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Effect of nanotube-nanotube coupling on the radial breathing mode of carbon nanotubes

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We study the radial breathing mode (RBM) of resonant single walled carbon nanotubes within individual bundles. As strain is applied, significant debundling of the nanotubes occurs, causing an upshift in the RBM frequency. The RBM frequency is found to change irreversibly with strain, correlating more strongly with the total number of strains and relaxations than with absolute strain, indicating that debundling is the dominant cause of the observed changes. The RBM upshift of semiconducting nanotubes is 70% larger than that of metallic nanotubes. We also observe a large drop in the Raman intensity as the nanotubes are debundled. This drop is not due to a change in the resonant electronic transition energies of the nanotube and indicates that neighboring nanotubes within a bundle play an important role in the resonant nanotube's Raman signal.

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Carbon nanotubes' mechanical properties have been proposed for a number of applications, including rotational actuators,[1] electromechanical switches,[2] and even space elevators.[3,4] Despite the wide range of sophisticated measurement techniques, now available for characterizing carbon nanotubes,[5–12] many questions remain unanswered about this complex and unique one-dimensional system including the effects of nanotube-nanotube interactions within bundles, which is the focus of this paper.

Internanotube coupling has been shown to redshift the energies of optical transitions of nanotubes by tens of meV.[13] Rao *et al.*[14] observed an increased radial breathing mode (RBM) frequency for solubilized nanotubes as compared to nanotube bundles and ropes. Individual semiconducting nanotubes showed a 40 cm^{-1} upshift in frequency as compared to bundles, while metallic nanotubes showed a 4 cm^{-1} upshift. In a different experiment, using atomic force microscope (AFM) manipulation, Jiang *et al.*[15] also observed an increase of 6–10 cm^{-1} in RBM frequency for individual nanotubes versus bundles. These results stand in contrast to theoretical calculations of the RBM frequency, which predict a decrease in the vibrational frequency as nanotubes are decoupled.[16–18]

In previous Raman measurements of nanotubes under strain, the RBM frequency was observed to upshift and downshift in frequency with applied strain.[19] However, in this previous work, bulk quantities of nanotubes were measured simultaneously, giving an ensemble average. The observed strain-induced changes arise from a change in the resonant electronic transition energies, E_{ii}, which shifts a different set of nanotubes, with slightly different diameters, onto resonance. In another previous publication, a detailed study of the *G* band Raman mode of individual carbon nanotube bundles was presented as a function of strain.[20] This study showed that only 10% of the applied strain was translated to the individual nanotubes within the bundle and that the primary effect of the strain was to debundle the nanotubes.

In the work presented here, the Raman spectra of an individual resonant single walled carbon nanotube (SWNT), within a bundle, are measured as strain is applied, eliminating the effects of ensemble averaging that were present in previous strain measurements. By increasing and decreasing the applied strain many times, we separate the reversible and irreversible changes observed in the Raman spectra and further corroborate that the primary effect is caused by debundling. Stokes (S) and anti-Stokes (AS) Raman spectra show that these changes are not caused by a change in the transition energy E_{ii} and are solely due to the effects of mechanical decoupling. Changes in the RBM Raman intensity and frequency are measured under strain-induced debundling.

The sample fabrication follows the general procedure illustrated schematically in Fig. 1. Polydimethylsiloxane (PDMS), created from a Sylgard 184 silicone kit (Corning, Inc.), is cut into strips that serve as elastomeric substrates. SWNTs synthesized by the laser ablation method[21] are sonicated in an isopropyl alcohol solution for 20 min and deposited on top of the PDMS [Fig. 1(b)]. The ends of the bundle are fixed to the PDMS substrate with metal strips of Cr-Au, patterned on top of the SWNTs using photolithography [Fig. 1(c)].[20,22] AFM imaging is used to ensure that both ends of the resonant nanotube bundle are pinned beneath the strips. These images also determine the angle between the nanotube and the metal strips and, hence, the angle of the applied strain. The entire PDMS substrate is then strained, as shown in Fig. 1(d). A Renishaw *inVia* Raman microprobe is used to obtain Raman spectra with a 532 nm Spectra Physics solid-state laser and a 633 nm HeNe laser, as the PDMS substrate is incrementally strained and unstrained.

For the nanotube bundles measured in this experiment, several nanotubes may contribute to the *G* band spectrum,

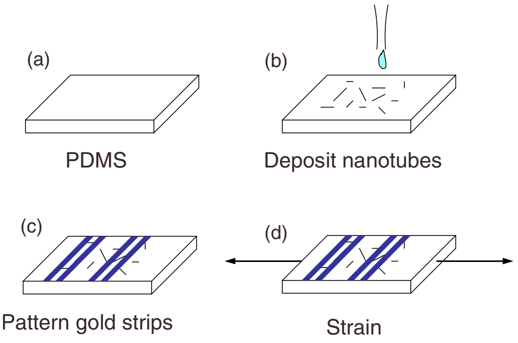

FIG. 1. (Color online) Fabrication steps for inducing strain in individual carbon nanotube bundles.

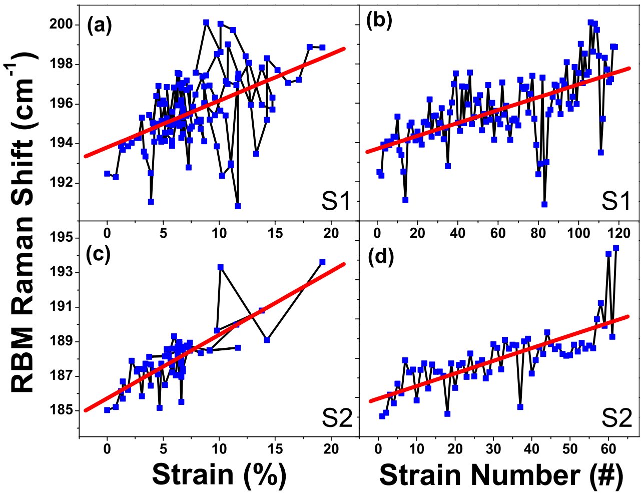

FIG. 2. (Color online) Radial breathing mode frequency versus strain (%) and total number of strains and relaxations (#) of two semiconducting nanotubes strained on PDMS substrates.

yet only one nanotube within the bundle produces a RBM. Figure 2 shows the effect of strain-induced debundling on two semiconducting nanotubes, S1 and S2, measured with a 532 nm laser. These samples were strained and unstrained many times to separate the reversible and irreversible strain-induced effects. The Raman shift of the RBM is plotted as a function of strain (%) and total number of strains and relaxations (#). The data correlate better with the number of strains and relaxations (#) than with absolute strain (%). That is, the RBM frequency tends to increase irreversibly with both increases and decreases in strain. This behavior indicates that debundling is the primary effect on the nanotubes rather than strain since an increase in strain will cause nanotubes to separate from the bundle while a decrease will not cause the nanotubes to reversibly reinsert themselves into the bundle. The RBM frequencies (ω_{RBM}) of these two resonant nanotubes S1 and S2 (from two separate bundles) were observed at 199 and 194 cm^{-1}, implying nanotube diameters (d_t) of 1.19 and 1.23 nm, respectively, by the relation $\omega_{\text{RBM}}=A/d_t+B$.[23] A total of four semiconducting nanotubes were measured in this study, all of which showed consistent upshifts in the RBM frequency with applied strain. In a previous publication,[20] slippage of the nanotubes underneath the metal strips was found to occur in discrete jumps and could therefore be determined quantitatively from the Raman data. The irreversible changes in the RBM, however, show no such discrete jumps, further indicating that slippage of the nanotubes within the bundle is the mechanism of debundling we are observing.

Figure 3 shows the RBM frequency of two metallic nanotubes measured with a 633 nm laser plotted as a function of strain (%) and number of strains and relaxations (#). Again, we see a better correlation to strain number (#), implying that irreversible debundling is the main cause for the observed changes in ω_{RBM}. Interestingly, the increases in the RBM frequency with strain are larger for semiconducting nanotubes than those for metallic nanotubes. This difference may be caused by the Kohn anomaly in metallic carbon nanotubes, which already causes a damping of this phonon mode.[24–26] The RBM frequencies of these two resonant nanotubes M1 and M2 (from two separate bundles) were observed at 154 and 205 cm^{-1}, implying nanotube diameters of 1.6 and 1.2 nm, respectively.[23] A total of four metallic nanotubes were measured in this study, all of which showed consistent upshifts in the RBM frequency with applied strain.

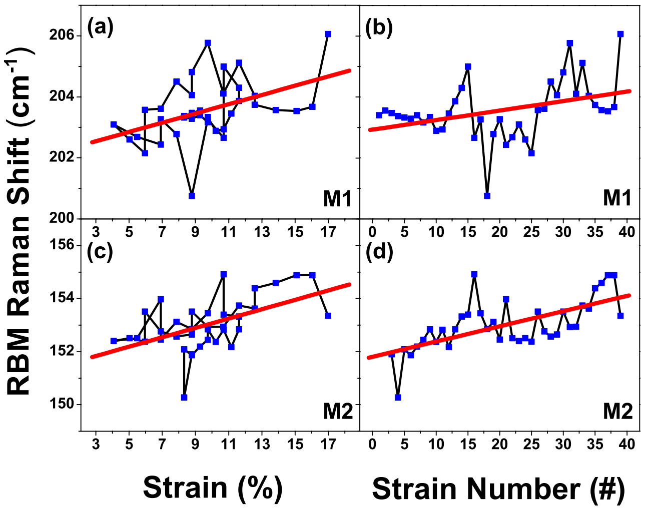

FIG. 3. (Color online) Radial breathing mode frequency versus strain (%) and total number of strains and relaxations (#) of two metallic nanotubes strained on PDMS substrates.

In addition to irreversible changes in the RBM frequency, we also observe a significant drop in the Raman intensity of the RBM with strain-induced debundling. Figure 4 shows the Raman intensity of nanotubes M1 and S1 plotted as a function of strain (%) and number of strains and relaxations (#). The data show a significant decrease in intensity with strain-induced debundling. Again, the Raman data correlate more strongly with strain number (#) than with absolute strain (%). It is tempting to attribute this drop in RBM intensity to strain-induced shifting of the electronic band energies off of resonance with the laser energy. However, we observe no

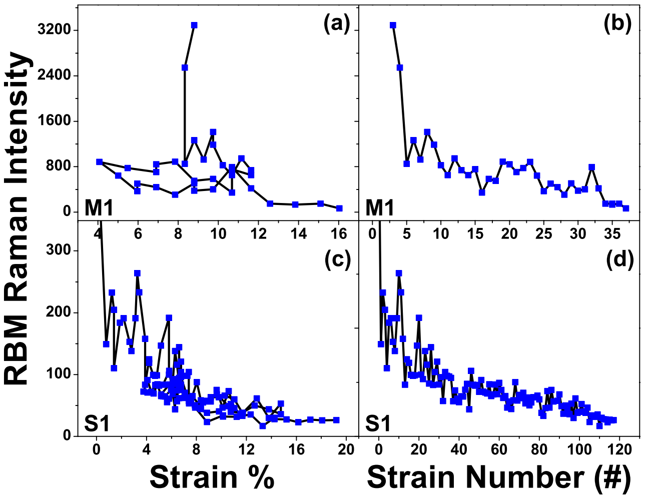

FIG. 4. (Color online) Radial breathing mode Raman intensity for nanotubes M1 and S1 plotted as a function of strain (%) and number of strains and relaxations (#).

change in the S/AS Raman intensity ratio, which is known to be very sensitive to small changes in the resonance condition ($E_{ii}-E_{\text{laser}}$).[27] Therefore, we can rule out changes in the electronic transition energies, E_{ii}, as playing a role in the observed changes in the RBM intensity. We believe that the intensity is reduced through the antenna effect as the nanotube bundle, acting as an antenna to the incident electromagnetic field, changes its physical configuration with applied strain.[28] This nanotube decoupling mechanism is further evidenced by the universal decrease in Raman intensity. One would expect some of the nanotubes to shift *onto* resonance if this was due to a change in ΔE_{ii}, as was previously observed.[29] Therefore, we attribute these irreversible effects to a change in the nanotube-nanotube coupling within the bundle. The behavior in Fig. 4 was observed consistently in all of the nanotubes measured in this study. The G band Raman mode also experiences a similar drop in intensity. Lebedkin *et al.*[30] reported a drop in the RBM intensity under hydrostatic pressures in the range of 4–10 GPa. However, this drop occurs from a radial deformation of the nanotubes and is unrelated to the physical mechanism reported here, where nanotubes within a bundle are separated by a sheer or tangential force.

An upshift in the RBM frequency is expected with applied strain due to a reduction in the diameter of the nanotube by the Poisson ratio.[31] However, these changes would correlate with absolute strain (%), reversibly, which is not observed. Instead, the changes observed in the RBM frequency are due to the decoupling of nanotubes within the bundle. In the bundle, neighboring SWNTs tend to damp the vibrational motion of the resonant nanotube. We can represent this system as a damped harmonic oscillator following the equation

$$\frac{d^2x}{dt^2}+\frac{b}{m}\frac{dx}{dt}+\omega_0^2x=0,$$

where x, t, b, and m are the position, time, damping coefficient, and mass, respectively. Here, the damping coefficient, b, is an experimentally determined quantity satisfying the relationship $F=-bv$ and m corresponds to the mass of the nanotube per unit length. The frequency of the damped harmonic oscillator is given by

$$\omega=\sqrt{\omega_0^2-R_m^2},$$

where

$$R_m=\frac{b}{2m}.$$

The decoupling of the nanotubes tends to reduce the amount of damping. From the upshifts observed in Figs. 2 and 3, we can specify the relative change in the damping coefficient for nanotubes in a bundle. In Fig. 2(b), an upshift of 6 cm^{-1} is observed for a RBM of approximately 196 cm^{-1}. This corresponds to a damping frequency of $R_m=48.9\ \text{cm}^{-1}$. Using a mass per unit length of $m=6.3\times10^{-24}$ kg, for a 1.22 nm diameter nanotube, the relative change in the damping coefficient per unit length is $\Delta b=8.3\times10^{-3}\ \text{N s/m}^2$. This value gives a lower limit for the damping due to neighboring nanotubes since the RBM is not observed to saturate and the extent of debundling is unknown. This extreme sensitivity of the RBM frequency and intensity to nanotube-nanotube coupling reflects the high surface-to-volume nature of nanotubes. The basic mechanism underlying these RBM frequency shifts is expected to arise from van der Waals forces between the nanotubes in the bundle. These forces decrease as the nanotubes are debundled under the applied strain, causing an upshift in the RBM vibrational frequency.

In conclusion, the radial breathing mode of carbon nanotube bundles is studied under strain-induced debundling. Consistent upshifts in the RBM frequency of approximately 5 and 2 cm^{-1} are observed for semiconducting and metallic nanotubes, respectively, due to a reduction in the damping of this mode by neighboring nanotubes. The RBM frequency is found to correlate more strongly with the number of strains and relaxations than with absolute strain (%), indicating that debundling is, in fact, responsible for the observed changes. Semiconducting carbon nanotubes exhibit a more significant upshift than metallic SWNTs. A large drop in the Raman intensity is also observed as the nanotubes are debundled, indicating that neighboring nanotubes play a significant role in nanotubes' Raman signal, through the antenna effect. No change in the resonant electronic transition energy E_{ii} is observed under the applied strain and debundling.

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