One-Dimensional Characteristics of Third-Order Nonlinear Optical Response in Single-Walled Carbon Nanotubes

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Abstract. Third-order nonlinear optical susceptibilities have been investigated for individually suspended single walled carbon nanotubes in solution. The imaginary part of susceptibility $\mathrm{Im}\chi^{(3)}$ shows the resonant enhancement at each optical transition of the specific (n,m) tube. We have found that the diameter D dependence of the figure of merit $\mathrm{Im}\chi^{(3)}/\alpha$ (α:absorption coefficient) is $D^{6.1\pm0.9}$.

Keywords: Carbon nanotubes, One-dimensional system, Nonlinear optical response, Femtosecond spectroscopy.
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INTRODUCTION

The quasi-one-dimensional (1D) electronic states in carbon nanotubes show a van Hove singularity of the density of states and a strong exciton effect[1,2]. These effects are expected to enhance optical nonlinearities in the near-infrared region[3], which have the potential for applications in optical telecommunication systems. However, the contributions of a van Hove singularity and excitons to the nonlinear susceptibility $\chi^{(3)}$ in single-walled carbon nanotubes (SWNTs) are not quantitatively understood. In addition, the dependence of $\chi^{(3)}$ on the diameter and chirality is essential for understanding 1D features of SWNTs.

In this paper, third-order nonlinear optical response in individually suspended SWNTs in solution was investigated using femtosecond pump-probe spectroscopy. We report on the resonance enhancement of $\chi^{(3)}$ and its diameter dependence in semiconducting SWNTs.

EXPERIMENT

HiPco (high-pressure CO conversion)-SWNTs were dispersed in deuterium oxide (D_2O)-sodium dodecyl sulfate (SDS) to obtain individual nanotubes, each encased in a cylindrical micelle. Nanotube bundles were separated and purified by sonification and centrifugation at 85000g for 4 hours. Pump-probe measurements were made using an amplified Ti:sapphire laser system with the pump photon energy of 3.12 eV and the pulse duration of 150 fs[4]. Nonlinear absorption spectra were measured with a white continuum probing beam generated by self-phase modulation in a water cell. Values of $\chi^{(3)}$ in the nondegenerate configuration were measured in the spectral range of 0.85 to 3.0 eV.

RESULTS AND DISCUSSION

Figure 1 (solid curve) shows the absorption spectrum in the photon energy range 0.85–1.45 eV for SWNT-SDS suspensions in D_2O. The spectrum in this energy range indicates sharp structures corresponding to different diameters and chiral angles of semiconducting nanotubes. Each optical transition was assigned to a specific (n,m) nanotube[5]. For example, the peak at 1.110 eV is assigned to the transition between the lowest conduction and valence bands of

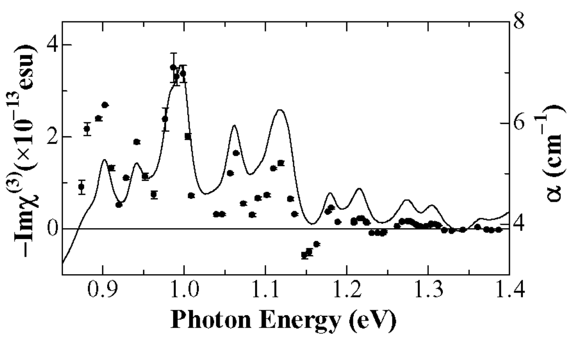

FIGURE 1. Absorption and $\mathrm{Im}\chi^{(3)}$ spectra of SWNTs in D_2O/SDS.

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the (7,6) tube. The peak at 0.999 eV is ascribed to (9,5), (10,3) and (10,5), which are not separated.

In Fig. 2 we show the linear absorption spectrum and differential absorption spectra with various delay times between the pump and probe pulses. The photon energy of the pump pulse is 3.12 eV, which corresponds to the higher band states of the SWNTs. The differential spectrum $\Delta\alpha$ exhibits absorption bleaching at each peak, and $\Delta\alpha$ slightly decays in the range 0-2.4 ps. The sharp structure corresponding to each optical transition due to the specific (n,m) nanotube suggests the resonance enhancement of the nonlinearities.

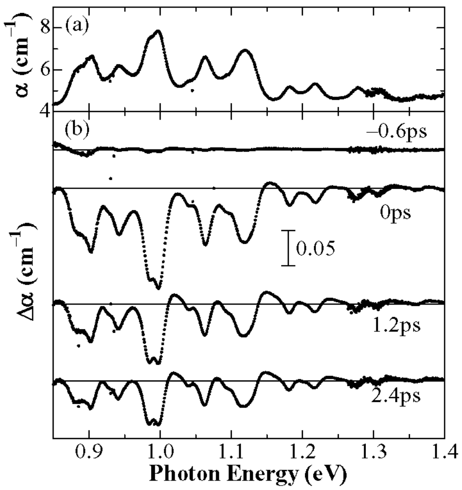

FIGURE 2. (a) Linear absorption spectrum and (b) differential absorption spectra for different delay times.

For a moderate laser intensity of the pump pulse, I, the change in the absorption coefficient $\Delta\alpha$ is described by $\Delta\alpha = \beta I$, where β is a nonlinear absorption coefficient. The imaginary part of $\chi^{(3)}$ ($\mathrm{Im}\chi^{(3)}$) is related to β by

$$\mathrm{Im}\,\chi^{(3)} = \frac{n^2 c^2}{240\pi^2 \omega_{probe}}\beta \qquad (1)$$

where n represents the linear refractive index of the SWNTs at the probe frequency and c is the velocity of light in vacuum. From the dependence of $\Delta\alpha$ on I we can estimate $\mathrm{Im}\chi^{(3)}$ values. The obtained values of $\mathrm{Im}\chi^{(3)}$ are plotted in Fig.1 by closed circles. Comparing the result with the absorption spectrum, we have found that $-\mathrm{Im}\chi^{(3)}$ shows a peak at each optical transition. The figure of merit $\mathrm{Im}\chi^{(3)}/\alpha$ for the E_{11} transition of the (7,6) tube is $-1.3\mathrm{x}10^{-13}$ esu cm.

Utilizing the assignment of the optical transitions in the absorption spectrum we investigated the diameter D dependence of $\mathrm{Im}\chi^{(3)}$ in semiconducting SWNTs. Shown in Fig. 3 is the diameter dependence of the figure of merit. The least-squares fit to the data indicates that $\mathrm{Im}\chi^{(3)}/\alpha$ depends on $D^{6.1\pm0.9}$. As the band gap E_g of the semiconductor nanotubes is proportional to D^{-1}, the dependence of $\mathrm{Im}\chi^{(3)}$ on the band gap is -6.1 ± 0.9. This dependence is comparable to the exciton energy dependence of $E^{-5.5}$ observed in polysilanes[6] in which the 1D exciton effect plays an important role in the resonant enhancement of the nonlinearity. Therefore, we have found that the observed diameter dependence is a feature characteristic of the optical nonlinearity in the 1D exciton system.

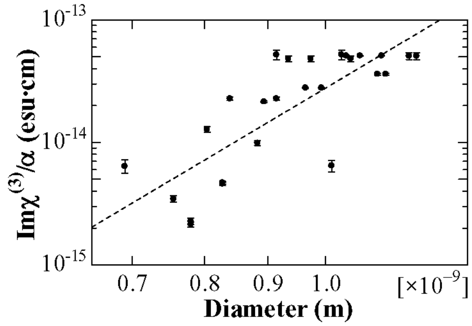

FIGURE 3. Log-log plot of $\mathrm{Im}\chi^{(3)}/\alpha$ vs. diameter for E_{11} transitions of semiconducting nanotubes. The dashed line is the least-squares fit to the data.

CONCLUSIONS

We have investigated third-order nonlinear optical susceptibilities and their dependence on the tube diameter in individual SWNTs. The imaginary part of susceptibility shows the resonant enhancement at each optical transition of the specific (n,m) tube. It is found that the diameter D dependence of $\mathrm{Im}\chi^{(3)}/\alpha$ is $D^{6.1\pm0.9}$.

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