Synthesis of Fullerene Nanotubes by Liquid-liquid Interfacial Precipitation Method in the System of C₆₀-pyridine and Isopropyl Alcohol

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ABSTRACT

Nanotubes composed of C₆₀ molecules (C₆₀NTs) were prepared at ambient pressure and temperature by liquid-liquid interfacial precipitation (LLIP) method using pyridine and isopropyl alcohol (IPA) for the solvent of C₆₀ powder. The pyridine solution saturated with C₆₀ 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 (C₆₀-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. C₆₀NTs also form faster when prepared using 1:10 and 1:9 solvent ratios and incubated at 5°C temperature. Further, the diameter of C₆₀NTs 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 C₆₀ [3] and C₇₀ [2] fullerene molecules and their derivatives [5,6]. Fullerenic nanowhiskers with hollow structures, “fullerene nanotubes”, have also been synthesized by a modified LLIP method [7-10]. Using pure C₆₀ and pyridine as solvent and by a slow addition of IPA, C₆₀ nanotubes (C₆₀NTs) are precipitated and grown. These C₆₀NTs, 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 C₆₀NTs 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 C₆₀NTs 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 C₆₀NTs. Variations in the morphological and structural characteristics of the C₆₀NTs resulting from each experimental setting will also be investigated.

2 METHODS

The C₆₀NTs were prepared at room temperature (23-25°C) and ambient pressure in a small-scale experimental set-up using 99.5+% pure C₆₀ fullerene (MTR Ltd.) powder. The C₆₀ powder was pulverized and dissolved in pyridine (0.9819 g/ml density) by applying a solubility factor of 0.3 mass% to form C₆₀-saturated pyridine solution. The resulting solution of C₆₀-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 C₆₀ to form the liquid-liquid interface. The interface was prepared in a water bath set at 5°C where both the IPA and the C₆₀-pyridine solutions were cooled before mixing. The nanotube solutions were mixed according to the following solvent ratios of C₆₀-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 5°C, 10°C, and 15°C to grow the C₆₀NTs. Depending on the conditions set, C₆₀NTs 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<sub>60</sub>NTs. Raman analyses were done immediately after the samples were air-dried.

3 RESULTS AND DISCUSSION

3.1 Yield and Growth Rate of C<sub>60</sub>NTs

It has been reported that the growth rate of C<sub>60</sub> 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<sub>60</sub>NTs is also enhanced by irradiation of light having wavelengths of 302 nm and 436 nm (with intensity of 13.7 mW/cm<sup>2</sup>). 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<sub>60</sub>NTs due to the increase absorption of the C<sub>60</sub>-saturated pyridine solution in the 400-480 nm region [13].

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

3.2 Morphology and Structure of C<sub>60</sub>NTs

In view of the above results, morphological and structural analyses were conducted only on C<sub>60</sub>NTs...
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 C₆₀NTs produced have a surface area of 26.2 m²/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 C₆₀-pyridine (Fig. 2d-f). In the case of 1:10 ratio, thinner C₆₀NTS 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 C₆₀NTs, hence the tube diameter is dependent on the solvent ratio rather than temperature.

The uniformity of the tube wall along its growth axis (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 15°C (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 C₆₀ molecules along the tube wall (Fig. 3b).

Fig. 4. Raman spectroscopic measurements of selected C₆₀NTs 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