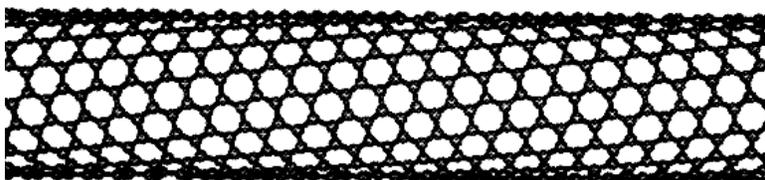


# Fibers of Aligned Single Wall Carbon Nanotubes

Single walled carbon nanotubes are a relatively new form of carbon discovered less than 10 years ago by Sumio Iijima<sup>1</sup>. Due to their relatively new appearance on the stage, there is still a lot of work to be done on basic characterization. Because The tubes are very long compared to their diameters (~10  $\mu\text{m}$  length but only ~ 1 nm diameter) their properties are expected to be highly anisotropic. Characterization of this anisotropy is important to understanding the nature of the nanotubes. One obstacle to the study of this anisotropy is that the tubes in bulk samples are highly entangled with each other and randomly oriented. One can pin individual tubes down on a substrate, however their extremely small size makes certain experiments hard, if not impossible to perform. It is therefore important to try to achieve some sort of alignment on a macroscopic scale.

Single walled nanotubes are long tubes made entirely out of carbon, more exactly from a planer sheet of graphite (a hexagonal planer carbon network). This sheet is



wrapped into a seamless tube, which is nanometers in diameter and microns in

**Figure 1. A nanotube midsection**

length. The tubes are then either capped at either or both ends with half a spheroidal Fullerene, or left open. The nanotubes are characterized by what is referred to as a roll up vector. Which specifies the helicity of the nanotube. Depending on its helicity, a nanotube can be either semiconducting or metallic in its electronic transport characteristics (for a good overview, see ref. 2 and references therein).

The nanotubes we used were produced by the pulsed laser vaporization method<sup>3</sup>. This method produces tubes that have a diameter distribution sharply peaked at  $\approx 1.4\text{nm}$ . After an acid based purification the tubes were suspended in N,N-dimethylformamide (DMF) with a concentration of  $\approx .01\text{ mg/ml}$  and ultrasonicated for approximately 15 minutes in order to ensure dispersion of the tubes. A highly graphitized commercial

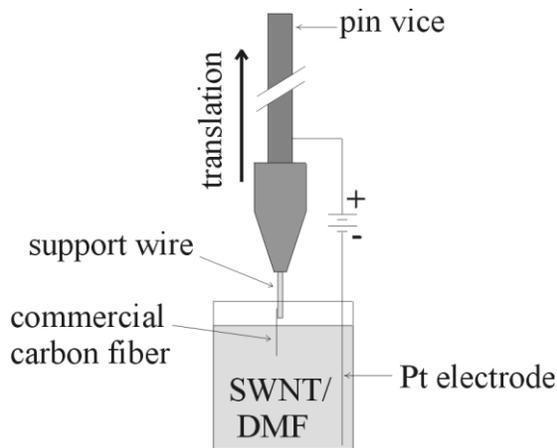


Figure 2: The Experimental Setup

carbon fiber  $\approx 8\ \mu\text{m}$  in diameter,  $\approx 12\text{ mm}$  long and was attached to support wire with a drop of silver paint. This was placed into a pin vice, which was held in a motorized translation stage. The carbon fiber was lowered  $\approx 8\text{ mm}$  into the solution. A voltage

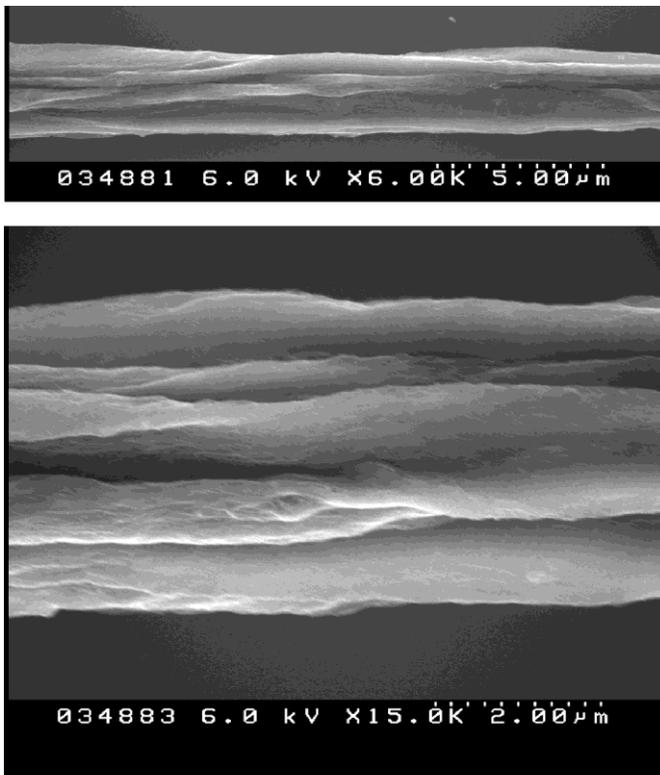
between 1-2 volts was applied between the fiber and the solution. Over a period of between 10-

30 minutes (depending on concentration and voltage) a cloud forms around the carbon fiber. The carbon fiber is withdrawn slowly from the solution with a velocity  $\approx 1 \times 10^{-2}\text{ mm/sec}$ , with the stage and motor providing a smooth withdrawal. As the carbon fiber pulls out of the solution a fiber of nanotubes is observed to form on the end of the carbon fiber, linking the carbon fiber with the cloud in the solution. This fiber continues to be formed until the translation stage reaches the end of its travel, the cloud is depleted, or some vibration causes the fiber to break. We have grown these fibers up to 5 cm in length and with typical diameters between 3 and 10  $\mu\text{m}$ .

The process that forms this SWNT fiber can be likened to pulling kelp out of the sea. Beneath the surface lies a tangled web of kelp, linked together and intertwined.

When you reach in and pull some out, there is a vertical force pulling the kelp taught between you and that beneath underneath the surface, this tends to stretch the kelp out, causing it to align with the vertical axis. Also surface tension helps to pull the kelp together, and align it into a single bundle.

The formation of the cloud in the DMF about the positively charged electrode shows us that the SWNT are negatively charged in the solution. This is to be expected, since other poly-cyclic aromatic carbon species pick up negative charge in solution due to



**Figure 2. SEM images of a fiber**

their high electronegativity. Once in contact the tubes become positively charged and tend to repel each other. This keeps the cloud from collapsing in upon itself.

We have examined these fibers under scanning electron microscopy (SEM) and transmission electron microscopy (TEM) which has given us a feel for the amount of alignment on the fibers. However these techniques gave us no real

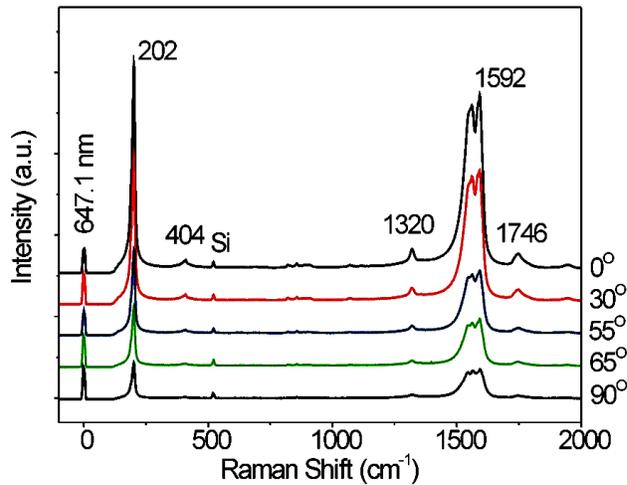
quantitative data. So we turned to selected area electron diffraction (SAED). In SAED a beam of electrons is diffracted by the sample. This was restricted to the sides of the fiber due to the thickness of the fiber. If our tubes are aligned perfectly with the axis, the fiber should act like a diffraction grating,

producing two spots on either side of a main spot. However since our sample is not perfect, there should be widening of the two spots, into arcs whose angular extent is representative of the distribution of the nanotubes. This indicates that the majority of the tubes lie within  $\approx 25^\circ$  of the fiber axis. Which is consistent with our observations under the TEM and SEM.

We have further studied these fibers with polarized Raman Spectroscopy. In polarized Raman spectroscopy a polarized laser beam is focused onto the sample and the scattered light is passed through a polarizer (called an analyzer) into a spectrometer. This scattered light contains, in addition to the wavelength of the incident beam, wavelengths that are shifted relative to the incident light. These shifts in the scattered light, and their intensity, provide information about the vibrational modes of the atoms in the sample. These vibrational modes have different symmetries depending on the relative motions of the atoms in the sample. For oriented samples, analyzer allows certain vibration symmetries to be distinguished from others depending on whether the ~~analyser~~analyzer is perpendicular (VH mode) or parallel (VV mode) to the incident radiation. Predictions of the angular dependence of polarized Raman spectra have been made by Saito et. al.<sup>4</sup>. Their model predicts the Raman peak intensity dependence on the angle between the nanotube axis and the incident polarization for each analyzer configuration (VV or VH). We have carried out experiments to try and corroborate this predicted angular dependence.

Spectra were recorded with a micro-Raman Spectrometer (Renishaw Ramanscope 1000) fitted with a 50X 0.65 NA objective. This was done in the backscatter

geometry (the light collected was scattered back along the path of the laser) with the incident beam the 647.1 nm line of a polarized krypton ion laser. The laser spot was  $\approx 1\text{-}2\ \mu\text{m}$  in diameter with a total power of  $100\ \mu\text{W}$ . The nanotube fibers were adhered to a polished silicon substrate with a drop of methanol to prevent their vibration. A motorized x-y stage was used to position the sample and a rotary stage was used to rotate the sample. For each angle, spectra were recorded at several points up and down the fiber and averaged together to take into account local variations in the alignment.



In the VV geometry, we observed a monotonic decrease in all the Raman lines with increasing angle from the axis of the laser polarization. This is contrary to what has been predicted by Saito et. al.<sup>3</sup> and suggests that there is another dominant effect not accounted for in their model. -

Consideration of what might cause this angle dependent decrease in all the Raman lines has led us to conclude that it is due in fact to the highly anisotropic nature of the nanotubes. The exceptionally strong Raman scattering intensity from the nanotubes occurs because of resonant enhancement. That is, our laser energy lies near an allowed optical absorption of the tubes in our sample. Such “resonance” of the incident light with allowed transitions is known to enhance Raman signals by orders of magnitude. What our

data allows us to conjecture is that the efficiency of the resonant absorption is strongly angle dependent. That is light which is polarized parallel to the nanotubes can be absorbed (leading to the intense, resonantly enhanced Raman signal) while light which is polarized perpendicular to the nanotubes can not be absorbed (hence a much weaker Raman signal for all lines). Such an angular dependence for the absorption efficiency for polarized light was in fact predicted for the nanotubes as occurring due to their highly anisotropic nature<sup>5</sup>. Our results constitute the first experimental evidence for this effect.

Based on this ideas we have moreover developed a simple model that allows us to determine the degree of alignment in an imperfectly aligned nanotube sample. Applied to our fibers the data indicates that 86% of the tubes within  $\pm 31^\circ$  of the fiber axis. Close agreement with the information provided by the SAED, and the TEM and SEM images. (see ref. 6 for more information about this work) The ability to determine the degree of nanotube alignment in a sample by this relatively simple technique should prove increasingly useful as nanotubes are incorporated into structural composite materials where alignment leads to greatly improved mechanical properties.

---

<sup>1</sup> S. Iijima, Nature **354** 56 (1991).

<sup>2</sup> B. I. Yakobson, R. E. Smalley, American Scientist **85** 324 (1997).

<sup>3</sup> A. Thess, R. Lee, P. Nikolaev, H. J. Dai, P. Petit, J. Robert, C. H. Xu, Y. H. Lee, S. G. Kim, A. G. Rinzler, D. T. Colbert, G. E. Scuseria, D. Tomanek, J. E. Fischer, R. E. Smalley, Science **273** 483 (1996)

<sup>4</sup> R. Saito, T. Takeya, T. Kimura, G. Dresselhaus, M. S. Dresselhaus, Physical Review B (Condensed Matter) **57** 4145 (1998).

<sup>5</sup> H. Ajiki, T. Ando, Solid State Communications **102** 135 (1997).

<sup>6</sup> H. H. Gommans, J. W. Alldredge, H. Tashiro, J. Park, J. Magnuson, A. G. Rinzler, submitted to Journal of Applied Physics (2000).