

Synthesis of C₆₀ Fullerene Nanotubes by the Liquid-Liquid Interfacial Precipitation Method

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High yield (100%) of C₆₀ fullerene nanotubes have been successfully produced by the liquid-liquid interfacial precipitation method in a small-scale experimental set-up. These nanotubes were grown in the irradiated C₆₀-saturated pyridine and isopropyl alcohol (IPA) system combined at different ratios (1:10, 1:9, 1:8, 1:6 C₆₀-pyridine:IPA) and incubated at varying temperatures (15°C, 10°C, 5°C). Solutions irradiated under visible light (436 nm) produces higher yield of production and higher reproducibility compared with that illuminated with ultraviolet light (302 nm). The volume of nanotubes grown also increases with increasing ratio of C₆₀-pyridine:IPA and decreasing temperature of incubation. Scanning electron microscopic observations show thinner nanotubes prepared with lower amount of IPA. At present, the process of scaling up the procedure to obtain gram quantities of nanotubes is under investigation. Such work will prove beneficial in obtaining more information on its physical and mechanical properties.

Key words: C₆₀ fullerene, liquid-liquid interfacial precipitation, synthesis, nanotubes

1. INTRODUCTION

Over the past few years, the liquid-liquid interfacial precipitation (LLIP) method has been effectively used to create nanowhiskers, nanofibers, and nanotubes composed of fullerene molecules such C₆₀, C₇₀, and their derivatives [1-9]. Since then, there has been a growing demand to discover their unique physical and chemical properties for promising applications in the field of energy storage, electronics, and semiconductors [10]. In particular, C₆₀ fullerene nanotubes (C₆₀NTs) have attracted considerable attention because of their novel and optoelectronic properties not reported in related structures and materials to date [11]. Our group has successfully fabricated C₆₀NTs at ambient pressure and temperature and is now providing C₆₀NTs to other research institutions and metal industries which are working in developing more functional devices from such materials. For example, the use of nanotubes for absorbing metals in waste liquid was recently investigated [12].

The LLIP method is a simple and direct approach in synthesizing C₆₀NTs and has the advantage of having very low production cost. However, a major drawback in the previous syntheses is the low production yield (25%) and growth speed of C₆₀NTs (1-2 weeks). We provide an improved method in fabricating C₆₀NTs that produces higher yield (as much as 100%) at a considerably shorter time frame (1-3 days).

2. METHODS

The experimental procedures for the fabrication of C₆₀NTs described in [5-7] were modified. The C₆₀ fullerene used has a 99.5+0% purity (MTR Ltd.) and was finely powdered using mortar and pestle. The pulverized C₆₀ was dissolved using 99.5% pyridine

(density 0.9819 g/ml) in an ordinary glass vial by applying the dissolution factor of 0.3% mass to form the C₆₀-saturated pyridine solution. To obtain maximum dissolution of the C₆₀ fullerene, the solution was ultrasonicated for 30 min and was filtered afterwards using Kiriya funnel (no. 5C filter and 21φ mm funnel). It was reported that the growth of C₆₀ nanowhiskers is significantly promoted by illumination with visible light at wavelengths between 600-625 nm [13]. For comparison, the filtered solution was exposed to UV (302 nm) and visible light (436 nm) for 24 h which resulted to a change in color from dark purple to yellowish brown. The observed color change was proposed to be a result of a stepwise addition of pyridine to C₆₀ [15]. After irradiation, the solution was filtered one more time using the same materials. The second solvent used is isopropyl alcohol (IPA; density 0.79 g/ml) which forms poor-solvent systems and having low solvency for fullerenes. IPA was gently added to the C₆₀-saturated pyridine solution using autoclavable pipette to form the liquid-liquid interface. The set-up was done at room temperature in a water bath fixed at 5°C and using transparent glass vials with 21 mm external diameter and 10 ml capacity. After adding IPA, the solution was mixed in a ~5°C ultrasonic bath for 1 min, followed by manual mixing, and another 1 min sonication. The vials were then sealed to avoid evaporation of the solvents and were stored in an incubator to grow C₆₀NTs.

Various conditions were established during the experimentation. These conditions include the different wavelengths of light used to irradiate the initial C₆₀-saturated pyridine solution, the ratio of fullerene

solution and the second solvent used to form the liquid-liquid interface, and the temperature of the incubators where the C_{60} NTs were stored. The starting C_{60} -pyridine solution was irradiated using wavelengths of 436 nm and 302 nm and was mixed with IPA using 1:10, 1:9, 1:8, and 1:6 ratio (C_{60} -pyridine:IPA). The C_{60} NTs were grown in refrigerators at three different settings, 15°C, 10°C and 5°C. In this work, yield is defined as the ratio between the number of specimens with nanotubes and the total number of specimens.

Ultra-high resolution scanning (Hitachi S-5500) and transmission (JEOL JEM 4010, 400 kv) electron microscopes were used to determine the morphology and structural character of the C_{60} NTs.

3. RESULTS AND DISCUSSION

3.1 Yield of C_{60} NTs

Illumination with UV light (302 nm): Out of 20 specimens prepared using 1:10 ratio of C_{60} -pyridine:IPA and incubated at 10°C, only 11 bottles contained C_{60} NTs (55% yield), which grew after 3-7 days (Fig. 1). The amount of C_{60} NTs (done through visual examination only) varies from very low-low. For 1:9 ratio, the results show a 50% yield of C_{60} NTs (10 out of 20 bottles have nanotubes). It took 2-22 days for the nanotubes to grow and deposited very low-low amounts. For 1:8 ratio, this condition generates a 49% yield of C_{60} NTs (11 out of 23 bottles contain very low-low amount of nanotubes), which became visible starting from 2-21 days. For 1:6 ratio, 1 out of 5 bottles (20% yield)

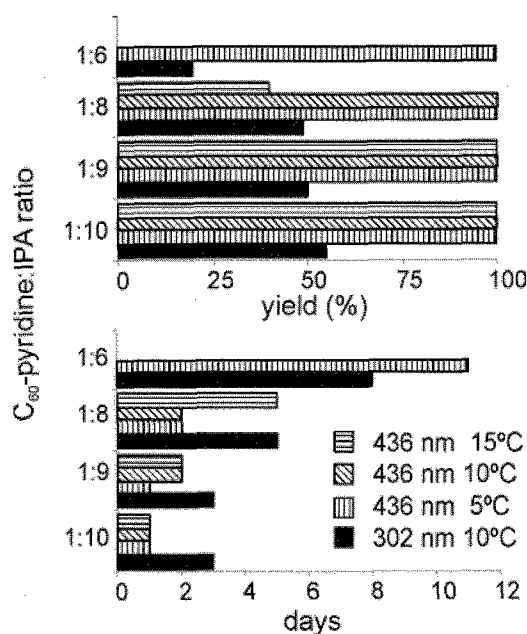


Fig. 1. Comparison of the yield and growth speed of C_{60} NTs between UV and visible light-illuminated specimens prepared using varying ratios of C_{60} -saturated pyridine:IPA and grown at different temperatures.

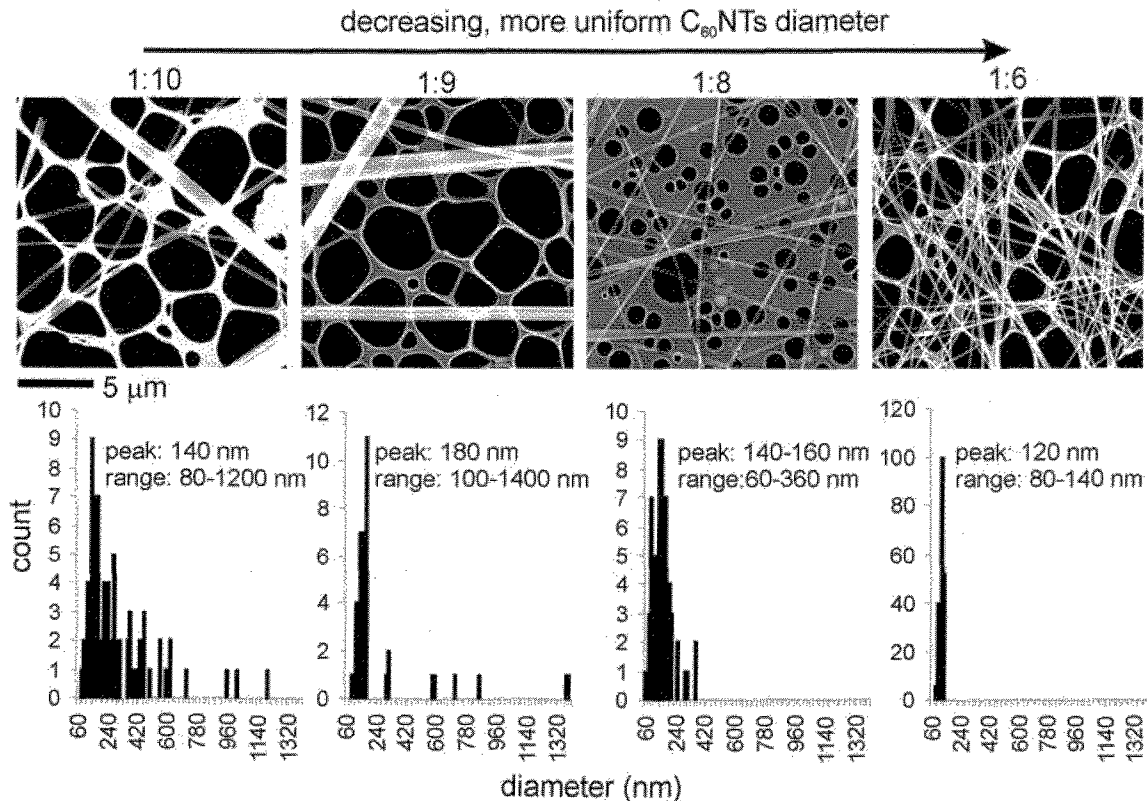


Fig. 2. SEM images of C_{60} NTs illuminated with visible light (436 nm) and grown at 5°C using varying solvent ratios. Histograms show the outer diameter of C_{60} NTs measured using a series of SEM photos. The diameter of the tubes decreases with increasing amount of concentrated C_{60} -pyridine in the solution.

contained very low amount of C₆₀NTs which started to grow after 8 days.

Illumination with visible light (436 nm): Irradiation under this wavelength generated a radical increase in the amount of C₆₀NTs within shorter periods of time (Fig. 1). This occurrence is possibly due to a variation in the UV-visible absorption of the irradiated C₆₀-saturated pyridine solution which is known to increase visibly in the 400-480 nm region [14]. The specimens stored in an incubator set at 5°C produces 100% yield for 1:10 (20 bottles), 1:9 (20 bottles), 1:8 (20 bottles), and 1:6 (5 bottles) ratios of C₆₀-pyridine:IPA which grew within 1 day, 1-2 days, 1-4 days and 8-14 days, respectively (Fig. 1). About 18 mg of dried C₆₀NT can be collected for 1 L of solution containing 1:10 mixture of C₆₀-pyridine:IPA in one day. The amount of C₆₀NTs is comparable for 1:10, 1:9, and 1:8 ratios while it becomes lesser using the ratio of 1:6. It is worth noting that for specimens irradiated using 436 nm wavelength, only at 5°C does the ratio of 1:6 C₆₀-pyridine:IPA successfully produced nanotubes.

In conditions when the growth temperature is 10°C and the C₆₀-pyridine:IPA ratio is 1:10, a 100% yield (10 bottles) of relatively higher amounts of C₆₀NTs also occurred within 1 day. For 1:9 and 1:8 ratios, the yield is still 100% but the C₆₀NTs grew within 1-5 days. No nanotubes were formed when prepared using the 1:6 C₆₀-pyridine:IPA ratio.

For C₆₀NTs stored in an incubator set at 15°C, higher C₆₀-pyridine:IPA ratio produces more nanotubes within shorter period of time. For 1:10 ratio, all the 10 specimens have started growing C₆₀NTs (100% yield) at a rate of 1-3 days. For 1:9 ratio, it took 2-15 days for the all the nanotubes to grow (100% yield for 10 bottles). For 1:8 ratio, only 4 out of 10 bottles produced nanotubes (40%) within 5 days. As with 10°C growth temperature, no C₆₀NTs were formed in the 10 specimens prepared using 1:6 ratio of C₆₀-pyridine:IPA.

It is evident that the optimum growth condition of C₆₀NTs is confined in solutions with 1:10 and 1:9 mixture of C₆₀-pyridine:IPA incubated at 5°C. It is unclear how the growth of C₆₀NTs is diminished in solutions containing more concentration of C₆₀-saturated pyridine. At the interface between C₆₀-pyridine and IPA, the nucleation conditions are expected to be the same in different mixture of solutions. It is possible that when the solutions are homogenized, IPA acts as an efficient catalyst for nanotube formation. Another

factor is the role of light in the promotion of C₆₀NTs growth. The possibility that light is less absorbed in solutions with more amount of C₆₀-pyridine during incubation may also hinder the formation of C₆₀NTs. It is expected that further studies will provide a more detailed explanation for the growth mechanism of C₆₀NTs by LLIP method.

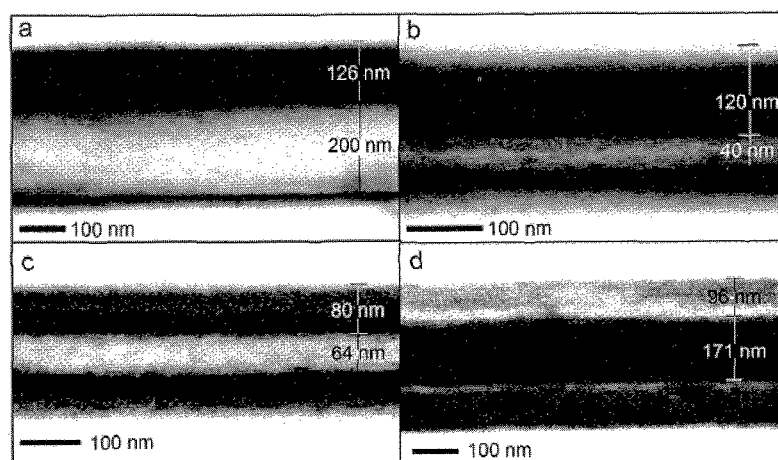
3.2 Morphology and Structure of C₆₀NTs

SEM images of specimens illuminated with 436 nm show that the diameter of nanotubes generally increases with increasing C₆₀-pyridine:IPA ratio (Fig. 2). C₆₀NTs also exhibit large variation in width at higher ratios but are more uniform at solutions with more amount of C₆₀-saturated pyridine. This variation was observed at 5°C, 10°C, and 15°C incubation temperatures indicating that C₆₀NT thickness is more dependent on the solvent ratio. For mixtures of 1:10 and 1:9 C₆₀-pyridine:IPA, although the peaks of the histograms point to relatively thinner tubes, (140 nm and 180 nm in diameter, respectively), quite a number of very thick nanotubes, (>400 nm) were also observed. In contrast, for solutions prepared using lower ratios, 1:8 and 1:6, there is a drastic shift to the lower values in the histograms. C₆₀NTs are predominantly 140-160 nm thick in 1:8 ratio, but a few have diameter of more than 200 nm. However, for 1:6 ratio, the tubes are very thin, ≤120 nm, and do not exceed 150 nm in diameter.

A closer look shows C₆₀NTs with different thickness of tube wall and inner diameter (Fig 3). About 126 nm thick wall and 200 nm width of inner diameter were measured from a C₆₀NT prepared using 1:10 C₆₀-pyridine:IPA ratio and grown at 15°C (Fig 3a). Another tube, on the other hand, has a very small hole, 40 nm, and has a thick tube wall, 120 nm (Fig 3b). Using 1:8 ratio, but incubated at the same temperature setting, a C₆₀NT was found which has approximately 80 nm thick tube wall and smaller inner diameter of about 64 nm (Fig. 3c). Another measurement was taken from a tube formed from a solution of 1:10 C₆₀-pyridine:IPA and stored at 10°C (Fig. 3d). The tube wall is about 96 nm thick and the inner diameter is relatively wider, 171 nm.

Figure 4 shows a TEM image of a C₆₀NT fabricated using 1:9 ratio of C₆₀-pyridine:IPA and grown at a temperature of 15°C. The nanotube is at least 218 μm long and has an outer and inner diameter of approximately 741 nm and 518.5 nm, respectively. The tube wall is about 148 nm and is virtually uniform

Fig. 3. SEM images of C₆₀NTs prepared using different solvent ratios (C₆₀-pyridine:IPA) and incubation temperature. (a, b) 1:10, 15°C, (c) 1:8, 15°C, and (d) 1:10, 10°C.



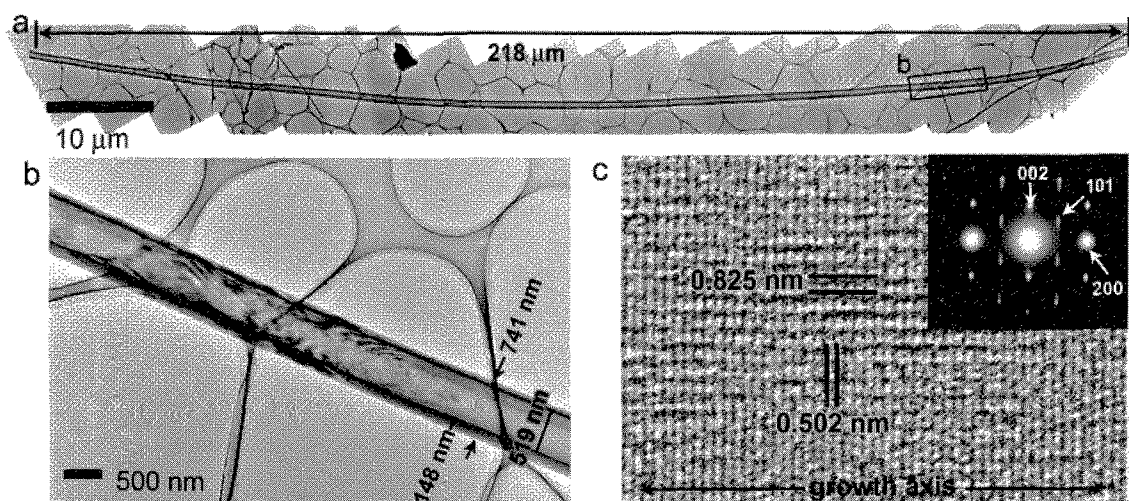


Fig. 4. TEM image of a C_{60} NT illuminated with visible light (436 nm) and prepared in a 1:9 solution of C_{60} -pyridine:IPA at 15°C. (a) The tube is free of internal impurities along its growth axis and shows (b) extinction fringes in some areas. (c) HRTEM image shows densely packed C_{60} molecules along the tube wall. Assuming a body-centered tetragonal structure, the lattice constants a and c derived from the electron diffraction pattern (inset) are calculated to be 0.985 nm and 1.60 nm, respectively.

along its growth axis. The tube is also free from clogging along its entire length and exhibit extinction fringes (Fig. 4a) in some areas indicating that the C_{60} NT is single crystalline [9]. The crystalline structure of the C_{60} NT is more evidently manifested in a high resolution TEM image taken on the tube wall (Fig. 4b). Densely packed C_{60} molecules are distinctly recognizable along the growth axis of the nanotube. The lattice plane spacings were calculated using the inset electron diffraction pattern shown in Fig. 4c. The (002), (101) and (200) plane spacings have respective values of 0.824 nm, 0.833 nm, and 0.493 nm. Assuming a body-centered tetragonal structure [3], the lattice constants a and c are calculated to be 0.985 nm and 1.65 nm, respectively.

4. CONCLUSIONS

Synthesis of C_{60} NTs by photo-irradiation of C_{60} -pyridine using 436 nm wavelength produces higher yield of nanotubes and higher reproducibility compared with that illuminated with ultraviolet light (302 nm). In both cases, though, the ratios of C_{60} -pyridine:IPA that create significant amount of nanotubes at a much higher speed (which means that nanotubes are visibly grown on the first day of incubation) are both 1:10 and 1:9. The growth of nanotubes is also definitely affected by the incubation temperature. The lowest temperature, 5°C, results in higher and faster production of nanotubes. At 15°C, the growth rate decreases with decreasing C_{60} -pyridine:IPA ratio.

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