Probing the doping in metallic and semiconducting carbon nanotubes by Raman and transport measurements

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In-situ Raman experiments together with transport measurements have been carried out on carbon nanotubes as a function of gate voltage. In metallic tubes, a large increase in the Raman frequency of the $G^-$ band, accompanied by a substantial decrease of its line-width, is observed with electron or hole doping. In addition, we see an increase in Raman frequency of the $G^+$ band in semiconducting tubes. These results are quantitatively explained using ab-initio calculations that take into account effects beyond the adiabatic approximation. Our results imply that Raman spectroscopy can be used as an accurate measure of the doping of both metallic and semiconducting nanotubes.

In metallic tubes, the Raman $G^-$ modes harden for both electron and hole doping by 7 cm$^{-1}$ for a $V_g$ of -1 and +1 V [14, 15, 16]. Ref. [17] qualitatively attributed the frequency shift of metallic tubes to the KA. However, the shift of the Fermi level, a key parameter to understand the results, so far has not been quantified.

In this work, we demonstrate that the shift of the $G$ bands can be used to measure the doping level not only in metallic but also in semiconducting nanotubes. This is done by performing a combined Raman and electron-transport experiments and by comparison with ab-initio calculations based on density functional theory (DFT).

We use electrochemical gating of the nanotubes with a solid polymer electrolyte to shift the Fermi level, which is quantified by electron-transport measurements. This allows a shift of the Fermi level at much smaller gate voltages as compared to SiO$_2$ gating [18, 19, 20].

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SWNTs are synthesized by arc-discharge followed by purification [21]. AC dielectrophoresis [22] is used to align and connect the nanotubes between two gold electrodes at 15 µm separation. The average diameter of the bundles connected to the electrodes is 10-50 nm from the SEM image, Fig. 1(b). We have used as gating material a solid-polymer electrolyte [19, 20] prepared by dissolving LiClO₄ and PEO (1:0.12) in methanol to form a precursor. The gate is applied by placing a platinum electrode into the polymer layer. The advantage of the solid electrolyte over the electrolytes in solution phase is that it does not degrade the sample and electrodes and solid electrolyte over the electrolytes in solution phase is the gate-voltage (∼gate-current is extremely small (∼nA) even at high gate voltages (∼1V). A DIOR triple grating spectrometer equipped with charge-couple device is used to record the Raman spectra using a He-Ne (1.96 eV) laser. Fig. 1(c) shows the RBM of our tubes. It has two bands with average diameter d=1.4 and 1.6 nm. The laser at 1.96 eV is in resonance with E₂₂ of tube diameter 1.4 nm and lies in between the E₁₁ and E₃₃ of 1.6 nm diameter tubes [23]. Therefore, Raman spectra has contributions from metallic tubes of d=1.4 nm as well as from both semiconducting and metallic tubes of d=1.6 nm.

Fig. 1(a) shows the ambipolar behavior of our nanotube FET device at a drain-source voltage V_DS of 50 mV. At gate voltage V_g=0, I_DS ~ 500 nA. The behavior of the current through the SWNT is reversible with V_g and the leakage current is very small (∼10 nA at V_g ~ 2V). Since the current increases on either side of the starting zero V_g, we infer that the initial Fermi energy (ε_F=0) is at the middle of the gap of semiconducting tubes (charge neutrality point-CNP) [20]. The sharp increase in current, as shown in Fig. 1(a), for large positive (negative) V_g is due to addition of electrons (holes) to the first van Hove singularity on conduction (valence) band side of the semiconducting tubes present in the sample along with the metallic tubes. The onset of this increase in current is observed for V_g=2.02 V and -0.8 V, inset of Fig. 1(a). For the semiconducting tubes of average diameter ~ 1.5 nm, E₁₁~ 0.5 eV and for metallic tubes E₁₁~ 1.8 eV [23]. As the metallic tubes have larger energy separation between the van Hove singularities, the sharp increase in conductivity in Fig. 1(a) is mostly governed by the semiconducting tubes. Therefore, the semiconducting tubes of the sample act as an internal read out to estimate the V_g-induced ε_F shift. We define the proportionality factor α_e (α_h), to estimate ε_F at different positive (negative) gate voltages (ε_F = αV_g). For electron doping, a positive voltage of ∼ 2.02 V shifts ε_F into the first conduction band, which is 0.25 eV from the CNP. Therefore, α_e = 0.25/2.02 = 0.12 e and similarly α_h = 0.25/0.8 = 0.31 e. The difference between α_e and α_h is probably due to double layer formation of different ions Li⁺ and ClO₄⁻ in PEO matrix at the interfaces.

Fig. 2(a) shows the Raman spectra recorded at different V_g. A constant gate voltage is applied for 15 minutes to stabilize I_DS and then the Raman spectra were recorded for next 15 minutes at the same V_g. For a V_g in the -1.25/+2.5 V range, the Raman spectra as well as the source-drain current fully recover to the starting condition (V_g=0) within about one hour after removing the gate voltage. There are three prominent Raman modes and the spectra are fitted with three Lorentzians L1 (∼1540 cm⁻¹), L2 (∼1567 cm⁻¹) and L3 (∼1590 cm⁻¹). The Raman frequency, linewidth and total area thus obtained for L1, L2 and L3 modes are plotted in Figs. 2(b), 2(c) and 2(d), as a function of V_g. Following Fig.19 of Ref. [6], the L1 line is attributed to the LO mode of the metallic tubes with diameter 1.4 nm [6]. The L1 line can be equally well fitted by a Lorentzian or a Fano-
resonance line-shape. We use a Lorentzian line-shape to minimize the number of fitting parameters. In our spectra, the L2 has a large line-width of ~ 40 cm\(^{-1}\) and the doping dependence is similar to that of L1 mode. Therefore the L2 line is attributed to a combination of the LO mode of metallic tubes and of the TO mode of semiconducting tubes with diameter 1.6 nm (Fig.19 of Ref. [6]).

The L3 line is attributed to a combination of the TO of metallic and the LO of semiconducting tubes. The EPC determines an important broadening of the LO mode of metallic tubes. This explains the large width of the L1 (~ 60 cm\(^{-1}\)) and L2 (~ 40 cm\(^{-1}\)) lines. The sharpness of the L3 line (~ 10 cm\(^{-1}\)) is explained considering that the semiconducting LO and the metallic TO modes are not broadened by EPC and that their frequencies are almost independent from diameter (Fig.19 of Ref. [6]).

As shown in Fig. 2(b), the largest effect is the frequency increase of the L1 line by 15/10 cm\(^{-1}\) on hole/electron doping. The substantial decrease of its linewidth is also remarkable. Both effects are due to the dependence of the KA on \(V_g\) in metallic tubes. The L2 line displays a similar behavior due to the metallic tubes associated with this line. The intensity of the L1 line (entirely due to metallic tubes) drops to zero at high doping (positive or negative). This suggests that, at high doping, the Raman signal from metallic tubes is negligible. Thus, the behavior of the L3 line at high doping is mostly due to semiconducting tubes. Interestingly, the frequency upshift of the L3 line is perfectly correlated to the \(I_{DS}\) current (Fig.1), indicating that the L3 shift is due to the change of the electron (hole) populations in the conduction (valence) bands of semiconducting tubes.

We now compare measurements with DFT calculations, done using i) the adiabatic Born-Oppenheimer approximation (BOA, Eq.6 of Ref. [3]) and ii) time-dependent perturbation theory (TDPT, Eq.7 of Ref. [3]) to include dynamical effects beyond BOA. Within BOA, the phonon frequency is obtained from the forces resulting from a static displacement of the atoms. However, a phonon is not a static perturbation to the system but a dynamic one, oscillating in time, that should be treated within TDPT. Dynamic effects beyond BOA are usually assumed to be negligible, but they are crucial to reproduce the Raman spectra of nanotubes and doped graphene [4, 5, 11, 11]. Our DFT calculations are based on a linear response approach [24] as described in Ref. [11]. Calculations are done on a metallic (10,10) and on a semiconducting (20,0) tube, having diameters 1.4 and 1.6 nm. We compute the variation of the LO and TO phonon frequency (\(\Delta \omega_{LO}\) and \(\Delta \omega_{TO}\)) as a function of the doping. We also compute the intrinsic linewidth (\(\gamma_{LO}\) and \(\gamma_{TO}\)) due to EPC (Eq.29 of Ref. [11]), owing to the decay of the phonon into electron-hole pairs, which is nonzero only for metallic tubes. The electronic occupations are determined according to a Fermi Dirac distribution at 315 K.

For metallic tubes \(\Delta \omega_{TO}\) and \(\gamma_{TO}\) are negligible, since the EPC between occupied and empty electronic states is zero (see Eq.9 of Ref. [11]). For diameter \(d\) larger than 1 nm, \(d \times \Delta \omega_{LO}\) and \(d \times \gamma_{LO}\) are universal, i.e. independent of both \(d\) and chirality [5, 11]. Fig.3 reports these universal behaviors, as functions of \(\epsilon_F\), computed within TDPT. BOA results are not reported, since they are very similar for \(h\omega_{LO}/2 < |\epsilon_F| < 1.0 eV\) [11]. The hardening of \(\Delta \omega_{LO}\) for \(|\epsilon_F| > h\omega_{LO}/2\) is understood by considering the modification of the electronic band structure in the presence of the LO phonon. An atomic distortion following the LO phonon pattern opens a gap at the CNP [3]. The filling of the electronic states with doping increases the energy required to open this gap, thus inducing a hardening of the LO frequency [25].

We assume that \(\epsilon_F\) has a Gaussian distribution (with a standard deviation \(\sigma\)) to take into account the spatial fluctuation of \(\epsilon_F\) in the actual device. In Fig.3 we report the average frequency and the FWHM of the LO peak profile obtained by an ensemble of tubes with such a distribution. To include the experimental data in Fig.3 we multiply the measured \(V_g\) by \(\alpha_e\) and \(\alpha_h\). The calculations best describe the experiment with \(\sigma = 0.055\) eV. The agreement between theory and measurements is excellent for \(\Delta \omega_{LO}\). The theoretical LO linewidth is smaller than the experimental one, probably because of other ef-
metallic and semiconducting tubes does not depend on line, since, at small doping, the position of $G$ is directly compared to the theoretical $\Delta G$ of metallic tubes. We can instead compare the theoretical $\Delta G$ with the L3 line. At the minimum $V_g$, L3 upshifts by $\sim 5 \text{ cm}^{-1}$. According to TDPT, this corresponds to a doping of $4.0 \times 10^{-3}$ holes per C atom and to $-0.15 \text{ eV}$ shift of $\epsilon_F$ below the first vHs.

In semiconducting tubes, $\Delta G$ depends on the positions of the band edges, i.e., on $d$ and, to a lesser extent, on the chirality. Fig. 4 shows $\Delta v_{\text{LO}}$ and $\Delta v_{\text{TO}}$ computed within BOA and TDPT. Within the more accurate TDPT, $\Delta v_{\text{LO}}$ and $\Delta v_{\text{TO}}$ upshift when $\epsilon_F$ reaches the vHs. To understand this behavior, we have to consider how the electrons screen a phonon vibration. The electronic screening can be expressed in terms of inter- and intraband EPC transitions between electronic states [9]. Within TDPT only the interband transitions between occupied valence and empty conduction electronic states contribute (Eq.(7) of [9]). By doping the tube, the valence (conduction) band is emptied (filled). Both processes correspond to a reduction of the number of allowed transitions. The consequent reduction of the screening upshifts $\omega$. The shift is more pronounced for the TO phonon that has a larger EPC for transition between valence and conduction band edges. Within BOA, the presence of intraband transitions (second line of Eq. (6) of [3]) contrasts the hardening due to interband transition [9,11].

The $G^-$ of both metallic and semiconducting tubes are affected in a different way by $V_g$. Thus, the behavior of $G^-$ of semiconducting tubes in the L2 line cannot be separated from that of metallic tubes. We can instead directly compare the theoretical $\Delta v_{\text{LO}}$ with the L3 line, since, at small doping, the position the $G^+$ of both metallic and semiconducting tubes does not depend on $V_g$ and, at large doping, the metallic-tube intensity vanishes. TDPT calculations for the LO mode compare very well with the measured behavior of the L3 line, that we report in Fig. 4 using the transport-derived ratios $\alpha_e, \alpha_h$. At the minimum $V_g$, L3 upshifts by $\sim 5 \text{ cm}^{-1}$. According to TDPT, this corresponds to a doping of $4.0 \times 10^{-3}$ holes per C atom and to $-0.15 \text{ eV}$ shift of $\epsilon_F$ below the first vHs.

Concluding, by combining transport, in-situ Raman experiments and ab-initio calculations we quantified the effect of the doping on the phonons in carbon nanotubes. By electron and hole doping, the Raman $G^-$ peak of metallic tubes and both the $G^-$ and $G^+$ of semiconducting tubes harden. Moreover, the $G^-$ linewidth of metallic tubes narrows. Important consequences of the present results are that: i) The metallicity of the system is not always associated with the presence of a broad $G^-$ peak, as often assumed. Indeed, in a doped metallic tube, the $G^-$-peak width can be much smaller than in the undoped case if the Fermi level is far from the $\pi$ band-crossing. ii) Given the strong dependence of the Raman $G$ bands on the Fermi energy, Raman spectroscopy can be used as an accurate measure of the doping of both metallic and semiconducting nanotubes, with important technological implications for nano electronics.

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[1] S. Reich, C. Thomsen, and J. Maultzsch, Carbon nanotubes: basic concepts and physical properties, (Wiley-VCH, 2004)
[2] R. Saito, G. Dresselhaus, and M.S. Dresselhaus, Physical properties of carbon nanotubes, (Imperial College Press, 1998)
[3] S. Tans, A. Verschueren, and C. Dekker, Nature 393, 49 (1998).
[4] S. Ghosh, A.K. Sood, and N. Kumar, Science 299, 1042 (2003).
[5] O. Dubay, G. Kresse, and H. Kuzmany, Phys. Rev. Lett. 88, 235506 (2002).
[6] S. Piscanec et al., Phys. Rev. B 75, 035427 (2007).
[7] M. Lazzeri et al., Phys. Rev. B 73, 155426 (2006).
[8] S. Piscanec et al., Phys. Rev. Lett. 93, 185503 (2004).
[9] M. Lazzeri and F. Mauri, Phys. Rev. Lett. 97, 266407 (2006).
[10] S. Pisana et al. Nature Materials 6, 198 (2007); J. Yan et al., Phys. Rev. Lett. 98, 166802 (2007).
[11] N. Caudal et al., Phys. Rev. B 75, 115423 (2007).
[12] M. Stoll et al., Chem. Phys. Lett. 375, 625 (2003).
[13] L. Kavan et al., J. Phys. Chem. B. 105, 10764 (2001).
[14] N. Bendiab et al., Phys. Rev. B. 64, 245424 (2001).
[15] C.P. An et al., Synth. Met. 116, 411 (2001).
[16] P. Corio et al., Chem. Phys. Lett. 370, 675 (2003).
[17] P.M. Rafailov et al., Phys. Rev. B. 72, 045411 (2005).
[18] M. Krüger et al., Appl. Phys. Lett. 78, 1291 (2001).
[19] C. Lu et al., Nano Lett. 4, 623 (2004).
[20] G.P Siddons et al., Nano Lett. 4, 927 (2005).
[21] S.R.C. Vivekhand et al. Small 1, 920 (2005).
[22] R. Krupke et al. Science 301, 344 (2003).
[23] T. Michel et al. Phys. Rev. B 75, 155432 (2007).
[24] S. Baroni et al. Rev. Mod. Phys. 73, 515 (2001).

[25] The behavior of $\Delta \omega_{LO}$ in metallic tubes can be equally understood within perturbation theory, in terms of inter-band electronic transitions, as we explained in ref. [11]. Here we adopt this approach to interpret the behavior of the semiconducting tubes.