Competition between the Spring Force Constant and the Phonon Energy Renormalization in Electrochemically Doped Semiconducting Single-Walled Carbon Nanotubes

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ABSTRACT

A detailed analysis of the in situ Raman spectroelectrochemical behavior of individual semiconducting single-walled carbon nanotubes (SWCNTs) is presented. Special attention has been paid to the development of the tangential (TG) mode frequency, which shifts when the externally applied potential $V_e$ is shifted away from $V_e = 0$. The magnitude and direction (upshift or downshift) of the tangential mode band has been found to be dependent on the diameter of the semiconducting tubes. For negative charging, the small-diameter tubes exhibit a downshift while the large-diameter tubes exhibit an upshift. This behavior is explained by a competition between two effects which cause opposite shifts in the TG mode frequency during negative charging: a phonon renormalization effect and a C–C bond weakening during the charging process. Positive charging always causes an upshift of the TG mode frequency. However, the magnitude of the upshift is dependent on the tube diameter.

An understanding of the electronic structure of single-walled carbon nanotubes (SWCNTs) is a crucial issue for their application in nanoelectronic devices. Changes in electronic structure of SWCNTs can be realized by chemical doping,1 electrostatic,2 or electrochemical gating.3–5

Probing the sensitivity of carbon nanostructures by electrochemical charging provides important information on the electronic structure of these materials. In situ Raman spectroelectrochemistry is a well-established method for investigating the change in physical properties of SWCNTs during charging.3 We have shown previously that electrochemical charging has a strong impact on the development of the Raman spectra of SWCNT bundles.3 These observations inspired several spectroelectrochemical studies on SWCNTs,5–7 double-walled carbon nanotubes (DWCNTs)8 and fullerene peapods.9,10 It should be noted that electrochemical charging is different from chemical doping. In the latter case, the redox-active molecule (chemical dopant) can penetrate into the interior of carbon nanostructures. In some cases (for example, in fullerene peapods),11,12 the chemical doping is highly irreversible and the chemical dopant cannot be removed even by extraction with solvent. Electrochemical charging, on the other hand, mimics a double-layer capacitor,3 where the charge carriers are injected into the nanotube from the electrode and the electrolyte ions only compensate the injected charge.

Previous measurements have been typically performed on samples containing large bundles of SWCNTs, which complicated the interpretation of the results since the individual properties of specific tubes are averaged. Furthermore, nanotubes in a bundle have been shown to exhibit different properties as compared to those of individual nanotubes.13 Therefore, it is desirable to focus attention on spectroelectrochemical studies of small bundles and ideally of individual carbon nanostructures.
Group theory predicts six Raman-active features in the TG band region for chiral nanotubes: $2A_{1g} + 2E_{1g} + 2E_{2g}$, which are reduced to three Raman-active bands for the symmorphic zigzag or armchair tubes. For semiconducting tubes, the transverse optical modes $E_{1}^{TO}$ and $E_{2}^{TO}$ are predicted to be stiffer than the longitudinal ones $E_{1}^{LO}$ and $E_{2}^{LO}$, while the $A_{1}^{TO}$ mode is softer than the $A_{1}^{LO}$ mode due to the different stiffness for the axial and circumferential bonds. For unpolarized Raman studies of semiconducting tubes, only two main components of the TG band are often considered in the analysis. They are usually referred to as the $G^+$ and $G^-$ lines, which are found around 1590 cm$^{-1}$ (composed of $A_{1}^{LO}$, $E_{1}^{TO}$, and $E_{2}^{TO}$) and around 1560 cm$^{-1}$ (composed of $A_{1}^{TO}$, $E_{1}^{LO}$, and $E_{2}^{LO}$), respectively. Note that the frequency of the $A_{1}^{TO}$ mode is diameter-dependent. The value of 1560 cm$^{-1}$ is appropriate for tubes with a diameter of about 1.3 nm. The $E_{1}$ and $E_{2}$ modes have a much weaker Raman intensity than the totally symmetric $A_{1}$ modes. Thus, for semiconducting tubes, the $G^+$ line is attributed mainly to the diameter-independent $A_{1}^{LO}$ modes, while the $G^-$ line is assigned to the $A_{1}^{TO}$. A proper interpretation for the TG mode during the positive charging of individual tubes is the calculation of the sign of the frequency shift with the applied potential ($V_c$). Also, several laser lines were typically probed to ensure that the laser spot does not contain several tubes.

Here, we report the effects of electrochemical charging on the Raman spectra of semiconducting SWCNTs as a function of their diameters. In contrast to SWCNT bundles, it is possible for individual tubes to find the dependence of the $G^+$ mode frequency on the diameter of the nanotube. The $G^+$ band can be either downshifted or upshifted during negative charging. We show experimentally for the first time that this effect exhibits a dependence on diameter of SWCNTs. The change of the sign of the frequency shift with applied potential ($\delta \omega / \delta V_c$) is rationalized by a competition between two effects: namely, a phonon renormalization effect and a C–C bond weakening during the charging process. Furthermore, we show here the first data on the development of the TG mode during the positive charging of individual semiconducting SWCNTs. These electrochemical data cannot be obtained using a back gate due to the low gate coupling efficiency. The diameter dependence of the behavior of $\delta \omega / \delta V_c$ observed here experimentally during both negative and positive charging has been found to be consistent with the recent theoretical predictions of Tsang et al.

SWCNTs were synthesized directly on a SiO$_2$/Si substrate using Fe as a catalyst. For the electrochemical charging experiments, SWCNTs were subsequently contacted using Au evaporated on a part of the substrate, and served as a working electrode. The cell was completed with a Pt-counter electrode and an Ag-wire pseudoreference electrode. The electrolyte gel was 0.1 M LiClO$_4$ dissolved in dry propylene carbonate/PMMA (PMMA = polymethylmethacrylate, Aldrich). Electrochemical charging of the working electrode on which SWCNTs were placed was carried out by varying the applied potential $V_c$ between $1.5$ and $1.5$ V vs the Ag pseudoreference electrode (PAR potentiostat). The Raman spectra were excited by a dye laser (R6G dye, Coherent), a Ti:Sapphire laser (Coherent), or a Nd:YAG laser (Coherent).

The spectrometer resolution was about 5 cm$^{-1}$. The spectrometer was interfaced with a microscope (Carl-Zeiss, objective 100×). The diameter of the laser spot was about 500 nm.

Figure 1 shows a SEM image of SWCNTs grown directly on a Si/SiO$_2$ substrate. The nanotubes are typically individual and are parallel to each other. The distance between adjacent SWCNTs is usually greater than 10 nm. This geometry simplifies finding a tube and also enables alignment of the laser polarization parallel to the SWCNT axis, which is important for obtaining a reasonably strong Raman signal and for establishing a well-defined reproducible geometry. Note that it is difficult to completely exclude the situation where more than one tube is present in the laser spot (500 nm in diameter) from which Raman spectra are taken. However, for our analysis, we selected spectra where, to the best of our knowledge, only one SWCNT band was present. Also, several laser lines were typically probed to ensure that the laser spot does not contain several tubes.

Figure 2 shows the development of the $G^+$ and $G^-$ bands for two different tubes (denoted by A and B referring to the particular charts of Figure 2) during electrochemical charging. The TG mode region of both tubes is dominated by the $G^+$ band at around 1585 cm$^{-1}$. For tube A, the $G^+$ band is at a slightly higher frequency than for tube B. The $G^-$ part of the TG band for both tubes is very weak and thus is almost unresolved. There is no obvious broadening of the $G^-$ band, which suggests that both tubes are semiconducting or are of nearly zigzag chirality. An exact assignment of the $(n,m)$ indices is difficult since the $E_{2g}$ can be distorted by strain, interaction with the substrate, and/or interactions with the polymer electrolyte.

The insets in Figure 2A,B show the respective spectra in the RBM region of tubes A and B, respectively, at $V_c = 0$ V. The frequencies of the RBM bands for tubes A and B are about 175 and 135 cm$^{-1}$, respectively. The diameter of the SWCNTs can be approximated by the simple equation $d = A/\rho + B$ where $A = 217.8$ cm$^{-1} \cdot$ nm and $B = 15.7$ cm$^{-1}$. Hence, the RBM frequencies of tubes A and B correspond to tube diameters of about 1.37 and 2.00 nm, respectively.

For both tubes, the intensities of both the $G^+$ and $G^-$ modes are decreased as the magnitude of the electrode...
potential is increased from 0 to -1.5 V. Metallic tubes are expected to exhibit a narrowing and a simultaneous increase of the G-band intensity during electrochemical charging. This is because electrochemical charging leads to a change of the Fermi level position, and subsequently the electron-phonon coupling in metallic tubes is decreased. Thus, the line broadening associated with electron-phonon coupling is suppressed by the application of an electrochemical potential and the peak intensity of the G-band increases. In contrast, semiconducting tubes do not exhibit such a broadening due to electron-phonon interaction. Hence, neither a narrowing of the G-band nor an intensity increase is expected. (Note that a slight increase of the intensity can be observed for the special case where the charging causes a better resonance of the tube with the particular laser.)

The attenuation of the intensity of both the G+ and G- bands is continuous and is attributed to a weakening of the resonance effect. In other words, the electrochemical charging of carbon nanotubes can be used to distinguish between semiconducting and metallic SWCNTs. The behavior of tubes A and B during electrochemical charging is consistent with a semiconducting character for both tubes as suggested above. A change in $\omega_{G^+}$ of the most intense component of the TG band (G+) is observed in going from the electrode potential 0 V to -1.5 V. However, the sign of the shift is different for tubes A and B. While for tube A the phonon frequency is decreased, for tube B it is increased as the magnitude of the electrode potential is increased from 0 to -1.5 V.

There is also a change of the frequency of the weak (G-) component, which appears at around 1570 cm$^{-1}$ (for $V_e = 0$ V) for both tubes A and B. It seems that, for tube A, the G-component of the TG band is upshifted by applying a negative electrode potential. However, the G-mode can be followed only up to a potential of about -0.5 V and then the signal disappears into the background. For tube B, it is difficult to distinguish the G-mode even at 0 V.

Figure 3 shows the spectra of the TG band (G+) of tubes A and B observed in going from the electrode potential 0 to 1.5 V (positive potential). The intensity of the G+ spectra is bleached similarly as in the case of negative charging, both for tubes A and B. However, in contrast to negative charging, both tubes A and B exhibit an upshift in $\omega_{G^+}$ as the magnitude of the potential is increased (same sign of $\delta \omega_{G^+}/\delta V_e$). Note that the upshift of $\omega_{G^+}$ from $V = 0$ to $V = 1.5$ V is larger for tube B than for tube A. The same individual tubes were tested in experiments shown in Figures 2 and 3.
Extensive studies of alkali metal doped graphite have established that electron doping leads to the filling of antibonding states. This results in the weakening of the C–C bond. A similar behavior could be expected for the analogous high-frequency G⁺ phonons in SWCNTs. The negative electrochemical charging is analogous to the doping by alkali metals: in this case electrons are injected into the tube and the Fermi level is increased. Thus, similar effects should be observed as in the case of alkali metal doping.

On the other hand, Tsang et al. recently showed that, due to the renormalization of the phonon energy, the frequency of the A₁LO mode of semiconducting tubes increases monotonically with increasing gate potential. (The energy renormalization in perturbation theory reduces the phonon energy and has its maximum effect on the undoped state of SWCNTs. Reducing the phonon renormalization energy by charging thus leads to a general upshift of Raman modes.) Ref 2 shows the effect to be valid for both the LO and TO modes of semiconducting SWCNTs, and it is predicted to be larger in magnitude for large-diameter tubes. For smaller-diameter tubes, the renormalization effect is predicted to be weaker. However, this prediction has not yet been proven experimentally.

In this study, we show that both phonon energy renormalization and changes in the strength of the C–C bond play an important role in the behavior of the G⁺ feature of semiconducting SWCNTs during electrochemical charging. Let us now analyze the consequences of the electrochemical charging in detail. Obviously, for negative charging of a SWCNT, the renormalization of the phonon energy and the effect of the weakening of the C–C bond due to the filling of antibonding orbitals have opposite signs and thus may cancel each other. The renormalization of the phonon energy is predicted to be strong for large-diameter tubes. Hence, it can be expected that this effect will dominate for large-diameter tubes and the frequency of the G⁺ band would then increase with charging. On the other hand, the weakening of the C–C bond due to the filling of the antibonding orbitals would dominate in the case of small-diameter tubes, and consequently, the electron doping would lead to a softening of the G⁺ mode frequency in this case.

Indeed, our experimental results show that the smaller-diameter tube (A) exhibits a downshift, while the larger-diameter tube (B) exhibits an upshift of the G⁺ mode frequency under negative charging.

Figure 3. (A,B) In situ Raman spectroelectrochemical data for two different individual SWCNTs in the range from $V_e = 0$ to 1.5 V (from bottom to top). The spectra are excited by 2.03 and 1.70 eV laser excitation energies, respectively. The electrochemical potential change between adjacent curves is 0.1 V. The spectra are offset for clarity, but the intensity scale is the same for all spectra in their respective charts. The vertical dashed lines are a guide to the eye and correspond to the position of the G⁺ phonon feature at 0 and 1.5 V, respectively. Arrows point to the positions of the G⁺ mode at $V_e = 0$. 

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Indeed, our experimental results show that the smaller-diameter tube (A) exhibits a downshift, while the larger-diameter tube (B) exhibits an upshift of the G⁺ mode frequency under negative charging.
The positive charging should lead to a strengthening of the C–C bond and thus to an upshift of the G$^+$ mode. The shift of the G$^+$ mode due to the renormalization of the phonon energy is independent of the sign of the charging (negative or positive charging) and always corresponds to an upshift of the G$^+$ mode. Since both effects are shifting the G$^+$ mode in the same direction, only an upshift is expected for all kinds of tubes in the experimental spectra. Nevertheless, the magnitude of the upshift should be diameter-dependent, since the phonon energy renormalization is stronger for large-diameter tubes. Indeed, our experimental results show that tube B (with larger diameter) exhibits a stronger upshift than tube A (smaller diameter).

Figure 4 shows a summary plot of the dependence of the relative change of $\omega_{G^+}$ on the electrode potential $V_e$ for tubes A and B and for three additional SWCNTs with identified RBM positions (145 cm$^{-1}$, 125 cm$^{-1}$, and 120 cm$^{-1}$). The frequencies of the G$^+$ mode for each SWCNT at different applied potentials are referenced to $\omega_{G^+}$ at $V_e = 0$ V. For tube B, the dependence of the relative $\omega_{G^+}$ on applied potential is shown for two laser excitation energies ($E_{\text{laser}} = 1.70$ and 1.68 eV). It is obvious that for positive charging the larger diameter SWCNT (smaller frequency of the RBM) corresponds to a steeper dependence of $\omega_{G^+}$ on electrode potential. This is in agreement with our conclusion and previous prediction, where the larger diameter tube experiences a stronger phonon energy renormalization effect. For negative doping, the sign of the frequency shift ($\delta\omega_{G^+}/\delta V_e$) is changed from negative to positive and increases in going from small diameter tubes to the large-diameter tubes.

However, we should note that the frequency shift ($\delta\omega_{G^+}/\delta V_e$) is not a simple function of the diameter of the tube. For example, there is a relatively small difference in the diameter of the largest and the second-largest SWCNTs, but the difference in behavior is quite significant. Hence, there are probably other effects which modulate the dominant dependence of $\delta\omega_{G^+}/\delta V_e$ on tube diameter, but their contribution seems to be minimal if individual nanotubes are considered. Here, we also tested the dependence on laser excitation energy. For tube B, the data using two laser excitation energies (1.70 (empty squares) and 1.68 eV (filled squares)) are shown in Figure 4. Despite the slight variation in the magnitude of the frequency shift of the G$^+$ mode, the trends do not exhibit a dependence on laser excitation energy for the $E_{\text{laser}}$ values that were probed. It is important to note that the experiments on individual tubes are limited to the resonance window of a particular SWCNT, and thus, $\delta\omega_{G^+}/\delta V_e$ due to a large change of $E_{\text{laser}}$ cannot be studied. This is different for the case of nanotube bundles where at each laser excitation energy there are several tubes in resonance.

It seems that the dependence of the G$^+$ mode frequency on electrode potential is generally not monotonic. The frequency is unchanged up to a potential of approximately −0.5 V, and then there is a sudden change, which in some cases is followed again by a range of almost constant frequency. The potential of the sudden change of the frequency is close to the first van Hove singularity ($E_{1S}$). Note, that the $E_{1S}$ is in resonance with $E_{33S}$. Thus, we believe that the filling of this particular $E_{1S}$ singularity is responsible for the observed effects in the Raman spectra of
Figure 4. This is particularly important for the hardening/softening of the C–C bond due to extracted/added electrons. The contribution of the phonon renormalization effect is predicted to increase when the potential is moved away from \( V_e = 0 \) V. The phonon renormalization effect is strongly diameter dependent,\(^2\) and consequently, it should manifest itself at a lower potential for large-diameter tubes than for small-diameter tubes. Furthermore, the constant frequency range being larger is indicative of the larger energy spacing between the van Hove singularities for small-diameter tubes. Indeed, our data in Figure 4 show that the range with a constant frequency is broader for the smaller-diameter tube than for the large-diameter tubes. The reason for the asymmetry in this behavior with respect to positive and negative charging is not clear, but it can be tentatively explained by an asymmetry in the electronic structure with respect to \( V_e = 0 \). The negative and positive contributions of the two effects mentioned above or the difference in the gating efficiency of positive/negative ions also can cause the observed asymmetry.

In conclusion, we show that \( \omega_G^+ \) of semiconducting SWCNTs is dependent on the electrode potential \( V_e \). The sign of the frequency shift (\( \delta \omega_G^+ / \delta V_e \)) was found to be different for different tubes for negative charging, but in contrast, the sign of (\( \delta \omega_G^- / \delta V_e \)) was found to be the same for positive charging. We have observed that the response of the \( G^+ \) band to a potential is dependent on SWCNT diameter: for negative charging, the large-diameter tube exhibits an upshift of the \( G^+ \) band, while the small-diameter tube exhibits a downshift of the \( G^+ \) band upon negative charging. For positive charging, the \( G^+ \) mode frequency is always upshifted, but the larger-diameter tube exhibited a stronger upshift than the smaller-diameter tube. More detailed analysis of the data showed that the change of \( \omega_G^+ \) starts at an electrode potential which is close to the first van Hove singularity \( E_1 \) of the studied semiconducting tube.

Our data furthermore demonstrate the importance of making measurements at the single nanotube level, since it is difficult to analyze the effects specific to tubes with a particular \((n, m)\) systematically when they are in bundles due to the averaging of the data measured for different nanotubes.

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