

POLYMER COMPOSITE NANOFIBRES

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ABSTRACT

Electrospinning has been used to prepare poly(vinyl alcohol) (PVA) nanofibres, with diameters ranging from 1 μm down to 20 nm, that contain dispersions of isolated, well-aligned, single wall carbon nanotubes (SWNTs). The nanofibres 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 nanofibre axes. The nanofibres were subjected to deformation and the position of the G- and G'-bands was followed as a function of strain. It was found that large band shifts were obtained indicating that there was good stress transfer from the PVA matrix to the nanotubes. A band shift of up to 40 cm^{-1} for 1% strain was found for the G' band which is similar to that reported for the deformation of isolated nanotubes. This indicates that the Young's modulus of the SWNTs is in excess of 800 GPa.

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 [1-4]. The highest levels of stiffness and strength are obtained for composites with the reinforcing fibres 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) nanofibres, with diameters ranging from 1 μm down to 20 nm, that contain dispersions of isolated, well-aligned, single wall carbon nanotubes (SWNTs). The nanofibres were characterized by Raman spectroscopy. Single radial breathing modes (RBMs) have been found for the SWNTs in the nanofibres indicating possible debundling of the original SWNT ropes. Polarized Raman spectroscopy has indicated the presence of isolated SWNTs, aligned along the nanofibre axes.

It is well established that the positions and relative intensities of the Raman bands of SWNTs are affected by mechanical stressing. In particular, the G and G' bands shift to lower wavenumber in tension [1-7] and the relative intensities of the RBMs [2,6] change with stress. Hence Raman spectroscopy has been employed widely to monitor SWNT deformation in a variety of situations [1-7]. In the case of SWNT composite nanofibres it is vital to know the extent to which the high modulus nanotubes can offer reinforcement to the low modulus polymer. Hence in this present study upon nanofibres containing SWNTs, Raman spectra have been obtained while the nanofibres were subjected to axial tensile deformation in order to determine the level of stress transfer from the PVA matrix polymer to the SWNTs. This has been monitored by obtaining Raman spectra from the nanotubes within the nanofibres and observing the stress-

induced shifts of the G and G' Raman bands. The behaviour has then been correlated with similar studies upon the deformation of other nanotube composites [1] and that of isolated SWNTs [5].

2. EXPERIMENTAL

PVA nanofibres 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 $72,000 \text{ gmol}^{-1}$ 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 nanofibres 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 \times objective lens giving a spot size of the order of 1 μm [1,2].

In order to prepare samples for mechanical testing, a square window of 10 mm was made on a square paper card and placed on top of a two small metal blocks being used as the collector for the electrospun fibres. The fibres become aligned between the metal blocks which in turn collect between two opposite sides of the paper card. The two sides on which the fibres were deposited are glued on top by paper cards to grip the fibres firmly in a uniaxial direction. A custom-made rig was used for stretching the paper card in the fibre directions after its sides were cut to allow the strain to be applied to the fibres. The rig has two horizontal holders, one fixed and other movable to which a micrometer is attached to calculate the strain applied to the fibres on the paper card. The rig was mounted onto the optical microscope stage in the Raman spectrometer and the fibre direction was aligned parallel to the axis of incident laser polarisation. A HeNe laser of wavelength 633 nm (1.96 eV) was again used as the excitation source and the scattered radiation was passed through a polarizer (VV scattering configuration). The fibres were stretched by rotating the micrometer attached to a moveable holder and the strain to the fibres was calculated by dividing the change in gauge length by the original length.

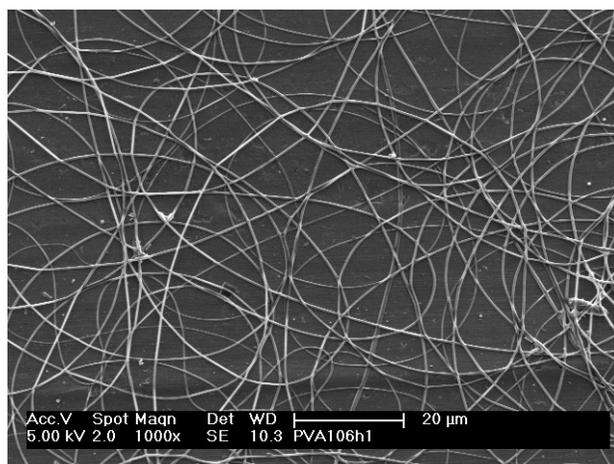


Figure 1: SEM micrograph of the PVA/SWNT composite nanofibres produced by electrospinning.

3. CHARACTERISATION OF THE NANOFIBRE STRUCTURE

3.1 Scanning Electron Microscopy

Figure 1 shows an area of the foil containing a high density of the nanofibres and it can be seen that the individual nanofibres have approximately constant cross-sectional areas and the diameter of the nanofibres ranges from around 1 μm down to about 20 nm.

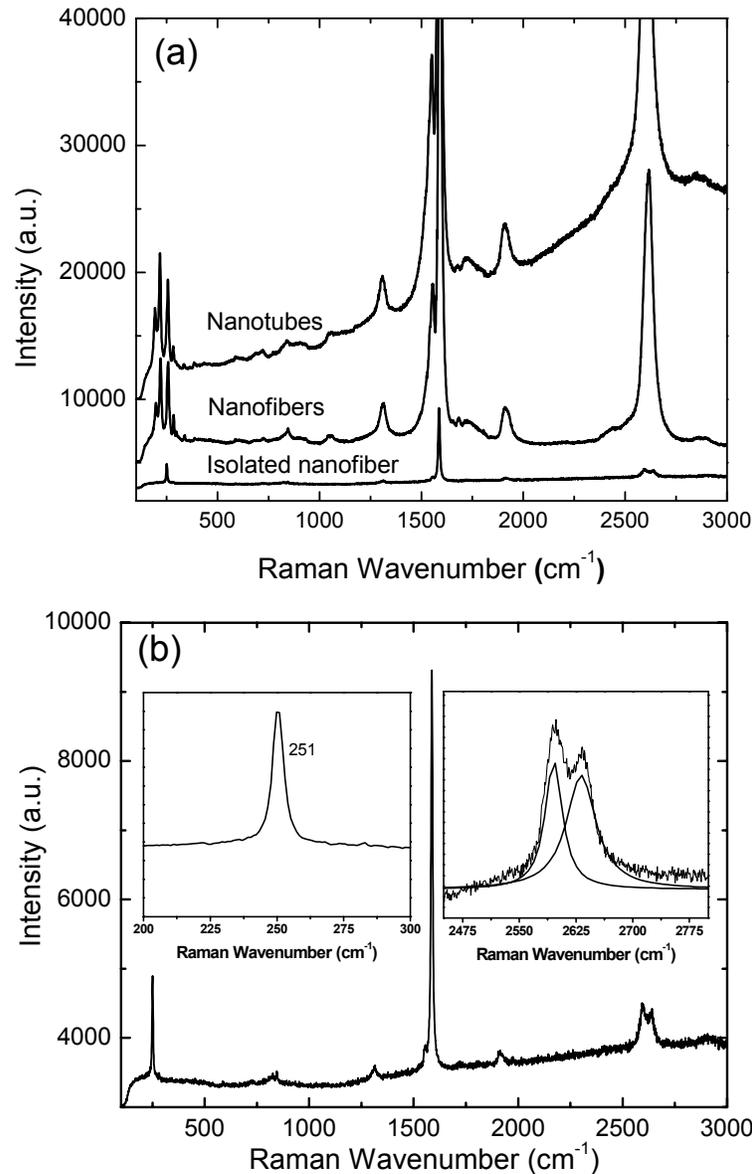


Figure 2: Raman spectra of (a) the HiPco nanotubes, a nanofiber bundle and an isolated nanofiber. (b) Isolated nanofiber showing detail (inset) of the RBM (left) and G' band (right).

3.2 Raman Spectroscopy

The Raman spectrum of the original HiPco nanotubes is shown in Figure 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 nanofibres (e.g. Figure 2(a)) gives

well-defined Raman bands from the SWNTs even though the concentration of nanotubes is very low (only 0.04 % in the nanofibres) because they undergo intense resonance Raman scattering [8]. The spectrum is somewhat weaker than 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.

A Raman spectrum from an isolated nanofibre (as identified in the optical microscope of the spectrometer) in a region with a low density of nanofibres is also shown in Figure 2(a). In this case the spectrum is rather weak and it is shown in more detail in Figure 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 nanofibre. 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 nanofibre bundles in Figure 2(a). Such anomalous two-peak G'-band behavior was first reported and explained by Souza Filho *et al* [9] 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_{ji} van Hove singularities in the joint density of states (JDOS) [9]. 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 nanofibres and determine firstly the orientation of the SWNTs and secondly if they are isolated from other nanotubes [10].

Figure 3(a) shows the results of the analysis of the intensity of the G-band scattering from a single nanofibre in a region of low nanofibre density as a function of the angle, ϕ , between the nanofibre 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 ϕ between the polarization axis and the nanotube axis is found to be [6]

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

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 nanofibre axis. The spectrum obtained for low frequency the breathing mode region, inset in Figure 3(a), showed a single RBM for this nanofibre 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 [11] that the variation of the intensity of scattering with ϕ is given by

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

The data in Figure 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 nanofibre axis.

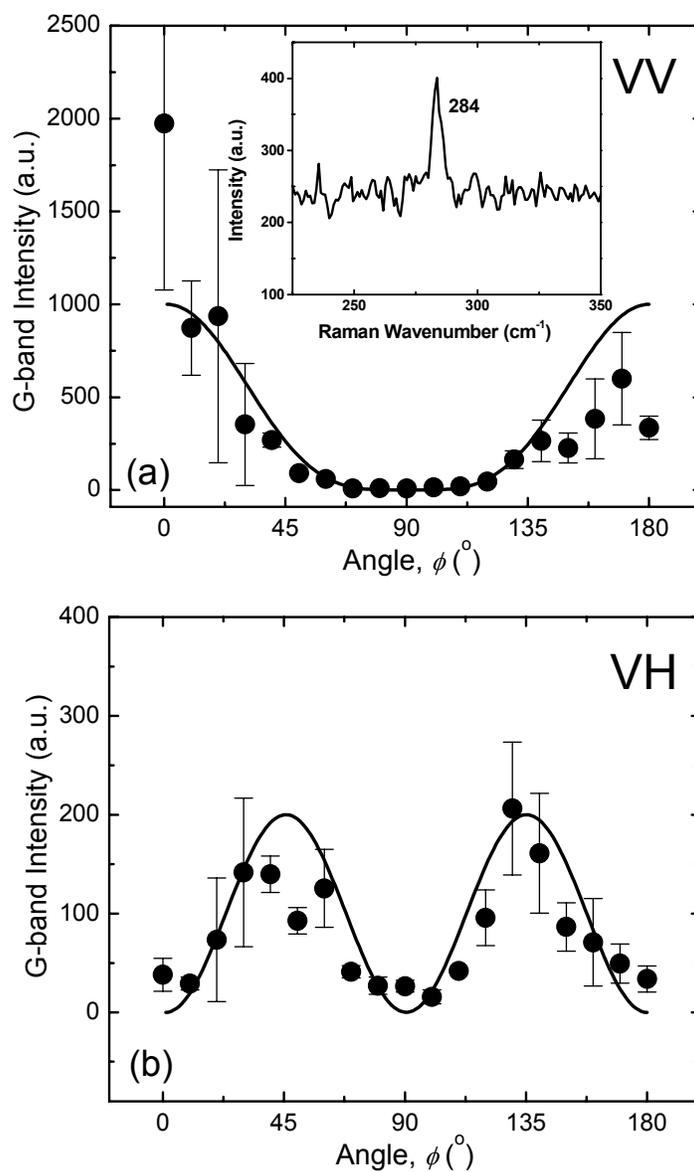


Figure 3: G-band intensity for an isolated nanofibre as a function of orientation angle, ϕ , for the two scattering geometries (a) VV (with the RBM inset), (b) VH. (Average of 3 measurements for each data point).

3.3 Proposed Nanofibre Microstructure

It is possible to estimate the number of SWNTs in the nanofibres 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 nanofibre axis, then for 1 nm diameter SWNTs you should expect to find on average at least one SWNT in the nanofibre 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 nanofibres. A fibre of 1 μm diameter, on the other hand, such as that used to obtain the data in Figure 2(b) & 3 would be expected to contain the order of 400 aligned SWNTs.

Shin *et al* [12] 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 nanofibres containing nanotubes and suggest that the SWNTs may be aligned by a combination of the applied electric field and the mechanical stretching of the fibres. They found that better alignment was obtained for smaller diameter fibres 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 nanofibres. The issue of nanotube isolation is clearly worthy of further study and one way forward might be to use TEM upon fractured nanofibres in which the pulled-out nanotubes can be examined.

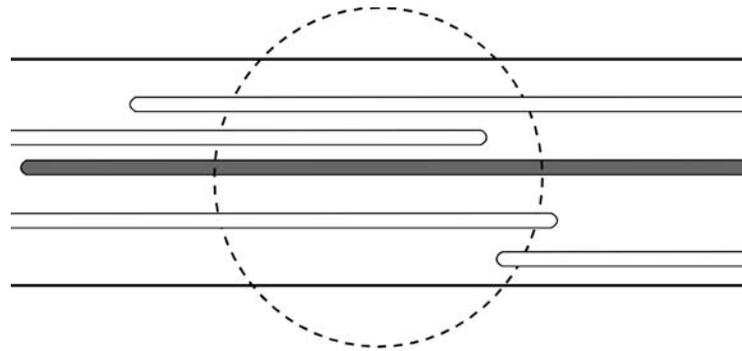


Figure 4: Schematic diagram of the microstructure of a large nanofibre (not to scale). The shaded nanotube is in resonance with the laser excitation whereas the majority of the nanotubes (unshaded) are not. The dashed circle represents the laser spot of the order of 1 μm in diameter.

Figure 4 gives a schematic representation of the structure of the nanofibres in which a number of nanotubes are aligned parallel to the fibre axis [13]. 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 nanofibre, with a large number of potential applications.

4. DEFORMATION OF THE NANOFIBRES

Figure 5 shows the positions of the G and G' Raman bands measured simultaneously for the same isolated semiconducting SWNT in a nanofibre subjected to different levels of applied strain. The shifts were determined using the VV configuration and it can be seen that for both bands there is a significant shift to lower wavenumber and that the rate of shift decreases with increasing nanofibre strain. The initial shift rate is about $-15 \text{ cm}^{-1}/\%$ strain for the G band and around $-35 \text{ cm}^{-1}/\%$ strain for the G' band. This behaviour demonstrates that when the nanofibres are being subjected to deformation stress is being transferred from the PVA matrix of the nanotubes – hence they are acting as reinforcement in the nanofibres [1]. For this level of nanotube content (0.04%), however, the effect of this reinforcement upon the nanofibre modulus would be expected to be minimal. Stress-induced Raman bands shifts for SWNTs are

generally linear with strain [5] and the non-linearity of the behaviour shown in figure 5 at high strains may be an indication of the breakdown of interfacial adhesion.

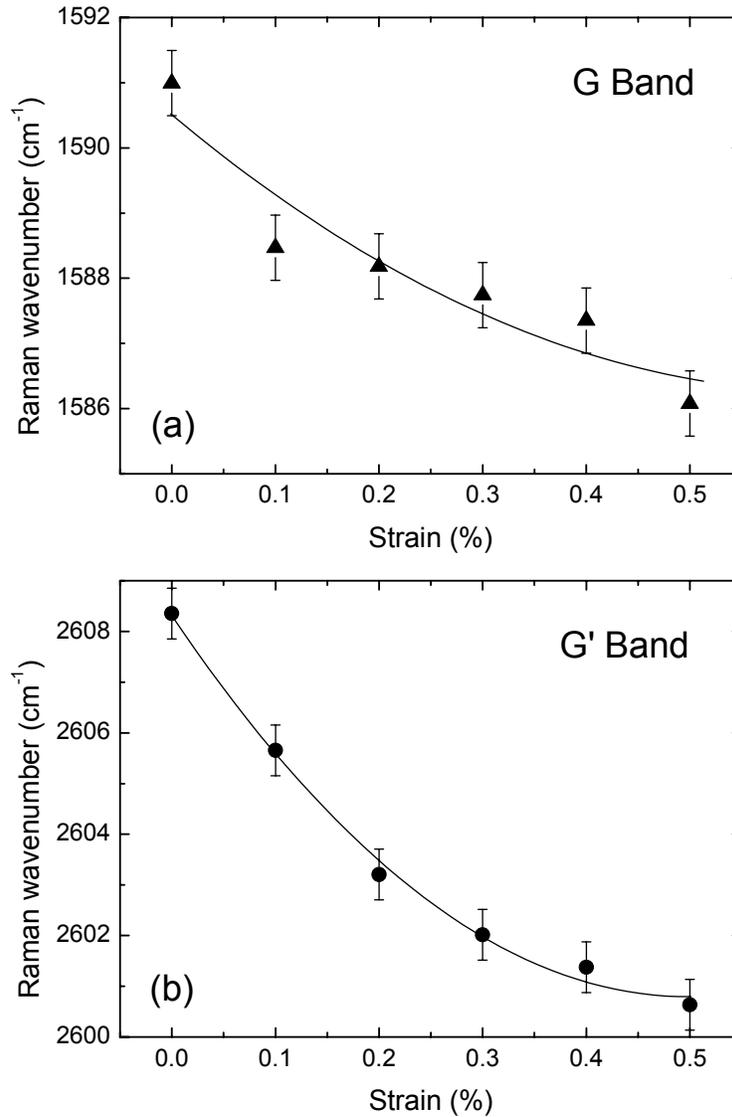


Figure 5: Shift of the peak position of the SWNT Raman bands as a function of nanofibre strain during the deformation of a single nanofibre. (a) G band and (b) G' band. (Solid lines are least square fits to the data points).

Similar band shifts were found during the deformation of other semiconducting nanofibres and the behaviour of the fibre in Figure 5 and that of another nanofibre is shown in figure 6. The dashed line is the variation of G'-band position with strain found by Cronin *et al.* [5] during the deformation of isolated semiconducting SWNTs on a substrate using an AFM probe. It can be seen that the data from this present study fall either on or just above the dashed line. This behaviour would only be expected if the nanotubes were aligned parallel to the nanofibre axis, relatively long and adhering well to the PVA matrix, at least at low strains.

It is possible to model the mechanics of the deformation if the nanofibre is considered to be a nanocomposite and continuum micromechanics assumed to be applicable at the nano level. For reinforcement by a continuous fibre in a unidirectional composite (c.f. Figure 4), as long as the fibre-matrix interface remains intact, the matrix strain will be the same as the fibre strain [14] and the dashed line in Figure 6 should be followed. If the electrospinning process damages the SWNTs and reduces their length then there will be a drop in reinforcement efficiency since the stress decreases to zero at the reinforcing fibre ends [14]. In this case the slope of the line in figure 6 will be lower. As mentioned earlier, if the interface breaks down as the strain is increased then the slope of the curves in figure 5 will decrease with increasing strain. The behaviour shown in figure 6 indicates that the reinforcement of the nanofibre by the SWNTs is relatively good.

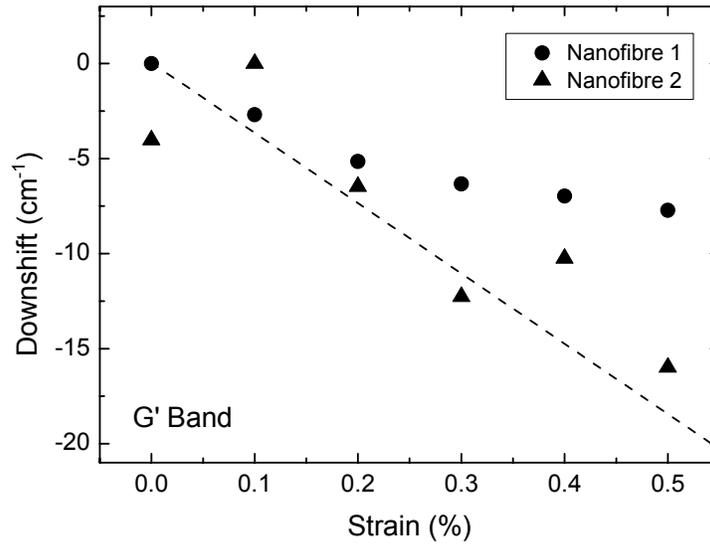


Figure 6: Shift of the peak position of the SWNT G' band Raman band as a function of nanofibre strain during the deformation of two different nanofibres. The dashed line is taken from the work of Cronin *et al.* [5].

The final aspect of the work that needs to be commented upon is that it is possible to estimate the Young's modulus of the nanotubes from the dependence of the band positions upon strain following the analysis of Cooper *et al.* [1]. It was found [1] for a series of carbon fibres that the rate of shift of the G' band per unit strain $d\alpha_{G'}/de$ was proportional to the fibre modulus, E_f , with a shift rate of $50 \text{ cm}^{-1}/\%$ strain corresponding to a modulus of 1000 GPa. If it is assumed that the G' band shifts in SWNTs have the same dependence upon Young's modulus as those in carbon fibres then the universal calibration shows that the semiconducting nanotubes in Figure 6 for which $d\alpha_{G'}/de \approx 40 \text{ cm}^{-1}/\%$ strain have Raman band shift rates corresponding to a modulus of at least 800 GPa.

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