Nonlinear and ultrafast optical response in single-walled carbon nanotubes

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Abstract. We measured third-order nonlinear susceptibility ($\chi^{(3)}$) spectra in semiconducting single-walled carbon nanotubes (SWNTs) by the Z-scan method. $|\text{Im}\chi^{(3)}|$ is remarkably enhanced under resonant excitation to the lowest interband transition, reaching $4.2 \times 10^{-6}$ esu. A comparison of the transient absorption changes evaluated by degenerate and nondegenerate pump-probe measurements suggests that the resonant enhancement of $|\text{Im}\chi^{(3)}|$ is dominated by a coherent process rather than by incoherent one such as saturation of absorption.

1. Introduction

The rapid progress of the optical communication network demands all optical switching devices which enables terahertz control of phase, amplitude, and route of lights. For the realization of such ultrafast control of lights, nonlinear optical (NLO) materials with large third-order nonlinear susceptibility $\chi^{(3)}$ and small relaxation time of photocarriers are indispensable. One-dimensional materials are good candidates of NLO materials, since quantum confinement of electron-hole motion on one-dimensional space can enhance $\chi^{(3)}$. Recently, the high potential of single-walled carbon nanotubes (SWNTs) as NLO materials has been suggested from both the experimental and the theoretical viewpoints [1-7]. Semiconducting SWNTs (SC-SWNTs) have the absorption peak around the optical fiber communication wavelength (1.55 μm). Its optical nonlinearity is therefore attracting interest concerning possible applications to optical switching devices as well as academic interest in the field of physics and chemistry.

In previous NLO studies on SWNTs, observed third-order optical nonlinearity around the gap transition has been attributed to saturation of absorption. There has, however, been no spectroscopic study of $\chi^{(3)}$, and therefore the mechanism for the enhancement of $\chi^{(3)}$ has not been fully understood yet. The time characteristic of the optical response has also been investigated by several groups using pump-probe (PP) methods [4,5,8-10]. Those studies revealed that the relaxation time of photoexcited states in SC-SWNTs is very small, being less than 1 ps. The origin for such an ultrafast optical response has, however, not been clarified yet.
In this paper, we report quantitative $\text{Im}\chi^{(3)}(-\omega; \omega, -\omega, \omega)$ spectra of the two kinds of SWNTs synthesized by the laser ablation and the HiPco method, which are abbreviated in the following as L-SWNT and H-SWNT, respectively. Using the Z-scan method [11], $\text{Im}\chi^{(3)}$ was evaluated in the whole energy region of the gap transition in the SC-SWNTs. $|\text{Im}\chi^{(3)}|$ was found to be remarkably enhanced under resonant excitation to the gap transition, reaching $4.2 \times 10^{-6}$ esu in L-SWNTs and $1.5 \times 10^{-7}$ esu in H-SWNTs. We also studied time characteristics of the optical response in the two SWNTs by the PP measurements under the resonant excitation condition and evaluated the relaxation time $T_1$ of the photoexcited states. The results revealed that the figure of merit (FOM) for third-order optical nonlinearity in SWNTs is very large as compared with that of conventional semiconductors. In addition, by comparing the response for the resonant excitation and off-resonant one, we demonstrate that the enhancement of optical nonlinearity under the resonant excitation condition is dominated mainly by a coherent process rather than by an incoherent one, such as saturation of absorption.

2. Experiment

![Figure 1. Absorption spectra of L-SWNTs [(a)] and H-SWNTs [(b)].](image)

L-SWNTs were made by the method previously reported [12]. From the energy dispersive x-ray spectroscopy, the catalyst impurities (Ni) were found to be very small, being just 1 at. %. H-SWNTs were purchased from Carbon Nanotechnologies, Inc. and used without further purification. Thin film samples were prepared by spraying SWNTs suspended in ethanol under sonication on CaF$_2$ substrates. The spectrum of the absorption coefficient $\alpha$ in the L- (H-)SWNT film with the thickness $L_s$ of ~160 nm (130 nm) is presented in Figure 1. The absorption band at 0.6-1.1 eV corresponds to the lowest interband transition of SC-SWNTs, on which we focus in this study. The broadening of this band especially in H-SWNTs is due to finite distributions of tube diameter $d$. It is known that the average $d$ value of H-SWNTs (~0.9 nm) is smaller than that of L-SWNTs (~1.4 nm), and the interband transition energy is approximately proportional to $d^{-1}$ [13]. As a result, the peak energy of the absorption band is higher and its band width is larger in H-SWNTs as compared with L-SWNTs.

In both the Z-scan and PP measurement, we used laser pulses with 110 fs duration obtained from optical parametric amplifiers pumped by a Ti:Al$_2$O$_3$ regenerative amplifier system operating at 1 kHz. To evaluate $\text{Im}\chi^{(3)}$ of the films by the Z-scan method, we used a SiO$_2$ plate as a reference, in which the absolute value of the nonlinear refractive index $n_2$ is known. The detailed procedure to determine $\text{Im}\chi^{(3)}$ is as follows [14]. First, the transmittance $T$ of a sample is measured as a function of the sample position $z$ (Z-scan profile) under the open aperture condition. Second, the Z-scan profile of a SiO$_2$ plate with 0.5-mm thickness is measured under closed aperture condition. Typical Z-scan profiles for the L-SWNTs and the SiO$_2$ plate are presented in the upper and lower panels of Figure 2, respectively. These profiles are well reproduced by the theoretical profiles for third-order optical nonlinearity (solid lines),
which are described as 
\[ T(z)=\frac{f(a_1[1+(z/a_2)^2])}{1} \]
for the open aperture signal and 
\[ T(z)=1+4a_3(z/a_2)[(z/a_2)^2+1][(z/a_2)^2+9]^{-1} \]
for the closed aperture signal. Here, \( f(x) \) is defined as 
\[ f(x)=\frac{\ln(x+1)}{x} \]
and \( a_1, a_2, \) and \( a_3 \) are fitting parameters. Magnitudes of the Z-scan signals are characterized by the peak intensity, \( T(0) \), for the open aperture signal of the sample and by the peak-to-valley value, \( \Delta T_{p-v} \), for the closed aperture signal of the reference. We can calculate \( \text{Im}\chi^{(3)} \) by putting \( T(0) \) and \( \Delta T_{p-v} \) into the following relation,
\[
\text{Im}\chi^{(3)} = \frac{1.08 \pi \varepsilon_0 c n_0^2 \kappa_0 (1 - S)^{0.25} L_r}{\lambda r [1 - \exp(-4 \pi \kappa_0 L_s / \lambda)]} \frac{f^{-1}(T(0))}{\Delta T_{p-v}} n_2.
\]
Here, \( \varepsilon_0 \) is the permittivity of vacuum and \( c \) the light velocity. \( n_0 \) and \( \kappa_0 \) are linear refractive index and extinction coefficient, respectively, which were determined by analyzing the results of ellipsometry, absorption, and reflectance measurements. \( S \) is the aperture linear transmittance in the closed aperture measurement of the SiO2 plate (see ref. [11]), \( L_r \) the thickness of the SiO2 plate, and \( \lambda \) the wavelength of light. \( r \) is defined by \( r = P_s / P_r \), where \( P_s \) and \( P_r \) show power of the incident laser pulses for the sample and the SiO2 plate, respectively.

**Figure 2.** Typical Z-scan profiles of the L-SWNT film in open aperture configuration (upper panel) and of the SiO2 plate in closed aperture configuration (lower panel). Solid lines show the theoretical lines (see text). The excitation energy is set at 0.704 eV.

In the PP measurement, we detect time evolution of the transmittance change \( \Delta T(t)/T \) and deduce the photoinduced change of \( \alpha \), \( \Delta \alpha(t) \), from \( \Delta T(t)/T \) using the following relations:
\[
\Delta \alpha(t) = \Delta \alpha_0(t) \times \exp(-\alpha_{\text{pump}} x),
\]
\[
\Delta \alpha_0(t) = -\frac{\alpha_{\text{pump}} \ln[\Delta T(t)/T + 1]}{1 - \exp(-\alpha_{\text{pump}} L_s)}.
\]
Here, \( \alpha_{\text{pump}} \) is the linear absorption coefficient for the pump light in the sample, \( \Delta \alpha_0(t) \) the absorption change of the probe light at the sample surface, and \( x \) the distance from the sample surface.

### 3. Results and discussions

We present the \( -\text{Im}\chi^{(3)} \) spectrum of L-SWNTs and H-SWNTs obtained by the Z-scan method (the solid circles) together with the \( \alpha \) spectrum (the dashed line) in Figure 3. Maximum values of \( |\text{Im}\chi^{(3)}| \) (max[|\text{Im}\chi^{(3)}|]) are very large, reaching \( 4.2 \times 10^6 \) esu in L-SWNTs and \( 1.5 \times 10^7 \) esu in H-SWNTs. To compare the spectral shape of \( |\text{Im}\chi^{(3)}| \) with that of the linear absorption for the interband transition, we subtracted the background from the \( \varepsilon_2 (= 2n_0\kappa_0) \) spectrum around the band gap region. The obtained \( \varepsilon_2 \) spectra are shown by the gray lines, the spectral shapes of which are quite similar to those of \( -\text{Im}\chi^{(3)} \). This similarity indicates that the observed NLO response is due to the photoinduced change of the absorption spectrum associated with SC-SWNTs.
Figure 3. $-\text{Im}(\chi^{(3)})$ spectra (solid circles) of L-SWNTs (a) and H-SWNTs (b). $\alpha$ is also shown by the dashed lines. The gray lines show the normalized $\epsilon_2$ spectra, in which the background [the straight line from 0.50 eV (0.60 eV) to 0.83 eV (1.31 eV) for L- (H-)SWNTs] is excluded. The solid and open arrows indicate the energy positions of the pump light used in the degenerate and nondegenerate PP measurements shown in Figure 4, respectively.

Another important result about the optical nonlinearity is the time characteristics of the response. In Figures 4(a) and 4(b), we present the time evolutions of $-\Delta\alpha_0$ obtained by the PP measurement with degenerate configuration, in which both the pump energy ($E_{\text{pump}}$) and the probe energy ($E_{\text{probe}}$) are set at the absorption peak indicated by the solid arrow in Figure 3 (0.688 eV for L-SWNTs and 0.953 eV for H-SWNTs). The observed time characteristics cannot be explained by a single exponential decay but are composed of the two components: the ultrafast component and the slower one, the decay times of which are much shorter and longer than the pulse duration of 110 fs, respectively. We simulated $-\Delta\alpha_0$ with the following equation including the convolution of the pump and probe pulses:

$$-\Delta\alpha_0(t) = A_1 \exp\left[-\left(\frac{t}{\tau}\right)^2\right] + A_2 \exp\left(-\frac{t}{T_1}\right) \int_{-\infty}^{t} \exp\left[\frac{t'/T_1 - (t'/\tau)^2}{2}\right] dt'.\,$$

Here, $\tau$ is the parameter associated with the pulse duration. $A_1$ and $A_2$ are the amounts of the ultrafast and slow components at $t = 0$, respectively. $-\Delta\alpha_0(t)$ is well reproduced by this equation, as shown by the solid lines in Figures 4(a) and 4(b). $\tau$ is set to 110 fs, and the other parameters are $A_1 = 1.24 \times 10^4$ ($1.57 \times 10^3$), $A_2 = 4.37 \times 10^3$ ($5.06 \times 10^3$), and $T_1 = 0.90$ ps (0.35 ps) for L- (H-)SWNTs. The calculated ultrafast and slow components are represented by the shaded area and the broken line, respectively. $A_1/(A_1 + A_2)$ is about 0.75 in both SWNTs, indicating that the ultrafast response dominates the large optical nonlinearity.
The experimental configuration of the degenerate PP measurement at \( t = 0 \) ps is the same as that of the Z-scan method, so we can compare the \( \text{Im} \chi^{(3)} \) values deduced in the two methods. \( \text{Im} \chi^{(3)} \) can be calculated from the magnitudes of \( \Delta \alpha(0) \) using the formula \( \text{Im} \chi^{(3)} = \frac{\varepsilon_0 c n_0^2 \lambda}{6 \pi I_{\text{pump}}} \Delta \alpha(0) \). Here, \( I_{\text{pump}} \) is the pump power. The obtained -\( \text{Im} \chi^{(3)} \) is \( 3.0 \times 10^{-6} \) esu \( (1.8 \times 10^{-7} \) esu) for L- (H-)SWNTs, which is fairly consistent with that evaluated from the Z-scan method.

To clarify the origin of the two components in the time characteristics, we performed nondegenerate (two-color) PP measurements, in which only \( E_{\text{pump}} \) is shifted to the higher energy at \( 0.739 \text{ eV} \) \( (1.022 \text{ eV}) \) for L- (H-)SWNTs, which is indicated by the open arrow in Figure 3. The time evolutions of -\( \Delta \alpha_0(t) \) are shown in Figures 4(c) and 4(d), which can be reproduced by the single exponential component as shown by the solid line. The obtained parameters are \( A_2 = 1.53 \times 10^3 \) \( (1.22 \times 10^3) \) and \( T_1 = 1.0 \text{ ps} \) \( (0.35 \text{ ps}) \) for L- (H-)SWNTs. The values of \( T_1 \) are almost equal to those evaluated from the degenerate PP measurements. Since the similar slower component is observed in the degenerate and two-color PP measurements in common, it is attributable to saturation of absorption, that is, incoherent NLO response. Namely, \( T_1 \) reflects the decay time of the photoexcited states. Very recently, it has been reported that the relaxation process of the photoexcited states in the micelle-suspended isolated SC-SWNTs occurs with the decay time of \( \sim 10 \) ps [15], which is much longer than that reported previously in the SWNT films [4,5,8-10] and that evaluated in our SWNT films. It has been ascertained from the transmission electron microscope measurement that our SWNT films are composed of the bundles. It is, therefore, reasonable to consider that the relaxations with \( T_1 \) of \( 1 \) ps \( (0.35 \text{ ps}) \) for L-SWNTs (H-SWNTs) will be dominated by charge transfer and/or energy transfer of the photoexcited electrons and holes to neighboring metallic tubes, as suggested previously [9].

On the other hand, the ultrafast component is observed only for the degenerate PP measurement. Therefore, it is reasonably attributed to the coherent NLO response. This coherent response is interpreted as an optical Stark effect and a stimulated emission. As for the NLO response of SC-SWNTs, the theoretical study by Margulis et al. suggests the importance of the coherent response characteristic of the two-level system [3], supporting our experimental results and interpretations.

As detailed above, the NLO response at \( t = 0 \) ps in the degenerate PP measurement is dominated mainly by the ultrafast response, that is, the coherent process. In fact, max|\( \Delta \alpha_0 \)| at \( t = 0 \) ps in the two-color PP measurement is about one-sixth (one-eleventh) of that observed in the degenerate PP one for L- (H-)SWNTs. From these results, large |\( \text{Im} \chi^{(3)} \)| obtained by the Z-scan method is also attributable mainly to the coherent process.

The max|\( \text{Im} \chi^{(3)} \)| values in the L-SWNTs obtained by the Z-scan measurement is about 30 times as large as that in the H-SWNT. It is reasonable to consider that such a difference is due to the difference in the spectral width \( (\Gamma) \) of the absorption band and the magnitude of the transition dipole moment \( (\mu) \) for the gap transition in both the coherent and incoherent processes. With decrease of the band energy, \( \Gamma \) decreases as seen in Figure 1 and \( \mu \) will increase. Both of these two effects will be responsible for the enhancement of |\( \text{Im} \chi^{(3)} \)| in the L-SWNTs as compared with the H-SWNTs.

In addition to \( \text{Im} \chi^{(3)} \), we measured Re\( \chi^{(3)} \) in L-SWNTs at 0.756 eV \( (1.64 \mu \text{m}) \) using the closed-aperture condition of the Z-scan method (not shown). The obtained Re\( \chi^{(3)} \) reaches \( (1.3 \pm 0.2) \times 10^{-6} \) esu, which is as large as \( \text{Im} \chi^{(3)} \). It demonstrates that the optical control of the refractive index will also be possible in SWNTs.

When we consider the applications of NLO materials, it is more practical to evaluate FOM defined as \( \text{FOM} = |\text{Im} \chi^{(3)}|/(\alpha T_1) \). In this sense, the bundled SWNTs with \( T_1 \sim 1 \) ps will be more advantageous than the isolated SWNTs with \( T_1 \sim 10 \) ps. By using the values of |\( \text{Im} \chi^{(3)} \)|, \( \alpha \), and \( T_1 \) evaluated in this study, FOM is deduced to be 68 esu cm/s at 1.8 \( \mu \text{m} \) in L-SWNTs and 6.3 esu cm/s at 1.4 \( \mu \text{m} \) in H-SWNTs. The value in L-SWNTs is tremendously larger than those of other semiconductors: 0.010 esu cm/s at 0.90 \( \mu \text{m} \) in GaAs [16,17] and 2.6 esu cm/s at 0.94 \( \mu \text{m} \) in polydiacetylene [18-21], which is well known to show large optical nonlinearity. In SWNTs, the optical gap is tunable by the control of tube diameter and large FOM will be obtained at 1.55 \( \mu \text{m} \). Judging from these facts, it can be concluded that SWNTs are strong candidates for future NLO materials.
4. Summary

We have measured \( \text{Im}^{(3)} \) spectra by the Z-scan method in SWNTs. The max|\( \text{Im}^{(3)} \)| is fairly large, reaching \( 4.2 \times 10^{-6} \) esu and \( 1.5 \times 10^{-7} \) esu in L-SWNTs and H-SWNTs, respectively. A comparison of degenerate and nondegenerate pump-probe measurements suggests that the enhancement of |\( \text{Im}^{(3)} \)| under resonant excitation is due mainly to a coherent process rather than to an incoherent one such as saturation of absorption. In addition, the value of the figure of merit for SWNTs is much larger than that for other semiconductors, demonstrating the high potential of SWNTs as NLO materials.

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