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Ultrafast carrier dynamics in purified and as-grown single-walled carbon nanotube films*

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Ultrafast time-resolved optical transmissions in purified and as-grown single-walled carbon nanotube films are measured at a temperature of 200K. The signal of the purified sample shows a crossover from photobleaching to photoabsorption. The former and the latter are interpreted as the state filling and the red shift of the π-plasmon, respectively. The signal of the as-grown sample can be perfectly fitted by a single-exponential with a time constant of 232fs. The disappearance of the negative component in the as-grown sample is attributed to the charge transfer between the semiconducting nanotubes and the impurities.

Keywords: carbon nanotubes, carrier dynamics, π-plasmon resonance, charge transfer
PACC: 7847, 7125X, 6148, 3470

1. Introduction

Single-walled carbon nanotubes(SWNTs) have stimulated extensive attention due to their striking properties in mechanics,[1,2] conductivities,[3] electronics[4]and optics.[5] Spurred by the interest in understanding the electronic structure and developing nano-electronic devices, carrier dynamics in this 1-D nanostructure has been investigated employing femtosecond pump-probe technique.[6−12] Two main results reported are that the intraband relaxation time of the semiconducting nanotubes in the nanotube films or mats is about 130 fs, and the interband relaxation time is about 1 ps through nonradiative channels.[6−10] On the other hand, two-component dynamics is observed in the isolated semiconducting type single-walled carbon nanotubes, which is interpreted as intraband carrier relaxation (0.3–1.5ps for fast component) and radiative carrier relaxation (5–20ps for slow component).[11,12]

Though much work has been done on SWNT, a complete understanding of the carrier dynamics in SWNT films needs more investigations. The uncertainty in sample state, the wide diameter distribution of the nanotubes and the probable interaction between the nanotubes and between the nanotubes and other impurities make things more complicated. In our previous paper, we have revealed two competing processes in carrier dynamics of the purified SWNT films.[10] In this paper we will report for the first time that the photo-induced electrons can be transferred from semiconducting nanotubes to the impurities in the as-grown SWNT films by comparing the carrier dynamics between the as-grown and purified SWNT films.

2. Experiment

The SWNT samples with areas up to several tens of square centimeters were prepared directly by floating chemical vapour deposition method.[13] The SWNT nonwoven was oxidized in air at 400–500°C for 48 h and subsequently treated with concentrated HCl to remove the impurities. Inspection by SEM indicated that the as-grown SWNT sample was decorated with very small nanoparticles(Fe and amorphous carbon).[13] Electron-loss spectrometry showed that the percent weight of the Fe catalyst of the as-

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grown sample was about 8.29 and that of the purified sample was about 0.37. Both the as-grown and the purified SWNT films were composed of thousands of highly entangled single-walled carbon nanotube bundles with 20–30nm in diameter, several hundred microns in length and about several micrometers in thickness. For the experiment of ultrafast time-resolved optical transmission, both the as-grown and the purified films with an area of about 5mm×8mm were spread on a pre-cleaned glass slide. Then these pretreated SWNT films on the glass slides were kept in an electric furnace at 80°C under the normal atmosphere for about 10h.

We used the standard femtosecond pump-probe transient transmission change technique to study ultrafast relaxation dynamics in the SWNTs. A mode-locked Ti:sapphire laser beam with a central wavelength of 790nm, a pulse width of 100fs, and a repetition rate of 82MHz, was split into an intense pump beam and a weak probe beam. The pump beam, perpendicularly polarized to the probe beam, was modulated at a frequency of about 1kHz by a chopper. The pump and probe beams were focused through a single lens to the same spot with a diameter of about 50 microns on the surface of the SWNTs. The pump and probe fluences were about $30\mu J/cm^2$ and $2.0\mu J/cm^2$, respectively. The samples were mounted inside an Oxford static exchange-gas continuous flow cryostat and the temperature was kept at 200K in order to prevent the sample from being heated by the laser beams. The detailed description of the experiment setup, can be found in Ref.[14].

3. Results and discussion

The optical absorption (OA) spectra of the purified sample are shown in Fig.1. In our previous studies, sharp peaks at 207 cm^{-1}in Raman spectra of samples represent that the (12, 4) nanotubes are dominant in the original and purified films.[13,15] On the other hand, two peaks in the OA spectra (A, 0.92eV; B, 1.43eV) are consistent with the first (0.924eV) and second (1.447eV) transitions in the (12, 4) nanotubes, respectively. The peaks in the OA spectra are broad compared with those of the samples used in Refs.[8, 10]. The relatively flat OA spectra suggest that the interaction between nanotubes and π-plasmon tail plays a more important role in our sample. We have also measured the OA spectra of the as-grown samples, and no obvious difference is observed, suggesting that the impurities in the as-grown samples have little effects on the OA spectra.

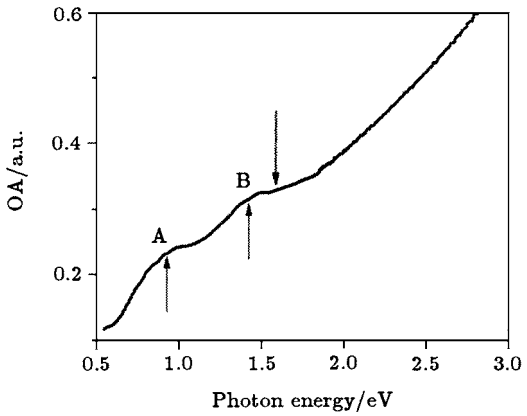


Fig.1. Linear near-infrared OA spectrum of the sample. Peak A(0.9eV) and peak B(1.4eV) are related to the first and second interband transitions of the semiconducting nanotubes, respectively. The thick arrow on the OA spectrum indicates the pump/probe energies.

The time resolved optical transmission $\Delta T/T$ of the purified sample as a function of the delay time is shown in Fig.2. The most important characteristic observed from this figure is that the signal shows a crossover from photobleaching to photoabsorption. The data perfectly fit a double-exponential described by $\Delta T(t)/T = \Delta T(0)/T + A_1(0)e^{-t/\tau_1} + A_2(0)e^{-t/\tau_2}$, where τ_1=160fs and τ_2=0.72ps. There is a fast initial decay with a characteristic time τ_1=160fs, followed by a relatively long component (τ_2=0.72ps) with a negative amplitude. This result is consistent with the previously reported intraband relaxation time (130fs) and the interband relaxation time(1ps) in the semiconducting nanotubes,[8] respectively.

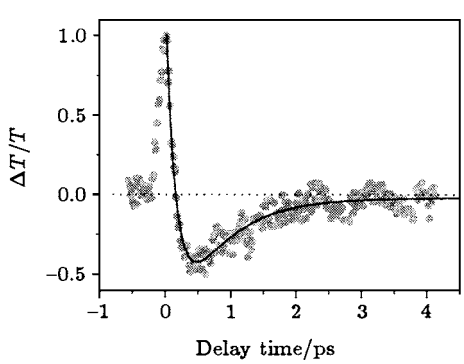


Fig.2. Normalized transient transmission $\Delta T/T$ for the purified sample. Grey points represent experimental data; black curve is for fitted data; dotted line is a zero-line.

The pump pulse excites a population of electrons in the conduction band, occupying the final states of the optical transition (1.57eV). Before these excited

electrons are scattered to other states in the conduction band, few electrons can be further excited from the valence band by the following probe pulse because the corresponding states in the conduction band have been filled. This state filling effect leads to a photobleaching signal. After the photo-created electrons decay down to the conduction band edge (E_{11}) in about 0.13ps, the relaxation process in the semiconducting tubes is dominated by the interband relaxation (on 1-ps time scale) of the electrons through nonradiative channels. Recent time-resolved experiments on unbundled nanotubes show that the intrinsic lifetime is long(5–20ps), and attributed to the fluorescence relaxation.[11,12] The fluorescence quenching in the bundled nanotube films can be derived from the carrier trapping by the defect and the charge transfer between the nanotubes. The carrier trapping channels assisted by the phonons can be excluded since no change in the relaxation time is observed in the low temperature experiments(down to 10K). Similar experimental results have also been reported in Ref.[8]. The excited electrons in the semiconducting tubes are transferred to the metallic tubes due to the tube-tube interaction, followed by the rapid carrier cooling in the metallic tubes, which quenches the fluorescence.

The excessive electrons in the band edge lead to a transient saturation at E_{11}, and change the imaginary part of the dielectric constant $\varepsilon_i(\omega_{11})$ at E_{11}. The real part of the dielectric constant $\varepsilon_r(\omega)$ throughout the spectra (Ω) is modified, according to Kramers–Kronig transformation[16]:

$$\Delta\varepsilon_r(\omega) = \frac{2}{\pi}\int_0^\infty \frac{\Omega\cdot\Delta\varepsilon_i(\Omega)}{\Omega^2-\omega^2}\mathrm{d}\Omega. \qquad (1)$$

The π-plasmon resonance, another relaxation mechanism determined by the equation $\varepsilon_{\mathrm{r}}(\Omega_{\mathrm{p}}) = 0$, is shifted to longer wavelengths. This red shift increases the absorption and decreases the transient transmission to the order of 10^{-5} (see Fig.2), which is in agreement with the measured data in Ref.[8]. Therefore, the decay of the photobleaching signal is attributed to the intraband relaxation of the photo-created electrons in the semiconducting nanotubes, and the photoabsorption signal is associated with the red shift of the π-plasmon resonance.

Figure 3 illuminates the time-resolved signal of the as-grown sample, which can be fitted well with a single-exponential with a time constant of 232fs. The figure indicates that the signal does not decay down to negative. According to Ref.[12], the thermal electron in the conduction band of a nanotube travels a distance of 60nm in the observed time of 200fs. The distance is much shorter than the length of the nanotube (several hundred micrometres). The end and length of the nanotubes have little influence on the carrier dynamics. The photobleaching signal should be attributed to the state filling in the semiconducting nanotubes rather than the impurities because i) the impurities have little effect on the OA spectra (mentioned above) ii) the OA spectra of the Fe nanoparticles have no peaks in the wavelength range from 300nm to 800nm [17] iii) the amplitude ($\Delta T/T$) and the relaxation time are of the same order of magnitude as those of the purified correspondingly . The disappearance of the negative part of the signal should be arising from absence of the red shift of the π-plasmon resonance, which indicates that the photo-generated electrons in the semiconducting nanotubes would be more likely to tunnel into the impurities than to decay to the fundamental bandgap of the semiconducting nanotubes.

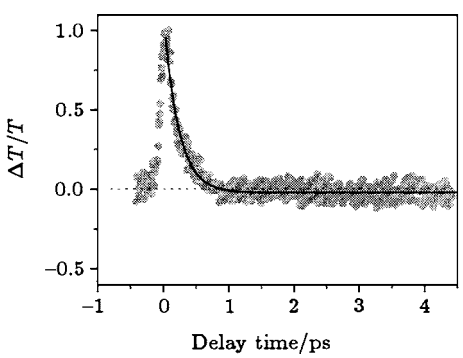


Fig.3. Normalized transient transmission $\Delta T/T$ for the as-grown sample. Gray points represent experimental data; black curve is for fitted data; dotted line is a zero-line.

4. Conclusion

In conclusion, we investigate the ultrafast carrier dynamics in the purified and the as-grown SWNT films. The signal of the purified sample shows the two-component behaviour. The fast component(160fs) and the slow component (0.72ps) are attributed to the intraband relaxation and interband relaxation in the semiconducting nanotubes. The amplitude of the signal shows a crossover from positive to negative, which can be interpreted as the state filling in the semiconducting nanotubes and the red shift of the π-plasmon resonance. Additionally, the signal of the as-grown sample can be fitted well with a time constant of 232fs. The disappearance of the photoabsorption in the as-grown sample results from the charge transfer from

the semiconducting nanotubes to the impurities in the sample.

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