EPJ Web of Conferences **41**, 04028 (2013)
DOI: 10.1051/epjconf/20134104028

Resonant Enhancement of Coherent Phonons in Carbon Nanotubes Observed with Sub-10fs Time Resolution

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Abstract. Using wavelength-resolved pump-probe spectroscopy with a sub-10-fs laser, we investigated resonant enhancement of radial breathing mode and G-mode coherent phonons in carbon nanotubes (CNTs), and successfully distinguished the electronic states of CNTs with different chiralities.

1 Introduction

Carbon nanotubes (CNTs) are one of the promising materials for next generation electronics. The electronic structure of CNTs changes from semiconductors to metals depending on the chirality [1]. The dynamics of carriers and electron-phonon coupling could also show strong dependence on their electronic structures, and thereby various ultrafast measurements have been investigated [2-5]. In most cases, mixture of CNTs with different chiralities and diameters is used for the measurements, making the analysis of the data complicated. Although single chirality samples are recently available [5, 6], it is still required to establish a way to distinguish the chirality of CNTs because the purity is at most in the order of 80 % even in the single chirality samples.

Sharp electronic resonance at the van-Hove singularities of density of states is a key to resolve the chirality of CNTs. One way to observe this singularity is to measure the photoluminescence excitation spectrum [7], but not all of the samples show the luminescence because of the inter-tube interactions. Raman spectroscopy to measure the frequency of radial breathing modes (RBM) is an alternate way to distinguish the chirality because the Raman scattering cross section of the RBM is strongly enhanced by the singularities [8]. However, observation of the resonant dynamics of the RBMs and also the high-frequency G-mode phonons cannot be achieved in conventional Raman measurements, because it requires a high time-resolution. In this work, we show that wavelength-resolved coherent phonon spectroscopy using 7.5-fs laser pulses enables us to distinguish the resonance of CNTs with different chiralities. The obtained results strongly show that the wavelength-resolved coherent phonon spectroscopy becomes a key technique not only for understanding the resonance of the RBM, but also for investigating the carrier dynamics in CNTs with different chiralities.

2 Experiment

CNTs purchased from Meijo Nano Carbon Co. Ltd. were filtrated several times to purify. The solution of the purified CNTs was dried on a glass plate. The diameter of the CNTs ranges from 1.1 to 1.6 nm. A 7.5-fs Ti-sapphire laser was used for pump-probe transmission measurements. The output of the laser was separated into pump and probe beams. The pump pulse is delayed by an optical shaker with a scanning range of 15 ps, and focused on the sample together with the probe pulse. The probe pulse transmitted through the sample was delivered to a photodiode for detecting the probe signal. To balance the current of the photodiode for the probe signal, the reference signal was also detected. The difference between the probe and reference signals was amplified and collected by an analogue-to-digital converter. We placed a bandpass filter with a 10 nm bandwidth in front of the photodiodes to change the probe wavelength. The probe wavelength was tuned from 700 nm to 1000 nm by changing the bandpass filter.

3 Results and discussion

Figure 1(a) shows the obtained transmittance change as a function of time delay between pump and probe pulses. We observed positive electronic response near the time origin, as well as the interference between pump and probe pulses. By filtering out the interference, we see clearly the oscillations of the characteristic coherent phonons of CNTs as in Fig. 1(a). Figures 1(b) and 1(c) are the Fourier transform spectra for the observed coherent phonons of RBM (4-7 THz) and D- and G-modes (37-50 THz), respectively. The observed frequency range of the RBM agrees well with that expected in the CNTs used in this experiment (diameters of 1.1-1.6 nm). Note that even though the interference between pump and probe pulses lasts about 0.1 ps, the high frequency coherent phonons can be clearly observed.

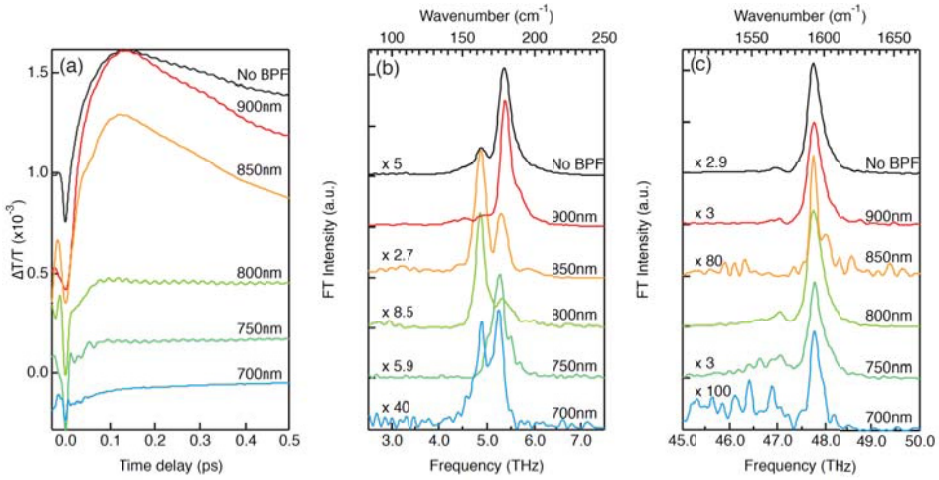

Fig. 1. (a) Observed transient transmittance of the CNTs with different probe wavelengths. (b) Fourier transform spectra of the coherent phonons observed near the RBM frequency. (c) Those near the G-mode frequency.

As shown in Figs. 1(b) and 1(c), the spectra of the observed coherent phonons depend on the probe wavelength. Especially, in the RBM spectra (Fig. 1(b)), we found that there are a few peaks whose intensity depends strongly on the probe wavelength. It is well known that the electronic resonance depends on the tube diameter, which is summarized as Kataura-plot. Therefore, the observed experimental results directly reflect difference of resonant enhancement of the Raman scattering cross section among different chiralities/diameters of CNTs. Considering the tube diameter of the sample and the observed wavelength dependence of the RBM Raman intensity, there exist three

possible electronic transitions: E22 transition of the semiconductor nanotubes at 900-1000 nm, E11 transition of the metallic nanotubes at 850-700 nm, and E33 transition of the semiconductor tubes below 700 nm. As shown in Fig. 1(b), the peak intensity at 4.8 THz becomes stronger at 850 nm, corresponding to the E11 resonance for metallic CNTs. The peak intensity at 5.6 THz is stronger at 900 nm, which corresponds to the E22 resonance for the semiconductor CNTs. The peak at 5.3 THz can be attributed to the E33 resonance for semiconductor CNTs. On the other hand, in the G-mode signal (Fig. 1(c)), the change of the peak frequency is not as pronounced as that in the RBM. However, the spectral shape of the G-mode exhibits a shoulder structure at 46.5 THz of 700-800 nm probe wavelengths, implying Fano resonance between the G-mode and conduction electrons. The wavelength of 700-800 nm corresponds to the E11 resonance of metallic CNTs, supporting the existence of Fano resonance.

4 Conclusion

In conclusion, we observed the resonant enhancement of the coherent phonons in CNTs using the wavelength-resolved coherent phonon spectroscopy. Because of the broad bandwidth of the 7.5-fs laser, we can distinguish the electronic resonance of CNTs with different chiralities and diameters, which could be useful for the dynamical spectroscopy on CNTs with chirality resolution.

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