# COMPOSITE NANOFIBERS CONTAINING ISOLATED AND ALIGNED SINGLE WALL CARBON NANOTUBES

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## Abstract

*Electrospinning has been used to prepare poly(vinyl alcohol) (PVA) nanofibers, with diameters ranging from 1 μm down to 20 nm, that contain dispersions of isolated, well-aligned, single wall carbon nanotubes (SWNTs). The nanofibers were characterized by Raman spectroscopy and single radial breathing modes (RBMs) were found for the SWNTs in the nanofibers indicating debundling of the original SWNT ropes. Moreover a split G' band for some nanotubes and the results of polarized Raman spectroscopy were consistent with the presence of highly aligned and possibly isolated SWNTs along the nanofiber axes.*

## 1 Introduction

It is known that carbon nanotubes have impressive mechanical properties and it is thought that one of the best ways to realize them is to incorporate nanotubes into composites [1,2]. The highest levels of stiffness and strength are obtained for composites with the reinforcing fibers aligned in one direction. It has also been recognized that for any nanocomposite to realize its full potential in terms of mechanical properties, the nanophase has to be well-dispersed. Hence, the isolation of the nanotubes and their alignment are critical in the development of these potentially useful materials.

In this study electrospinning has been used to prepare poly(vinyl alcohol) (PVA) nanofibers, with diameters ranging from 1 μm down to 20 nm, that contain dispersions of isolated, well-aligned, single wall carbon nanotubes (SWNTs). The nanofibers were characterized by Raman spectroscopy. Single radial breathing modes (RBMs) have been found for the SWNTs in the nanofibers indicating possible debundling of the original SWNT ropes. Polarized Raman spectroscopy has indicated the presence of isolated SWNTs, aligned along the nanofiber axes.

## 2 Experimental

PVA nanofibers were prepared, with low loadings (~0.04%) of HiPco SWNTs relative to the PVA, by the electrospinning an aqueous PVA solution (8.8% by weight of polymer of molar mass 72,000 $gmol^{-1}$ in de-ionised water with no surfactant added) containing dispersions of the nanotubes. The electrospinning conditions were as follows: rate of flow = 0.08-2 ml/hour; voltage = 15-25 kV; tip-to-collector distance = 60-120 mm. The nanofibers were collected on aluminum foil, coated with carbon and examined in a FEG SEM operated at 5 kV. Raman spectra were obtained using a Renishaw 2000 spectrometer fitted with a 632 nm HeNe laser. Spectra were obtained using a 50× objective lens giving a spot size of the order of 1 μm [1,2].

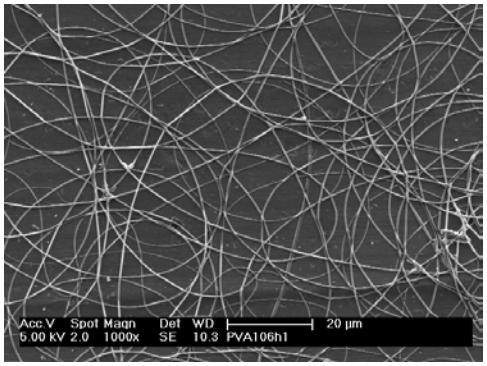


Fig. 1. SEM micrograph of the PVA/SWNT composite nanofibers produced by electrospinning.

## 3 Results

### 3.1 Scanning Electron Microscopy

Fig. 1 shows an area of the foil containing a high density of the nanofibers and it can be seen that the individual nanofibers have approximately

constant cross-sectional areas and the diameter of the nanofibers ranges from around 1 μm down to about 20 nm.

### 3.2 Raman Spectroscopy

The Raman spectrum of the original HiPco nanotubes is shown in Fig. 2(a) which shows well-defined RBMs, along with the D, G and G' bands for the SWNTs. The Raman spectra from a region containing bundles of nanofibers (e.g. Fig. 2(a)) gives well-defined Raman bands from the SWNTs even though the concentration of nanotubes is very low (only 0.04 % in the nanofibers) because they undergo intense resonance Raman scattering [3]. The spectrum is somewhat weaker that that from the original HiPco material as there are fewer nanotubes in the 1 μm laser spot but the RBM region is very similar in both cases.

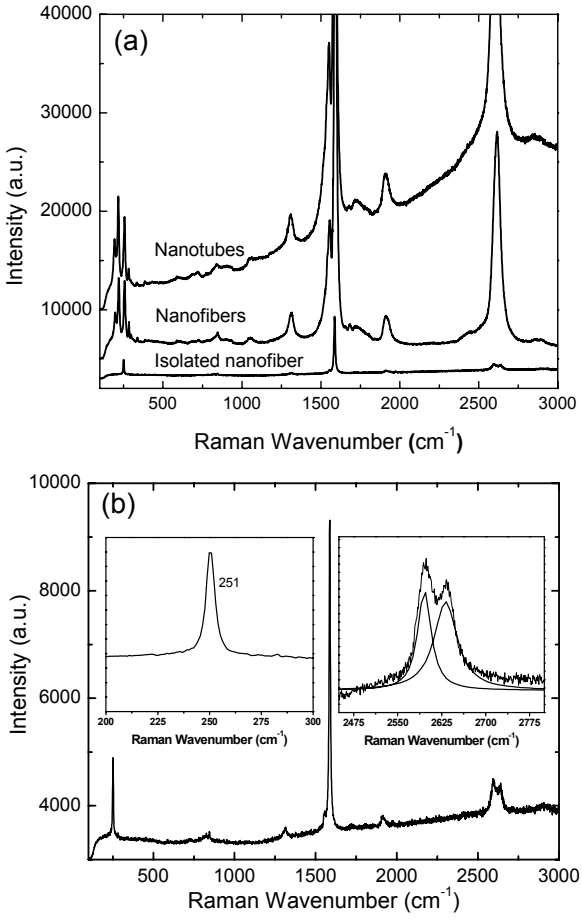


Fig. 2. Raman spectra of (a) the HiPco nanotubes, a nanofiber bundle and an isolated nanofiber. (b) Isolated nanofiber showing detail (inset) of the RBM (left) and G' band (right).

A Raman spectrum from an isolated nanofiber (as identified in the optical microscope of the spectrometer) in a region with a low density of nanofibers is also shown in Fig. 2(a). In this case the spectrum is rather weak and it is shown in more detail in Fig. 2(b). Closer inspection of the RBM region shows that in this case only a single RBM at 251 $cm^{-1}$ (see inset) can be seen, implying that the nanotube contributing to this spectrum is isolated in the nanofiber. The most remarkable feature of the spectrum is found for the G' band which is split into two well-defined peaks, one at 2596 and the other 2632 $cm^{-1}$, i.e. equally either side of the G'-band position of 2614 $cm^{-1}$ for the nanofiber bundles in Fig. 2(a). Such anomalous two-peak G'-band behavior was first reported and explained by Souza Filho *et al* [4] who demonstrated clearly that it can occur only in the spectra of a few special $(n,m)$ isolated SWNTs. The peaks occur due to a double-resonance process, one in connection with the incident photon and the other with the scattered photon, with each of the two photons resonant with different $E_{ii}$ van Hove singularities in the joint density of states (JDOS) [4]. This phenomenon is found only for specific *isolated* SWNTs and not for nanotube bundles. There are, however, other reasons why the G'-band may split such as being due to the presence of defects or interactions with the matrix

### 3.3 Nanotube Alignment

It is possible to use polarized Raman spectroscopy to follow the characteristics of the Raman scattering from the SWNTs in the nanofibers and determine firstly the orientation of the SWNTs and secondly if they are isolated from other nanotubes [5].

Fig. 3(a) shows the results of the analysis of the intensity of the G-band scattering from a single nanofiber in a region of low nanofiber density as a function of the angle, $\phi$, between the nanofiber axis and direction of incident laser polarization for the VV configuration, where the polarizer and analyzer are parallel to each other. For perfectly-aligned SWNTs using a VV scattering geometry, the dependence of the intensity of the scattering $I_{VV}(\phi)$ upon the angle $\phi$ between the polarization axis and the nanotube axis is found to be [6]

$$I_{VV}(\phi) \propto \cos^4 \phi \qquad (1)$$

The data have been fitted using Eqn. 1 for isolated SWNTs and it can be seen that there is good agreement with the data points. This implies that in the SWNTs are isolated and highly oriented along

the nanofiber axis The spectrum obtained for low frequency the breathing mode region, inset in Fig. 3(a), showed a single RBM for this nanofiber at 284 $cm^{-1}$, consistent with the nanotube being isolated.

In the case where the analyzer is perpendicular to the excitation polarization axis (VH geometry) it is predicted [6] that the variation of the intensity of scattering with $\phi$ is given by

$$I_{VH}(\phi) \propto \cos^2\phi \sin^2\phi \qquad (2)$$

The data in Fig. 3(b) have been fitted to this function and it can be seen that there is again good agreement between the experimental data and theoretical curve. This is further confirmation of the alignment of the SWNTs parallel to the nanofiber axis.

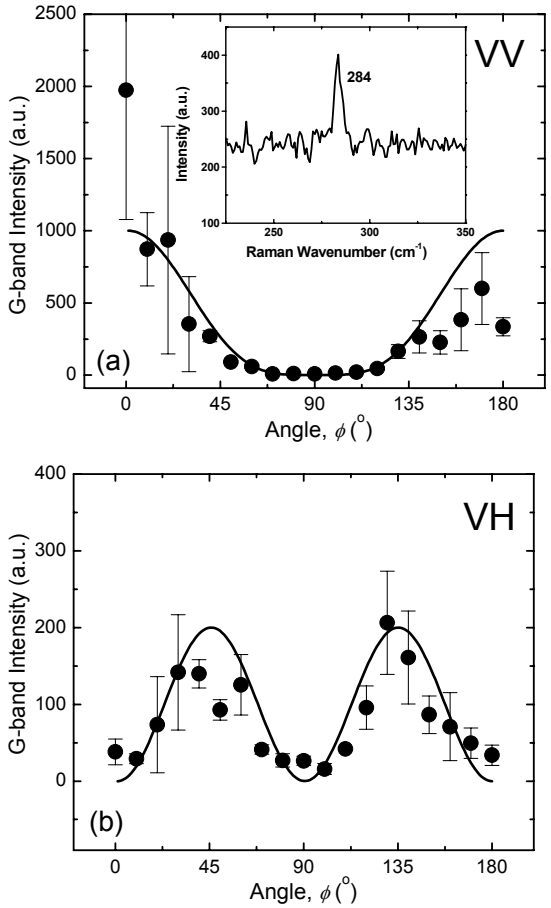


Fig. 3. G-band intensity for an isolated nanofibre as a function of orientation angle, $\phi$, for the two scattering geometries (a) VV (with the RBM inset), (b) VH. (Average of 3 measurements for each data point).

## 4 Discussion

It is possible estimate the number of SWNTs in the nanofibers from the concentration (0.04 %) of SWNTs. Assuming that they have approximately the same density as the PVA polymer and they are aligned parallel to the nanofiber axis, then for 1 nm diameter SWNTs you should expect to find on average at least one SWNT in the nanofiber as long as it is greater than about 50 nm in diameter. This explains why it was not possible to use TEM to image the SWNTs in the nanofibers. A fiber of 1 μm diameter, on the other hand, such as that used to obtain the data in Fig. 2(b) & 3 would be expected to contain the order of 400 aligned SWNTs.

Shin *et al* [7] have analyzed the process of electrospinning in terms of a whipping instability that causes bending and stretching of the jet of fluid which facilitates the break up of the SWNT bundles. The processes that occur during the electrospinning of nanofibers containing nanotubes and suggest that the SWNTs may be aligned by a combination of the applied electric field and the mechanical stretching of the fibers. They found that better alignment was obtained for smaller diameter fibers than larger diameter ones. It appears from this present study that the nanotube ropes have been debundled by the electrospinning process and then become aligned and possibly isolated by being confined within the nanofibers. The issue of nanotube isolation is clearly worthy of further study and one way forward might be to use TEM upon fractured nanofibers in which the pulled-out nanotubes can be examined.

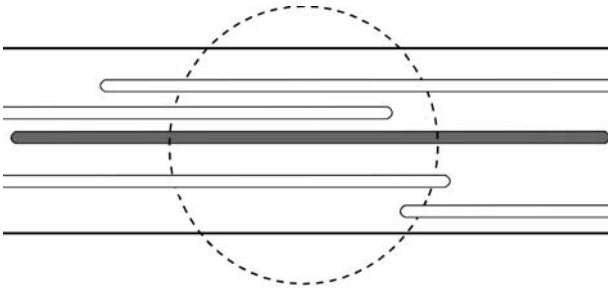

Fig. 4. Schematic diagram of the microstructure of a large nanofibre (not to scale). The shaded nanotube is in resonance with the laser excitation whereas the majority of the nanotubes (unshaded) are not. The dashed circle represents the laser spot of the order of 1 μm in diameter.

Fig. 4 gives a schematic representation of the structure of the nanofibers in which a number of nanotubes are aligned parallel to the fiber axis. Most will not be in resonance with the laser excitation but a small number, such as the one shaded, will be in resonance. This microstructure can be considered to

be that of the ultimate model nanocomposite of a nanotube within a nanofiber, with a large number of potential applications.

## 5. Conclusions

It has been demonstrated that it is possible to produce polymer nanofibers in which the nanotubes are both isolated and aligned parallel to the nanofiber axis. Examples will be given of how this microstructure can be used to follow the fundamental properties of SWNTs. For example, it will be demonstrated [8] that axial deformation of the nanofibers allows the effect of stress upon the Raman spectrum of SWNTs to be followed in detail.

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