Formation mechanism of fullerene peapods and coaxial tubes: a path to large scale synthesis

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Abstract

A method to functionalize nanotubes by filling could enable the creation of new materials for molecular scale devices. Here we report the synthesis of chains of $C_{60}$ molecules inside single-wall carbon nanotubes (SWNTs). $C_{60}$ molecules are seen to deposit on the surfaces of SWNTs from the gas phase and to enter the tubes, ostensibly via defects. They subsequently self-assemble into Van der Waals interacting chains, called 'bucky-peapods.' Upon high temperature annealing, encapsulated $C_{60}$ molecules coalesce into interior tubes, forming pairs of nested graphene cylinders. The synthesis methods described herein suggest a more general way in which nanotubes may be functionalized.

Following the production of single wall carbon nanotubes by the pulsed laser vaporization (PLV) method [1], it was proposed that the most abundant nanotube was optimally sized to encapsulate a $C_{60}$ molecule [2]. We recently discovered that this is correct. These unique 'peapods' naturally occur, albeit at low concentrations, in PLV synthesized material that has been acid purified and vacuum annealed at 1100°C [3]. Two-wall nanotubes whose inner tubes have the same diameter as the $C_{60}$ molecule are seen to exist in this same material in even lesser abundance [4]. Due to the linear confinement of their constituent $C_{60}$ molecules [4], peapods enable for the first time the empirical study of one-dimensional phenomena including diffusion and phase transformations. Furthermore, electronic band structure calculations have shown that a peapod could exhibit a superconducting transition upon doping [5]. Mechanics theory predicts that a two-wall tube has superior resistance to bending [6] than an empty nanotube, whose elastic modulus (~1 TPa) is already the largest that has ever been measured [7]. These properties are highly desirable for use in molecular electronics and composite materials applications. However, the mechanism by which these structures are formed cannot be explained in analog to the filling of large diameter multiwall nanotubes (MWNTs) with low surface tension liquids by capillarity [8–16] due to fundamental differences in size and chemistry. This mechanism must be understood if bulk quantities are to be produced for study or application.

In this Letter, two materials are employed. The first was synthesized by the laser ablation of a...
graphitic target impregnated with 0.6 at% each Ni/Co catalyst. This raw nanotube ‘mat’ was refluxed in HNO₃ for 48 h, rinsed and neutralized, suspended in surfactant, and filtered to form a thin paper [17]. The second was synthesized by carbon arc (CA) discharge using 4.2/1.0 at% Ni/Y catalyst [18] and then similarly purified [19]. Such wet chemical etching is known to open the ends of nanotubes [15,20] as well as attack their sidewalls [21].

High resolution transmission electron microscopy (HRTEM) remains the only technique that can reliably detect these hybrid structures. We examined a number of materials by HRTEM in the as-synthesized condition, after acid purification, and after subsequent ex-situ or in-situ anneals under a vacuum of 20–40 μPa at temperatures of 100–1200°C. Temperature was monitored continuously via thermocouples. During in-situ experiments, only a few minutes were required to ramp between temperatures due to the small mass of the heater. Specimens were prepared from nanotube paper by tearing away a small sliver and fixing it inside an oyster TEM grid, thereby forgoing additional chemical or thermal processing.

It has proven impossible to determine by observation if peapods are present in raw PLV material due to the large quantity of carbonaceous impurities that decorate individual nanotubes and nanotube ropes. Even after acid purification and drying, the isolated nanotubes as well as bundles remain coated with a thin layer of surfactant that obscures fine detail and makes it difficult to assess whether or not peapods are present. The HRTEM micrograph in Fig. 1a shows this condition. Nevertheless, we have examined thousands of as-purified nanotubes and have

Fig. 1. HRTEM micrographs of nanotubes produced by PLV and subsequently acid purified. (a) A bundle in the unannealed, as-purified sample. (b) The same sample after vacuum annealing for 63 h at 225°C. A tube severed by acid treatment is indicated with an arrow. (c) The same sample after reannealing for 2 h at 450°C. Many peapods are present. The arrow indicates a well-focused area. Scale bar, 10 nm.
never detected the conspicuous periodic contrast of peapods.

We have found that baking as-purified material in vacuo at 225°C produces a general cleaning of the nanotubes. Fig. 1b shows the same sample of Fig. 1a after additional treatment for 63 h at 225°C. The nanotubes are free of most impurities, although X-ray diffraction [17] and TEM observation confirm the presence of C₆₀ crystallites. The walls of the nanotubes appear as dark parallel lines and are seen to have breaks and disclinations (as indicated with arrows) that are the result of acid attack. Several hundred tubes were observed at various locations and were found to be empty.

The sample of Fig. 1a and b was reannealed for 2 h at 450°C. Fig. 1c shows a representative micrograph of the resultant material. The walls of the tubes are partially healed. Many tubes, both isolated and comprising ropes, are seen to contain C₆₀ chains. These appear as regularly spaced strings of 0.7 nm diameter circles (C₆₀ molecules) between two parallel lines separated by 1.4 nm (corresponding to the diameter of the surrounding nanotube). Although many tubes are unavoidably defocused due to the large depth of the sample, the contrast signature of each C₆₀ chain remains clearly recognizable. A well-focused area is indicated with an arrow.

The data indicate that peapods are formed during the annealing treatment following acid purification, requiring that residual exterior C₆₀ arrives at nanotube ends or sidewall defects via surface diffusion and/or transport in the vapor phase. This phenomenon is demonstrated by the following experiment. A specimen was prepared from PLV material and subsequently cleaned by baking for 24 h at 225°C. The temperature was then cycled in the range 225–375°C, equilibrating at 25°C increments for observation. The sequence in Fig. 2 was recorded at

Fig. 2. Consecutive micrographs taken 15–30 s apart during in situ annealing of PLV material at 350°C. The sequence shows the mobility of exterior C₆₀ molecules, which appear as circles 0.7 nm in diameter and occupy different positions in each image. A fixed position is indicated with an arrow. Scale bar, 5 nm.
350°C with 15–30 s between images. The nanotubes, which were originally clean, now have C$_{60}$ molecules adsorbed to their surface. The fullerenes adsorb to locations on the nanotubes for only transient times before vanishing so quickly as to be undetectable to the eye. The occupied locations appear to be random. During exposure to the electron beam, individual fullerenes are damaged and become fixed in position.

Mobility has been observed in situ only at furnace temperatures exceeding 325°C. At the microscope column vacuum of 40 μPa, the sublimation temperature of solid C$_{60}$ is reported to be approximately 375°C [22]. The agreement of these temperatures suggests that C$_{60}$ is most likely to arrive at a nanotube via the vapor phase. At the sublimation temperature of solid C$_{60}$, it might be expected that C$_{60}$ molecules are more strongly bound to a SWNT than to each other due to the greater number of carbon–carbon Van der Waals interactions in the former case. Thus once a fullerene arrives at a nanotube, surface diffusion to an open end or sidewall defect could occur. As the temperature is increased, the residence time of C$_{60}$ on the surface of the SWNT – and thus the probability of that molecule entering the SWNT – decreases. Once the C$_{60}$ molecules enter, the stabilizing Van der Waals coordination with the surrounding tube causes them to be retained inside. Self-assembly into chains subsequently occurs because the interior fullerenes are still mobile, thereby increasing each molecule’s coordination even further.

A test of the mechanism of peapod formation was conducted using acid purified CA material, which is expected to have little exterior C$_{60}$ due to its comparatively high catalyst concentration. Two specimens were prepared from the as-received paper. The first served as a control, while a drop of C$_{60}$ suspended in dimethyl formamide was added to the second, which was then air dried. Preliminary TEM observation of both samples confirmed that the tubes were damaged with open ends, that peapods were absent, and that C$_{60}$ crystallites were sparse in the control sample and abundant in the experimental sample. Each was annealed for 1 h at 400°C. Large numbers of peapods were found in the experimental sample as shown in Fig. 3. In the control sample, a very low concentration of peapods was found, consistent with the small amount of C$_{60}$ seen in the as-purified CA material. In general, no difference could be detected between the peapods produced in the PLV synthesized SWNTs and those in the CA synthesized SWNTs.

The positive correlation between the amount of exterior C$_{60}$ pre-annealing and the amount of interior C$_{60}$ post-annealing evidences that C$_{60}$ molecules enter the tubes during heat treatment. This is corroborated by the fact that large (≈ 3 nm) diameter tubes

Fig. 3. A bundle of CA produced nanotubes vacuum annealed for 1 h at 450°C after C$_{60}$ suspended in dimethyl formamide was added to the sample. A very high fraction of the tubes contain C$_{60}$ chains. Scale bar, 10 nm.
are observed to contain irregularly arranged clusters of C$_{60}$ near their ends, as shown in Fig. 4. Previous reports of microscopic and macroscopic inhomogeneities in the distribution of peapods [4] are now easily explained. Encapsulated C$_{60}$ chains are expected in samples having a high exterior C$_{60}$ concentration, and intra-sample microsegregation is related to the initial distribution of C$_{60}$ throughout the bulk as well as to the time and temperature of heat treatment.

The related CAT structures, consisting of nested 0.7 nm and 1.4 nm diameter tubes, can be synthesized by high-temperature processing of C$_{60}$ chains. Consider that no CATs have been observed in nanotube samples annealed in situ at temperatures up to 900°C, while they were initially discovered in material that was annealed above 1100°C. We have investigated this by annealing a PLV sample ex situ for 2 h at 450°C in order to produce C$_{60}$ chains and subsequently holding the sample for 24 h at 1200°C. After furnace cooling, the sample was examined in the microscope, where CATs were observed in lieu of interior C$_{60}$. It is conceivable that at 1200°C, neighboring C$_{60}$ molecules have a reasonable probability of colliding with sufficient kinetic energy to cause them to coalesce within the time frame of the experiment. The surrounding SWNT thus acts as a reaction container, ensuring a near-zero impact parameter and templating the fused product into a 0.7 nm diameter SWNT. The fusion of two C$_{60}$ molecules during unconstrained, high kinetic energy impact has been confirmed in tight-binding molecular-dynamics simulations [23].

The mechanism for the formation of encapsulated C$_{60}$ chains is now apparent. We have successfully synthesized them in large fractions of the tubes that comprise our samples as well as explained why they are not present in raw and acid purified material. In contrast to prior studies showing the uptake of liquid into large diameter MWNTs, the mechanism involves transport in the vapor phase, and SWNTs with small interior diameters are completely filled over long lengths. The extent of filling argues for the entrance of C$_{60}$ through sidewall defects as well as open ends. A minimum temperature of ~325°C must be achieved in order to promote exterior C$_{60}$ to enter the tubes on a reasonable time scale. Similarly, a maximum temperature is imposed by the fact that high temperature limits the residence time of C$_{60}$ on a SWNT as well as heals the nanotubes’ walls, thereby eliminating access to their interiors. Since formation is governed by both time and temperature, nanotube material must be soaked in, and not ramped through, this critical temperature window in order to produce peapods in abundance.

The ability to synthesize these unique hybrid materials in bulk now permits scaled-up empirical study. Furthermore, there is no reason why SWNTs could not be filled with any appropriately sized molecule having an affinity for nanotubes and existing in the gas phase at temperatures within the critical temperature window. The present report opens the possibility for the general functionalization of SWNTs, regardless of the means by which they were produced.

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