Raman frequency shift in oxygen-functionalized carbon nanotubes

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Abstract

Based on density functional theory, the geometrical and electronic structures of oxygen-functionalized single-wall carbon nanotubes (O-SWCNs) are obtained, of which the vibrational properties are calculated in terms of lattice dynamics theory. Both bond expansion and contraction are found to coexist in O-SWCNs. A distinct Raman shift is observed in the radial breathing mode (RBM) and the G modes, depending not only on the tube diameter and chirality but also on oxygen coverage and adsorption configurations. With the oxygen coverage increasing, interestingly, a nonmonotonic upshift and downshift is observed in the G modes, which is attributed to the competition between the bond expansion and contraction. In addition, the resonance Raman effect at different oxygen coverage, which may be observable in O-SWCNs, is discussed.

Chemical functionalization of carbon nanotubes could offer new and promising avenues to process and assemble tubes, add sensing capabilities, or tune their electronic properties, which are the subject of intensive research [1, 2]. When the functional groups are chemically bonded to the nanotube wall, the tube geometry can be significantly changed. As a result, the C–C force constant and thus the vibrational properties of the nanotube will be largely modified. For example, an obvious upshift in the tangential mode vibrations (so-called G modes) was observed experimentally in both single-walled carbon nanotubes (SWCNs) and multi-walled carbon nanotubes (MWCNs) in an acid treatment [3, 4]. For physically doped nanotubes, such a frequency shift was usually attributed to the variations in the C–C bonds on the nanotube, induced by charge transfer [5–8]. In chemically processed nanotubes, however, there exists much stronger interaction between the functional groups and the nanotubes, which is of particular importance in the characterization of nanotube-based devices. Some works have been reported on this subject. For example, the effects of chemisorption of CrO3 on the Raman shift of carbon nanotubes was investigated [9], and the chemical bond between the nanotube and the functional group was also obtained through the analysis of the D band [9, 10]. For nanotube-based device applications, the chemisorption effect on the Raman shift is still an outstanding issue and its clarification is greatly desirable.

An oxygen molecule (O2) can be regarded as a simplest kind of functional group. It was reported that the oxygen molecule is very reactive to SWCNs with diameter below 1 nm, and that oxidation can even occur at room temperature [11, 12], forming an oxygen-functionalized SWCN (O-SWCN). Such oxidation can dramatically influence the nanotubes’ electrical resistance, thermoelectric power, and local density of states. The Raman shift and even some new vibrational modes may be expected in such an O-SWCN, which may be characterized by Raman spectroscopy. Therefore, the study of the oxygen chemisorption effects on Raman modes can be very helpful to explore the underlying mechanism of the Raman shift in the functionalized nanotubes.

As two types of the most important Raman modes, the radial breathing mode (RBM) and the G modes are widely used in the estimation of the diameter distribution of nanotubes [13, 14]. To assign the Raman peaks of an O-SWCN, the frequency shift in these modes should be fully taken into account. In addition, an O-SWCN can form several possible configurations, leading to different electronic properties, which depend not only on the adsorbed sites and coverage but also on whether there is O–O bond breaking.
or not [11, 12]. It was reported that an SWCN with high adsorbed oxygen has a higher electrical conductance than one with less adsorbed oxygen [15]. In the lattice dynamics, it is still an open question to explore the influence of the adsorption configuration and coverage on the vibrational properties of an O-SWCN.

In this work, the geometrical and electronic structures of the O-SWCNs are first obtained, based on density functional theory. The vibrational properties of the O-SWCNs are then calculated in terms of lattice dynamics theory. Both the bond expansion and contraction are found in O-SWCNs, induced by the sp$^2$-like rehybridization and by the charge transfer. A distinct Raman shift is observed in the RBM and G modes, depending not only on the tube diameter and chirality but also on oxygen coverage and adsorption configurations. With the oxygen coverage increasing, interestingly, a nonmonotonic upshift and downshift is observed in the G modes, which is attributed to the competition between the bond expansion and contraction that coexist in the functionalized carbon nanotube. In addition, the resonance Raman effect at different oxygen coverage, which may be observable in O-SWCNs, is discussed.

As a typical example, we consider the cycloaddition structure for O$_2$ adsorption on an achiral tube. From a previous report, the two configurations, O$_2$ on top of an axial C–C bond (site TA) and on top of a zigzag C–C bond (site TZ), can lead to chemisorbed structures via cycloaddition (see figure 1), which will be the focus of the present work. A nanotube was modeled by a periodically repeating supercell. With a tube lying along the $c$ direction, the lattice parameters $a$ and $b$ were chosen to ensure a minimum distance of more than 10 Å between two nearest neighbors, so that the interactions between a tube and its periodic images were negligible. For a simplification, a unit cell of the zigzag tube is chosen to be a supercell, as in [16]. The validity of the optimum results is also confirmed by using a larger supercell.

In the calculations, the first-principles plane-wave pseudopotential density functional theory (DFT) was used, performed in the CASTEP code [17]. GGA (generalized gradient approximation) exchange–correlation functional and ultrasoft potentials were employed [18, 19]. An energy cut-off of 340 eV and the Monkhorst–Pack scheme [20] with a distance of 0.04 Å$^{-1}$ between the sampling points in reciprocal space were used in the calculations. Optimal atomic positions were determined until the magnitude of the forces acting on all atoms became less than 0.02 eV Å$^{-1}$, which also converged the total energy within 0.01 meV. The electronic structures of the O-SWCNs were calculated, based on the optimized geometries obtained above. For the lattice dynamic calculations, the vibrations of the carbon atoms on the nanotube can be modeled by the force constant model in terms of the force constants of graphene, up to the fourth next-neighboring interaction [21]. To incorporate the oxygen adsorption effects, the C–C force constants have been corrected through the distorted bond lengths obtained above [22, 23]. For the C–O and O–O bond interactions, we use the well-known Tersoff–Brenner bond order potential [24] and the potential parameters in [25].

Figure 1 shows the optimized geometries of a (10, 0) O-SWCN in both TA and TZ configurations. The optimized structures are very similar to previous results [11, 12]. Interestingly, both the expansion and contraction of the C–C bonds are obtained from the optimized structures of the O-SWCNs, in contrast to that of physically doped SWCNs with only a bond expansion or contraction [5–8]. In the TA configuration, for example, three C–C bonds at the adsorbed site are markedly expanded to be 1.500, 1.498 and 1.521 Å, respectively, while the bonds near the adsorbed site are contracted, there appearing a minimal length of about 1.374 Å, shorter than 1.417 Å of the bare tube. Far from the adsorbed site, little change in the C–C bonds is observed; they are almost unaffected by the oxidation. It is well known that in physically doped SWCNs, C–C bond expansion (contraction) may be induced by the gain (removal) of electrons, which may result in a downshift (upshift) in the G modes [5–8]. Therefore, the coexistence of the bond expansion and contraction may indicate a new mechanism of Raman shift in functionalized SWCNs.

The bond expansion can be understood by the fact that strong C–O covalent bonds are formed in the O-SWCNs. In figure 2 we present the electronic charge density contour plots of the (10, 0) O-SWCN in the TA configuration. From figure 2(a) and (b), an obvious charge density overlapping is observed between the O and C atoms, the strong C–O covalent bonds existing there. Three C–C bonds plus the C–O bond form a structure of sp$^2$-like rehybridization at the adsorbed site [26–28]. This may lead to the much larger bond length, near that of 1.540 Å in diamond with sp$^2$ rehybridization. As for the bond contraction, it is mainly attributed to the charge transfer from SWCN to O atoms. From the calculations, an amount of about 0.50 electronic charge is found to be transferred from the SWCN to O$_2$ in the TA configuration.
where the O atom acts as an acceptor. The removed electrons of the SWCN mainly originate from the C atoms at and near the adsorbed sites. This leads to a bond contraction, similar to that in physically doped SWCNs, which may induce an upshift of the G modes in the O-SWCNs [9].

In figure 3 we present the electronic structures of (10, 0) SWCN and O-SWCNs in the TA and TZ configurations. The zero energy is set to be at the top of the valence band. From figure 3, many degenerate electronic bands are split in the O-SWCNs and the SWCN levels are highly perturbed; they are strongly hybridized with the O$_2$ levels [11]. This is very different from the case of physically doped SWCNs, in which the SWCN levels are only perturbed near the Fermi level [29, 30]. Also, the modified energy gap in the TZ configuration is larger than that in the TA configuration, and the splitting of the band structures in the former is very different from that in the latter. The band structure and its adsorption-configuration dependence may indicate a new characteristic of resonance Raman spectroscopy.

Shown in table 1 are the RBM and G mode frequencies of (10, 0) SWCN and O-SWCNs in both TA and TZ configurations. For the bare (10, 0) SWCN, the RBM frequency is obtained to be of 294 cm$^{-1}$, in good agreement with the experiment and the first-principles results [31, 32]. In the TA (TZ) configuration of the O-SWCN, the RBM frequency downshifts to be 278 cm$^{-1}$ (276 cm$^{-1}$), decreased by 16 (18) cm$^{-1}$, while the upshifts are obtained in the G modes, increasing by 8 (4) cm$^{-1}$ in $E_{2g}$, 6 (13) cm$^{-1}$ in $A_{1g}$, and 7 (3) cm$^{-1}$ in $E_{1g}$, respectively. It is shown that the frequency shift in both the RBM and G modes depends strongly on the adsorption configurations, which should be considered in the nanotube characterization by the Raman spectroscopic experiment.

To explore the dependence of the Raman shift on the tube diameter and chirality, we calculate the RBM of armchair (5, 5) and zigzag (8, 0) O-SWCNs, which have a similar tube diameter. For the (5, 5) O-SWCN, the O–O bond direction is perpendicular to the tube axis. In the case of the (8, 0) SWCN, the TA configuration is considered. For the bare and oxygenated (8, 0) SWCNs, the RBM frequencies are obtained to be 359 cm$^{-1}$ and 329 cm$^{-1}$, respectively. The frequency shift in the RBM, $\Delta \omega = -30$ cm$^{-1}$, is much larger than that of (10, 0) O-SWCN. This indicates the dependence of the Raman shift on the tube diameter, i.e., the larger the frequency shift, the smaller the tube diameter. For the bare and oxygenated (5, 5) O-SWCN, on the other hand, the RBM frequencies are obtained to be 336 cm$^{-1}$ and 272 cm$^{-1}$, respectively. The frequency shift ($\Delta \omega = -64$ cm$^{-1}$) is larger than two times that of the (8, 0) O-SWCNs. At a given tube diameter, obviously, an armchair tube is more sensitive to oxidation than a zigzag one, showing a chirality dependence of the Raman shift. The results give the possibility to determine the tube diameter and chirality of O-SWCNs by Raman spectroscopic experiments.

In the following discussions, we further study the dependence of the Raman shift on the coverage (defined by O/C ratio x). In real cases, the oxygen distribution may be somewhat disordered, making it very time consuming, even impossible, to simulate. To obtain a quick impression of the relationship between the vibrational properties and oxygen coverage, we assume that the oxygen molecules are

![Figure 2.](image-url) (a) Charge density contour plots of the (10, 0) O-SWCN in TA configuration (a) on a plane perpendicular to the tube axis, which also contains a C–O bond; (b) on a plane containing an oxygen molecule and the nearest C–C bond.

![Figure 3.](image-url) Electronic structures of (10, 0) SWCN (a) and O-SWCNs in (b) TA and (c) TZ configurations.

|                  | RBM | $E_{1g}$ | $A_{1g}$ | $E_{2g}$ |
|------------------|-----|----------|----------|----------|
| SWCN             | 294 | 1585     | 1566     | 1535     |
| Site TA          | 278 | 1592     | 1572     | 1543     |
| Site TZ          | 276 | 1588     | 1579     | 1539     |
evenly distributed along the tube circumference. Such an approximation is favorable in most cases, since its system energy is lower than the disordered case. Figure 4 shows eigenfrequencies and eigenvectors of the RBM and \(E_{1g}\) mode in the (10, 0) O-SWCNs with TA configuration at \(x = 0, 0.05,\) and 0.10. Due to the C–O interactions and the symmetry destruction, obviously, the atomic displacements of the Raman modes depend on the oxygen coverage, slightly different from that in the bare SWCN [21, 33, 34]. Moreover, the frequencies of both RBM and \(E_{1g}\) change dramatically with \(x\) increasing. This means that the vibrational properties of the O-SWCNs are very sensitive to the oxygen coverage.

In figure 5 we further show the frequency of the \(E_{1g}\) mode in the (10, 0) O-SWCN with TA configuration as a function of \(x\). From figure 5, the \(E_{1g}\) mode first upshifts and then downshifts with \(x\) increasing. There exists a maximum of \(1611\) cm\(^{-1}\) at \(x = 0.25\), showing a nonmonotonic behavior of the frequency shift. At half coverage (\(x = 0.5\)), it even downshifts to be \(1580\) cm\(^{-1}\), lower than \(1585\) cm\(^{-1}\) of the bare SWCN. For other G modes, the frequency shift in both \(A_{1g}\) and \(E_{2g}\) modes is also calculated, which has the similar dependence on coverage to that in the \(E_{1g}\) mode. Experimentally, a similar change in G modes with \(x\) had been observed via vapor phase doping or redox reaction [35, 36].

In order to explore the origin of the G mode shift, we remove the C–O interactions and recalculate \(E_{1g}\) mode in terms of the same optimum geometry above. From figure 5, the frequencies are overall downshifted in the absence of the C–O interaction, lower than those in the presence of the C–O interactions. It is shown that the C–O interaction has a large contribution to the upshift in G modes. In the absence of the C–O interactions, interestingly, the nonmonotonic behavior is still obtained in the \(E_{1g}\) frequency shift. This can be understood by the following consideration. At low coverage, the bond contraction effect is dominant, leading to the upshift in G modes. With the coverage increasing, the number of the expansionary bonds increases continuously. At a critical coverage, the bond expansion effect would become predominant, resulting in an decrease of the G mode frequency with \(x\). Therefore, the nonmonotonic behavior of the frequency shift may be attributed to the competition between the bond expansion and contraction, coexisting in O-SWCNs. The former is induced by the sp\(^3\)-like rehybridization and the latter
by the charge transfer. Our results indicate a new competition mechanism between the upshift and downshift in G modes.

In the absence of the C–O interactions, in addition, there exists a locally minimal frequency of the $E_{1g}$ mode at $x = 0.1$. In this case, the O-SWCN is considered to have its highest symmetry, that of mirror symmetry. To understand this local minimum, we recalculate the $E_{1g}$ mode at the same coverage but an asymmetrical configuration. The obtained frequency of 1592 cm$^{-1}$ is higher than 1586 cm$^{-1}$ in the symmetrical case, which further shows the dependence of Raman shift on the configurations.

Experimentally, Raman spectroscopy is a nondestructive, non-dissipative measurement at ambient conditions. In particular, resonance Raman spectroscopy is widely used to select nanotubes in the nanotube sample, which are resonant with excitation laser energy [37]. To explore the dependence of the resonance Raman effect on coverage, we calculate in figure 6 the optical adsorption spectra of (10, 0) O-SWCNs in the TA configuration at various $x$, using the CASTEP code. The laser excitation energies of 1.58, 1.96 and 2.41 eV are usually used in resonance Raman spectroscopy, indicated by three dotted lines in figure 6. At $x = 0.10$ and 0.15, obviously, an adsorption peak is newly observed at about 1.58 eV, which is absent in the bare SWCN. For such coverages, therefore, the resonance Raman effects may be observable at 785 nm laser excitation (1.58 eV). This is because the resonant Raman scattering occurs only when the incident photon energy matches the energy of strong optical absorption electronic transitions [34, 38, 39]. At 633 nm laser excitation (1.96 eV), similarly, there may be resonance Raman effects for the O-SWCNs with $x = 0.05$ and 0.10. At 514 nm laser excitation (2.41 eV), especially, large adsorption strength and/or adsorption peaks are obtained at various coverages, indicating that the resonance Raman effects exist there. The results show that the Raman frequency shift in O-SWCNs should be observable by resonance Raman experiments.

In summary, the geometrical and electronic structures of O-SWCNs have been obtained, based on density functional theory. Both bond expansion and contraction are found in O-SWCNs, the former induced by the $sp^3$-like rehybridization and the latter by the charge transfer. The vibrational properties have been studied in terms of lattice dynamics theory. A distinct Raman shift is found in the RBM and G modes, depending not only on the tube diameter and chirality but also on oxygen coverage and adsorption configurations. With the oxygen coverage increasing, interestingly, a nonmonotonic upshift and downshift is observed in the G modes, which is attributed to the competition between the bond expansion and contraction, coexisting in the functionalized carbon nanotube. In addition, the resonance Raman effects, which may be observable in O-SWCNs, have been discussed at various oxygen coverages. The results may be helpful in the characterization and practical application of functionalized carbon nanotube-based device.

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