown C60 needle-like crystals exhibited a very high mobility up to 11 cm$^2$ V$^{-1}$ s$^{-1}$ [69]. As the measured carrier mobility of C60NWs, or needle-like crystals of C60, depends largely on the measurement conditions (solvent impurities, oxygen impurity, crystal structure, and lattice defects), electrical properties of the materials were investigated under controlled conditions. Only C60NWs with clearly defined chemical and structural properties were used.

Figure 3. Model showing the liquid–liquid interface (a) changing with manual mixing (b). The interface front between the C60-saturated toluene solution and IPA is assumed to move with a velocity $v$ along the vertical direction of the glass bottle (c).

Figure 4. Cylindrical model used to calculate the number density $N$ of C60NW nuclei for the region of the liquid–liquid interface shown in figure 3(c).
The electrical resistivity of C$_{60}$ whiskers with diameters greater than 1 μm (~10–a few hundred micrometers) was measured using a two-terminal method at ambient temperature [70]. The electrical resistivity of the C$_{60}$ whiskers decreased dramatically with decreasing diameter (figure 5(a)). The resistivity of C$_{60}$NWs is expected to be several Ohm centimeters (Ω cm), based on extrapolation of the curve-fitted data. Subsequently, Larsson et al measured the electrical resistivity using a four-point probe method [71]. Figure 5(b) summarizes their results including figure 5(a) [70]. The four-point probe method also showed a decrease in resistivity of C$_{60}$ whiskers with decreasing diameter (FIB-spot (4PP)), figure 5(b)). A C$_{60}$NW with a diameter of 650 nm showed a low resistivity of 3 Ω cm [71]. The decrease in resistivity with decreasing diameter suggested that C$_{60}$NWs with smaller diameters and shorter C$_{60}$ intermolecular distances are more crystalline and thus have a greater overlap of π electrons [70].

Recently, this fact was further confirmed by Barzegar et al using thinner C$_{60}$NWs [93]. It was shown that the electrical mobility of as-grown C$_{60}$NWs with diameters less than 300 nm increases with decreasing the diameter of C$_{60}$NWs [64, 93–95].

If the line measured using the four-point probe method is extrapolated to a diameter of 100 nm in figure 5(b), the resistivity will decrease to the order of $10^{-3}$ Ω cm. This result suggests that C$_{60}$NWs may exhibit metallic conductivity when their diameters are sufficiently small. Xu et al showed that C$_{60}$NWs are conductive only if the surface is not covered by oxygen [72].

To determine the electrical properties of a semiconductor, it is necessary to measure the temperature dependence of electrical conductivity. Ji et al performed these measurements using C$_{60}$NWs with either a face-centered cubic (fcc) or a hexagonal closed packed (hcp) structure [73]. The fcc C$_{60}$NW displayed higher electrical conductivity than did the hcp C$_{60}$NW. This result confirms that the crystal structure influences the electrical properties of C$_{60}$NWs. However, the effect of solvent molecules contained in the hcp C$_{60}$NW is still under some debate. If C$_{60}$ molecules adopt a closely packed structure, a greater overlap between π electrons would lead to higher electrical conductivity in these C$_{60}$NWs [70, 73].

Carbon superconductors have been investigated for many years. The superconductivity of graphite (C$_8$) specimens doped with alkali metals, including K (superconducting transition temperature ($T_c$) < 0.55 K [74], 0.128–0.198 K [75]), Cs ($T_c = 0.020–0.135$ K [74]), and Rb ($T_c = 0.023–0.151$ K [74]) has been reported. Graphite superconductors such as C$_6$Ca ($T_c = 11.5$ K) and C$_6$Yb ($T_c = 6.5$ K) were also synthesized [76]. C$_{60}$NWs can be transformed into glassy carbon nanofibers by heat treatment [77–79]. When heated to 3000 °C, C$_{60}$NWs transform into carbon nanofibers with up to 17 graphene layers [77]. The number of stacked graphene layers increases with increasing temperature between 2000 and 3000 °C [77]. Those C$_{60}$NWs heated at high temperatures with developed graphitic ribbons are promising materials that may exhibit superconductivity if doped with alkali metals and alkaline-earth metals. In addition, the high-temperature-treated C$_{60}$NWs become electron emission tips showing striped patterns that reflect the atomic structure of the crumpled graphitic layers [78, 79]. However, since long amorphous carbon nanofibers prepared by high-

Figure 5. Electrical resistivity of C$_{60}$ whiskers measured as a function of diameter. The resistivity measurement was performed by the two-point probe method (2PP) in (a) and by the four-point probe method (4PP) in (b). [6] in the inset of (b) is identical with [70]. FIB stands for focused ion beam. Part (a) reprinted with permission from [70], copyright © 2003 John Wiley & Sons, Ltd. Part (b) reproduced by permission of ECS—The Electrochemical Society from [71].
temperature heat treatment of C60NWs showed cytotoxicity like long multiwall carbon nanotubes [96], special care will be necessary in the practical uses of the glassy carbon nanofibers. In 2004, boron-doped diamond was observed to exhibit superconductivity \( (T_c \approx 4 \text{ K}) \) [80]. Takano et al found that the \( T_c \) of a boron-doped diamond film was 7.4 K [81].

Hebard et al discovered that C60 doped with potassium (K) exhibited superconductivity [82]. A superconducting transition temperature \( (T_c) \) of 18 K was observed for both K-doped C60 films and bulk samples. Tanigaki et al reported the highest \( T_c \) value (18 K) for both K-doped C60 films and bulk samples. Tanigaki et al reported the highest \( T_c \) value (18 K) for both K-doped C60 films and bulk samples.

Of the three known phases of K-doped C60 (fcc (\( \text{K}_3\text{C}_{60} \)), body-centered tetragonal (bct) (\( \text{K}_4\text{C}_{60} \)), and body-centered cubic (bcc) (\( \text{K}_6\text{C}_{60} \)), only the fcc phase exhibits superconductivity [84]. Although C60NWs that are grown in solution display a solvated hexagonal structure, they transform into an fcc structure upon drying and removal of the internal solvent molecules [85]. Hence, these fcc C60NWs should be superconducting if doped with alkali metals [15]. C60 nanotubes were doped with Li, Na, and K, and the crystal structures were examined using Raman spectroscopy [86].

Superconductive C60NWs were also successfully fabricated by doping with K [87, 88]. Although the \( T_c \) value (17 K) of the K-doped C60NWs with a nominal composition of \( \text{K}_3\text{C}_{60} \) was lower than the reported value of 18 K [82], the superconducting, shielding volume fraction was as high as 80\%, and the critical current density \( J_c \) was more than \( 3 \times 10^5 \text{ A cm}^{-2} \) under 50 kOe [87, 88], although the doping was performed at 200 °C for 24 h. The shielding volume fraction of the K-doped C60 crystal powder was less than 1\% when doped using the same process (figure 6). The high shielding volume fraction in the K-doped C60NWs may allow for light, flexible, and recyclable superconducting carbon cables. Initially, the superconducting shielding volume fraction of K-doped C60 crystals was at most 35\%, even after prolonged heat treatment (20 days) at temperatures up to 250 °C [89].

Efforts to increase the \( T_c \) value of alkali-doped C60NWs are continuing. Values up to 26 K have been achieved by doping with Rb [90]. The volume fraction of Rb-doped C60NWs was approximately five times greater than that of Rb-doped C60 powder. As Rb is an abundant alkali metal like the other common metals such as copper, lead, or zinc [91], lightweight Rb-doped C60NWs are expected to find use in a variety of superconducting applications, including motor cars, cables for power delivery, and wind generators.

4. Summary

A variety of fullerene nanofibers and nanosheets have been synthesized using LLIP methods. These materials have found use in a wide range of applications, including solar cells, chemical sensors, photo sensors, photocatalysts, and ambipolar field-effect transistors. The synthesis of C60NWs using a dynamic LLIP method with a C60-saturated toluene solution and IPA suggests that nucleation is governed by the volume of the liquid–liquid interface produced by interdiffusion between the two solvents.

Alkali-metal-doped C60NWs are the first carbon fibers to display superconductivity while being lightweight and flexible. K- or Rb-doped C60NWs are promising superconductors with \( T_c \) values that are higher than those of any other practically used metal superconductors. Additionally, they are composed of non-toxic, abundant, and recyclable elements. Fullerene nanomaterials show great promise for a variety of applications in electrical and optical fields.

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