CHAPTER 9

Raman Spectroscopy of Carbon Nanotube–Polymer Hybrid Materials

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9.1 Introduction

Carbon nanotubes (CNTs) have received much attention as a class of next-generation nanomaterials due to their unique physical and chemical properties. The potential utility of CNTs in a variety of technologically important applications, such as polymer composites, supercapacitors, lithium rechargeable batteries, sensors, photovoltaic and solar cells, high-resolution printable conductors and so on, is now well established. However, due to their poor solubility and strong aggregation, enhancing the processability of CNTs while preserving their properties has been a main challenge before CNTs could be integrated into functional hybrids for the fabrication of advanced devices.

The hybridization of various types of CNTs, such as single-walled CNTs (SWCNTs), double-walled CNTs (DWCNTs) or multi-walled CNTs (MWCNTs), with insulating or conducting polymers at the molecular level is an efficient strategy to: (i) obtain the emerging properties through the synergistic effects of the two components while overcoming the intrinsic limitations of the individual materials, (ii) reinforce the macromolecular
compound and (iii) introduce novel electronic properties based on morphological modifications or interactions between the two constituents. Moreover, from the materials engineering perspective, the characteristics of the CNT–polymers interface should be rationally designed to make CNTs chemically compatible for polymeric matrices with enhanced mechanical/electrical properties for the final composite.

In the past decade, the development of Raman spectroscopy (RS) in the field of CNTs and, recently, of graphene is truly impressive. The level of information and details that have become available has allowed the development of nanotechnology from a more fundamental perspective. In this process, Raman spectroscopy is one of the most useful and versatile tool to characterize and investigate CNT samples. It is a fast and non-invasive probing technique with high resolution giving the maximum structural, vibrational and electronic information. Raman spectroscopy has been widely used to investigate the structure, physical and chemical properties of CNTs. The unique optical properties observed in SWCNTs are largely due to the one-dimensional confinement of electronic and phonon states, resulting in the so-called van Hove singularities (vHs) in the nanotube electronic density of states (DOS) (see below in the text). In combination with the intriguing electronic structure, the resonantly enhanced Raman scattering intensity allows one to obtain detailed information about the vibrational properties of nanotubes, even at the isolated individual SWCNT level.

Raman scattering has been employed successfully to determine the diameter, chirality and curvature of nanotubes, their structural integrity, the metallic vs. semiconducting behaviour, physical adsorption and/or wrapping of polymers to CNTs surface, defects and other crystal disorder, as well as strain or stress that the nanotubes experience under external loads or environmental effects. Also, it is extremely sensitive for detecting local changes in the hybridization state of carbon atoms from \( sp^2 \) to \( sp^3 \) and/or modifications of the electronic and phonon structure caused by the functionalization of the graphitic network. Charge transfer effects between the CNTs and the polymer molecules and the concomitant alterations of the electronic structure can be effectively traced using Raman spectroscopy.

This Chapter provides an overview of micro-Raman spectroscopy of CNTs and its application in studying CNT reinforced polymer composites. By choosing and presenting various important and characteristic paradigms, we intend to elucidate the usefulness of Raman scattering as a valuable tool to characterize different types of composite materials and probe the interactions between CNTs and polymer molecules. More detailed information is available in topical reviews.

### 9.2 Chemical Modification of CNTs with Polymers

As already mentioned, the usage of CNTs as a starting material in different applications has been largely limited due to their poor processability,
insolubility and infusibility. To bypass this disadvantage, an efficient key is the functionalization of CNTs with polymers, leading to functional composite materials. The modification strategies of CNTs by polymers can be divided into two categories based on the type of bonds between CNTs and polymers, namely non-covalent or covalent bonding.

Non-covalent CNT modification concerns the physical adsorption and/or wrapping of polymers to the surface of the CNTs. The graphitic sidewalls of CNTs provide the possibility for $\pi$-stacking interactions with conjugated polymers, as well as organic polymers containing heteroatoms with free electron pairs. An advantage of non-covalent functionalization is that it does not destroy the conjugated system of the CNT sidewalls and therefore it does not affect the final structural properties of the material.\footnote{3}

The second modification is covalent chemical bonding (grafting) of polymer chains to CNTs, in which strong chemical bonds between CNTs and polymers are created. There are two main methodologies for the grafting of CNTs depending on the building of polymer chains. Firstly, the “grafting to” approach involves the synthesis of a polymer with a specific molecular weight terminated with reactive groups or radical precursors. In a subsequent reaction, this polymer chain is attached to the surface of nanotubes by addition reactions.\footnote{9} A disadvantage of this method is that the grafted polymer content is limited because of the relatively low reactivity and high steric hindrance of macromolecules. In comparison, the “grafting from” approach involves growing polymers from CNT surfaces via in situ polymerization of monomers initiated by chemical species immobilized on the CNT sidewalls and tips. The advantage of this method is that the high reactivity of monomers makes efficient, controllable and tailored grafting feasible.\footnote{3}

9.3 Background of Raman Spectroscopy of CNTs

9.3.1 Electronic Structure of CNTs

Owing to their one-dimensional nature, the $\pi$-derived electronic DOS of a SWCNT (the prototype material of CNT family) forms sharp singularities, the so-called van Hove singularities. The sharp vHs define narrow energy ranges for which the electronic DOS intensity becomes quite large (Figure 9.1a–9.1c). Therefore, a SWCNT exhibits a “molecular-like” behaviour, with well-defined electronic energy levels at each singularity. The vHs closer to the Fermi level originate from cutting lines closer to the K point in the 2D Brillouin zone.\footnote{7} To a first approximation, the vHs are energetically symmetrical with respect to the Fermi level of the individual SWCNT. Dipole-allowed optical transitions (designated as $E_{ii}$) occur between the i-th valence band vHs and the i-th conduction band vHs. Each individual (n, m) SWCNT exhibits a different set of valence and conduction band vHs and a different set of optical transition energies $E_{ii}$. For this reason, optical experiments can be used for the structural determination of a given (n, m) CNT.\footnote{7}
It is quite useful in CNT characterization by Raman spectroscopy to consider the plots of $E_{ii}$ vs. $d_t$ (nanotube diameter). Figure 9.1(d) presents $E_{ii}(d_t)$ values for all the (n, m) SWCNTs with diameters between 0.5 and 3.0 nm, calculated using the tight-binding approximation. As can be clearly seen, the electronic transition energies vary, exhibiting an almost $1/d_t$ dependence. Each point in this plot corresponds to one optically allowed $E_{ii}$ from a given (n, m) semiconducting (Figure 9.1d, crosses) or metallic (Figure 9.1d, circles) SWCNT. The so-called Kataura plot has been widely used to interpret the optical spectra from CNTs.

More specifically, an observable Raman signal from a CNT can be obtained when the laser excitation energy ($E_{\text{laser}}$) is equal to the energy separation between two vHs in the valence and conduction bands. Because Raman scattering is a resonance process in CNTs, Raman spectra even at the single nanotube level allow us to study the electronic and phonon structure of SWCNTs in great detail. Since the observable Raman spectra come predominantly from tubes in resonance with $E_{\text{laser}}$, a Kataura plot specifies which nanotubes will be detected for a particular laser line. When Raman spectra of SWCNT bundle samples are taken, only those SWCNTs with $E_{ii}$ in resonance with the $E_{\text{laser}}$ will contribute strongly to the detected Raman signal. It should be stressed that the transition energies that apply to an individual suspended SWCNT, e.g. wrapped by a surfactant, do not necessarily hold for

**Figure 9.1** (a–c) Electronic DOS of different metallic (M) and semiconducting (S) CNTs, and (d) Kataura plot derived from a simple first neighbour tight-binding approximation. Adapted from Jorio et al.\textsuperscript{5}
SWCNT in a bundle where the transition energies for bundled SWCNTs are downshifted and the resonance widths are found to be broadened.\textsuperscript{5,12}

9.3.2 Raman Spectrum of CNTs

Figure 9.2 shows the main spectral features of the Raman spectrum of a SWCNT, namely the radial breathing modes (RBMs) (150–300 cm\textsuperscript{-1}), the D band at 1250–1450 cm\textsuperscript{-1}, the G-band at 1580 cm\textsuperscript{-1} and the 2D band at 2500–2750 cm\textsuperscript{-1}. Each feature corresponds to different vibration modes associated with the structure of SWCNTs and will be discussed briefly below.

9.3.2.1 The Radial Breathing Modes

The RBM bands correspond to the coherent vibration of the carbon atoms where all the tube atoms vibrate radially in phase. These features are unique in CNTs and occur with frequencies between 120 and 350 cm\textsuperscript{-1} for SWCNTs with diameters in the range 0.7 nm < \(d_t\) < 2 nm. The RBM frequency (\(\omega_{\text{RBM}}\)) varies as 1/\(d_t\) through the relation: \(\omega_{\text{RBM}} = A/d_t + B\), where the parameters \(A\) and \(B\) are determined experimentally. Different values of the constants \(A\) and \(B\) have been reported in the literature,\textsuperscript{7,10} whereas the variations in the \(A\) and \(B\) parameters are often attributed to environmental effects, namely whether the SWCNTs are present as isolated, supported or in the form of bundles.\textsuperscript{13} Therefore, from the \(\omega_{\text{RBM}}\) measurement of an individual SWCNT, it is possible to obtain its diameter value. Also, by recording Raman spectra using

![Figure 9.2 Typical Raman spectrum of SWCNT excited at 514.5 nm; the more intense Raman features are marked.](image-url)
many laser lines, the nanotubes diameter distribution in a sample can be extracted. In this line, the RBM spectrum of SWCNT bundles contains RBM peaks corresponding to different SWCNTs in resonance with the $E_{\text{laser}}$.

The RBM is a highly resonant feature and very sensitive to electronic and structural changes as well as environmental, e.g. polymer wrapping on to CNT sidewalls. The Raman intensity is enhanced by some orders of magnitude if the energy of the incident or scattered light matches the energy of an electronic transition $E_{ii}$. These resonance conditions are called incoming and outgoing resonance, respectively. A resonance profile for a given RBM mode is rendered by recording the Raman intensity as a function of excitation energy using tunable laser systems. From the resonance profiles it is possible to obtain the transition energies $E_{ii}$ and assign the chiral index (n, m).

The Raman resonance profile for a single resonance is a superposition of an incoming and an outgoing resonance and can be described by eqn (1):

$$I(E_{\text{laser}}) = \left( \frac{Mc}{\hbar \omega_{\text{RBM}}} \right)^2 \left[ \frac{1}{(E_{\text{laser}} - E_{ii} - i\gamma/2)} - \frac{1}{(E_{\text{laser}} - \hbar \omega_{\text{RBM}} - E_{ii} - i\gamma/2)} \right]^2 \quad (1)$$

where $E_{\text{laser}}$ is the laser energy, $E_{ii}$ is the energy of the allowed optical transition and $\gamma$ is the lifetime broadening of the intermediate electronic states. The $M$ contains all of the matrix elements and $c$ summarizes the remaining factors. An incoming resonance occurs when $E_{\text{laser}} = E_{ii}$ and an outgoing resonance when $E_{1} = E_{ii} + \hbar \omega_{\text{RBM}}$. If the incoming and outgoing resonances are not resolved in the resonance profile, the recorded spectral profile exhibits a Lorentzian-like shape with a resonance maximum at approximately $E_{ii} + 0.5\hbar \gamma_{\text{RBM}}$. It should be stressed that in practice the energy distance between the maxima of the incoming and outgoing resonances is in the range of 20 to 40 meV, which is too small to appear as two distinct maxima.

The above-mentioned RBM properties have been extensively employed to characterize chemically modified CNTs. CNT–polymer interactions that are sensitive to the diameter as well as the electronic structure (metallic or semiconducting) of the SWCNTs can be easily followed. On the other hand, recording resonance profiles in the case of functionalized material only makes sense by comparing both reference and functionalized nanotubes, as the absolute values of the optical transitions are often modified during preparation procedures and due to environmental changes. Covalent modification disrupts the electronic band structure, thus reducing the resonance enhancement of the Raman process significantly affecting the resonant profiles. In many cases the optical transitions are broadened due to functionalization which causes longer lifetimes and thus larger values for the $\gamma$ parameter.

9.3.2.2 The D-band

The D-band is a disorder-induced feature arising from double resonance Raman scattering process from a non-zero-centre phonon mode. It is also an
energy dispersive feature, namely the peak frequency increases with increasing laser excitation energy. It is well-documented that sidewall functionalization breaks the translational symmetry along the tube axis causing this mode to become Raman active. Therefore, an increase in the D-band intensity comprises a fingerprint for successful sidewall functionalization. In general, the ratio of intensities of the D- to the G-band (see below) is widely used to evaluate the degree of CNTs graphitization and the functionalization degree of chemically modified nanotubes. Alternatively, Maultzsch et al.\textsuperscript{16} argue that the G-band itself can be defect-induced and suggest that the intensity of the D-band should be normalized to the intensity of the second order mode 2D (overtone of the D-mode) as a measure for the defect concentration in SWCNTs. It should be mentioned that the presence of amorphous or disordered carbon in a pristine material also contributes in the recorded Raman intensity of the D-peak.

Finally, the D’ band, which is a weak shoulder of the G-band at $\sim 1615$ cm$^{-1}$ (with 514.5 nm excitation), is also a double resonance energy dispersive feature induced by disorder and defects and provides a complementary peak to assess the degree of modification in carbon-based nanomaterials.

\subsection*{9.3.2.3 The G-band}

The high energy region in the Raman spectrum of SWCNTs contains two main first-order components, resulting from the in-plane C–C carbon displacements parallel and perpendicular to the tube axis (tangential G-band), usually labelled as G$^+$ (1590 cm$^{-1}$) and G$^-$ (1570 cm$^{-1}$).\textsuperscript{7} In metallic CNTs, the G$^-$ component exhibits a broad asymmetric Breit–Wigner–Fano (BWF) line-shape, resulting from the phonon coupling to an electronic continuum, which is assumed to be proportional to the DOS at the Fermi level and quantified by the asymmetry parameter $1/q$.\textsuperscript{17} This BWF coupling results in the broadening and softening of the G$^-$ peak, as well as in a more pronounced inverse tube diameter ($d_t$) frequency dependence than that in semiconducting tubes.\textsuperscript{18}

As pointed out by Dresselhaus et al.,\textsuperscript{7} G$^+$ is sensitive to charge transfer arising from dopant additions to SWCNTs. The G$^+$ mode up-shifts for acceptors and downshifts for donors as in graphite intercalation compounds.\textsuperscript{7} Additionally, charge transfer to SWCNTs can lead to an intensity increase or decrease in the BWF feature. Also, the $\omega(G^+)$ is essentially independent of $d_t$ or the chiral angle, whereas $\omega(G^-)$ is dependent on $d_t$ (not on chiral angle) and whether the SWCNT is metallic or semiconducting.\textsuperscript{7} The G$^+ - G^-$ splitting is relatively small for large diameter MWCNTs and smeared out because of the diameter distribution in a certain sample. As a result, in MWCNTs the G feature predominantly exhibits a weakly asymmetric characteristic line-shape, with a peak appearing at the graphite frequency $\sim 1580$ cm$^{-1}$.\textsuperscript{5}
9.4 Raman Characterization of CNT–Polymer Hybrid Materials

The transition from fundamental research to materials engineering and applications involves good knowledge of the physico-chemical properties of the investigated materials, and their electronic and vibrational features provide primary information. In the following, via the presentation of some specific cases, we demonstrate the ability of Raman scattering to characterize, in detail, chemically modified CNT–polymers hybrid materials.

Tasis et al.\cite{19} successfully introduced polyacrylamide chains on to SWCNT and MWCNT surfaces via ceric ion-induced redox radical polymerization (Figure 9.3). The resulting polymerized nanotubes were carefully analyzed by UV–Vis spectroscopy, X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and scanning electron microscopy (SEM) techniques. Raman spectra showed strong evidence for the significant alteration of the conjugated network of the graphitic cylinders. The D- to G-band intensity ratios, \( \frac{I(D)}{I(G)} \) for starting and polyacrylamide-modified SWCNTs are 0.07 and 0.16, respectively. Thus, the enhancement of the \( \frac{I(D)}{I(G)} \) ratio indicates a relative increase in the defect sites due to covalent attachment of chemical functionalities, resulting in a conversion of a significant amount of \( sp^2 \)- to \( sp^3 \)-hybridized carbon.

In the same line, high-Pressure carbon monoxide (HiPco) SWCNTs were functionalized along their sidewalls with hydroxyalkyl groups using a radical addition scheme.\cite{20} These moieties were found to be active in the polymerization of acrylic acid from the surface of the nanotubes by a redox radical mechanism. In Figure 9.4 (left-hand panel) the Raman response of pristine, ethanol-treated and polymer-modified samples is illustrated. Compared with

![Figure 9.3](image-url)  
**Figure 9.3** Functionalization strategy. The first step is a radical addition to the CNTs sidewalls, whereas the second one is a redox radical grafting of polyacrylamide chains. Adapted from Tasis et al.\cite{19}
the pristine, the modified materials exhibit drastic differences in the relative intensity of the D-band with respect to the main G$^+$ peak assigned to C–C vibrations along the nanotube axis. Evaluation of the relative intensities $I(G^+)/I(D)$ for the studied samples shows that the ratio is 5.4 for pristine, 1.62 for SWCNT–ethanol and 0.76 for SWCNT–polymer, indicating a significant alteration of the graphitic network. It is worth mentioning that Raman scattering originated from the polymer chains themselves is expected to contribute in the spectral intensity of polymer-modified CNTs. Also, the absence of the strong peaks at 1450 cm$^{-1}$ and 1700 cm$^{-1}$ belonging to the Raman spectrum of neat poly(acrylic acid) implies a minor contribution of the polymer in the observed Raman scattering intensity. Therefore, it is suggested that the polymer grafting not only takes place from the initiating groups but from some polymer chains that are attached directly to the sidewalls. The absorption spectroscopy of CNTs is a complementary experimental technique which provides direct information for the vHs in the visible region and their changes upon functionalization. In the absorption spectrum of pristine and ethanol-treated tubes, the characteristic vHs are clearly observed.

On the contrary, the spectrum of the polymer-modified material shows a complete loss of the van Hove transitions. This is clear evidence of covalent attachment of chemical species on to the π-system.

Müller et al. presented a resonant Raman scattering study on SWCNTs decorated with side chain dendritic terpyridine–Ru(II)–terpyridine [tpy–Ru(II)–tpy] complexes in order to understand how the latter substances will affect the processability and, most importantly, the electronic properties of CNTs. The resonance profiles for the nanotube RBMs were recorded using a tunable excitation laser (Ti:sapphire) and a dye laser. The scattering signal of CaF$_2$ was used to normalize the signal intensity at different excitation energies. Following the procedure of Maultzsch et al. from the transition energies of

![Figure 9.4 Raman spectra in the D- and G-band regions, ethanol-treated and polymer-modified CNTs excited with the 514.5 nm laser line (left-hand panel); and SEM image of polymer-modified SWCNTs (right-hand panel). Adapted from K. Papagelis et al.](image-url)
the $E_{22}^S$ (semiconducting tubes) and $E_{11}^M$ (metallic tubes), the signal is assigned to certain tube chiral index $(n, m)$. Comparing the pristine tubes with the tpy- and poly-tpy-decorated samples, an additional downshift of the transition energies is observed with functionalization, as it can be seen in Figure 9.5 (left-hand panel). This trend holds for all the recorded profiles. Also a broadening of the resonance profile is obvious for the polymer-decorated tubes (Figure 9.5). The full width at half maximum is increased by approximately 50%. For the monomeric sample, this effect is less pronounced.

Concerning the RBM frequencies, a hardening with functionalization can be observed. Shifts of approximately 2 and 5 cm$^{-1}$ for monomeric or polymeric decoration are observed, respectively (see Figure 9.5, right-hand panel). The pronounced shift in the polymeric sample is most probably due to wrapping of the polymer chain around the tube, as it has been observed for certain polymers.23

The frequency shifts are accompanied by drastic effects on the intensity of the RBM signal. In general, the RBM intensity decreases with functionalization. For excitation energies below 1.8 eV, Raman signal from both monomeric and polymeric samples could hardly be recorded, because the signal almost vanishes with functionalization. Interestingly, the decrease of the intensity and therefore the chemical reaction seems to be driven by two effects:
small diameters are highly affected, as it can be observed, \textit{e.g.}, for the (11, 1) tube, but also for tubes with relatively larger diameters like the entire (15, 0) branch (Figure 9.5, right-hand panel). This effect holds for different tube chiralities observed at different excitation energies (Figure 9.5). The preferred reaction of small diameter tubes is expected due to higher strain relaxation and has been reported for various moieties\textsuperscript{24,25}. Also, it may possibly be due to defect functionalization, because, even if the defect density is the same in all starting materials, larger tube diameters lead to a higher amount of defects in absolute numbers. Steric effects may also come into play, with less curved material offering more space for the reactants to attack the CNT sidewalls.

Further interesting works on CNTs functionalized with polymeric chains and extensively characterized by means of Raman spectroscopy have been published previously\textsuperscript{26,27}.

In another study, Ma and co-workers\textsuperscript{28} prepared thermotropic liquid crystalline polyester (TLCP) nanocomposites reinforced with a small quantity of MWCNTs (up to 5 wt\%) by an \textit{in situ} polymerization method. The MWCNTs were well dispersed in the host matrix due to aromatic interactions. The interactions between the TLCP molecules and CNTs were tuned through Raman spectroscopy using an excitation wavelength of 532 nm. RBMs are particularly sensitive probes to study interactions between CNTs and “foreign” molecules absorbed on the CNT surface, as they correspond to vibrations of the carbon atoms perpendicular to the nanotube axis. The authors detected a distinct Raman shift of the RBMs, suggesting that CNTs interacted with the surrounding liquid crystal molecules, most likely through aromatic interactions (\(\pi-\pi\) stacking). Also, in a blank experiment in which nanotubes were embedded in a different liquid crystal host, formed by molecules having a similar molecular structure but without phenyl rings, no shift was observed in the RBM band.\textsuperscript{28} This further justifies the observation that the RBM shift is directly associated with \(\pi-\pi\) stacking interactions at the CNT surface, involving the aromatic core structure of the TLCP molecules.

Hybrid materials consisting of SWCNTs and a conductive block copolymer, perchlorate-doped poly(3,4-ethylenedioxythiophene)-block-poly(ethyleneoxide) (P-PEDOT-b-PEO), were successfully prepared.\textsuperscript{29} Using an excitation wavelength of 532 nm, the authors observed several SWCNT RBM bands in the range of 180–250 cm\(^{-1}\) corresponding to a diameter range from 0.9 to 1.3 nm. According to the authors,\textsuperscript{29} the noticeable weakness of the RBM bands in SWCNT/P-PEDOT-b-PEO relative to the bundled SWCNTs for frequencies lower than 200 cm\(^{-1}\) indicates that P-PEDOT-b-PEO effectively coated, isolated and dispersed the small-diameter nanotubes because of the weak intertube interactions of small SWCNTs.\textsuperscript{30} Also, the band broadening and shift in the low-frequency range of 150–200 cm\(^{-1}\) was attributed to effective exfoliation of SWCNTs. The negligible changes in the \(I(D)/I(G)\) ratio of SWCNTs indicate that the non-covalent functionalization by P-PEDOT-b-PEO prevents the destruction of intrinsic electronic structures of SWCNTs.
Based on the observations that the UV–Vis and Fourier transform infrared (FT-IR) spectra of P-PEDOT-b-PEO were changed after the hybridization with SWCNTs, the authors assumed that charge transfer may occur in the supramolecular assembly of hybrids. The G-band of SWCNTs is quite sensitive to the charge transfer.\(^{31}\) As a result, the authors compared the G-band of SWCNTs with the one of SWCNT/P-PEDOT-b-PEO nanohybrids to verify the presence of electronic interactions. As a matter of fact, the G-band of the pristine material (approximately \(1578 \text{ cm}^{-1}\)) was blue-shifted by \(8 \text{ cm}^{-1}\) for SWCNT/P-PEDOT-b-PEO hybrids. The up-shift of the G-band was attributed to either p-doping (such as bromine as an electron acceptor) or oxidation (similar to that by \(\text{HNO}_3\) or \(\text{H}_2\text{SO}_4\)).\(^{32}\) The carbon bonds are stiffened due to a reduction in the delocalized electron density on the SWCNTs, resulting in hole injection from P-PEDOT-b-PEO to SWCNT. Consequently, the spectroscopic analysis of SWCNT/P-PEDOT-b-PEO materials indicates that the charge transfer in the CNT–polymer nanohybrids was facilitated by the electronic interactions between SWCNTs and P-PEDOT blocks.\(^{29}\)

Conducting polythiophene (PTh)–SWCNTs composites were synthesized by the \textit{in situ} chemical oxidative polymerization method.\(^{33}\) Using an excitation wavelength of 514 nm, the authors studied the pristine and the derived materials. The Raman spectrum for the SWCNT–PTh composites is clearly an addition of the corresponding spectra of PTh and SWCNTs, demonstrating that SWCNTs served as templates in the formation of a co-axial nanostructure for the composites.\(^{33}\)

In the work of Yi \textit{et al.},\(^{34}\) the authors prepared a composite material by grafting a carbonizable polymer, poly(furfuryl alcohol) (PFA), to arylsulfonic acid (SA)-modified SWCNTs (Figure 9.6). The Raman spectrum of the PFA-SWCNT has similar features to those of the SA–SWCNT. The intensity ratio of the D-band to G-band was almost the same as that of the SA–SWCNT, suggesting that the PFA wrapping did not alter the hybridization of the carbon atoms within the SWCNT framework. They also observed that the RBMs of the PFA–SWCNT composite became even weaker than that of the SA–SWCNT. This would be expected if the attachment of the macromolecule would restrict the radial breathing of SWCNTs more than the SA group alone.

On the other hand, the RMB peaks of the carbonized, at 600 °C, nanocomposite—yielding a nanoporous carbon–CNT hybrid (NPC/SWCNT)—slightly shifted to higher wavelength numbers. As the RBMs of the NPC/SWCNT hybrid material show intensities comparable with those of the purified material, the authors concluded that there is no chemical bonding or charge transfer between the SWCNT and NPC. They attribute these shifts to molecular forces being exerted by the NPC on the SWCNT. It has been well established that the Raman features exhibit a blue shift under the influence of hydrostatic pressure.\(^{35}\) Therefore, it can be calculated that the molecular pressure of the NPC on the SWCNT is hundreds of MPa based on RMB shifts. Although there is an obvious frequency change in RBMs, tangential modes remain at almost the same frequency. This experimental finding is attributed to
the anisotropic behaviour of the NPC on the SWCNTs. When PFA was pyrolyzed to form NPC, there is considerable volume shrinkage in all dimensions, which may induce compressive stress on the SWCNT. The compressive stress more strongly affects the radially modes than the tangentially ones.

In another work, Nogueira et al.\textsuperscript{36} presented a covalent modification approach with thiophene groups located at the edges and defects of SWCNTs in order to modify the interaction with the polymer matrix with the aim of its application in solar cells. Raman spectra of the pristine SWCNTs, purified material (SWCNT-COOH) and the modified material (SWCNT-THIOP) were obtained. For the non-purified SWCNT, at least four distinct tube radii were observed in the Raman spectrum excited with a wavelength of 632.8 nm. The main peak for the RBMs occurs at \(\sim 162 \text{ cm}^{-1}\) (1.4 nm diameter), whereas

\[\begin{align*}
\text{p-SWNT} & + \text{H}_2\text{N}\text{-SO}_3\text{H} & \xrightarrow{\text{NaNO}_2, \text{AlBN, Oleum, 80 °C, 1hr}} & \text{HO}_3\text{S-}\text{-SO}_3\text{H} \\
\text{SA-SWNT} & \xrightarrow{\text{polymerization}} & & \text{NPC/SWNT}
\end{align*}\]
other less intense peaks appear at \( \sim 144, 176 \) and \( 186 \text{ cm}^{-1} \). According to the authors, the introduction of carboxylic and thiophene groups is expected to change the force constant of the RBM mode, and as a consequence this band was reduced in intensity and shifted to higher energy values. This upshift is difficult to quantify, given the low frequency and the weak nature of the RBM after the chemical treatment. Only two weak peaks were observed at \( \sim 163 \) and \( 187 \text{ cm}^{-1} \) after both the purification (SWCNT-COOH) and functionalization (SWCNT-THIOP) processes. The G-band profile for the pristine SWCNT shows a higher-frequency component (approximately 1573 cm\(^{-1}\)) and a lower-frequency component (approximately 1540 cm\(^{-1}\)) with a BWF line-shape. These features are attributable to the presence of metallic SWCNT in the sample used. Also, after purification significant upshifts by approximately 4, 10 and 21 cm\(^{-1}\) for the D-, G- and 2D-bands were observed, respectively. As mentioned above, the removal of electrons from SWCNTs (i.e., p-doping or oxidizing conditions) results in an upshift of the G-peak, whereas the concomitant upshifts of the D- and 2D-bands are another signal of charge transfer. After the chemical modification with thiophene-containing groups, G- and 2D-bands upshifted again by 4 and 3 cm\(^{-1}\), respectively.

In a recent work, Imin et al. have successfully synthesized a new class of highly soluble alternating copolymers of fluorene and dithieno[3,2-b:2',3'-d]pyrrole. Sample preparation for Raman measurements involved drop casting dilute polymer–SWCNT solutions in tetrahydrofuran (THF) on to a glass microscope slide and air-drying prior to measurement. The authors collected Raman data using the 785 nm excitation wavelength because the RBM spectra at this excitation wavelength can be used to evaluate the extent of aggregation occurring in a sample. RBM spectra of the as-received HiPco sample, sodium dodecylbenzenesulfonate (SDBS)-wrapped SWCNTs as well as the soluble polymer–SWCNT hybrids were reported. All of the peaks of the polymer–SWCNT complexes and SWCNT–SDBS show a characteristic red shift of 3–6 cm\(^{-1}\) relative to the same peaks in the spectrum of the starting material. The signal at 284 cm\(^{-1}\) is much more dominant in the spectra of pristine bundled SWCNTs, and this feature nearly disappeared in the polymer-functionalized samples as well as the SDBS (surfactant)-dispersed sample. This result indicates that the nanotubes are individually dispersed by the polymeric chains in solution, and there is no evidence of aggregation when they are drop-casted on to the glass substrate. Interestingly, both polymer–SWCNT complexes exhibit a strong signal at 247 cm\(^{-1}\) (\( d_t = 0.96 \text{ nm} \)), indicating that both polymers selectively bring a specific nanotube species into resonance when excited at 785 nm.

### 9.5 Conclusions

Modification of CNTs with polymers has been widely investigated with the primary purpose to control their solubility and processibility, either through covalent or non-covalent bonding. The non-covalent attachment does not alter
the structure of the SWCNTs, As the interactions between the wrapping polymeric chains and the nanotube are, in principle, weak. Besides, much stronger interactions between SWCNTs and polymer molecules might be achieved by covalent modification using a variety of functionalization strategies. Raman spectroscopy has been successfully utilized to determine the influence of chemical functionalization on the vibrational and electronic properties of CNTs. The dependence of the resonant Raman spectrum of CNT–polymer hybrids on the laser excitation energy can be used to understand the type of bonding between the two constituents and the effect of individual polymer molecules on the structure and the overall symmetry of the tubes. Following the resonance of particular tube chirality, the different reactivity of nanotubes can be traced. Metallic or semiconducting nanotubes exhibit different reactivity, quantified by the different DOS at the Fermi level, and may be affected differently by polymer reactions. Also, the reactivity depends on the steric demands of the functionalities. Moreover, the charge transfer between the CNTs and the addends creates alterations in the electronic structure of the tubes, causing red shifts in the optical transitions, accompanied by a broadening of the resonance conditions. Finally, covalent sidewall functionalization can be proven due to the intensity enhancement of the defect-induced D-mode in combination with attenuated RBMs.

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