Synthesis of Fullerene Nanotubes by Liquid-liquid Interfacial Precipitation Method in the System of C_{60}-pyridine and Isopropyl Alcohol

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ABSTRACT

Nanotubes composed of C_{60} molecules (C_{60}NTs) were prepared at ambient pressure and temperature by liquid-liquid interfacial precipitation (LLIP) method using pyridine and isopropyl alcohol (IPA) for the solvent of C_{60} powder. The pyridine solution saturated with C_{60} was (a) exposed to UV (302 nm) and visible (436 nm) light, (b) mixed with IPA at 1:10, 1:9, 1:8, and 1:7 (C_{60}-pyridine:IPA) ratios, and (c) grown at temperature settings of 15°C, 10°C, and 5°C. Results show that specimens irradiated under visible light have higher yield of nanotubes, higher reproducibility, and faster growth rate. C_{60}NTs also form faster when prepared using 1:10 and 1:9 solvent ratios and incubated at 5°C temperature. Further, the diameter of C_{60}NTs varies widely when prepared using higher ratio but is relatively smaller and more uniform in solutions with lower ratio.

Keywords: fullerene, nanotubes, liquid-liquid interfacial precipitation, synthesis

1 INTRODUCTION

A fundamental problem relating to the synthesis of carbon nanotubes is the high production cost which hinders fabrication of sufficient amount of material. As a consequence, this also inhibits further discoveries of its many exceptional properties that may lead to various practical applications. The liquid-liquid interfacial precipitation (LLIP) method has recently demonstrated the feasibility of producing fullerene nanowhiskers at ambient pressure and temperature, and hence at a much sustainable cost [1-4]. These whiskers, which are single crystalline, have submicrometer diameters and hundred micrometers to millimeter in length, are precipitated at the liquid-liquid interface of fullerene-dissolved solution and isopropyl alcohol (IPA). LLIP has successfully produced single crystalline tubular fibers composed C_{60} [3] and C_{70} [2] fullerene molecules and their derivatives [5,6]. Fullerene nanowhiskers with hollow structures, "fullerene nanotubes", have also been synthesized by a modified LLIP method [7-10]. Using pure C_{60} and pyridine as solvent and by a slow addition of IPA, C_{60} nanotubes (C_{60}NTs) are precipitated and grown. These C_{60}NTs, with diameters larger than 300 nm, can be re-dissolved in proper solvents and can be useful as adsorbents, catalysts, and membranes [8]. The LLIP method is therefore a very promising technique for directly growing carbon nanotubes at low production costs.

In this work the LLIP method was further modified to produce significantly higher yield (~100%) of C_{60}NTs within a span of a few (1-3) days (yield is defined as the ratio of specimens with nanotubes and the total number of samples). It was found that the growth and morphology of C_{60}NTs are effectively influenced by (a) illumination with UV and visible light, (b) solvent ratio, and (c) incubation temperature. In this paper, we present a framework of the different experimental conditions applied (based on the parameters mentioned) that produce optimum reproducibility and growth yield of C_{60}NTs. Variations in the morphological and structural characteristics of the C_{60}NTs resulting from each experimental setting will also be investigated.

2 METHODS

The C_{60}NTs were prepared at room temperature (23-25ºC) and ambient pressure in a small-scale experimental set-up using 99.5+% pure C_{60} fullerene (MTR Ltd.) powder. The C_{60} powder was pulverized and dissolved in pyridine (0.9819 g/ml density) by applying a solubility factor of 0.3 mass% to form C_{60}-saturated pyridine solution. The resulting solution of C_{60}-pyridine was exposed to UV (302 nm) and visible light (436 nm) for 24 h before mixing with IPA (0.79 g/ml density). IPA was gently added to the pyridine solution saturated with C_{60} to form the liquid-liquid interface. The interface was prepared in a water bath set at 5ºC where both the IPA and the C_{60}-pyridine solutions were cooled before mixing. The nanotube solutions were mixed according to the following solvent ratios of C_{60}-pyridine:IPA, 1:10, 1:9, 1:8, and 1:7, and were later subjected to ultrasonic mixing for 2 minutes to enhance diffusion. The final products were stored in incubators with temperature settings of 5ºC, 10ºC, and 15ºC to grow the C_{60}NTs. Depending on the conditions set, C_{60}NTs can form within 24 h.

Ultra-high resolution SEM (Hitachi S-5500) and TEM (JEOL JEM 4010, 400 kv) images were taken combined with microscopic Raman spectrophotometer (JASCO, NRS-3100) analyses to determine disparities in the

morphology and structural character of the C_{60}NTs. Raman analyses were done immediately after the samples were air-dried.

3 RESULTS AND DISCUSSION

3.1 Yield and Growth Rate of C_{60}NTs

It has been reported that the growth rate of C_{60} nanowhiskers is significantly promoted by light illumination with wavelengths between 600-625 nm [11, 12]. It was suggested that photo-induced crystallization occurs as a consequence of direct interaction between the solute molecules and the electric field of the light. In this work, we found that the growth of C_{60}NTs is also enhanced by irradiation of light having wavelengths of 302 nm and 436 nm (with intensity of 13.7 mW/cm^2). Between the two spectra however, the use of visible light produced abundant yield of nanotubes at a much faster pace in contrast to UV light (Fig. 1). Visible light results to a more favorable formation of C_{60}NTs due to the increase absorption of the C_{60}-saturated pyridine solution in the 400-480 nm region [13].

High yield and growth rate of C_{60}NTs irradiated with visible light is more pronounced in mixtures with less amount of C_{60}-pyridine and incubated at cooler temperatures (Fig. 1). In particular, solutions prepared using 1:10, 1:9, and 1:8 (C_{60}-pyridine:IPA) ratios and stored at 5ºC and 10ºC produced 100% yield within 1-3 days only. In the case of 1:7 ratio, however, C_{60}NTs only formed when incubated at 5ºC (100% yield) and the growth is much slower (~2 weeks).

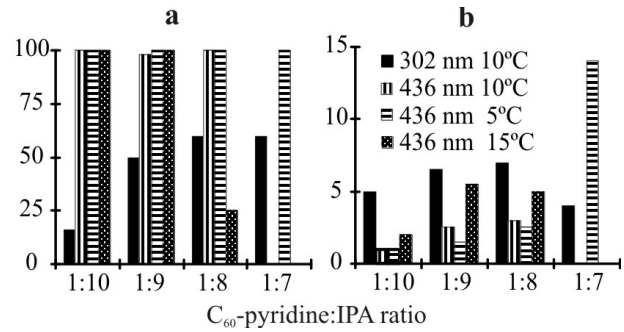

Fig. 1. Comparison of the yield (%; a) and growth rate (days; b) of C_{60}NTs synthesized at various experimental conditions.

3.2 Morphology and Structure of C_{60}NTs

In view of the above results, morphological and structural analyses were conducted only on C_{60}NTs

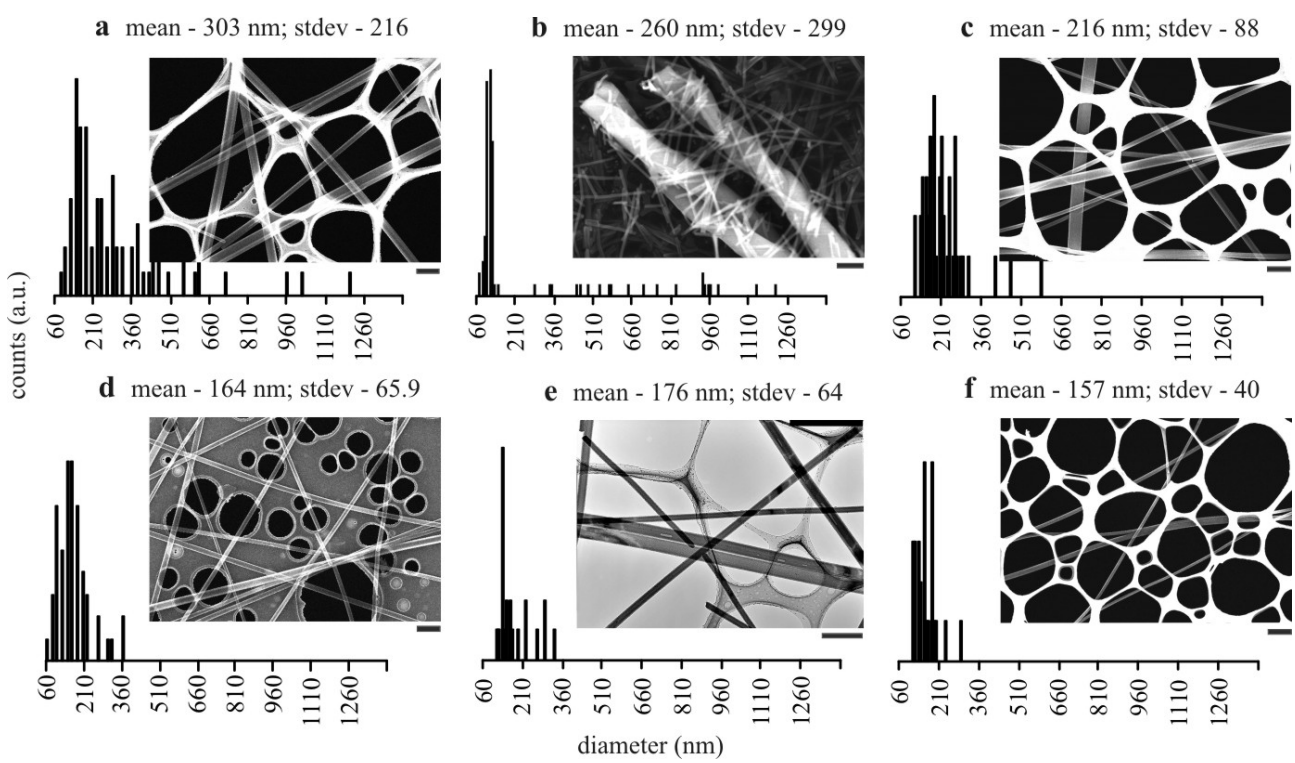

Fig. 2. Histograms of C_{60}NTs diameter derived from SEM and TEM micrographs show relatively thicker and more varied tube diameter in solutions with higher C_{60}-pyridine:IPA ratio (a-c) compared with lower ratios (d-f). The C_{60}NTs were prepared using 1:10 (a-c) and 1:8 (d-f) solvent ratios and grown at 5°C (a, d), 10°C (b, e) and 15°C (c, f) temperatures. Also calculated are the mean diameters and the standard deviations (stdev). Bar scale is 1 μm.

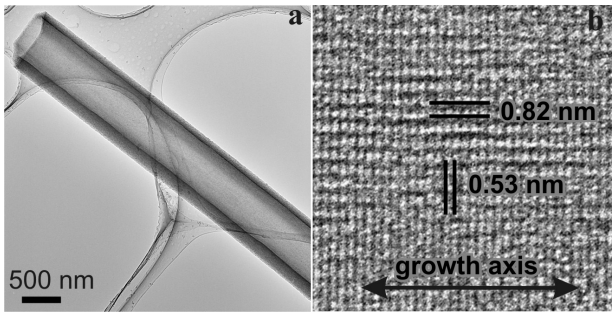

Fig. 3. TEM (a) and HRTEM (b) images of a typical nanotube prepared using 1:9 solvent ratio and stored at 15°C.

illuminated with visible light. The C_{60}NTs produced have a surface area of 26.2 m^2/g (BELSORP-max-2, Japan) and grow up to a few millimeters long. The diameter of the nanotubes prepared at different experimental conditions was measured using a series of SEM and TEM images and plotted on histograms (Fig. 2). Comparison of the results shows that the diameter of nanotubes is relatively more uniform and thinner (histogram peaks at 130-160 nm and ranges at 80-360 nm) in solutions more saturated with C_{60}-pyridine (Fig. 2d-f). In the case of 1:10 ratio, thinner C_{60}NTS are still dominant but the over-all thickness of the nanotubes has a much broader range (histogram peaks at 110-180 nm and ranges at 80-1200 nm; Fig. 2a-c). This trend is similar regardless of the growth temperature of C_{60}NTs, hence the tube diameter is dependent on the solvent ratio rather than temperature.

The uniformity of the tube wall along its growth axis and (Fig. 3a) and the crystalline structure of the nanotubes are evident in the TEM images taken on a nanotube prepared using 1:9 solvent ratio and grown at 15ºC (Fig. 3b). The nanotubes formed have external diameters ranging from 125-500 nm with inner diameters of about 40-200 nm. Wall thickness varies from less than 50 nm to above 100 nm. More detailed observation by high-resolution transmission electron microscopy shows densely packed C_{60} molecules along the tube wall (Fig. 3b).

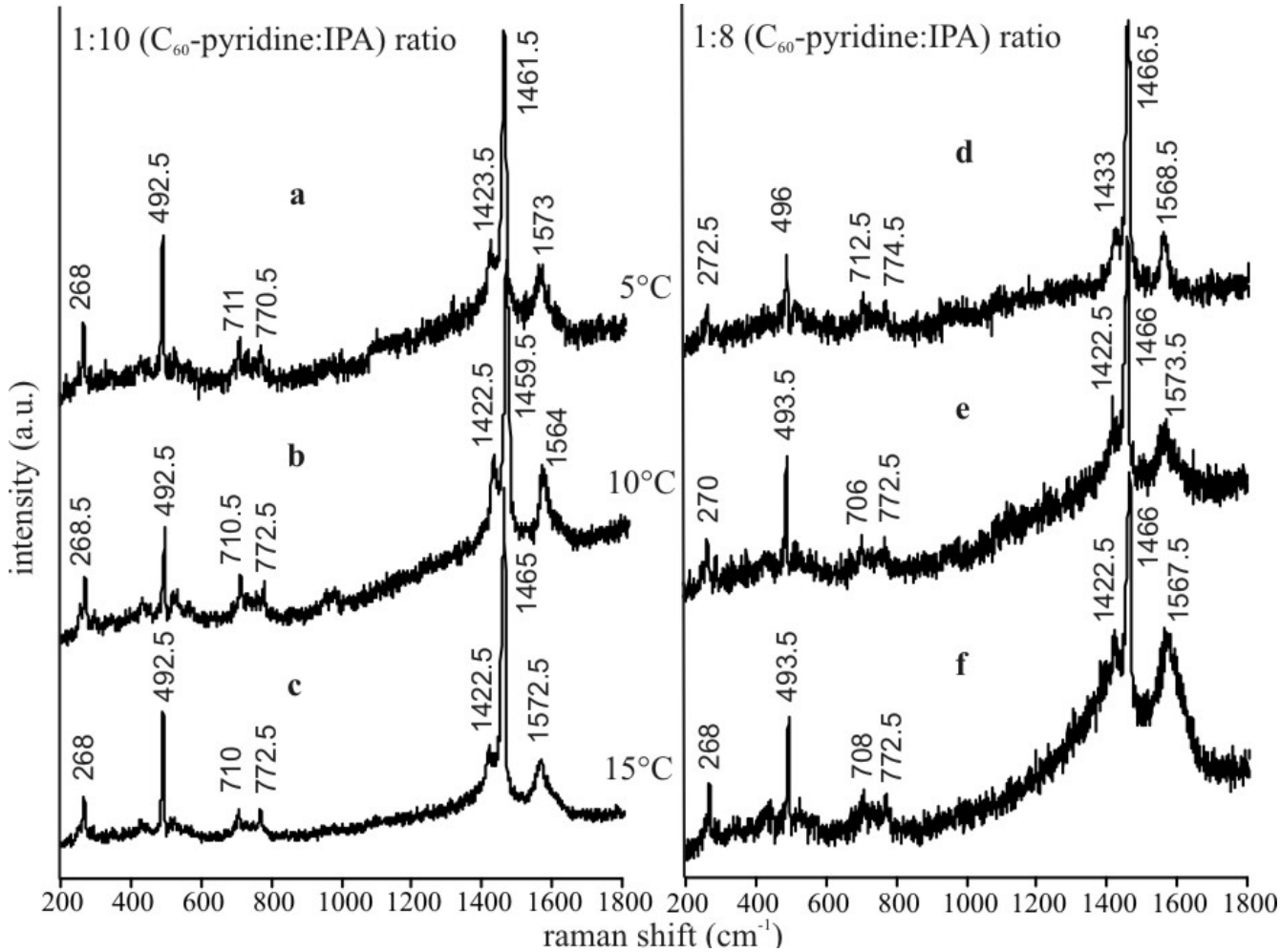

Fig. 4. Raman spectroscopic measurements of selected C_{60}NTs dried in air. The specimens were synthesized accordingly: (a) 1:10 solvent ratio and grown at 5°C; (b) 1:10 solvent ratio and grown at 10°C; (c) 1:10 solvent ratio and grown at 15°C; (d) 1:8 solvent ratio and grown at 5°C; (e) 1:8 solvent ratio and grown at 10°C; and (f) 1:8 solvent ratio and grown at 15°C.

Raman spectroscopic analyses of the C_{60}NTs show an overall similarity in the patterns of the raman shifts for both specimens synthesized with 1:10 and 1:8 (C_{60}-pyridine:IPA) mixtures and stored at 5ºC, 10ºC, and 15ºC temperatures (Fig. 4). However, a closer examination shows that the 1:8 spectra (Fig. 4 d-f) behave similar to the pristine C_{60} powder [14] while the 1:10 spectra (Fig. 3 a-c) have shifted to lower values in the 1400-1500 cm^{-1} region.

4 CONCLUSIONS

The yield and growth rate of C_{60}NTs are significantly promoted by irradiation with visible light (436 nm). Moreover, incubation at lower temperature, preferably 5ºC and using higher solvent ratio (1:10 and 1:9) also result to faster growth rate. The diameter of the C_{60}NTs is dependent on the solvent ratio rather than the growth temperature. C_{60}NTs are thinner and has more uniform width when fabricated using solutions mixed with relatively higher amounts C_{60}-pyridine solution.

REFERENCES

[1] K. Miyazawa and K. Hamamoto, J. Mater. Res., 17, 2205-2208, 2002.

[2] K. Miyazawa, K. Hamamoto, S. Nagata, and T. Suga, J. Mater. Res., 18, 1096-1103, 2003.

[3] K. Miyazawa, Y. Kuwasaki, K. Hamamoto, S. Nagata, A. Obayashi, and M. Kuwabara, Surf. Interface Anal., 35, 117-120, 2003.

[4] J. Minato and K. Miyazawa, Carbon, 43, 2837-2841, 2005.

[5] K. Miyazawa, T. Mashino, T. Suga, J. Mater. Res., 18, 2730-2735, 2003.

[6] K. Miyazawa, J. Minato, T. Mashino, S. Nakamura, M. Fujino, and T. Suga, Nukleonika, 51, S41-S48, 2006.

[7] K. Miyazawa and T. Suga, J. Mater. Res., 19, 3145-3148, 2004.

[8] J. Minato, K. Miyazawa and T. Suga, Sci. Tech. Adv. Mater., 6, 272-277, 2005.

[9] K. Miyazawa, J. Minato, T. Yoshii, M. Fujino, and T. Suga, J. Mater. Res., 20, 688-695, 2005.

[10] J. Minato and K. Miyazawa, Diamond Relat. Mater., 15, 1151-1154, 2006.

[11] K. Kobayashi, M. Tachibana, and K. Kojima, J. Cryst. Growth, 274, 617-621, 2005.

[12] M. Tachibana, K. Kobayashi, T. Uchida, K. Kojima, M. Tanimura and K. Miyazawa, Chem. Phys. Lett., 374, 279-285, 2003.

[13] J. Cheng, Y. Fang, Q. Huang, Y. Yan, X. Li, Chem. Phys. Lett., 330, 262-266, 2000.

[14] K. Miyazawa, C. Ringor, K. Nakamura, M. Tachibana, T. Masino, and S. Nakamura, this volume