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Surface-Enhanced Raman Scattering from small numbers of single-walled carbon nanotubes and oxidised single-walled carbon nanotubes

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Abstract
Temporal fluctuations of surface-enhanced Raman scattering spectra of purified and oxidised single walled carbon nanotubes have been observed. SERRS spectra were recorded that possessed fluctuating spectral profiles, these profiles possessed randomly fluctuation peak intensities and positions. Observation of bands in the 1000 to 1200 cm⁻¹ frequency window was observed. A series of peaks in this window were observed to coincide with peak positions that have been assigned to arise from Stone-Thrower-Wales and heptagonal-pentagonal intramolecular junction defects on the nanotubes surface. We find that these peaks also occur for chemically treated SWCNTS.

1. Introduction
Single-walled carbon nanotubes (SWCNT) have attracted considerable research effort in understanding and applying their properties [1,2]. One way of tailoring the electronic properties of carbon nanotubes is to add chemical groups to the carbon nanotube [2-4]. The addition of a chemical group via covalent bonding alters the conjugative network of the graphene sheet and creates changes in the electronic structure of the SWCNT. In addition to this the exposure to chemical treatments potentially results in the displacement of carbon atoms from graphite network creating vacancies [5-8]. The effect of adding chemical groups to the surface of the nanotube potentially enhances such properties as field emission, chemical detection sensitivity and electrochemical capacity as well as interface interactions between the nanotube surface and other materials or surfaces [9,10].

Surface enhanced Raman scattering (SERRS) can enhance the Raman signal of SWCNTs by up to 14 orders of magnitude [1,11-13]. SERRS can occur when the SWCNT is placed in contact with metallic (such as silver or gold) nanostructured materials [12,13]. These nanomaterials enable enhancement via localised optical fields. The size of these localised regions can be on the order of 5 nm. This enables small numbers of nanotubes to be probed down to the single nanotube level [12-14]. Raman spectroscopy is able to detect the presence of topological defects on SWCNT. Raman spectroscopy enables characterization of alternations in the graphene network though monitoring the Raman D band. This band assigned to a phonon mode originates from the hexagonal structure of graphite [1,12-14], whereby the presence of pentagon, heptagon, and octagon configurations in place of the hexagonal structure is referred to as topological defects [5,7,8].

The presence of defects in SWCNTs has implications for their application. This has motivated the characterization of defects such as topological defects in SWCNTs. One such topological defect are adjacent pentagon/heptagon pairs, called Stone-Thrower-Wales (STW) and heptagonal-pentagonal intramolecular junction defects [7,8]. As outlined by Miyamoto et al a STW defect consists of a localised π/2 rotation of a C-C bond, such that two pentagons and heptagons are created [15]. These pentagon and heptagon arrangements potentially translocate along the structure, creating either dislocation centres in regions of positive
(pentagons) or negative (heptagons) Gaussian curvature, which ultimately lead to the closing of the nanostructure. A limited number of studies have been performed applying Raman spectroscopy to study defects on SWCNTs. The presence of STW defects changes the structural symmetry of the SWCNT and consequently vibrational modes associated with the topological defects are expected. Fujimori et al reported temporally fluctuating SERRS spectra from SWCNTs [8]. The authors applied SERRS to detect STW defects in SWCNTs. Temporally fluctuating spectra in SERRS occurred with additional peaks not observed in the non-SERRS spectra. These peaks were assigned to dynamic reconstruction of defective structures of SWCNTs arising from STW defects in the vicinity of SERRS-active sites under irradiation of the laser light.

Here we perform SERRS studies on commercially sourced SWCNTs and purified SWCNTs that have been chemically treated to improve their purity and also to alter the structure of the nanotube surface via covalently attaching carboxylic acid groups [4]. The purification process removing impurities such as graphene or fullerenes which may be present in untreated SWCNT samples. This aide’s definitive assignment of the observed Raman peaks as such impurities potentially possess Raman active peaks that overlap with peaks associated with defects. SWCNTs with chemical groups covalently to the SWCNT surface were investigated assessing the impact of altering the electronic arrangement of the nanotube surface. The presence of structural changes in the SWCNT in the vicinity of SERRS-active sites (namely STW defects) has been asserted here to explain the occurrence of bands observed in the SERRS spectrum of purified SWCNT via comparison with reported theoretical calculated band positions for defects [7,8]. SERRS spectra were recorded that possessed fluctuating spectral profiles, these profiles possessed randomly fluctuation peak intensities and positions. Observation of bands in the 1000 to 1200 cm⁻¹ frequency window was observed. A series of peaks in this window were observed to coincide with peak positions that have been assigned to arise from defects on the nanotubes surface. We find that these peaks also occur for chemically treated SWCNTs.

2. Experimental
SERRS measurements were carried out with a single monochromator (Roper Acton SP2300s) and EMCCD (Andor Ixon) in a backscattering configuration using a 60× objective to excite and collect the scattered light. The spectral resolution was >1.5 cm⁻¹. SERRS measurements were conducted with 532 nm (Nd:YAG laser) excitation. The SERRS substrates consisted for a thin film of silver of 40 nm in thickness which was deposited onto a glass slide. Following this silver nanoparticles were then deposited onto the substrate surface, carbon nanotubes where then deposited onto the silver substrate. This created the SERRS active support which the SWCNTs were dispersed at low concentration in ethanol (abs) by sonication, spray coated onto freshly prepared SERRS substrates and dried in a desiccator. Purified commercially sourced SWCNTs (p-SWCNTs) were purchased from Carbon Nanotechnologies, Inc. and used as supplied. Highly purified and selectively oxidised SWCNTs (o-SWCNTs) were prepared according to a recently published purification/oxidation protocol [4]. Briefly, this method involves a short nitric acid oxidation to minimize structural/electronic degradation of SWCNTs and sodium hydroxide treatments to remove carboxylated carbonaceous impurities. A hydrogen peroxide oxidation step efficiently etches remaining carbonaceous impurities and ensures full oxidation of oxygenated species to carboxylic acid moieties. Persistence of characteristic optical properties indicating the preservation of the electronic structure during chemical treatment has been demonstrated [4]. Atomic Force Microscopy (AFM) images were recorded using an explorer AFM system.
3. Results and discussion

SERRS and Raman spectra of p-SWCNT are shown in Fig. 1. Fig 1a shows SERRS spectra of p-SWCNT recorded sequentially with a 10 s interval as an intensity plot. The SERRS spectra show temporally fluctuating peaks superimposed on the G and D band regions. Areas of the sample that show the presence of these fluctuating peaks are found randomly across the sample with some regions of the sample showing no sharp fluctuating peaks, only broadened G and D bands with stable profiles. Fig 1b shows two SERRS spectra taken from different regions of the sample. One spectra show broadened G and D band features, the second spectrum shows sharp features within the G and D band region. The G and D modes are broadened compared to the Raman spectra. Broadening of the G and D band regions in SWCNT has been reported to occur for nanotubes on thin (c.a. >20 nm) silver films [16]. Fig 1c shows a sequence of ten spectra recorded over a concurrent period of p-SWCNTs. Fluctuating peaks are seen in this spectral sequence with band positions and band intensities changing. Carbon nanotubes possess strong Raman scattering cross sections which when coupled with plasmonic enhancement enables small number of nanotubes to be observed down to the single nanotube level. The effect of ensemble averaging potentially gives rise to temporal fluctuations of intensities and frequencies. With SWCNTs of different sizes and orientations been observed at different times creating temporally fluctuating spectral signals.

In order to assess the type of nanotube probed a study of the radial breathing mode (RBM) region was undertaken. Fig 1d and e shows the RBM region of the SERRS spectrum. The spectrum recorded at 532 nm has peaks at 271, 240 and 188 cm⁻¹. The RBM peak at 270 cm⁻¹ equates to a nanotube d_t = 0.92 nm as calculated by the relation, ω_{RBM} = 248/ d_t , where ω_{RBM} and d_t indicate the RBM frequency and tube diameter, respectively [12-13]. The band at 240 cm⁻¹ has a d_t = 1.03 nm. The RBM peak at 192 cm⁻¹ has a d_t = 1.29 nm. Using the Kataura plot the nanotubes excited at 532 nm (2.33 eV) are predominantly metallic nanotubes for p-SWCNT were all tubes c.a. <275 cm⁻¹ and >200 cm⁻¹ arise from metallic nanotubes and those above are from semiconducting tubes [17]. Maultzsch et al applied resonant Raman to study the radial breathing mode of nanotubes for more than 50 chiral indices with diameters between 0.6 and 1.5 nm [17]. The authors noted that ω_{RBM} = 248/ d_t + C is required to more correctly account for additional external forces, e.g., from interactions with a substrate or neighbouring tubes in a bundle. The silver SERRS active potential creates additional external forces on the nanotube thus requiring correction for estimation of the ω_{RBM}, however it is noted that changes in the environment of the tubes probed so far lead to small changes in the RBM frequencies. Changing the excitation wavelength to 632 nm, changes also the RBM spectrum compared to the spectrum recorded at 532 nm. The spectra show that the p-SWCNT has a RBM peak at 283, 257 217 and 196 cm⁻¹. These bands equate to metallic nanotubes for the bands <225 cm⁻¹ with the bands above this arising from semiconducting nanotubes. Thus on this basis the RBM spectra for p-SWCNT indicates that for 532 nm excitation predominantly metallic nanotubes are excited at 532 nm and predominantly semiconducting nanotubes are excited at 632 nm.

Fig 1d and e shows the RBM spectra for o-SWCNT recorded at 532 and 632 nm. The spectrum recorded at 532 nm has two peaks at 241 and 268 cm⁻¹. The RBM peak at 241 cm⁻¹ equates to a nanotube d_t = 1.02 nm as calculated by the relation, ω_{RBM} = 248/ d_t [12-13]. The band at 261 cm⁻¹ has a d_t = 0.95 nm. Using the Kataura plot as above the nanotubes excited at 532 nm (2.33 eV) are predominantly metallic nanotubes for p-SWCNT were all tubes c.a. <275 cm⁻¹ and >200 cm⁻¹ arise from metallic nanotubes [17]. Changing the excitation wavelength to 632 nm, changes also the RBM spectrum compared to the spectrum recorded at 532 nm as for p-SWCNT. The spectra show that the o-SWCNT has a RBM peak at 282,
255, 218 and 198 cm\(^{-1}\). These bands equate to metallic nanotubes for the bands <225 cm\(^{-1}\) with the bands above this arising from semiconducting nanotubes. Thus on this basis the RBM spectra for p-SWCNT indicates that for 632 nm excitation predominantly from semiconducting nanotubes where when the nanotubes are excited at 532 nm predominantly metallic nanotubes are observed.

These sizes of nanotube can be related tentatively to nanotube chirality. Kurti et al using density functional theory obtained the geometrical properties and the radial breathing mode (RBM) frequency of a series of 40 different single-wall carbon nanotubes [18]. The authors predicted that a (9,9) nanotube would have a RBM peak at 192 cm\(^{-1}\) and a (12,0) nanotube would have a RBM peak at 240 cm\(^{-1}\). However it is noted for example that there the assignment of the chirality of the nanotube at the diameter 1.3 nm can be made to several nanotubes such as (9,9) and also to (10,n) were n = 7, 8 or 9. The broad RBM peaks potential possess a number of peaks corresponding to different nanotube chirality within this broad RBM envelop. Maultzsch et al applied resonant Raman to study the radial breathing mode of nanotubes for more than 50 chiral indices with diameters between 0.6 and 1.5 nm [17]. The authors noted that \(\omega_{RBM} = 248/d + C\) is required to more correctly account for additional external forces, e.g., from interactions with a substrate or neighbouring tubes in a bundle. The silver SERRS active potential creates additional external forces on the nanotube thus requiring correction for estimation of the \(\omega_{RBM}\), however it is noted that changes in the environment of the tubes probed so far lead to small changes in the RBM frequencies.

Studies of defects in nanotubes such as STW have been performed by Fujimori et al and Vandescuren et al [7,8]. Fujimori et al reported temporally fluctuating SERRS spectra from SWCNTs with peaks in the D and G band regions and also peaks outside this region at 1139 and 1184 cm\(^{-1}\) which were assigned to dynamic reconstruction of defective structures of SWCNTs arising from STW defects in the vicinity of SERRS-active sites under irradiation of the laser light [8]. This study was based on semiconductor nanotubes with diameters of c.a. 1.5 and 1.3 nm. Theoretical calculations by Vandescuren et al predicted Raman peaks for STW defects for (10, m) (were m is an integer between 0 and 10) nanotubes and for heptagonal-pentagonal defects for (9,0) and (12,0) nanotubes [7]. The SERRS study here potentially probes both (10, m) and (12,0) nanotube type as evidenced by the RBM spectra (see above).

Fig 2 displays SERRS spectra, i to iii, selected from the spectra shown in Fig 2a. Spectra i and ii possess peaks at 1143 cm\(^{-1}\) as well as peaks at 1186 cm\(^{-1}\) both marked \(\alpha\). These bands are outside of the D and G wavelength region. The presence of the \(\alpha\) bands is accompanied by a strong band in the G band region at c.a. 1590 cm\(^{-1}\). Fig 2b shows that the bands marked \(\alpha\) are persistent over seconds. Analysis of the spectral features in Fig 2a show the presence of a band at 1270 cm\(^{-1}\) (marked \(\beta\)). Spectrum iii in Fig 2a does not possess spectral features at \(\alpha\) or \(\beta\). Peaks (marked \(\chi\)) are seen at 1276 and 1310 cm\(^{-1}\).

The intensity of several peaks as a function of time was assessed by plotting band intensity vs. time over a 250 sec interval (as shown in Fig 2c). Inspection of Fig 2c shows that the bands at 1142 and 1186 cm\(^{-1}\) (assigned to STW defects) show similar fluctuations in Raman signal intensity with time. The band at 1270 cm\(^{-1}\) can also be assigned to arise from STW defects and shows a similar fluctuation in Raman signal intensity over time compared to the bands at 1142 and 1186 cm\(^{-1}\). Looking at the Raman intensity over time for a band at 1599 cm\(^{-1}\), which is associated with a SWCNT G mode, the intensity fluctuations visible differ to the bands associated with STW defects. Calculating the Pearson product-moment correlation...
coefficient r for the intensity allows for analysis of the ‘randomness’ in the intensity of peaks [19]. Values close to zero indicate a random intensity variation while large values present a strong linear correlation. The Pearson product-moment correlation coefficient for the fluctuations in the $\alpha$ peak at 1183 cm$^{-1}$ over the observed time-frame was as calculated to be $r = 0.27$. This indicates that the intensity variation is random over the recorded time window. Pearson product-moment correlation coefficient was employed to calculate the correlation between two Raman peaks by comparing the Raman signal intensities as a function of time i.e. when comparing two peaks. The variation of peak intensity of the two peaks at 1183 and 1142 cm$^{-1}$ yields a correlation coefficient $r = 0.98$. This value demonstrates a strong correlation between the two Raman bands. Both bands are predicted to arise from STW defects. Another band that was predicted to be associated with STW defects is the band at 1270 cm$^{-1}$. Comparing the peaks at 1142 cm$^{-1}$ with the band at 1270 cm$^{-1}$ revealed a strong correlation $r = 0.94$. This supports the assertion that the peaks at 1270 cm$^{-1}$ is associated with STW defects. A relatively minor correlations ($r = 0.47$ and 0.46 respectively) were found between the STW peaks at 1142 or 1183 cm$^{-1}$ when compared to the peak at 1598 cm$^{-1}$ which is associated with the G band in SWCNTs.

Fig 3 outlines the variation in Raman frequencies and intensities recorded for p-SWCNTs recorded at 632 nm. Fig 3a shows ten spectra recorded successively. Fig 3b shows the un-normalized spectra as shown in Fig 3a. The spectra show the presence of fluctuating peaks and a changing intensity in the spectral features. Magnifications of three spectra from Fig 3a are displayed in Fig 3c. The upper spectrum in Fig 3c shows peaks at 1144 and 1185 cm$^{-1}$ (marked $\alpha$). A band at 1269 cm$^{-1}$ (marked $\beta$) is observed. These peaks are in the same position as the bands observed at 532 nm excitation. On this basis these peaks are assigned to dynamic reconstruction of defective structures of SWCNTs arising from STW defects in the vicinity of SERRS-active sites under irradiation of the laser light [8]. A small shift from 1139 to 1143 cm$^{-1}$ or 1184 to 1186 cm$^{-1}$ is present however. Theoretical calculations by Vandescuren et al predicted further Raman peaks for STW defects at 1270 and 1020 cm$^{-1}$ [7]. The peak positions and intensities predicted by Vandescuren et al was for (10, m) SWCNT [7]. Analysis of the spectral features in Fig 2 and 3 show the presence of a band at 1270 cm$^{-1}$ (marked $\beta$). While a band at 1020 cm$^{-1}$ does not clearly appear. However, it is noted that the predicted band intensity at 1020 cm$^{-1}$ is much weaker than the predicted band intensity at 1270 cm$^{-1}$. Spectra in Fig 2 and 3 also can show peaks (marked $\chi$) at 1276 and 1310 cm$^{-1}$. These bands can be assigned, on the basis of theoretical calculations by Vandescuren et al, to heptagonal-pentagonal intramolecular junctions in carbon nanotubes, which correspond to defect modes localized on the pentagon and slightly around it [7]. These bands are reported to occur at 1275 and 1315 cm$^{-1}$.

Fig 4 outlines the variation in Raman frequencies and intensities recorded for o-SWCNTs recorded at 632 nm. Fig 4a shows ten spectra recorded successively. Fig 4b shows normalized spectra as shown in Fig 4a. The spectra show the presence of fluctuating peaks and a changing intensity in the spectral features. The upper spectrum possesses peaks at 1143 cm$^{-1}$ as well as peaks at 1186 cm$^{-1}$ both marked $\alpha$. Analysis of the spectral features shows also the presence of a band at 1270 cm$^{-1}$ (marked $\beta$). The lower spectrum in Fig 4a does not possess spectral features at $\alpha$ or $\beta$. Peaks (marked $\chi$) are seen at 1276 and 1310 cm$^{-1}$. These bands are in the same position and possess similar relative intensities are the bands marked correspondingly for p-SWCNT excited at 632 nm (as shown in Fig 3). This shows the treatment to produce the oxidised SWCNT (o-SWCNT) does not change the presence of bands potentially arising from defect sites.
The substrate was analysed using microscopy. Fig 5a shows an AFM microscopy image recorded of the SWCNTs on a glass slide. The dispersed sample shows the presence of aggregates on the sample surface containing few nanotubes. The presence of single nanotubes was not definitively found due to a combination of the small size of these structures making it difficult for the AFM to image them. Images of the carbon nanotubes were obtained on a cleaned glass slide to determine their dispersion, whereby the glass forms a smooth surface. The distribution of the nanotubes was seen to be inhomogeneous across the sample surface. The presence of aggregates of nanotubes and the inhomogeneous distribution of silver on the substrate indicates that there is expected to be a variation in the Raman spectral features expected when probing a small area of the sample. The use of a high powered objective (ie 60X) enables the probing of areas of the sample on the few micron length scales. The inhomogeneous distributions of plasmonic active silver and nanotube dispersion explains the occurrence of some regions of the sample randomly occurring as you scan the sample that show temporal fluctuations in the SERRS spectra. The inset shows an optical reflection contrast image of the substrate. The image in Fig 5a shows a selection of the sample area of the silver film substrate which has present on its surface deposited silver nanoparticles, which were deposited after the silver film was made. The image shows that the silver is not a continuous film but is fragmented into small and large areas or islands on the substrate on length scales on the scale of microns or larger. This means that the silver substrate is an inhomogeneous plasmon active substrate layer on which the carbon nanotubes are located. AFM studies were undertaken of the samples surface to enable more spatially resolved information to be obtained. Fig 5b show an AFM topography image of the surface features of the silver film which the SWCNTs are deposited onto. Inset i) shows a potential observation of SWCNTS on the substrate. An inhomogeneous surface topography was found. The topography profile plot (inset ii) indicates that certain regions of the samples surface are rough on the order of 100’s of nm and others rough on the length scale of 10’s of nm. ‘Hot spot’ areas of high plasmon enhancement may be present on this sample as a result of the fragmentation of the silver on the micron length scale, in addition to the presence of the nm roughed surface features as a result of the presence of silver nanoparticles. This nm sized roughness potentially can create plasmon enhancement ‘hot spots’. Fluctuations in the SERRS Raman band intensities and positions have been observed previously and have been proposed to arise from the presence of such create plasmon enhancement “hot spots” on SERRS-active metals such as silver.

Molecular dynamic simulations were undertaken using MM+ methodology. The simulation was based on silver ions and a nanotube structure. The ions were calculated to interact with the nanotube. The ions were found to enter the nanotube and assemble with the nanotube and around its external structure, were the silver was placed at the beginning of the calculation. This simulation provides evidence that the silver ions are in proximity to the nanotube surface and as a consequence may interact with defect sites such as a mobile STW defect that may be present from a vacancy in the tube. The presence of these silver ions potentially influence the nanotubes structure and in turn the resulting Raman spectra. In addition it is noted that the presence of the nanoscale rough silver environment may lead to restricting the vibration motion of the nanotube leading to in turn a change in the frequency and intensity of the resulting Raman. The observed SERRS temporal Raman spectral features may result from a perturbation of the Raman modes and not by the presence of defects.

o-SWCNTs are prepared from p-SWCNTs using acid based treatment, creating the addition of oxide groups at the end of the nanotubes or in areas of vacancies in the nanotubes surface. The presence of the oxide groups do not remove the occurrence of bands associated with
STW defects. The observed SERRS spectrum is modified compared to the Raman spectra for both the p-SWCNT and o-SWCNT as evidenced by the large D band SERRS intensity compared to the spectral features for the resonance Raman spectral features [ref]. The intense D band in the SERRS indicates a change in the degree of disorder. The D band in the SERRS increases its intensity and displays a change in profile. The broadening of the D and G band region has been assigned to an interaction between the silver and the nanotube centring on the charge transfer mechanism responsible (in part) for the SERRS enhancement [16]. The presence of the silver nanoparticle layer potentially contributes also to this broadening and enhancement of the D band region.

Photo-induced structural changes such as the decomposition of the nanotube can potentially lead to the observation of bands in the c.a. 1150 cm\(^{-1}\) region assigned to STW defects as outlined above. Lefrant et al showed that SERRS from SWCNT could be interpreted in terms of degradation of the single-walled nanotubes and the formation of particles similar to highly oriented pyrolytic graphite e.g. C\(_{60}\) and amorphous carbon [16]. Lefrant et al demonstrated that the presence of materials such as C\(_{60}\) is expected to result in Raman spectra with marker bands at 1458 cm\(^{-1}\) [16]. No bands were observed at this position in the SERRS spectra indicating that the no C\(_{60}\) was formed. However the broad G and D bands seen in Fig 1b and 3a indicates that there is strong coupling between the SWCNT and the silver substrate. This coupling is expected to lead to strong SERRS.

4. Conclusion

SERRS studies on commercially available purified SWCNTs and oxidized SWCNTs have been carried out. For both samples SERRS spectra with and without temporal fluctuations in peak frequencies and intensities were found depending upon the area probed. The origin for the SERRS spectra with temporal fluctuations in peak frequencies and intensities was ascribed to single and/or few nanotubes been located in regions of the sample that possessed high plasmon localisation. Areas of relatively high and low plasmon localisation result from the rough surface topography of the silver substrate. In p-SWCNTs and o-SWCNT temporal fluctuating peaks in the region between 1000 to 1350 cm\(^{-1}\) Raman shift have been ascribed to the dynamic behaviour of STW and heptagonal-pentagonal intramolecular junction defects based on comparing the band positions observed to simulated values for the occurrence of such defects in nanotubes. Evidence for carbonaceous impurities photochemically generated in the sample was not definitively found, e.g. no occurrence of Raman bands at c.a. 1458 cm\(^{-1}\) (definitive for C\(_{60}\)) was observed when Raman bands for STW defects were observed. The effect of chemical introduction of carboxylic acid moieties to the surface of the nanotubes was seen to alter the spectral profile in the frequency region associated with bands arising from of Stone-Thrower-Wales and heptagonal-pentagonal intramolecular junction defects in the nanotube.

The treatment that creates the o-SWCNT nanotubes potentially can lead to a covalent bond occurring at a defect site. The occurrence of bands that can be assigned to defect sites indicates that the presence of oxides on the nanotube does not remove the defects. In addition the occurrence of strong D band intensities indicates further that potentially disorder/defects may be present on the nanotubes surface. MM+ calculations show that silver ions may be present within the tubes structure as well as near its external wall structure, these ions potentially perturbing the nanotubes structure and Raman spectral features. While the presence of photo-induced decomposition cannot be ruled out and also potentially impurities
from the atmosphere or from contamination elsewhere may explain the observed bands, the occurrence of bands in the positions labelled $\alpha$ and $\beta$ have been calculated to occur from defects in grapheme. Furthermore the calculations by Fujimori et al were performed on a sheet which is applicable to nanotubes of different sizes and chirality.

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References


Fig 1. a) Temporally fluctuating SERRS spectra of p-SWCNTs. $\lambda_{\text{excitation}} = 532$ nm. The power density was 0.65 MW cm$^{-2}$. Each SERRS spectrum was acquired for 1s with a time interval of 10s. A series of SERRS spectra recorded consequently. Note the tilt in the spectra shown is accounted for in extracting the data shown in following figures c). b) SERRS spectra taken at different regions of the sample. i) show a region where no temporal variation in band intensities are seen and ii) a region of the sample showing variation in the spectral profile over time. c) Shows ten spectra taken from the series shown in a), the band intensities have been normalised for clarity. d) and e) SERRS spectra in the RBM spectral region.
Fig 2. Temporally fluctuating SERRS spectra of p-SWCNTs. $\lambda_{\text{excitation}} = 532$ nm. The power density was 0.65 MW cm$^2$. Each SERRS spectrum was acquired with a time interval of 10s. a) shows three spectra taken from Fig 1c, $\alpha$, $\beta$ and $\chi$ mark band positions. b) shows magnified sections of the spectra shown Fig 1d, the band intensities have been normalised for clarity. c) a plot of peak intensity vs time for temporally fluctuating SERRS peak intensities acquired with a time interval of 2s as a function of time over 250 s.
Fig 3. Temporally fluctuating SERRS spectra of p-SWCNTs. $\lambda_{\text{excitation}} = 632$ nm. Each SERRS spectrum was acquired with a time interval of 10s. The power density was 0.65 MW cm$^{-2}$. The spectra are normalized for clarity. a) Two spectra taken from different parts of the sample. b) A series of ten spectra taken consecutively. c) Three spectra were taken from Fig 3a shown for clarity.
Fig 4. a) Temporally fluctuating SERRS spectra of o-SWCNTs. $\lambda_{\text{excitation}} = 632$ nm. Each SERRS spectrum was acquired with a time interval of 10s. The power density was 0.65 MW cm$^{-2}$. The spectra are normalized for clarity. b) Two spectra were taken from Fig 3a shown for clarity. c) Schematic drawing of o-SWCNT, the COOH group attached at the end of the nanotube.
Fig 5. a) AFM topography image of o-SWCNTs dispersed onto a glass slide, using the same dispersion methods employed to prepare all the samples studied. The AFM image showing features in white which are assigned to arise potentially from clusters of carbon nanotubes c.a. 4 nm in height (from the background substrate) present on the substrate surface. These clusters potentially containing few nanotubes where 1 nanotube is c.a. 1 nm in height and potentially microns in length. The presence of single nanotubes was not definitively found. The inset shows an optical reflection contrast images of the sample surface of the silver film following the addition of silver nanoparticles. The images were recorded with a standard CMOS camera mounted onto a AFM system. b) AFM topography image of the substrate surface. The inset ii) shows a AFM topography profile plot showing that the roughness of the silver film is inhomogeneous with a parts of the sample surface been rough on the order of 100 nm and others been on the order of 10’s of nm. inset ii) shows features associated with SWCNTS on the silver surface. The topography image shows features associated with SWCNT present on the silver surface, noting that only a relatively smooth part of the surface enabled features assigned to SWCNTs to be seen. c) Molecular dynamics simulation of the interaction of silver ions and a nanotube structure.
Figure

(a) Time series of Raman intensity versus wavenumber. (b) Spectra showing two distinct peaks labeled i and ii. (c) Series of Raman intensity plots across different wavenumbers. (d) Comparison of Raman intensity for p-SWCNT and o-SWCNT. (e) Additional spectra for p-SWCNT and o-SWCNT at lower wavenumber range.
Highlights

Surface-enhanced Raman scattering spectra of purified and oxidised single walled carbon nanotubes

Potential evidence for the presence of Stone-Thrower-Wales and heptagonal-pentagonal intramolecular junction defects.

Effect of chemical introduction of carboxylic acid moieties to the surface of the nanotubes