Formation of iodine-doped C_{60} whiskers by the use of liquid–liquid interfacial precipitation method

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Iodine-doped whiskers of C_{60} (I–C_{60} whiskers) with diameters ranging from submicrometers to micrometers and lengths longer than 100 μm were successfully obtained by the use of the liquid–liquid interfacial precipitation method. Transmission electron microscopy observations showed that the I–C_{60} whiskers were single crystalline and had a growth axis parallel to the close-packed direction of C_{60} molecules and expanded (002) lattice planes indicative of the intercalation of iodine and oxygen atoms between the (002) planes of a body-centered-tetragonal crystal system. The I–C_{60} whiskers showed nonlinear *I-V* curves. The electrical resistivity of the I–C_{60} whiskers was more than three orders of magnitude lower than that of pristine face-centered-cubic C_{60} crystals.

Since the discovery of C_{60} in 1985,[1] tremendous efforts have been made to understand its fundamental physical and chemical properties.[2,3] C_{60} has been investigated in various forms such as films, powders, bulk single crystals, and composites with metals, ceramics, and polymer matrices.[4–7] Linear-shaped structures of C_{60} have been also reported. For example, Michaud *et al.*[8] obtained needlelike solvated C_{60} crystals by slowly evaporating solutions of C_{60} in 1,2-dichloroethane (DECAN) at room temperature. The needlelike crystals had a composition of C_{60}:DECAN = 1:1 in molar ratio and exhibited a decagonal shape with a length of 500 μm and a diameter of 150 μm. Céolin *et al.*[9] formed hexagonal needlelike crystals of C_{60} with a length of 200 μm and a diameter of about 20 μm by evaporating the dichloromethane solutions of C_{60}. Further, Ogawa *et al.*[10] formed a needlelike substance with a length of 20 mm and a diameter of 100 μm through a slow evaporation of a toluene solution of C_{60}. This substance had a structure composed of thin layers with thickness of about 30 nm and was found to be amorphous by transmission electron microscopy (TEM).

Recently, on the other hand, we accidentally discovered fine fibrous structures of C_{60} in the course of preparing a mixture of lead zirconate titanate (PZT) sol–toluene with dissolved C_{60}.[11] This experiment was done with the expectation that addition of a small amount of C_{60} into a PZT sol prepared from lead acetate and alcoxides of Zr and Ti would effectively enhance the nucleation of perovskite PZT crystals at a low temperature. The C_{60} fibers with submicrometer diameters and lengths more than 100 μm were proved to be single-crystalline whiskers of C_{60} and called "C_{60} nanowhiskers" (C_{60}NWs).[11]

Since isopropyl alcohol was used in the PZT-C_{60} sol as the solvent, we further considered that the C_{60} nanowhiskers would be produced in a system of a C_{60}-saturated toluene and isopropyl alcohol.[12] A toluene solution with saturated C_{60} was put into a glass bottle, and then isopropyl alcohol was gently added into the bottle to form a liquid–liquid interface of C_{60}–saturated toluene and isopropyl alcohol at a temperature of about 21 °C. Fine whiskers of C_{60} nucleated at the interface, and the bottle was aged at room temperature for 30 days to grow the C_{60} whiskers. The C_{60} whiskers fabricated by this "liquid–liquid interfacial precipitation (LLIP) method" had diameters ranging from submicrometers to micrometers and lengths of more than 100 μm. The C_{60} whiskers are considered to nucleate at the toluene–isopropyl alcohol interface with supersaturated C_{60} molecules. The supersaturated state is assumed to be caused by a loss of toluene, which diffuses into isopropyl alcohol.

An example of the single-crystalline whiskers of C_{60} is shown in Fig. 1(a), where we can see straight or flexibly curved C_{60} whiskers with constant diameters along their growth axes. The C_{60} whiskers were well dispersed in the toluene–isopropyl alcohol solution. We also found bundled C_{60} whiskers, as shown in Fig. 1(b). This result indicates that the flexible C_{60} whiskers can be spun into a yarn. The yarns of C_{60} whiskers would be processed further into various cages, nets, and cloths.

The LLIP method was repeated for C_{70} and single-crystalline whiskers of C_{70} with diameters ranging from submicrometers to micrometers were successfully obtained.[13] The C_{70} single-crystalline (nano)whiskers had a curved structure, and the C_{70} molecules polymerized along their close-packed direction parallel to the growth axis as well as the C_{60} NWs.

The second stage of our study was confined to examination of the possibility that the C_{60} (nano)whiskers can incorporate impurity elements, since we found an example in which $CHBr_3$-intercalated C_{60} single crystals with expanded lattice parameters exhibited a high-T_c superconductivity.[14]

This paper shows an attempt to obtain single-crystalline whiskers of C_{60} doped with impurity atoms by the LLIP method. Iodine was selected for this purpose because it can be easily dissolved into isopropyl alcohol, and iodine-doped C_{60} crystals have been reported to exhibit interesting optical and magnetic properties. For example, Grigoryan *et al.* showed that iodine-doped C_{60} samples exhibited a magnetic transition temperature (60 K) higher than that of the tetrakis (dimethylamino) ethylene (TDAE)-C_{60} and IBr–C_{60} systems,[15] and Yue *et al.* showed that the photoconductivity of a toluene derivative of C_{60} increased by one order of magnitude after iodine doping.[16]

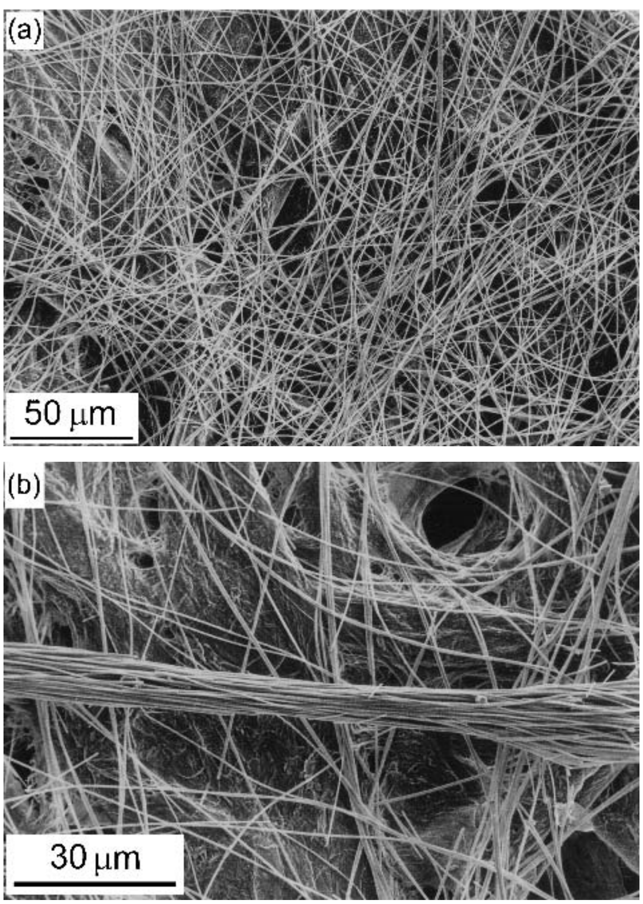

FIG. 1. (a) SEM image of single-crystalline C_{60} (nano)whiskers on a paper filter. (b) SEM image of bundled C_{60} (nano)whiskers.

The experimental procedure was as follows. First, a toluene (99.5%, Wako Pure Chemical Industries, Ltd., Japan) solution of C_{60} (99%, MER Corp., Tucson, AZ) with a concentration of 0.2 mass% C_{60} was prepared. Secondly, an isopropyl alcohol (99.5%, Wako) solution of iodine with a concentration of 2.3 mass% iodine was prepared by ultrasonically dissolving iodine (99.9%, Wako). A 5-mL aliquot of the toluene with dissolved C_{60} was poured into a 10-ml glass bottle, and a 5-ml aliquot of the isopropyl alcohol with dissolved iodine was gently added into the bottle. The C_{60} whiskers nucleated instantly at the toluene–isopropyl alcohol interface when the iodine–isopropyl alcohol solution was added into the C_{60}–toluene solution. This glass bottle was kept still for two days at about 21 °C to allow the precipitates of C_{60} whiskers to settle on the bottom of the glass bottle, shaken by hand to disperse the C_{60} whisker precipitates that were expected to act as the seed crystals for longer C_{60} whiskers, and then aged for 30 days at room temperature to grow the iodine-doped C_{60} whiskers.

Specimens for structural investigation for TEM (JEOL, JEM-4000FXII, 400kV, Tokyo, Japan) and scanning electron microscopy (SEM; Hitachi S-4200, Tokyo, Japan) with energy dispersive x-ray spectrometry (EDX; Kevex Instruments, SuperDry, Scotts Valley, CA) were prepared by placing droplets of the aged solution containing the iodine-doped C_{60} (nano)whiskers on TEM microgrids.

Straight iodine-doped C_{60} (I–C_{60}) whiskers were successfully fabricated as shown in the SEM image of Fig. 2(a). Figure 2(b) shows that the whisker had clear habit planes. The I–C_{60} whiskers had diameters ranging submicrometers to micrometers. Long I–C_{60} whiskers had lengths of more than several hundreds of micrometers.

The chemical composition of an I–C_{60} whisker was analyzed by EDX of the SEM and was calculated to be C:I:O = 74:2:24 in atomic percentage by a semi-quantitative analytical program. The C:I atomic percentage ratio was calculated as C:I = 60:1.6, and this ratio is the same as the reported value of a compound $C_{60}I_{1.6}$.[15] A semi-quantitative SEM-EDX analysis of a single crystalline C_{60} whisker without iodine doping showed C:O = 87.5:12.5 = 1.0:0.14 in atomic percentage, while the above I–C_{60} whisker had the atomic percentage ratio of C:O = 1.0:0.32. This increase in the oxygen content in the I–C_{60} whisker may be explained by the expanded (002) plane spacing that will be discussed later. A SEM-EDX analysis of the C_{60} powder used for the preparation of the C_{60} and I–C_{60} whiskers showed C:O = 92.4:7.6 = 1:0.08 in atomic percentage. The C_{60} powder must have absorbed impurity oxygen from air.

The possible sources of oxygen contained in the C_{60} and I–C_{60} whiskers are air and isopropyl alcohol. The oxygen atoms are assumed to have been incorporated into the I–C_{60} whiskers through a strong interaction with iodine.

Single-crystalline I–C_{60} whiskers with diameters less than 1 μm were also fabricated as shown in the TEM image in Fig. 3. The crystalline nature of the I–C_{60} whisker of Fig. 3(a) is shown by the areas of differing contrast as marked by arrows. The single crystallinity of the I–C_{60} whisker was confirmed by the selected-area electron diffraction pattern shown in Fig. 3(b).

A high-resolution TEM observation is shown in Fig. 4(a), which was taken at the edge of an I–C_{60} whisker. Figure 4(b) shows a magnified image for the enclosed area of Fig. 4(a), and the (001) and (100) lattice-plane spacings are indicated as 2.10 nm and

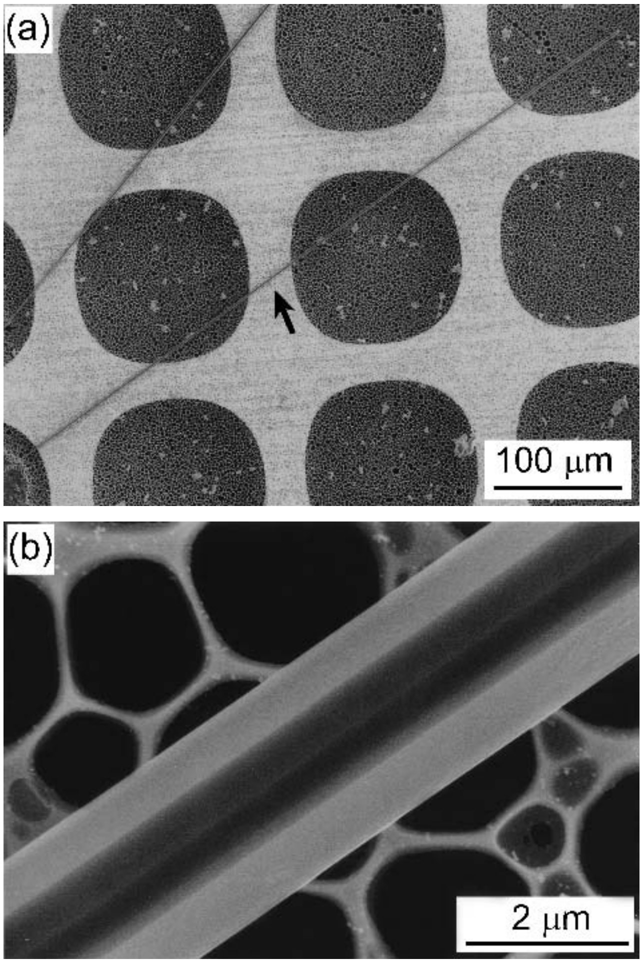

FIG. 2. (a) SEM image of iodine-doped C_{60} whiskers. (b) Magnified SEM image of the arrowed whisker of photo (a).

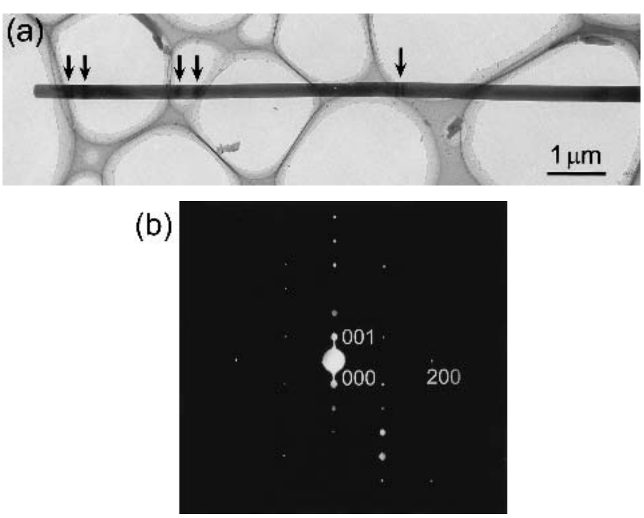

FIG. 3. (a) TEM image of an iodine-doped single-crystalline C_{60} nanowhisker with a diameter of 280 nm, and (b) its selected-area electron diffraction pattern. Bend contours are indicated by arrows.

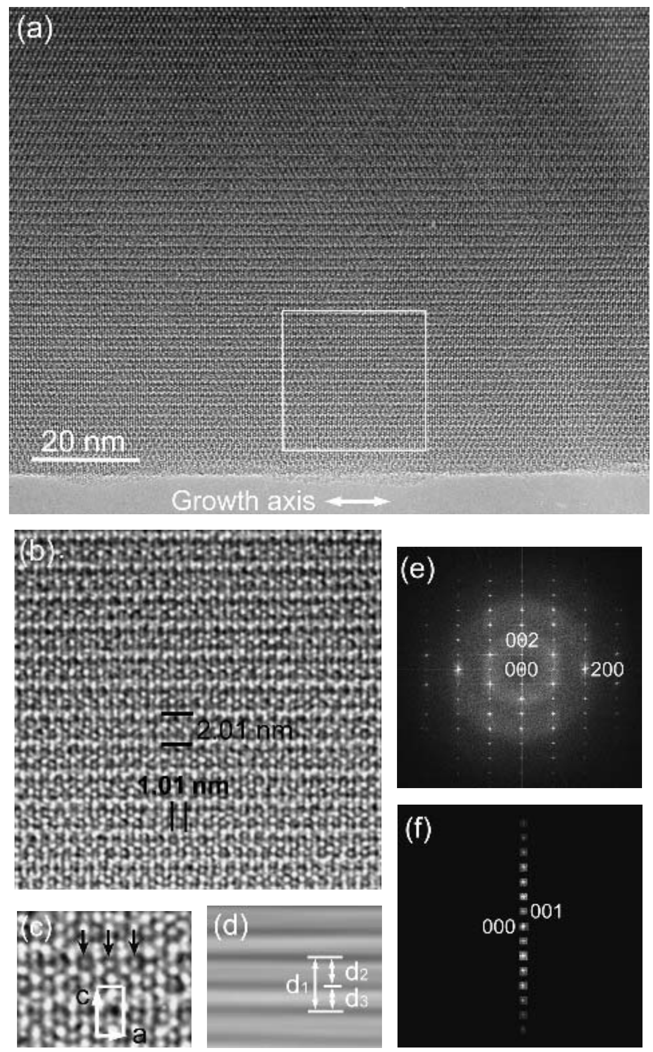

FIG. 4. (a) HRTEM image of a single-crystalline iodine-doped C_{60} nanowhisker taken at an underfocusing condition. (b) Enlarged image of the enclosed area of photo (a). (c) The *a* (= 1.01 nm) and *c* (= 2.10 nm) axes of the bct unit cell. (d) Filtered inverse FFT image for photo (c) ($d_1 = 2.10$ nm, $d_2 = 1.17$ nm, $d_3 = 0.93$ nm). (e,f) FFT patterns for photos (c) and (d), respectively.

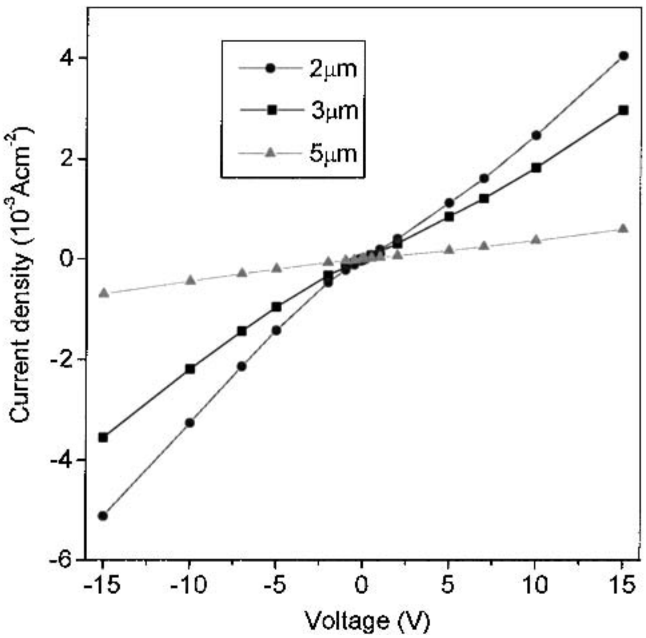

FIG. 5. *I-V* curves for the iodine-doped C_{60} whiskers with diameters of 2, 3, and 5 μm.

1.01 nm, respectively. The Miller indices are tentatively given by a body-centered-tetragonal (bct) system whose unit cell is indicated in the magnified image in Fig. 4(c), with the lattice constants $a = 1.01$ nm and $c = 2.10$ nm ($= d_1$). The arrows in Fig. 4(c) show the structure image of C_{60} molecules. Figure 4(d) is a filtered inverse fast fourier transform (FFT) image for Fig. 4(c), which was obtained by using the FFT spots of the 00*n* series ($n = 0, \pm 1, \pm 2, \ldots$). The (002) planes modulated and consisted of the wider planes with a spacing of 1.17 nm ($= d_2$) and the narrower planes with a spacing of 0.93 nm ($= d_3$). The corresponding (002) lattice plane spacing was 0.71 nm in face-centered-cubic (fcc) pristine C_{60} crystals with a lattice constant $a = 1.4166$ nm.[17] The wider planes with the spacing d_2 showed darker contrast than the narrower planes with the spacing d_3. Hence, it is conjectured that more impurity atoms were incorporated between the wider planes than the narrower planes.

The center-to-center distance between adjoining C_{60} molecules was 1.01 nm and very close to that of a pristine C_{60} crystal measured along its close-packed direction (1.00 nm). The above results suggest that impurity atoms were not interstitially incorporated between the adjoining C_{60} molecules polymerized along the close-packed direction of the I–C_{60} whisker. The expansion of (002) plane spacing is of great interest with respect to superconductivity, since higher superconducting transition temperature T_c could be obtained by increasing the lattice constant of C_{60} crystals.[14]

The *I-V* curves for iodine-doped C_{60} whiskers were obtained as shown in Fig. 5 by the use of the two-terminal method and In–Ga electrodes (impedance analyzer, Hewlett Packard 4192A, Tulsa, OK). The electrical resistivity of the iodine-doped C_{60} whiskers was measured to be about 1.4×10^6, 8.1×10^5 and 1.3×10^6 Ω cm for the whiskers with diameters of 2, 3, and 5 μm, respectively. These values of electrical resistivity were more than three orders of magnitude lower than that of pristine C_{60} crystals in the range 10^8 to 10^{14} Ω cm.[18] The nonlinear *I-V* curves indicated that the doped iodine acted as the source of carriers. A detailed study is necessary to clarify the origin of the nonlinear *I-V* curves.

In summary, the above results demonstrate that the LLIP method is a promising technique to fabricate halogen-doped single-crystalline fullerene whiskers and may be applicable to the formation of fulerene whiskers doped with the other elements such as alkali metals.

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