

# A STUDY OF CARBON NANOTUBE PEAPOD MATERIALS

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## ABSTRACT

*The remarkable electronic and mechanical properties of carbon nanotubes are widely acclaimed, but these molecules also have a unique structure that encapsulates a one-dimensional volume of space. The promise afforded by this structure is often overlooked. Carbon nanotubes have the capability to contain or transport other atoms, molecules, or crystalline materials inside. The constrained lumen of a nanotube could be a novel reaction chamber, catalyzing the synthesis of new compounds by forcing reactants and products to adopt specific conformations. Perhaps most importantly, the intrinsic properties of nanotubes could be modified by filling with species that have opportune magnetic, electronic charge transfer, absorption, mechanical, catalytic, or thermal characteristics.*

*Such nanoscale heterostructures could have broadly tunable properties, but the components are not covalently associated, so the chemistry and mechanical integrity of the underlying nanotube is preserved. Because of this potential, filling methods are certain to play a critical role in the evolution of carbon nanotubes as engineering materials.*

**Keywords-** carbon nanotubes, synthesis, nanostructure.

## I. INTRODUCTION

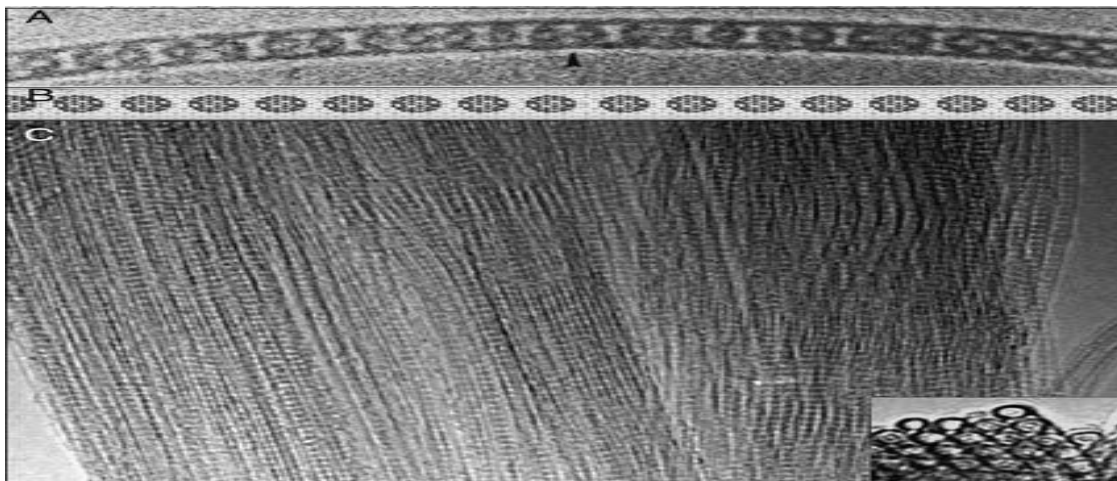
The deceptively simple one-dimensional structure of a carbon nanotube gives rise to a host of fascinating mechanical, electrical, field emission, and optical properties. Among carbon nanotubes, single-wall nanotubes have

been the most extensively studied because a direct comparison can often be made between theoretical properties and experimental measurements. As nanotubes encompass a lumen in their structure, they afford a rich reaction space for nanoscale experiments, such as insertion and manipulation of atomic, ionic, or molecular species. This has afforded the potential of tuning the intrinsic properties of carbon nanotubes. Initial efforts to create hierarchical nanotube materials focused on filling multiwall carbon nanotubes (MWNTs) with metal complexes and related

species. Following the discovery of single-wall carbon nanotubes (SWNTs) and their bulk synthesis, various attempts were made to fill them with metal chloride and metal species by capillarity. However, these attempts

suffered from heterogeneity and limited yield. Thus, it was somewhat surprising when a new class of filled nanotube materials based instead on encapsulated fullerenes was discovered in 1998. The canonical structure was referred to as a peapod (C60@SWNT) and consisted of C60 molecules self-assembled inside the lumen of a single-wall nanotube, obtained by a vapor phase filling process. Since then, various molecular species have been considered for filling and modifying SWNTs, yielding myriad new hybrid materials with unique structural characteristics. **C60@SWNT**

The first peapods, depicted in Fig.1, were discovered by transmission electron microscopy (TEM) as self-assembled C60 molecules inside SWNTs produced by laser vaporization and processed by chemical etching and annealing. The fullerene molecules were co-formed during the laser vaporization process along with the nanotubes and assembled during the vacuum annealing process. This novel material is termed C60@SWNT, where @ is read “contained by” by analogy to the naming convention used in metallofullerene chemistry. An example of a fullerene-filled rope illustrating the characteristic peapod contrast is shown in 1. Following the initial discovery, chemical characterization corroborated that the discrete molecules inside the SWNTs were indeed C60 fullerenes. However, experiments to characterize the structure and property

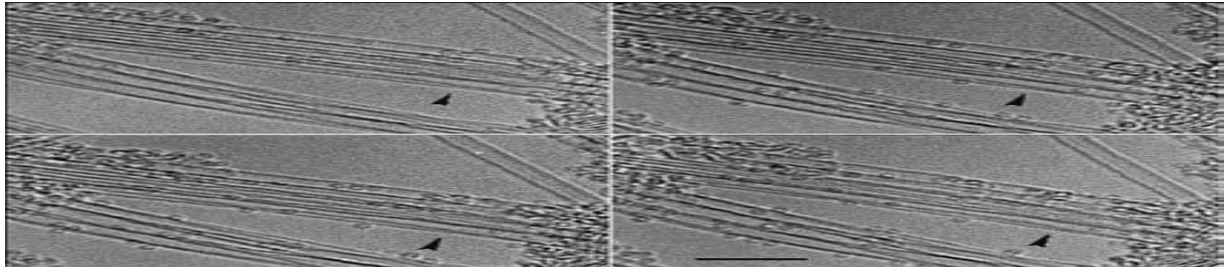


**Figure 1 High-resolution transmission electron microscopy (HRTEM) micrograph of isolated peapod illustrating the one-dimensional array of fullerene C60 molecules filled inside a SWNT. (b) The molecular model of the peapod structure showing the spherical molecules of C60 of 0.7 nm diameter encapsulated inside a ~1.4-nm (10, 10) nanotube. (c) Illustrates the TEM micrograph of a SWNT rope filled with C60 molecules showing characteristic image contrast.**

## II. MECHANISM OF FORMATION

To determine the mechanism of peapod formation, Smith and Luzzi performed a novel *in situ* experiment involving the exposure of a nanotube bucky paper sample to a fullerene vapour generated *in situ* during TEM imaging.<sup>16</sup> As the temperature of the stage was ramped to about 325°C, corresponding to the sublimation temperature of C60 at the microscope column pressure, impurity C60 fullerenes present in the sample vaporized and bombarded the surfaces of SWNTs via dynamic adsorption and desorption. It was proposed that diffusion of the fullerenes along the nanotubes facilitated access to the nanotubes' interiors through defective regions, e.g. Open caps or sidewall defects. The micrographs illustrating the successive events during this experiment are

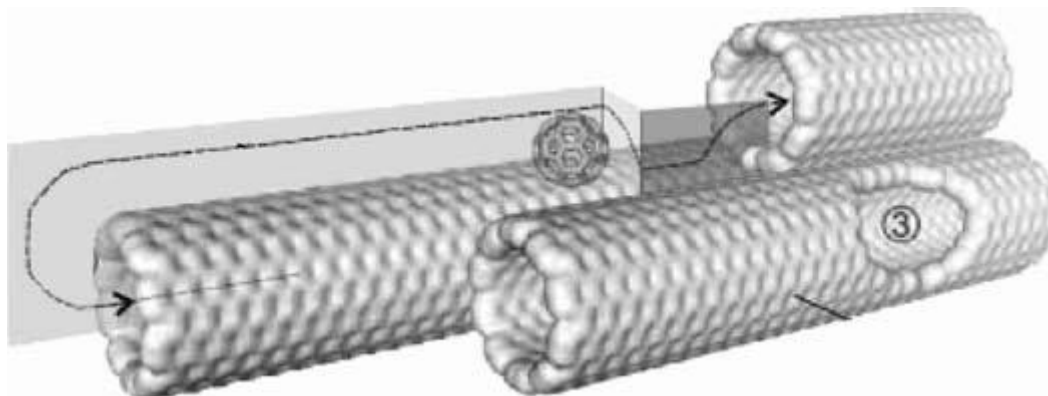
shown in Figure 2. The molecules are seen to be mobile in successive frames, and they ostensibly fill the nanotubes once they encounter openings. Once the fullerenes are encapsulated by a nanotube, they evidently self-assemble into a linear chain, which has been found to be the energetically favoured configuration



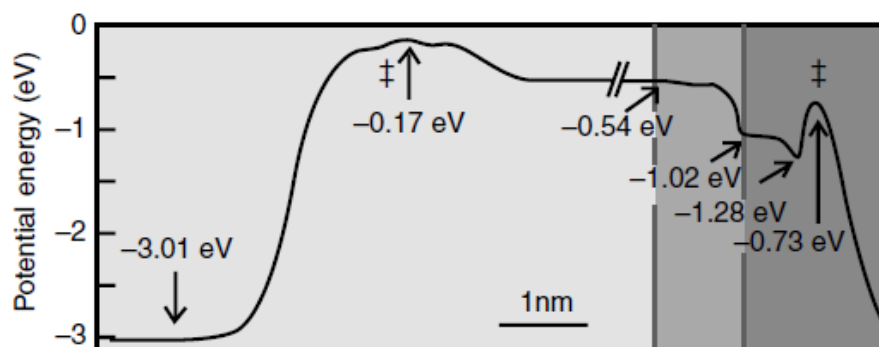
**Figure 2 (a–d) Successive micrographs taken during the *in situ* annealing of nanotubes' bucky paper material at 350°C. The sequence shows the mobility of exterior C60 molecules on the surface of SWNTs, which appear as circles 0.7 nm in diameter. A fixed position is indicated with an arrow to infer the mobility of molecules. Scale bar is 5 nm**

Theoretical studies have supported this proposed mechanism of fullerene encapsulation. Calculations have been based on the intermolecular binding potentials for graphitic materials and other related experimental parameters, such as filling temperature, vapor pressure, and process kinetics. Using a continuum model with a Lennard–Jones potential, Girifalco et al.<sup>17</sup> have calculated that the binding energy of C60 molecules inside a (10, 10) nanotube is six times higher than that of C60 on the exterior of the nanotube. Thus, any C60 molecule physisorbed to the surface of a SWNT near an opening to the interior will be drawn down a potential gradient and into the tube. A C60 molecule physisorbed on the exterior of a SWNT can diffuse along the surface very easily at the relevant temperatures, as the energy barrier for sliding is only ~0.1% of the binding energy to the wall.<sup>17</sup> Berber et al.<sup>18</sup> carried out molecular dynamics calculations using an electronic Hamiltonian to study the mechanism of peapod encapsulation. In their model they predicted a barrierless filling process and an optimal filling temperature of ~400°C. Encapsulation occurred predominantly through wall defects and open ends of nanotubes. A more quantitative treatment of the filling mechanism was proposed by Ulbricht and Hertel,<sup>19</sup> who experimentally

deduced the interaction potential of fullerene molecules on a graphite surface through temperature-programmed thermal desorption (TPD) spectroscopy. Using molecular mechanics and molecular dynamics, the authors further described a system where fullerene molecules were allowed to fill inside a rope comprising three open-ended nanotubes, with one of the tubes having a wall defect. Potential energy calculations for various filling geometries indicated a lip barrier at the entrance of an open tube (groove, position 2), while encapsulation through open ends and defects.



**Figure 3** A cut through the three-dimensional potential energy surface of a small (10, 10) tube bundle with three defect positions, which facilitate the filling of fullerene molecules. Calculations show that encapsulation is most efficient via the head-on approach along the reaction path labelled



**Figure 4** Position along minimum energy path.

(positions 1 and 3) was barrier-free. The successful encapsulation rates estimated by the authors for filling through these three sites (isolated end, groove, and wall defect) were respectively 105 sec<sup>-1</sup>, 107 sec<sup>-1</sup>, and 103 sec<sup>-1</sup>.

It may soon become possible to investigate these findings experimentally by filling isolated nanotubes with carefully controlled defects. This understanding of the fundamental mechanism of C<sub>60</sub> encapsulation enabled the development of methods for milligram-scale peapod synthesis. Efficient processing schemes were necessary to remove amorphous carbon (a-C) coverage from the starting nanotube material and to introduce openings in the nanotube structure. Treatment with acids or oxidizers, and particularly treatment with peroxide (H<sub>2</sub>O<sub>2</sub>) followed by HCl suspension, has yielded the best results for filling experiments.<sup>20,21</sup> This has been attributed to the efficient decomposition and solubilization of overcoated a-C by aqueous peroxide and the concomitant oxidation of nanotubes resulting in open

end caps and sidewall defects. It is also necessary to select temperature–pressure conditions that balance the C<sub>60</sub> vapor pressure and the surface diffusivity to optimize encapsulation probability. Good yields are generally obtained

when syntheses are performed under an inert, static C<sub>60</sub> atmosphere around 400°C. Under these conditions, the fullerene molecules can efficiently access the lumens of nanotubes through defect sites.

### III. STRUCTURAL CHARACTERIZATION OF PEAPODS

#### 3.1 Electron diffraction

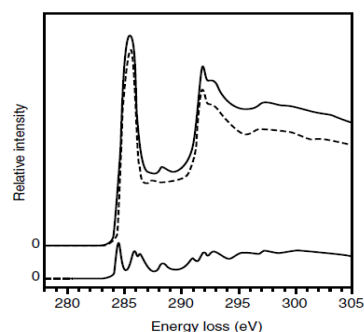
Because of the initial unavailability of bulk material, the first quantitative investigations of peapod structure utilized electron diffraction. Smith et al. performed electron diffraction studies on individual ropes containing C<sub>60</sub>

peapods at 94 K. The obtained patterns showed characteristic broken streaks oriented parallel to the rope lattice reflections and perpendicular to the real space direction of the bundle axis. These features corresponded to the intersection of the Ewald sphere with the form factor of a one-dimensional lattice of C<sub>60</sub>. The spacing of the streaks indicated a real space center-to-center distance of  $\sim 10 \text{ \AA}$ , which is similar to the nearest-neighbour separation in face-centered cubic (fcc) C<sub>60</sub>, 10.01  $\text{ \AA}$ . These measurements were performed using an internal calibration standard such that any tilt of the rope out of the imaging plane would not affect the determined lattice parameter, and they were validated by simulation. Similar studies by other investigators<sup>22</sup> have concluded that the lattice parameter is 9.7  $\text{ \AA}$ , which is slightly less than the bulk  $\langle 110 \rangle$  separation. This discrepancy has never been reconciled but could be due to differences in experimental conditions, sample material, or measurement error. Hirahara et al. characterized one-dimensional crystals of a variety of larger fullerenes encapsulated in SWNTs using high-resolution transmission

electron microscopy (HRTEM) and electron diffraction. They concluded that the intermolecular distances of various fullerenes in SWNTs are considerably smaller than those for bulk fullerene crystals, suggesting an effect of confinement in the one-dimensional channels inside SWNTs.

### 3.2 EELS spectroscopy

Microscopy is a local probe that cannot provide an accurate assessment of bulk filling fraction. A *quantitative* measurement of yield was first obtained by Liu et al. using electron energy loss spectroscopy (EELS). However, the spectrum from the peapod sample showed an additional fine structure that was attributed to the presence of the encapsulated fullerenes. The difference spectrum obtained after normalization of the peapod and reference spectra by the C1s edge jump was then compared to C1s spectra for fcc and polymerized C<sub>60</sub> Fig 5. From these data, it was possible to determine that the filling fraction in the peapod sample was  $\sim 60\%$ . Notably, this study also concluded that the electronic and optical properties of encapsulated fullerene molecules were similar to those for fcc C<sub>60</sub>, except for small changes in the relative intensities of the derived molecular orbitals.



**Figure 5 C1s core-level excitation spectra of peapods (solid line) and reference empty SWNTs (dashed line). The difference spectrum at the bottom is the resulting response of the C<sub>60</sub> peas. (From Liu, X. et al., Phys. Rev. B, 65, 045419, 2002.)**

### 3.3 X-Ray Diffraction



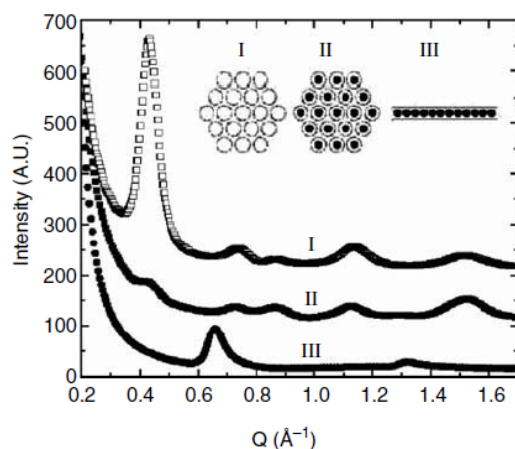
X-ray diffraction is typically applied to SWNTs to determine the crystalline ordering of nanotube bundles. For 1.4-nm-diameter SWNTs, the bundles are packed in a two-dimensional triangular lattice with a parameter of 17.4 Å,

yielding an intense (1, 0) rope lattice reflection at  $0.42 \text{ \AA}^{-1}$ . The intensity of this reflection is strongly attenuated by the presence of encapsulated C<sub>60</sub> due to the destructive interference of the form factors of the two component molecules. Therefore, the attenuation of this peak can be used as a metric to quantify the filling yield. Zhou et al. analysed x-ray scattering from peapod samples using a two-dimensional detector and measured the filling

fraction by this method to be 60 to 85%. Fig 6 shows the x-ray diffraction patterns of peapod and control (empty) samples. The control sample shows the intense first-order peak due to the crystalline lattice of nanotubes. For the peapod sample, this reflection is weak in intensity due to the diminished overall form factor.

### 3.4 Raman Spectroscopy

Raman spectroscopy has proven to be a key technique in the study of SWNTs<sup>29</sup> and peapods. In the case of C<sub>60</sub>, two modes with Ag symmetry and eight modes with Hg symmetry are Raman active. Most prominent is the pentagonal pinch mode Ag(2), located at  $1469 \text{ cm}^{-1}$  at room temperature. Low-temperature Raman spectroscopy characterization of peapods using laser excitations in the range 1.24 to 3.0 eV was reported by Pfeiffer et al.



**Figure 6** X-ray diffraction patterns from the starting SWNT film (control sample) and C<sub>60</sub>@SWNT film (peapod sample). Note the filling of C<sub>60</sub> molecules into nanotubes significantly changes the diffraction profile. The (001) and (002) peaks from the C<sub>60</sub> chains are easily detected. (From Zhou, W. et al., Appl. Phys. Lett., 84, 2172, 2004.)

## IV. PROPERTIES OF PEAPODS

### 4.1 Band Structure

One prospect afforded by the ability to encapsulate heteromolecules within a nanotube is the possibility to modify that SWNT's intrinsic electronic structure. Interactions between the component molecules result in a mixed band structure that differs from that of either isolated species. As we describe below, this has been experimentally verified primarily by scanning tunnelling microscopy (STM) studies of individual peapods

performed at low temperature and ultrahigh vacuum. Theoretical models of a one-dimensional chain of C60 molecules inside a semiconducting SWNT have predicted hybridization of the C60 lowest unoccupied molecular orbital (LUMO) with the conduction band of the nanotube. Even though no electron charge transfer is predicted (which, independently, would result in a rigid shift of the relevant Fermi levels), this partial mixing leads to new states that are not present in the band structure of either component. This prediction was empirically verified by Hornbaker et al. who studied individual peapods by STM and found that these assemblies can be distinguished from empty nanotubes by a characteristic periodic modulation. This modulation, present only for peapod structures at certain bias voltages, was superimposed on the usual honeycomb lattice image of the SWNT cage and showed a characteristic spacing of  $\sim 10 \text{ \AA}$ . This study also generated detailed information about the spatially resolved density of states (DOS) by obtaining differential conductance ( $dI/dV$ ) spectra at the STM junction as a function of the bias voltage ( $V$ ) while moving the tip along the peapod. The authors observed that the occupied electronic states (imaged at negative sample bias) were equivalent to those expected for an unfilled semiconducting SWNT. However, the unoccupied states (imaged at positive sample bias) showed a strong periodic modulation in the bias range of 1.0 to 1.25 eV that corresponded to the features detected in the lattice images. Calculations suggested that these modulations appeared *between* the C60 molecules, i.e., out of phase with the peas. The observation of energy-dependent periodic variations in the unoccupied DOS suggests that C60@SWNT should have significantly different conduction properties than an empty SWNT. Okada et al. used a total energy approach to predict the electronic band structure for peapods derived from various armchair nanotubes. Calculations showed that encapsulation was exothermic into (10, 10) SWNTs but endothermic into the slightly smaller (9, 9) and (8, 8) structures. Peapods based on (10, 10) tubes showed a unique band structure having additional free electron states near the Fermi level of the unperturbed SWNT. endothermic into the slightly smaller (9, 9) and (8, 8) structures. Peapods based on (10, 10) tubes showed a unique band structure having additional free electron states near the Fermi level of the unperturbed SWNT.

#### **4.2 Electrical And Thermal Conduction**

Initial progress toward measurement of the electrical and thermal properties of peapods was slow due to the relative unavailability of bulk samples. However, transport measurements have been successfully performed on bucky paper materials in which a significant fraction of the SWNTs are filled with C60 molecules. Four probe resistivity measurements<sup>35</sup> of such samples have shown decreased resistivity at low temperature with respect to control samples of unfilled nanotubes. This has been attributed to availability of additional conduction channels afforded by the one-dimensional C60 chains (as described in the previous section). It is not likely that the lower resistivity is due to charge transfer, as is known to occur with ion-doped nanotube samples.<sup>36</sup> Despite this consistent finding, there have been conflicting reports of the electrical transport properties of C60@SWNT.<sup>37</sup>

#### **4.3 Optical Properties**

Optical absorption characterization of thin films of nanotubes and peapods has been carried out by Kataura et al.<sup>25</sup> There are no literature reports evidencing distinct, unique optical characteristics for peapods in comparison to nanotubes. However, it has been recently shown that individual semiconducting nanotubes can be isolated from bundles in surfactant micelles and show characteristic signatures in UV-vis absorption and fluorescence spectra.

38,39 Efforts to isolate peapod samples for optical characterization are still in progress, so the effect of filling on optical behaviour of individual nanotubes remains unknown.

## V. CONCLUSION

The nanotube provides the special structural feature of a lumen, a characteristic through which this material is imbued with a clearly defined inside. For the case of a single-wall nanotube, nature has provided us with the fascinating structure in which the inside and the outside are separated by stable, single atomic sheet. Through scientific research, methods have been devised to controllably open nanotubes, and to fill these structures with a variety of materials.

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