Chemical doping by sulfuric acid in double wall carbon nanotubes

P Puech[*], A Ghandour[***], A Sapelkin[***], C Tinguely[**], E Flahaut[**], D Dunstan[***] and W Bacsa[*]

[*]CEMES CNRS UPR, 29 rue Jeanne Marvig, Univ. Toulouse, 31055 Toulouse France, wolfgang.bacsa@cemes.fr
[**] CIRIMAT-LCMIE, CNRS UMR, 118 route de Narbonne, Univ. Toulouse, 31062 Toulouse, France
[***] Physics Department, Queen Mary, University of London, London E1 4NS, United Kingdom

ABSTRACT

Charge transfer due to chemical doping in carbon nanotubes can be detected through changes in the band shape and spectral shifts of the Raman G-band. In double wall carbon nanotubes, the inner tube is well protected from the environment and contributions of the inner tube to the Raman G-band can be detected when applying hydrostatic pressure. We find that by combining doping with sulfuric acid and high hydrostatic pressure, we can determine the ratio of single to double wall carbon nanotubes and we propose empirical parameters to fit the G-band line shape. We observe a spectral band at 1560 cm^{-1} which shifts with pressure at the same rate as the outer tube and which attribute to electronic coupling of the two tube walls.

Keywords: Raman spectroscopy, carbon nanotubes, double wall, chemical doping, hydrostatic pressure

1 INTRODUCTION

Double wall carbon nanotubes (DWs) are the simplest form of multi-wall carbon nanotubes. While single wall carbon nanotubes (SW) can either be semi-conducting or metallic depending on the way the graphene sheet is rolled up, multi-wall carbons nanotubes (MWs) are electrical conductors due to their larger diameter. DWs are the ideal system to study the inter-wall coupling. The electrical conductivity perpendicular to the graphene layer is less than 1% of the in-plane electrical conductivity [1]. Electronic conductivity has been extensively studied, and inter-shell conductance in MWs is consistent with tunneling through orbitals of neighboring walls [2].

Two main synthesis methods for DWs are known to day: conversion of peapods into DWs leading to DWs with uniform diameter distribution [3] and the use of the catalytical chemical vapor deposition (CCVD) method resulting in 80−100% of DWs with a larger diameter distribution [4, 5]. Peapods or single wall carbon nanotubes filled with C_{60} molecules. Raman spectroscopy is routinely used to screen the diameter distribution using the low frequency radial breathing mode, by changing the excitation wavelength and by measuring defect induced scattering (D band) [6]. The G band in DWs contains contributions from the internal and external tubes which depend on external parameters such as pressure, temperature and applied electric field [7]. We combine the influence of the G band shape as a function chemical doping and hydrostatic pressure to separate contributions from inner and outer tubes. The internal tube does not experience any pressure from the inside and is only slightly affected by doping (10%) [8,9].

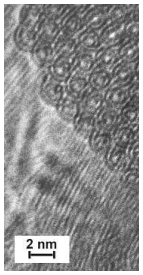

FIG. 1: Transmission electron microscopy images of a bundle of DWs of uniform diameter distribution.

The G band frequency of the outer tube in DWs is about the same as that for SWs making it impossible to separate both G band contributions applying pressure or changing the temperature. Kim et al [10] have recently proposed a scheme to determine the purity of the sample using chemical doping. Chemical doping with sulphuric acid has a large effect on the G band of SWs [11] depending on the excitation wavelength, while the shape change is more subtle in the case of DWs as will be shown in our study. Raman scattering of DW doped with H_2SO_4 reported in literature [12] have not been able to discriminate contribution form the inner and outer tubes to the Raman G band. Hydrostatic pressure experiments give us the opportunity to separate contributions from the inner and outer tubes [13, 14].

2 EXPERIMENTAL

The DWs were prepared by CCVD [15]. High-resolution transmission electron microscopy images show the presence of individual and small bundles of DWs with diameters ranging from 0.6 to 3 nm (see figure1). The tubes are single(15%), double (80%) or triple walled (< 5%). For the high pressure experiment Raman spectra were recorded at room temperature using a Renishaw Raman microprobe instrument. The high-pressure Raman measurements were performed in a diamond anvil cell. Raman spectra were also

recored using a XY-Dilor spectrometer. All spectra have been recorded in air using 1 mW before entering the optical microscope and spectrometer for the high pressure experiment to prevent any heating of the tubes. We can estimate that the tubes are heated less than 10 K using Stokes and Anti-Stokes scattering and G, D band shifts.

3 RAMAN BANDS OF DOPED DWS

Kim et al [10] propose to use chemical doping with sulphuric acid to determine the composition of DW samples. Here we conduct hydrostatic pressure experiment with sulphuric acid as a medium to identify a set of empirical parameters that can be used to determine the fraction of DW to SW. Zhou et al [11] has shown that the G band frequency is diameter dependent. In figure 2, we show Raman spectra excited at 633 nm in the spectral region of the D and G band and the G′ 2D band of SWs of 1.4 nm and 0.8 nm diameter and DWs.

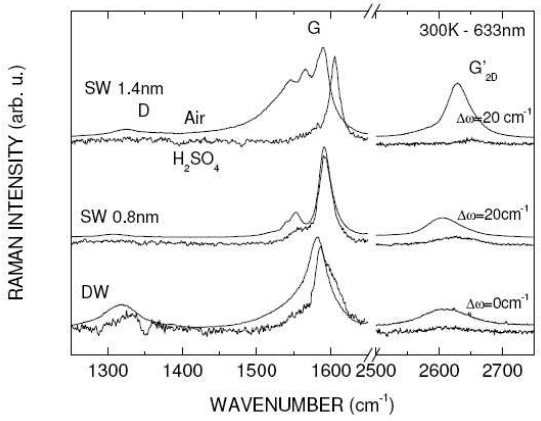

FIG. 2: First and second order Raman spectra of SWs and DWs recorded at 633nm in air and doped with sulphuric acid.

We note that with diameters larger than 1.4nm, chemical doping leads to a considerable upshift of the G band. Contribution from the G− band in SWs, as well as a band associated with electronic coupling are strongly reduced in intensity when doped. As the mean tube diameters of SWs and DWs are larger than 1.4nm in our DW sample, a large upshift is expected as a result of the chemical doping. This results in the change of the G band shape of our DW sample containing 15% of SWs

4 HYDROSTATIC PRESSURE

Figure 3 shows on the left side the G band of DWs at 5 GPa using four different pressure media. A clear difference in the G band shape is observed when using argon or sulphuric acid as pressure medium.

The G band splits when increasing pressure due to the different pressure experienced by the inner and outer tubes. The differences as a function of pressure between the media demonstrate that the pressure experienced by the tube depends on them. At normal pressure, ie without anvil cell, the signal of the outer tubes on the higher energy side of the G band is not present. The signal from the outer tube increases with pressure and its intensity is comparable to the G band of the inner tube. The signal from the remaining SWs in the DW is also present but is less intense. At around 5GPa we observe a decrease in the intensity of the entire G band.

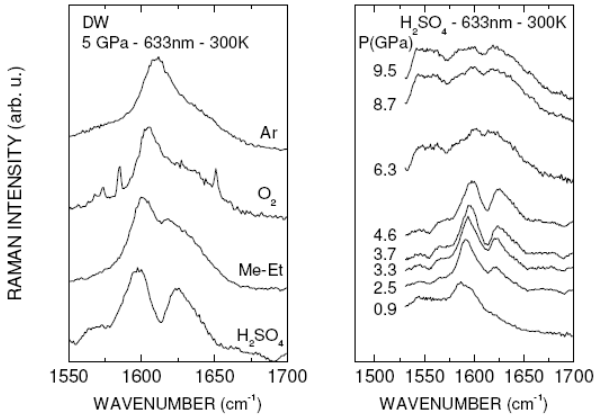

FIG. 3: Left side: Raman G band of DWNTs at 5 GPa for 4 different pressure transmitting media. Right side: G band of DWNTs and pressures upto 9.5 GPa for H2SO4 as pressure transmitting medium.

We used the spectrum recorded without anvil cell for the value at zero pressure. In graphite intercalation compounds the G band shifts by 16 cm^{-1} for the first H_2SO_4 intercalation stage and shifts two or three times more for the second and third intercalation stage [16]. Doping of graphite induces strain [17]. It has been found from high pressure experiments [18] that the lattice parameter a/a is 8×10^{-4} for each stage leading to a total shift of 4 cm^{-1}. Consequently, strain alone cannot explain the observed shift in DWs upon doping. The remaining shift of 12 cm^{-1} has clearly a different origin. This effect is related to electron-phonon interaction [19].

In table I, we report the spectral G band position. The spectral G band position at zero pressure depends also on the medium. The larger effect of oxygen on the G band position compared to alcohol or argon can be explained by p-doping of the tubes by oxygen which is expected to up shift the G band. It is important to notice that a shoulder is observed on the lower side of the G band at 1560 cm^{-1}. This band persists with increasing pressure for DWs in contrast with what is observed for SWs [20-22].

It is observed that D band is more intense after pressure loading. Doping has clearly the effect of reducing the

NSTI-Nanotech 2008, www.nsti.org, ISBN 978-1-4200-8503-7 Vol. 1

intensity of the G band. Reduction of the G band intensity through doping of up to 50% has been reported in the literature [10].

TABLE I: G band position of inner and outer tube of DWs, pressure coefficients for four different pressure transmitting media (i: inner, o: outer).

Medium	$\omega_i(P=0)$ (cm^{-1})	$\omega_o(P=0)$ (cm^{-1})
Me-Et	1582	1594
O_2	1584	1598
Argon	1581	1592
H_2SO_4	1587	1618

The splitting of the G band with pressure allows to determine contributions of inner and outer tubes and to extrapolate the G band frequencies at zero pressure. In the low pressure regime (< 3GPa) the two bands overlap and the numerical fitting is not stable. A change in shape can be either due to intensity variation or change of spectral position. There are clear differences seen between the DWs obtained from peapods and DWs grown with CCVD. The spectral position of the inner tube at zero pressure deduced from linear fitting is at 1579 cm^{-1} [14] for the DW from peapods but at 1581 cm^{-1} for DW grown by CCVD and we find that the shifting of the G band of the inner tube with pressure is delayed. This implies that the coupling of the two walls is not the same which is consistent with differences observed for the band at 1560 cm^{-1}.

5 SPECTRAL ANALYSIS

Figure 4 shows DW G band spectra recorded at three different locations (A, B, C) and recorded at different laser power levels (right hand side). The left hand side shows Stokes and anti-Stokes spectra at location B and a spectrum of DWs in H_2SO_4. To obtain the same background level for Stokes and anti Stokes spectra, we have corrected the Anti-Sokes part by the factor ω^4 and the Bose-Einstein factor corresponding to T = 775K. This high Temperature can be attributed to the single particle excitations [23]. On the right side of figure 4 we have subtracted a linear background for each spectra for the spectra of the three locations A, B and C. To fit the data, only the 4 intensities of the four main contributions are taken as free parameters. Even if a small spectral shift for the four bands is added the intensity ratio remains unchanged. For location B we show spectra from two different laser powers. The fit is stable and higher power reduces the spectral noise. We associate the two intense bands to the G band of SWs and the inner tubes of the DWs and we correlate the intensity ratio with experimentally observed SW/DW ratio.

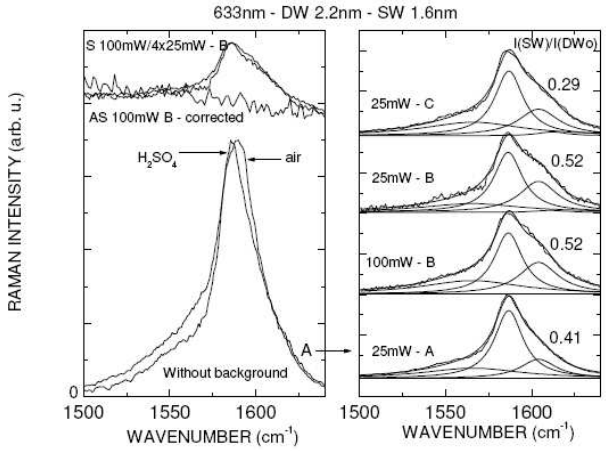

FIG. 4: Fraction of SW in our sample: 3 places (A,B and C), S for Stokes, AS for Anti-Stokes.

Using the determined purity (80%) using transmission electron microscopy, and the average value of I_S/I_D reported in figure 4, we find an empirical relation: $N_{SW}/N_{DW}=0.3I_S/I_D$. We note that with increasing pressure and doping the intensity decreases and increases the contribution of the outer tube. We use the parameters deduced on the CCVD grown DWs to test the consistency of our approach. We consider 3 bands at fixed spectral position and fixed HWHM for a given temperature. The data used for the fitting are reported in the table II.

We have fitted our data using the set of parameters determined in the first part. We use 2 parameters for the linear background and 3 parameters for the intensities and include a small shift for all associated to temperature increase. Two sets of spectra have been used to test the scheme and the results are reported in figure 5.

Figure 5 shows the G band as a function of laser power using two different microscope objectives.

TABLE II: Parameters for fitting G bands of SWs and DWs in H_2SO_4 using 647 nm excitation wavlength.

Wavenumber (cm^{-1})	HWHM (cm^{-1})
$\omega_{DW-inner} = 1587$	$\Gamma = 10$
$\omega_{DW-outer} = 1618$	$\Gamma = 10$
$\omega_{SW} = 1606$	$\Gamma = 10$
$\omega_{DW_{ei}} = 1568$	$\Gamma = 35$

6 CONCLUSION

We find that chemical doping with H_2SO_4 allows us to accurately determine the composition of CCVD DW samples by using a set of parameters obtained from hydrostatic pressure experiments to fit the Raman G band by keeping the spectral position of contributions from the inner and outer tubes fixed.

ACKNOWLEDGMENT

We thank Jenny Patterson, Intel Ireland, for stimulating discussions.

REFERENCES

[1] K. Matsubara, K. Sugihara, and T. Tsuzuku, Phys. Rev. B 41, 969 (1990)
[2] B. Bourlon, C. Miko, L. Forro, D. C. Glattli, and A. Bachtold, Phys. Rev. Lett. 93, 176806 (2004)
[3] S. Bandow, M. Takizawa, K. Hirahara, M. Yudasaka, S. Iijima, Chem. Phys. Lett. 337, 48 (2001)
[4] E. Flahaut, A. Peigney, Ch. Laurent, A. Rousset, J. Mater. Chem. 10, 249 (2000)
[5] M. Endo, H. Muramatsu, T. Hayashi, Y. A. Kim, M. Terrones, and M. S. Dresselhaus, Nature London 433, 476 (2005)
[6] C. Thomsen and S. Reich, Light Scattering in Solids IX, Ed. M. Cardona and R. Merlin (2005)
[7] Ladislav Kavan , Lothar Dunsch, Chemphyschem.8, 974 (2007)
[8] G. Chen, S. Bandow, E.R. Margine, C. Nisoli, A.N. Kolmogorov, V.H. Crespi, R. Gupta, G.U. Sumanasekera, S. Iijima,and P.C. Eklund, Phys. Rev. Lett. 90, 257403 (2003)
[9] P. Puech, E. Flahaut, A. Sapelkin, H. Hubel, D.J. Dunstan, G. Landa, and W.S. Bacsa, Phys. Rev. B73, 233408 (2006)
[10] Y.A. Kim et al Chem. Phys. Lett. 420, 377 (2006)
[11] W. Zhou, J. Vavro, N.M. Nemes, J.E. Fischer, F.Borondics, K. Kamaras and D.B. Tanner, Phys. Rev. B 71, 205423 (2005)
[12] E.B. Barros et al Phys. Rev. B 76, 045425 (2007)
[13] P. Puech, H. Hubel, D.J. Dunstan, R.R. Bacsa, C. Laurent and W.S. Bacsa, Phys. Rev. Lett. 93, 095506 (2004)
[14] J. Arvanitidis, D. Christofilos, K. Papagelis, K.S. Andrikopoulos, T. Takenobu, Y. Iwasa, H. Kataura, S. Ves, and G.A. Kourouklis, Phys. Rev. B 71, 125404 (2005)
[15] E. Flahaut, R. Bacsa, A. Peigney and Ch. Laurent, Chemical Communication 12, 1442 (2003)
[16] R. Nishitani, Y. Sasaki and Y. Nishina, Phys. Rev. B37, 3141 (1988)
[17] C.T. Chan, W.A. Kamitakahara, K.M. Ho and P.C. Eklund, Phys. Rev. Lett.58, 1528 (1987)
[18] M. Hanfland, H. Beister, and K. Syassen, Phys. Rev. B 39, 12598 (1989)
[19] S. Piscanec, M. Lazzeri, J. Robertson, A.C. Ferrari, and F. Mauri, Phys. Rev. B 75, 035427 (2007)
[20] A. Merlen, N. Bendiab, P. Toulemonde, A. Aouizerat, A. San Miguel, J. L. Sauvajol, G. Montagnac, H. Cardon, and P. Petit, Phys. Rev. B 72, 035409 (2005)
[21] R. Pfeiffer, F. Simon, H. Kuzmany and V.N. Popov, Phys. Rev. B72, 161404 (2005)
[22] P. Puech, A. Bassil, J. Gonzalez, Ch. Power, E. Flahaut, S. Barrau, Ph. Demont, C. Lacabanne, E. Perez, and W. S. Bacsa, Phys. Rev. B 72, 155436 (2005)
[23] D.S. Kim and P.Y. Yu, Phys. Rev. B43, 4158 (1991)